

β -Diketiminato complexes of group 13 elements and their use in small molecule activation and catalysis



Alexa Caise

Worcester College, Oxford

A thesis submitted in partial fulfilment of the
requirements for the degree of Doctor of
Philosophy

September 2019

Acknowledgements

I am immensely grateful to both of my supervisors Prof. Simon Aldridge and Prof. Jose Goicoechea for their dedicated supervision throughout this project and for the constant support. Applying to the Aldridge group for a position as a Part II (over four years ago!), I did not know how much this decision would affect the next few years of my life – I am certainly glad I did apply! Since I joined the group, I have been offered so many opportunities which have enriched my DPhil experience and taught me so much. For these, and for all of the constant help he has offered, I am very thankful. Moreover, I am particularly grateful to Prof. Goicoechea for (despite not knowing much about me) agreeing to co-supervise me. I know all of those hours going over my confusing NMRs were probably not how he envisioned spending every Friday morning – I owe a huge debt of gratitude for that. I feel immensely privileged to have worked with both of them.

Further thanks go to Prof. Cameron Jones for allowing me to work in his group for three months. Despite the fact that the chemistry might not have been the most successful and the Australian sun didn't make an appearance for my whole time in Melbourne, I am so grateful for everything that I learnt in those months – they were truly some of the most enjoyable of my DPhil.

Many people have passed through the Aldridge group during my time as a Part II and DPhil student. Each one of them has contributed to my experience in some manner (whether it has been educationally or socially). Every single person that I have worked with have made my years as an occupant of S12 truly enjoyable. Everyone has always been so helpful and full of suggestions when the going got tough. A special mention goes to Dr. Joe Abdalla for supervising me when I was a part II. Little did I know then how useful everything you were teaching me would be! I truly feel that working with you for 8 months set me in good stead for my DPhil (and I'll always remember the hours we spent playing celebrity rhyme time). A further special mention goes to the members of 'spaghetti measuring': Dr. Jamie 'back door' Hicks, Dr. Petra 'big rock' Vasko, Huan 'no offense but....' Do and Anna 'little but concentrated' Booth. You guys really made the last couple of years of my DPhil really fun, whether it was the bi-daily coffee, distraction in the form of animal videos or teasing Huan about his low-talent chemistry, you made every day fun in one way or another. Moreover, I am truly grateful that Jamie and Petra have been able to fill in the blanks of basic things I should know (being able to filter something and use computer shortcuts have been surprisingly useful in the last year) and never losing patience with me when they hear me say "Can I ask a question?". I truly look forward to experiencing #postdoc life with all of you.

I count myself very fortunate to have supervised Dafydd Jones (someone we could probably class as a 'medium talent' Part II). His hard work and dedication meant that I found my job as a supervisor enjoyable (most of the time!). I am very grateful for his contributions to the early work on the electronically modified β -diketiminato-ligated aluminium hydrides and their reactivity.

Furthermore, I am very grateful to the Goicoechea group. It has always been great to know there is a second place to turn to when I need to find a chemical (or a few beers at the Uni club).

Many thanks to all of the Aldridge group crystallographers for running all of my crystals and solving them: Dr. Jesus Campos, Dr. Evgeny Kolychev, Dr. Rémi Tirfoin, Dr. Jamie Hicks and Dr. Maria Fuentes-Dominguez. Despite always trying to give you the best crystals I could grow, I know how many hours of effort were put in to obtaining all the crystal structures for my thesis and for those, I am forever grateful. Moreover, Dr. Nick Rees has been immensely helpful throughout the course of my DPhil. He was always available to help with any of my NMR queries and always happy to book me extra time on the NMR machines – without that I’m not sure this thesis would have been completed until 2020 (at least!).

I would like to thank Luka who has, from the moment I received an offer of funding, supported me throughout this whole journey and always kept a smile on my face. From the 18 months in which I became a slave to the NMR machine, to the last year which has been particularly difficult – I could not have done it without him!

While there are countless other people (from the real, non-science world) that I could thank, I owe the most to my parents. The things that they have done for me are too numerous to list so I summarise to say thank you for your unwavering support and everything that you did that allowed me to get to this point. While it was always my mum who insisted it was from her who I got my brains from, I almost certainly wouldn’t have got to this point academically without inheriting my dad’s ability to recall a wealth of information (proven pub quiz champion!). While I perhaps applied this skill in a less profitable manner, I couldn’t have done it without you. Without a doubt however, it is all the skills I learnt from my mum that helped me with the more practical lab aspects. I am most thankful however for the lesson from her to “not take things so personally”. Without this, I am certain I wouldn’t have survived working four years of working in the same lab as Huan.

This thesis is dedicated to my Mum, Pia, who passed away shortly before it was ready to be submitted. She was the epitome of strength and a beautiful person, who put all others before herself.

Abstract

This thesis examines the potential of hydrides of the group 13 metals aluminium and gallium to function as homogeneous catalysts for the reduction of unsaturated substrates including CO₂, aldehydes and ketones. In addition, it reports on studies designed to probe the mechanisms by which these processes occur.

Chapter 3 details the preparation of a series of novel β -diketiminate (or Nacnac) ligated aluminium hydrides of the form $\{\text{HC}(\text{XCNDipp})_2\}\text{Al}(\text{R})\text{H}$ $\{\text{X} = \text{Me}, \text{NMe}_2; (\text{DippNacnac})\text{Al}(\text{R})\text{H}\}$, which differ in the nature of the auxiliary R substituent and the Nacnac backbone itself. These systems show considerable variation in the nature of the Al-H bond and significant differences in reactivity with respect to the hydroalumination of carbon dioxide. Electron-donating R substituents give rise to weaker and more hydridic Al-H bonds, which exhibit enhanced rates of insertion of the CO₂ molecule. The treatment of the resulting κ^1 -formate complexes with B-H containing reductants under stoichiometric and catalytic conditions reveals that no Al-O/B-H metathesis occurs, even under forcing conditions. This study did however lead to the isolation of a range of novel boryloxy complexes, $(\text{DippNacnac})\text{Al}(\text{R})(\text{OBXX}')$ ($\text{X} = \text{X}' = \text{cat}, 9\text{-BBN}$; $\text{X} = \text{H}, \text{X}' = \text{OMe}$) and borohydride complexes $(\text{DippNacnac})\text{Al}(\text{R})(\text{H}_2\text{BX}_2)$ ($\text{X}_2 = (9\text{-BBN}), \text{H}_2$). It is concluded that no catalytic turnover can be achieved in the reduction of CO₂ by boranes mediated by these aluminium hydrides, presumably due to the excessive strength of the Al-O bond, and the consequent lack of viability of Al-O/B-H metathesis.

Chapter 4 describes a number of synthetic routes for the preparation of unsymmetrically substituted Nacnac-ligated gallium monohydride complexes, including a rare example of a base-stabilised cationic gallium hydride. The range of novel hydrides reported offers variation in the steric and electronic properties of the auxiliary R substituent. Studies of stoichiometric reactivity reveal that, as with related alanes, gallium hydrides which bear more σ -donating R substituents are more amenable to the hydrogallation of CO₂. In addition, studies were undertaken to establish the impact of both the gallium-bound R substituent and the borane on Ga-O/B-H metathesis processes leading to the regeneration of a Ga-H bond from the corresponding formate complex $\{\text{HC}(\text{MeCNDipp})_2\}\text{Ga}(\text{R})(\text{OC}(\text{O})\text{H})$, $[\text{Dipp}^1]\text{Ga}(\text{R})(\text{OC}(\text{O})\text{H})$. With the factors influencing

both the insertion and metathesis processes established, the ability of these Nacnac gallium hydrides to catalyse the borane-mediated reduction of CO₂ was then investigated.

The work presented in Chapter 5 demonstrates that the Nacnac-ligated gallium hydride complex, [Dipp¹]**1**Ga(Ad)H, can be employed in tandem with B(C₆F₅)₃ to effect the catalytic hydrosilylation of CO₂. Whilst forcing conditions are required to bring about catalytic turnover (and only modest TOF values can be achieved), this system represents a rare example of a main group hydride catalyst for this process. In addition, it can be shown that selectivity can be controlled through the ratio of Lewis acid co-catalyst employed. A series of mechanistic studies is described which shows that the B(C₆F₅)₃ co-catalyst leads to the activation of the gallium complex towards *both* processes (insertion, metathesis) that are key to catalytic turnover. During the course of this study, the first examples of three-coordinate β-diketimate-ligated gallium cations were synthesised.

Chapter 6 describes a study of the mechanisms of the reduction of organic carbonyl substrates, mediated by aluminium and gallium hydrides. It is demonstrated that the hydrogallation of aldehydes by β-diketimate-ligated gallium hydrides is relatively limited and only one gallium hydride of this nature, [Dipp¹]**1**GaH₂, could be found to hydrogallate benzaldehyde, requiring forcing conditions to bring about such reactivity. However, the gallium alkoxide product so generated is amenable to rapid Ga-O/B-H metathesis to regenerate a Ga-H bond and release the reduced organic product. Thus, in accordance with the research reported in Chapters 4 and 5, the hydroboration of C=O bonds can be effected by gallium systems based on an inner-sphere mechanism involving insertion and Ga-O/B-H metathesis steps. By contrast, a wide range of β-diketimate-ligated aluminium hydrides can be shown to hydroaluminate benzaldehyde under ambient conditions. However, in this case the resulting metal alkoxides are resolutely unreactive towards B-H containing reagents. This behaviour is consistent with the reactivity towards CO₂ reported in Chapter 3 and can be rationalized by the underlying thermodynamics of Al-O/B-H metathesis (which are unfavourable). Nonetheless, literature reports of the catalytic hydroboration of benzaldehyde by aluminium hydrides are confirmed to be correct – and a series of mechanisms based on outer-sphere processes which avoid ‘net cleavage’ of the Al-O bond have therefore been investigated.

Abbreviations

The following abbreviations will be used throughout this thesis:

Ad – Adamantyl	L – A general ligand
Ar – Aryl	LUMO – Lowest occupied molecular orbital
Ar ^f – 3,5-(F ₃ C) ₂ C ₆ H ₃	<i>m</i> – Meta
br – Broad	m – Multiplet
<i>ca.</i> – Circa	Me – Methyl
calc. – Calculated	MeLi – Methyllithium
cat – 1,2-C ₆ H ₄ O ₂	MeOH – Methanol
Cp* - Pentamethylcyclopentadienyl	MeOTf – Methyltrifluoromethane sulfonate
Cy – Cyclohexyl	meas. – Measured
d – Doublet	Mes – 2,4,6-trimethylphenyl
DCM – Dichloromethane	Mins – Minutes
Dep - 2,6-Et ₂ C ₆ H ₃	MS – Mass spectrometry
DFT – Density functional theory	ⁿ Bu – <i>n</i> -Butyl
Dipp – 2,6-diisopropylphenyl	ⁿ BuLi – <i>n</i> -Butyllithium
DMAP – 4-(<i>N,N</i> -dimethylamino)pyridine	NHC – <i>N</i> -heterocyclic carbene
EI – Electron impact	NMR – Nuclear magnetic resonance
Equiv. – Equivalents	<i>o</i> – Ortho
ESI – Electrospray ionisation	Obs. – Observed
Et – Ethyl	OTf – -OSO ₂ CF ₃
Et ₂ O – Diethyl ether	<i>p</i> – Para
FLP – Frustrated Lewis pair	Ph – Phenyl
FT-IR – Fourier transform infrared spectroscopy	pin - -OCMe ₂ CMe ₂ O-
h – Hours	ppm – Parts per million
HMDS – Hexamethyldisilazane	q – Quartet
HOMO – Highest occupied molecular orbital	qn – Quintet
Hz – Hertz, s ⁻¹	rt – Room temperature
ⁱ Pr – Isopropyl	s – Singlet or strong
IR – Infrared	sept – Septet
J – Joule	t – Triplet
ⁿ J _{XY} – Coupling constant between nuclei X and Y, over <i>n</i> bonds, in Hz	t _{1/2} – Half-life
K – Kelvin	^t Bu – <i>tert</i> -butyl
k – Rate constant	^t BuLi – <i>tert</i> -butyllithium
κ ⁿ – Denotes binding mode for polydentate ligand, <i>n</i> denotes bridging index	THF – Tetrahydrofuran
	TOF – Turnover frequency

TON – Turnover number

OTS – Tosylate ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$)

Tripp – 2,4,6-*i*Pr₃C₆H₂

vs – *Versus*

VT-NMR – Variable temperature NMR

δ – NMR chemical shift

λ – Wavelength

ν – Wavenumber

μ – Bridging

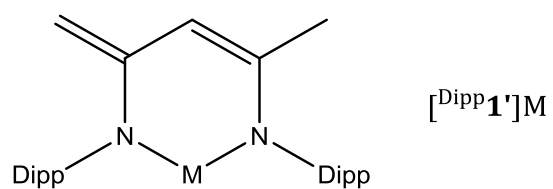
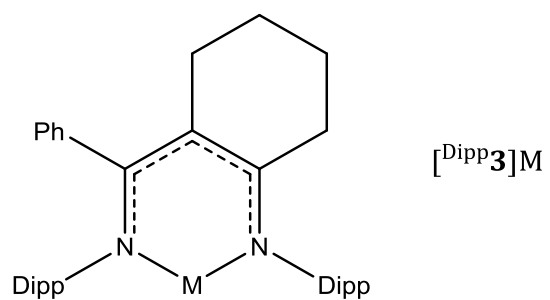
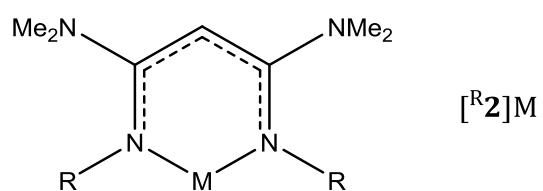
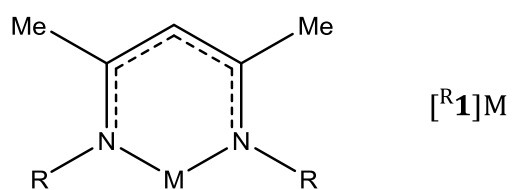


Table of Contents

1.	Introduction	1
1.1	Hydrides of the group 13 metals: aluminium and gallium	1
1.1.1	Physical properties of the binary hydrides	1
1.1.2	Binary hydrides of aluminium and gallium	3
1.1.3	Lewis base adducts of M(III) hydrides: AlH_3 and GaH_3	4
1.1.4	Organo-alanes and gallanes: preparation	6
1.1.5	Organo-alanes and gallanes: examples	8
1.1.6	Borohydride derivatives of aluminium and gallium	12
1.1.7	Alanes and gallanes: spectroscopic analysis	15
1.2	β-diketiminato ligands	17
1.2.1	Steric modification of β -diketiminato ligands	18
1.2.2	Electronic modification of β -diketiminato ligands	19
1.2.3	β -diketiminato-ligated alanes	22
1.2.4	β -diketiminato-ligated gallanes	28
1.3	The use of main group elements in catalytic reductive processes	29
1.3.1	Catalytic reduction of CO_2	31
1.3.2	Catalytic hydroboration of CO_2	34
1.3.2.1	<i>Transition metal hydride catalysts</i>	34
1.3.2.2	<i>Main group and non-metal catalysts</i>	37
1.3.2.3	<i>Catalytic hydroboration of CO_2: Mechanistic considerations</i>	41
1.3.3	Catalytic hydrosilylation of CO_2	47
1.3.4	Catalytic hydroboration of aldehydes and ketones	52
1.4	The use of alanes and gallanes in small molecule activation and catalysis	55
1.4.1	The use of Group 13 complexes in small molecule activation	55
1.4.2	Group 13 complexes as catalysts for reductive processes	59
1.4.2.1	<i>Stoichiometric reactions of alanes: critical steps for substrate activation in catalysis</i>	60
1.4.2.2	<i>Alanes as catalysts for hydroboration reactions</i>	61
1.4.2.3	<i>Alanes as catalysts for hydrosilylation reactions</i>	65
1.4.2.4	<i>The use of gallanes as catalysts for the reduction of unsaturated substrates</i>	68
1.5	References	71

2.	Experimental Techniques	81
2.1	Manipulation of air-sensitive compounds	81
2.1.1	Inert atmosphere techniques	81
2.2	Spectroscopic and analytical techniques	83
2.2.1	NMR spectroscopy	82
2.2.2	Infrared spectroscopy	83
2.2.3	Mass spectrometry	83
2.2.4	Elemental analysis	84
2.2.5	X-ray crystallography	84
2.3	Preparation and purification of starting materials	85
2.4	References	88
3.	On the viability of catalytic turnover <i>via</i> Al-O/B-H metathesis: the reactivity of β-diketiminato aluminium hydrides towards CO₂ and boranes	91
3.1	Introduction	91
3.2	Project aims	97
3.3	Experimental details	98
3.4	Results and discussion	126
3.4.1	Synthesis of novel β -diketiminato-ligated aluminium hydrides	126
3.4.1.1	<i>Synthesis of novel β-diketiminato-ligated aluminium halide precursors: iodination of aluminium-carbon bonds</i>	126
3.4.1.2	<i>Synthesis of novel β-diketiminato-ligated aluminium halide precursors: salt metathesis reactions</i>	127
3.4.1.3	<i>Synthesis of novel β-diketiminato-ligated aluminium hydrides: metathetical reactions of aluminium halides with hydride sources</i>	130
3.4.1.4	<i>Synthesis of novel β-diketiminato-ligated aluminium hydrides: the use of electronically-modified ligands</i>	133
3.4.1.5	<i>Structural analysis of novel β-diketiminato-ligated aluminium complexes</i>	136
3.4.1.6	<i>Spectroscopic analysis of novel β-diketiminato-ligated aluminium hydride complexes</i>	140
3.4.2	Reactivity of β -diketiminato-ligated aluminium hydrides towards CO ₂	143
3.4.2.1	<i>Reactivity of "conventional" β-diketiminato-ligated aluminium hydrides towards CO₂</i>	143
3.4.2.2	<i>Reactivity of "electronically modified" β-diketiminato-ligated aluminium hydrides towards CO₂</i>	151
3.4.3	Can aluminium hydrides act as catalysts for the reduction of CO ₂ by boranes?	156
3.4.3.1	<i>Catalytic and stoichiometric studies: pinacolborane as the reductant</i>	156

3.4.3.2	<i>Catalytic studies: catecholborane as the reductant</i>	158
3.4.3.3	<i>Stoichiometric studies: catecholborane as the reductant</i>	158
3.4.3.4	<i>Catalytic studies: {H(9-BBN)}₂ as the reductant</i>	164
3.4.3.5	<i>Stoichiometric studies: the formation of dialkylborohydride complexes</i>	166
3.4.3.6	<i>Stoichiometric studies: the reactivity of aluminium formates towards {H(9-BBN)}₂</i>	177
3.4.3.7	<i>Catalytic studies: Me₂S·BH₃ as the reductant</i>	186
3.4.3.8	<i>Stoichiometric studies: the formation of borohydride complexes</i>	187
3.4.3.9	<i>Stoichiometric studies: borane dimethylsulfide as the reductant</i>	192
3.4.3.10	<i>Stoichiometric studies: regeneration of aluminium hydrides?</i>	198
3.5	Conclusions and suggestions for further work	199
3.6	References	202
4.	Synthesis of novel gallium hydrides and their potential as catalysts for the borane-mediated reduction of CO₂	207
4.1	Introduction	207
4.2	Project aims	212
4.3	Experimental details	213
4.4	Results and discussion	231
4.4.1	Synthesis of novel β-diketiminato-ligated gallium hydrides	231
4.4.2	Reactivity of gallium hydrides towards CO ₂	250
4.4.3	Stoichiometric reactivity studies of gallium formate complexes with boranes	259
4.4.3.1	<i>Stoichiometric reactivity studies of gallium formate complexes with HBpin</i>	260
4.4.3.2	<i>Stoichiometric reactivity studies of gallium formate complexes with HBcat</i>	265
4.4.3.3	<i>Stoichiometric reactivity studies of gallium formate complexes with {H(9-BBN)}₂</i>	266
4.4.3.4	<i>Stoichiometric reactivity studies of gallium formate complexes with Me₂S·BH₃</i>	268
4.4.4	Exploring the catalytic potential of these systems	270
4.4.4.1	<i>Investigating the mechanistic steps key to catalytic turnover</i>	271
4.4.4.2	<i>Further investigation of the system under catalytic conditions</i>	275
4.5	Conclusions and suggestions for further work	276
4.6	References	279
5.	β-diketiminato complexes of group 13 elements as catalysts for the hydrosilylation of CO₂	281
5.1	Introduction	281
5.2	Project aims	287
5.3	Experimental details	288
5.4	Results and discussion	297

5.4.1	Gallium formate complexes: amenable to Ga-O/Si-H σ -bond metathesis?	297
5.4.2	Investigation of the two steps key to catalytic turnover	307
5.4.3	Catalytic hydrosilylation of CO ₂ using stoichiometric B(C ₆ F ₅) ₃	317
5.4.4	The use of excess B(C ₆ F ₅) ₃ : impact on rate and selectivity	321
5.4.5	Catalytic hydrosilylation of CO ₂ using excess B(C ₆ F ₅) ₃	324
5.4.6	Can B(C ₆ F ₅) ₃ activate aluminium complexes towards Al-O/E-H σ -bond metathesis?	327
5.5	Conclusions and suggestions for further work	332
5.6	References	334
6.	Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms	337
6.1	Introduction	337
6.2	Project aims	344
6.3	Experimental details	346
6.4	Results and discussion	360
6.4.1	Activation of aldehydes by group 13 hydrides	360
6.4.1.1	<i>Reactivity of β-diketiminato-ligated aluminium hydrides towards aldehydes</i>	360
6.4.1.2	<i>Investigation of the factors which influence aldehyde insertion</i>	365
6.4.1.3	<i>Can β-diketiminato-ligated gallium hydrides hydrogallate aldehydes?</i>	371
6.4.2	Regenerating the metal hydride: exploring M-O/B-H σ -bond metathesis (M = Al, Ga)	374
6.4.3	Consideration of alternative mechanisms	377
6.4.3.1	<i>Activation of the borane</i>	377
6.4.3.2	<i>Aluminium hydrides: Nothing but a pre-catalyst?</i>	382
6.4.3.3	<i>Aluminium complexes: catalysts for the Tishchenko reaction</i>	383
6.4.3.4	<i>Does the Tishchenko reaction play a role in the catalytic cycle?</i>	388
6.5	Conclusion	389
6.6	References	391

1. Introduction

1.1 Hydrides of the group 13 metals: aluminium and gallium

1.1.1 Physical properties of the binary hydrides

Property	B	Al	Ga	In
Continental crust abundance (ppb)	10 ⁴	8.2 x 10 ⁷	1.8 x 10 ⁴	2.5 x 10 ²
World production (tonnes year ⁻¹)	2 x 10 ⁶	4 x 10 ⁷	100	450
Electronegativity (Pauling scale) χ	2.04	1.61	1.81	1.78
Atomic radius (Å)	0.80 – 0.90	1.431	1.22 – 1.40	1.62 – 1.68
Single bond covalent radius M(III) (Å)	0.88	1.25	1.25	1.50
$E^\ominus$ (M(III)/M), $a_{H^+} = 1$ (V)	-0.870	-1.662	-0.549	-0.3382
$E^\ominus$ (M(III)/M(I)), $a_{H^+} = 1$ (V)	-	-2.7	-0.72	-0.443
Covalent bonds in M(III) compounds (kJ mol ⁻¹)				
M-H	377	282	260	225
M-Cl	444	426	363	327
M-C	376	280	245	162
M-O	559	585	430	360

Table 1.1: Some of the intrinsic properties of group 13 elements.¹

The binary hydrides of the group 13 elements feature bonds which are polarised in the sense $M^{\delta+}-H^{\delta-}$. The negative charge carried by the hydride ligand increases with the reducing power of the metal and the susceptibility of the hydrogen atom towards electrophilic attack typically follows this pattern. Conversely, the metal centres display a tendency towards nucleophilic attack; their electrophilic character depends on both their partial positive charge and the presence of a vacant orbital of accessible energy. The similar size, but greater electronegativity of gallium compared to aluminium (Table 1.1), a direct outcome of the d-block contraction, accounts for the weaker Lewis acidity of GaH₃ (and related GaX₃ complexes) compared with AlH₃, and the reduced polarity of the Ga-H bond.^{1,2} Therefore while both Al(III) and Ga(III) display a tendency to avoid

Chapter I: Introduction

coordinative unsaturation by forming higher nuclearity species, aluminium tends to expand its coordination sphere to a greater degree than gallium, favouring coordination numbers of 5 or 6, compared to 4 or 5 for gallium.

The kinetic and thermodynamic stability of the group 13 hydrides decreases upon descending the group, whereby unimolecular decomposition of MH_3 to MH and H_2 becomes increasingly favourable.²⁻⁴ This arises as an effect of the combination of the “inert pair effect” and the increasing stability of the +1 oxidation state for the heavier group 13 elements, with the reduced strength of the M-H bond.¹

$\Delta_f H^\ominus_{298\text{ K}} (\text{kJ mol}^{-1})$	Al	Ga	In	Tl
MH_3	+ 123	+ 151	+ 222	+ 293
M_2H_6	+ 92 - +184	+ 105 - + 118	+ 175	+ 245

Table 1.2: Standard enthalpies of formation of group 13 hydrides.^{1,4}

The formation of bridging three-centre, two-electron bonding interactions (M-H-M) is proposed to aid in the stabilisation of the uncoordinated lighter group 13 hydrides. The formation of such bridging interactions is enabled by partial donation of electron density from the hydride ligand into the empty valence p-orbital of an adjacent metal.

While decomposition of a discrete molecular hydride MH_n may be initiated by homolytic dissociation of an M-H bond, it is proposed that an associative mechanism which may precede elimination of H_2 offers a lower barrier to decomposition than does a simple dissociative mechanism.⁴ Therefore, the association of binary group 13 hydrides *via* the formation of bridging M-H-M interactions is suggested to be kinetically relevant in their decomposition.¹ Thus, the tendency of group 13 hydrides to associate, and the resulting strength of the M-H-M bridges are likely to be decisive factors in lowering the barrier to homolytic decomposition processes.^{4,5}

1.1.2 Binary hydrides of aluminium and gallium

The aluminium analogue of diborane, $\text{H}_2\text{Al}(\mu\text{-H})_2\text{AlH}_2$, has been characterised as a transient intermediate in the preparation of polymeric alane, $[\text{AlH}_3]_n$, from the laser-ablation of aluminium at 3.5 K in dihydrogen matrices. Due to its highly unstable nature, Al_2H_6 polymerises into $[\text{AlH}_3]_n$ upon removal of the matrix.^{6,7} The most commonly employed route for the preparation of polymeric alane, $[\text{AlH}_3]_n$, is *via* the reaction of LiAlH_4 with AlCl_3 , which allows for the isolation of the donor-free alane or solutions of the ethereal or THF solvates; alane is stable in THF for up to 48 h at room temperature.⁸⁻¹¹ The solid state structure of donor-free $\alpha\text{-AlH}_3$, as determined by X-ray crystallography, features aluminium atoms in 6-coordinate octahedral environments, each bound by six Al-H-Al bridging interactions.¹¹ Donor-free gallane, which may be prepared from the reaction of monochlorogallane, $\text{H}_2\text{Ga}(\mu\text{-Cl})_2\text{GaH}_2$, and LiGaH_4 at -30°C , is considerably less thermally stable than its lighter homologues.^{12,13} Whilst the lack of thermal stability of gallane has precluded its structural characterisation in the solid state, a series of studies such as infra-red spectroscopy (in the vapour phase), low temperature ^1H NMR, gas-phase electron diffraction and trapping experiments are indicative of the presence of Ga_2H_6 , with a structure comparable to B_2H_6 .

The stabilisation of reactive MH_n fragments ($\text{M} = \text{Al}, \text{Ga}$), by the suppression of aggregation, may be achieved by a variety of chemical methods. These methods are based on stabilisation of the group 13 hydrides (i) electronically, by coordinative saturation of the metal centre and (ii) sterically, by the use of bulky ligands which spatially inhibit the formation of M-H-M bridges.

1.1.3 Lewis base adducts of M(III) hydrides: AlH_3 and GaH_3

The thermal fragility and propensity of binary hydrides of aluminium and gallium towards aggregation render them unattractive MH_3 sources for synthetic purposes. This has led to the development of a range of Lewis base adducts of the hydrides, formed by coordination of a charge neutral or anionic donor. Such adducts are more synthetically convenient reagents due to their improved solubility, increased thermal stability and lower degree of aggregation.¹ Whilst these adducts may be accessed by the addition of the donor to the parent hydride, more extensively employed approaches are based on the displacement of a weakly-bound donor, such as NMe_3 or H^- .^{14–17} Structural characterisation of charge-neutral adducts of alane or gallane has been achieved predominantly for adducts featuring nitrogen-, phosphorus-, oxygen- or carbene-based donors. Structurally, charge-neutral adducts of group 13 hydrides exhibit a number of trends which relate to the differing Lewis acidities and covalent radii of the metals, together with the electronic and steric properties of the ligand.

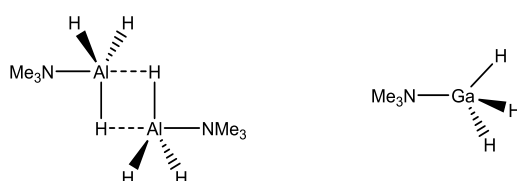


Figure 1.1: Contrasting solid-state structures of $[\text{Me}_3\text{N}\cdot\text{AlH}_3]_2$ and $\text{Me}_3\text{N}\cdot\text{GaH}_3$.

Alane and gallane exhibit disparate coordination numbers and geometries, even when provided with an identical ligand environment.^{14,15} Typically, neutral complexes of alane adopt higher coordination numbers than those of gallane. This is demonstrated by the solid state structures of the trimethylamine adducts $[\text{Me}_3\text{N}\cdot\text{AlH}_3]_n$ ($\text{M} = \text{Al}$, $n = 2$; $\text{M} = \text{Ga}$, $n = 1$): $\text{Me}_3\text{N}\cdot\text{GaH}_3$ is monomeric in the solid state, exhibiting a tetrahedral gallium centre, whilst the aluminium analogue exists as a hydride-bridged dimer with each

aluminium centre adopting 5-fold coordination.^{18,19} This arises due to the greater Lewis acidity of aluminium compared to gallium.^{20,21} The more electropositive nature of aluminium also renders the 2:1 Lewis base complex stable – $[(\text{Me}_3\text{N})_2\cdot\text{AlH}_3]$ is stable at room temperature.²² By contrast, the gallium analogue, $[(\text{Me}_3\text{N})_2\cdot\text{GaH}_3]$ may be prepared, but the second NMe_3 donor is labile and lost above -23°C .^{12,23}

The steric and electronic nature of the ligand also plays a significant role in influencing the coordination geometries adopted. Due to the proclivity of aluminium to form pentacoordinate adducts, the formation of monomeric four-coordinate adducts ($\text{L}\cdot\text{AlH}_3$) is observed only when strongly σ -donating or sterically demanding ligands are employed. Examples of ligands which have allowed for the isolation of monomeric alane adducts include quinuclidine and PCy_3 .^{24,25} Additionally, a dimeric gallane $[\text{L}\cdot\text{GaH}_2(\mu\text{-H})_2\text{H}_2\text{Ga}\cdot\text{L}]$ has been prepared, where the use of a smaller amine ligand (NHMe_2 cf. NMe_3) induces higher coordination numbers at the gallium centre.²⁶

Some of the most thermally stable, monomeric group 13 adducts feature *N*-heterocyclic carbene (NHC) donors. The high nucleophilicity of NHCs makes them attractive ligands for the formation of particularly thermally robust adducts of group 13 metal hydrides.²⁷ Additionally, the flanking aryl substituents afford steric protection to the metal centre and reduce the kinetic lability of these complexes. Examples of NHCs which have been employed as donor ligands for the stabilisation of alane and gallane include 5-membered NHCs, such as IMes, IPr and *i*PrMe [^{28,29; 30,31; 31}] and expanded-ring NHCs, such as 6Mes/6Dipp and 7Dipp.^[32,33;34] The alane and gallane adducts of IMes are particularly thermally robust, with $\text{IMes}\cdot\text{AlH}_3$ melting (without decomposition) at 246°C , and $\text{IMes}\cdot\text{GaH}_3$ decomposing at 214°C .^{28,29}

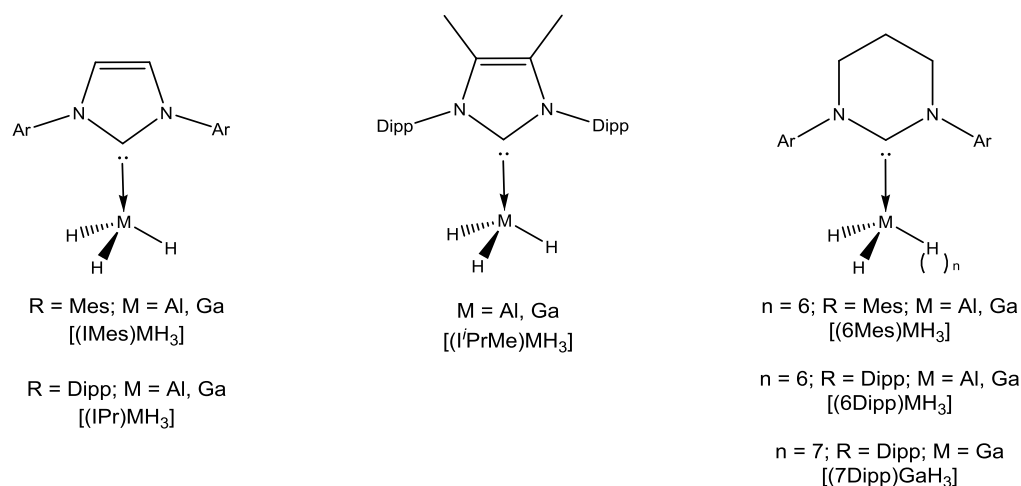


Figure 1.2: Examples of NHC-adducts of alane and gallane.

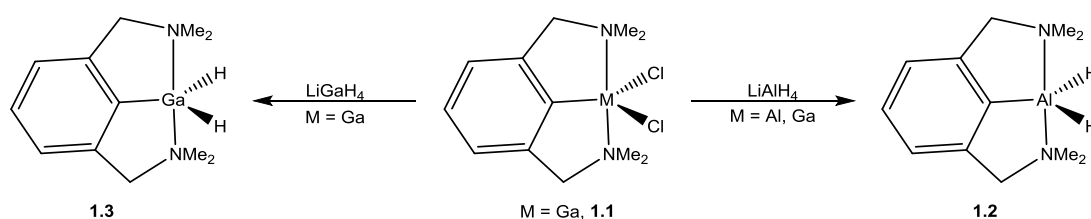
The group 13 hydrides show no tendency towards forming chelating adducts with bidentate, charge neutral donors and instead typically form polymeric structures with a 1:1 ligand: metal stoichiometry.^{2,35}

1.1.4 Organo-alanes and gallanes: preparation

General approaches for the preparation of main-group metal hydrides comprise four routes: (i) addition of H₂ or an E-H functionality to the metal in the elemental or a low-valent oxidation state; (ii) metathesis involving a hydride source and a metal halide; (iii) decomposition or elimination reactions; and (iv) acid-base reactions.² Many of these methods can be used in the preparation of complexes featuring bonds between hydrogen and a group 13 metal, including neutral organo-alane and gallane complexes.

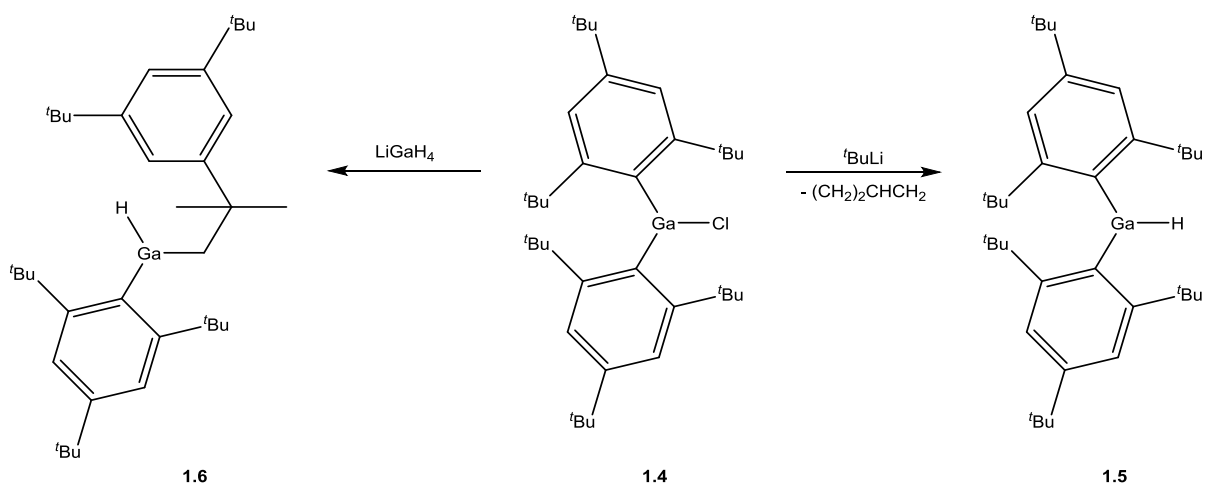
One of the simplest strategies for the preparation of neutral group 13 hydrides is the salt metathesis reaction between the corresponding metal halide complex and a hydride source, such as LiAlH₄, NaBH₄ or M[HBEt₃]. Silanes such as Me₃SiH and stannanes such as Bu₃SnH have also been used as hydride sources.^{36,37} However, the successful preparation of such complexes relies on the selection of the appropriate hydride source, often dictated by its activity. As such, this can severely reduce the synthetic options for

the preparation of aluminium hydrides *via* this preparative route due to the strength of aluminium halide bonds. Thus, whilst the treatment of Ga_2Cl_6 with two equivalents or excess Me_3SiH leads to the formation of Me_3SiCl and $[\text{HGaCl}_2]_2$ or $[\text{H}_2\text{GaCl}]_2$, respectively, the corresponding reaction for aluminium is unsuccessful.^{4,5,37} The fact that the thermodynamics of this reaction are unfavourable for aluminium is shown by the treatment of Me_3SiCl with aluminium hydride sources such as LiAlH_4 , which leads to the formation of Me_3SiH , at the expense of one of the Al-H bonds of LiAlH_4 .



Scheme 1.1: The preparation of group 13 element dihydrides stabilised by aryl ligands functionalised in the 2- and 6-positions *via* salt metathesis or transmetallation reactions.

Additionally, the choice of hydride source may be dictated by the possibility that exchange may also lead to mixed hydride derivatives, such as group 13 borohydride complexes (see section 1.1.6) or that transmetallation can offer a competing reaction pathway.⁴ This is illustrated by the preparation of aluminium and gallium dihydride complexes that feature pincer aryl ligands. The metathetical reactions of $[(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{MCl}_2$ (M = Al, Ga **1.1**) with LiAlH_4 and LiGaH_4 , respectively, yield the corresponding dihydride complexes $[(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{MH}_2$ (M = Al **1.2**, Ga **1.3**). By comparison, the treatment of **1.1** with LiAlH_4 yields **1.2** *via* a transmetallation reaction.^{38,39} The importance of the use of an appropriate hydride source is reflected in the reactivity of $\text{Mes}^*_2\text{GaCl}$ (**1.4**) with two different reagents. Treatment with $^t\text{BuLi}$ leads to the isolation of the gallium monohydride Mes^*_2GaH (**1.5**),⁴⁰ while reaction with LiGaH_4 leads to the isolation of an “aryl-rotated” isomer of the monohydride (**1.6**).⁴¹



Scheme 1.2: The choice of hydride source can greatly influence the product obtained.

Another method utilised for the preparation of organoalanes and gallanes is the addition of H_2 or an E-H functionality to the metal in a low-valent oxidation state.¹ The photoinduced addition of H_2 or HCl to molecular derivatives of the subvalent group 13 metals, such as MCl ($\text{M} = \text{Al}, \text{Ga}$) in argon matrices has been demonstrated to lead to the formation of monomeric $\text{M}(\text{Cl})\text{H}_2$ or $\text{M}(\text{Cl})_2\text{H}$, respectively.^{42,43} In a similar fashion, the monohydrides AlH and GaH can function as precursors to AlH_3 and $\text{Ga}(\text{Cl})\text{H}_2$, respectively.^{44,45} Such studies are however limited to matrix-isolation and the viability of such methods as a means of preparation on a large scale is questionable.

1.1.5 Organo-alanes and gallanes: examples

The partial replacement of hydrides from MH_n fragments by other ligands is a commonly employed strategy to improve the thermal stability of such systems. This may be achieved thermodynamically or kinetically by the use of ligands which provide steric and/or electronic protection. In the past decade, this has led to the isolation of numerous mixed hydrides of the form $[\text{RMH}_2]_n$ and $[\text{R}_2\text{MH}]_n$ ($\text{M} = \text{Al}, \text{Ga}$), for a variety of organic and inorganic R substituents including halides, alkoxides, aryloxides, phosphides, arsenides, amides and imides.¹¹⁷ The substitution of hydrides for halides

may be used as a method for the stabilisation of group 13 hydrides by increasing the bond enthalpies of the remaining M-H bonds by inductive polarisation of the MX_n core.⁴⁶ Additionally, the increased Lewis acidity of the halohydrides relative to the trihydrides leads to increased thermal stability of their neutral-donor adducts.⁴⁷ However, unless the R substituent is sufficiently bulky or tailored to function as a multidentate ligand, these “base-free” hydrides tend to exist as oligomers under ambient conditions, with bridging M-X-M (X = N, P, As, O, Cl, H) interactions, leading to the formation of 4- or 6-membered cyclic arrays.

As such, *monomeric* organoalanes and gallanes incorporate ligands which curb their tendency to participate in bridging M-H-M interactions. This may be achieved through the use of sterically encumbering substituents which reduce the extent of aggregation or those that are multidentate and coordinatively saturate the metal centre.^{1,2}

The steric bulk of the R substituent has been shown to play a key role in determining the extent of oligomerisation in charge neutral alane and gallanes of the form R_2MH and RMH_2 (R = alkyl or aryl substituent).^{41,48–54} The use of very sterically bulky aryl ligands has enabled the isolation of a range of monomeric group 13 mono- and dihydride complexes. Thus, the employment of the Mes^* ligand ($\text{Mes}^* = 2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2$) has allowed for the isolation of monomeric, non-donor stabilised group 13 monohydrides (Mes^*_2MH (M = Ga (**1.5**), Al), $\text{Mes}^*\text{AlH}(\text{Cl})$) and the gallium dihydride complex Mes^*GaH_2 (**1.7**) (Figure 1.3).^{40,41,50,53} The analogous aluminium dihydride is dimeric $[\text{Mes}^*\text{AlH}(\mu\text{-H})]_2$ (**1.8**) in both the solid and solution state. The contrasting extent of oligomerisation of **1.7** and **1.8** reflects both the greater propensity of aluminium to adopt higher coordination numbers and the greater polarity of the Al-H bond (cf. Ga-H).⁴⁹

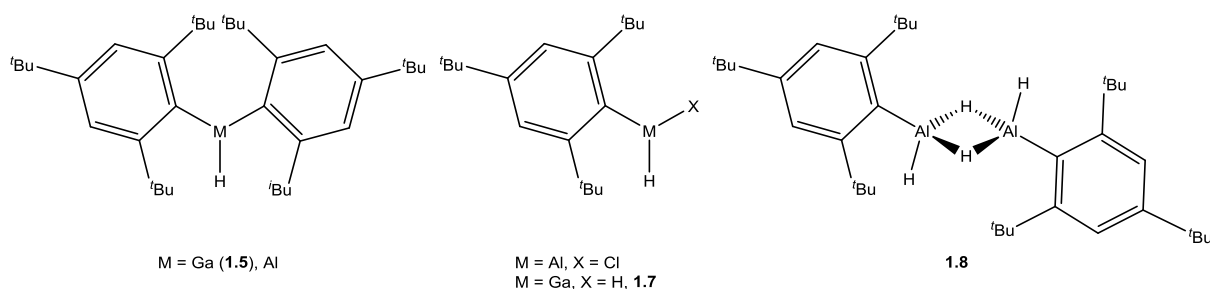


Figure 1.3: Examples of alanes and gallanes which feature the super bulky Mes* ligand.

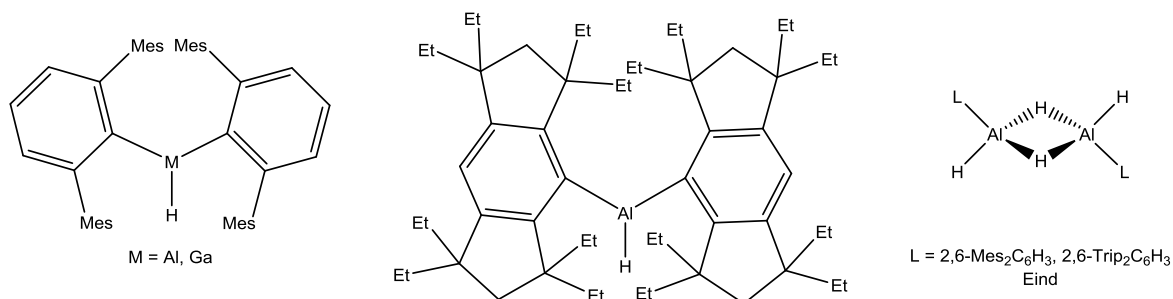


Figure 1.4: Group 13 monohydrides that feature bulky terphenyl^{18,19} or Eind⁵⁴ ligands are monomeric whereas the corresponding aluminium dihydrides are dimeric.

By contrast, attempts to isolate analogues of these species that bear the marginally less sterically encumbering Tripp ligand lead to the isolation of the hydride-bridged dimers $(\text{Tripp}_2\text{MH})_2$ ($\text{M} = \text{Al}, \text{Ga}$).⁴⁰ Additionally, reported attempts to isolate monomeric, base-free alanes that are ligated by a single terphenyl ligand lead to the isolation of the dimeric alanes $(\text{LAlH}_2)_2$ ($\text{L} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$ or $2,6\text{-Tripp}_2\text{C}_6\text{H}_3$).^{40,53} This suggests that these planar aryl substituents possess the ability to rotate into an orientation which provides reduced steric and electronic protection to the metal centre.

An alternative approach to inhibit thermal decomposition of intrinsically fragile group 13 metal hydride fragments involves coordination of the metal centre by a suitable Lewis base. Hence, a methodology that is heavily employed in the isolation of monomeric group 13 M(III) hydrides is the use of aromatic ligands which feature tethered Lewis basic substituents that may coordinate to the metal centre.^{16,38,39,48,57–63}

Chapter I: Introduction

Examples of such ligands include those based on aryl substituents which are functionalised in the 2- and 6-positions e.g. $(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3$. The use of this class of ligand has allowed for the isolation of the monomeric aluminium and gallium dihydride complexes $[(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{MH}_2$ ($\text{M} = \text{Al}, \text{Ga}$), in which the metal adopts a trigonal bipyramidal coordination geometry.^{38,39} The impact of this intramolecular coordination on the thermal stability is illustrated by the decomposition temperature of $[(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{GaH}_2$ ($T_{\text{decomp}} > 350^\circ\text{C}$), compared to that of $(\text{Me}_3\text{N})_2\text{GaH}_3$ ($T_{\text{decomp}} < -23^\circ\text{C}$).²³ Additionally, the presence of two tethered Lewis basic functionalities is apparently crucial to achieve coordinative saturation of the metal centre in many cases. Thus, whilst the gallium hydride complex which features organo-substituents which bear one tether arm, $[(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{GaH}_2$ is monomeric, the corresponding alane exists as a hydride-bridged dimer.⁵⁷ Additionally, while the gallium dihydride monomer $[(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{GaH}_2$ is initially formed, it undergoes a redistribution reaction over the course of several days at -20°C to form $[(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{GaH}$. Evidently, the employment of aryl ligands which bear a single intramolecularly-coordinating substituent results in a significantly diminished ability to electronically and sterically saturate the metal centre.

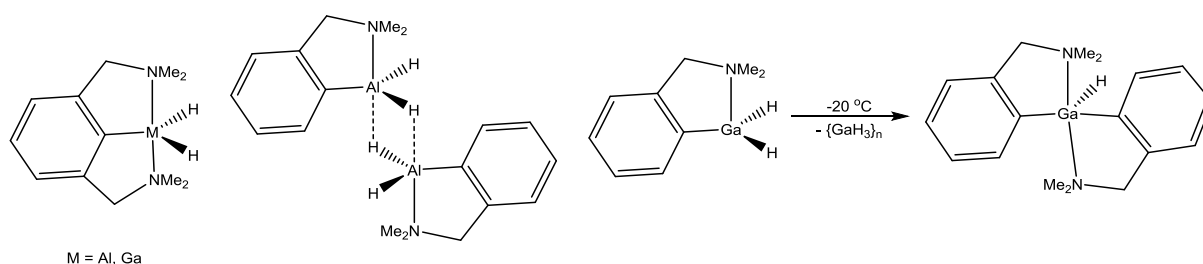


Figure 1.5: The use of aryl ligands with chelating amino donors can stabilise M(III) alanes and gallanes.

This has led to an investigation of ligands which feature both an intramolecularly-coordinating substituent and high steric bulk, to saturate the metal centre and hence stabilise monomeric group 13 hydrides ($M = \text{Al}, \text{Ga}$). A number of ligands which bring success to this field have been reported including, but not limited to, β -diketiminate ligands (discussed in more depth in Section 1.2.) (**A**),^{64,65} ketiminate (**B**),^{66,67} amidinate (**C**),^{68,69} guanidinate,⁷⁰ triazenide,⁷¹ phosphinimine-amide (**D**),^{72,73} aminotroponimine (**E**),⁷⁴ and 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxanthene) ligands (**F**) (Figure 1.6).⁷⁵

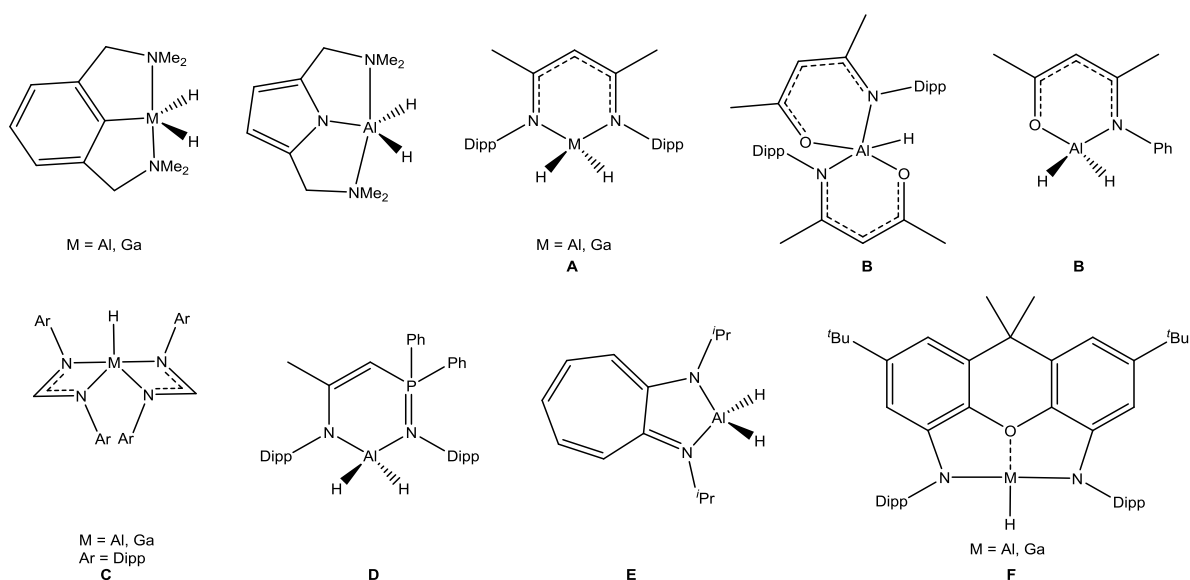


Figure 1.6: Examples of ligands which have led to the isolation of monomeric group 13 hydrides.

1.1.6 Borohydride derivatives of aluminium and gallium

The prevailing structural feature of organo-group 13 hydrides is their tendency to form bridging $M\text{-H-M}$ linkages.² The bridging hydride may not always be located between two identical group 13 metals, and a bridging $M\text{-H-M'}$ interaction may include another main group element⁷⁶ or a transition metal.⁷⁷⁻⁸⁰ Of particular relevance to this thesis is the formation of bridging interactions between a heavier group 13 metal and boron, not

least because borohydride reagents are commonly used as hydride sources for the metathetical generation of heavier hydrides.² For example, the treatment of $[\text{H}_2\text{GaCl}]_2$ with LiBH_4 at 250 K leads to the formation of the mixed-metal hydride complex $[\text{H}_2\text{Ga}(\text{BH}_4)]_n$ rather than gallane $(\text{GaH}_3)_n$.⁸¹ The treatment of group 13 halide complexes with alkali borohydride reagents has been established as a synthetic route for the preparation of heavier borohydride complexes.^{82,83} This is illustrated in the synthesis of $\text{Al}(\text{tmp})_2(\text{BH}_4)$, formed from the addition of LiBH_4 to $\text{Al}(\text{tmp})_2\text{Br}$.⁸³ Alternatively, these borohydride complexes may be synthesised by ligand distribution reactions between metal alkyl (MR_3) and metal borohydride reagents ($\text{M}(\text{BH}_4)_3$) ($\text{M} = \text{Al}, \text{Ga}$), or by the nucleophilic displacement of X from masked boranes of the nature $\text{X} \cdot \text{BH}_3$ ($\text{X} = \text{SMe}_2, \text{THF}, \text{DippNH}_2$) by an alane or gallane.⁸⁴ This is illustrated by the reaction of $(\text{AlH}_3)_n$ with $\text{THF} \cdot \text{BH}_3$, yielding a range of species of the type $\text{AlH}_{3-n}(\text{BH}_4)_n$.⁸⁴

Despite their thermal fragility, a number of examples of borohydride derivatives of aluminium and gallium have been structurally characterised by gas-phase electron diffraction,^{4,85} including $\text{H}_2\text{Ga}(\text{BH}_4)$,^{81,86} $\text{HGa}(\text{BH}_4)_2$,⁸⁷ $\text{Me}_2\text{M}(\text{BH}_4)$ ($\text{M} = \text{Al}, \text{Ga}$),^{82,88} $\text{MeAl}(\text{BH}_4)_2$ ⁸⁹ and $\text{Al}(\text{BH}_4)_3$.⁹⁰ The investigation of such complexes in the solid state is frustrated by their thermal lability, with gallium borohydride complexes displaying a marked tendency towards decomposition to the metal, dihydrogen and diborane under ambient conditions.^{86,91,92} Solid-state structural characterisation of such complexes has been achieved in only a few cases, and examples of mixed group 13 hydrides whose structures have been elucidated in both the solid and vapour phases include $\text{Me}_2\text{Al}(\text{BH}_4)$, $\text{Al}(\text{BH}_4)_3$ and $\text{H}_2\text{Ga}(\text{BH}_4)$.^{81,82,86,88,90} Derivatives of the form $\text{R}_2\text{M}(\text{BH}_4)$ ($\text{M} = \text{Al}, \text{R} = \text{Me}; \text{M} = \text{Ga}, \text{R} = \text{H}$) exist as discrete molecules of the form $\text{R}_2\text{M}(\mu\text{-H})_2\text{BH}_2$ in the gaseous phase, featuring a bidentate mode of ligation of the BH_4 ligand, but adopt $[\text{BH}_4]$ -bridged

polymeric structures in the solid phase. This bidentate mode of ligation of the $[\text{BH}_4]$ ligand, featuring bridging 3-centre, 2-electron M-H-B interactions, is common in complexes featuring both group 13 elements and other elements, including transition metals, lanthanides and actinides.⁹³

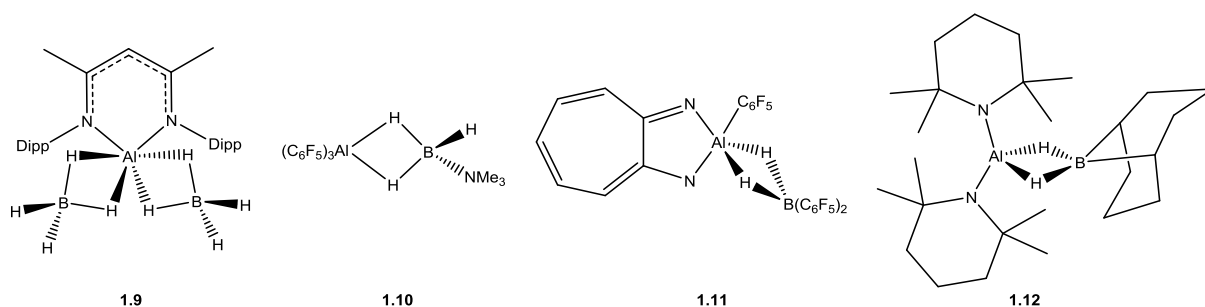


Figure 1.7: Examples of aluminium borohydride complexes.

Within the field of mixed hydrides of the group 13 elements, aluminium borohydride complexes have attracted the most attention, and many examples have been characterised crystallographically. These include complexes of the form $\text{L} \cdot \text{Al}(\text{BH}_4)_3$ ($\text{L} = \text{NMe}_3, \text{NH}_2\text{Me}$),^{94,95} $[\text{L}][\text{Al}(\text{BH}_4)_4]$ ($\text{L} = \text{Ph}_3\text{MePh}$ or PPN),⁹⁶ $[\text{Al}(\text{BH}_4)_2(\text{OSiMe}_3)]_2$ ⁹⁷ and $[\text{Al}(\text{BH}_4)(\text{H}_2\text{TiCp}_2)]_2$.⁸⁰ While the majority of aluminium borohydride complexes feature the $[\text{BH}_4]^-$ ligand, a number of examples have been reported in which the boron centre bears substituents other than hydrides, including $\text{B}(\text{C}_6\text{F}_5)_2$ and 9-BBN fragments.^{83,98–100} In addition, it has been demonstrated that the installation of bulky, chelating ligands at the aluminium centre leads to significant improvement of the thermal stability of borohydride complexes. As such, the complex $\{\text{HC}(\text{MeCNDipp})_2\}\text{Al}(\kappa^2\text{-H}_2(\text{BH}_2))_2$ ($[\text{Dipp}^1]\text{Al}(\kappa^2\text{-H}_2(\text{BH}_2))_2$) (**1.9**), which features a chelating Nacnac ligand and two κ^2 borohydride ligands, is sufficiently thermally stable to be crystallographically characterised in the solid state.⁸⁴ The bulky Nacnac ligand kinetically stabilises the complex by saturating and immobilising the metal coordination sphere, impeding decomposition processes.⁹³

Whilst examples of amine adducts of gallium borohydride complexes such as $\text{Me}_3\text{N}\cdot\text{Ga}(\text{BH}_4)_2\text{H}$ and $\text{Me}_3\text{N}\cdot\text{Ga}(\text{BH}_4)\text{Me}_2$ have been reported, the scope of such complexes in which the gallium centre is ligated by substituents other than hydride or methyl substituents is relatively limited (Figure 1.8).^{91,101,102} Presumably this relates, at least in part, to both the reduced Lewis acidity of the metal centre and reduced polarity of the M-H bond of gallanes relative to alanes. Despite this, it has been demonstrated that the use of more sterically bulky/chelating ligands significantly improves the thermal stability of these systems: $\text{Me}_3\text{N}\cdot\text{Ga}(\text{BH}_4)\text{Me}_2$ decomposes below -45°C , but the closely related complexes **1.13** and **1.14** are stable up to 100°C .¹⁰²

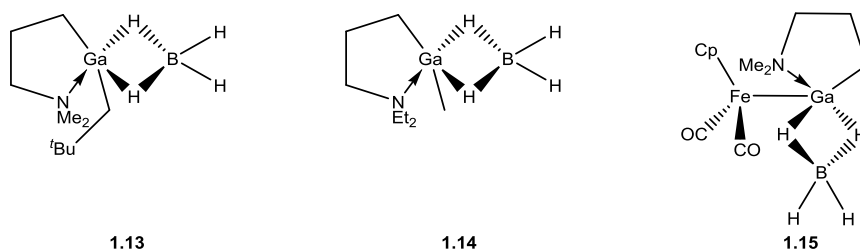


Figure 1.8: Examples of gallium borohydride complexes.¹⁰²

1.1.7 Alanes and gallanes: spectroscopic analysis

Infra-red spectroscopy is one of the most widely used spectroscopic tools for analysis of main-group metal hydrides. In particular, this method is valuable for the analysis of species which are transient under ambient conditions, or those for which the presence of the hydride cannot be reliably established by X-ray diffraction. Additionally, infra-red spectroscopy is a particularly valued tool for the characterisation of group 13 hydrides due to its capacity to distinguish bridging from terminal M-H units. The M-H stretching frequencies ($\nu_{\text{M-H}}$) are typically intense, and occur at sufficiently high wavenumbers that they may be treated as well-defined, localised motions with minimal coupling to other vibrations of the molecule. The positions of bands associated with M-H stretching modes

allow for their secure assignment and their response to deuteration may further support the assignment.

	B(III)	Al(III)	Ga(III)
$\nu(\text{M-H}) \text{ (cm}^{-1}\text{)}$	2200 – 2650	1700 – 1970	1720 – 2050
$\nu(\text{M-H-M}) \text{ (cm}^{-1}\text{)}$	1525 – 2200	930 – 1790	900 – 1720

Table 1.3: Observed (anharmonic) wavenumber ranges of M-H stretching fundamentals for group 13 elements.

The wavenumbers associated with the M-H stretch are particularly sensitive to the nature of the M-H bond and its surroundings. The ranges associated with the stretching frequencies of terminal (M-H) and bridging (M-H-M) group 13 hydrides are shown in Table 1.3. As noted in a review of main group metal hydrides, any changes in the charge separation of this bond affect the $\nu_{\text{M-H}}$ wavenumbers. Specifically any factor that increases the electron density on the metal, such as ligand substitution, typically leads to a reduction in the $\nu_{\text{M-H}}$ wavenumber.² This is reflected in the stretching frequencies associated with the asymmetric ($\nu_{\text{Ga-H}}$, cm^{-1}) mode of gallane and its substituted derivatives: H_2GaCl 1978,⁴² H_3Ga 1923,⁴⁴ $\text{H}_2\text{Ga}(2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2)$ 1887,⁴¹ $\text{Me}_3\text{N}\cdot\text{GaH}_3$ 1820¹⁰³ and LiGaH_4 1760.¹⁰⁴ A similar effect is observed with variation of the oxidation state of the metal and whilst other factors such as coordination geometry play a role, these are less influential.

By contrast, the use of NMR spectroscopy to characterise group 13 hydrides, particularly hydrogen-bridged systems, is somewhat less useful. Broadening of the ^1H NMR resonance associated with the hydride through coupling to a quadrupolar metal nucleus ($^{11}\text{B}/^{69/71}\text{Ga}$: $I = 3/2$; ^{27}Al : $I = 5/2$; ^{115}In $I = 9/2$) may help to identify the presence of a metal-bound hydride. However, this broadening may also lead to difficulty in locating

such resonances in ^1H NMR spectra, in anything other than highly symmetrical environments.

1.2 β -Diketiminato ligands

First reported in 1968, the widespread use of β -diketiminato (Nacnac) ligands for the stabilisation of an extensive range of complexes featuring elements from the *s*-, *p*-, *d*- and *f*-blocks, in a range of oxidation states demonstrates the versatility and popularity of this class of donor.^{105,106} In part, this arises from their synthetically accessible nature but is also due to the facile tuneability of the steric and electronic characteristics of these monoanionic N-donor ligands.¹⁰⁷⁻¹⁰⁹

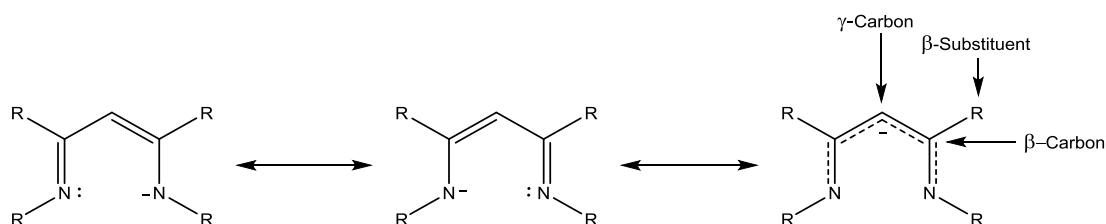


Figure 1.9: Resonance structures for β -diketiminato ligands demonstrating two equally weighted resonance forms (left) and labelling scheme for Nacnac complexes (right).

While a diverse range of coordination modes of Nacnac ligands have been reported, the most common ligation mode is a $\kappa^2-(N,N')$ bidentate coordination mode involving both nitrogen atoms, affording a six-membered metallacycle ring.¹⁰⁵ The resonance structures (Figure 1.9), corroborated by DFT calculations, show the ability of both nitrogens to σ -bond to the metal centre, formally rendering the Nacnac ligand a 4-electron, bidentate donor.¹¹⁰ This ligation mode thermodynamically favours complexation of the metal due to the chelate effect. Moreover, the widespread use of Nacnac ligands has arisen from their ability to kinetically stabilise the resulting metal complexes. This is due to both the strongly σ -donating imine/amido donors and the

sterically protecting flanking groups provided by Nacnac ligands. These features can lead to steric and coordinative saturation of ligated metal centres, thereby inhibiting aggregation, and obstructing potential associative decomposition reaction pathways. The combination of these features leads to the widespread use of Nacnac ligands for the stabilisation of reactive main group metal centres/functionalities.¹⁰⁹

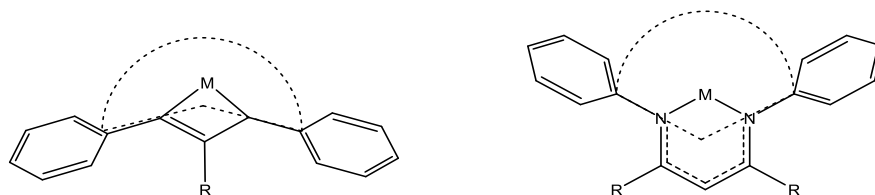


Figure 1.10: The steric protection provided by the flanking aryl substituents in 4 and 6 membered N, N-chelating ligand frameworks.

1.2.1 Steric modification of β -diketiminate ligands

The steric properties of Nacnac ligands may be modulated by variation of the substituents bound to the backbone (γ -C or β -C) or N positions.¹⁰⁹ The installation of a variety of substituents at the β -C position, including t Bu, Ph, CF_3 , NR_2 ($\text{R} = \text{Me}, \text{Et}$) and Me, has been reported and unsubstituted ligands are also known. In a similar fashion, the nature of the N-bound substituent may be varied to modulate access to the metal centre. The use of substituted N-bound aryl groups allows for further control of the steric environment surrounding the metal centre.

Typically, the employment of smaller β -C or N-bound substituents reduces the steric protection of the metal coordination sphere. This can allow oligomerisation of the resulting metal complexes or an increase in the coordination number. It is also observed that the installation of more sterically hindering N-bound substituents may cause unfavourable interactions with the metal, pushing the metal centre out of the plane of the Nacnac ligand. Additionally, an increase in the size of the β -C substituents can lead to

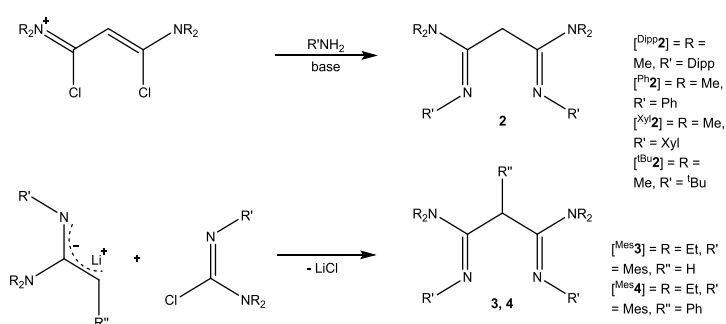
steric conflict between these substituents and those bound to nitrogen, particularly in the case of aryl substituents. This typically pushes the N-aryl ring closer to the metal, causing it to move deeper into the Nacnac binding pocket. These structural changes can have profound effects on both the rate and selectivity of reactivity at the metal centre.¹⁰⁹

1.2.2 Electronic modification of β -diketiminate ligands

The modulation of the electronic properties of Nacnac ligands may be achieved through the functional groups on the backbone (γ - or β -position) or on the N-bound aryl substituents. Whilst this may lead to a change in electron density at the metal centre, the use of these substituents can also significantly impact its steric environment, particularly those located on the β -C or ortho-position of N-aryl substituents.

Typically, modification of the substituents at the γ -C and β -C positions leads to greater variation of the electronic character of the metal centre compared to the N-aryl substituents. The N-aryl ring in Nacnac-ligated complexes typically lies approximately perpendicular to the plane of the ligand, thereby limiting conjugation and the effect that the electronically-modifying substituents may have. As such, effects are more pronounced when there are no substituents at the ortho-position and the N-aryl group can rotate closer to planarity with the ligand backbone.¹¹¹ In most cases, substituents that are located on the ligand backbone lie in the plane of the ligand and impact the electron density of the metal centre to a greater degree.¹⁰⁹ This is nicely demonstrated by an electrochemical study of copper and nickel complexes of the types $\text{LCu}(\text{NCCH}_3)$, $\text{LCu}(\text{OAc})$, L_2Cu and L_2Ni featuring Nacnac ligands of varying electronic properties.¹¹² The redox potentials obtained suggest that NO_2 and CF_3 have the strongest electronic effect, followed by CN and the 3,5-bis(trifluoromethyl)-phenyl substituent.

Most of these efforts have primarily focused on electronic modification of the σ -framework of the ligand system and the use of π -donor substituents including -OMe and -NR₂ (R = Me, Et) is in its infancy.¹¹³ A range of -NR₂ (R = Me, Et) functionalised Nacnac (N-nacnac) ligands have recently been shown to be synthetically accessible. Ligands of this type may be prepared using two distinct synthetic methodologies, the first involving the condensation of a primary amine with a pre-formed bifunctional backbone, and the second by linking two amino-imine units through the α -carbon (Scheme 1.3).¹¹³ The first route yields a range of -NMe₂ functionalised Nacnac ligands with different nitrogen-bound R' substituents whilst the second route allows for functionalisation of the γ -C position, yielding potential for further modification of electronic and steric properties.



Scheme 1.3: Two synthetic routes which yield N-nacnac ligands; the nomenclature used for these ligands.

	X	ΔE_{S-T}
	OMe	74.12
	NMe ₂	27.70
	Me	18.02

Figure 1.11: The ΔE_{S-T} energies (kJ mol⁻¹) determined by DFT for a range of theoretical boron(I) complexes featuring variously substituted Nacnac ligands.

Calculations on model borylene systems indicate that the presence of a backbone π -donor substituent should increase the singlet-triplet energy gap (ΔE_{S-T}), yielding a

more stable complex.¹¹⁴ Similar effects have been experimentally verified in the stabilities of low oxidation state group 13 element complexes which feature amidinate and guanidinate ligands.¹¹⁵ The use of guanidinate ligands (which feature a pendant π -donating amino substituent on the ligand backbone) has allowed for the successful isolation of a Ga(I) complex (Figure 1.12).¹¹⁶ By contrast, attempts to synthesise the corresponding amidinato-gallium(I) complex leads to the isolation of a gallium(II) dimer, arising from a disproportionation reaction.¹¹⁷ The stability of the guanidinate complex is proposed to arise from an increase in the electron donor capabilities of the ligand due to the presence of the π -donating amino group, and it is proposed that this effect is also present in the N-nacnac ligand, leading to enhanced donor properties.¹¹³

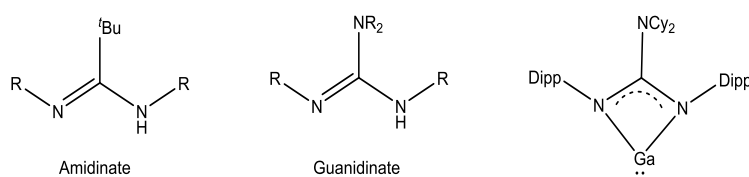


Figure 1.12: Amidine and guanidine protio-ligands and the corresponding gallium(I) guanidinate complex.

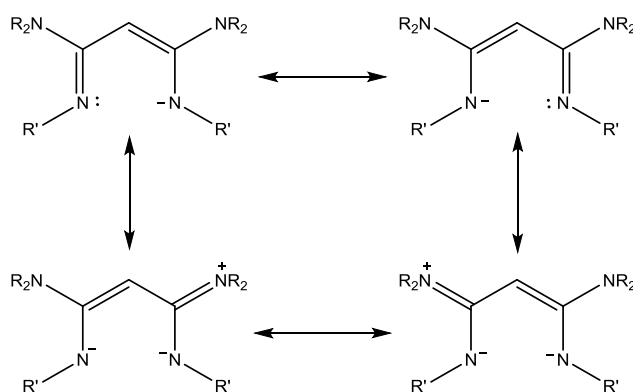


Figure 1.13: Resonance structures of the N-nacnac ligand system. The β -amino substituents can donate electron density into the ligand framework.

The enhanced donor properties of the N-nacnac ligand, arising from inclusion of the pendant NR_2 substituents, is proposed to arise, in Valence Bond terms, from additional

dianionic “double amido” resonance structures incorporating a backbone $=\text{NR}_2^+$ function (Figure 1.13).¹¹³

Studies of the coordination chemistry of N-nacnac ligands are fairly preliminary in nature. Most of the reported metal complexes which feature this novel ligand incorporate group 14 elements although complexes of other *s*-, *p*- and *f*-block elements have also been reported.^{113,118} A number of structural and spectroscopic features are present for these N-nacnac-ligated complexes which are suggestive of some degree of π -delocalisation into the ligand system from the dimethylamino substituents. For example, in the solid state, analysis of all reported N-nacnac ligated complexes by single crystal X-ray crystallography reveals that a common feature is that the C-N distances involving the β -nitrogens lie between typical C-N double and single bonds.^{113,119} In other respects, however, these complexes closely resemble their traditional Nacnac analogues and only minor differences are observed. The use of this ligand has, however, allowed for the isolation of complexes that have not been successfully isolated for the more traditional Nacnac ligands. Thus, for example, the chlorosilylene $[\text{Dipp}2]\text{SiCl}$ is isolable and a diverse range of reactivity, employing this halide complex as a precursor, has been demonstrated.¹¹⁸ By contrast, analogous attempts to synthesise $[\text{Dipp}1]\text{SiCl}$ are unsuccessful, with deprotonation of the *exo*-cyclic methyl substituent occurring to yield an ylide-like N-heterocyclic silylene.¹²⁰ This disparate reactivity arises from the absence of acidic protons at the β -carbon substituent, rather than the electronic properties of the ligand.¹⁰⁵

1.2.3 β -diketiminato-ligated alanes

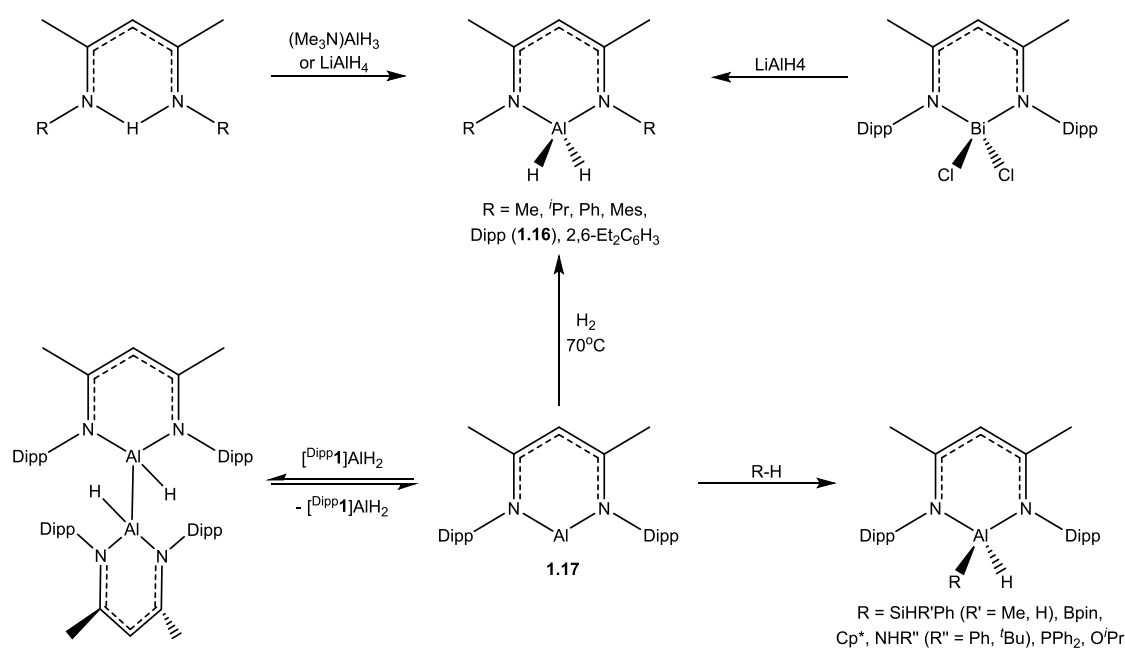
The use of Nacnac ligands in group 13 chemistry has gained prominence through their ability to stabilise the metals ($\text{M} = \text{Al}, \text{Ga}, \text{In}$) in their +1 oxidation state.^{121–123} As a result

of this, a multitude of organometallic M(III) complexes ($M = \text{Al, Ga}$) have been described in the literature, arising either as precursors for these low oxidation state complexes, or as a result of their reactivity. Nacnac ligands have been demonstrated to be particularly adept at stabilising monomeric aluminium hydride complexes, and a range of examples of such complexes have been reported. The kinetic stabilisation provided by the Nacnac ligand is seen in the enhanced thermal stability of the Nacnac complexes relative to the binary hydrides; for example, the decomposition temperature of polymeric $(\text{AlH}_3)_n$ is 80°C whilst that of $[\text{Mes}\mathbf{1}]\text{AlH}_2$ is 200°C .^{124,125}

The most well known of these hydrides are the dihydride complexes of the form $[\text{R}\mathbf{1}]\text{AlH}_2$, which have been reported with a range of *N*-bound substituents of varying steric bulk ($\text{R} = \text{Me, }^i\text{Pr, Ph, Mes, Dipp, 2,6-Et}_2\text{C}_6\text{H}_3$).^{67,125–128} These complexes are typically generated by deprotonation of the corresponding protio-ligand with aluminium hydride sources such as $\text{Me}_2\text{RN}\cdot\text{AlH}_3$ ($\text{R} = \text{Me, Et}$) or LiAlH_4 , or by transmetallation reactions. Thus treatment of $[\text{Dipp}\mathbf{1}]\text{BiCl}_2$ with LiAlH_4 leads to the quantitative generation of $[\text{Dipp}\mathbf{1}]\text{AlH}_2$ (**1.16**).¹²⁹ **1.16** can also be synthesised from the oxidative addition of H_2 at the Al(I) centre of $[\text{Dipp}\mathbf{1}]\text{Al(I)}$ (**1.17**) when heated to 70°C .¹³⁰

One of the primary modes of reactivity of reagents containing aluminium in the +1 oxidation state is the oxidative addition of substrates (including E-H bonds) across the Al(I) centre.^{130–134} Since 2014, this reactivity has been exploited to access unsymmetrically substituted aluminium hydride complexes of the form $[\text{Dipp}\mathbf{1}]\text{Al(R)H}$, for a range of *R* substituents (e.g. $\text{R} = \text{SiHR}'\text{Ph}$ $\{\text{R}' = \text{Me, H}\}$, *Bpin*, *Cp**, NHR' $\{\text{R}' = \text{Ph, }^t\text{Bu}\}$, PPh_2 , *OⁱPr*).¹³⁰ Interestingly, **1.17** oxidatively adds the Al-H bond of **1.16** when the complexes are mixed in an equimolar ratio in C_6D_6 . An equilibrium is set up between these complexes and the aluminium(II) hydride $\{[\text{Dipp}\mathbf{1}]\text{Al(H)}\}_2$.¹³⁰ Whilst the chemistry

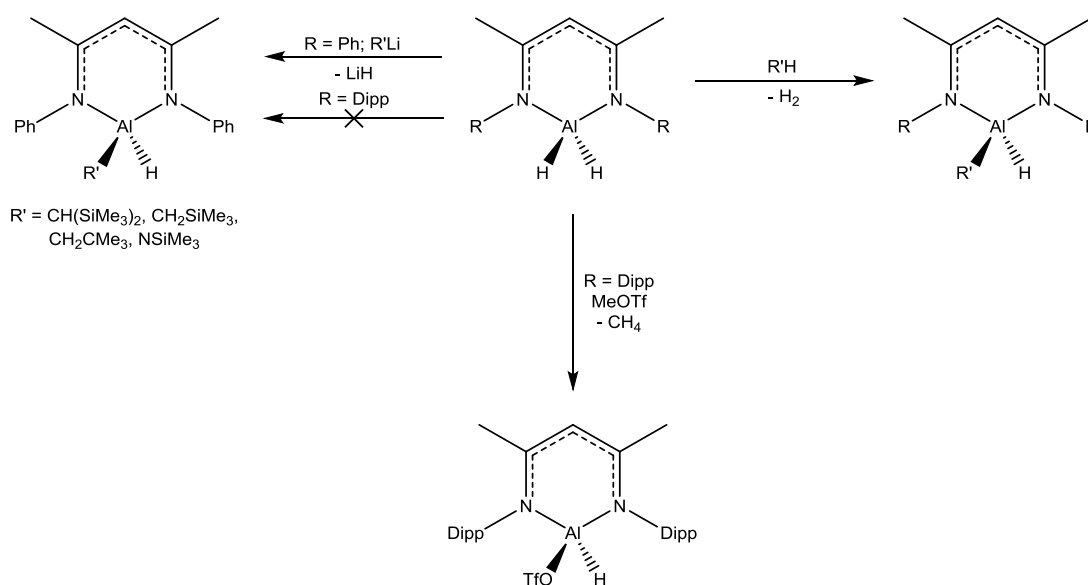
of Nacnac-ligated aluminium hydride complexes is significantly more well-developed than that of gallium, the use of **1.17** as a precursor for unsymmetrically substituted aluminium hydrides is far less utilised than the gallium analogue.^{135,136} Aluminium(I) compounds show the greatest tendency of the group 13 metal(I) species to reduce substrates and form aluminium(III) compounds.¹ Conversely, monomeric Al(I) fragments are far less stable than their heavier group 13 homologues, a direct consequence of the inert pair effect, rendering them less accessible synthetic reagents.



Scheme 1.4: Some of the routes employed for the preparation of Nacnac-ligated alanes.

Given the difficulty in accessing Al(I) precursors, a range of alternative synthetic methodologies for the preparation of unsymmetrically substituted aluminium hydrides has been developed. The most commonly employed strategy is the exchange of one of the hydride substituents of the dihydride complexes $[R^1]AlH_2$. In many cases, this method utilises the basic nature of the Al-H bond to deprotonate substrates such as alcohols, amines, anilines and alkynes, producing hydrogen and the unsymmetrically substituted alane.¹³⁷⁻¹⁴² Alternatively, the reaction of **1.16** with trifluoromethane

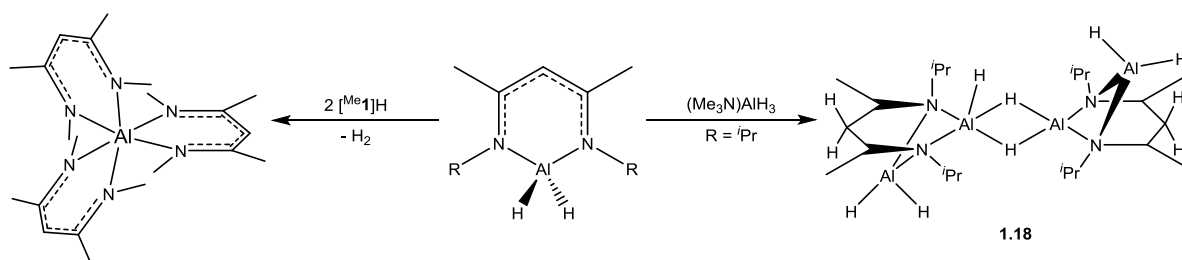
sulfonate (MeOTf), installs a triflate substituent at the aluminium centre, generating methane as the co-product.¹⁴³ An alternative method involves metathesis chemistry: complexes $[\text{Ph}\mathbf{1}]\text{Al}(\text{R})\text{H}$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2, \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{CMe}_3, \text{NSiMe}_3$) may be synthesised by treatment of $[\text{Ph}\mathbf{1}]\text{AlH}_2$ with the corresponding alkyl lithium/amidolithium source, eliminating LiH as the co-product.^{67,144,145} Other routes which yield unsymmetrically substituted aluminium hydrides are somewhat more esoteric. The reaction of $[\text{m-Xyl}\mathbf{1}]\text{AlH}_2$ with Ph_3PCH_2 cleaves the P-C bond of the phosphonium ylide at 60°C , yielding $[\text{m-Xyl}\mathbf{1}]\text{Al}(\text{Ph})\text{H}$.¹²⁸ Additionally, stepwise hydrolysis of the dihydrides $[\text{R}\mathbf{1}]\text{AlH}_2$ ($\text{R} = \text{m-Xyl}, \text{Mes}$) yields dialuminoxane hydride complexes $[[\text{R}\mathbf{1}]\text{Al}(\text{H})]_2(\mu\text{-O})$ ($\text{R} = \text{m-Xyl}, \text{Mes}$).^{125,137}



Scheme 1.5: The functionalisation of aluminium dihydrides $[\text{R}\mathbf{1}]\text{AlH}_2$ can lead to the formation of unsymmetrically substituted aluminium monohydride complexes.

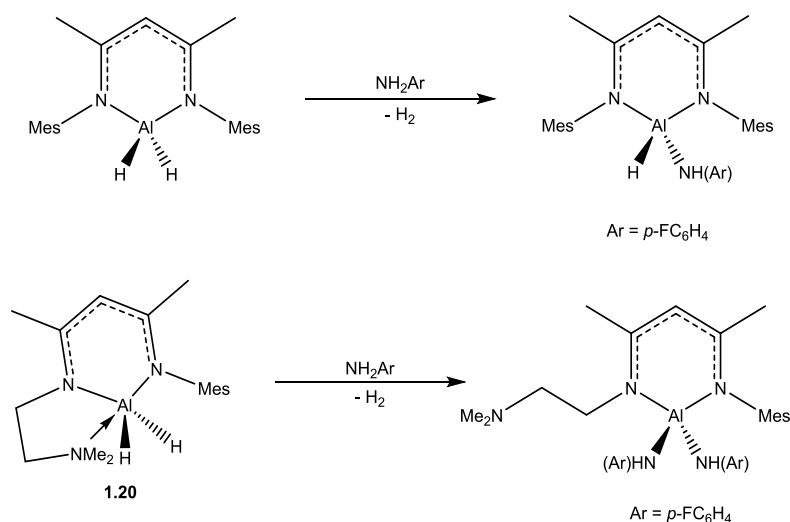
Variation of the steric properties of the Nacnac ligand in aluminium hydride chemistry is limited to modification of the N-bound substituents.^{64,67,146,127} The steric bulk of the R substituent can influence selectivity in the preparation of these dihydride complexes. In the case of $[\text{iPr}\mathbf{1}]\text{H}$, for example, the addition of excess $\text{Me}_3\text{N}\cdot\text{AlH}_3$ results in imine

reduction and the isolation of an unusual tetraaluminium compound (**1.18**; Scheme 1.6).¹⁴⁶ In the presence of excess $[\text{Me}\mathbf{1}]\text{H}$, $[\text{Me}\mathbf{1}]\text{AlH}_2$ yields the tris(β -diketiminate) complex $[\text{Me}\mathbf{1}]_3\text{Al}$.¹⁴⁷ Additionally, the steric profile of the N-bound substituents may also influence the reactivity at the aluminium centre. For example, $[\text{Ph}\mathbf{1}]\text{AlH}_2$ is amenable to elimination of LiH when treated with select alkyl lithium/amidolithium reagents whilst $[\text{Dipp}\mathbf{1}]\text{AlH}_2$ is resolutely unreactive.^{67,144,145}



Scheme 1.6: The presence of smaller N-bound substituents can significantly influence the stability of aluminium dihydride complexes.

The variation of the electronic properties of the Nacnac ligand in group 13 hydride chemistry has not been reported. The use of Nacnac ligands which have been electronically-modified by variation of the N-aryl groups within group 13 chemistry is relatively limited but a number of alkyl aluminium complexes ligated by Nacnac complexes which bear fluorinated aryl substituents have been reported, e.g. $[\text{C}_6\text{F}_5\mathbf{1}]\text{Al}(\text{Me})\text{R}$ ($\text{R} = \text{Me}, \text{Cl}, \text{I}$), $[\text{C}_6\text{F}_5\mathbf{1}]\text{Al}(\text{R}')_2$ ($\text{R}' = \text{Br}, \text{OTf}$). A different method used to modulate the electronic properties of the Nacnac ligand is *via* the backbone C-bound groups.¹¹³ The application of these ligands towards group 13 chemistry is largely unexplored and only one example of such a complex has been reported: $[\text{Dipp}\mathbf{2}]\text{Al}(\text{Me})_2$ (**1.19**).¹¹³ **1.19** appears to show very few differences, spectroscopically and structurally, when compared to its Nacnac-counterpart.^{148–151} The impact of the modification of the electronic properties of the ligand on the chemistry of these complexes is largely unexplored.^{150,152}



Scheme 1.7: The use of a Nacnac-ligand which features an N-bound amino donor functionality influences both the coordination number of the aluminium centre and the dehydrocoupling reactivity of the dihydride.

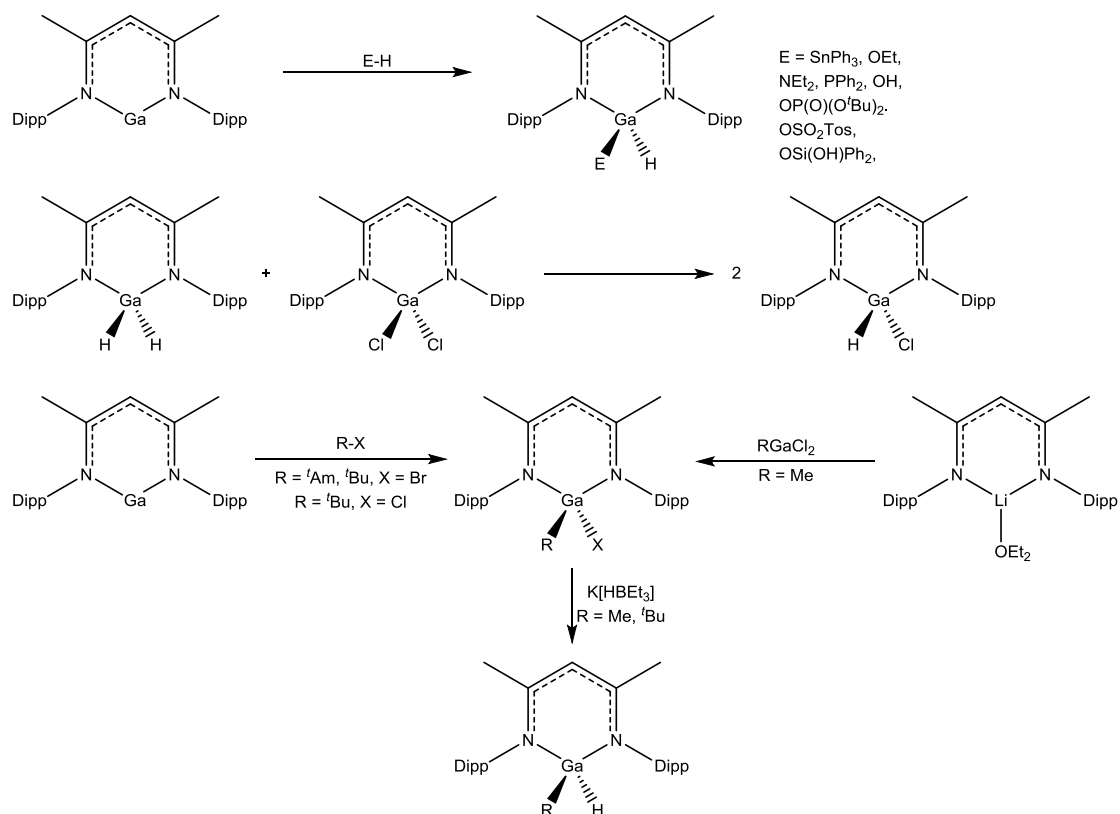
A further modification of the Nacnac ligand which can modulate the coordination number of the aluminium centre is *via* incorporation of additional donors. The replacement of one of the Dipp substituents of $[\text{Dipp}\mathbf{1}]\text{H}$ with an amino-tether leads to the formation of a novel ligand $[\text{DippNC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NMe}_2]$, which has been shown to react with LiAlH_4 or $\text{Me}_3\text{N}\cdot\text{AlH}_3$ to yield the corresponding aluminium dihydride complex $[\kappa^3\text{-DippNC}(\text{Me})\text{CHC}(\text{Me})\text{NCH}_2\text{CH}_2\text{NMe}_2]\text{AlH}_2$ (**1.20**). The aluminium centre of **1.20** is found in a trigonal bipyramidal geometry in both the solid and solution phases.¹²⁸ The coordination of the amino substituent leads to a significant reduction in the Al-H stretching frequency associated with the aluminium hydride ($\nu_{\text{Al-H}}$ 1743 cm^{-1}) compared to the related four-coordinate aluminium hydride **1.16** ($\nu_{\text{Al-H, av}}$ 1814 cm^{-1}). The influence of this additional donor group on the chemistry of this hydride is relatively unexplored.^{141,153} However, differences in the reactivity compared to $[\text{Mes}\mathbf{1}]\text{AlH}_2$ (**1.21**) are reflected in their dehydrocoupling reactivity towards anilines. While **1.21** reacts with *p*-fluoroaniline to yield the corresponding mono-substituted product, **1.20** reacts spontaneously with *p*-fluoroaniline to yield the *bis*-substituted

product and the hydrido/amide intermediate could not be isolated. It is proposed that dissociation of the pendant amine functionality occurs following the first Al-N bond formation, opening up the coordination sphere at aluminium and favouring the second dehydrocoupling.

1.2.4 β -diketiminato-ligated gallanes

The library of reported Nacnac-ligated gallium hydrides is significantly less well developed than for aluminium, and most of their established chemistry is derived from the gallium dihydride complexes $[\text{R}\mathbf{1}]\text{GaH}_2$. As for the alanes, the Nacnac ligand renders these hydrides monomeric and imparts thermal stability; the decomposition temperature of $\{\text{GaH}_3\}_n$ is -30°C whilst that of $[\text{Mes}\mathbf{1}]\text{GaH}_2$ is 149°C .^{12,154} Variation of Nacnac-ligated gallium hydride complexes by modification of the ligand is limited to that of the N-bound aryl substituents $[\text{R}\mathbf{1}]\text{GaH}_2$ ($\text{R} = \text{Ph}, \text{Mes}, \text{Dipp}$).^{65,67,154} The reported application of electronically-modified Nacnac ligands to gallium chemistry is restricted to two complexes $[\text{C}_6\text{F}_5\mathbf{1}]\text{GaR}_2$ ($\text{R} = \text{Me}, \text{Cl}$) and the difference in the chemistry arising from the use of this ligand is not well established.^{149,155}

Nacnac-ligated gallium hydride complexes have been synthesised by a variety of routes. Deprotonation of the protio-ligand by donor-stabilised sources of GaH_3 , such as $\text{EtMe}_2\text{N}\cdot\text{GaH}_3$ or LiGaH_4 leads to the formation of $[\text{Ph}\mathbf{1}]\text{GaH}_2$.⁶⁷ Alternatively, metathetical reactions of Nacnac-ligated gallium halide complexes such as $[\text{Dipp}\mathbf{1}]\text{GaX}_2$ ($\text{X} = \text{Cl}, \text{I}$) or $([\text{Mes}\mathbf{1}]\text{GaCl})_2(\mu\text{-O})$ with hydride sources such as $\text{M}[\text{HBEt}_3]$ ($\text{M} = \text{Li}, \text{K}$) or $\text{Me}_3\text{N}\cdot\text{AlH}_3$, respectively, yield the corresponding dihydride complexes.^{65,154}



Scheme 1.8: Synthetic routes reported in the literature for the unsymmetrically substituted Nacnac-ligated gallium hydride complexes.^{65,156,157}

Additionally, the more readily accessible nature of $[\text{Dipp}1]\text{Ga}$ (**1.22**) has led to its use as a precursor for the synthesis of hydride complexes *via* oxidative addition chemistry.¹²¹ A range of hydrides of the form $[\text{Dipp}1]\text{Ga(E)H}$ have been isolated from the activation of dihydrogen or polarised E-H bonds at the Ga(I) centre of **1.22**.^{135,136} Alternatively, alkyl-substituted complexes $[\text{Dipp}1]\text{Ga(E)H}$ may be prepared by metathesis between a gallium halide and a hydride source, such as $\text{K}[\text{HBEt}_3]$.^{65,156} The precursor halide complexes may be prepared from the activation of the C-X bond of a haloalkane by $[\text{Dipp}1]\text{Ga}$ or *via* metathesis between $[\text{Dipp}1]\text{Li(OEt)}_2$ and RGaCl_2 .^{65,156,158}

1.3 The use of main group elements in catalytic reductive processes

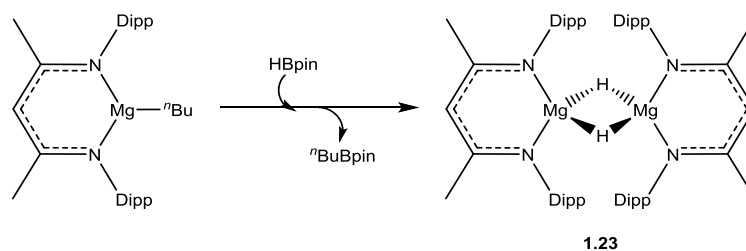
The activation of E-X bonds is fundamental to a wide range of industrially relevant chemical reactions, being a key step in a number of catalytic processes. Bond cleavage

can be accomplished through a variety of routes, the most widely exploited, and hence studied, involves oxidative addition at a transition metal centre. This is generally a facile process owing to both the coordinative flexibility and readily accessible " $n/n+2$ " redox states of "noble" transition metals. Recently however, there has been interest in the development of main group systems that are capable of activating E-X bonds, and hence effecting the catalysis of organic transformations.^{159,160} This has been driven by economical and environmental imperatives, specifically the lower cost, greater abundance and reduced toxicity of main group elements relative to "noble" transition metals.

It was previously conceived that the activation of E-X bonds in simple molecules was solely the domain of transition metals. However, following the first report of the activation of H_2 by a main group system in 2005, it became clear that catalytic transformations using main-group compounds are a genuine possibility.¹⁶¹ In the years following this report, a number of strategies to coax "precious-metal type" behaviour from main-group elements have been investigated. Crucially, in doing this, species have been synthesised which feature characteristics more commonly associated with transition metals: orbitals of the correct symmetry to engage in donation/backdonation interactions with the E-X bond and a small HOMO-LUMO energy gap.

Common strategies for E-X bond activation at heavier p-block element centres include activation by multiply-bonded systems (including tetranelenes and tetrynes), oxidative addition at a low-valent element centre (e.g. Al(I), Ga(I) or Sn(II)) and activation by frustrated Lewis pairs (FLPs). Additionally, a number of approaches based on cooperative reactivity between of a low-valent metal centre with a non-innocent ligand have been developed.

Main group element-containing complexes which feature highly reactive E-X bonds may also be employed for the activation of small molecules. Molecular main group metal *hydrides* have demonstrated particular efficacy for the activation of small molecules, especially those that feature unsaturated functionalities, and such compounds have a long history in the stoichiometric reduction of unsaturated compounds. It is only in the past decade however that such hydrides have been employed to effect reductive transformations in a *catalytic* manner. Thus, a range of main group hydride systems have been developed (e.g. {[^{Dipp}**1**]MgH}₂, **1.23**) which effect the catalytic hydroboration of a wide range of unsaturated functionalities.^{162–164}



Scheme 1.9: The generation of magnesium hydride catalyst **1.23** from the reaction of magnesium alkyl precatalyst, [Dipp¹]**1**Mg(ⁿBu), with HBpin.

1.3.1 Catalytic reduction of CO₂

Within the expanding field of small molecule activation, the reduction and transformation of CO₂ has received appreciable attention, not least because it can produce compounds such as methanol, carbon monoxide, formaldehyde or methane, all of which may be used as simple synthetic building blocks.^{165–170} In addition, CO₂ is an abundant and inexpensive carbon source and is both non-toxic and non-flammable.

Heterogeneously and electrochemically catalysed processes are prominent in this chemistry,¹⁷¹⁻¹⁷⁴ but forays have been made into homogeneous catalysis, particularly based on transition metals, in the past decade.¹⁷⁵⁻¹⁷⁸ By contrast, until 2010, little

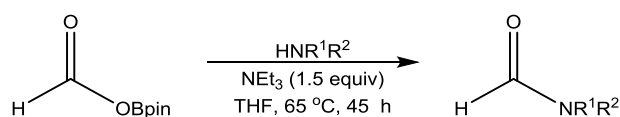
Chapter I: Introduction

attention was given to catalysts based on main group metal and non-metal elements.^{160,176}

The catalytic reduction of CO₂ typically occurs with concomitant abstraction of one of the oxygen atoms, and this type of process has been investigated with H₂,^{179–183} silanes¹⁸⁴ (Section 1.3.3) and boranes both as reductants and oxygen scavengers.^{176,185} The use of H₂ as a reductant can yield methanol or formamides, methylamines and aliphatic alcohols, when the catalytic hydrogenation is undertaken in the presence of amines, imines or olefins, respectively.¹⁸⁶ While the hydrogenation of CO₂ can afford a variety of products and is a desirable process in terms of atom economy, the use of silanes and boranes as reductants allows for the use of significantly milder reaction conditions ($T < 100^{\circ}\text{C}$, $P_{\text{CO}_2} < 3 \text{ atm}$).¹⁸⁵ In addition, the use of silanes or boranes has allowed for the development of catalytic systems which exercise greater control of selectivity in the reduction of CO₂ into C₁ compounds such as CO, CH₂O, HC(O)OH, CH₃OH and CH₄.

Catalytic systems based on ambiphilic compounds, strong Lewis bases, borohydride complexes, Lewis acids, organic compounds and Brønsted bases have all been developed.¹⁶⁰ One such approach that has been exploited to mediate the catalytic reduction of CO₂ is the use of metal hydrides. Metal hydride systems, including both those based on transition metal and main group elements, have demonstrated competence for this process, despite the intrinsic thermodynamic stability of CO₂.^{186–194} Generally, the activation of CO₂ occurs by insertion of one of the C=O bonds into the M-H unit, followed by liberation of the derived formate moiety from the metal centre and regeneration of the metal hydride catalyst, by employing a reductant such as a borane or silane.¹⁹⁵

These catalytic procedures have been demonstrated to yield boryl and silyl derivatives of formaldehyde and methanol, which may be hydrolysed *via* B-O/Si-O bond cleavage.^{167,176} During the course of such studies, a number of other methodologies have been developed which focus on the reductive functionalisation of CO₂ and its transformation into formamides,¹⁸⁹ imines,¹⁹² methyl amines,^{196–198} amins¹⁹⁹ and other functionalised organic molecules.¹⁸⁶

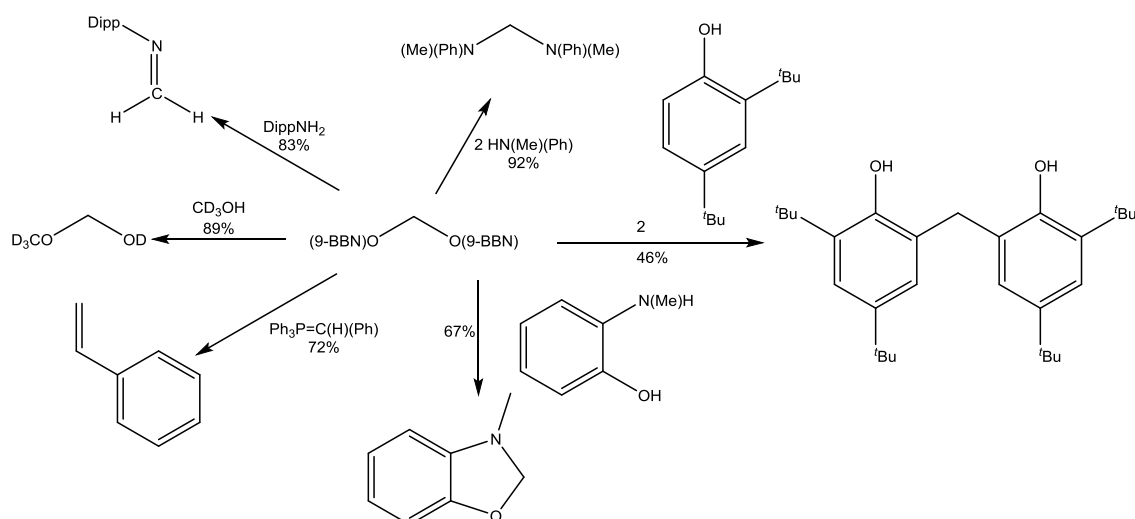


Scheme 1.10: The reaction of HC(O)OBpin with amines yield formamides.

Formic acid derivatives, such as HC(O)OBpin, obtained from the catalytic hydroboration of CO₂, may be used as a formylation reagent for a range of primary, secondary and cyclic amines, yielding the corresponding formamides in good yields (81 – 98%).¹⁸⁹ In addition, where such catalytic procedures generate significant quantities of formaldehyde, it may be used to form imines *via in situ* condensation with primary amines, such as DippNH₂.¹⁹² The hydrolysis of such imines regenerates the corresponding amine and a formalin solution, demonstrating that CO₂ may be used as a C₁ feedstock to generate formaldehyde.

Additionally, bis(boryl)acetal complexes, H₂C(OBR₂)₂ (R₂ = (9-BBN), pin), have been demonstrated to function as a versatile methylene transfer agent in the formation of novel C-N, C-O, C-C, C=N and C=C bonds (Scheme 1.11).^{186,200}

A number of catalysts have been described which effect the methylation of primary and secondary amines *via* the reduction of CO₂.^{196–198} This has been achieved employing boranes, silanes and H₂ as reductants.



Scheme 1.11: Bis(bora)acetal complexes may act as methylene transfer agents.

1.3.2 Catalytic hydroboration of CO₂

Hydroboration of CO₂ is a valuable methodology for the reduction of CO₂ and a variety of catalysts for this process have been reported. Up to three hydroboration reactions may occur, giving rise to formoxyborane compound HC(O)OBR₂, bis(boryl)acetal compound H₂C(OBR₂)₂ or methoxyborane compound MeOBR₂, with concomitant formation of the diboroxane, O(BR₂)₂. The driving force for the reaction is the formation of strong B-O bonds and, in particular, the formation of the diboroxane. Initial activation of CO₂ typically occurs by hydride transfer and catalysts which can effect this process include metal hydride complexes, ambiphilic compounds, strong Lewis bases or borohydride complexes.¹⁸⁵

1.3.2.1 Transition metal hydride catalysts

Some examples of transition metal hydride catalysts for this process include those based on iron,¹⁸⁶ ruthenium,^{192–194,201} molybdenum,²⁰² nickel,^{187,203} copper¹⁸⁹ and palladium.¹⁹⁰ These compounds have demonstrated efficient catalytic reduction of CO₂

under ambient conditions, generating borane precursors to formaldehyde, methanol or formic acid, respectively.

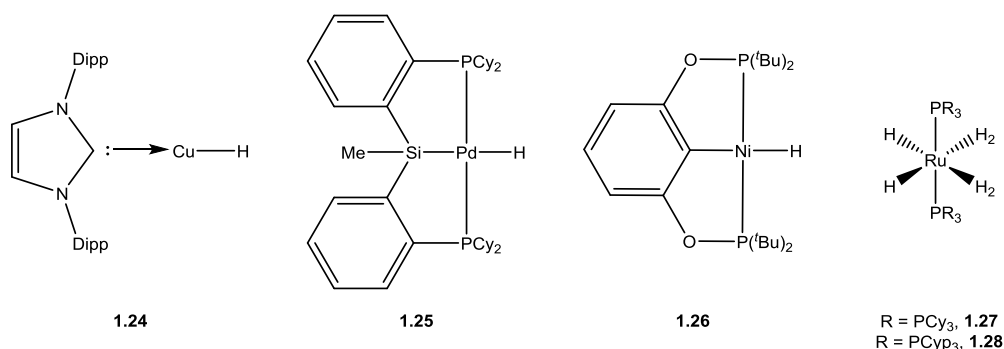


Figure 1.14: Examples of transition metal hydride catalysts which effect the catalytic reduction of CO_2 , employing boranes as reductants.

It was demonstrated in 2013, that an NHC-supported Cu(I) hydride complex, $(\text{IPr})\text{Cu}(\text{H})$ (**1.24**), generated *in situ* from the reaction of $(\text{IPr})\text{Cu}(\text{OtBu})$ and HBpin, effects the selective reduction of CO_2 to formic acid (after acidic work up) with HBpin at 35°C and 10 mol% catalyst loading (max TOF 0.4 h^{-1}).¹⁸⁹ The activation of CO_2 by its insertion into the Cu-H bond was demonstrated by the isolation of the corresponding formate complex, $(\text{IPr})\text{Cu}(\text{OC}(\text{O})\text{H})$ (**1.24^{OCOH}**). It was demonstrated that **1.24^{OCOH}** could catalyse the hydroboration of CO_2 with comparable activity to that of **1.24** and, on the basis of these studies, it was proposed that the mechanism of this catalysis proceeds *via* insertion of CO_2 into the Cu-H bond, followed by liberation of the formate functionality *via* Cu-O/B-H σ -bond metathesis.¹⁸⁹

In a similar fashion, a palladium hydride complex (**1.25**) was described which promotes the selective catalytic reduction of CO_2 to the formic acid derivative $\text{HC}(\text{O})\text{OBpin}$.¹⁹⁰ **1.25** operates at room temperature and displays high activity at particularly low catalyst loadings (0.001 mol%), with a TOF of 529 h^{-1} (0.01 mol%, TOF $> 8500 \text{ h}^{-1}$). Whilst the catalysis is highly selective ($> 90\%$) towards $\text{HC}(\text{O})\text{OBpin}$ when HBpin is employed as

the reductant, the use of HBcat leads to the formation of a mixture of products, including HC(O)OBcat, MeOBcat and O(Bcat)₂.¹⁹⁰ A similar dependence of the product distribution on the borane employed is reported when a Ni(II) hydride POCOP-pincer complex **1.26** is used as a catalyst.^{187,188,195,204} The use of HBpin as the reductant leads to the selective formation of HC(O)OBpin, while the use of HBcat (and closely related boranes such as {H(9-BBN)}₂) reduces CO₂ to the methanol oxidation level, yielding MeOBR₂ and diboroxane, O(BR₂)₂ (R = cat, 9-BBN).^{187,188} **1.26** (0.2 mol%), in conjunction with HBcat, catalyses the reduction of CO₂ at room temperature with a TOF of 495 h⁻¹. By contrast, the use of *more* Lewis acidic H₃B·THF as a reductant for the reduction of CO₂ shuts down the catalytic activity at room temperature.¹⁸⁸ In the presence of more Lewis acidic boranes (HBcat, {H(9-BBN)}₂, H₃B·THF), complexes of the type (XPOCOP)NiH (X = ^tBu, ⁱPr) form the corresponding borohydride complexes, (XPOCOP)Ni(μ-H)₂BR₂ (R₂ = H₂, cat, 9-BBN). In the case of H₃B·THF, **1.26** is trapped as the borohydride complex and therefore deactivated. By contrast, the corresponding borohydride complexes derived from HBcat and {H(9-BBN)}₂ are labile at room temperature and catalytic activity is retained.¹⁸⁸

The ruthenium polyhydride complexes [Ru(H)₂(H₂)₂(PR₃)₂] (10 mol%) (R = Cy **1.27**, Cyp **1.28** {Cyp = cyclopentyl}) catalyse the reduction of CO₂ at room temperature to yield a mixture of products including HC(O)OBpin, O(Bpin)₂, MeOBpin, H₂C(OBpin)₂, HC(O)OCH₂OBpin and, in the case of **1.28**, formaldehyde.^{192,193} The formation of HC(O)OCH₂OBpin represents an unusual example of the reductive coupling of two CO₂ molecules and is not a product that is commonly reported for the borane-mediated reduction of CO₂.

In addition to this, metal hydride catalysts Fe(H)₂(dmpe)₂ (dmpe = 1,2-bis(dimethylphosphino)ethane) (**1.29**) and nickel hydride **1.30** (Figure 1.15)

represent relatively rare examples of catalysts which reduce CO₂ to formaldehyde equivalents.^{186,200} In both cases, the formation of *bis*(boryl) acetal products of the type H₂C(OBR₂) (R = 9-BBN, pin) is favoured, with the formation of H₂C(OBpin)₂ being 97% selective in the case of reduction by **1.30** (0.2 mol%, 25°C, TOF 122 h⁻¹).²⁰⁰

It is of particular note that the most efficient homogeneous catalysts reported for the reduction of CO₂ to methanol are not metal hydride catalysts but nickel and palladium thiolate complexes (Figure 1.15).^{178,205} These complexes operate, in conjunction with HBcat, at low catalyst loadings (0.2 mol%) and at room temperature.

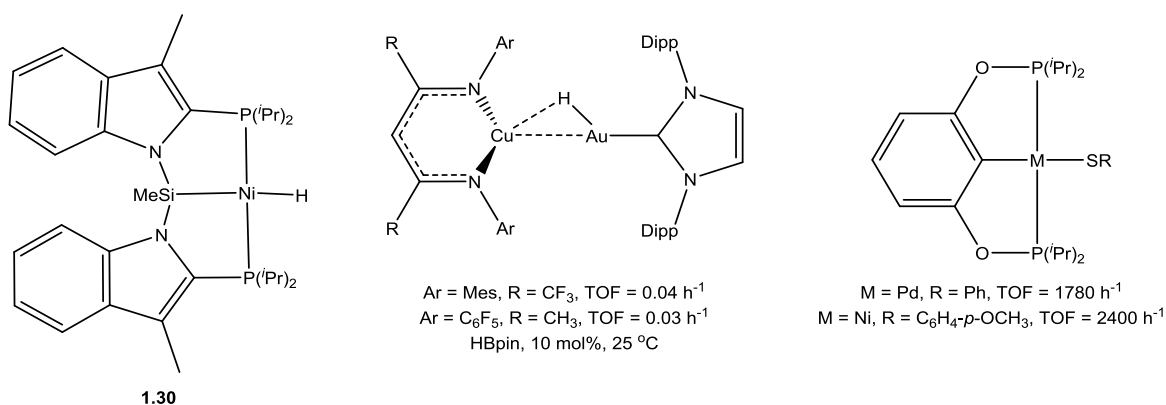


Figure 1.15: Further examples of transition catalysts including a heterobimetallic complex based on coinage metals²⁰⁶ and the most active homogenous catalysts to date.

1.3.2.2 Main group and non-metal catalysts

Stoichiometric reduction of CO₂ has been achieved using main group compounds such as FLPs and Lewis acidic species.^{176,185} It is only very recently however that the potential for catalytic reduction by main group systems has been probed. The first example of CO₂ reduction under a metal-free system was reported in 2013.²⁰⁷ The phosphine/borane FLP system (1-Bcat-2-PPh₂-C₆H₄) (0.33 mol%) reduces CO₂ to the methanol derivative (CH₃OBO)₃ at 70°C, with a maximum TOF of 973 h⁻¹ when Me₂S·BH₃ is used as the reductant. This activity drops significantly however when a less reactive borane and

lower temperatures are employed (e.g. HBcat, 25°C, max TOF 17 h⁻¹). Since this initial report of borane-mediated catalytic reduction of CO₂, a variety of both intra- and intermolecular FLP catalysts have been reported.^{208–212} These include the FLP system consisting of P^tBu₃ (0.02 mol%) and {H(9-BBN)}₂ which selectively reduces CO₂ to the methanol derivative MeO(9-BBN) at 60°C with a TOF of 170 h⁻¹ (5 atm CO₂).²¹⁰ Other phosphines such as PPh₃, P(4-MeC₆H₄)₃ and P(3,5-Me₂C₆H₃)₃ also exhibit reasonable catalytic activity, although such systems were only probed at higher catalyst loadings (1 – 4 mol%), and were far less selective, yielding mixtures of HC(O)O(9-BBN), H₂C{O(9-BBN)}₂ and MeO(9-BBN).

In an analogous manner to this latter system, nitrogen bases (**1.31** – **1.34**), NHCs (**1.35**) and proazaphosphatranes (**1.36**) (Figure 1.16) have also been shown to catalyse the reduction of CO₂ to methanol derivatives.^{196,209} Within the field of nitrogen bases **1.31** – **1.34**, a maximum TOF of 33 h⁻¹ was achieved at room temperature, employing **1.32** (at 0.1 mol%) and {H(9-BBN)}₂. It is apparent in these catalytic systems that the activity is highly dependent on both the nitrogen base and borane reagent, as no catalytic reduction is observed when **1.31** or **1.33** are employed in conjunction with HBcat.²⁰⁹ In addition, proazaphosphatrane superbase **1.36** is a highly efficient catalyst for this process with {H(9-BBN)}₂ as the reductant, operating at low catalyst loadings (0.01 – 2.5 mol%) with TOFs of 31 h⁻¹ (25°C) and 287 h⁻¹ (70°C).¹⁹⁶ Other metal-free catalysts for the hydroboration of CO₂ include carbodiimides,²¹³ zwitterionic (azo)indenides and diazafluorenides,^{214–216} abnormal NHCs,²¹⁷ carbenoid,²¹⁸ and proton sponge.²¹⁹ In addition to this, a number of metal salts of borohydride complexes have been reported to catalyse this transformation.^{220–225}

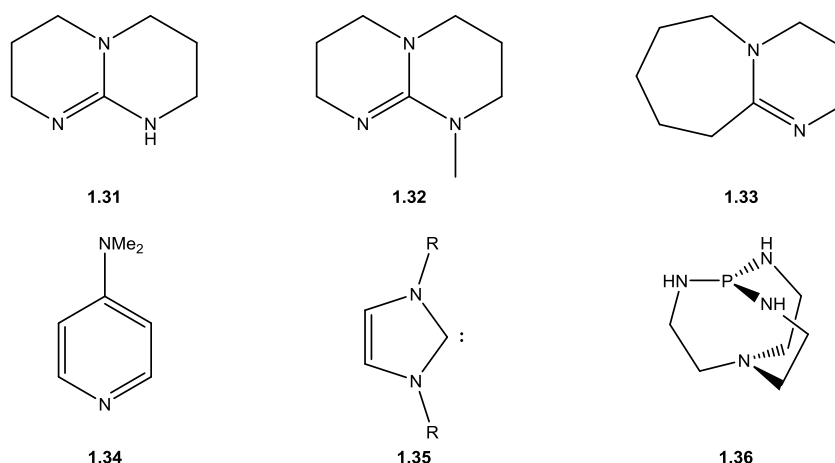
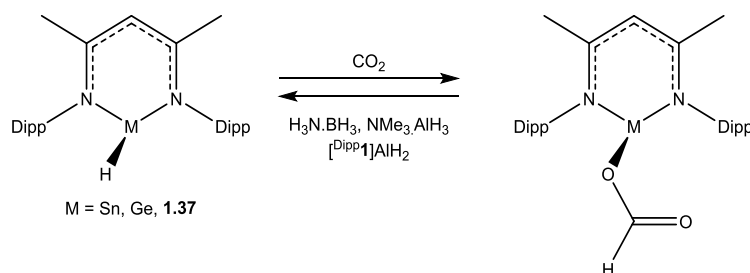


Figure 1.16: Examples of Lewis base catalysts for CO₂ reduction.

A number of main group metal hydride catalysts for this process have been reported. These include derivatives of inexpensive alkaline earth metals, group 13 and 14 elements.^{156,220,221,226–230}

In 2009, it was demonstrated that hydridogermylene and stannylene complexes of the form [Dipp $\mathbf{1}$]MH (M = Ge **1.37**, Sn) possess the ability to hydrometallate CO₂ at room temperature, yielding the corresponding metal formate complexes [Dipp $\mathbf{1}$]M(OC(O)H) (M = Ge, **1.37**^{OCOH}).^{227,228} Regeneration of **1.37** was shown to be possible by treating **1.37**^{OCOH} with a variety of borane and alane reagents including LiH₂NBH₃, H₃N · BH₃, Me₃N · AlH₃ and [Dipp $\mathbf{1}$]AlH₂.^{229,231} Despite showing competence in the two steps key to catalytic turnover for the reduction of CO₂ into methanol derivatives, the catalytic potential of this system was not probed further.



Scheme 1.12: Group 14 metal hydrides hydrometallate CO₂. It has been demonstrated that the hydride may be regenerated by separate treatment of [Dipp $\mathbf{1}$]Ge(OC(O)H) with boranes or alanes.

The ability of a number of main group hydrides to function as catalysts for this process has recently been demonstrated. In each case, the ability of the metal hydride to hydrometallate CO_2 was shown under stoichiometric conditions. In the case of catalysts **1.40**, **1.41** and **1.42** (Figure 1.17), the corresponding metal formate complexes, $\text{LM}(\text{OC}(\text{O})\text{H})$ ($\text{L} = \text{N}(\text{Si}(\text{iPr})_3\text{Ar})$ ($\text{Ar} = \text{C}_6\text{H}_2\text{Pr}^i\text{-}\{\text{C}(\text{H})\text{Ph}_2\}_{2-4,2,6}$) ($\text{M} = \text{Ge}$, **1.40**^{OCOH}; $\text{M} = \text{Sn}$, **1.41**^{OCOH}) and $[\text{Dipp}]\text{Ga}(\text{iBu})(\text{OC}(\text{O})\text{H})$ (**1.42**^{OCOH}), were isolated and crystallographically characterised.^{156,230} By contrast, the stoichiometric addition of CO_2 to catalyst **1.38** produces a highly unusual complex which features two bridging formate functionalities.²²⁶

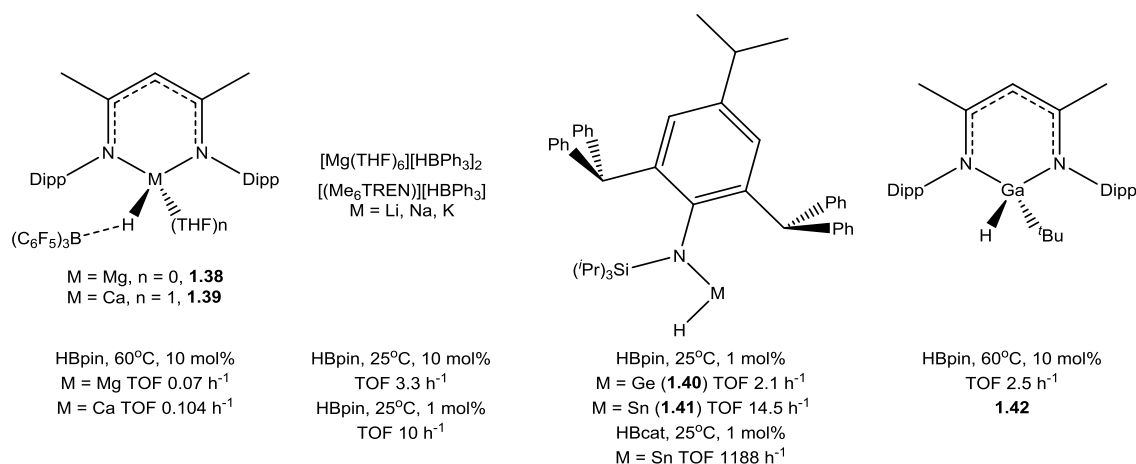
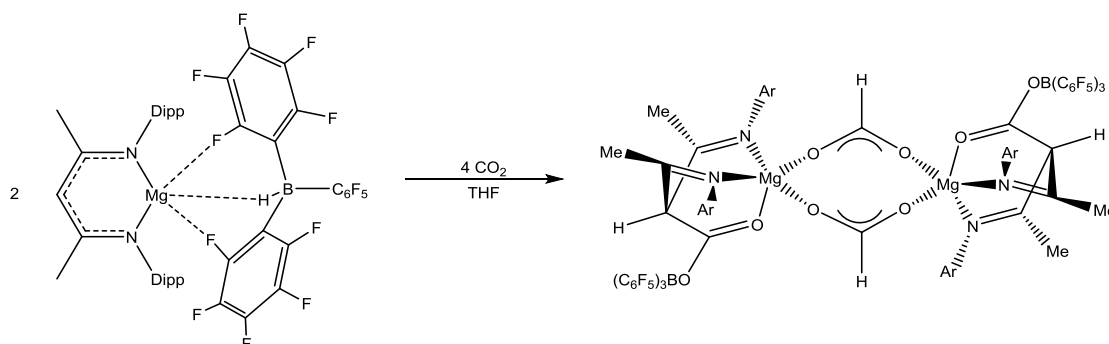


Figure 1.17: Examples of main group metal hydride complexes which catalyse the borane-mediated reduction of CO_2 .



All of these systems selectively reduce CO_2 to methanol derivatives, MeOBR_2 , using HBpin or HBcat as a reductant. For **1.42**, the use of THF, rather than benzene- d_6 , as the solvent is reported to lead to the selective reduction of CO_2 to the formic acid oxidation level. In the case of **1.38**, **1.39** and **1.42**, high catalyst loadings (10 mol%) and elevated temperatures (and a Lewis acid co-catalyst for **1.38/1.39**) are required to achieve low turnover frequencies (0.07, 0.1 and 2.5 h^{-1} , respectively), employing HBpin as the reductant.^{156,226} By contrast, the group 14 M(II) hydrides ligated by bulky amido ligands ($\text{L} = \text{N}(\text{Si}(\text{iPr})_3\text{Ar})$ ($\text{Ar} = \text{C}_6\text{H}_2\text{Pr}^i\text{-}\{\text{C}(\text{H})\text{Ph}_2\}_2\text{-4,2,6}\}$) under ambient conditions and yield turnover frequencies which rival those reported for transition metal hydride catalysts (1 mol% **1.41**, 298 K; HBpin TOF = 14.5 h^{-1} ; HBcat TOF = 1188 h^{-1}).²³⁰

1.3.2.3 Catalytic hydroboration of CO_2 : Mechanistic considerations

A wealth of literature describes the mechanisms by which borane-mediated reduction of CO_2 is proposed to proceed, employing metal hydride catalysts.^{195,230} Mechanistic investigations have involved demonstration of the viability of the two steps key to catalytic turnover: activation of CO_2 (in the majority of cases by insertion into the M-H bond) and regeneration of the hydride by cleavage of the formate functionality.

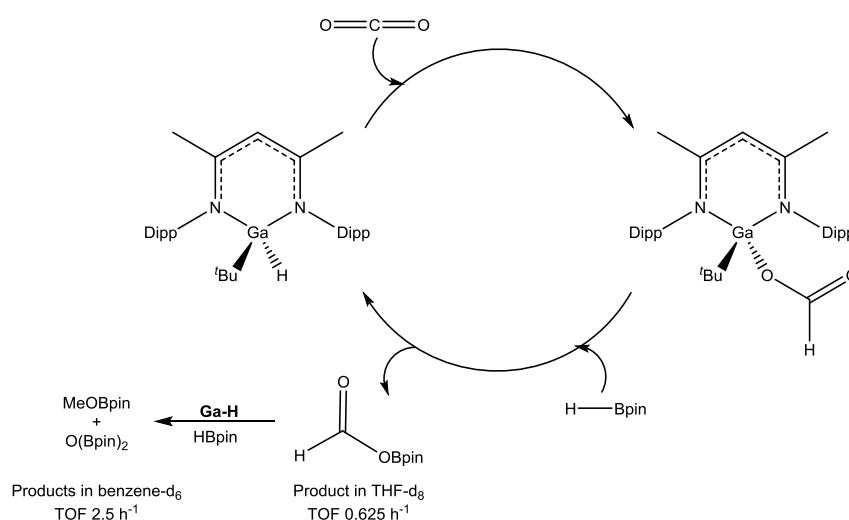


Figure 1.18: The catalytic cycle proposed for the reduction of CO_2 , catalysed by **1.42**.

It is typically considered that activation of CO₂ occurs by insertion into the metal hydride bond and, in many studies of catalytic systems, this step has been independently verified: the corresponding metal formate complexes have been isolated and characterised (Figure 1.18). For example, **1.42** is demonstrated to react with CO₂ over the course of approximately 12 h to yield the gallium formate complex [Dipp¹]₃Ga(^tBu)(OC(O)H), which has been isolated and crystallographically characterised.¹⁵⁶

Regeneration of the corresponding hydride by the treatment of the independently isolated formate complex with a borane under stoichiometric conditions is considered to be indicative of the potential of such complexes to function as intermediates within the catalytic cycle. Alternatively, this may be demonstrated by the observation of comparable catalytic activity for the formate complexes under catalytic conditions.¹⁸⁹

These steps have been successfully demonstrated for a range of catalyst systems and it is proposed that, when formic acid derivatives HC(O)OBR₂ are selectively yielded as the product of catalysis, the mechanism proceeds *via* insertion of CO₂ into the M-H bond, followed by straightforward M-O/B-H σ-bond metathesis.^{189,190}

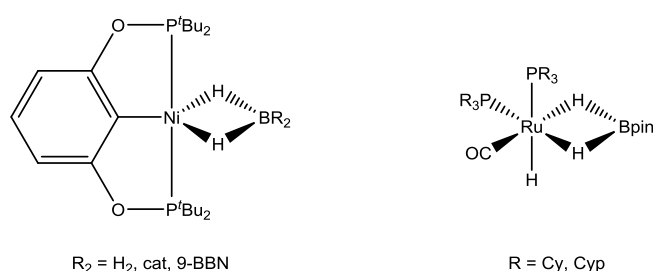


Figure 1.19: Borohydride complexes have been identified as catalyst resting states within catalytic reduction mixtures.

An alternative mechanism has been proposed which involves initial activation of the borane instead of CO₂.¹⁸⁸ A number of transition metal borohydride complexes (Figure

1.19) have been isolated and observed during catalytic hydroboration reactions. However, it was subsequently shown that these complexes are resting states rather than active species.¹⁸⁸

The formation of formoxyborane complexes HC(O)OBR_2 is not always selective under catalytic conditions, and a number of metal hydride catalysts bring about further reduction of such species to give acetal and/or formaldehyde and ultimately methoxy/diboroxane species. The mechanism for such transformations have been the subject of great deliberation and have recently been computationally assessed, employing either HBpin or HBcat as reductants (Figure 1.20).^{195,230} Two potential routes that have similar energetic barriers have been deemed viable; the first steps, leading to a metallo-bora-acetal intermediate of the form $\text{MOCH}_2\text{OBR}_2$, are common to both cycles.²³⁰

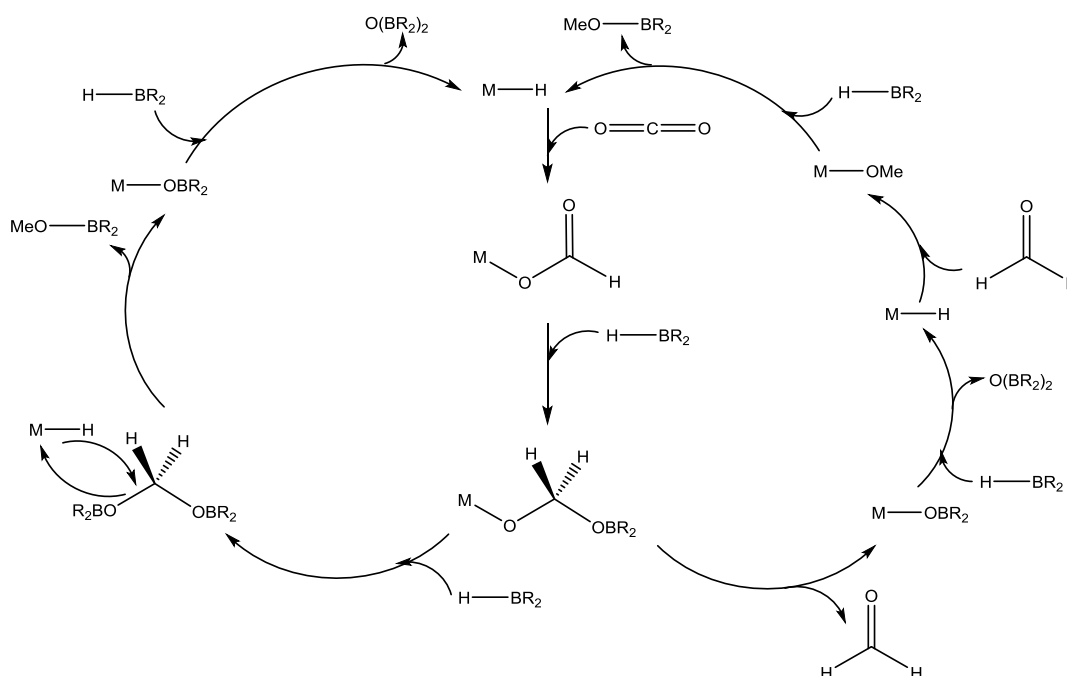
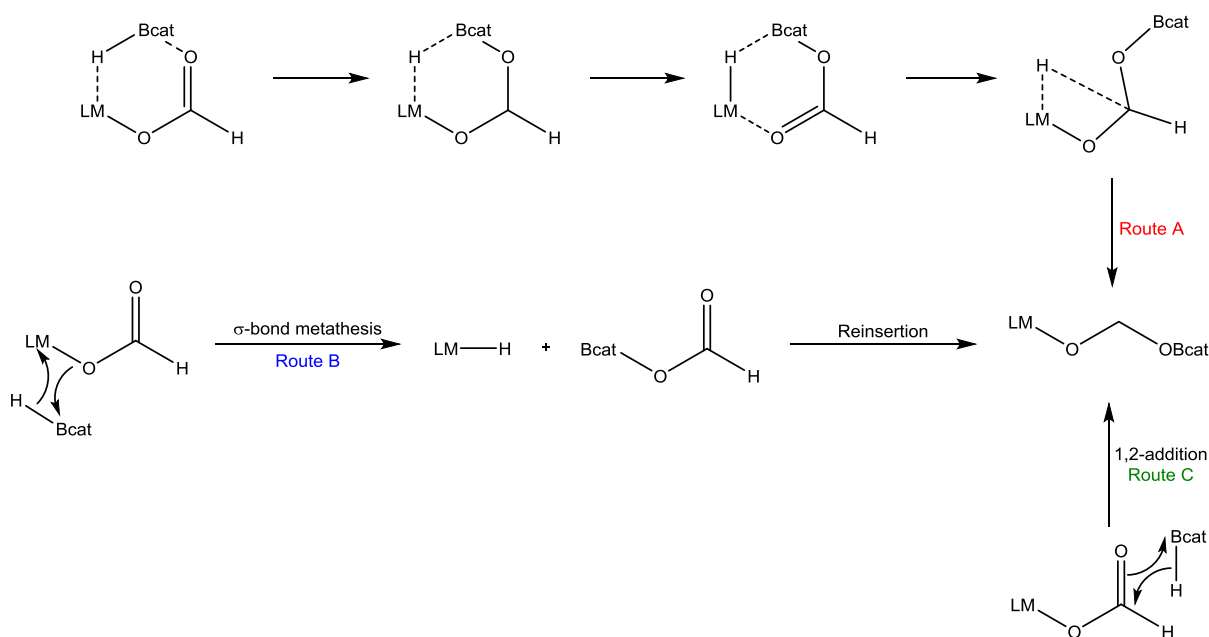


Figure 1.20: The proposed generic catalytic cycle for the metal hydride-catalysed reduction of CO_2 , when a borane is employed as the reductant. This mechanism shows the reduction of CO_2 through to a methanol derivative, with concomitant formation of diboroxane.^{195,230}



Scheme 1.14: Computationally assessed routes for the formation of metallo-bora-acetal complexes from the reaction of boranes with metal formate complexes.

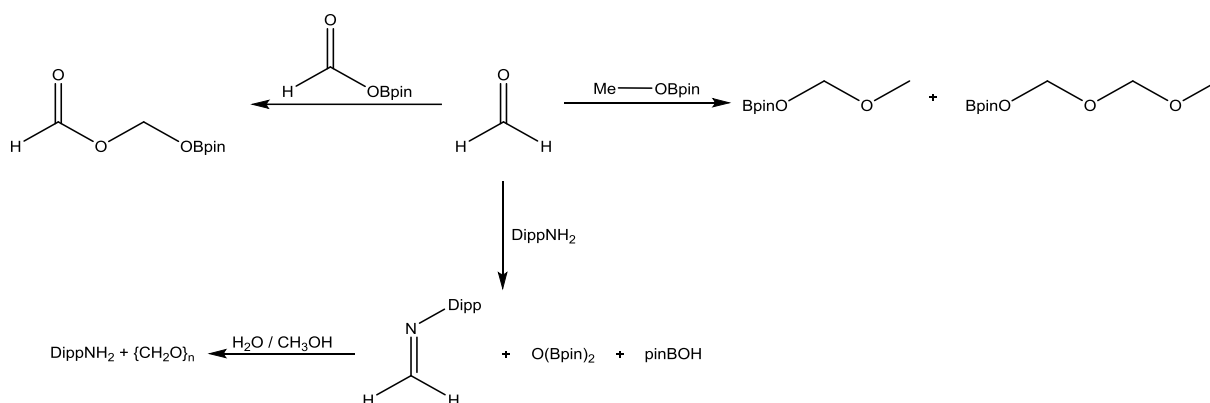
Three pathways for the formation of metallo-bora-acetal intermediates from the corresponding formate complexes with borane were computationally assessed (for a system based on the hydridogermylene catalyst **1.40**, with HBpin as the borane).²³⁰ The first proceeds by a cycloaddition reaction involving the formate complex **1.40**^{OCOH}, with HBpin adding across one Ge-O bond to give a 6-membered transition state and thence to an intermediate which is described as an adduct of HC(O)OBpin with **1.40**. Hydrogen migration from **1.40** then occurs to the electrophilic carbon of the formate functionality (Route A). This route was determined to be the most likely to operate under catalytic conditions. An alternative mechanism that was considered to lead to a reaction dead-end involves formal σ -bond metathesis across the Ge-O bond of **1.40**^{OCOH} to yield **1.40** and free HC(O)OBpin, which react together to give the acetal (Route B). The third route involves the 1,2-addition reaction of HBpin across one CO bond of **1.40**^{OCOH} which was found to be marginally less accessible kinetically ($\Delta H^\ddagger = 122.2 \text{ kJ mol}^{-1}$) (Route C).²³⁰

Experimental evidence has been offered, however, which suggests that route B may be operative in alternative systems.^{195,230} It was demonstrated that HC(O)OBpin, which has been independently prepared, is resolutely unreactive towards HBpin but, upon the addition of **1.27**, is readily reduced to MeOBpin and O(Bpin)₂, suggesting that reinsertion of HC(O)OBpin into the Ru-H bond of **1.27** is possible.¹⁹⁴ Additionally, the relative abilities of HC(O)OBpin and HC(O)OBcat to insert into the Pd-H bond of **1.25** is used to rationalise the product distributions obtained when HBpin and HBcat are employed as reductants.¹⁹⁰ It is suggested that HC(O)OBpin is too sterically bulky to reinsert into the Pd-H bond and hence undergoes no further reduction whilst the less sterically hindered catechol derivative is readily reduced.

Metallo-bora-acetal intermediates may react onwards *via* two potential pathways which have very similar activation energies.²³⁰ In the first route, M-O/B-H σ -bond metathesis with HBR₂ regenerates the M-H and forms H₂C(OBR₂). These two species recombine in the rate determining step ($\Delta H^\ddagger = 150.6 \text{ kJ mol}^{-1}$), yielding MeOBR₂ and a metallo-borate ester intermediate M(OBR₂) (Figure 1.20). The latter then reacts readily with HBR₂ to regenerate the catalyst and give the diboroxane product O(BR₂)₂. The proposed alternative route involves the direct extrusion of formaldehyde from M(OCH₂OBR₂), as the rate-determining step, *via* a cyclic MOCO four-membered transition state.^{194,230} The barrier for this process ($\Delta H^\ddagger = 153.6 \text{ kJ mol}^{-1}$) is only marginally higher than that observed in the first route. The metallo-borate-ester intermediate readily reacts with borane and the formaldehyde may be further reduced by the metal hydride catalyst (Figure 1.20).

Experimental evidence has also been proffered to support the postulated elimination of formaldehyde within the mechanism of the subsequent reduction of HC(O)OBpin to

MeOBpin/O(Bpin)₂.^{192–194} Thus, in the HBpin-mediated reduction of CO₂ employing **1.27** as a catalyst, HC(O)OCH₂OBpin (**1.43**) was obtained as up to 20% of the product mixture.¹⁹³ **1.43** was shown independently formed, in the absence of a catalyst, by the addition of formaldehyde to a solution of HC(O)O(Bpin).¹⁹⁴ Moreover, the use of the closely related catalyst, [Ru(H)₂(H₂)₂(PCyp₃)₂] (**1.28**), leads to the formation of greater quantities of formaldehyde such that (i) it is observed in the catalytic reaction mixture and (ii) no formation of HC(O)OBpin was observed due to its complete conversion to **1.43** in the presence of a greater concentration of CH₂O. In addition to this, it was observed that MeOBpin also reacts with CH₂O (Scheme 1.15).¹⁹²



Scheme 1.15: Trapping agents have been employed to provide evidence for the extrusion of formaldehyde within the borane-mediated reduction of CO₂.¹⁹²

In addition, metalloborate ester intermediates {(*i*Pr₃Si)(Ar*)N}M(OBpin) (M = Ge, Sn; Ar* = C₆H₂^{*i*}Pr-4-{C(H)Ph₂}_{2-2,6}) have been isolated and crystallographically characterised. These complexes were reported to be formed from the addition of one equivalent of HBpin to **1.40**^{OCOH}/**1.41**^{OCOH}.²³⁰ Both complexes readily react with HBpin (1 equiv.), regenerating the metal hydride and forming one equivalent of diboroxane, O(Bpin)₂. This provides strong evidence that metalloborate ester complexes are likely intermediates within the catalytic cycle.²³⁰

1.3.3 Catalytic hydrosilylation of CO₂

An alternative approach to effect the functionalisation of CO₂ focuses on hydrosilylation, a process which has several advantages. A range of inexpensive and environmentally benign hydrosilanes are readily available and hydrosilylation of CO₂ may proceed in a stepwise manner, allowing for the controlled isolation of a range of products with different carbon oxidation levels, including silyl formates, silyl acetals, methoxy silanes and methane (formed in conjunction with bis(silyl)ethers).¹⁸⁴ Reduction of CO₂ to methane is unknown when boranes are employed as reductants.

A variety catalysts have been developed which effect the hydrosilylation of CO₂, including complexes of precious metals such as Pd/Pt,^{232,233} Rh,²³⁴ Re,^{235,236} Ru,^{237–241} and Ir.^{184,242–245} Additionally, catalysts based on cheaper and more abundant “base” transition metals such as Co,²⁴⁶ Zr,^{247,248} Cu,^{249–252} Ni,^{253,254} Sc,^{191,255} and Zn^{256–261} have been developed. Furthermore, a number of promising strategies which avoid the use of transition metals have been developed for the catalytic hydrosilylation of CO₂; these include systems based on Lewis acid catalysts (for examples based on aluminium and gallium see section 1.4),^{262–266} FLPs,^{267,268} organocatalysts,^{199,216,265,269,270} alkali metal carbonates,²⁷¹ metal borohydrides²²⁴ and even polar solvents such as DMF have all shown promise.²⁶⁹

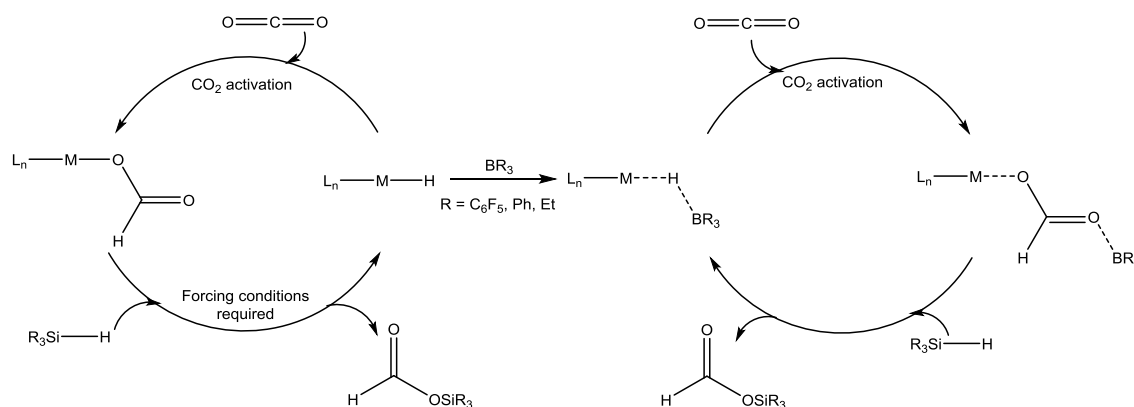
Many of these metal-based catalytic systems feature reactive metal hydride or alkyl moieties, which effect the initial activation of CO₂. Despite the wealth of literature describing metal hydride-catalysed hydrosilylation of CO₂, there is a dearth of examples of main group element hydride catalysts for this process.²⁷² One such example is the ion pair [{Tism^{PriBenz}}Mg][HB(C₆F₅)₃] (**1.44**), featuring the tris[(1-isopropylbenzimidazol-2-yl)-dimethylsilyl]methyl ligand, which is formed by the treatment of the corresponding

magnesium hydride with $\text{B}(\text{C}_6\text{F}_5)_3$.²⁶¹ When **1.44** is employed in conjunction with excess $\text{B}(\text{C}_6\text{F}_5)_3$, a catalytic system is generated which effects the hydrosilylation of CO_2 by R_3SiH ($\text{R}_3\text{SiH} = \text{PhSiH}_3, \text{Et}_3\text{SiH}, \text{Ph}_3\text{SiH}$) at room temperature.

Typically, metal-based systems which operate in the *absence* of a Lewis acid co-catalyst require elevated temperatures and high pressures of CO_2 to bring about catalytic hydrosilylation of CO_2 . Such systems do however tend to exhibit greater selectivity, typically yielding silylformate products.^{256–258} One example of such a system is $[\text{Ru}^{\text{II}}\text{Cl}(\text{NCMe})_5][\text{trans-Ru}^{\text{III}}\text{Cl}_4(\text{NCMe})_2]$, which was found to be an excellent catalyst for the hydrosilylation of CO_2 to silylformates at high CO_2 pressures (*ca.* 70–88 bar) at 353 K.^{239,240} It has also been demonstrated that copper hydride complexes, such as the carbene-stabilised copper hydride $(\text{IPr})\text{Cu}(\text{H})$, will selectively hydrosilylate CO_2 to silylformate complexes, but under ambient CO_2 pressures (1 atm) and comparably low temperatures (60 – 100°C), rendering them some of the most active catalysts to selectively yield this product (e.g. TON 8100).^{249,250} More reactive catalytic metal hydride systems, which operate under ambient conditions, tend to exhibit reduced selectivity. For instance, the pincer-ligated cobalt hydride, $(^t\text{BuPNP})\text{CoH}$, reduces CO_2 at room temperature when a primary silane, PhSiH_3 , is employed but yields oligomers which feature silyl formate, bis(silyl)acetal and silyl ether subunits.^{243–246}

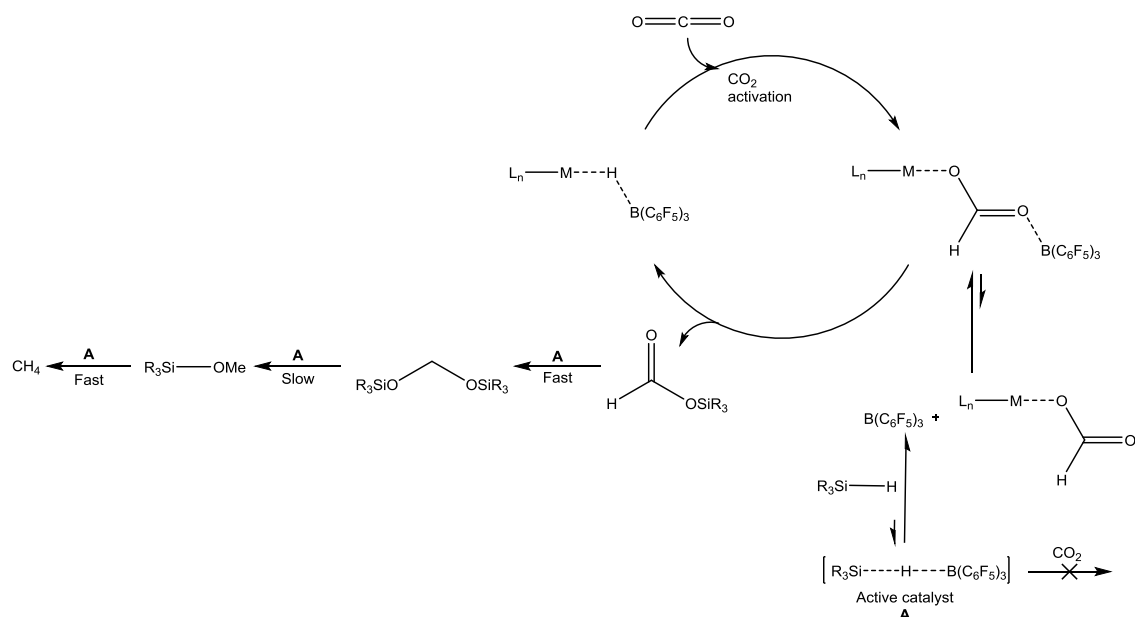
An emerging approach to enhance catalytic performance in reductive hydrosilylation systems is to couple them with a strong organo-Lewis acid; such as $\text{B}(\text{Et})_3$,²⁵⁴ BPh_3 ,^{232,265} or, more commonly, $\text{B}(\text{C}_6\text{F}_5)_3$.²⁷³ $\text{B}(\text{C}_6\text{F}_5)_3$ is a known co-catalyst in hydrosilylation reactions in the reduction of carbonyl or alcohol functions,^{274–276} in which it is demonstrated that the borane activates the silane through the formation of the “adduct” $\text{R}_3\text{Si-H}\cdots\text{B}(\text{C}_6\text{F}_5)_3$.^{277–280} This silane borane complex cannot hydrosilylate CO_2 on its own

due to its inability to invoke the first step, initial activation of CO_2 .^{211,247} However, in the presence of an additional catalyst, $\text{B}(\text{C}_6\text{F}_5)_3$ is involved in tandem catalysis for the hydrosilylation of CO_2 .



Scheme 1.16: The two catalytic cycles for metal hydride mediated catalytic hydrosilylation of CO_2 , with and without a borane Lewis acid co-catalyst.

A range of metal complexes have been reported to function as catalysts for the hydrosilylation of CO_2 when used in conjunction with $\text{B}(\text{C}_6\text{F}_5)_3$. Typically, these metal complexes are based on reactive M-H moieties or cationic metal centres. Generally, the metal component of the catalytic system activates CO_2 *via* either insertion into the M-H bond, to typically yield a $\text{B}(\text{C}_6\text{F}_5)_3$ -activated metal formate complex, or its fixation in a “frustrated Lewis pair” manner. The $\text{B}(\text{C}_6\text{F}_5)_3$ activated silane then transfers a $[\text{SiR}_3]^+$ silylium ion to the formate functionality, or activated CO_2 , forming a silyl formate and regenerating the metal hydride or metal complex.^{191,281} Silyl formate intermediates are rarely observed due to their propensity to be further reduced by $[\text{R}_3\text{Si-H}\cdots\text{B}(\text{C}_6\text{F}_5)_3]$ to bis(silyl)acetal complexes, intermediates which are typically accumulated in catalytic product mixtures yielded by tandem systems.²⁵⁵ The activated silane may also reduce bis(silyl)acetal species further to methane, *via* methoxy silane intermediates, although this is typically relatively slow.



Scheme 1.17: The general catalytic cycle proposed when metal hydrides are used in tandem with $B(C_6F_5)_3$ for catalytic hydrosilylation of CO₂.

While it has been demonstrated that the use of $B(C_6F_5)_3$ as a co-catalyst commonly leads to enhancement of catalytic activity, the presence of $B(C_6F_5)_3$ -activated silane often leads to over-reduction of the formic acid, formaldehyde and methanol derivatives to methane. As such, when $B(C_6F_5)_3$ is employed, silyl formate species are rarely observed as intermediates and methoxysilanes are rarely isolated in significant quantities due to their propensity to undergo subsequent reduction with the activated silane adducts. There have been a number of strategies developed, however, that allow for control of the reductive hydrosilylation of CO₂ to selectively yield products representing different carbon oxidation levels, even in the presence of $B(C_6F_5)_3$.

One such strategy is based on controlling the quantity of $B(C_6F_5)_3$ available for activation of the silane to form the reactive species – $[R_3Si-H \cdots B(C_6F_5)_3]$ – responsible for the further reduction of *bis*(silyl)acetal species.¹⁹¹ This is effected through the use of either sub-stoichiometric $B(C_6F_5)_3$ (which typically leads to reduced catalytic efficiency),²⁴⁷ or catalytic systems which sequester $B(C_6F_5)_3$ during the course of the catalysis, thereby

inhibiting the formation of the activated silane in sufficient quantities to reduce the bis(silyl)acetal species further.^{236,253,255,268}

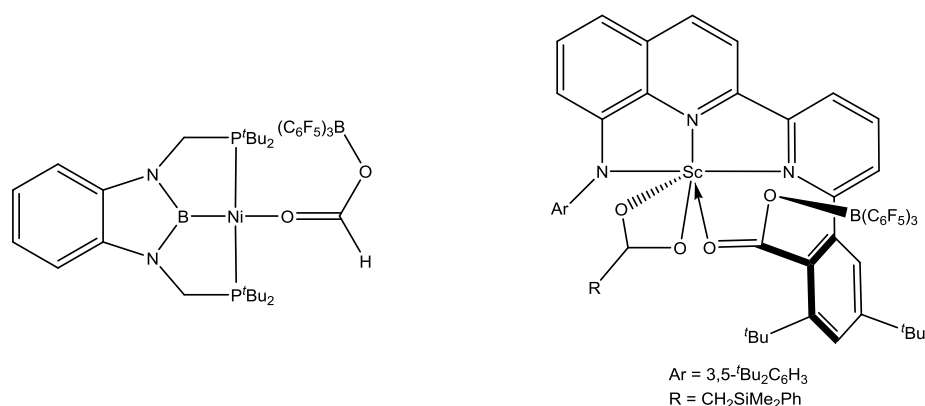


Figure 1.21: Examples of catalysts which effect the hydrosilylation of CO_2 , to selectively yield bis(silyl)acetal products by sequestering $\text{B}(\text{C}_6\text{F}_5)_3$ throughout the reaction.^{253,255}

An alternative method employed to minimise further reduction is the use of less Lewis acidic boranes such as BET_3 or BPh_3 .^{232,254,265} For example, the use of a nickel hydride catalyst, $[(\text{dippe})\text{Ni}(\mu\text{-H})_2]$, with excess BET_3 (10 equiv.) selectively yields $\text{Et}_3\text{SiOC(O)H}$, when Et_3SiH is employed as a reductant, at elevated temperatures.²⁵⁴ Additionally, it was recently demonstrated that BPh_3 catalyses the hydrosilylation of CO_2 to yield silyl formates with exceptional reactivity and under mild conditions (10 mol%, 40°C).²⁶⁵ A silyl formate species is obtained in each case, regardless of whether a primary (PhSiH_3), secondary (Ph_2SiH_2) or tertiary silane (Et_3SiH) is employed as the reductant but catalysis only operates in polar solvents such as acetonitrile.²⁶⁵

Additionally, it was demonstrated that the product distribution obtained may be directly affected by the nature of the silane reductant.^{247,261} The use of primary silanes can lead to the isolation of more complicated oligomeric products, through reactivity of the pendant Si-H bonds.²⁴⁶ For example, it was shown that **1.44**, in the presence of excess $\text{B}(\text{C}_6\text{F}_5)_3$, effects the catalytic hydrosilylation of CO_2 yielding CH_4 when PhSiH_3 is employed as the reductant, $\text{H}_2\text{C}(\text{OSiPh}_3)_2$ when Ph_3SiH is employed and a mixture with

Et_3SiH .²⁶¹ An explanation for the product selectivity was not given but it may arise due to the differing steric properties of the silanes. Furthermore, research has shown that control of temperature may also lead to selectivity, although this was not effected in the presence of a borane co-reagent.²³⁷

1.3.4 Catalytic hydroboration of aldehydes and ketones

The reduction of compounds featuring unsaturated functionalities such as $\text{C}=\text{X}$ ($\text{X} = \text{N}, \text{O}, \text{S}$) are some of the most significant conversions in organic synthesis. In particular, the reduction of aldehydes and ketones to alcohols is one of the most widely used chemical transformations.^{282–284} Traditionally, the reduction of carbonyl compounds is achieved by the employment of metal hydrides or transition metal-catalysed hydrogenation.^{285,286} The catalytic hydroboration of carbonyl compounds has however gained interest due to the mild reaction conditions required, and the avoidance of highly flammable dihydrogen gas. Typically, hydroboration involves the equimolar addition of a borane reagent to carbonyl compounds to form borate esters, which may be hydrolysed to alcohols. Until recently, the catalysts employed in the hydroboration of carbonyl compounds were primarily based on transition metals including Ru, Mo, Ti and Zn.¹⁷⁶

A variety of main group element catalysts have been developed which show impressive performance in the reduction of a range carbonyl compounds.^{162,176,287,288} Examples of catalysts which effect the hydroboration of aldehydes and ketones include a MOF-supported magnesium alkyl complex (max TOF at 0.0011 mol%: 1750 h^{-1}),²⁸⁹ tris(2,4,6-trifluorophenyl)borane (max TOF at 2 mol%: 50 h^{-1}),²⁹⁰ and systems based on germanium, tin and lead Lewis pairs,²⁹¹ alkali metal borohydrides,^{220,221} an N-heterocyclic germylene,²⁹² 1,2,4,3-triazaphosphenes,²⁹³ and an amidinato-stabilised calcium(II) iodide (Figure 1.22).²⁹⁴

Chapter I: Introduction

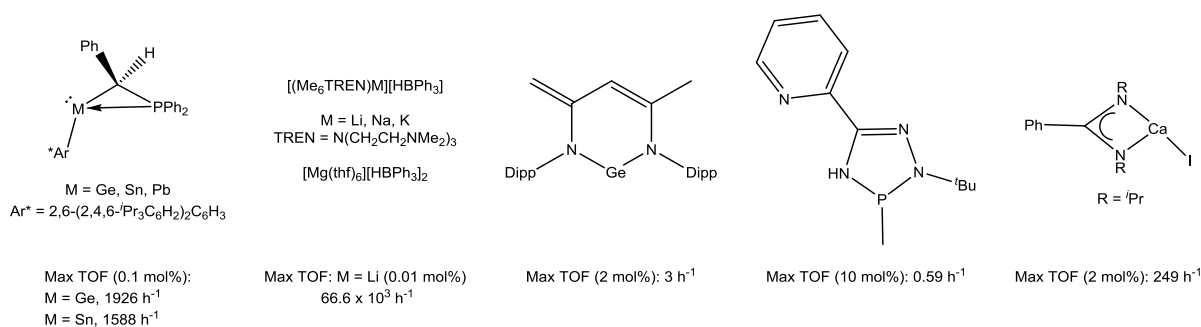


Figure 1.22: Examples of main group metal catalysts for the hydroboration of aldehydes and ketones and the maximum turnover frequencies exhibited by these systems.

Main group metal hydrides such as LiAlH_4 and LiBH_4 are valuable reagents for the reduction of carbonyl substrates.¹⁰ However, the disadvantages of such reagents include limited functional group tolerance, their pyrophoric nature and the need for stoichiometric reducing reagent. A number of main group metal hydrides have been employed to effect the hydroboration of aldehydes and ketones in a catalytic manner. A well-established hydride catalyst for hydroboration is the Corey-Bakshi-Shabata (CBS) catalyst which was first employed in 1987 for the asymmetric reduction of ketones.²⁹⁵⁻²⁹⁷ A number of variants of this catalyst have since been reported.

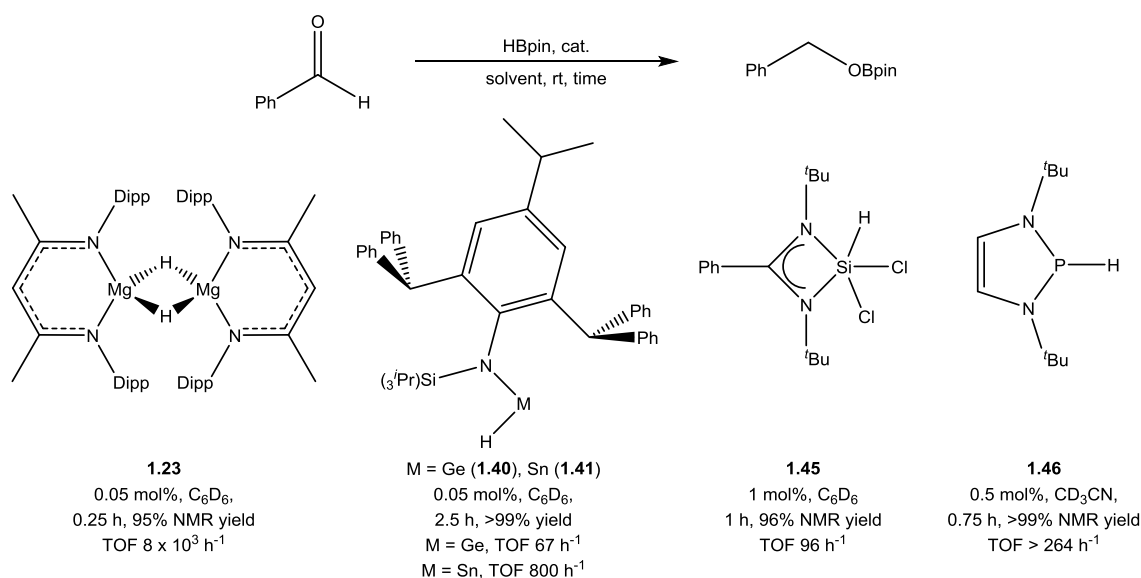


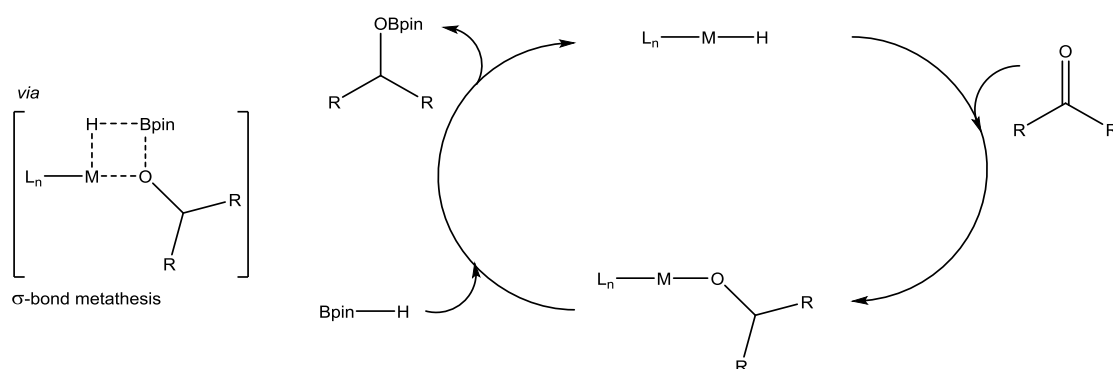
Figure 1.23: Examples of single site main group hydride catalysts for this process and the conditions required for each to bring about the hydroboration of benzaldehyde.

Other reported examples of main group metal hydride catalysts which catalyse the hydroboration of carbonyl functionalities are based on alkaline earth metals, or on group 13 (discussed in Section 1.4), group 14 and group 15 elements.^{298–302} Typically the reactive catalytic species contains a reactive E-H moiety. Many of these metal hydride systems effect the hydroboration of a wide range of aldehydes and ketones at room temperature, obtaining products in >90% yield, with the exception of silane **1.45**, which does not reduce ketones. Additionally, a magnesium hydride cluster, [LMgH]₄ (L = N(Dipp)PPh₂) has been reported which effects the catalytic hydroboration of ketones, with a maximum TOF of 4243 h⁻¹ for the reduction of 2-adamantone at 0.05 mol% catalyst loading.²⁹⁹

In 2014, the use of low valent group 14 M(II) hydrides **1.40** and **1.41** as catalysts for the hydroboration of a wide range of aldehyde and ketone substrates was reported.³⁰⁰ Hydridostannylene **1.41** (at 0.05 mol%) effects the hydroboration of aldehydes with TOF values between 400 and > 13 300 h⁻¹. The hydroboration of ketones requires higher catalyst loadings (0.5 – 5 mol%) to effect moderate TOF values (0.47 – 1330 h⁻¹). These systems are more efficient for this process than previously reported transition metal catalysed hydroboration employing HBpin as a reductant, but show similar efficiencies to other main group metal hydride catalysts.^{298,302}

The mechanism by which these catalytic processes proceed has been investigated in some depth.¹⁷⁶ It is typically considered that hydrometallation of the carbonyl functionality may be a common initial step. This has been validated by the isolation of the intermediate metal alkoxide complexes from the reaction of **1.40** and **1.41** with bulky carbonyl substrates, (*i*Pr₂C(O) or (*p*-MeOPh)C(O)H)).³⁰⁰ The corresponding hydrides can easily be regenerated from these metal alkoxide complexes by M-O/B-H

σ -bond metathesis, yielding the pinacolborate ester.³⁰⁰ Moreover, a first-order dependence of the reaction in both HBpin and catalyst, and a zero-order dependence in ketones were confirmed.³⁰⁰ This suggests that the metal alkoxide intermediates are resting states of the catalytic cycles and that the rate-determining step is the σ -bond metathesis step involving HBpin and the alkoxide intermediate. In addition to this, kinetic isotope effect studies conducted for catalysis by **1.46** illustrate that cleavage of B-H bonds is involved in the rate-determining step.³⁰²



Scheme 1.18: The general mechanism proposed for this reactivity.

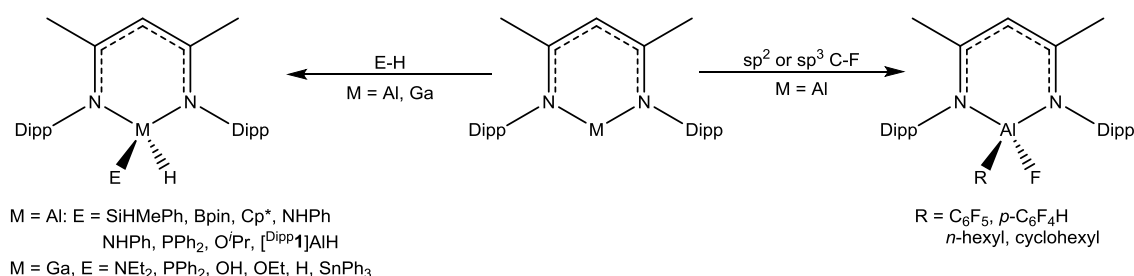
1.4. The use of alanes and gallanes in small molecule activation and catalysis

1.4.1 The use of group 13 complexes in small molecule activation

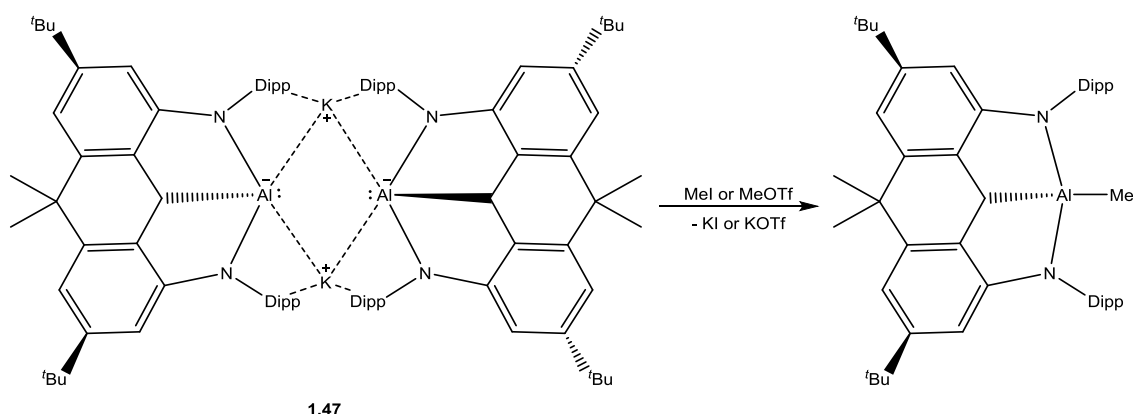
With respect to small molecule activation, the use of complexes which feature group 13 elements (specifically aluminium and gallium) generally fall into one of four types: (i) low coordinate, low oxidation state species, (ii) metal-ligand cooperativity, (iii) saturated metal compounds with highly reactive metal-X bonds and (iv) M(III) complexes acting as Lewis acids.

The primary mode of reactivity of low coordinate M(I) species (M = Al, Ga) involves oxidative addition at the metal centre to generate M(III) species.¹ This has been explored

in particular depth for Nacnac-ligated M(I) complexes, $[\text{Dipp}\mathbf{1}]\text{M}$ ($\text{M} = \text{Al}, \text{Ga}$), in particular for the oxidative addition of E-H bonds,^{130,135,136} sp^3 and sp^2 C-F bonds and the C-O bonds of THF and benzofuran.^{132–134} By contrast, the primary mode of reactivity of $[\text{K}\{\text{Al}(\text{NON})\}]_2$ (**1.47**) (NON = 4,5-bis(2,6-diisopropylanildo)-2,7-di-*tert*-butyl-9,9-dimethylxanthene) is as an aluminium-centred nucleophile; **1.47** reacts with MeI or MeOTf, forming a new Al-C bond and eliminating KI/KOTf, to give NONAlMe (Scheme 1.20).⁷⁵ Interestingly, **1.47** also reacts with benzene, giving clean conversion to $[\text{K}\{\text{Ph}(\text{H})\text{Al}(\text{NON})\}]_2$, *via* oxidative addition of a C-H bond of benzene at the Al(I) centre. This represents the first demonstration of intermolecular oxidative addition of a C-H bond in benzene at a single, well-defined main group metal centre.⁷⁵ Whilst low oxidation state complexes of group 13 elements show encouraging activity the field of small molecule activation, their poor chemical stability and non-trivial preparation typically render them less tractable for use in a catalytic manner.

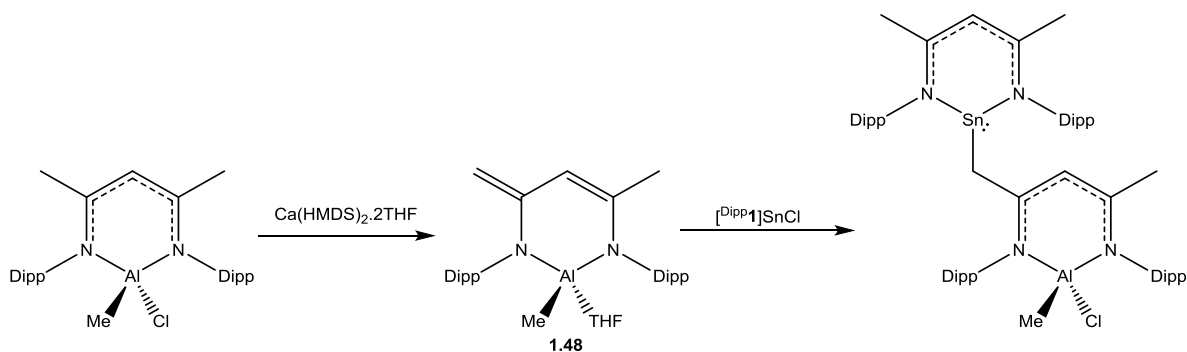


Scheme 1.19: Nacnac-ligated M(I) complexes oxidatively add a range of E-X bonds.

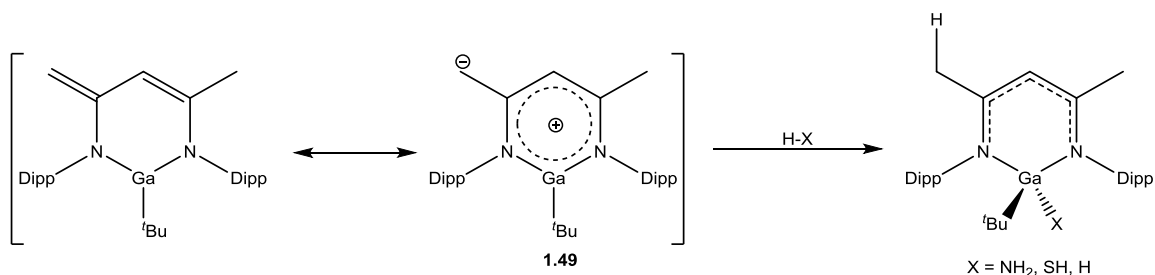


Scheme 1.20: The primary mode of reactivity of **1.47** is as an aluminium-centred nucleophile.

Metal-ligand cooperativity has been employed in both group 13 mediated E-X bond activation processes and aluminium-mediated catalytic processes. Single-site ambiphilic complexes based on aluminium and gallium have been prepared by the deprotonation of the exocyclic methyl substituent of Nacnac-ligated group 13 halide complexes, $[\text{Dipp}\mathbf{1}]\text{Al}(\text{Me})(\text{Cl})$ and $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{tBu})(\text{Br})$.^{156,303} The resulting complexes, $[\text{Dipp}\mathbf{1}']\text{Al}(\text{Me})(\text{THF})$ (**1.48**) and $[\text{Dipp}\mathbf{1}']\text{Ga}(\text{tBu})$ (**1.49**), which feature a dianionic, diamido Nacnac' ligand with a highly nucleophilic exocyclic methylene group and a vacant orbital centred at the metal centre (of **1.49**), are capable of activating a range of E-X bonds. Thus, **1.48** cleaves a number of E-X bonds including Sn-Cl, Ge-Cl bonds, and the Zn-C bonds in ZnMe_2 ,³⁰³ whilst **1.49** is shown to activate a range of acidic, hydridic and non-polar X-H bonds (Scheme 1.22), including the Si-H bonds of SiH_4 .¹⁵⁶



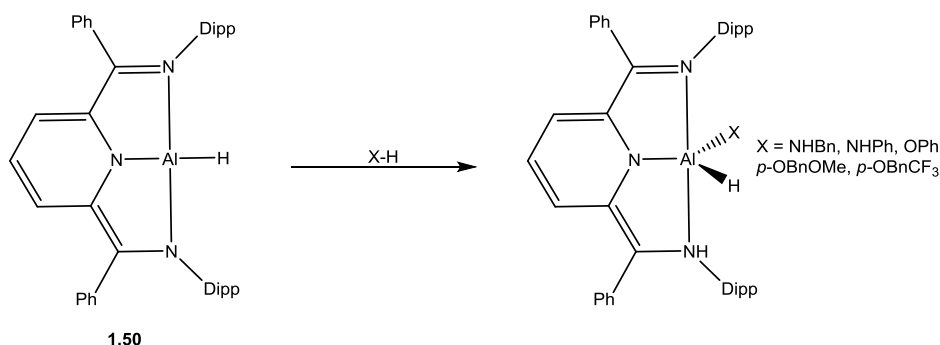
Scheme 1.21: Deprotonation of $[\text{Dipp}\mathbf{1}]\text{Al}(\text{Me})\text{Cl}$ to form **1.48**, and its activation of Sn-Cl bonds.



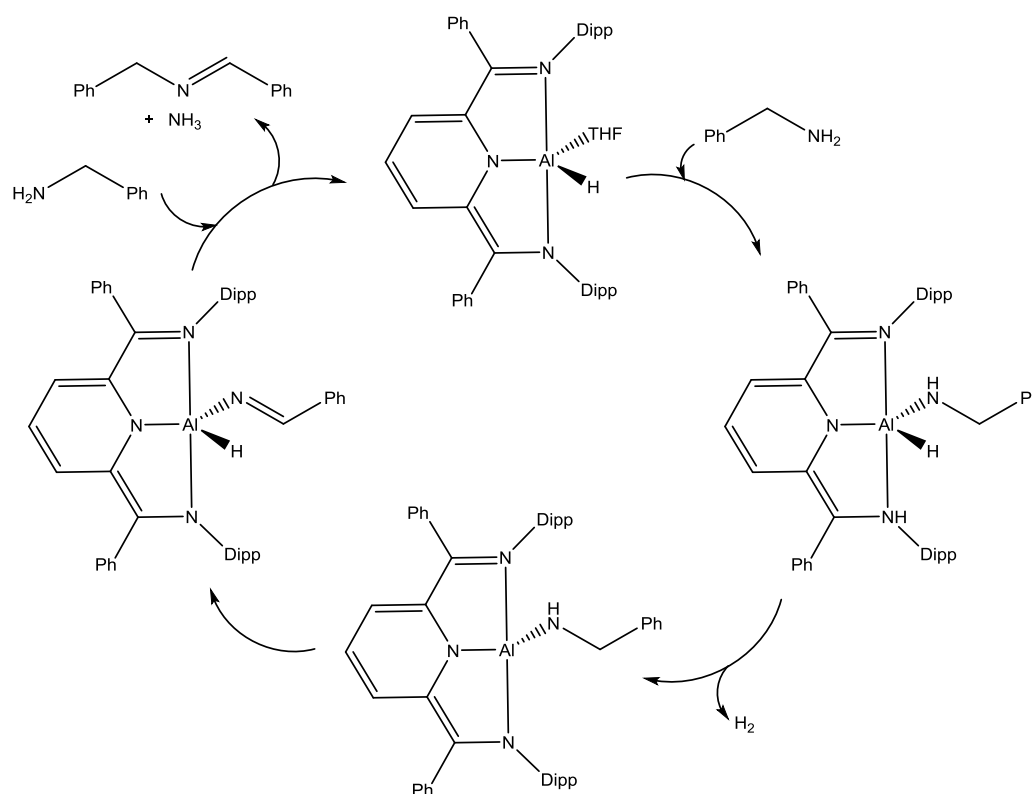
Scheme 1.22: Ambiphilic system **1.49** can activate a range of H-X bonds.

The ancillary ligands in Al(III) complexes have been demonstrated to play an important role in mediating proton transfer reactions.³⁰⁴ For example, Al(III) systems which

feature imino-pyridine NNN pincer ligands (**1.50**) have been recently reported to activate H-H, N-H and O-H bonds across the Al-N linkages.³⁰⁵⁻³⁰⁷ This aluminium-ligand cooperativity has been exploited to effect catalytic processes: **1.50**·THF catalyses the dehydrogenative coupling of benzylamine and the dehydrogenation of formic acid to CO₂ and H₂.^{308,309}



Scheme 1.23: Reaction of **1.50** with compounds containing X-H (X = NH, O) bonds.



Scheme 1.24: Proposed mechanism for dehydrogenative coupling of benzylamine by **1.50**·THF.

A more commonly employed strategy for small molecule activation by group 13 elements, particularly in a catalytic manner, exploits compounds which feature the

metals in the +3 oxidation state. Such compounds may function as potent Lewis acids or feature highly reactive M-X bonds, in particular M-H bonds. The chemistry of aluminium and gallium hydrides is well developed and complexes which feature these reactive moieties are widely used in organic transformations, inorganic synthesis and materials chemistry.^{16,304,310}

1.4.2 Group 13 complexes as catalysts for reductive processes

Aluminium was among the first elements employed in catalytic reduction chemistry. The initial use of aluminium complexes as catalysts for such processes was based upon the use of simple aluminium salts; aluminium alkoxides were the first catalysts employed for the Meerwein-Ponndorf-Verley reduction of ketones and aldehydes,^{311,312} and the use of aluminium trihalide salts as catalysts for the hydrosilylation of alkenes and alkynes dates back to 1978.³¹³ Indeed, Lewis acidic aluminium complexes still find uses in modern day catalytic processes. With the advent of LiAlH_4 in 1947 came its use as a commonplace reducing agent for a range of unsaturated functionalities.⁸ The use of aluminium (and gallium) hydrides as *catalysts* for reductive processes has received much less attention than the use of group 13 complexes as Lewis acid catalysts. Recently, however, a range of aluminium complexes have found uses as catalysts for a range of reductive processes including hydrogenation, hydrosilylation, hydroboration, hydroamination and hydrodefluorination processes.³¹⁰ The following discussion focuses on the use of aluminium and gallium catalysts (in particular those based on M-H functionalities) for hydroboration and hydrosilylation processes.

1.4.2.1 Stoichiometric reactions of alanes: critical steps for substrate activation in catalysis

The use of aluminium hydrides in stoichiometric reactions has been widely explored, and they have been demonstrated to be highly reactive towards protic reagents and C=O, C=NR, C $\equiv$ N, C=C and C $\equiv$ C multiple bonds.³⁰⁴ These stoichiometric reactions are of particular pertinence and in many cases can be considered to be the initial step in a catalytic reductive process.

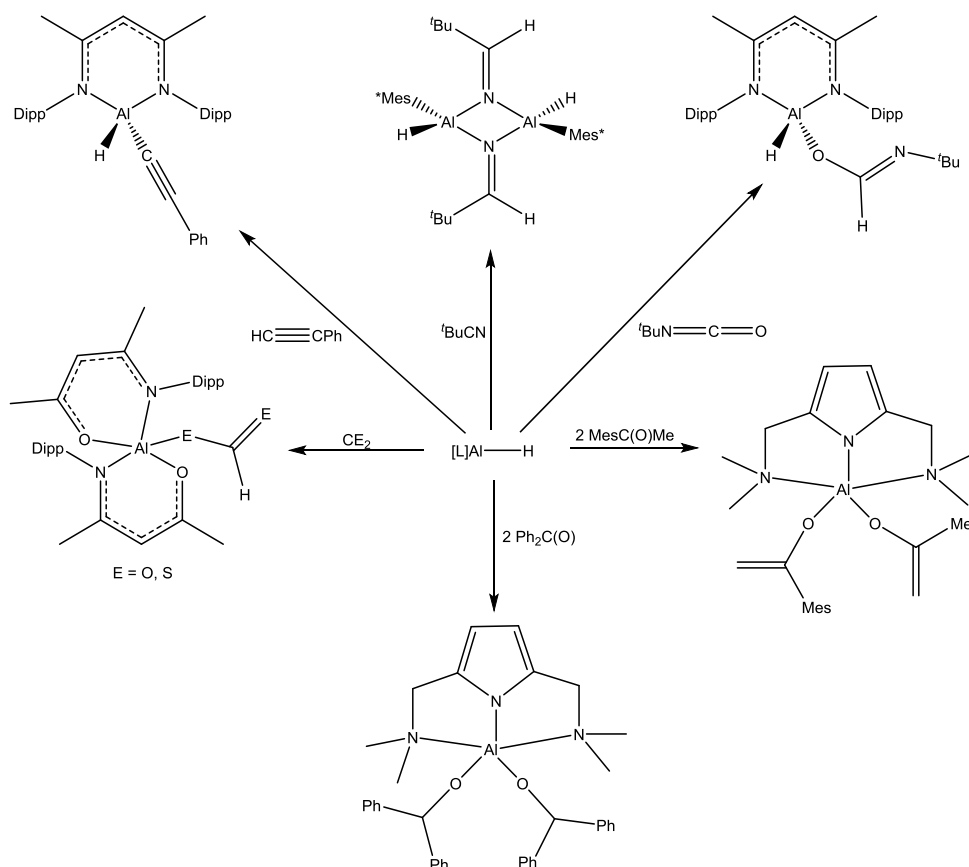


Figure 1.24: Examples of the reactions of aluminium hydrides towards terminal alkynes,¹³⁹ CE₂

(E = O, S),³¹⁴ ketones,³¹⁵ nitriles³¹⁶ and an isocyanate.³¹⁷

Of most relevance to reductive processes are the reactions of aluminium hydrides towards unsaturated substrates. Within this realm, binary aluminium hydrides and hydrides which bear ligands of low steric bulk have been demonstrated to undergo

reactions with alkene, alkyne and nitrile substrates, commonly generating aluminium clusters.³⁰⁴ The use of mono- and dimeric aluminium hydrides stabilised by bulky ligands has allowed for the study of the mechanisms of these processes.

In doing so, it has been demonstrated that the reaction of aluminium hydrides with terminal alkynes may proceed *via* hydroalumination or deprotonation. [Dipp $\mathbf{1}$] AlH_2 (**1.16**) reacts with phenylacetylene to yield the terminal acetylide complex *via* deprotonation of the alkyne.¹³⁹ A range of examples of the reduction of carbonyl compounds and small molecules such as CO_2 and CS_2 by aluminium hydrides have also been reported (Figure 1.24). Alternatively, aluminium hydrides can deprotonate ketones, thus forming aluminium enolates. **1.16** also reacts with isocyanate $t\text{BuNCO}$ *via* hydroalumination of the $\text{C}=\text{O}$ bond.³¹⁷

1.4.2.2 Alanes as catalysts for hydroboration reactions

A number of alane catalysts have been recently reported to effect the catalytic hydroboration of aldehydes and ketones at low catalyst loadings and under ambient conditions, employing HBpin as the reductant.^{143,318–321} In each of these cases, catalysis is proposed to proceed by initial hydroalumination of the unsaturated functionality to yield an aluminium alkoxide complex, followed by Al-O/B-H metathesis to form the borate ester product and regenerate the alane. This mechanism, which has been quantified by quantum mechanical calculations in the case of **1.51**, is comparable to those proposed for related main group metal hydride catalysts (Section 1.3.4).¹⁴³

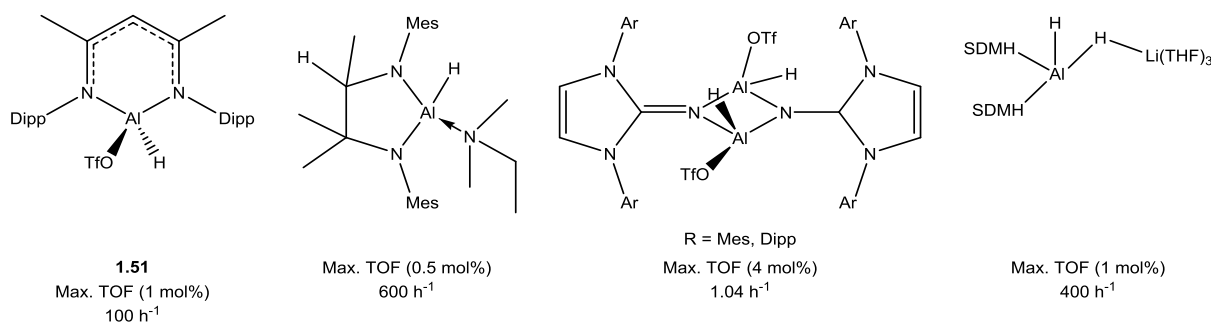


Figure 1.25: Examples of aluminium hydrides which catalyse the hydroboration of aldehydes and ketones with HBpin at room temperature.

It has been demonstrated, under stoichiometric conditions, that benzaldehyde will insert into the Al-H bonds of $[\text{Dipp}^1\text{AlH}_2]$ (**1.16**), yielding $[\text{Dipp}^1\text{Al}(\text{H})(\text{OCH}_2\text{Ph})]$ (**1.52**) and $[\text{Dipp}^1\text{Al}(\text{OCH}_2\text{Ph})_2]$.³²² However, in contrast to the reported behaviour of $[\text{Dipp}^1\text{Al}(\text{OTf})(\text{OCH}_2\text{Ph})]$, the stoichiometric reaction of **1.52** and HBpin produces a mixture of products with no evident formation of $\text{PhCH}_2\text{OBpin}$ or regeneration of **1.16**. This study may highlight the importance of the triflate substituent in reductive hydroboration processes when complexes of the form $[\text{Dipp}^1\text{Al}(\text{R})\text{H}]$ are employed as catalysts.

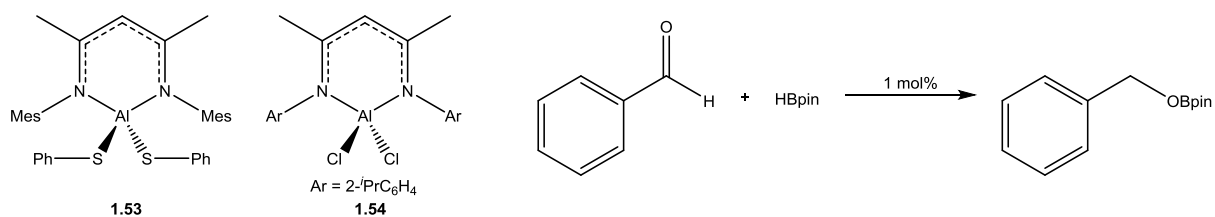


Figure 1.26: Examples of aluminium catalysts which *do not* bear hydride functionalities that bring about the catalytic hydroboration of carbonyl functionalities.³²³

However, it is of note that aluminium catalysts that are closely related to **1.51** have also been reported to effect the reduction of aldehydes/ketones.³²³ $[\text{Mes}^1\text{Al}(\text{SCH}_2\text{Ph})_2]$ (**1.53**) and $[\text{Ar}^1\text{AlCl}_2]$ ($\text{Ar} = 2\text{-}i\text{Pr-C}_6\text{H}_4$) (**1.54**), which *do not* bear hydride functionalities, catalyse this process with comparable activity to that of **1.51** (**1.53** or **1.54**, 1 mol%,

25°C, max TOF = 100 h⁻¹). The mechanism by which these catalysts effect this process is not clear.

A range of alane catalysts have been reported which are capable of bringing about the catalytic hydroboration of alkenes and alkynes.^{127,319,321,324} In 2016 it was reported that alane [Dep**1**]AlH₂ (**1.55**) acts as a pre-catalyst for the hydroboration of terminal alkynes, to give (E)-borylalkenes.¹²⁷ In the presence of phenylacetylene, for example, **1.55** deprotonates the alkyne to give the unsymmetrically substituted acetylide complex [Dep**1**]Al(H)(C≡CPh) (**1.56**). This process was also demonstrated under stoichiometric reaction conditions and is suggested to be the first step of the catalytic cycle, as probed by DFT calculations. **1.56** is proposed to undergo syn addition of B-H to the C=C bond, followed by Al-C/H-C metathesis with another alkyne equivalent to regenerate active catalyst. Al-C/H-C metathesis, proposed to be the rate-determining step, is associated with a relatively high barrier ($\Delta G^\ddagger = 189.5 \text{ kJ mol}^{-1}$). The system operates with maximum TOF of 2.1 h⁻¹ obtained with phenylacetylene as the substrate (**1.55** 3 mol%, 30°C, 75% yield).¹²⁷ It is of note that this system does not effect the hydroboration of internal alkynes.

Other alane catalysts for this process (ⁱBu₂AlH, Et₃Al·DABCO) are suggested to act by an alternative mechanism by which initial hydroalumination of the alkyne occurs, followed by Al-C/B-H σ -bond metathesis to regenerate the alane.³²⁴ This mechanism is proposed due to the ability of these systems to effect the hydroboration of internal alkynes. In addition, mechanistic studies do not support protonolysis of the Al-H bond in the case of terminal alkynes, in the absence of spectroscopically observed H₂ evolution. For comparison, if phenylacetylene is employed as the substrate, ⁱBu₂AlH and Et₃Al·DABCO catalyse hydroboration with TOFs of 4.3 h⁻¹ and 3.8 h⁻¹, respectively, albeit at higher

catalyst loadings and elevated temperatures (10 mol%, 110°C).³²⁴ Interestingly, alkenes are inert under these conditions, allowing for chemoselective reduction of $C\equiv C$ bonds to be accomplished. In addition, guanidinato-supported alanes $\{L(R)AlH_2\}_2$ ($R = \text{Mes}$ (**1.57**), Dipp) ($L(R)N = 1,3\text{-bis}(R)\text{-imidazolin-2-imino}$) have been employed to effect the hydroboration of alkynes, albeit under relatively harsh conditions, e.g. **1.57** 4 mol%, 80°C, TOF = 0.5 h⁻¹.³²⁵

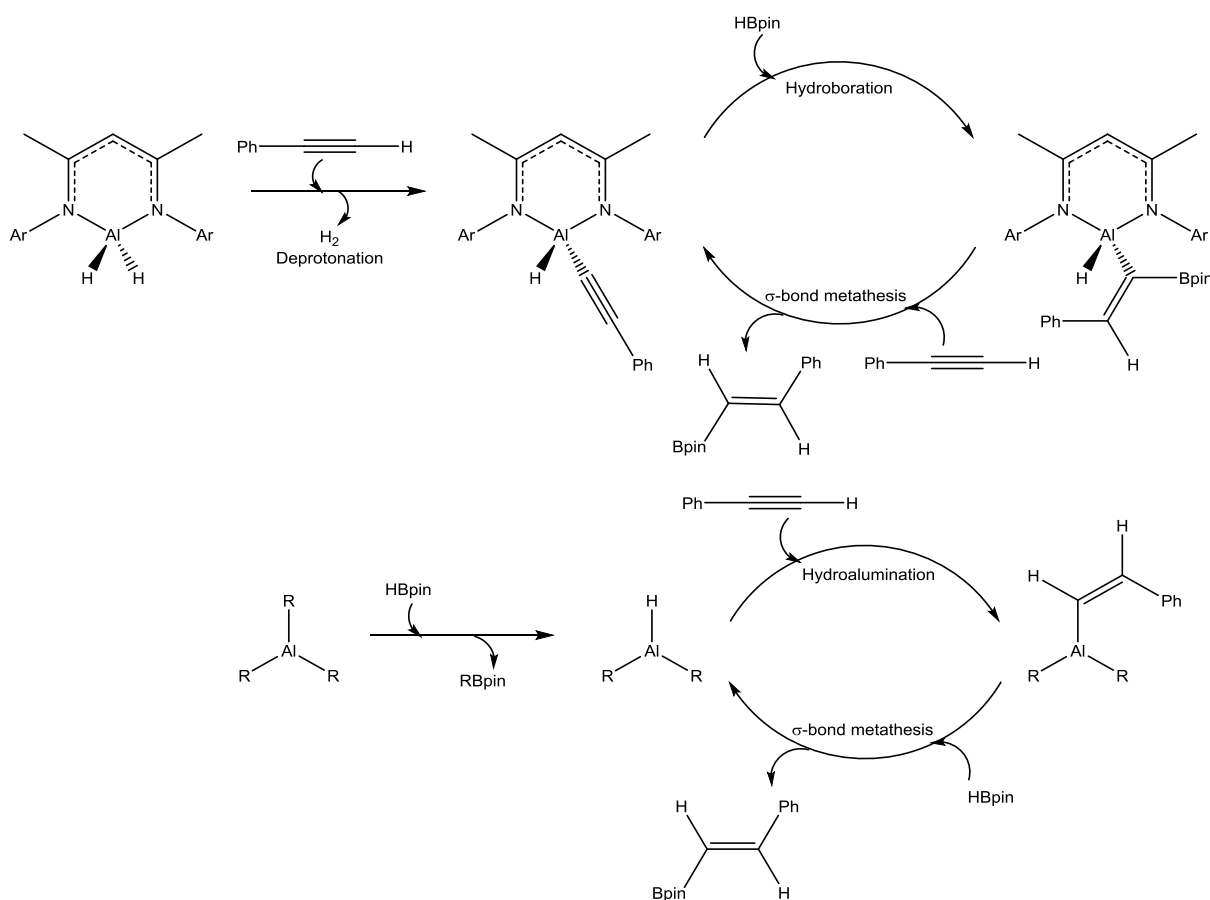
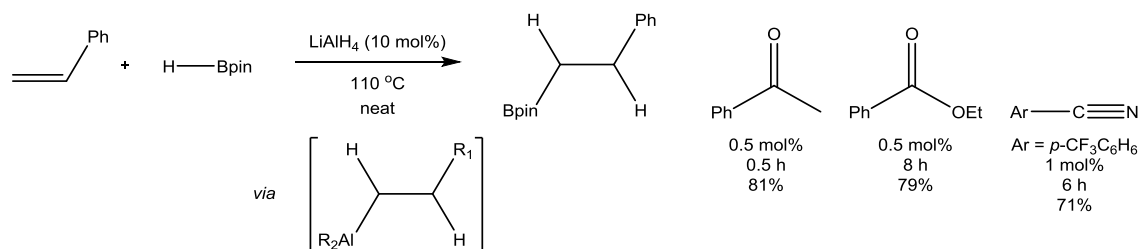


Figure 1.27: Proposed mechanistic cycles for catalytic hydroboration of alkynes using aluminium hydride catalysts.

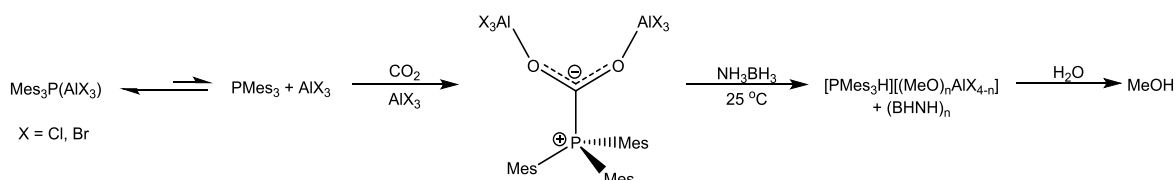
The extension of this methodology towards the hydroboration of alkenes has recently been made.³²¹ $LiAlH_4$ catalyses the hydroboration of a range of alkenes to yield the corresponding alkyl boronic esters with 99:1 linear:branched regioselectivity. For example, the catalytic hydroboration of styrene proceeds at 110°C with 10 mol% $LiAlH_4$

(TOF = 2.4 h⁻¹). This method is shown to have good substrate scope and functional group tolerance, with halide, silyl, and tosyl substituents remaining unaffected. As a preliminary study, this protocol was also applied to the hydroboration of ketone, ester and nitrile functional groups (Scheme 1.25).³²¹



Scheme 1.25: LiAlH₄ has been demonstrated to be a proficient catalyst for a range of unsaturated substrates.

Alanes have not been employed to effect the borane-mediated catalytic reduction of CO₂, but aluminium complexes have been used in CO₂ reduction processes as the Lewis acidic component of frustrated Lewis pairs.^{99,326–329}

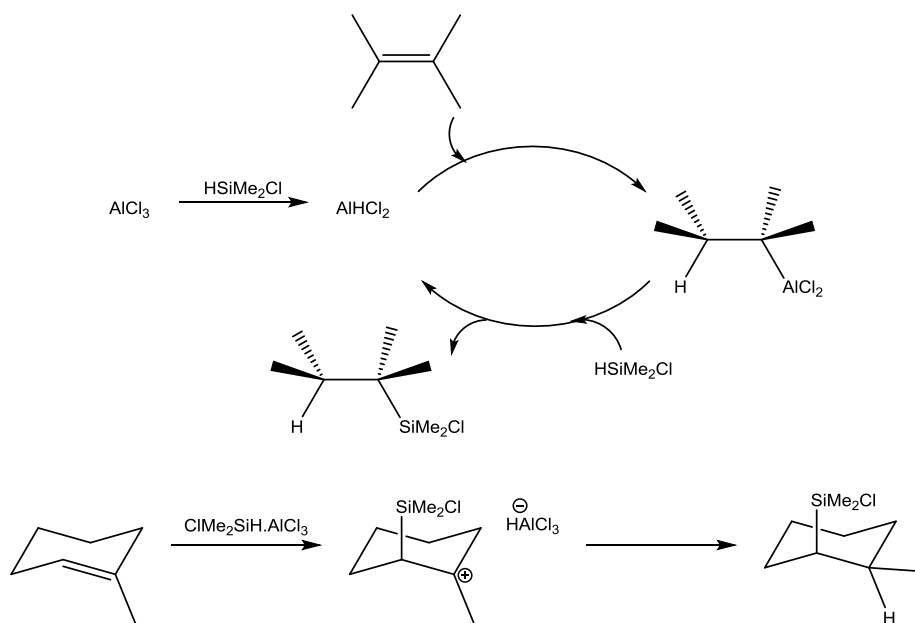


Scheme 1.26: Aluminium trihalides have been used as the Lewis acidic component of a FLP for the stoichiometric reduction of CO₂ to methanol.³²⁶

1.4.2.3 Alanes as catalysts for hydrosilylation reactions

Hydrosilylation is by far the most widely studied reaction catalysed by aluminium: aluminium halides are efficient catalysts for the hydrosilylation of alkenes and alkynes.³¹⁰ It has been demonstrated that AlCl₃ catalyses the hydrosilylation of tetrasubstituted alkenes, using HSiR₂Cl (R = Me, ^tBu).³³⁰ It was originally proposed that AlCl₃ reacts with the silane *via* Cl/H exchange, yielding the active hydride catalyst

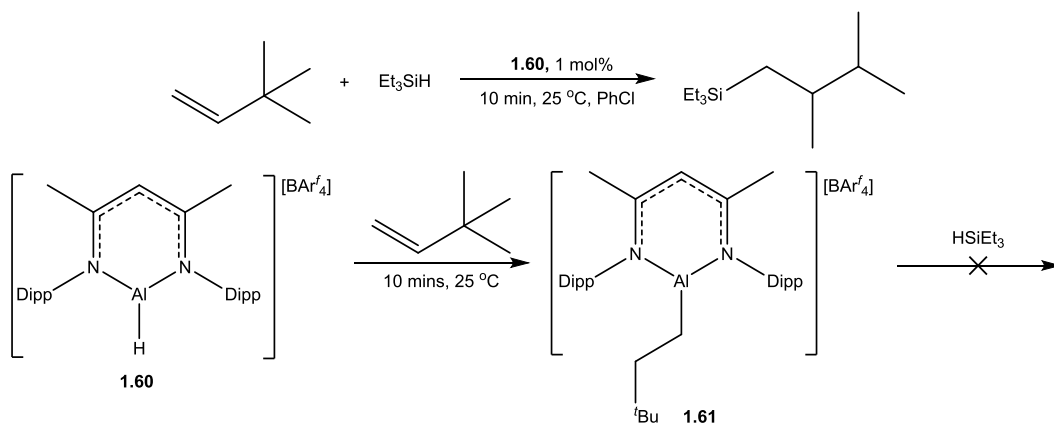
HAlCl_2 , which hydroaluminates the alkene. The alane catalyst would then be regenerated by Al-C/Si-H metathesis.



Scheme 1.27: Above: the original mechanism proposed for AlCl_3 -catalysed hydrosilylation of tetrasubstituted olefins; below: the mechanism is now considered to proceed by Lewis acid activation of the silane.

However, this mechanism has since been reconsidered and such reactivity is considered to proceed *via* an alternative electrophilic mechanism based on the activation of the *silane* by the aluminium Lewis acid, forming an adduct of the form $\text{R}_3\text{SiH}\cdot\text{AlCl}_3$, which transfers the silylium ion to the alkene to generate a carbocation.³¹⁰ This Lewis acid-catalysed process is closely related to the mechanism proposed for borane-catalysed hydrosilylation reactions.^{280,331} Indeed the highly electrophilic $\text{Al}(\text{C}_6\text{F}_5)_3$ (**1.58**) catalyses the hydrosilylation of 1-hexene (5 mol%, 0.5 h, 98%, TOF 39 h^{-1}), proceeding *via* formation of the “activated” silane adduct $[\text{Et}_3\text{Si}\cdot\text{H}\cdots\text{Al}(\text{C}_6\text{F}_5)_3]$ (**1.59**), which has been isolated and studied by X-ray diffraction.³³² **1.59** delivers a silylium ion to the alkene to give a carbocation, followed by the transfer of the hydride from $[\text{HAl}(\text{C}_6\text{F}_5)_3]^-$.

Even when the aluminium catalyst bears a hydride functionality, it has been demonstrated that the catalyst functions as a Lewis acid catalyst. This was revealed in a study of the hydrosilylation of alkenes and alkynes mediated by the cationic complex, $[[\text{Dipp}^1\text{AlH}][\text{BAR}^f_4]]$ (**1.60**).³³³ **1.60** readily hydroaluminates a range of alkenes, yielding alkylaluminium derivatives. However, these systems do not react with silanes to give hydrosilylation products, even at elevated temperatures (70°C, 24 h). In light of this, and the observation that alkene-insertion product **1.61** may also catalyse this process (with a turnover activity comparable to that of **1.60**), it was proposed that catalysis proceeds *via* Lewis acid activation of the silane by the cationic aluminium centre.



Scheme 1.28: Cationic aluminium hydride **1.60** is demonstrated to effect the catalytic hydrosilylation of alkenes.

It has therefore been demonstrated that hydrosilylation chemistry catalysed by aluminium complexes is dominated by their ability to operate as Lewis acid catalysts, for activation of the silane reductant.³¹⁰ A wide range of aluminium-based catalysts have been reported that effect the hydrosilylation of alkynes, carbonyls (including aldehydes, ketones and imines) and CO_2 .³¹⁰ For example, **1.58** catalyses the hydrosilylation of ketones, albeit with significantly reduced activity compared to that of $\text{B}(\text{C}_6\text{F}_5)_3$. This is thought to be due to the greater Lewis acidity of **1.58**, which coordinates ketones more strongly, thereby reducing the quantity of Lewis acid catalyst available for activation of

the silane.³³² A range of cationic aluminium complexes have also been reported which effect the catalytic hydrosilylation of CO₂, employing Et₃SiH as the reductant.^{262–264} The use of cationic Lewis acid catalysts (Figure 1.28) require harsh reaction conditions (T > 85°C) and a range of products are yielded including CH₄, HD, C₆D₅CH₃ and (C₆D₅)₂CH₂, with the latter two products arising from Lewis acid-catalysed Friedel–Crafts alkylation of the benzene-d₆ solvent. It has been demonstrated, however, that **1.58** catalyses the hydrosilylation of CO₂ when used in conjunction with B(C₆F₅)₃. While elevated temperatures are required (T = 80°C), catalysis proceeds selectively, yielding methane in 82% yield (**1.58** 5 mol% / B(C₆F₅)₃ 5 mol%, TOF 4 h⁻¹).²⁶²

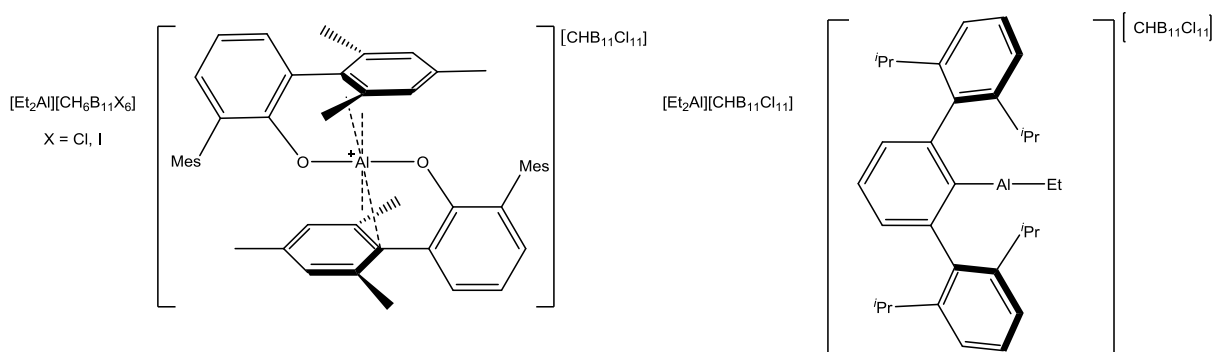
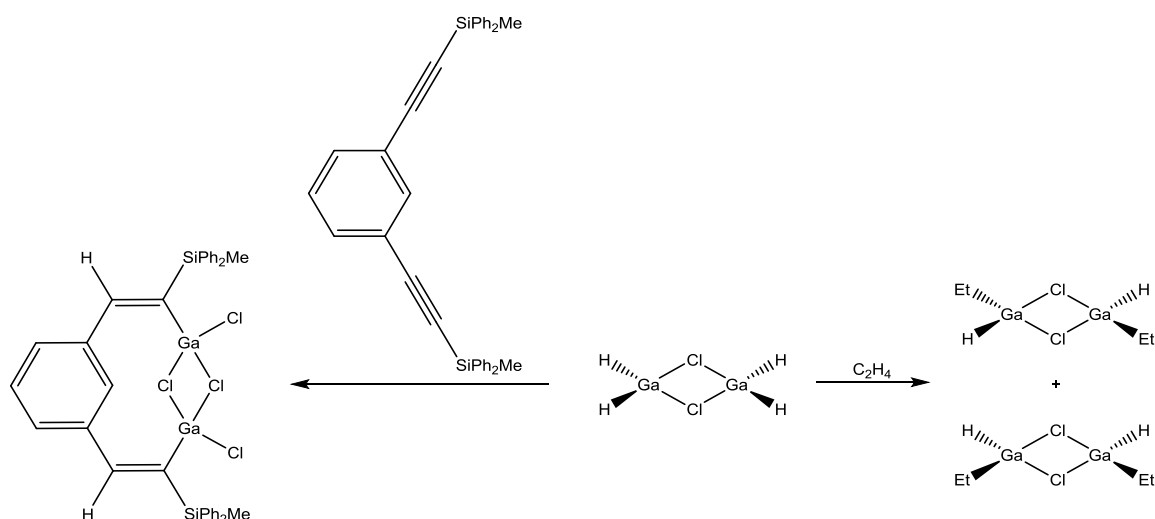


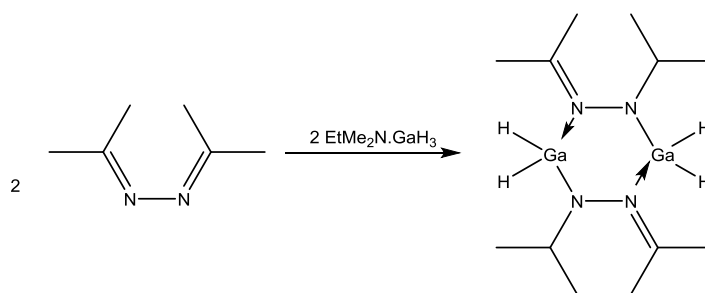
Figure 1.28: Examples of cationic aluminium catalysts for the hydrosilylation of CO₂.

1.4.2.4 The use of gallanes as catalysts for the reduction of unsaturated substrates

One of the primary modes of reactivity of gallium hydrides is hydrogallation of unsaturated C=E bonds. There are numerous reported examples of the insertion of Ga-H bonds into alkenes and alkynes,^{2,12,334–338} and examples of the hydrogallation of C=N bonds have also been described.^{339,340}



Scheme 1.29: Two examples of the use of monochlorogallane to effect the hydrogallation of alkynes and alkenes.³³⁷

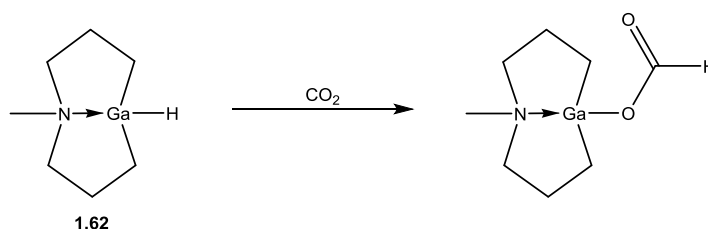


Scheme 1.30: An example of hydrogallation of an imine by donor-stabilised gallane.³³⁹

There is far less literature precedent for the insertion of Ga-H bonds into C=O bonds; and most of those reported only involve the stoichiometric reduction of these functionalities. Where gallanes are shown to hydrogallate C=O bonds, they operate as considerably milder reducing agents than their alane counterparts. For example, $\text{Me}_3\text{N} \cdot \text{GaH}_3$ reduces 4- $\text{BrC}_6\text{H}_4\text{C}(\text{O})\text{CH}_2\text{Br}$ to the corresponding alcohol, following work up, with only trace cleavage (*ca.* 6%) of the C-Br bond.³⁴¹ Key examples of the hydrogallation of C=O bonds include reactions of α,β -unsaturated ketones,³⁴² where insertion into the C=C and C=O bonds compete, and CO_2 . There are two reported examples of gallium hydrides which react with CO_2 *via* insertion of the Ga-H bond to yield a gallium formate complex.^{156,343} These include a Nacnac-ligated monohydride, $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{tBu})\text{H}$ (previously discussed in

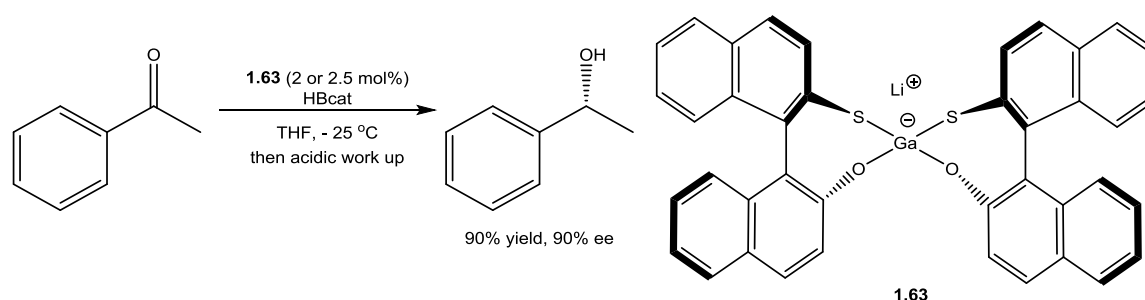
Chapter I: Introduction

Section 1.3.2.4), and a gallium hydride, $(\text{CH}_3)_3\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{GaH}$ (**1.62**), stabilised by an amino donor.



Scheme 1.31: Gallanes have been demonstrated to effect the hydrogallation of CO_2 .

Despite the ability of gallium hydrides to carry out the hydrometallation of unsaturated functionalities, there are very few reports of the exploitation of this reactivity catalytically. The use of $[\text{Dipp}^1]\text{Ga}(\text{tBu})\text{H}$ as a catalyst for the borane-mediated reduction of CO_2 (previously discussed in Section 1.3.2.4) represents a relatively rare example of a gallane-catalysed reductive process.¹⁵⁶

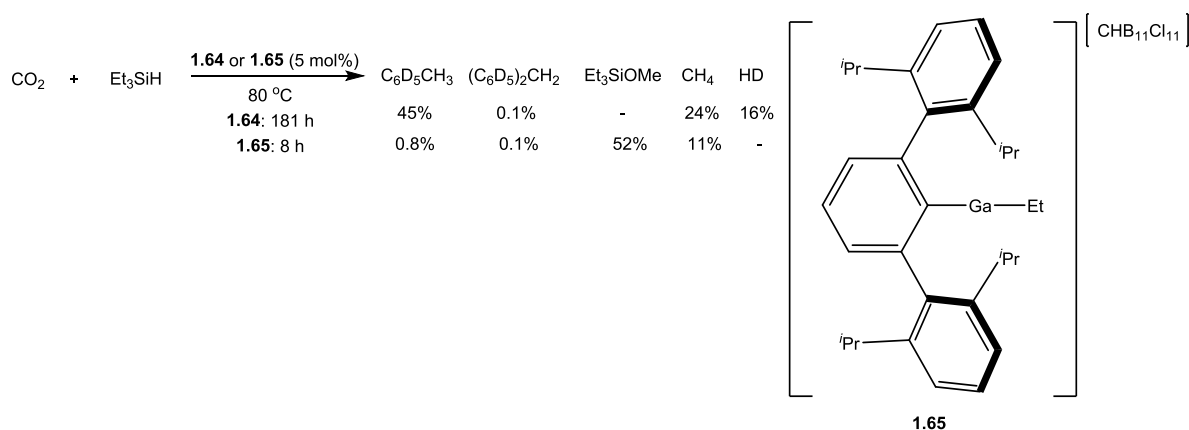


Scheme 1.32: Gallium catalyst **1.63** is employed for the enantioselective hydroboration of ketones.

In 2000, the enantioselective hydroboration of ketones catalysed by chiral gallium complexes was investigated.³⁴⁴ LiGaH_4 was used in combination with chiral ligands such as 1,1'-(bi-2-naphthol), 2,2'-dimercapto-1,1'-binaphthyl and 2-hydroxy-2'-mercapto-1,1'-binaphthyl (MTBH_2) to generate the active catalyst. The latter system exhibited the greatest activity for the hydroboration of acetophenone, employing HBcat as the reductant. This system reduces a range of aryl/alkyl ketones with 90 – 93% ee and dialkyl ketones $\text{RC}(\text{O})\text{Me}$ ($\text{R} = \text{iPr}, \text{tBu}$) with 60 – 72% ee. Mechanistic studies suggest

that the resting state of the catalyst is the dimer $[\text{Li}_2(\text{MTB})][\text{Ga}_2(\text{MTB})_3]$ which rearranges into the monomeric gallate $\text{Li}[\text{Ga}(\text{MTB})_2]$ (**1.63**).³⁴⁴ The nature of the reactive hydride species remains unclear.

Whilst not gallane-mediated, the catalytic hydrosilylation of CO_2 has been reported to have been effected by cationic gallium complexes $[\text{Et}_2\text{Ga}][\text{CHB}_{11}\text{Cl}_{11}]$ (**1.64**) and $[(2,6\text{-Dipp}_2\text{C}_6\text{H}_3)\text{Ga}(\text{Et})][\text{CHB}_{11}\text{Cl}_{11}]$ (**1.65**).²⁶⁴ Relatively forcing conditions are required (80%) and the reactions are not particularly selective, yielding products which arise as a result of alkylation of the solvent.



Scheme 1.33: Cationic gallium complexes have recently been shown to catalyse the hydrosilylation of CO_2 .

1.5 References

- (1) Downs, A. J.; Himmel, H. J. in *The Group 13 Metals Aluminium, Gallium, Indium and Thallium; Chemical Patterns and Peculiarities* (Eds.: S. Aldridge, A.J. Downs) Wiley, Chichester, UK.
- (2) Aldridge, S.; Downs, A. J. *Chem. Rev.* **2001**, *101* (11), 3305–3365.
- (3) Vest, B.; Klinkhammer, K.; Thierfelder, C.; Lein, M.; Schwerdtfeger, P. *Inorg. Chem.* **2009**, *48* (16), 7953–7961.
- (4) Downs, A. J.; Pulham, C. R. *Chem. Soc. Rev.* **1994**, *23* (3), 175–184.
- (5) Goode, M. J.; Downs, A. J.; Pulham, C. R.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1988**, (12), 768–769.
- (6) Wang, X.; Andrews, L.; Tam, S.; DeRose, M. E.; Fajardo, M. E. *J. Am. Chem. Soc.* **2003**, *125* (30), 9218–9228.
- (7) Andrews, L.; Wang, X. *Science* **2003**, *300* (5620), 741.
- (8) Finholt, A. E.; Bond, A. C.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69* (5), 1199–1203.
- (9) Schmidt, D. L.; Roberts, C. B.; Reigler, P. F.; Lemanski, M. F.; Schram, E. P. *Inorg. Synth.* **1973**, *14*, 47–52.
- (10) Brown, H. C.; Weissman, P. M.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88* (10), 1464–1472.
- (11) Turley, J. W.; Rinn, H. W. *Inorg. Chem.* **1969**, *8* (1), 18–22.
- (12) Pulham, C. R.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Am. Chem. Soc.* **1991**,

Chapter I: Introduction

- 113 (14), 5149–5162.
- (13) Downs, A. J.; Goode, M. J.; Pulham, C. R. *J. Am. Chem. Soc.* **1989**, *111* (5), 1936–1937.
- (14) Jones, C.; Koutsantonis, G. A.; Raston, C. L. *Polyhedron* **1993**, *12* (15), 1829–1848.
- (15) Raston, C. L. *Journal of Organometallic Chemistry*. **1994**, *475* (1–2), 15–24.
- (16) Gardiner, M. G.; Raston, C. L. *Coord. Chem. Rev.* **1997**, *166*, 1–34.
- (17) Downs, A. *Coord. Chem. Rev.* **1999**, *189* (1), 59–100.
- (18) Atwood, J. L.; Robinson, K. D.; Bennett, F. R.; Elms, F. M.; Jones, C.; Raston, C. L. *J. Am. Chem. Soc.* **1991**, *113* (21), 8183–8185.
- (19) Brain, P. T.; Brown, H. E.; Downs, A. J.; Greene, T. M.; Johnsen, E.; Parsons, S.; Rankin, D. W. H.; Smart, B. A.; Tang, C. Y. *J. Chem. Soc. Dalton Trans.* **1998**, (21), 3685–3692.
- (20) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, (21), 2832–2838.
- (21) Czerw, M.; Goldman, A. S.; Krogh-Jespersen, K. *Inorg. Chem.* **2000**, *39* (2), 363–369.
- (22) Heitsch, C. W.; Nordman, C. E.; Parry, R. W. *Inorg. Chem.* **1963**, *2* (3), 508–512.
- (23) Ii, N.; Greenwood, A.; Storr, A. M. G.; Wallbridge, H.; Wallbridge, T. H.; Finholt, A. E.; Bond, A. C.; Schlesinger, J. A.; Sot, M. *Inorg. Chem.* **1963**, *2* (5), 1036–1039.
- (24) Bennett, F. R.; Elms, F. M.; Gardiner, M. G.; Koutsantonis, G. A.; Raston, C. L.; Roberts, N. K. *Organometallics* **1992**, *11* (4), 1457–1459.
- (25) Atwood, J. L.; Butz, K. W.; Gardiner, M. G.; Jones, C.; Koutsantonis, G. A.; Raston, C. L.; Robinson. *Inorg. Chem.* **1993**, *32* (16), 3482–3487.
- (26) Tang, C. Y.; Coxall, R. A.; Downs, A. J.; Greene, T. M.; Parsons, S. *J. Chem. Soc. Dalton Trans.* **2001**, (14), 2141–2147.
- (27) Flidel, C.; Schnee, G.; Avilés, T.; Dagorne, S. *Coord. Chem. Rev.* **2014**, *275*, 63–86.
- (28) Arduengo, A. J.; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. J. *J. Am. Chem. Soc.* **1992**, *114* (24), 9724–9725.
- (29) Abernethy, C. D.; Cole, M. L.; Jones, C. *Organometallics* **2000**, *19* (23), 4852–4857.
- (30) Baker, R. J.; Davies, A. J.; Jones, C.; Kloth, M. J. *Organomet. Chem.* **2002**, *656* (1–2), 203–210.
- (31) Francis, M. D.; Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Smithies, N. A. *J. Chem. Soc. Dalton Trans.* **1998**, (19), 3249–3254.
- (32) Abdalla, J. A. B.; Riddlestone, I. M.; Tirfoin, R.; Phillips, N.; Bates, J. I.; Aldridge, S. *Chem. Commun.* **2013**, *49* (49), 5547–5549.
- (33) Abdalla, J. A. B.; Riddlestone, I. M.; Turner, J.; Kaufman, P. A.; Tirfoin, R.; Phillips, N.; Aldridge, S. *Chem. Eur. J.* **2014**, *20* (52), 17624–17634.
- (34) Leverett, A. R.; McKay, A. I.; Cole, M. L. *Dalton Trans.* **2015**, *44* (2), 498–500.
- (35) Baker, R. J.; Cole, M. L.; Jones, C.; Mahon, M. F. *J. Chem. Soc. Dalton Trans.* **2002**, (9), 1992–1996.
- (36) Miyai, T.; Inoue, K.; Yasuda, M.; Shibata, I.; Baba, A. *Tetrahedron Lett.* **1998**, *39* (14), 1929–1932.
- (37) Schmidbaur, H.; Findeiss, W.; Gast, E. *Angew. Chem. Int. Ed. Engl.* **1965**, *4* (2), 152–152.
- (38) Contreras, L.; Cowley, A. H.; Gabbai, F. P.; Jones, R. A.; Carrano, C. J.; Bond, M. R. *J. Organomet. Chem.* **1995**, *489* (1–2), 1–3.
- (39) Cowley, A. H.; Gabbai, F. P.; Atwood, D. A.; Carrano, C. J.; Mokry, L. M.; Bond, M. R. *J. Am. Chem. Soc.* **1994**, *116* (4), 1559–1560.
- (40) Wehmschulte, R. J.; Ellison, J. J.; Ruhlandtsenge, K.; Power, P. P. *Inorg. Chem.* **1994**, *33* (26), 6300–6306.
- (41) Cowley, A. H.; Gabbai, F. P.; Isom, H. S.; Carrano, C. J.; Bond, M. R. *Angew. Chem. Int. Ed. Engl.* **1994**, *33* (12), 1253–1255.
- (42) Köppe, R.; Tacke, M.; Schnöckel, H. Z. *Anorg. Allg. Chem.* **1991**, *605* (1), 35–41.
- (43) Köppe, R.; Schnöckel, H. *J. Chem. Soc. Dalton Trans.* **1992**, (23), 3393–3395.
- (44) Pullumbi, P.; Bouteiller, Y.; Manceron, L.; Mijoule, C. *Chem. Phys.* **1994**, *185* (1), 25–37.
- (45) Himmel, H.-J.; Downs, A. J.; Greene, T. M. *J. Am. Chem. Soc.* **2000**, *122* (5), 922–930.
- (46) Elms, F. M.; Koutsantonis, G. A. **1995**, *107* (8), 1669–1670.
- (47) Alexander, S. G.; Cole, M. L. *Eur. J. Inorg. Chem.* **2008**, (29), 4493–4506.
- (48) Cowley, A. H.; Gabbai, F. P.; Isom, H. S.; Decken, A. J. *Organomet. Chem.* **1995**, *500* (1–2), 81–88.
- (49) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1994**, *33* (25), 5611–5612.
- (50) Cowley, A. H.; Isom, H. S.; Decken, A. *Organometallics* **1995**, *14* (5), 2589–2592.
- (51) Wehmschulte, R. J.; Ellison, J. J.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1994**, *33* (26), 6300–6306.
- (52) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1996**, *35* (11), 3262–3267.
- (53) Wehmschulte, R. J.; Grigsby, W. J.; Schiemenz, B.; Bartlett, R. A.; Power, P. P. *Inorg. Chem.* **1996**, *35* (23), 6694–6702.

Chapter I: Introduction

- (54) Murosaki, T.; Kaneda, S.; Maruhashi, R.; Sadamori, K.; Shoji, Y.; Tamao, K.; Hashizume, D.; Hayakawa, N.; Matsuo, T. *Organometallics* **2016**, 35 (19), 3397–3405.
- (55) Wehmschulte, R. J.; Steele, J. M.; Khan, M. A. *Organometallics* **2003**, 22 (23), 4678–4684.
- (56) Young, J. D.; Khan, M. A.; Powell, D. R.; Wehmschulte, R. J. *Eur. J. Inorg. Chem.* **2007**, (12), 1671–1681.
- (57) Isom, H. S.; Cowley, A. H.; Decken, A.; Sissingh, F.; Corbelin, S.; Lagow, R. J. *Organometallics* **1995**, 14 (5), 2400–2406.
- (58) Bensiek, S.; Bangel, M.; Neumann, B.; Stammeler, H.-G.; Jutzi, P. *Organometallics* **2000**, 19 (7), 1292–1298.
- (59) Hair, G. S.; Battle, S. L.; Decken, A.; Cowley, A. H.; Jones, R. A. *Inorg. Chem.* **2000**, 39 (1), 27–31.
- (60) Dümichen, U.; Gelbrich, T.; Sieler, J. Z. *Anorg. Allg. Chem.* **2001**, 627 (8), 1915–1920.
- (61) Dümichen, U.; Thiele, K.-H.; Gelbrich, T.; Sieler, J. *J. Organomet. Chem.* **1995**, 495 (1–2), 71–75.
- (62) Chang, J. C.; Hung, C. H.; Huang, J. H. *Organometallics* **2001**, 20 (22), 4445–4447.
- (63) Lin, C. Y.; Tsai, C. F.; Chen, H. J.; Hung, C. H.; Yu, R. C.; Kuo, P. C.; Lee, H. M.; Huang, J. H. *Chem. Eur. J.* **2006**, 12 (11), 3067–3073.
- (64) Cui, C.; Roesky, H. W.; Hao, H.; Schmidt, H. G.; Noltemeyer, M. *Angew. Chem. Int. Ed.* **2000**, 39 (10), 1815–1817.
- (65) Singh, S.; Ahn, H.-J.; Stasch, A.; Jancik, V.; Roesky, H. W.; Pal, A.; Biadene, M.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2006**, 45 (4), 1853–1860.
- (66) Kuo, P. C.; Chen, I. C.; Chang, J. C.; Lee, M. T.; Hu, C. H.; Hung, C. H.; Lee, H. M.; Huang, J. H. *Eur. J. Inorg. Chem.* **2004**, (24), 4898–4906.
- (67) Jana, B.; Uhl, W. *Inorganica Chim. Acta* **2017**, 455 (1), 61–69.
- (68) Cole, M. L.; Jones, C.; Junk, P. C.; Kloth, M.; Stasch, A. *Chem. Eur. J.* **2005**, 11 (15), 4482–4491.
- (69) Duchateau, R.; Meetsma, A.; Teuben, J. H. *Chem. Commun.* **1996**, (2), 223–224.
- (70) Cole, M. L.; Davies, A. J.; Jones, C.; Junk, P. C.; McKay, A. I.; Stasch, A. *Z. Anorg. Allg. Chem.* **2015**, 641 (12–13), 2233–2244.
- (71) Alexander, S. G.; Cole, M. L.; Forsyth, C. M.; Furfari, S. K.; Konstas, K. *Dalton Trans.* **2009**, (13), 2326–2336.
- (72) Welch, G. C.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2004**, 23 (8), 1811–1818.
- (73) Masuda, J. D.; Walsh, D. M.; Wei, P.; Stephan, D. W. *Organometallics* **2004**, 23 (8), 1819–1824.
- (74) Rasika Dias, H. V.; Wiechang, J.; Ratcliff, R. E. *Inorg. Chem.* **1995**, 34 (24), 6100–6105.
- (75) Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. *Nature* **2018**, 557 (7703), 92–95.
- (76) Lehmkuhl, H.; Mehler, K.; Benn, R.; Rufinska, A.; Schroth, G.; Krüger, C. *Chem. Ber.* **1984**, 117 (1), 389–403.
- (77) Barron, A. R.; Wilkinson, G. *Polyhedron* **1986**, 5 (12), 1897–1915.
- (78) Bulychiev, B. M. *Polyhedron* **1990**, 9 (2–3), 387–408.
- (79) Erker, G.; Albrecht, M.; Werner, S.; Nolte, M.; Krüger, C. *Chem. Ber.* **1992**, 125 (8), 1953–1956.
- (80) Sizov, A. I.; Molodnitskaya, I. V.; Bulychiev, B. M.; Evdokimova, E. V.; Belskii, V. K.; Soloveichik, G. L. *J. Organomet. Chem.* **1988**, 344 (3), 293–301.
- (81) Pulham, C. R.; Brain, P. T.; Downs, A. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc. Chem. Commun.* **1990**, (2), 177–178.
- (82) Aldridge, S.; Blake, A. J.; Downs, A. J.; Gould, R. O.; Parsons, S.; Pulham, C. R. *J. Chem. Soc. Dalton Trans.* **1997**, (6), 1007–1012.
- (83) Knabel, K.; Krossing, I.; Noeth, H.; Schwenk-Kircher, H.; Schmidt-Amelunxen, M.; Seifert, T. *Eur. J. Inorg. Chem.* **1998**, (8), 1095–1114.
- (84) Harder, S.; Spielmann, J. *Chem. Commun.* **2011**, 47 (43), 11945–11947.
- (85) Downs, A. J.; Pulham, C. R. *Adv. Inorg. Chem.* **1994**, 41 (C), 171–232.
- (86) Downs, A. J.; Greene, T. M.; Johnsen, E.; Brain, P. T.; Morrison, C. A.; Parsons, S.; Pulham, C. R.; Rankin, D. W. H.; Aarset, K.; Mills, I. M.; Page, E. M.; Rice, D. A. *Inorg. Chem.* **2001**, 40 (14), 3484–3497.
- (87) Downs, A. J.; Greene, T. M.; Harman, L. A.; Souter, P. F.; Brain, P. T.; Pulham, C. R.; Rankin, D. W. H.; Robertson, H. E.; Hofmann, M.; Schleyer, P. v. R. *Inorg. Chem.* **1995**, 34 (7), 1799–1809.
- (88) Barlow, M. T.; Downs, A. J.; Thomas, P. D. P.; Rankin, D. W. H. *J. Chem. Soc. Dalton Trans.* **1979**, (11), 1793–1800.
- (89) Barlow, M. T.; Dain, C. J.; Downs, A. J.; Thomas, P. D. P.; Rankin, D. W. H. *J. Chem. Soc. Dalton Trans.* **1980**, (8), 1374–1378.
- (90) Almenningen, A.; Gundersen, G.; Haaland, A. *Acta Chem. Scand.* **1968**, 22 (1), 328–334.
- (91) Downs, A. J.; Harman, L. A.; Thomas, P. D. P.; Pulham, C. R. *Polyhedron* **1995**, 14 (7), 935–945.
- (92) Glass, J. A.; Kher, S. S.; Spencer, J. T. *Chem. Mater.* **1992**, 4 (3), 530–538.

Chapter I: Introduction

- (93) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, 77 (2), 263–293.
- (94) Bailey, N. A.; Bird, P. H.; Wallbridge, M. G. H. *Chem. Commun.* **1965**, (19), 438–439.
- (95) Bailey, N. A.; Bird, P. H.; Wallbridge, M. G. H. *Inorg. Chem.* **1968**, 7 (8), 1575–1581.
- (96) Bh, P. Al; Ii, E. A.; Dou, D.; Liu, J.; Krause, J. A.; Glenn, B.; Iv, T. J.; Shore, S. G. *Inorg. Chem.* **1994**, 33, 5443–5447.
- (97) Bissinger, P.; Mikulcik, P.; Riede, J.; Schier, A.; Schmidbaur, H. *J. Organomet. Chem.* **1993**, 446 (1–2), 37–43.
- (98) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, 123 (34), 8291–8309.
- (99) Ménard, G.; Stephan, D. W. *Dalton Trans.* **2013**, 42 (15), 5447–5453.
- (100) Erdmann, M.; Rösener, C.; Holtrichter-Rößmann, T.; Daniliuc, C. G.; Fröhlich, R.; Uhl, W.; Würthwein, E.-U.; Kehr, G.; Erker, G. *Dalton Trans.* **2013**, 42 (3), 709–718.
- (101) Downs, A. J.; Thomas, P. D. P. *J. Chem. Soc. Dalton Trans.* **1978**, (7), 809–817.
- (102) Fischer, R. A.; Priermeier, T.; Scherer, W. *J. Organomet. Chem.* **1993**, 459 (1–2), 65–71.
- (103) Durig, J. R.; Chatterjee, K. K.; Li, Y. S.; Jalilian, M.; Zozulin, A. J.; Odom, J. D. *J. Chem. Phys.* **1980**, 73 (1), 21–29.
- (104) Shirk, A. E.; Shriver, D. F. *J. Am. Chem. Soc.* **1973**, 95 (18), 5904–5912.
- (105) Camp, C.; Arnold, J. *Dalton Trans.* **2016**, 45 (37), 14462–14498.
- (106) Tsai, Y. C. *Coord. Chem. Rev.* **2012**, 256 (5–8), 722–758.
- (107) McGeachin, S. G. *Can. J. Chem.* **1968**, 46 (11), 1903–1912.
- (108) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, 102 (9), 3031–3065.
- (109) Chen, C.; Bellows, S. M.; Holland, P. L. *Dalton Trans.* **2015**, 44 (38), 16654–16670.
- (110) Randall, D. W.; George, S. D.; Holland, P. L.; Hedman, B.; Hodgson, K. O.; Tolman, W. B.; Solomon, E. I. *J. Am. Chem. Soc.* **2000**, 122 (47), 11632–11648.
- (111) Zhou, W.; Tang, L.; Patrick, B. O.; Smith, K. M. *Organometallics* **2011**, 30 (3), 603–610.
- (112) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Le Pape, L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, 41 (24), 6307–6321.
- (113) Do, D. C. H.; Keyser, A.; Protchenko, A. V.; Maitland, B.; Pernik, I.; Niu, H.; Kolychev, E. L.; Rit, A.; Vidovic, D.; Stasch, A.; Jones, C.; Aldridge, S. *Chem. Eur. J.* **2017**, 23 (24), 5830–5841.
- (114) Lee, P. T. K.; Clyburne, J. Masters Thesis, St. Mary's University, Halifax, Canada, **2009**.
- (115) Jones, C. *Coord. Chem. Rev.* **2010**, 254 (11–12), 1273–1289.
- (116) Jones, C.; Junk, P. C.; Platts, J. A.; Stasch, A. *J. Am. Chem. Soc.* **2006**, 128 (7), 2206–2207.
- (117) Jones, C.; Junk, P. C.; Kloth, M.; Proctor, K. M.; Stasch, A. *Polyhedron* **2006**, 25 (7), 1592–1600.
- (118) Do, D. C. H.; Protchenko, A. V.; Angeles Fuentes, M.; Hicks, J.; Kolychev, E. L.; Vasko, P.; Aldridge, S. *Angew. Chem. Int. Ed.* **2018**, 10.1002/anie.201807543.
- (119) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc. Perkin Trans.* **1987**, (12), S1.
- (120) Driess, M.; Yao, S.; Brym, M.; Van Wüllen, C.; Lentz, D. *J. Am. Chem. Soc.* **2006**, 128 (30), 9628–9629.
- (121) Hardman, N. J.; Eichler, B. E.; Power, P. P. *Chem. Commun.* **2000**, 53 (20), 1991–1992.
- (122) Cui, C.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem. Int. Ed.* **2000**, 39 (23), 4274–4276.
- (123) Hill, M. S.; Hitchcock, P. B. *Chem. Commun.* **2004**, 44 (16), 1818–1819.
- (124) Brower, F. M.; Matzek, N. E.; Reigler, P. F.; Rinn, H. W.; Roberts, C. B.; Schmidt, D. L.; Snover, J. A.; Terada, K. *J. Am. Chem. Soc.* **1976**, 98 (9), 2450–2453.
- (125) González-Gallardo, S.; Jancik, V.; Cea-Olivares, R.; Toscano, R. A.; Moya-Cabrera, M. *Angew. Chem. Int. Ed.* **2007**, 46 (16), 2895–2898.
- (126) Kuhn, N.; Fuchs, S.; Steimann, M. *Z. Anorg. Allg. Chem.* **2000**, 626 (6), 1387–1392.
- (127) Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H. W. *J. Am. Chem. Soc.* **2016**, 138 (8), 2548–2551.
- (128) Nako, A. E.; Gates, S. J.; White, A. J. P.; Crimmin, M. R. *Dalton Trans.* **2013**, 42 (42), 15199–15206.
- (129) Twamley, B.; Hardman, N. J.; Power, P. P. *Acta Crystallogr. E.* **2001**, 57 (6), 227–228.
- (130) Chu, T.; Korobkov, I.; Nikonov, G. I. *J. Am. Chem. Soc.* **2014**, 136 (25), 9195–9202.
- (131) Chu, T.; Boyko, Y.; Korobkov, I.; Kuzmina, L. G.; Howard, J. A. K.; Nikonov, G. I. *Inorg. Chem.* **2016**, 55 (17), 9099–9104.
- (132) Crimmin, M. R.; Butler, M. J.; White, A. J. P. *Chem. Commun.* **2015**, 51 (88), 15994–15996.
- (133) Chu, T.; Boyko, Y.; Korobkov, I.; Nikonov, G. I. *Organometallics* **2015**, 34 (22), 5363–5365.
- (134) Crimmin, M. R.; Bakewell, C.; White, A. *Angew. Chem. Int. Ed.* **2018**, 57 (22), 6638–6642.
- (135) Seifert, A.; Scheid, D.; Linti, G.; Zessin, T. *Chem. Eur. J.* **2009**, 15 (44), 12114–12120.
- (136) Herappe-Mejía, E.; Trujillo-Hernández, K.; Carlos Garduño-Jiménez, J.; Cortés-Guzmán, F.;

- Martínez-Otero, D.; Jancik, V. *Dalton Trans.* **2015**, 44 (38), 16894–16902.
- (137) Yang, Y.; Li, H.; Wang, C.; Roesky, H. W. *Inorg. Chem.* **2012**, 51 (4), 2204–2211.
- (138) Hao, H.; Mou, Z.; Zhuang, J.; Wan, P.; Li, H. *Faming Zhuanhi Shiqing* **2014**.
- (139) Chu, C.; Yang, Y.; Zhu, H. *Sci. China Chem.* **2010**, 53 (9), 1970–1977.
- (140) Zhu, H.; Yang, Z.; Magull, J.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **2005**, 24 (26), 6420–6425.
- (141) Nako, A. E.; Gates, S. J.; Schädel, N.; White, A. J. P.; Crimmin, M. R. *Chem. Commun.* **2014**, 50 (67), 9536–9538.
- (142) Yang, Z.; Hao, P.; Liu, Z.; Ma, X.; Roesky, H. W.; Sun, K.; Li, J. *Organometallics* **2012**, 31 (17), 6500–6503.
- (143) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, 54 (35), 10225–10229.
- (144) Uhl, W.; Jana, B. *J. Organomet. Chem.* **2009**, 694 (7–8), 1101–1106.
- (145) Uhl, W.; Jana, B. *Chem. Eur. J.* **2008**, 14 (10), 3067–3071.
- (146) Kuhn, N.; Fuchs, S.; Steimann, M. *Z. Anorg. Allg. Chem.* **2000**, 626 (6), 1387–1392.
- (147) Kuhn, N.; Fuchs, S.; Steimann, M. *Eur. J. Inorg. Chem.* **2001**, 2001 (2), 359–361.
- (148) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, 121 (37), 8673–8674.
- (149) Vidovic, D.; Jones, J. N.; Moore, J. A.; Cowley, A. H. *Z. Anorg. Allg. Chem.* **2005**, 631 (13–14), 2888–2892.
- (150) Yang, Z.; Zhu, H.; Ma, X.; Chai, J.; Roesky, H. W.; He, C.; Magull, J.; Schmidt, H. G.; Noltemeyer, M. *Inorg. Chem.* **2006**, 45 (4), 1823–1827.
- (151) Vidovic, D.; Findlater, M.; Reeske, G.; Cowley, A. H. *J. Organomet. Chem.* **2007**, 692 (26), 5683–5686.
- (152) Bai, G.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G. *J. Am. Chem. Soc.* **2005**, 127 (10), 3449–3455.
- (153) Nako, A. E.; Tan, Q. W.; White, A. J. P.; Crimmin, M. R. *Organometallics* **2014**, 33 (11), 2685–2688.
- (154) Bernabé-Pablo, E.; Jancik, V.; Moya-Cabrera, M. *Inorg. Chem.* **2013**, 52 (12), 6944–6950.
- (155) Yang, Z.; Ma, X.; Roesky, H. W.; Yang, Y.; Zhu, H.; Magull, J.; Ringe, A. *Z. Anorg. Allg. Chem.* **2008**, 634 (9), 1490–1492.
- (156) Abdalla, J. A. B.; Riddlestone, I. M.; Tirfoin, R.; Aldridge, S. *Angew. Chem. Int. Ed.* **2015**, 54 (17), 5098–5102.
- (157) Turner, J.; Abdalla, J. A. B.; Bates, J. I.; Tirfoin, R.; Kelly, M. J.; Phillips, N.; Aldridge, S. *Chem. Sci.* **2013**, 4 (11), 4245–4250.
- (158) Kempter, A.; Gemel, C.; Fischer, R. A. *Inorg. Chem.* **2008**, 47 (16), 7279–7285.
- (159) Power, P. P. *Nature* **2010**, 463 (7278), 171–177.
- (160) Revunova, K.; Nikonov, G. I. *Dalton Trans.* **2015**, 44 (3), 840–866.
- (161) Spikes, G. H.; Fetting, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, 127 (35), 12232–12233.
- (162) Hill, M. S.; Liptrot, D. J.; Weetman, C. *Chem. Soc. Rev.* **2016**, 45 (4), 972–988.
- (163) Weetman, C.; Anker, M. D.; Arrowsmith, M.; Hill, M. S.; Kociok-Köhn, G.; Liptrot, D. J.; Mahon, M. F. *Chem. Sci.* **2016**, 7 (1), 628–641.
- (164) Yang, Y.; Anker, M. D.; Fang, J.; Mahon, M. F.; Maron, L.; Weetman, C.; Hill, M. S. *Chem. Sci.* **2017**, 8 (5), 3529–3537.
- (165) Huang, K.; Sun, C.-L.; Shi, Z.-J. *Chem. Soc. Rev.* **2011**, 40 (5), 2435–2452.
- (166) Schneider, J.; Jia, H.; Muckerman, J. T.; Fujita, E. *Chem. Soc. Rev.* **2012**, 41 (6), 2036–2051.
- (167) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *Nature Communications* **2015**, 6, 5933–5948.
- (168) Murphy, L. J.; Robertson, K. N.; Kemp, R. A.; Tuononen, H. M.; Clyburne, J. A. C. *Chem. Commun.* **2015**, 51 (19), 3942–3956.
- (169) Tlili, A.; Blondiaux, E.; Frogneux, X.; Cantat, T. *Green Chem.* **2015**, 17 (1), 157–168.
- (170) Laitar, D. S.; Müller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2005**, 127 (49), 17196–17197.
- (171) Kortlever, R.; Shen, J.; Schouten, K. J. P.; Calle-Vallejo, F.; Koper, M. T. M. *J. Phys. Chem. Lett.* **2015**, 6 (20), 4073–4082.
- (172) Costentin, C.; Robert, M.; Savéant, J.-M. *Chem. Soc. Rev.* **2013**, 42 (6), 2423–2436.
- (173) Sahara, G.; Ishitani, O. *Inorg. Chem.* **2015**, 54 (1), 5096–5104.
- (174) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. *Chem. Soc. Rev.* **2009**, 38 (1), 89–99.
- (175) Wang, W. H.; Himeda, Y.; Muckerman, J. T.; Manbeck, G. F.; Fujita, E. *Chem. Rev.* **2015**, 115 (23), 12936–12973.
- (176) Chong, C. C.; Kinjo, R. *ACS Catal.* **2015**, 5 (6), 3238–3259.
- (177) Lu, Z.; Williams, T. J. *ACS Catal.* **2016**, 6 (10), 6670–6673.
- (178) Ma, Q.-Q.; Liu, T.; Li, S.; Zhang, J.; Chen, X.; Guan, H. *Chem. Commun.* **2016**, 52 (99), 14262–14265.
- (179) Jessop, P. G.; Joó, F.; Tai, C.-C. *Coord. Chem. Rev.* **2004**, 248 (21–24), 2425–2442.

Chapter I: Introduction

- (180) Wang, W.; Wang, S.; Ma, X.; Gong, J. *Chem. Soc. Rev.* **2011**, 40 (7), 3703–3727.
- (181) Li, Y.-N.; Ma, R.; He, L.-N.; Diao, Z.-F. *Catal. Sci. Technol.* **2014**, 4 (6), 1498–1512.
- (182) Alberico, E.; Nielsen, M. *Chem. Commun.* **2015**, 51 (31), 6714–6725.
- (183) Klankermayer, J.; Wesselbaum, S.; Beydoun, K.; Leitner, W. *Angew. Chem. Int. Ed.* **2016**, 55 (26), 7296–7343.
- (184) Fernández-Alvarez, F. J.; Aitani, A. M.; Oro, L. A. *Catal. Sci. Technol.* **2014**, 4 (3), 611–624.
- (185) Bontemps, S. *Coord. Chem. Rev.* **2016**, 308 (2), 117–130.
- (186) Jin, G.; Werncke, C. G.; Escudié, Y.; Sabo-Etienne, S.; Bontemps, S. *J. Am. Chem. Soc.* **2015**, 137 (30), 9563–9566.
- (187) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. *J. Am. Chem. Soc.* **2010**, 132 (26), 8872–8873.
- (188) Chakraborty, S.; Zhang, J.; Patel, Y. J.; Krause, J. A.; Guan, H. *Inorg. Chem.* **2013**, 52 (1), 37–47.
- (189) Shintani, R.; Nozaki, K. *Organometallics* **2013**, 32 (8), 2459–2462.
- (190) Suh, H.-W.; Guard, L. M.; Hazari, N. *Chem. Sci.* **2014**, 5 (10), 3859–3872.
- (191) Berkefeld, A.; Piers, W. E.; Parvez, M.; Castro, L.; Maron, L.; Eisenstein, O. *Chem. Sci.* **2013**, 4 (5), 2152–2162.
- (192) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2014**, 136 (11), 4419–4425.
- (193) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2012**, 51 (7), 1671–1674.
- (194) Bontemps, S.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2013**, 52 (39), 10253–10255.
- (195) Huang, F.; Zhang, C.; Jiang, J.; Wang, Z. X.; Guan, H. *Inorg. Chem.* **2011**, 50 (8), 3816–3825.
- (196) Blondiaux, E.; Pouessel, J.; Cantat, T. *Angew. Chem. Int. Ed.* **2014**, 53 (45), 12186–12190.
- (197) Li, Y.; Fang, X.; Junge, K.; Beller, M. *Angew. Chem. Int. Ed.* **2013**, 52 (36), 9568–9571.
- (198) Li, Y.; Sorribes, I.; Yan, T.; Junge, K.; Beller, M. *Angew. Chem. Int. Ed.* **2013**, 52 (46), 12156–12160.
- (199) Frogneux, X.; Blondiaux, E.; Thuéry, P.; Cantat, T. *ACS Catal.* **2015**, 5 (7), 3983–3987.
- (200) Murphy, L. J.; Hollenhorst, H.; McDonald, R.; Ferguson, M.; Lumsden, M. D.; Turculet, L. *Organometallics* **2017**, 36 (19), 3709–3720.
- (201) Sgro, M. J.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2012**, 51 (45), 11343–11345.
- (202) Pal, R.; Groy, T. L.; Trovitch, R. J. *Inorg. Chem.* **2015**, 54 (15), 7506–7515.
- (203) Suh, H. W.; Guard, L. M.; Hazari, N. *Polyhedron* **2014**, 84, 37–43.
- (204) Chakraborty, S.; Patel, Y. J.; Krause, J. A.; Guan, H. *Polyhedron* **2012**, 32 (1), 30–34.
- (205) Liu, T.; Meng, W.; Ma, Q.-Q.; Zhang, J.; Li, H.; Li, S.; Zhao, Q.; Chen, X. *Dalton Trans.* **2017**, 46 (14), 4504–4509.
- (206) Crimmin, M. R.; Hicken, A.; White, A. J. P. *Angew. Chem. Int. Ed.* **2017**, 56 (47), 15127–15130.
- (207) Courtemanche, M. A.; Légaré, M. A.; Maron, L.; Fontaine, F. G. *J. Am. Chem. Soc.* **2013**, 135 (25), 9326–9329.
- (208) Wang, T.; Stephan, D. W. *Chem. Eur. J.* **2014**, 20 (11), 3036–3039.
- (209) Das Neves Gomes, C.; Blondiaux, E.; Thuéry, P.; Cantat, T. *Chem. Eur. J.* **2014**, 20 (23), 7098–7106.
- (210) Wang, T.; Stephan, D. W. *Chem. Commun.* **2014**, 50 (53), 7007–7010.
- (211) von Wolff, N.; Lefèvre, G.; Berthet, J.-C.; Thuéry, P.; Cantat, T. *ACS Catal.* **2016**, 6 (7), 4526–4535.
- (212) Declercq, R.; Bouhadir, G.; Bourissou, D.; Légaré, M. A.; Courtemanche, M. A.; Nahi, K. S.; Bouchard, N.; Fontaine, F. G.; Maron, L. *ACS Catal.* **2015**, 5 (4), 2513–2520.
- (213) Ramos, A.; Antiñolo, A.; Carrillo-Hermosilla, F.; Fernandez-Galan, R.; Rodríguez Diéguez, A.; García-Vivó, D. G. *Chem. Commun.* **2018**, 4700 (54), 4700–4703.
- (214) Yang, Y.; Xu, M.; Song, D. *Chem. Commun.* **2015**, 51 (56), 11293–11296.
- (215) Yang, Y.; Yan, L.; Xie, Q.; Liang, Q.; Song, D. *Org. Biomol. Chem.* **2017**, 15, 2240–2245.
- (216) Janes, T.; Yang, Y.; Song, D. *Chem. Commun.* **2017**, 53 (83), 11390–11398.
- (217) Sau, S. C.; Bhattacharjee, R.; Vardhanapu, P. K.; Vijaykumar, G.; Datta, A.; Mandal, S. K. *Angew. Chem. Int. Ed.* **2016**, 55 (48), 15147–15151.
- (218) Ho, S. Y.-F.; So, C.-W.; Saffon-Merceron, N.; Mézailles, N. *Chem. Commun.* **2015**, 51 (11), 2107–2110.
- (219) Légaré, M.-A.; Courtemanche, M.-A.; Fontaine, F.-G. *Chem. Commun.* **2014**, 50 (77), 11362–11365.
- (220) Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. *Chem. Commun.* **2016**, 52 (89), 13155–13158.
- (221) Mukherjee, D.; Osseili, H.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2016**, 138 (34), 10790–10793.
- (222) Mukherjee, D.; Wiegand, A.-K.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2017**, 46 (19), 6183–6186.
- (223) Lafage, M.; Pujol, A.; Saffon-Merceron, N.; Mézailles, N. *ACS Catal.* **2016**, 6 (5), 3030–3035.
- (224) Lu, Z.; Hausmann, H.; Becker, S.; Wegner, H. A. *J. Am. Chem. Soc.* **2015**, 137 (16), 5332–5335.
- (225) Fujiwara, K.; Yasuda, S.; Mizuta, T. *Organometallics* **2014**, 33 (22), 6692–6695.
- (226) Anker, M. D.; Arrowsmith, M.; Bellham, P.; Hill, M. S.; Kociok-Köhn, G.; Liptrot, D. J.; Mahon, M. F.; Weetman, C. *Chem. Sci.* **2014**, 5 (7), 2826–2830.
- (227) Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. *J. Am. Chem. Soc.* **2009**, 131

- (3), 1288–1293.
- (228) Jana, A.; Roesky, H. W.; Schulzke, C.; Döring, A. *Angew. Chem. Int. Ed.* **2009**, *48* (6), 1106–1109.
- (229) Tan, G.; Wang, W.; Blom, B.; Driess, M. *Dalton Trans.* **2014**, 43 (16), 6006–6011.
- (230) Hadlington, T. J.; Kefalidis, C. E.; Maron, L.; Jones, C. *ACS Catal.* **2017**, *7* (3), 1853–1859.
- (231) Jana, A.; Tavčar, G.; Roesky, H. W.; John, M. *Dalton Trans.* **2010**, 39 (40), 9487–9489.
- (232) Mitton, S. J.; Turculet, L. *Chem. Eur. J.* **2012**, *18* (48), 15258–15262.
- (233) Rios, P.; Diez, J.; Lopez-Serrano, J.; Rodriguez, A.; Conejero, S. *Chem. Eur. J.* **2016**, *22* (47), 16791–16795.
- (234) Huckaba, A. J.; Hollis, T. K.; Reilly, S. W. *Organometallics* **2013**, *32* (21), 6248–6256.
- (235) Morris, D. S.; Weetman, C.; Wennmacher, J. T. C.; Cokoja, M.; Drees, M.; Kühn, F. E.; Love, J. B. *Catal. Sci. Technol.* **2017**, *7* (13), 2838–2845.
- (236) Jiang, Y.; Blacque, O.; Fox, T.; Berke, H. J. *Am. Chem. Soc.* **2013**, *135* (20), 7751–7760.
- (237) Metsänen, T. T.; Oestreich, M. *Organometallics* **2015**, *34* (3), 543–546.
- (238) Deglmann, P.; Ember, E.; Hofmann, P.; Pitter, S.; Walter, O. *Chem. Eur. J.* **2007**, *13* (10), 2864–2879.
- (239) Jansen, A.; Pitter, S. *J. Mol. Catal. A Chem.* **2004**, *217* (1–2), 41–45.
- (240) Jansen, A.; Görls, H.; Pitter, S. *Organometallics* **2000**, *19* (2), 135–138.
- (241) Koinuma, H.; Kawakami, F.; Kato, H.; Hirai, H. *J. Chem. Soc. Chem. Commun.* **1981**, (1), 213–214.
- (242) Julián, A.; Jaseer, E. A.; Garcés, K.; Fernández-Alvarez, F. J.; García-Orduña, P.; Lahoz, F. J.; Oro, L. A. *Catal. Sci. Technol.* **2016**, *6* (12), 4410–4417.
- (243) Park, S.; Bézier, D.; Brookhart, M. *J. Am. Chem. Soc.* **2012**, *134* (28), 11404–11407.
- (244) Eisenschmid, T. C.; Eisenberg, R. *Organometallics* **1989**, *8* (7), 1822–1824.
- (245) Lalrempuia, R.; Iglesias, M.; Polo, V.; Sanz Miguel, P. J.; Fernández-Alvarez, F. J.; Pérez-Torrente, J. J.; Oro, L. A. *Angew. Chem. Int. Ed.* **2012**, *51* (51), 12824–12827.
- (246) Scheuermann, M. L.; Semproni, S. P.; Pappas, I.; Chirik, P. J. *Inorg. Chem.* **2014**, *53* (18), 9463–9465.
- (247) Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2006**, *128* (38), 12362–12363.
- (248) Giambastiani, G.; Luconi, L.; Tuci, G.; Rossin, A.; Cicchi, S.; Gafurov, Z.; Yakhvarov, D.; Lyubov, D.; Trifonov, A.; Ba, H.; Pham-Huu, C. *ChemCatChem* **2018**. 10.1002/cctc.201800077
- (249) Zhang, L.; Cheng, J.; Hou, Z. *Chem. Commun.* **2013**, 49 (42), 4782–4784.
- (250) Motokura, K.; Kashiwame, D.; Miyaji, A.; Baba, T. *Org. Lett.* **2012**, *14* (10), 2642–2645.
- (251) Motokura, K.; Kashiwame, D.; Takahashi, N.; Miyaji, A.; Baba, T. *Chem. Eur. J.* **2013**, *19* (30), 10030–10037.
- (252) Tani, Y.; Kuga, K.; Fujihara, T.; Terao, J.; Tsuji, Y. *Chem. Commun.* **2015**, 51 (65), 13020–13023.
- (253) Rios, P.; Curado, N.; Lopez-Serrano, J.; Rodriguez, A. *Chem. Commun.* **2016**, 52 (10), 2114–2117.
- (254) González-Sebastián, L.; Flores-Alamo, M.; García, J. J. *Organometallics* **2013**, *32* (23), 7186–7194.
- (255) Leblanc, F. A.; Piers, W. E.; Parvez, M. *Angew. Chem. Int. Ed.* **2014**, *53* (3), 789–792.
- (256) Rit, A.; Zanardi, A.; Spaniol, T. P.; Maron, L.; Okuda, J. *Angew. Chem. Int. Ed.* **2014**, *53* (48), 13273–13277.
- (257) Sattler, W.; Parkin, G. *J. Am. Chem. Soc.* **2012**, *134* (42), 17462–17465.
- (258) Specklin, D.; Fliedel, C.; Gourlaouen, C.; Bruyere, J. C.; Avilés, T.; Boudon, C.; Ruhlmann, L.; Dagorne, S. *Chem. Eur. J.* **2017**, *23* (23), 5509–5519.
- (259) Deshmukh, M. M.; Sakaki, S. *Inorg. Chem.* **2014**, *53* (16), 8485–8493.
- (260) Tüchler, A. M.; Gärtner, L.; Fischer, S.; Boese, D.; Belaj, F.; Mösch-zanetti, N. C. *Angew. Chem. Int. Ed.* **2018**, *57* (23), 6906–6909.
- (261) Rauch, M.; Parkin, G. *J. Am. Chem. Soc.* **2017**, *139* (50), 18162–18165.
- (262) Chen, J.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2016**, *138* (16), 5321–5333.
- (263) Khandelwal, M.; Wehmschulte, R. J. *Angew. Chem. Int. Ed.* **2012**, *51* (29), 7323–7326.
- (264) Saleh, M.; Powell, D. R.; Wehmschulte, R. J. *Organometallics* **2017**, *36* (24), 4810–4815.
- (265) Mukherjee, D.; Sauer, D. F.; Zanardi, A.; Okuda, J. *Chem. Eur. J.* **2016**, *22* (23), 7730–7733.
- (266) Schäfer, A.; Saak, W.; Haase, D.; Müller, T. *Angew. Chem. Int. Ed.* **2012**, *51* (12), 2981–2984.
- (267) Berkefeld, A.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2010**, *132* (31), 10660–10661.
- (268) Del Rio, N.; Lopez-Reyes, M.; Baceiredo, A.; Saffon-Merceron, N.; Lutters, D.; Müller, T.; Kato, T. *Angew. Chem. Int. Ed.* **2017**, *56* (5), 1365–1370.
- (269) Courtemanche, M.-A.; Pulis, A. P.; Rochette, É.; Légaré, M.-A.; Stephan, D. W.; Fontaine, F.-G. *Chem. Commun.* **2015**, 51 (48), 9797–9800.
- (270) Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem. Int. Ed.* **2009**, *48* (18), 3322–3325.
- (271) Fang, C.; Lu, C.; Liu, M.; Zhu, Y.; Fu, Y.; Lin, B.-L. *ACS Catal.* **2016**, *6* (11), 7876–7881.
- (272) Chong, C. C.; Kinjo, R. *Angew. Chem. Int. Ed.* **2015**, *54* (41), 12116–12120.
- (273) Piers, W. E. *Advances in Organometallic Chemistry*. **2004**, *52*, 1–76.

Chapter I: Introduction

- (274) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, 65 (10), 3090–3098.
- (275) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, 118 (39), 9440–9441.
- (276) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J. X.; Yamamoto, Y. *J. Org. Chem.* **2000**, 65 (19), 6179–6186.
- (277) Houghton, A. Y.; Hurmalainen, J.; Mansikkamäki, A.; Piers, W. E.; Tuononen, H. M. *Nat. Chem.* **2014**, 6 (11), 983–988.
- (278) Hog, D. T.; Oestreich, M. *Eur. J. Org. Chem.* **2009**, (29), 5047–5056.
- (279) Oestreich, M.; Hermeke, J.; Mohr, J. *Chem. Soc. Rev.* **2015**, 44 (8), 2202–2220.
- (280) Rendler, S.; Oestreich, M. *Angew. Chem. Int. Ed.* **2008**, 47 (32), 5997–6000.
- (281) Ríos, P.; Rodríguez, A.; López-Serrano, J. *ACS Catal.* **2016**, 6 (9), 5715–5723.
- (282) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. *Acc. Chem. Res.* **2015**, 48 (7), 1995–2003.
- (283) Magano, J.; Dunetz, J. R. *Organic Process Research and Development.* **2012**, 16 (6), 1156–1184.
- (284) Cho, B. T. *Chem. Soc. Rev.* **2009**, 38 (2), 443–452.
- (285) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, 30 (2), 97–102.
- (286) Mäki-Arvela, P.; Hájek, J.; Salmi, T.; Murzin, D. Y. *Applied Catalysis.* **2005**, 292 (1-2), 1–49.
- (287) Barman, M. K.; Baishya, A.; Nembenna, S.; Kociok-Koehn, G.; Edwards, A. J.; McIntyre, G. J.; Lemaire, M.; Pudalov, N. J.; Knapp, S. M. M.; Chianese, A. R. *Dalton Trans.* **2017**, 46 (13), 4152–4156.
- (288) Mukherjee, D.; Ellern, A.; Sadow, A. D. *Chem. Sci.* **2014**, 5 (3), 959–964.
- (289) Manna, K.; Ji, P.; Greene, F. X.; Lin, W. J. *Am. Chem. Soc.* **2016**, 138 (24), 7488–7491.
- (290) Lawson, J. R.; Wilkins, L. C.; Melen, R. L. *Chem. Eur. J.* **2017**, 23 (46), 10997–11000.
- (291) Schneider, J.; Sindlinger, C. P.; Freitag, S. M.; Schubert, H.; Wesemann, L. *Angew. Chem. Int. Ed.* **2017**, 56 (1), 333–337.
- (292) Wu, Y.; Shan, C.; Sun, Y.; Chen, P.; Ying, J.; Zhu, J.; Liu, L.; Zhao, Y.; Horwich, T.; Januzzi, J. L.; Johnson, M. R.; Kasper, E. K.; Levy, W. C.; Masoudi, F. A.; McBride, P. E.; McMurray, J. J. V.; Mitchell, J. E.; Peterson, P. N.; Riegel, B.; Sam, F.; Stevenson, L. W.; Tang, W. H. W.; Tsai, E. J.; Wilkoff, B. L. *Chem. Commun.* **2016**, 52 (95), 13799–13802.
- (293) Tien, C.-H.; Adams, M. R.; Ferguson, M. J.; Johnson, E. R.; Speed, A. W. H. *Org. Lett.* **2017**, 19 (20), 5565–5568.
- (294) Yadav, S.; Pahar, S.; Sen, S. S. *Chem. Commun.* **2017**, 53 (33), 4562–4564.
- (295) Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, 109 (18), 5551–5553.
- (296) Corey, E. J.; Shibata, S.; Bakshi, R. K. *J. Org. Chem.* **1988**, 53 (12), 2861–2863.
- (297) Corey, E. J.; Helal, C. J. *Angew. Chem. Int. Ed.* **1998**, 37 (15), 1986–2012.
- (298) Arrowsmith, M.; Hadlington, T. J.; Hill, M. S.; Kociok-Köhn, G. *Chem. Commun.* **2012**, 48 (38), 4567–4569.
- (299) Fohlmeister, L.; Stasch, A. *Chem. Eur. J.* **2016**, 22 (29), 10235–10246.
- (300) Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. J. *Am. Chem. Soc.* **2014**, 136 (8), 3028–3031.
- (301) Bisai, M. K.; Pahar, S.; Das, T.; Vanka, K.; Sen, S. S. *Dalton Trans.* **2017**, 46 (8), 2420–2424.
- (302) Chong, C. C.; Hirao, H.; Kinjo, R. *Angew. Chem. Int. Ed.* **2015**, 54 (1), 190–194.
- (303) Sarish, S. P.; Nekoueishahraki, B.; Jana, A.; Roesky, H. W.; Schulz, T.; Stalke, D. *Chem. Eur. J.* **2011**, 17 (3), 890–894.
- (304) Li, W.; Ma, X.; Walawalkar, M. G.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2017**, 350, 14–29.
- (305) Myers, T. W.; Berben, L. A. *J. Am. Chem. Soc.* **2013**, 135 (27), 9988–9990.
- (306) Myers, T. W.; Berben, L. A. *Organometallics* **2013**, 32 (22), 6647–6649.
- (307) Sherbow, T. J.; Carr, C. R.; Saisu, T.; Fettingner, J. C.; Berben, L. A. *Organometallics* **2016**, 35 (1), 9–14.
- (308) Berben, L. A. *Chem. Eur. J.* **2015**, 21 (7), 2734–2742.
- (309) Myers, T. W.; Berben, L. A. *Chem. Sci.* **2014**, 5 (7), 2771–2777.
- (310) Nikonov, G. I. *ACS Catal.* **2017**, 7 (10), 7257–7266.
- (311) Graves, C. R.; Campbell, E. J.; Nguyen, S. T. *Tetrahedron: Asymmetry* **2005**, 16 (21), 3460–3468.
- (312) Cha, J. S. *Organic Process Res. and Dev.* **2006**, 10 (5), 1032–1053.
- (313) Finke, U.; Moretto, H. DE 2804204 A1, 1978.
- (314) Kuo, P. C.; Chen, I. C.; Chang, J. C.; Lee, M. T.; Hu, C. H.; Hung, C. H.; Lee, H. M.; Huang, J. H. *Eur. J. Inorg. Chem.* **2004**, (24), 4898–4906.
- (315) Chen, I. C.; Ho, S. M.; Chen, Y. C.; Lin, C. Y.; Hu, C. H.; Tu, C. Y.; Datta, A.; Huang, J. H.; Lin, C. H. *Dalton Trans.* **2009**, (40), 8631–8643.
- (316) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1998**, 37 (26), 6906–6911.
- (317) Peng, Y.; Bai, G.; Fan, H.; Vidovic, D.; Roesky, H. W.; Magull, J. *Inorg. Chem.* **2004**, 43 (4), 1217–1219.
- (318) Jakhar, V. K.; Barman, M. K.; Nembenna, S. *Org. Lett.* **2016**, 18 (18), 4710–4713.
- (319) Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S. Z. *Anorg. Allg. Chem.* **2016**, 642 (22), 1245–1250.
- (320) Pollard, V. A.; Orr, S. A.; McLellan, R.; Kennedy, A. R.; Hevia, E.; Mulvey, R. E. *Chem. Commun.* **2018**,

Chapter I: Introduction

- 54 (10), 1233–1236.
- (321) Bismuto, A.; Cowley, M. J.; Thomas, S. P. *ACS Catal.* **2018**, 8 (3), 2001–2005.
- (322) Keyes, L. K.; Todd, A. D. K.; Giffin, N. A.; Veinot, A. J.; Hendsbee, A. D.; Robertson, K. N.; Geier, S. J.; Masuda, J. D. *RSC Adv.* **2017**, 7 (59), 37315–37323.
- (323) Liu, Y.; Liu, X.; Liu, Y.; Li, W.; Ding, Y.; Zhong, M.; Ma, X.; Yang, Z. *Inorg. Chim. Acta* **2018**, 471, 244–248.
- (324) Bismuto, A.; Thomas, S. P.; Cowley, M. J. *Angew. Chem. Int. Ed.* **2016**, 55 (49), 15356–15359.
- (325) Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S. Z. *Anorg. Allg. Chemie* **2016**, 642 (22), 1245–1250.
- (326) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, 132 (6), 1796–1797.
- (327) Ménard, G.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2011**, 50 (36), 8396–8399.
- (328) Boudreau, J.; Courtemanche, M.-A.; Fontaine, F.-G. *Chem. Commun.* **2011**, 47 (39), 11131–11133.
- (329) Courtemanche, M. A.; Larouche, J.; Légaré, M. A.; Bi, W.; Maron, L.; Fontaine, F. G. *Organometallics* **2013**, 32 (22), 6804–6811.
- (330) Oertle, K.; Wetter, H. *Tetrahedron Lett.* **1985**, 26 (45), 5511–5514.
- (331) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, 65 (10), 3090–3098.
- (332) Chen, J.; Chen, E. Y.-X. *Angew. Chem. Int. Ed.* **2015**, 54 (23), 6842–6846.
- (333) Jakobsson, K.; Chu, T.; Nikonov, G. I. *ACS Catal.* **2016**, 6 (11), 7350–7356.
- (334) Uhl, W.; Claesener, M. *Inorg. Chem.* **2008**, 47 (2), 729–735.
- (335) Uhl, W.; Claesener, M. *Inorg. Chem.* **2008**, 47 (11), 4463–4470.
- (336) Uhl, W. *Coord. Chem. Rev.* **2008**, 252 (15–17), 1540–1563.
- (337) Uhl, W.; Hentschel, A.; Kovert, D.; Kösters, J.; Layh, M. *Eur. J. Inorg. Chem.* **2015**, (14), 2486–2496.
- (338) Zaidlewicz, M.; Wolan, A.; Budny, B. *Comprehensive Organic Synthesis: Second Edition.* **2014**, 8, 877–963.
- (339) Uhl, W.; Molter, J.; Neumüller, B. *J. Organomet. Chem.* **2001**, 634 (2), 193–197.
- (340) J. L. Atwood; S. G. Bott; C. Jones; C. L. Raston. *Inorg. Chem.* **1991**, 30 (25), 4868–4870.
- (341) Raston, C. L.; Siu, A. F. H.; Tranter, C. J.; Young, D. J. *Tetrahedron Lett.* **1994**, 35 (32), 5915–5918.
- (342) Ohshita, J.; Schmidbaur, H. *J. Organomet. Chem.* **1993**, 453 (1), 7–12.
- (343) Schumann, H.; Just, O.; Seub, T. D.; Weimann, R. *J. Organomet. Chem.* **1994**, 472, 15–25.
- (344) Blake, A. J.; Cunningham, A.; Ford, A.; Teat, S. J.; Woodward, S. *Chem. Eur. J.* **2000**, 6 (19), 3586–3594

2. Experimental Techniques

2.1 Manipulation of air-sensitive compounds

The majority of compounds handled during the work presented this thesis are highly sensitive to air and moisture. In order to manipulate such compounds, inert atmosphere techniques were utilised, rather than traditional bench-top techniques.

2.1.1 Inert atmosphere techniques

The two techniques most frequently employed for the handling of air and moisture sensitive compounds are the use of a glove box or a Schlenk line. The use of such techniques enable the storage and manipulation of compounds under an inert atmosphere of argon or nitrogen.^{1,2} Solution-phase reactions involving sensitive compounds are typically carried out using a Schlenk line, which is both an efficient and effective way to minimise the risk of decomposition by oxidation or hydrolysis.³ The line utilised consisted of a dual Pyrex manifold; one manifold was connected to a source of purified argon gas, and the other to a high vacuum pump. A series of two-way taps allows for the connection of reaction vessels employed to both manifolds, allowing them to be evacuated and back-filled with a positive pressure of argon gas (Figure 2.1). The pressure within the vacuum manifold was monitored by use of a Pirani pressure gauge and was typically maintained at *ca.* 10^{-2} mbar.

To generate an environment inside reaction vessels that was as free as possible from air and moisture, a sequence of three 'pump and purge' cycles were applied, in which the

Chapter II: Experimental Techniques

vessel was evacuated to *ca.* 10^{-2} mbar, before being back-filled with argon gas. During the first evacuation cycle, glassware was heated strongly under vacuum using a Bunsen burner, to remove traces of moisture from the inside of the glassware. Excess pressure in the argon manifold was vented through a mercury bubbler. The vacuum manifold was used in conjunction with a liquid nitrogen trap, the purpose of which to ensure that no solvents or other volatile substances enter the vacuum pump. Ground glass joints were lubricated with high vacuum grease to produce an air-tight seal. Liquids were transferred between vessels using cannulae or syringes to minimize exposure to air. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS.

A glove box featuring a nitrogen atmosphere was used for the manipulation and storage of moisture sensitive solids. Neoprene gloves were installed into the side of the box to allow access to the sealed system. The atmosphere was purified by passage through an activated copper catalyst and molecular sieves, to remove oxygen and moisture, respectively. Compounds entered the box *via* an antechamber, which was subject to three 'pump and purge' cycles.

2.2 Spectroscopic and analytical techniques

A range of characterisation techniques were employed in this project, the details of which are given below.

2.2.1 NMR spectroscopy

NMR spectra were measured on a Bruker Avance III HD Nanobay 400 MHz NMR spectrometer equipped with a 9.4T magnet, Bruker Avance III 500 MHz NMR spectrometer equipped with a 11.75T magnet or a Bruker Avance 500 MHz NMR

Chapter II: Experimental Techniques

spectrometer equipped with a 11.75T magnet and a ^{13}C detect cryoprobe. ^1H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ^{11}B , ^{19}F , ^{29}Si and ^{27}Al NMR spectra were referenced with respect to $\text{BF}_3\cdot\text{OEt}_2$, CFCl_3 , $\text{Si}(\text{CH}_3)_4$ and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. NMR spectra were measured in benzene- d_6 or toluene- d_8 (which were dried over potassium), THF- d_8 (which was dried over LiAlH_4), bromobenzene- d_5 (which was dried over CaH_2) or dichloromethane- d_2 (which was dried over molecular sieves), with the solvent then being distilled under reduced pressure, degassed by three freeze-pump-thaw cycles and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves.

2.2.2 Infrared spectroscopy

Infrared spectra were measured on a Nicolet 500 FT-IR spectrometer. Samples were measured as a Nujol mull or a KBr disc and were prepared inside a glovebox before being sealed in an airtight cell.

2.2.3 Mass spectrometry

EI-MS measurements on neutral samples were carried out by Mr. James Wickens, University of Oxford.

2.2.4 Elemental analysis

Elemental analyses were carried out by Mr. Stephen Boyer, London Metropolitan University. Analyses were conducted on all novel compounds reported in this thesis that were isolated in the solid state.

2.2.5 X-ray crystallography

Structure determinations were carried out by Drs Rémi Tirfain, Jesus Campos, Evgeny Kolychev, Jamie Hicks or Maria Fuentes-Dominguez of the University of Oxford. Single-crystal X-ray diffraction data were collected using a Bruker Nonius Kappa-CCD or an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on Micromount loops and quench-cooled using an Oxford Cryosystems open flow N₂ cooling device.⁴ Data were collected at 150 K (unless otherwise stated), and reduced using DENZO/SCALEPACK⁶ or the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).⁶ Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. The structures were subsequently solved using SIR92,⁷ Superflip⁸ or SHELXT-2014 and refined with full-matrix least-squares within CRYSTALS^{8,9} or SHELXL 2014 package.¹¹⁻¹⁴

2.3 Preparation and purification of starting materials

Reagents and solvents were typically purified before use. Details of suppliers and purification procedures for all commercially available materials are provided in the Appendix. The following compounds were prepared according to literature procedures:

$\{\text{HC}(\text{MeCNDipp})_2\}\text{H}$ ([Dipp¹]H),¹⁵ $\text{Me}_3\text{N}\cdot\text{AlH}_3$,¹⁶ $\{\text{HC}(\text{MeCNDipp})_2\}\text{AlH}_2$,¹⁷
 $\{\text{HC}(\text{MeCNDipp})_2\}\text{Li}\cdot\text{OEt}_2$,¹⁷ $\{\text{HC}(\text{MeCNDipp})_2\}\text{AlCl}_2$,¹⁸ $\{\text{HC}(\text{MeCNDipp})_2\}\text{Al}(\text{OTf})\text{H}$,¹⁹
 $\{\text{HC}(\text{MeCNDipp})_2\}\text{AlMe}_2$,²⁰ $\{\text{HC}(\text{MeCNDipp})_2\}\text{Al}(\text{Me})\text{Cl}$,²¹ $\{\text{HC}(\text{MeCNDipp})_2\}\text{Ga}(\text{tBu})\text{Br}$,²²
 $\{\text{HC}(\text{MeCNDipp})_2\}\text{Ga}(\text{tBu})\text{H}$,²² $\{\text{HC}(\text{MeCNDipp})_2\}\text{Ga}(\text{tBu})(\text{OC}(\text{O})\text{H})$,²²
 $\{\text{HC}(\text{MeCNDipp})_2\}\text{Ga}(\text{tAm})\text{Br}$,²² $\{\text{HC}(\text{Me}_2\text{NCNDipp})_2\}\text{H}$ ([Dipp²]H),²³
 $\{\text{HC}(\text{Me}_2\text{NCNDipp})_2\}\text{Li}\cdot\text{OEt}_2$,²³ $\text{B}(\text{C}_6\text{F}_5)_3$,²⁴ and $\text{Na}[\text{B}(3,5\text{-CF}_3\text{-C}_6\text{H}_3)_4]$ ($\text{Na}[\text{BAr}^{\text{f}}_4]$).²⁵ Other compounds were prepared by modified literature procedures, as detailed below.

Preparation of $\{\text{HC}(\text{MeCNDipp})_2\}\text{Al}(\text{Et})\text{Cl}$ – [Dipp¹]Al(Et)Cl

The preparation of [Dipp¹]Al(Et)Cl followed a modified version of the method reported by Yang *et al.*²⁶ [Dipp¹]Li·OEt₂ (4g, 8.03 mmol) was dissolved in toluene (30 mL) and cooled to –78°C. AlEtCl₂ (1.0 M in *n*-hexane, 9.64 mL, 9.64 mmol) was added dropwise *via* syringe and the reaction mixture subsequently allowed to warm to room temperature overnight with stirring. The resulting yellow solution was filtered, and the remaining colourless precipitate washed with a further portion of toluene (10 mL). The two portions of toluene were combined, and volatiles removed *in vacuo*, to yield a spectroscopically pure orange oil. The oil was extracted into *n*-hexane, filtered and concentrated until incipient crystallisation. Gentle warming of the solution to redissolve the solid and storage of the solution at –30°C overnight yielded large yellow crystals, suitable for X-ray crystallography. The crystals were isolated and dried *in vacuo*. Further

concentration and cooling of the supernatant yielded a second crop of crystals. Total yield: 3.23 g, 79%. ^1H NMR data are consistent with those reported in the literature.²⁶

Preparation of $\{\text{HC}(\text{MeCNDipp})_2\}\text{GaCl}_2 - [\text{Dipp1}]\text{GaCl}_2$

The synthesis of $[\text{Dipp1}]\text{GaCl}_2$ followed a modified version of the method reported by Stender *et al.*¹⁸ $[\text{Dipp1}]\text{Li}\cdot\text{OEt}_2$ (4.00 g, 8.03 mmol) was dissolved in toluene (30 mL) and added dropwise to a cooled (0°C) solution of GaCl_3 (1.70 g, 9.64 mmol), also in toluene (20 mL). The reaction mixture was stirred overnight, whilst being allowed to warm to room temperature. The yellow solution was filtered, and volatiles removed *in vacuo*. The resulting solid was washed with cold pentane (0°C) and a small amount of cold diethyl ether (0°C) to yield a colourless powder, which was dried *in vacuo*. Yield: 3.53 g, 79%. ^1H NMR data are consistent with those reported in the literature.¹⁸

Preparation of $\{\text{HC}(\text{MeCNDipp})_2\}\text{GaH}_2 - [\text{Dipp1}]\text{GaH}_2$

The synthesis of $[\text{Dipp1}]\text{GaH}_2$ followed a modified version of the method reported by Singh *et al.*,²⁷ employing $[\text{Dipp1}]\text{GaCl}_2$ rather than $[\text{Dipp1}]\text{GaI}_2$. $[\text{Dipp1}]\text{GaCl}_2$ (3.50 g, 6.27 mmol) was dissolved in toluene (35 mL) and cooled to -78°C . $\text{K}[\text{HBEt}_3]$ (1.0 M in THF, 13.8 mL, 13.8 mmol) was added dropwise *via* syringe and the reaction mixture subsequently allowed to warm to room temperature overnight. The yellow solution was filtered, and volatiles removed *in vacuo*. The resulting solid was extracted into diethyl ether, filtered and concentrated to the point of incipient crystallisation. Storage of the solution at -30°C overnight produced large colourless crystals, which were isolated by filtration and dried *in vacuo*. Further concentration of the supernatant and storage at -30°C overnight yielded a second crop of colourless crystals. Yield: 2.77 g, 90%. ^1H NMR data are consistent with literature values.²⁷

Preparation of {HC(MeCNDipp)₂}GaI₂ – [Dipp1]GaI₂

[Dipp1]Li·OEt₂ (4.50 g, 9.04 mmol) was dissolved in toluene (30 mL) and added dropwise to a rapidly stirred slurry of GaI₃ (4.48 g, 9.40 mmol), also in toluene (20 mL), at –78°C. The reaction mixture was allowed to warm to room temperature overnight, whereby a bright yellow solution was formed, together with a colourless precipitate. The solution was filtered, and the precipitate washed with toluene (20 mL). Volatiles were removed *in vacuo* from the combined toluene fractions, and the resulting yellow residue extracted into boiling toluene. The solution was filtered, concentrated to the point of incipient crystallisation and stored at –30°C, producing large colourless crystals. A second crop of crystals could be obtained from further concentration of the supernatant and storage at –30°C. Yield: 5.87 g, 88%. ¹H NMR data are consistent with those reported in the literature.¹⁸

Preparation of {HC(MeCNDipp)₂}Ga(Cl)H – [Dipp1]Ga(Cl)H

The synthesis of [Dipp1]Ga(Cl)H followed a modified version of the method reported by Aldridge *et al.*²⁸ To a solution of [Dipp1]GaH₂ (1.00 g, 2.01 mmol) in toluene (20 mL) at –78°C was added dropwise a solution of [Dipp1]GaCl₂ (1.14 g, 2.01 mmol), also in toluene (20 mL). The solution was allowed to warm to room temperature and stirred for 48 h. Volatiles were removed *in vacuo* to yield a colourless powder which was extracted into diethyl ether. Filtration, concentration and cooling of this ethereal solution to –30°C yielded colourless crystals. Yield: 1.86 g, 87%. ¹H NMR data are consistent with those reported in the literature.²⁸

Preparation of {HC(MeCNDipp)₂}Ga – [Dipp¹]Ga

To a solution of [Dipp¹]GaI₂ (2.2 g, 2.97 mmol) in toluene (30 mL) at –78°C was added dropwise a solution of {[^{Mes}1]Mg}₂ (2.55 g, 3.56 mmol), also in toluene (30 mL). The reaction mixture was allowed to warm to room temperature, stirred for 24 h and filtered. The precipitate was washed with toluene (10 mL) and volatiles removed *in vacuo* from the combined toluene fractions, yielding a yellow solid. The solid was extracted into hot *n*-hexane, and the resulting solution filtered while hot and cooled to –30°C. Storage overnight yielded yellow crystals of [Dipp¹]Ga, which were isolated and dried *in vacuo*. Yield: 1.05 g, 72 %. ¹H NMR data are consistent with those reported in the literature.²⁹

2.4 References

- (1) Dodd, R. E.; Robinson, P. L. *Experimental Inorganic Chemistry. A Guide to Laboratory Practice*; Elsevier, Amsterdam.
- (2) Errington, R. J. *Advanced Practical Inorganic and Metalorganic Chemistry*; Blackie Academic and Professional, London.
- (3) Shriver, D.; Drezdon, M. *The Manipulation of Air-Sensitive Compounds*; Wiley-Interscience.
- (4) Cosier, B. J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, 19 (2), 105–107.
- (5) Otwinowski, Z.; Minor, W. *Processing of X-ray Diffraction Data collected in Oscillation Mode, Methods Enzymol.*
- (6) CrysAlisPro v.1.171.35.8 Agilent Technologies. 2011.
- (7) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, 26 (3), 343–350.
- (8) Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, 40 (4), 786–790.
- (9) Thompson, A. L.; Watkin, D. J. *J. Appl. Crystallogr.* **2011**, 44 (5), 1017–1022.
- (10) Cooper, R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Crystallogr.* **2010**, 43 (5 PART 1), 1100–1107.
- (11) Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112–122.
- (12) Sheldrick, G. M. *SHELX-2014* **2014**.
- (13) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, 42 (2), 339–341.
- (14) Barbour, L. J. *J. Supramol. Chem.* **2001**, 1 (4–6), 189–191.
- (15) Stender, M.; Wright, R. J.; Eichler, B. E.; Prust, J.; Olmstead, M. M.; Roesky, H. W.; Power, P. P. *J. Chem. Soc. Dalt. Trans.* **2001**, 23, 3465–3469.
- (16) Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, 82, 2141–2144.
- (17) Cui, C.; Roesky, H. W.; Hao, H.; Schmidt, H. G.; Noltemeyer, M. *Angew. Chem. Int. Ed.* **2000**, 39 (10), 1815–1817.
- (18) Stender, M.; Eichler, B. E.; Hardman, N. J.; Power, P. P.; Prust, J.; Noltemeyer, M.; Roesky, H. W. *Inorg. Chem.* **2001**, 40 (12), 2794–2799.
- (19) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, 54 (35), 10225–10229.
- (20) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, 120 (36), 9384–9385.
- (21) Zhu, H.; Chai, J.; He, C.; Bai, G.; Roesky, H. W.; Jancik, V.; Schmidt, H. G.; Noltemeyer, M. *Organometallics* **2005**, 24 (3), 380–384.

Chapter II: Experimental Techniques

- (22) Abdalla, J. A. B.; Riddlestone, I. M.; Tirfoin, R.; Aldridge, S. *Angew. Chem. Int. Ed.* **2015**, *54* (17), 5098–5102.
- (23) Do, D. C. H.; Keyser, A.; Protchenko, A. V.; Maitland, B.; Pernik, I.; Niu, H.; Kolychev, E. L.; Rit, A.; Vidovic, D.; Stasch, A.; Jones, C.; Aldridge, S. *Chem. Eur. J.* **2017**, *23* (24), 5830–5841.
- (24) Wang, C.; Erker, G.; Kehr, G.; Wedeking, K.; Fröhlich, R. *Organometallics* **2005**, *24* (20), 4760–4773.
- (25) Reger, D. L.; Wright, T. D.; Little, C. A.; Lamba, J. J. S.; Smith, M. D. *Inorg. Chem.* **2001**, *40* (15), 3810–3814.
- (26) Yang, Y.; Schulz, T.; John, M.; Yang, Z.; Jiménez-Pérez, V. M.; Roesky, H. W.; Gurubasavaraj, P. M.; Stalke, D.; Ye, H. *Organometallics* **2008**, *27* (4), 769–777.
- (27) Singh, S.; Ahn, H.-J.; Stasch, A.; Jancik, V.; Roesky, H. W.; Pal, A.; Biadene, M.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2006**, *45* (4), 1853–1860.
- (28) Turner, J.; Abdalla, J. A. B.; Bates, J. I.; Tirfoin, R.; Kelly, M. J.; Phillips, N.; Aldridge, S. *Chem. Sci.* **2013**, *4* (11), 4245–4250.
- (29) Hardman, N. J.; Eichler, B. E.; Power, P. P. *Chem. Commun.* **2000**, *53* (20), 1991–1992.

3. On the viability of catalytic turnover *via* Al-O/B-H metathesis: the reactivity of β -diketimate aluminium hydrides towards CO₂ and boranes

3.1 Introduction

The activation of E-X bonds is fundamental to a wide range of industrially relevant chemical reactions, being a key step in a number of catalytic processes. Recently there has been interest in the development of main group systems that are capable of activating E-X bonds, and hence effecting the catalysis of organic transformations. This has been driven in part by economic and environmental imperatives, specifically the lower cost, greater abundance and reduced toxicity of main group elements relative to "noble" transition metals.

In the past decade, several strategies to coax "precious-metal type" behaviour from main-group elements have been investigated. One such approach is the synthesis of species containing highly reactive M-R bonds (M = main group element; R = hydride, alkyl, aryl, amido etc.) that can activate small molecules, ideally in a catalytic manner. Within this field of small molecule activation, the reduction and transformation of CO₂ has recently received appreciable attention. In part, this is because CO₂ is an inexpensive carbon source, non-toxic and non-flammable. Additionally, the reduction of CO₂ can produce many compounds, such as methanol, carbon monoxide, formaldehyde or methane, all of which may be used as simple synthetic building blocks.¹⁻⁵

The use of metal hydrides to mediate the catalytic reduction of CO₂ is an approach that has been exploited in recent years. Several metal hydride systems, including both transition metal and main group elements, have been shown to be effective catalysts for the reduction of CO₂.^{6–14} Generally, the activation of CO₂ occurs by insertion of one of the C=O bonds into the metal hydride bond, followed by liberation of the formate group from the metal centre and regeneration of the metal hydride catalyst, by employing a reductant such as a borane or silane.¹⁵

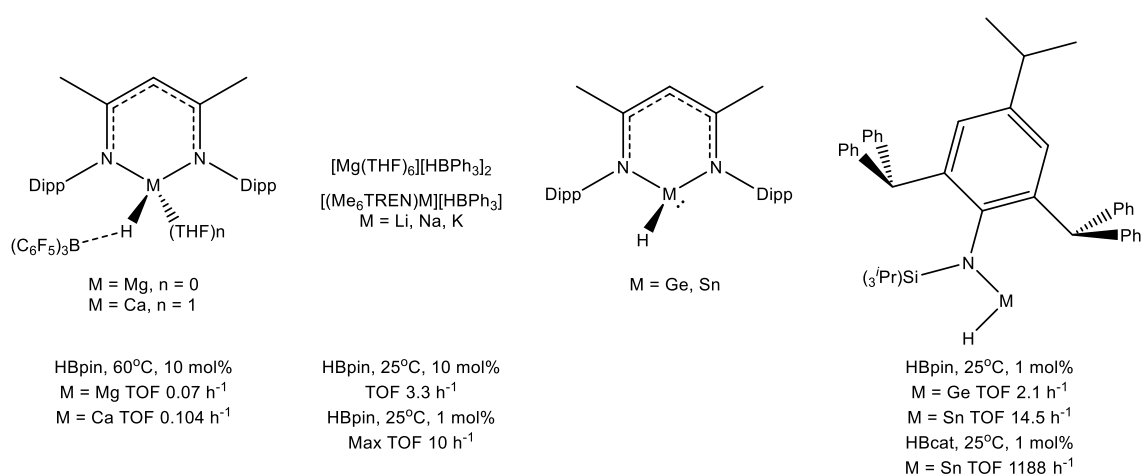
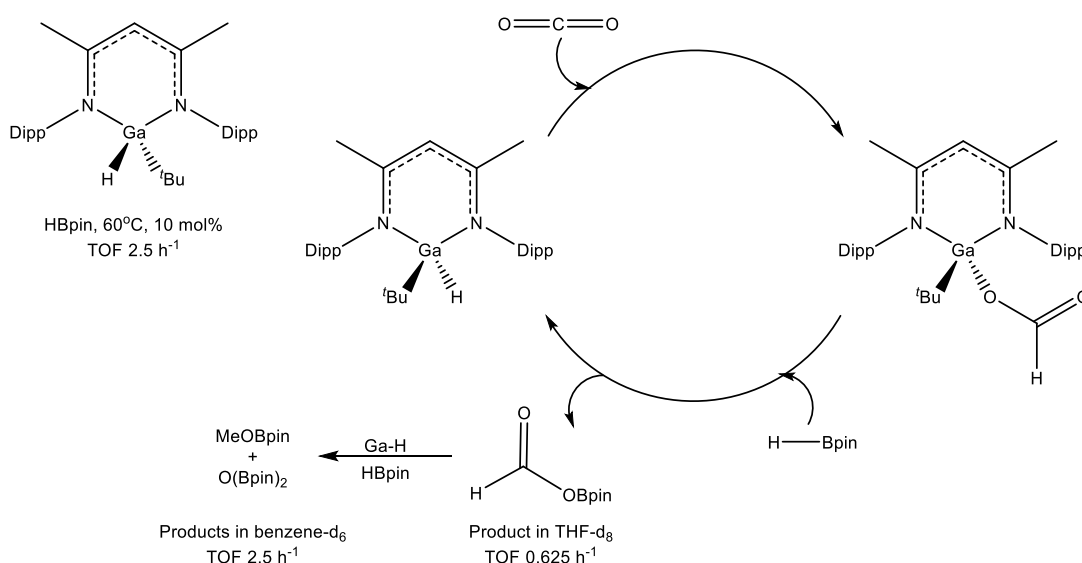


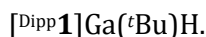
Figure 3.1: Examples of main group metal hydride complexes which catalyse the borane-mediated reduction of CO₂.

Examples of metal hydrides that function as catalysts for this process include derivatives of inexpensive alkaline earth metals, group 13 and 14 elements (Figure 3.1).^{16–23} Species of the form {HC(MeCNDipp)₂}MH ([^{Dipp}1]MH) (M = Ge, Sn), for example, insert CO₂ at room temperature, yielding the corresponding metal formate complexes [^{Dipp}1]M(OC(O)H).^{19,20} For M = Ge, it was demonstrated that the formate reacts with hydride sources such as Me₃N·AlH₃ and H₃N·BH₃, producing methanol derivatives and regenerating the germanium hydride; the catalytic potential of this system has, however, not been probed.^{21,24} In 2015, a gallium(III) hydride was reported – [^{Dipp}1]Ga(^tBu)H – that selectively catalyses the reduction of CO₂ into either methanol or formic acid

equivalents when employed in conjunction with HBpin (Scheme 3.1).²³ It was proposed that the rate-determining step for this catalysis is insertion of CO₂ into the Ga-H bond. Whilst the maximum TOFs obtained (2.5 h⁻¹, 10 mol%, 2 bar CO₂, 60°C) do not rival those of transition metal hydrides, at the time of report this complex was the most efficient single-site main group catalyst for this process.



Scheme 3.1: The proposed catalytic cycle for the reduction of CO₂ by the gallium hydride



The extension of this chemistry towards aluminium hydrides is unreported, despite the greater polarity of their M-H bonds which might be expected to render them more amenable to rapid insertion of CO₂.²⁵ Moreover, aluminium has a lower cost and greater terrestrial abundance than gallium - both of which favour its use for industrial applications (cost per kg: Al: \$2, Ga: \$500; abundance in earth's crust: Al 82000 ppm, Ga 16.9 ppm). There are a few reported examples of hydroalumination of CO₂ by molecular aluminium hydrides. The aluminium mono-hydrides ^{Ph}dimpyrAlH(THF) (^{Ph}dimpyr = H₃C₅N(2,6-C(Ph)=NDipp)₂) and (OCMeCHCMeNAr)₂AlH (Ar = Dipp) both undergo facile reactions with CO₂ at room temperature to yield the corresponding formate complexes ^{Ph}dimpyrAl(OC(O)H) and (OCMeCHCMeNAr)₂Al(OC(O)H) (Figure 3.2).^{26,27} Moreover, the

Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO_2 and boranes

use of LiAlH_4 to reduce carbon dioxide, producing formaldehyde, formic acid and methanol derivatives dates back to 1952.²⁸

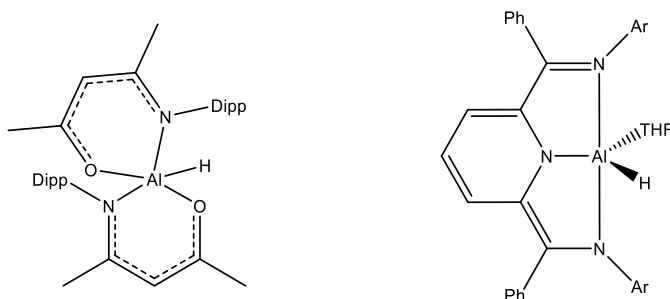


Figure 3.2: Two examples of aluminium hydrides which hydroaluminate CO_2 .

In recent years, the isolation of mono- and dimeric aluminium hydrides stabilised by bulky ligands has allowed for the exploration of their reactivity towards protic E-H and unsaturated E=X functionalities. The basic and hydridic character of the Al-H bond allows for the activation of such functionalities by deprotonation or hydroalumination reactions. There are numerous publications on the stoichiometric reactivity of aluminium hydrides towards a range of substrates.^{29,30} Despite this, there are comparatively few examples of the use of aluminium hydrides as catalysts for organic transformations, where the hydride initiates the first step of the catalytic cycle.^{29,30} The basic character of the Al-H bonds in $[\text{Ar}1]\text{AlH}_2$ ($\text{Ar} = 2,6\text{-Et}_2\text{C}_6\text{H}_3$) was recently exploited to apparently effect the catalytic dehydrogenative coupling of a range of alcohols, thiols and amines with boranes.³¹ However, it was later demonstrated that this reactivity proceeds under ambient conditions in the absence of a catalyst.³²

A range of catalysts have been reported which are capable of bringing about the catalytic hydroboration of alkenes and alkynes; this chemistry is typically proposed to proceed by initial hydroalumination of the $\text{C}=\text{C}/\text{C}\equiv\text{C}$ functionality, followed by Al-C/B-H σ -bond metathesis.^{31,33-35} Additionally, the cationic aluminium hydride complex $[[\text{Dipp}1]\text{AlH}][\text{BAR}^{\text{f}}_4]$ catalyses the hydrosilylation of alkenes and alkynes, although this is

proposed to proceed by Lewis acid activation of the silane or alkyne/alkene, rather than *via* insertion into the Al-H bond.³⁶

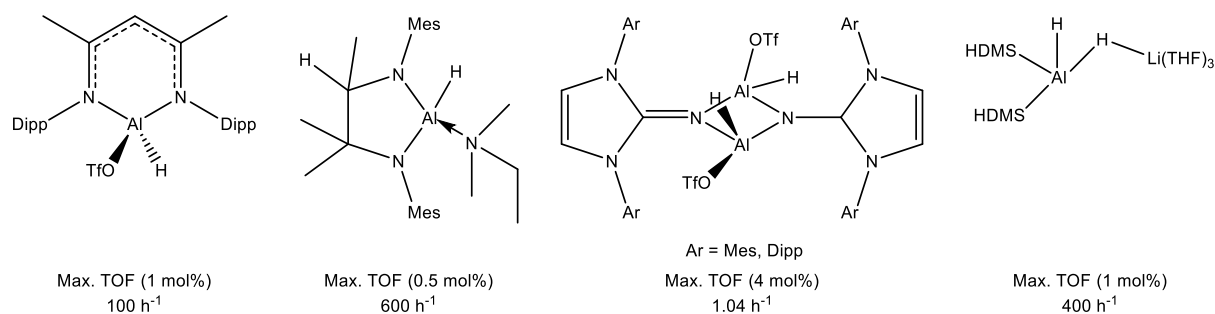


Figure 3.3: Examples of aluminium hydrides which catalyse the hydroboration of aldehydes and ketones with HBpin at room temperature.

A range of aluminium hydrides have been reported which have the ability to catalyse the hydroboration of aldehydes and ketones under ambient conditions with moderate TOF values at low catalyst loadings (Figure 3.3).^{35,37–39} These systems are more efficient for aldehydes than ketones and are all proposed to proceed by initial hydroalumination of the C=O functionality to yield an aluminium alkoxide complex, followed by the reaction with HBpin *via* Al-O/B-H σ -bond metathesis to regenerate the hydride. The proposed mechanism is superficially similar to that reported for the gallium hydride catalysed reduction of CO_2 (Figure 3.4) and this, together with the known capabilities of aluminium hydrides in the hydroalumination of CO_2 , suggests that they might be capable of functioning as catalysts for this process. To the best of our knowledge, however, the catalytic reduction of CO_2 by an aluminium hydride has not been reported. The main use of aluminium complexes in the area of catalytic CO_2 reduction chemistry is as the Lewis acidic component of a frustrated Lewis pair, or as a Lewis acid catalyst for the deoxygenative hydrosilylation of CO_2 .^{40–45}

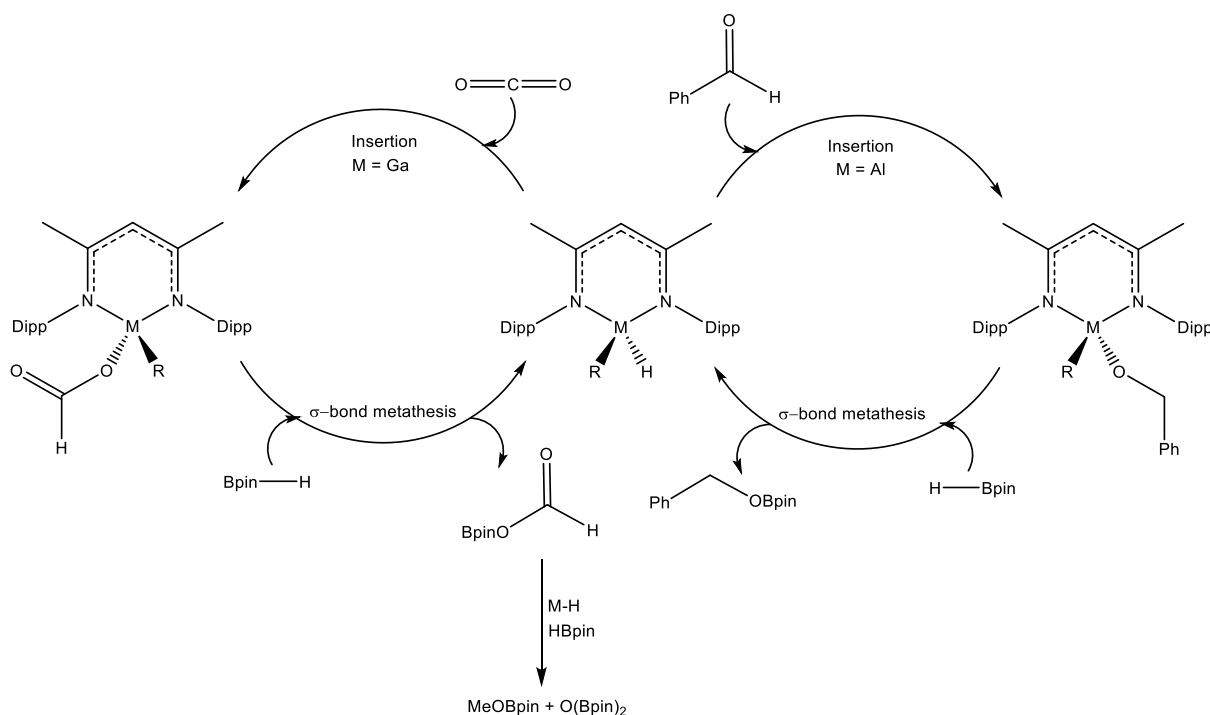


Figure 3.4: The proposed catalytic cycles for the catalytic reduction of CO_2 (left) and benzaldehyde (right), catalysed by Nacnac-ligated group 13 monohydrides.

β -Diketiminate (Nacnac) ligands have been shown to be particularly successful for the stabilisation of monomeric aluminium hydride complexes, due to the presence of the strongly σ -donating imine/amido donors and sterically protecting flanking groups. As a result, a wide range of aluminium hydride complexes which feature this ligand have been reported, the most widespread being aluminium dihydride complexes of the type $[\text{R}^1]\text{AlH}_2$, which have been reported with a range of substituents of varying steric bulk ($\text{R} = \text{Me}$, $i\text{Pr}$, Ph , Mes , Dipp , $2,6\text{-Et}_2\text{C}_6\text{H}_3$).^{31,46–49} Unsymmetrically substituted aluminium hydrides are typically synthesised *via* oxidative addition of an E-H bond at the $\text{Al}(\text{I})$ centre of $[\text{Dipp}^1]\text{Al}$ or *via* exchange of one of the hydride substituents in $[\text{R}^1]\text{AlH}_2$. The first method was used in the isolation of a range of complexes including $[\text{Dipp}^1]\text{Al}(\text{R})\text{H}$ ($\text{R} = \text{SiHR}'\text{Ph}$ $\{\text{R}' = \text{Me}, \text{H}\}$, Bpin , Cp^* , NHR' $\{\text{R}' = \text{Ph}, t\text{Bu}\}$, PPh_2 , $\text{O}^i\text{Pr}\}$).⁵⁰ The second method utilises the basic nature of the Al-H bond to deprotonate substrates such as alcohols, amines and alkynes, producing hydrogen and the unsymmetrically substituted

complex.⁵¹⁻⁵⁵ Additionally, the alkyl-substituted complexes [Dipp $\mathbf{1}$]Al(CH₂RMe₃)H (R = Si, C) may be synthesised by the elimination of LiH from [Dipp $\mathbf{1}$]AlH₂ following the addition of Li(CH₂RMe₃).⁵⁶

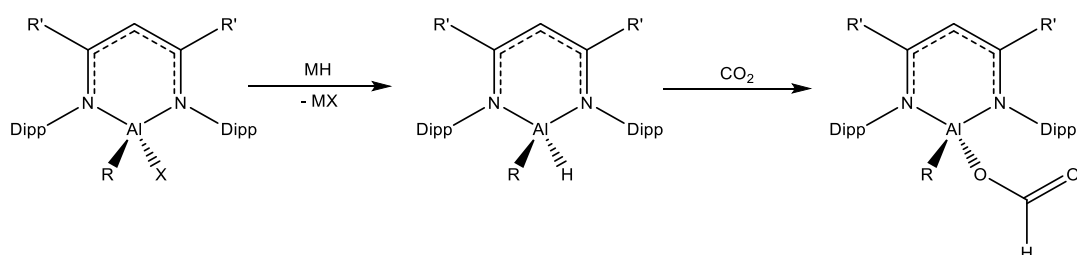
3.2 Project aims

The reported use of aluminium hydrides as catalysts for the hydroboration of organic carbonyl functionalities suggests that they may be able to function in a similar fashion to transition metal catalysts. At the outset, the main focus of this chapter was to probe the possibility for extending the catalytic reactivity of gallium hydride complexes, into aluminium hydride chemistry, particularly towards the aluminium hydride-catalysed reduction of CO₂.

While a wide range of unsymmetrically substituted Nacnac-ligated aluminium hydride complexes have been reported, examples of such complexes which bear alkyl substituents - aluminium analogues of [Dipp $\mathbf{1}$]Ga(*t*Bu)H - are relatively limited and their synthetic routes are not well established. A commonly utilised method for the synthesis of gallium hydrides is metathesis utilising a gallium halide and a hydride source. The treatment of gallium halides [Dipp $\mathbf{1}$]GaRX (R = X = I, Cl; R = Me, X = Cl; R = *t*Bu, X = Br) with reagents of the form M[HBET₃] (M = Li, K) at low temperatures readily leads to the selective formation of gallium hydrides [Dipp $\mathbf{1}$]GaRH (R = H, Me, *t*Bu).^{23,57} By contrast, the extension of this method towards the synthesis of Nacnac-ligated aluminium hydrides is relatively unexplored.⁵⁷

A range of precursor halide complexes [Dipp $\mathbf{1}$]Al(R)X (R = Me, Et, *t*Bu, Ph; X = Cl) have been reported and the work in this chapter initially aimed to explore the synthesis of the corresponding hydride complexes *via* their treatment with hydride sources.^{23,58-60}

Additionally, the use of such methods was to be extended to the synthesis of novel aluminium hydrides featuring an electronically modified amino-functionalised Nacnac ligand ($\text{L} = \{\text{HC}(\text{R}'\text{CNDipp})_2\}$; $\text{R}' = \text{NMe}_2$).⁶¹ Variation of the Nacnac ligand within group 13 hydride chemistry is currently limited to steric modification of the N-bound groups and the use of the electronically modified ligand may have significant ramifications on their chemistry.



Scheme 3.2: The proposed method of synthesis for alkyl-substituted aluminium hydrides and their subsequent reactivity with CO_2 .

The subsequent treatment of a range of Nacnac-ligated aluminium hydrides with CO_2 was targeted, to allow for comparison with the related gallium systems and to provide a systematic basis to understand the influence of the aluminium-bound R substituent and the Nacnac ligand on hydroalumination chemistry. The complexes that showed greatest propensity for the hydroalumination of CO_2 under ambient conditions would then undergo investigation of their ability to catalyse the borane-mediated reduction of CO_2 .

3.3 Experimental details

Preparation of $\{\text{HC}(\text{MeCNDipp})_2\}\text{Al}(\text{Me})\text{I}$ – $[\text{Dipp}^1]\text{Al}(\text{Me})\text{I}$ (3.1)

I_2 (0.740 g, 2.93 mmol) was dissolved in toluene (15 mL) and added dropwise to a stirred solution of $[\text{Dipp}^1]\text{AlMe}_2$ (1.39 g, 2.93 mmol) in toluene (15 mL) at -78°C . The reaction mixture was allowed to warm to room temperature and stirred overnight,

during which time the solution colour developed from deep purple to yellow. Volatiles were removed *in vacuo* to yield a spectroscopically pure, pale yellow powder, which was washed with *n*-hexane and dried *in vacuo*. Yield: 1.61 g, 94%. Large single crystals (of the toluene solvate), suitable for X-ray crystallography, could be obtained from the storage of a concentrated solution of [Dipp¹]Al(Me)I in toluene at -30°C overnight.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} -0.31 (3H, s, CH₃Al), 1.01, 1.18, 1.28, 1.49 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.52 (6H, s, CH₃ of β -diketiminato backbone), 3.22 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.88 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 5.04 (1H, s, γ -CH), 7.04 – 7.16 (6H, m, aromatic CH). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_{C} -6.5 (br, CH₃Al), 23.8 (CH₃ of β -diketiminato backbone), 24.4, 24.5, 24.9, 28.4 (CH₃ of Dipp ⁱPr), 28.7, 29.1 (CH of Dipp ⁱPr), 99.7 (γ -CH), 124.2, 125.7, 127.9, 139.7, 143.8, 146.0 (ArC of Dipp), 171.4 (NC). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} 127. **EI-MS:** *m/z* calc for C₂₉H₄₁N₂AlI ([M-Me]⁺) 571.2310, meas. 571.2110 (20%), calc for C₃₀H₄₄AlN₂ 459.3320 ([M-I]⁺), meas. 459.3334 (100%). **Elemental microanalysis:** calc. for C₃₀H₄₄N₂AlI: C 61.43% H 7.56% N 4.78% meas. C 61.61% H 7.41% N 4.72%.

Preparation of {HC(Me₂NCNDipp)₂}Al(Et)Cl – [Dipp²]Al(Et)Cl (3.3)

To a stirred solution of [Dipp²]Li(OEt₂) (0.530 g, 0.95 mmol) in toluene (15 mL) at -78°C was added dropwise a solution of AlEtCl₂ (1 M solution in *n*-hexane, 1.14 mL, 1.14 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The solution was filtered, and the precipitate washed with toluene (5 mL); the filtrate and washings were then combined, and the resulting pale yellow solution dried *in vacuo*. The residual solid was extracted into *n*-hexane, filtered and concentrated to the point of incipient crystallisation. Storage of the solution at -30°C

overnight yielded colourless block-like crystals, suitable for X-ray crystallography. Yield: 0.29 g, 53%.

Spectroscopic data: ^1H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} 0.09 (2H, q, $^3J_{\text{HH}} = 8.2$ Hz, CH₃CH₂Al), 0.71 (3H, t, $^3J_{\text{HH}} = 8.2$ Hz, CH₃CH₂Al), 1.10, 1.25, 1.29, 1.60 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH₃ of Dipp ⁱPr), 2.19 (12H, s, CH₃ of NMe₂), 3.05 (2H, sept, $^3J_{\text{HH}} = 6.7$ Hz, CH of Dipp ⁱPr), 3.78 (1H, s, γ -CH), 4.42 (2H, sept, $^3J_{\text{HH}} = 6.7$ Hz, CH of Dipp ⁱPr), 7.06 – 7.17 (6H, m, aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene-d₆, 298 K): δ_{C} 0.6 (br, CH₃CH₂Al), 9.1 (CH₃CH₂Al), 24.3, 24.5, 26.8, 26.9 (CH₃ of Dipp ⁱPr), 28.4, 28.6 (CH of Dipp ⁱPr), 41.2 (CH₃ of NMe₂) 77.1 (γ -CH), 124.6, 125.5, 126.3, 141.6, 144.3, 146.0 (ArC of Dipp) 167 (NC). ^{27}Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} 124. **MS(ESI):** m/z calc for C₃₃H₅₂AlClN₄ ([M-CH₂CH₃]⁺) 537.3305, meas. 537.3295 (100%). **Elemental microanalysis:** calc. for C₃₃H₅₂N₄AlCl: C 69.88% H 9.24% N 9.88% meas. C 69.68% H 9.21% N 9.71%.

Preparation of {HC(MeCNDipp)₂}Al(Me)H – [Dipp¹]Al(Me)H (3.4^{Me})

Method A: To a solution of [Dipp¹]Al(Me)Cl (0.400 g, 0.81 mmol) in diethyl ether (10 mL) at –78°C was added dropwise a solution of LiAlH₄ (0.031 g, 0.81 mmol), also in diethyl ether (5 mL). The reaction mixture was allowed to warm to room temperature and stirred for 5 h, over which time a colourless precipitate was formed. The reaction mixture was filtered, and volatiles subsequently removed *in vacuo* to yield a white residue. The residue was extracted into *n*-hexane, filtered (leaving a colourless powder that reacted violently with water) and concentrated to the point of incipient crystallisation. Storage of the solution at –30°C for 24h produced large, colourless block crystals suitable for X-ray crystallography. Yield: 0.24 g, 65%.

Method B: To a solution of [Dipp¹]Al(Me)I (0.250 g, 0.426 mmol) in diethyl ether (10 mL) at -78°C was added dropwise a solution of LiAlH₄ (0.017 g, 0.447 mmol), also in diethyl ether (5 mL). The reaction mixture was allowed to attain room temperature and stirred for 5 h, over which time the yellow solution decolourised, and a colourless precipitate was formed. The reaction mixture was then treated with a workup method identical to that detailed in method A. Yield: 0.12 g, 61%. **N.B** Increasing the scale of the reaction to 1 g using this method yields significant quantities of [Dipp¹]AlH₂, which could not be separated from the product.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} -0.74 (3H, s, CH₃Al), 1.11, 1.18, 1.33, 1.36 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.56 (6H, s, CH₃ of β -diketiminato backbone), 3.35 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.51 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.64 (1H, br s, AlH), 4.93 (1H, s, γ -CH), 7.07 – 7.16 (6H, m, aromatic CH). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_{C} -11.7 (br, CH₃Al), 23.1 (CH₃ of β -diketiminato backbone), 24.2, 24.3, 24.8, 26.4 (CH₃ of Dipp ⁱPr), 28.2, 28.8 (CH of Dipp ⁱPr), 97.2 (γ -CH), 124.2, 124.9, 127.3, 140.5, 143.6, 145.3 (ArC of Dipp), 170.1 (NC). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ 143. **EI-MS:** *m/z* calc for C₂₉H₄₂N₂Al ([M-Me]⁺) 445.3163, meas. 445.3151 (100%), calc for C₃₀H₄₄N₂Al ([M-H]⁺) 459.3320, meas. 459.3308 (80%). **IR (nujol/cm⁻¹)** $\nu_{\text{Al-H}}$: 1767 (s). **Elemental microanalysis:** calc. for C₃₀H₄₅N₂Al: C 78.22% H 9.85% N 6.08% meas. C 77.99% H 9.85% N 6.14%.

Preparation of {HC(MeCNDipp)₂}Al(Et)H – [Dipp¹]Al(Et)H (3.4^{Et})

The preparation of 3.4^{Et} followed the method reported for the preparation of 3.4^{Me} (method A) using: [Dipp¹]Al(Et)Cl (3.25 g, 6.38 mmol) and LiAlH₄ (0.242 g, 6.38 mmol). Large, colourless, single crystals, suitable for X-ray crystallography could be obtained from storage of a *n*-hexane solution of 3.4^{Et} at 6°C for several. The isolation of the

crystals, and further concentration and cooling of the supernatant yielded a second crop of large crystals. Yield: 2.40 g, 79%.

Spectroscopic data: $^1\text{H NMR}$ (400 MHz, benzene- d_6 , 298 K): δ_{H} -0.13 (2H, q, $^3J_{\text{HH}} = 8.2$ Hz, $\text{CH}_3\text{CH}_2\text{Al}$), 0.79 (3H, t, $^3J_{\text{HH}} = 8.2$ Hz, $\text{CH}_3\text{CH}_2\text{Al}$), 1.11, 1.17, 1.35, 1.39 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH_3 of Dipp ^iPr), 1.56 (6H, s, CH_3 of β -diketiminato backbone), 3.34 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ^iPr), 3.51 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ^iPr), 4.57 (1H, br s, AlH), 4.92 (1H, s, γ -CH), 7.08-7.15 (6H, m, aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene- d_6 , 298 K): δ_{C} -0.9 (br, $\text{CH}_3\text{CH}_2\text{Al}$), 9.1 ($\text{CH}_3\text{CH}_2\text{Al}$) 23.0 (CH_3 of β -diketiminato backbone), 24.2, 24.4, 24.9, 26.4 (CH_3 of Dipp ^iPr), 28.2, 28.9 (CH of Dipp ^iPr), 97.0 (γ -CH), 124.1, 124.9, 127.3, 140.5, 143.6, 145.2 (ArC of Dipp), 170.0 (NC). $^{27}\text{Al NMR}$ (104 MHz, benzene- d_6 , 298 K): δ_{Al} not observed. **EI-MS:** m/z calc for $\text{C}_{29}\text{H}_{42}\text{N}_2\text{Al}$ ($[\text{M-Et}]^+$) 445.3163, meas. 445.3155 (100%), calc. for $\text{C}_{31}\text{H}_{46}\text{N}_2\text{Al}$ ($[\text{M-H}]^+$) (20%). **IR (nujol/ cm^{-1})** $\nu_{\text{Al-H}}$: 1776 (s). **Elemental microanalysis:** calc. for $\text{C}_{31}\text{H}_{47}\text{N}_2\text{Al}$: C 78.44% H 9.98% N 5.90% meas. C 78.10% H 9.89% N 5.75%.

Preparation of $\{\text{HC}(\text{MeCNDipp})_2\text{Al}(\text{Cl})\text{H} - [\text{Dipp}^1]\text{Al}(\text{Cl})\text{H}$ (**3.4^{Cl}**)

The preparation of **3.4^{Cl}** followed the method reported for the preparation of **3.4^{Me}** (method A) using: $[\text{Dipp}^1]\text{AlCl}_2$ (3.00 g, 5.82 mmol) and LiAlH_4 (0.221 g, 5.82 mmol). In this case, the reaction mixture was stirred for only 90 min at room temperature. Storage of an *n*-hexane solution of **3.4^{Cl}** at -30°C overnight yielded colourless block crystals, suitable for X-ray diffraction. Yield: 2.15 g, 77%.

Spectroscopic data: $^1\text{H NMR}$ (400 MHz, benzene- d_6 , 298 K): δ_{H} 1.10, 1.13, 1.34, 1.47 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH_3 of Dipp ^iPr), 1.52 (6H, s, CH_3 of β -diketiminato backbone), 3.30 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ^iPr), 3.47 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ^iPr), 4.55

(1H, br s, Al-H), 4.88 (1H, s, γ -CH), 7.06 – 7.17 (6H, m, aromatic CH). **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_c 23.3 (CH₃ of β -diketiminato backbone), 24.7, 24.9, 25.3, 25.5 (CH₃ of Dipp ⁱPr), 28.6, 28.9 (CH of Dipp ⁱPr), 97.70 (γ -CH), 124.7, 125.1, 127.9, 138.7, 144.1, 145.3 (ArC of Dipp), 171.2 (NC). **²⁷Al NMR** (104 MHz, benzene-d₆, 298K): δ_{Al} 116. **EI-MS**: m/z calc for C₂₉H₅₁N₂AlCl ([M-H]⁺) 479.2774, meas. 479.2752 (70%). **IR (nujol/cm⁻¹)** ν_{Al-H} : 1865, 1842 (s). **Elemental microanalysis**: calc. for C₂₉H₄₂N₂AlCl: C 72.40% H 8.80% N 5.82% meas. C 72.10% H 8.70% N 5.67%.

Preparation of {HC(Me₂NCNDipp)₂}AlH₂ – [Dipp₂]AlH₂ (3.5^H)

To a stirred solution of Me₃N·AlH₃ (0.130 g, 1.46 mmol) in toluene (10 mL) at 0°C was added dropwise a solution of [Dipp₂]H (0.500 g, 1.05 mmol), also in toluene (15 mL). The reaction mixture was allowed to warm to room temperature and stirred for 24 h, after which time the solution was filtered and volatiles removed *in vacuo*. The resulting white solid was extracted into hexane, filtered to remove traces of Me₃N·AlH₃, and volatiles removed *in vacuo* to yield a spectroscopically pure white powder. Colourless acicular crystals, suitable for X-ray crystallography, were obtained from the storage of a saturated solution in *n*-hexane at –30°C overnight. The crystals were isolated and dried *in vacuo*. A second crop of crystals was obtained on further concentration of the supernatant solution and storage at –30°C. Yield: 0.34 g, 64%.

Spectroscopic data: **¹H NMR** (400 MHz, benzene-d₆, 298 K): δ_H 1.19, 1.43 (12H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 2.20 (12H, s, CH₃ of NMe₂), 3.58 (4H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.84 (1H, s, γ -CH), 4.52 (2H, br s, AlH), 7.11 (6H, s, aromatic CH). **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_c 23.8, 26.8 (CH₃ of Dipp ⁱPr), 28.6 (CH of Dipp ⁱPr), 40.9 (CH₃ of NMe₂) 75.3 (γ -CH), 124.7, 125.9, 141.8, 144.8 (ArC of Dipp), 166.9 (NC). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **EI-MS**: m/z calc for C₃₁H₄₈N₄Al

([M-H]⁺) 503.3689, meas. 503.3686 (5%). **IR (nujol/cm⁻¹)** $\nu_{\text{Al-H}}$: 1840, 1793. **Elemental microanalysis**: calc. for C₃₁H₄₉N₄Al: C 73.77% H 9.79% N 11.10% meas. C 73.56% H 9.43% N 10.89%.

Preparation of {HC(Me₂NCNDipp)₂}Al(Et)H – [Dipp₂]Al(Et)H (3.5^{Et})

The preparation of 3.5^{Et} followed the method reported for the preparation of 3.4^{Me} (method A) using: [Dipp₂]Al(Et)Cl (2.80 g, 4.94 mmol) and LiAlH₄ (0.280 g, 7.38 mmol). The reaction mixture was stirred for 24 h at room temperature in this case. Storage of an *n*-hexane solution of 3.5^{Et} at –30°C, yielded colourless plate-like crystals suitable for X-ray crystallography. Yield: 1.36 g, 52%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} –0.27 (2H, q, ³J_{HH} = 8.2 Hz, CH₃CH₂Al), 0.72 (3H, t, ³J_{HH} = 8.2 Hz, CH₃CH₂Al), 1.15, 1.23, 1.33, 1.58 (6H, d, ³J_{HH} = 6.7 Hz, CH₃ of Dipp ⁱPr), 2.23 (12H, s, CH₃ of NMe₂), 3.08 (2H, sept, ³J_{HH} = 6.7 Hz, CH of Dipp ⁱPr), 3.68 (1H, s, γ -CH), 4.04 (2H, sept, ³J_{HH} = 6.7 Hz, CH of Dipp ⁱPr), 4.90 (1H, br s, AlH), 7.08 – 7.17 (6H, m, aromatic CH). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_{C} 1.2 (br, CH₃CH₂Al), 9.9 (CH₃CH₂Al), 24.2, 24.4, 26.5, 26.6 (CH₃ of Dipp ⁱPr), 28.3, 28.5 (CH of Dipp ⁱPr), 41.0 (CH₃ of NMe₂) 75.1 (γ -CH), 124.5, 125.0, 125.9, 142.1, 144.1, 145.3 (ArC of Dipp), 166.6 (NC). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **IR (nujol/cm⁻¹)** $\nu_{\text{Al-H}}$: 1788 (s). **Elemental microanalysis**: calc. for C₃₃H₅₃N₄Al: C 74.39% H 10.03% N 10.52% meas. C 74.24% H 9.89% N 10.42%.

Preparation of {HC(MeCNDipp)₂}Al(Me)(OC(O)H) – [Dipp₁]Al(Me)(OC(O)H) (3.6^{Me})

[Dipp₁]Al(Me)H (0.246 g, 0.53 mmol) was dissolved in toluene (3 mL) in an ampoule fitted with a J. Young's valve and degassed by three freeze-pump-thaw cycles. The ampoule was then back-filled with carbon dioxide (*ca.* 1 bar) and stirred for 5 h at room

temperature, after which time volatiles were removed *in vacuo*. The resulting white solid was extracted into minimal pentane (1 mL), filtered and concentrated to the point of incipient crystallisation. Single crystals suitable for X-ray crystallography were obtained from storage of this solution at -30°C for several days. Yield: 0.17 g, 65%. (¹H NMR monitoring indicates that the reaction proceeds with > 95% conversion; the relatively low isolated yield represents the high solubility of the product in alkane solvents).

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} -0.80 (3H, s, CH₃Al), 1.03, 1.18 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.28 (12H, 2 x overlapping d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.55 (6H, s, CH₃ of β -diketiminato backbone), 3.19 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.42 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 5.14 (1H, s, γ -CH), 7.05 – 7.16 (6H, m, aromatic CH), 8.46 (1H, s, Al(OC(O)H)). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_{C} Signal for the CH₃Al group could not be observed, 23.4 (CH₃ of β -diketiminato backbone), 24.1, 24.3, 24.8, 26.1 (CH₃ of Dipp ⁱPr), 27.4, 29.1 (CH of Dipp ⁱPr), 100.1 (γ -CH), 124.2, 125.0, 127.7, 140.0, 143.5, 145.7 (ArC of Dipp), 162.4 (Al(OC(O)H), 171.0 (NC). ²⁷Al NMR (104 MHz, benzene-d₆, 298K): δ_{Al} 109. **EI-MS:** *m/z* calc. for C₃₁H₄₄AlN₂O₂ ([M-H]⁺) 503.3213, meas. 503.3217 (100%), calc. for C₃₀H₄₂AlN₂O₂ ([M-Me]⁺) 489.3062, meas. 489.3051 (5%), calc. for C₂₉H₄₂AlN₂O ([M-CO-Me]⁺) 461.3113 meas. 461.3100 (30%). **IR (nujol/cm⁻¹)** $\nu_{\text{C=O}}$: 1673 (s). **Elemental microanalysis:** calc. for C₃₁H₄₅N₂AlO₂: C 73.78% H 8.99% N 5.55% meas. C 73.58% H 9.17% N 5.67%.

Preparation of {HC(MeCNDipp)₂}Al(Et)(OC(O)H) – [Dipp¹]Al(Et)(OC(O)H) (3.6^{Et})

The preparation of 3.6^{Et} followed the method reported for the preparation of 3.6^{Et} using: [Dipp¹]Al(Et)H (1.50 g, 3.16 mmol). Storage of a solution of 3.6^{Et} in *n*-hexane at

Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂ and boranes

-30°C produced fine, colourless, acicular crystals over the course of several hours, which were isolated and dried *in vacuo*. Yield: 1.47 g, 90%. Storage of a concentrated solution in *n*-hexane at -30°C for three days yielded single, colourless, block-crystals of the hexane hemi-solvate suitable for X-ray crystallography.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} -0.15 (2H, q, $^3J_{\text{HH}} = 8.1$ Hz, CH₃CH₂Al), 0.74 (3H, t, $^3J_{\text{HH}} = 8.1$ Hz, CH₃CH₂Al), 1.03, 1.19 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ⁱPr), 1.31 (12H, 2 x overlapping d, $^3J_{\text{HH}} = 6.8$ Hz, 2 x CH₃ of Dipp ⁱPr), 1.57 (6H, s, CH₃ of β -diketiminato backbone), 3.19 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 3.41 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 5.15 (1H, s, γ -CH), 7.00 – 7.15 (6H, m, aromatic CH), 8.49 (1H, s, Al(OC(O)H)). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_{C} -3.2 (br, CH₃CH₂Al), 8.6 (CH₃CH₂Al) 23.3 (CH₃ of β -diketiminato backbone), 24.0, 24.4, 24.9, 25.9 (CH₃ of Dipp ⁱPr), 27.3, 29.2 (CH of Dipp ⁱPr), 100.1 (γ -CH), 124.1, 125.1, 127.7, 140.0, 143.5, 145.6 (ArC of Dipp), 162.7 (Al(OC(O)H), 171.0 (NC). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **EI-MS:** *m/z* calc for C₃₀H₄₂N₂AlO₂ ([M-Et]⁺) 489.3062, meas. 489.3057 (80%), C₂₉H₄₂N₂AlO ([M-Et-CO]⁺) 461.3113, meas. 461.3312 (100%). **IR (nujol/cm⁻¹)** $\nu_{\text{C=O}}$: 1680 (s). **Elemental microanalysis:** calc. for C₃₂H₄₇N₂AlO₂: C 74.10% H 9.13% N 5.40% meas. C 73.80% H 8.92% N 5.36%.

Method for testing the reactivity of [Dipp¹]AlH₂ with CO₂, and the isolation of ([Dipp¹]AlO)CH₂)₂ (3.7)

NMR scale: [Dipp¹]AlH₂ (0.010 g, 0.022 mmol) was dissolved in benzene-d₆ (0.5 mL) in an NMR tube fitted with a J. Young's valve and degassed by three freeze-pump-thaw cycles. The tube was pressurised with *ca.* 1 bar of CO₂ at room temperature and the progress of the reaction monitored by ¹H NMR spectroscopy.

Preparative scale: [Dipp¹]AlH₂ (0.060 g, 0.135 mmol) was dissolved in benzene-d₆ (0.5 mL) in an NMR tube fitted with a J. Young's valve and degassed by three freeze-pump-thaw cycles. The tube was pressurised with *ca.* 1 bar of CO₂ at room temperature and monitored by ¹H NMR spectroscopy. When single crystals were yielded from the benzene-d₆ solution, they were analysed by X-ray crystallography and ¹H NMR spectroscopy. The ¹H NMR data were consistent with those reported in the literature.²¹

Preparation of {HC(Me₂NCNDipp)₂}Al(Et)(OC(O)H) – [Dipp²]Al(Et)(OC(O)H) (3.8^{Et})

[Dipp²]Al(Et)H (0.500 g) was dissolved in toluene (15 mL) in an ampoule fitted with a J. Young's valve. The ampoule was attached to a Schlenk line *via* a glass T-piece, the other end of which attached to a 500 mL ampoule filled with *ca.* 1 bar of CO₂, which had been pre-dried over P₂O₅ for 24 h. The solution of [Dipp²]Al(Et)H was then degassed by three freeze-pump-thaw cycles and back-filled with the dried CO₂ (*ca.* 1 bar) at room temperature and stirred for 6 h. The solution was subsequently concentrated and stored at –30°C for 3 d, yielding colourless, block-like crystals suitable for X-ray crystallography. Yield: 0.34 g, 62%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} –0.24 (2H, q, ³J_{HH} = 8.2 Hz, CH₃CH₂Al), 0.63 (3H, t, ³J_{HH} = 8.2 Hz, CH₃CH₂Al), 1.10, 1.24, 1.27, 1.52 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 2.20 (12H, s, CH₃ of NMe₂), 3.01 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.84 (1H, s, γ -CH), 3.89 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 7.06 – 7.16 (6H, m, aromatic CH), 8.76 (1H, s, Al{OC(O)H}). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_{C} –1.6 (br, CH₃CH₂Al), 9.0 (CH₃CH₂Al), 24.4 (CH₃ of Dipp ⁱPr), 24.5 (CH₃ of Dipp ⁱPr), 26.3 (CH₃ of Dipp ⁱPr), 26.6 (CH₃ of Dipp ⁱPr), 28.1 (CH of Dipp ⁱPr), 28.3 (CH of Dipp ⁱPr), 41.1 (CH₃ of NMe₂), 77.3 (γ -CH), 124.6, 125.2, 126.3, 141.5, 144.4, 145.6 (ArC of Dipp), 162.5 (Al{OC(O)H}), 167.5 (NC). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} not

observed. **IR (nujol/cm⁻¹)** $\nu_{C=O}$: 1678 (s). **Elemental microanalysis:** calc. for C₃₄H₅₃N₄AlO₂: C 70.80% H 9.26% N 9.71% meas. C 70.58% H 8.98% N 9.51%.

Preparation of {HC(Me₂NCNDipp₂)Al(H)(OC(O)H) – [Dipp₂]Al(H)(OC(O)H) (3.8^H)

A solution of [Dipp₂]AlH₂ (0.015 g, 0.030 mmol) in benzene-d₆ (0.5 mL) in an NMR tube fitted with a J. Young's valve was degassed by three freeze-pump-thaw cycles. The tube was pressurised with *ca.* 1 bar of CO₂ and the resulting solution monitored by ¹H NMR spectroscopy. Following complete conversion, volatiles were removed *in vacuo* and the resulting solid redissolved in benzene-d₆ for analysis by NMR spectroscopy.

Attempts were made to isolate 3.8^H in the solid state. A solution of [Dipp₁]AlH₂ (0.100 g, 0.198 mmol) was dissolved in toluene (2 mL) in an ampoule fitted with a J. Young's valve. The solution was degassed by three freeze-pump-thaw cycles and backfilled with *ca.* 1 bar of CO₂ at room temperature. The reaction mixture was stirred for 5 min and volatiles removed *in vacuo* to yield a colourless oil. Attempts to isolate crystalline samples of 3.8^H from compatible hydrocarbon solvents were unsuccessful, and analysis of the resulting oil by ¹H NMR spectroscopy showed the formation of a mixture of species.

Spectroscopic data: ¹H NMR (500 MHz, benzene-d₆, 298 K): δ_H 1.14, 1.20, 1.34, 1.47 (6H, d, ³J_{HH} = 6.9 Hz, CH₃ of Dipp ⁱPr), 2.18 (12H, s, CH₃ of NMe₂), 3.40 (2H, sept, ³J_{HH} = 6.9 Hz, CH of Dipp ⁱPr), 3.57 (2H, sept, ³J_{HH} = 6.9 Hz, CH of Dipp ⁱPr), 3.82 (1H, s, γ -CH), 5.22 (1H, br s, AlH), 7.06 – 7.16 (6H, m, aromatic CH), 8.31 (1H, s, Al(OC(O)H)). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): 24.0, 24.1, 26.6, 26.7 (CH₃ of Dipp ⁱPr), 28.3, 28.5 (CH of Dipp ⁱPr), 41.0 (CH₃ of NMe₂), 76.3 (γ -CH), 124.7, 124.9, 126.3, 140.4, 144.6, 145.1 (ArC of Dipp), 161.8 (Al(OC(O)H)), 167.1 (NC). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} 73.

Preparation of {HC(Me₂NCNDipp₂)Al(OC(O)H)₂ – [Dipp₂]Al(OC(O)H)₂ (3.8^{OC(O)H})

A solution of [Dipp₂]AlH₂ (0.015 g, 0.030 mmol) in benzene-d₆ (0.5 mL) in an NMR tube fitted with a J. Young's valve was degassed by three freeze-pump-thaw cycles. The tube was pressurised with *ca.* 1 bar of CO₂ and the resulting solution monitored by ¹H NMR spectroscopy. Following complete conversion, the solution was again degassed by three freeze-pump-thaw cycles and backfilled with CO₂ (1 bar). The resulting product was analysed by NMR spectroscopy.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} 1.15, 1.44 (12H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ⁱPr), 2.15 (12H, s, CH₃ of NMe₂), 3.42 (4H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 3.78 (1H, s, γ -CH), 6.94 – 7.15 (6H, m, aromatic CH), 8.06 (2H, br s, Al(OC(O)H)). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): 24.3, 26.4 (CH₃ of Dipp ⁱPr), 28.3 (CH of Dipp ⁱPr), 41.0 (CH₃ of NMe₂), 76.8 (γ -CH), 123.2, 124.8, 125.0, 144.9 (ArC of Dipp), 161.6 (Al(OC(O)H)), 167.4 (NC). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} 73.

General procedure for assessing rates of insertion of CO₂ into Al-H bonds

An NMR tube fitted with a J. Young's valve was charged with [Dipp₂X]Al(R)(OC(O)H) (**X** = 1, R = Me, Et, OTf, Cl; **X** = 2, R = Et, H) (0.021 mmol) and benzene-d₆ and degassed by three freeze-pump-thaw cycles. The tube was subsequently back-filled with 1 bar of CO₂, shaken vigorously and the progress of the reaction monitored by ¹H NMR spectroscopy.

General procedure for attempted catalytic reduction of CO₂

In a high-pressure NMR tube equipped with a J. Young's tap, [Dipp₂1]Al(Et)H (0.005 g, 0.011 mmol, 10 mol%) and borane (HBpin, HBcat, {H(9-BBN)}₂ {10 B-H equiv. used}, Me₂S·BH₃) (0.11 mmol) were dissolved in benzene-d₆ (0.5 mL). The solution was subject

to three freeze-pump-thaw cycles and then back-filled with CO₂ (1.5 bar) at -60°C. The solution was allowed to warm to room temperature, generating a pressure of *ca.* 2 bar. The solution was left at room temperature for 36 h, after which the ¹H and ¹¹B NMR spectra were obtained to monitor consumption of the borane. Pending no reaction, the solution was heated at 60°C for 24 h and ¹H and ¹¹B NMR spectra were again measured.

General procedure for study of stoichiometric reactions of aluminium formates with pinacolborane (HBpin)

An NMR tube fitted with a J. Young's valve was charged with [^{Dipp}1]Al(Et)(OC(O)H) (0.012 mg, 0.023 mmol), HBpin (0.030 g, 0.231 mmol) and benzene-d₆ (0.5 mL). The resulting solution was heated to 80°C for 48 h. The same method was used for [^{Dipp}1]Al(Me)(OC(O)H) and [^{Dipp}2]Al(Et)(OC(O)H).

Preparation of {HC(MeCNDipp)₂}Al(Et)(OBcat) – [^{Dipp}1]Al(Et)(OBcat) (3.9^{Et})

To a solution of [^{Dipp}1]Al(Et)(OC(O)H) (0.25 g, 0.48 mmol) in toluene (5 mL) was added HBcat (154 μ L, 1.45 mmol) at room temperature. The reaction mixture was stirred overnight, and volatiles were subsequently removed *in vacuo* to yield a colourless oil. The oil was extracted into hexamethyldisiloxane, filtered and concentrated to the point of incipient crystallisation. Storage of this solution at -30°C for several days yielded a colourless crystalline material. Yield: 0.21 g, 70%. Single crystals suitable for X-ray diffraction were obtained from the storage of a solution of 3.9^{Et} in Et₂O at -30°C.

Method for monitoring the progress of the reaction of [Dipp¹]Al(Et)(OC(O)H) with HBcat

An NMR tube fitted with a J. Young's valve was charged with [Dipp¹]Al(Et)(OC(O)H) (0.020 g, 0.0386 mmol) and benzene-d₆ (0.5 mL). To it was added 1 equivalent of HBcat (4 μ L, 0.0375 mmol) or 3 equivalents (12 μ L, 0.113 mmol) at room temperature. The resulting solution was monitored by ¹H and ¹¹B NMR spectroscopy.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} -0.06 (2H, q, ³J_{HH} = 8.1 Hz, CH₃CH₂Al), 0.91 (3H, t, ³J_{HH} = 8.1 Hz, CH₃CH₂Al), 1.03, 1.13, 1.27, 1.31 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.55 (6H, s, CH₃ of β -diketiminato backbone), 3.20 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.61 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.98 (1H, s, γ -CH), 6.75 – 6.77 (2H, m, CH of BCat), 7.03-7.13 (8H, m, aromatic CH of Dipp and BCat). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_{C} -2.6 (br, CH₃CH₂Al), 8.7 (CH₃CH₂Al) 23.3 (CH₃ of β -diketiminato backbone), 24.1, 24.3, 24.9, 25.8 (CH₃ of Dipp ⁱPr), 28.0, 29.1 (CH of Dipp ⁱPr), 98.6 (γ -CH), 111.7 (ArC of BCat), 121.7 (ArC of BCat), 124.1, 125.0, 127.6, 140.3, 143.3, 145.4 (ArC of Dipp), 149.6 (ArC of BCat), 170.4 (NC). ¹¹B{¹H} NMR (127 MHz, benzene-d₆, 298 K): δ_{B} 21.5. ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **MS(ESI):** *m/z* calc for C₃₅H₄₅AlBN₂O₃ ([M-CH₂CH₃]⁺) 579.3339, meas. 579.3349 (100%), C₃₇H₄₉AlBN₂O₃ ([M-H]⁺) 607.3730, meas. 607.3666 (5%).

Preparation of {HC(MeCNDipp)₂}Al(Me)(OBcat) – [Dipp¹]Al(Me)(OBcat) (3.9^{Me})

An NMR tube fitted with a J. Young's valve was charged with [Dipp¹]Al(Me)(OC(O)H) (0.020 g, 0.040 mmol), benzene-d₆ (0.5 mL) and HBcat (13 μ L, 0.119 mmol) at room temperature. The resulting solution was monitored by ¹H and ¹¹B NMR spectroscopy.

Following completion of the reaction, volatiles were removed *in vacuo* and the resulting solid redissolved in benzene-d₆; **3.9^{Me}** was characterised by *in situ* NMR spectroscopy.

In-situ spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} -0.67 (3H, s, CH₃ of AlMe), 1.05, 1.14, 1.25, 1.29 (6H, d, $^3J_{\text{HH}}$ = 6.9 Hz, CH₃ of Dipp ⁱPr), 1.55 (6H, s, CH₃ of β -diketiminato backbone), 3.20 (2H, sept, $^3J_{\text{HH}}$ = 6.9 Hz, CH of Dipp ⁱPr), 3.64 (2H, sept, $^3J_{\text{HH}}$ = 6.9 Hz, CH of Dipp ⁱPr), 5.00 (1H, s, γ -CH), 6.71 – 6.77 (2H, m, CH of BCat), 7.00 - 7.13 (8H, m, aromatic CH of Dipp and BCat). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_{C} -14.5 (br, CH₃ of AlMe), 23.4 (CH₃ of β -diketiminato backbone), 24.1, 24.2, 24.8, 25.9 (CH₃ of Dipp ⁱPr), 28.0, 29.1 (CH of Dipp ⁱPr), 98.7 (γ -CH), 111.7 (ArC of BCat), 121.7 (ArC of BCat), 124.1, 125.0, 127.6, 140.2, 143.3, 145.5 (ArC of Dipp), 149.6 (ArC of BCat), 170.5 (NC). ¹¹B{¹H} NMR (128 MHz, benzene-d₆, 298 K): δ_{B} 22. ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} 113. ¹¹B{¹H} NMR (128 MHz, benzene-d₆, 298 K): δ_{B} 22. ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} 113.

Preparation of {HC(MeCNDipp)₂}Al(Et)(H₂(9-BBN)) – [^{Dipp}1]Al(Et)(H₂(9-BBN)) (**3.10^{Et}**)

To a solution of [^{Dipp}1]Al(Et)H (0.300 g, 0.632 mmol) in toluene (5 mL) was added a solution of {H(9-BBN)}₂ (0.077 g, 0.316 mmol of the dimer), also in toluene (3 mL) at room temperature. The reaction mixture was stirred rapidly for 3 h, filtered and concentrated to the point of incipient crystallisation. Storage at -30°C for several days yielded single crystals suitable for X-ray diffraction. Yield: 0.27 g, 71%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} 0.52 (2H, q, $^3J_{\text{HH}}$ = 8.0 Hz, CH₃CH₂Al), 1.02, 1.23, 1.39, 1.43 (6H, d, $^3J_{\text{HH}}$ = 6.7 Hz, CH₃ of Dipp ⁱPr), 1.52 (6H, s, CH₃ of β -diketiminato backbone), 1.14 – 2.01 (14H, br m, 9-borabicyclo(3.3.1)nonane-

CH) 3.22 (2H, sept, $^3J_{\text{HH}} = 6.7$ Hz, CH of Dipp ⁱPr), 3.41 (2H, sept, $^3J_{\text{HH}} = 6.7$ Hz, CH of Dipp ⁱPr), 4.83 (1H, s, γ -CH), 7.10 – 7.19 (6H, m, aromatic CH). Signal for CH₃ of Al-Et obscured by Dipp ⁱPr, AlH₂B resonance not observed in either ¹H NMR spectra or ¹H{¹¹B} NMR spectra. **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_{C} 4.21 (br, CH₃CH₂Al), 10.70 (CH₃CH₂Al), 17.9 (br, B-CH), 24.3 (CH₃ of β -diketiminato backbone), 24.4 (CH₃ of Dipp ⁱPr), 24.7 (B-CHCH₂CH₂-), 25.0, 25.1, 26.1 (CH₃ of Dipp ⁱPr), 27.5, 29.4 (CH of Dipp ⁱPr), 34.2 (B-CHCH₂CH₂-), 99.5 (γ -CH), 124.4, 125.0, 127.5, 141.3, 143.1, 145.5 (ArC of Dipp), 172.2 (NC). **¹¹B{¹H} NMR** (128 MHz, benzene-d₆, 298 K): δ_{B} -16 (s, $\Delta\omega_{1/2} = 212$ Hz ¹H decoupled; $\Delta\omega_{1/2} = 285$ Hz ¹H coupled). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} 105. **EI-MS**: m/z calc for C₃₂₉H₄₂N₂Al ([M-(EtH{9-BBN})]⁺) 445.3163, meas. 445.3184 (100%). **IR (nujol/cm⁻¹)** $\nu_{\text{Al-H-B}}$: 2066 (w), 2026 (w). **Elemental microanalysis**: calc. for C₃₉H₆₂N₂AlB: C 78.50% H 10.47% N 4.69% meas. C 78.36% H 10.32% N 4.67%.

Preparation of {HC(MeCNDipp)₂}Al(Me)(H₂(9-BBN)) – [^{Dipp}1]Al(Me)(H₂(9-BBN)) (3.10^{Me})

A Schlenk was charged with [^{Dipp}1]Al(Me)H (0.110 g, 0.239 mmol) and {H(9-BBN)}₂ (0.029 g, 0.120 mmol of the dimer) and toluene was added (5 mL). The resulting solution was stirred for 3 h at room temperature, filtered and concentrated to the point of incipient crystallisation. Storage at -30°C for 48 h produced colourless block-like crystals which were isolated and dried *in vacuo*. Yield: 0.08 g, 55%.

Spectroscopic data: **¹H NMR** (400 MHz, benzene-d₆, 298 K): δ_{H} -0.10 (3H, s, AlMe), 1.01, 1.15, 1.38, 1.41 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ⁱPr), 1.53 (6H, s, CH₃ of β -diketiminato backbone), 1.32 – 1.96 (14 H, br m, 9-borabicyclo(3.3.1)nonane-CH), 3.27 (4H, 2 x overlapping sept, $^3J_{\text{HH}} = 6.8$ Hz, 2 x CH of Dipp ⁱPr), 4.91 (1H, s, γ -CH), 7.10 – 7.18 (6H, m, aromatic CH). AlH₂B not observed by ¹H NMR spectroscopy or ¹H{¹¹B}

spectroscopy. **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_C – 10.1 (br, CH₃ of AlMe), 18.0 (br, B-CHCH₂CH₂-), 24.0 (CH₃ of β -diketiminato backbone), 24.3, 24.6 (CH₃ of Dipp ⁱPr), 24.8 (B-CHCH₂CH₂-), 25.1, 26.4 (CH₃ of Dipp ⁱPr), 27.9, 29.6 (CH of Dipp ⁱPr), 34.2 (B-CHCH₂CH₂-), 98.4 (γ -CH), 124.2, 125.0, 127.5, 141.2, 143.0, 145.5 (ArC of Dipp), 171.5 (NC). **¹¹B{¹H} NMR** (128 MHz, benzene-d₆, 298 K): δ_B – 15.2 (s, $\Delta\omega_{1/2}$ = 420 Hz ¹H decoupled; $\Delta\omega_{1/2}$ = 604 Hz, ¹H coupled). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **EI-MS**: m/z calc for C₂₉H₄₂N₂Al ([M-Me-(H{9-BBN})]⁺) 445.3163, meas. 445.3169 (100%). **IR (nujol/cm⁻¹)** ν_{Al-H-B} : 2065 (w), 2030 (w). **Elemental microanalysis**: calc. for C₃₈H₆₀N₂AlB: C 78.33% H 10.38% N 4.81% meas. C 78.27% H 10.36% N 4.92%.

Preparation of {HC(MeCNDipp)₂}Al(H)(H₂(9-BBN)) – [Dipp¹]Al(H)(H₂(9-BBN)) (3.10^H)

A solution of {H(9-BBN)}₂ (0.181 g, 0.740 mmol of the dimer) in toluene (5 mL) was added to a solution of [Dipp¹]AlH₂ (0.60 g, 1.35 mmol), also in toluene (5 mL). The reaction mixture was stirred at room temperature overnight, leading to the formation of a colourless precipitate. Toluene was added until the precipitate redissolved, and the solution was filtered and concentrated to the point of incipient crystallisation. The solution was gently warmed to redissolve any solid and allowed to cool slowly to room temperature and then to -30°C. Storage of this solution at -30°C yielded colourless crystals suitable for X-ray diffraction. Yield: 0.70 g, 91%.

Spectroscopic data: **¹H NMR** (400 MHz, benzene-d₆, 298 K): δ_H 1.03, 1.15 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.39 (12H, 2 x overlapping d, ³J_{HH} = 6.8 Hz, 2 x CH₃ of Dipp ⁱPr), 1.53 (6H, s, CH₃ of β -diketiminato backbone), 1.26 – 1.93 (14 H, br m, 9-borabicyclo(3.3.1)nonane-CH), 3.18 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.33 (2H,

Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂ and boranes

sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 4.58 (1H, br s, Al-H), 4.90 (1H, s, γ -CH), 7.00 – 7.15 (6H, m, aromatic CH). AlH₂B not observed by ¹H NMR spectroscopy or ¹H{¹¹B} spectroscopy. **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_{C} 17.9 (br, B-CHCH₂CH₂-), 23.8 (CH₃ of β -diketiminato backbone), 23.9, 24.5 (2 overlapping signals) (CH₃ of Dipp ⁱPr), 24.7 (B-CHCH₂CH₂-), 25.9 (CH₃ of Dipp ⁱPr), 28.3, 29.5 (CH of Dipp ⁱPr), 34.0 (B-CHCH₂CH₂-), 97.8 (γ -CH), 124.1, 125.1, 127.6, 140.7, 142.6, 145.5 (ArC of Dipp), 171.4 (NC). **¹¹B{¹H} NMR** (128 MHz, benzene-d₆, 298 K): δ_{B} – 15.7 (s, $\Delta\omega_{1/2} = 391$ Hz ¹H decoupled; $\Delta\omega_{1/2} = 585$ Hz ¹H coupled). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **EI-MS**: m/z calc for C₂₉H₄₂N₂Al ([M-(H₂{9-BBN})]⁺) 445.3163, meas. 445.2885 (6%). **IR (nujol/cm⁻¹)** $\nu_{\text{Al-H-B}}$: 2065 (w), 2034 (w); $\nu_{\text{Al-H}}$: 1846 (s). **Elemental microanalysis**: calc. for C₃₇H₅₈N₂AlB: C 78.15% H 10.28% N 4.93% meas. C 77.87% H 10.15% N 4.87%.

Preparation of {HC(Me₂NCNDipp)₂}Al(Et)(H₂(9-BBN)) – [Dipp₂]Al(Et)(H₂(9-BBN)) (3.11^{Et})

To a solution of [Dipp₂](Et)H (0.25 g, 0.47 mmol) in toluene (7 mL) was added at room temperature a solution of {H(9-BBN)}₂ (0.058 g, 0.235 mmol of the dimer) also in toluene (5 mL). The reaction mixture was stirred at room temperature for 5 h, filtered and concentrated to the point of incipient crystallisation. Storage of this solution at –30°C overnight yielded colourless, block-like crystals (of the toluene solvate) suitable for X-ray diffraction. Yield: 0.14 g, 47%.

Spectroscopic data: **¹H NMR** (400 MHz, benzene-d₆, 298 K): δ_{H} 0.78 (2H, q, $^3J_{\text{HH}} = 8.0$ Hz, CH₃CH₂Al), 0.97 (3H, br t, CH₃CH₂Al), 1.07, 1.23, 1.40, 1.67 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ⁱPr), 1.09 – 1.94 (14 H, br m, 9-borabicyclo(3.3.1)nonane-CH), 2.22 (6H, s, CH₃ of Me₂N), 2.95 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 3.67 (1H, s, γ -CH), 3.77 (2H, sept,

Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂ and boranes

$^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 7.00 – 7.14 (6H, m, aromatic CH). AlH₂B not observed by ¹H NMR spectroscopy or ¹H{¹¹B} spectroscopy. **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_{C} 0.97 (br, CH₃CH₂Al), 11.0 (CH₃CH₂Al), 17.1 (br, B-CHCH₂CH₂-), 24.3, 24.4 (CH₃ of Dipp ⁱPr), 25.2 (B-CHCH₂CH₂-), 26.5, 26.7 (CH₃ of Dipp ⁱPr), 28.5, 28.6 (CH of Dipp ⁱPr), 33.6 (B-CHCH₂CH₂), 41.0 (CH₃ of Me₂N), 76.4 (γ -CH), 125.0, 125.4, 126.2, 142.6, 144.2, 145.7 (ArC of Dipp), 167.8 (NC). **¹¹B{¹H} NMR** (128 MHz, benzene-d₆, 298 K): δ_{B} -17.4 (s, $\Delta\omega_{1/2}$ 253.4 Hz ¹H decoupled; $\Delta\omega_{1/2} = 332.9$ Hz ¹H coupled). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} 109. **IR (nujol/cm⁻¹)** $\nu_{\text{Al-H-B}}$: 2104 (m). **Elemental microanalysis**: calc. for C₄₁H₆₈N₄AlB: C 75.20% H 10.47% N 8.56% meas. C 75.05% H 10.35% N 8.42%.

Preparation of {HC(Me₂NCNDipp)₂}Al(H)(H₂(9-BBN)) – [Dipp₂]Al(H)(H₂(9-BBN)) (3.11^H)

To a solution of [Dipp₂]AlH₂ (0.080 g, 0.159 mmol) in toluene (2 mL) at room temperature was added a solution of {H(9-BBN)}₂ (0.021 g, 0.0871 mmol of the dimer), also in toluene (1 mL). The reaction mixture was stirred for 1 h at room temperature, during which time a colourless precipitate was evolved. Toluene was subsequently added until this precipitate redissolved. The resulting solution was filtered and stored at -30°C for 48 h, yielding single colourless crystals which were isolated and dried *in vacuo*. Yield: 0.07 g, 66%.

Spectroscopic data: **¹H NMR** (400 MHz, benzene-d₆, 298 K): δ_{H} 1.07, 1.17, 1.40 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH₃ of Dipp ⁱPr), 1.53 (6H, s, CH₃ of β -diketiminato backbone), 1.65 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH₃ of Dipp ⁱPr), 1.13 – 2.00 (14H, br m, 9-borabicyclo(3.3.1)nonane-CH), 2.18 (12H, s, CH₃ of Me₂N), 2.91 (2H, sept, $^3J_{\text{HH}} = 6.7$ Hz, CH of Dipp ⁱPr), 3.61 (1H, s, γ -CH), 3.79 (2H, sept, $^3J_{\text{HH}} = 6.7$ Hz, CH of Dipp ⁱPr), 4.48 (1H, br s, Al-H), 6.94 – 7.12 (6H,

m, aromatic CH). AlH₂B not observed by ¹H NMR spectroscopy or ¹H{¹¹B} spectroscopy. **¹³C{¹H} NMR** (126 MHz, benzene-d₆, 298 K): δ_C 17.1 (br, B-CHCH₂CH₂-), 24.8, 25.0 (CH₃ of Dipp ⁱPr), 25.6 (B-CHCH₂CH₂-), 25.7 (CH₃ of Dipp ⁱPr), 28.5, 29.0 (CH of Dipp ⁱPr), 33.6 (B-CHCH₂CH₂), 41.3 (CH₃ of Me₂N), 75.2 (γ -CH), 124.8, 125.3, 126.4, 142.1, 143.7, 145.9 (ArC of Dipp), 166.8 (NC). **¹¹B{¹H} NMR** (128 MHz, benzene-d₆, 298 K): δ_B -17.4 (s, $\Delta\omega_{1/2}$ = 200 Hz ¹H decoupled; $\Delta\omega_{1/2}$ = 320 Hz ¹H coupled). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **EI-MS**: *m/z* calc for C₃₁H₄₈AlN₄ ([M-{H₂(9-BBN))}]⁺) 503.3694, meas. 503.3707 (100%). **IR (nujol/cm⁻¹)** ν_{Al-H-B} : 2103 (m), ν_{Al-H} : 1850 (s). **Elemental microanalysis**: calc. for C₃₉H₆₄N₄AlB: C 74.74% H 10.29% N 8.94% meas. C 74.84% H 10.16% N 8.79%.

Preparation of {HC(MeCNDipp)₂}Al(Et)(OCH₂(O(9-BBN))) - [Dipp₁]Al(Et)(OCH₂(O(9-BBN))) (3.12^{Et})

Method A: A solution of [Dipp₁]Al(Et)(H₂(9-BBN)) (0.018 g, 0.0302 mmol) in benzene-d₆ (0.5 mL) in an NMR tube fitted with a J. Young's valve was attached to a Schlenk line *via* a glass T-piece, the other end of which attached to a 500 mL ampoule fitted with a J. Young's valve filled with *ca.* 1 bar of CO₂, pre-dried over P₂O₅ for 24 h. The solution was then degassed by three freeze-pump-thaw cycles and back-filled with dried CO₂ (*ca.* 1 bar) at room temperature and the progress of the reaction monitored by ¹H and ¹¹B NMR spectroscopy.

Method B: An NMR tube fitted with a J. Young's valve was charged with [Dipp₁]Al(Et)(OC(O)H) (0.020 g, 0.0386 mmol), {H(9-BBN)}₂ (0.005 g, 0.0205 mmol of the dimer) and benzene-d₆ (0.5 mL). The resulting solution was monitored by ¹H and ¹¹B NMR spectroscopy.

In-situ spectroscopic data: ^1H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} -0.13 (2H, q, $^3J_{\text{HH}} = 8.2$ Hz, CH₃CH₂Al), 0.84 (3H, t, $^3J_{\text{HH}} = 8.2$ Hz, CH₃CH₂Al), 1.08 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ⁱPr), 1.31 (12H, 2 x overlapping d, $^3J_{\text{HH}} = 6.8$ Hz, 2 x CH₃ of Dipp ⁱPr), 1.47 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ⁱPr), 1.59 (6H, s, CH₃ of β -diketiminato backbone), 1.94 (14H, br m, 9-borabicyclo(3.3.1)nonane-CH), 3.21 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 3.76 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 5.02 (1H, s, γ -CH), 5.63 (2H, s, CH₂ of Al-OCH₂{O(9-BBN)}), 7.09 – 7.20 (6H, m, aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene-d₆, 298 K): δ_{C} -2.6 (br, CH₃CH₂Al), 9.2 (CH₃CH₂Al), 23.4 (CH₃ of β -diketiminato backbone), 23.9, 24.5, 24.6, 24.9 (CH₃ of Dipp ⁱPr), 25.8 (B-CHCH₂CH₂-), 27.7, 28.9 (CH of Dipp ⁱPr), 33.7 (B-CHCH₂CH₂-), 87.6 (CH₂ of Al-OCH₂{O(9-BBN)}), 99.1 (γ -CH), 124.2, 125.0, 127.4, 141.1, 143.5, 145.4 (ArC of Dipp), 169.9 (NC). Signal for B-CH not observed. ^{11}B NMR (128 MHz, benzene-d₆, 298 K): δ_{B} 56.0. ^{27}Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} 126.

[^{Dipp}1]Al(Me)(OCH₂(O(9-BBN))) (**3.12^{Me}**) and [^{Dipp}2]Al(Et)(OCH₂(O(9-BBN))) (**3.13^{Et}**) were prepared using identical methods A and B as used for the preparation of [^{Dipp}1]Al(Et(OCH₂(O(9-BBN)))) and were characterised by *in situ* NMR spectroscopy.

In-situ spectroscopic data: [^{Dipp}1]Al(Me)(OCH₂(O(9-BBN))) (**3.12^{Me}**) ^1H NMR (500 MHz, benzene-d₆, 298 K): δ_{H} -0.76 (3H, s, CH₃ of AlMe), 1.08 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ⁱPr), 1.29 (12H, 2 x overlapping d, $^3J_{\text{HH}} = 6.8$ Hz, 2 x CH₃ of Dipp ⁱPr), 1.45 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ⁱPr), 1.58 (6H, s, CH₃ of β -diketiminato backbone), 0.99 – 2.01 (14 H, br m, 9-borabicyclo(3.3.1)nonane-CH), 3.21 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 3.74 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 5.00 (1H, s, γ -CH), 5.53 (2H, s, CH₂ of Al-OCH₂{O(9-BBN)}), 7.08 – 7.20 (6H, m, aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, benzene-d₆, 298 K): δ_{C} 23.5 (CH₃ of β -diketiminato backbone), 23.6, 23.9, 24.5, 24.8 (CH₃ of Dipp ⁱPr), 25.8 (B-CHCH₂CH₂-), 27.9, 28.8 (CH of Dipp ⁱPr), 33.4 (B-CHCH₂CH₂-), 87.4 (CH₂ of Al-

OCH₂{O(9-BBN)}}, 99.8 (γ -CH), 124.3, 124.9, 127.4, 140.9, 143.7, 145.5 (ArC of Dipp), 169.9 (NC). Signal for B-CH and Al-Me not observed. **¹¹B NMR** (128 MHz, benzene-d₆, 298 K): δ_B 56.6. **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed.

In-situ spectroscopic data: [Dipp₂]Al(Et)(OCH₂(O(9-BBN))) (3.13^{Et}) **¹H NMR** (400 MHz, benzene-d₆, 298 K): δ_H -0.18 (2H, q, $^3J_{HH}$ = 8.2 Hz, CH₃CH₂Al), 0.66 (3H, t, $^3J_{HH}$ = 8.2 Hz, CH₃CH₂Al), 1.14, 1.29, 1.35, 1.60 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.80 – 1.97 (14 H, br m, 9-borabicyclo(3.3.1)nonane-CH), 2.25 (12H, s, CH₃ of Me₂N), 3.02 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ⁱPr), 3.77 (1H, s, γ -CH), 4.22 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ⁱPr), 5.84 (2H, s, CH₂ of Al-OCH₂{O(9-BBN)}}, 7.08 – 7.21 (6H, m, aromatic CH). **¹³C{¹H} NMR** (126 MHz, benzene-d₆, 298 K): δ_C -1.3 (br, CH₃CH₂Al), 9.4 (CH₃CH₂Al), 24.0 (CH₃ of Dipp ⁱPr), 24.3 (B-CHCH₂CH₂-), 24.7, 26.2, 26.8 (CH₃ of Dipp ⁱPr), 27.9, 28.3 (CH of Dipp ⁱPr), 33.6 (B-CHCH₂CH₂-), 41.2 (CH₃ of Me₂N), 76.3 (γ -CH), 87.8 (CH₂ of Al-OCH₂{O(9-BBN)}}, 124.6, 125.2, 126.0, 142.1, 144.2, 145.6 (ArC of Dipp), 167.2 (NC). Signal for B-CH not observed. **¹¹B NMR** (160.4 MHz, benzene-d₆, 298 K): δ_B 57. **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed.

Isolation of {HC(MeCNDipp₂)Al(Et)(O(9-BBN))} – [Dipp₁]Al(Et)(O(9-BBN)) (3.14^{Et})

A solution of {H(9-BBN)}₂ (0.118 g, 0.482 mmol of the dimer) in toluene (5 mL) was added at room temperature to a solution of [Dipp₁]Al(Et)(OC(O)H) (0.500 g, 0.964 mmol) (5 mL), with stirring. The reaction mixture was stirred overnight and volatiles were subsequently removed *in vacuo*, yielding a colourless oil. The oil was extracted into minimal diethyl ether, filtered and concentrated to *ca.* 1 mL. Storage of this solution at -30°C for 1 week yielded colourless single crystals suitable for X-ray diffraction. The identity of the crystalline material was shown to be [Dipp₁]Al(Et)(O(9-BBN)) rather than [Dipp₁]Al(Et)(OCH₂{O(9-BBN)}). Yield: 0.32 g, 55%.

Spectroscopic data: ^1H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} 0.02 (2H, q, $^3J_{\text{HH}} = 8.1$ Hz, CH₃CH₂Al), 1.02 (3H, t, $^3J_{\text{HH}} = 8.1$ Hz, CH₃CH₂Al), 1.10, 1.24, 1.30, 1.42 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH₃ of Dipp ⁱPr), 1.53 (6H, s, CH₃ of β -diketiminato backbone), 1.56 (4H, br m, 9-borabicyclo(3.3.1)nonane-CH), 2.04 (10H, br m, 9-borabicyclo(3.3.1)nonane-CH), 3.22 (2H, sept, $^3J_{\text{HH}} = 6.7$ Hz, CH of Dipp ⁱPr), 3.55 (2H, sept, $^3J_{\text{HH}} = 6.7$ Hz, CH of Dipp ⁱPr), 4.99 (1H, s, γ -CH), 7.07 – 7.14 (6H, m, aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene-d₆, 298 K): δ_{C} -1.7 (br, CH₃CH₂Al), 9.2 (CH₃CH₂Al), 23.5 (CH₃ of β -diketiminato backbone), 24.4, 24.7, 24.8, 25.2 (CH₃ of Dipp ⁱPr), 25.7 (B-CHCH₂CH₂-), 28.1, 28.5 (CH of Dipp ⁱPr), 29.2 (br, B-CH), 34.6 (B-CHCH₂CH₂-), 99.2 (γ -CH), 124.5, 125.0, 127.3, 140.9, 143.7, 145.0 (ArC of Dipp), 170.4 (NC). ^{27}Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. ^{11}B NMR (128 MHz, benzene-d₆, 298 K): δ_{B} 55.0. **EI-MS:** m/z calc for C₃₁H₄₆N₂Al-([M{O(9-BBN)}])⁺ 473.3476, meas. 473.3457 (3%), calc. for C₃₇H₅₅N₂AlBO ([M-Et]⁺) 581.4223, meas. 581.4216 (5%).

Preparation of {HC(MeCNDipp)₂}Al(Et)(OMe) – [Dipp1]Al(Et)(OMe) (3.15^{Et})

[Dipp1]Al(Et)H (0.200 g, 0.421 mmol) was dissolved in toluene (5 mL) and cooled to -78°C. MeOH (22 μ L, 0.547 mmol) was added dropwise and the solution allowed to warm to room temperature. Hydrogen was evolved, and the resulting colourless solution stirred at room temperature for 1 h, by which time gas evolution had ceased. Volatiles were removed *in vacuo* and the resulting white solid extracted with *n*-hexane, filtered and concentrated to the point of incipient crystallisation. Storage of this solution at -30°C for 48 h yielded large, single crystals, suitable for X-ray diffraction. Yield: 0.13 g, 61%.

Spectroscopic data: ^1H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} -0.18 (2H, q, $^3J_{\text{HH}} = 8.2$ Hz, CH₃CH₂Al), 0.82 (3H, t, $^3J_{\text{HH}} = 8.2$ Hz, CH₃CH₂Al), 1.07, 1.28, 1.31, 1.50 (6H, d, $^3J_{\text{HH}} =$

6.8 Hz, CH₃ of Dipp ⁱPr), 1.58 (6H, s, CH₃ of β -diketiminato backbone), 3.20 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.63 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.85 (3H, s, CH₃ of Al-OMe), 4.92 (1H, s, γ -CH), 7.08 – 7.18 (6H, m, aromatic CH). **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_c -3.2 (br, CH₃CH₂Al), 9.2 (CH₃CH₂Al) 23.2 (CH₃ of β -diketiminato backbone), 24.4, 24.7, 24.9, 25.6 (CH₃ of Dipp ⁱPr), 27.8, 28.9 (CH of Dipp ⁱPr), 51.8 (CH₃ of Al-OMe), 97.8 (γ -CH), 124.1, 124.9, 127.3, 141.0, 143.4, 145.3 (ArC of Dipp), 169.8 (NC). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} 111. **EI-MS**: *m/z* calc for C₃₀H₄₄N₂AlO ([M-Et]⁺) 475.3269, meas. 475.3285 (100%). **Elemental microanalysis**: calc. for C₃₁H₄₇N₂Al: C 76.15% H 9.79% N 5.55% meas. C 76.40% H 9.74% N 5.47%.

Preparation of {HC(MeCNDipp)₂}Al(Me)(OMe) – [^{Dipp}1]Al(Me)(OMe) (3.15^{Me})

To a solution of [^{Dipp}1]Al(Me)H (0.010 g, 0.022 mmol) in benzene-d₆ in an NMR tube fitted with a J. Young's valve was added MeOH (4 μ L, 0.109 mmol). Upon cessation of effervescence, volatiles were removed *in vacuo*. The resulting solid was redissolved in benzene-d₆ and *in-situ* NMR spectroscopic data was obtained.

In-situ spectroscopic data: **¹H NMR** (400 MHz, benzene-d₆, 298 K): δ_H -0.83 (3H, s, CH₃ of AlMe), 1.07, 1.26, 1.29, 1.46 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.57 (6H, s, CH₃ of β -diketiminato backbone), 3.20 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.66 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.77 (3H, s, CH₃ of Al-OMe), 4.93 (1H, s, γ -CH), 7.08 – 7.15 (6H, m, aromatic CH). **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_c -15.0 (br, CH₃ of AlMe), 23.3 (CH₃ of β -diketiminato backbone), 24.5, 24.6, 24.8, 25.8 (CH₃ of Dipp ⁱPr), 27.9, 28.9 (CH of Dipp ⁱPr), 51.7 (CH₃ of Al-OMe), 97.9 (γ -CH), 124.1, 124.9, 127.3, 141.0, 143.4, 145.4 (ArC of Dipp), 169.8 (NC). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} 112.

Preparation of {HC(MeCNDipp₂)Al(Et)(H₂(BH₂)) – [Dipp¹]Al(Et)(H₂(BH₂)) (3.16^{Et})

Me₂S·BH₃ (2.0 M in THF, 0.580 mL, 1.16 mmol) was added dropwise to a stirred solution of [Dipp¹]Al(Et)H (0.425 g, 0.895 mmol) in toluene (1 mL) at room temperature. The reaction mixture was stirred for 1 h at room temperature, and volatiles then removed *in vacuo* to yield a colourless solid. The solid was extracted into toluene, filtered and concentrated to the point of incipient crystallisation before being cooled to –30°C. Storage of this solution at –30°C for several days yielded colourless acicular crystals which were suitable for X-ray crystallography. Yield of isolated crystals: 0.19 g, 65%.

Spectroscopic data: ¹H{¹¹B} NMR (400 MHz, benzene-d₆, 298 K): δ_{H} –0.02 (2H, q, ³J_{HH} = 8.1 Hz, CH₃CH₂Al), 0.81 (3H, t, ³J_{HH} = 8.1 Hz, CH₃CH₂Al), 1.02 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.03 (4H, s, BH₄), 1.13, 1.35, 1.47 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.57 (6H, s, CH₃ of β -diketiminato backbone), 3.28 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.38 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.91 (1H, s, γ -CH), 7.08 – 7.16 (6H, m, aromatic CH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_{C} 0.9 (br, CH₃CH₂Al), 9.1 (CH₃CH₂Al), 23.7 (CH₃ of β -diketiminato backbone), 23.8, 25.1, 25.2, 26.6 (CH₃ of Dipp ⁱPr), 28.4, 29.2 (CH of Dipp ⁱPr), 97.9 (γ -CH), 124.1, 125.6, 127.8, 139.8, 144.0, 145.7 (ArC of Dipp), 170.4 (NC). ¹¹B NMR (128 MHz, benzene-d₆, 298 K): δ_{B} –36.6 (quint, ¹J_{BH} = 83.7 Hz). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} 111. **EI-MS:** *m/z* calc for C₂₉H₄₂N₂Al ([M–Et–BH₃]⁺) 445.6505, meas. 445.3157 (100%). **IR (nujol/cm^{–1})** $\nu_{(\text{B-Ht})}$ 2449 (s), 2400 (s), $\nu_{(\text{B-Hb})}$ 2201 (br).

Preparation of {HC(MeCNDipp)₂}Al(Me)(H₂(BH₂)) – [Dipp1]Al(Me)(H₂(BH₂)) (3.16^{Me})

To a solution of [Dipp1]Al(Me)H (12 mg, 0.026 mmol) in benzene-d₆ (0.5 mL) in an NMR tube fitted with a J. Young's valve was added Me₂S·BH₃ (8 μ L, 0.078 mmol). Volatiles were subsequently removed *in vacuo* and the resulting solid redissolved in benzene-d₆ and *in-situ* spectroscopic data was obtained. An analogous method was used for the *in-situ* synthesis of [Dipp2]Al(Et)(H₂(BH₂)).

In-situ spectroscopic data for [Dipp1]Al(Me)(H₂(BH₂)) (3.16^{Me}): ¹H NMR (500 MHz, benzene-d₆, 298 K): δ_{H} -0.48 (3H, s, CH₃ of AlMe), 1.06, 1.11, 1.30, 1.45 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.55 (6H, s, CH₃ of β -diketiminato backbone), 3.27 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.36 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.90 (1H, s, γ -CH), 7.06 – 7.15 (6H, m, aromatic CH). B-H and Al-H-B not observed in ¹H NMR or ¹H{¹¹B} NMR. ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_{C} -8.6 (br, CH₃ of AlMe), 24.0 (CH of Dipp ⁱPr), 24.7 (CH₃ of Dipp ⁱPr), 25.0 (two overlapping CH₃ of Dipp ⁱPr), 25.9 (CH₃ of Dipp ⁱPr), 28.8, 28.7 (CH of Dipp ⁱPr), 98.00 (γ -CH), 124.4, 125.3, 128.4, 140.0, 144.4, 146.1 (ArC of Dipp), 170.7 (NC). ¹¹B NMR (160 MHz, benzene-d₆, 298 K): δ_{B} -36.4 (quint, ¹J_{BH} = 82.8 Hz). ²⁷Al NMR (130 MHz, benzene-d₆, 298 K): δ_{Al} Not observed.

In-situ spectroscopic data for [Dipp2]Al(Et)(H₂(BH₂)) (3.17^{Et}): ¹H NMR (500 MHz, benzene-d₆, 298 K): δ_{H} 0.28 (2H, q, ³J_{HH} = 8.1 Hz, CH₃CH₂Al), 0.94 (3H, t, ³J_{HH} = 8.1 Hz, CH₃CH₂Al), 1.12, 1.23, 1.33, 1.48 (6H, d, ³J_{HH} = 6.7 Hz, CH₃ of Dipp ⁱPr), 2.16 (12H, s, CH₃ of Me₂N), 3.22 (2H, sept, ³J_{HH} = 6.7 Hz, CH of Dipp ⁱPr), 3.82 (1H, s, γ -CH), 3.89 (2H, sept, ³J_{HH} = 6.7 Hz, CH of Dipp ⁱPr), 7.06 – 7.13 (6H, m, aromatic CH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_{C} 3.5 (br, CH₃CH₂Al), 9.7 (CH₃CH₂Al), 24.3, 24.4, 26.3, 26.9 (CH₃ of Dipp ⁱPr), 28.3, 29.4 (CH of Dipp ⁱPr), 41.1 (CH₃ of Me₂N), 78.0 (γ -CH), 124.8, 125.3,

126.2, 141.8, 144.5, 145.2 (ArC of Dipp), 167.0 (NC). **¹¹B NMR** (128 MHz, benzene-d₆, 298 K): δ_B -39 (quint, $^1J_{BH}$ = 82.5 Hz). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed.

Preparation of {HC(MeCNDipp)₂}Al(Et)(OB(H)OMe) – [Dipp1]Al(Et)(OB(H)OMe) (3.18^{Et})

[Dipp1]Al(Et)(OC(O)H) (0.300 g, 0.579 mmol) was dissolved in toluene (5 mL) and Me₂S·BH₃ (165 μ L, 1.74 mmol) added. The reaction mixture was stirred overnight at room temperature, followed by the removal of volatiles *in vacuo*, yielding a sticky, colourless oil. The oil was dissolved in *n*-hexane (*ca.* 2 mL), filtered (leaving behind a white residue) and concentrated until the point of incipient crystallisation. The solution was stored at 6°C for several hours, yielding colourless rod-shaped crystals, suitable for X-ray diffraction. Yield: 0.13 g, 41%.

Method for monitoring the reaction of [Dipp1]Al(Et)(OC(O)H) with Me₂S·BH₃

An NMR tube fitted with a J. Young's valve was charged with [Dipp1]Al(Et)(OC(O)H) (0.020 g, 0.039 mmol) and benzene-d₆ (0.5 mL). To separate samples was added one (4 μ L, 0.039 mmol) and three (11 μ L, 0.116 mmol) equivalents of Me₂S·BH₃. The resulting solutions were monitored by ¹H and ¹¹B NMR spectroscopy.

Spectroscopic data: **¹H{¹¹B} NMR** (400 MHz, benzene-d₆, 298 K): δ_H -0.12 (2H, q, $^3J_{HH}$ = 8.1 Hz, CH₃CH₂Al), 0.83 (3H, t, $^3J_{HH}$ = 8.1 Hz, CH₃CH₂Al), 1.05, 1.23, 1.32, 1.38 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.55 (6H, s, CH₃ of β -diketiminato backbone), 3.22 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ⁱPr), 3.57 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ⁱPr), 3.63 (3H, s, CH₃ of B-OMe), 4.77 (1H, br s, BH), 4.96 (1H, s, γ -CH), 7.07 – 7.17 (6H, m, aromatic CH), **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_C -2.2 (br, CH₃CH₂Al), 9.0 (CH₃CH₂Al),

23.3 (CH of of Dipp ⁱPr) 24.1, 24.3, 24.9, 26.3 (CH₃ of Dipp ⁱPr), 27.7, 29.0 (CH of Dipp ⁱPr), 50.0 (CH₃ of BOMe), 98.3 (γ -CH), 124.1, 124.9, 127.5, 140.6, 143.4, 145.3 (ArC of Dipp), 170.1 (NC). **¹¹B{¹H} NMR** (128 MHz, benzene-d₆, 298 K): δ_B 25.1 (s, $\Delta\omega_{1/2}$ = 458 Hz ¹H decoupled, $\Delta\omega_{1/2}$ = 1102 Hz ¹H coupled). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **EI-MS**: *m/z* calc for C₃₀H₄₅N₂AlBO₂ ([M-Et]⁺) 503.3389, meas. 503.3400 (100%), calc for C₃₂H₅₁N₂AlBO₂ ([M+H]⁺) 533.3859, meas. 533.3517 (10%) **IR** (nujol/cm⁻¹) ν_{B-H} : 2434 (w).

Preparation of {HC(MeCNDipp)₂Al(Me)(OB(H)OMe) – [Dipp1]Al(Me)(OB(H)OMe) (3.18^{Me})

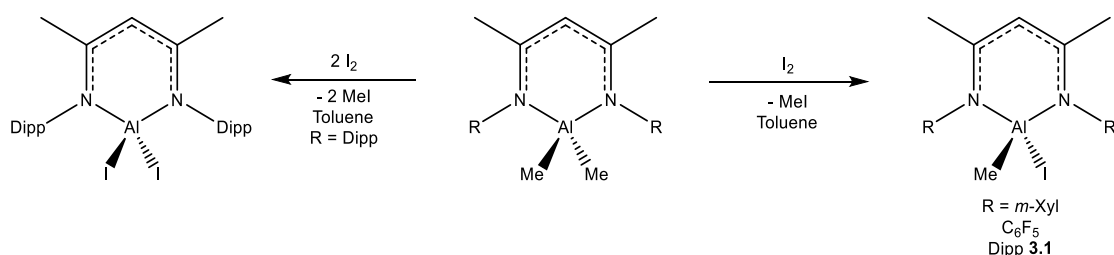
An NMR tube fitted with a J. Young's valve was charged with [Dipp1]Al(Me)(OC(O)H) (0.020 g, 0.043 mmol) and benzene-d₆ (0.5 mL). To this was added Me₂S·BH₃ (12 μ L, 0.13 mmol) and, after leaving the reaction mixture overnight at room temperature, volatiles were removed *in vacuo*. The resulting solid was dissolved in C₆D₆ and *in situ* NMR spectroscopic data was obtained.

In-situ spectroscopic data: **¹H{¹¹B} NMR** (400 MHz, benzene-d₆, 298 K): δ_H -0.78 (3H, s, CH₃ of AlMe), 1.06, 1.12, 1.23, 1.30 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.55 (6H, s, CH₃ of β -diketiminato backbone), 3.22 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.57 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.58 (3H, s, CH₃ of B-OMe), 4.70 (1H, br s, B-H), 4.98 (1H, s, γ -CH), 7.07-7.23 (6H, m, aromatic CH). **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_C -14.7 (br, CH₃ of AlMe), 23.4 (CH of of Dipp ⁱPr) 24.2, 24.3, 24.9, 26.4 (CH₃ of Dipp ⁱPr), 27.7, 29.0 (CH of Dipp ⁱPr), 50.2 (CH₃ of B-OMe), 98.4 (γ -CH), 124.2, 124.9, 127.5, 140.5, 143.4, 145.3 (ArC of Dipp), 170.2 (NC). **¹¹B{¹H} NMR** (128 MHz, benzene-d₆, 298 K): δ_B 25.5. **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} 109.

3.4 Results and discussion

3.4.1 Synthesis of novel β -diketiminato-ligated aluminium hydrides

3.4.1.1 Synthesis of novel β -diketiminato-ligated aluminium halide precursors: iodination of aluminium-carbon bonds



Scheme 3.3: Synthesis of aluminium iodide complexes by the reaction of aluminium methyl complexes with iodine.^{51,62,63}

The synthesis of β -diketiminato-ligated aluminium iodide complexes may be achieved by the addition of I₂ to the corresponding aluminium methyl complex, with elimination of iodomethane. This has been illustrated previously by the syntheses of [R¹]Al(Me)I (R = *m*-Xyl, C₆F₅) and [Dipp¹]AlI₂ *via* the addition of one or two equivalents of I₂ to [R¹]AlMe₂ and [Dipp¹]AlMe₂, respectively.^{51,62,63} Accordingly, the addition of one equivalent of I₂ to [Dipp¹]AlMe₂ at -78°C, followed by stirring at room temperature for 12 h leads to the selective formation of [Dipp¹]Al(Me)I (**3.1**), *via* partial iodination of [Dipp¹]AlMe₂. **3.1** was isolated in 94% yield and fully characterised by standard spectroscopic and analytical techniques, and by X-ray crystallography. Single crystals of **3.1** could be obtained by storage of a concentrated solution of **3.1** in toluene at -30°C; the molecular structure is displayed in Figure 3.5. A detailed structural analysis of **3.1** may be found in section 3.4.1.4.

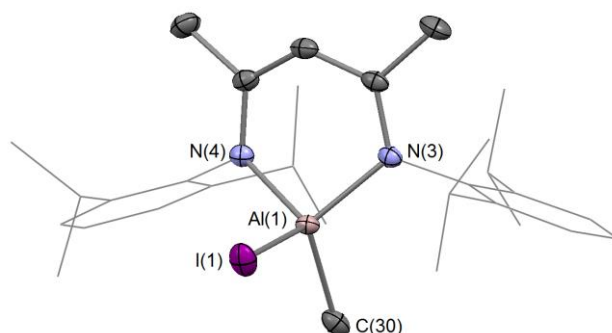


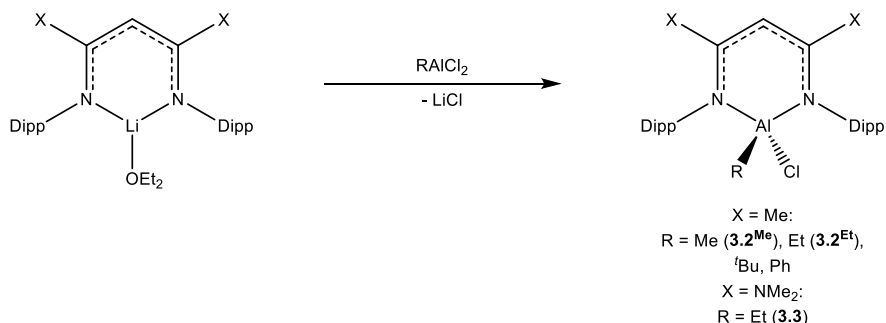
Figure 3.5: Molecular structure of [Dipp $\mathbf{1}$]Al(Me)I (**3.1**). Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths ($\text{\AA}$) and angles ($^\circ$): I(1)-Al(1) 2.5734(6), Al(1)-N(4) 1.891(2), Al(1)-N(3) 1.896(2), Al(1)-C(30) 2.023(3), N(4)-Al(1)-N(3) 99.01(8).

The ^1H NMR spectrum of **3.1** features four distinct doublets for the Dipp CH₃ groups and two septets for the Dipp CH groups, indicative of a reduction in symmetry around the aluminium centre, compared to that of [Dipp $\mathbf{1}$]AlMe₂, leading to inequivalent Dipp $i\text{Pr}$ groups. A singlet integrating to three hydrogens is observed at $\delta_{\text{H}} = -0.31$ ppm for the CH₃ group of the aluminium-bound methyl functionality, the upfield shift being characteristic of aluminium-bound alkyl groups. This signal is shifted downfield relative to that of [Dipp $\mathbf{1}$]AlMe₂ ($\delta_{\text{H}} = -0.50$ ppm) and is comparable to that of [$m\text{-Xyl}$ 1]Al(Me)I ($\delta_{\text{H}} = -0.25$ ppm).^{51,64} The ^{27}Al NMR spectrum displays a broad resonance ($\delta_{\text{Al}} = 127$ ppm), consistent with a four-coordinate aluminium centre.

3.4.1.2 Synthesis of novel β -diketiminato-ligated aluminium halide precursors: salt metathesis reactions

A more commonly utilised method for the synthesis of compounds of the type [R $\mathbf{1}$]Al(R')Cl (R' = alkyl group) is salt metathesis between [R $\mathbf{1}$]Li(OEt₂) and sources of R'AlCl₂. To date, the scope of this method is limited to that of four distinct alkyl groups

(R = Me, Et, *t*Bu, Ph)^{23,58-60} and exploration of the impact of modification of the β -diketiminato ligand limited to alteration of the N-bound aryl groups.^{51,59,62,64,65}



Scheme 3.4: Synthesis of [Dipp1]Al(R)(Cl) (**3.2^{Et, Me}**) and [Dipp2]Al(Et)(Cl) (**3.3**).

The complexes [Dipp1]Al(Et)Cl (**3.2^{Et}**) and [Dipp2]Al(Et)Cl (**3.3**) were synthesised *via* careful addition of an *n*-hexane solution of EtAlCl₂ to solutions of [Dipp1]Li(OEt₂) and [Dipp2]Li(OEt₂), respectively. These reactions occur cleanly at low temperature and, after work up and recrystallisation (both from concentrated solutions in *n*-hexane at -30°C), **3.2^{Et}** and **3.3** may be isolated in 79% and 53% yield, respectively. The ¹H NMR data obtained for **3.2^{Et}** is consistent with that reported in the literature, and the novel compound **3.3** was fully characterised by standard spectroscopic and analytical techniques.⁶⁰

In the absence of reported crystallographic data for **3.2^{Et}**, both **3.2^{Et}** and **3.3** were characterised by X-ray crystallography. Their molecular structures are shown in Figure 3.6 and display the expected molecular connectivity; an analysis of the molecular structures is undertaken in Section 3.4.1.4.

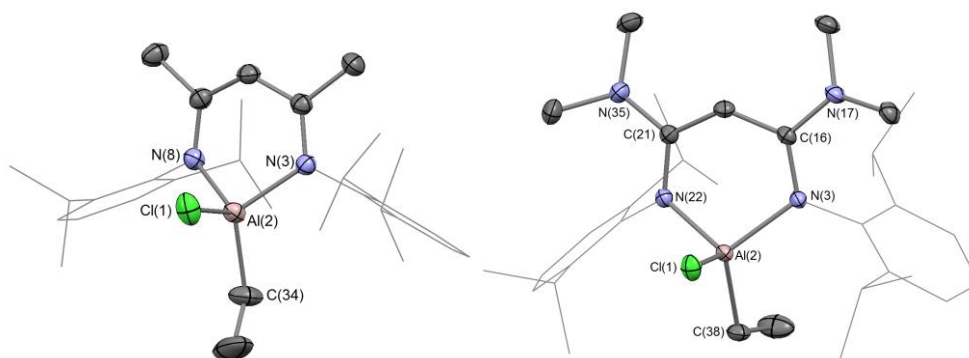


Figure 3.6: Molecular structures of [Dipp1]Al(Et)Cl (**3.2^{Et}**) (left) and [Dipp2]Al(Et)Cl (**3.3**) (right). Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°): **3.2^{Et}**: Cl(1)-Al(2) 2.1736(6), Al(2)-N(3) 1.8978(13), Al(2)-N(8) 1.8845(13), Al(2)-C(34) 1.9555(18), N(3)-Al(2)-N(8) 96.85(6). **3.3**: Al(2)-Cl(1) 2.1789(4), Al(2)-N(3) 1.8917(9), Al(2)-N(22) 1.8866(9), Al(2)-N(8) 96.85(6). **3.3**: Al(2)-Cl(1) 2.1789(4), Al(2)-N(3) 1.8917(9), Al(2)-N(22) 1.8866(9), Al(2)-C(38) 1.9703(11), N(3)-C(16) 1.3561(14), C(21)-N(22) 1.3611(14), C(16)-(N17) 1.3651(13), C(21)-N(35) 1.3684(14), N(3)-Al(2)-N(22) 101.73(4).

The ¹H NMR spectra of both **3.2^{Et}** and **3.3** feature four doublets for the Dipp CH₃ groups and two septets for the Dipp CH groups, consistent with Nacnac systems that lack C₂ symmetry, arising from unsymmetrical substitution of the aluminium centre. Both ¹H NMR spectra contain a quartet ($\delta_{\text{H}} = -0.04$ ppm for **3.2^{Et}**, 0.09 ppm for **3.3**) and a triplet ($\delta_{\text{H}} = 0.80$ ppm for **3.2^{Et}**, 0.71 ppm for **3.3**) for the methylene and methyl groups, respectively, of the aluminium-bound ethyl functionality.⁶⁰ The chemical shifts of the backbone γ -CH of **3.3** ($\delta_{\text{H}} = 3.78$ ppm, $\delta_{\text{C}} = 77.1$ ppm) are considerably upfield relative to those of **3.2^{Et}** ($\delta_{\text{H}} = 4.96$ ppm, $\delta_{\text{C}} = 98.7$ ppm). This difference is consistent with a more electron-rich ligand framework arising from π -donation from the NMe₂ groups, and is a feature common to metal complexes ligated by the [R²] (R = Ph, Xyl, Dipp) ligand family.⁶¹ Moreover, such an effect is consistent with well-documented effects of π -donor amino groups on alkene resonances.⁶⁶

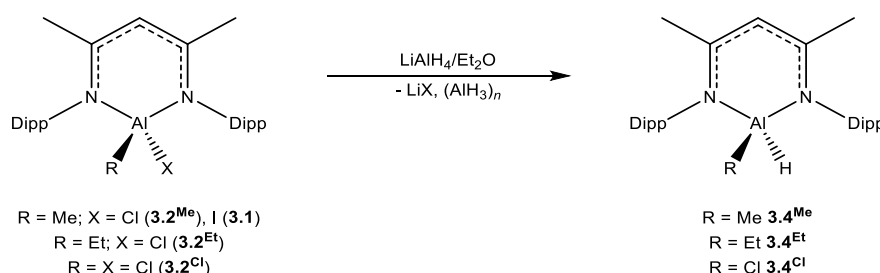
3.4.1.3 Synthesis of novel β -diketiminato-ligated aluminium hydrides: metathetical reactions of aluminium halides with hydride sources

A commonly utilised method for the synthesis of gallium hydrides is metathesis using a gallium halide precursor and a borohydride. The treatment of gallium halides [Dipp¹] $\text{Ga}(\text{R})\text{X}$ ($\text{R} = \text{X} = \text{I}, \text{Cl}$; $\text{R} = \text{Me}, \text{X} = \text{Cl}$; $\text{R} = \text{tBu}, \text{X} = \text{Br}$), for example, with $\text{M}[\text{HBEt}_3]$ ($\text{M} = \text{Li}, \text{K}$) readily leads to the selective formation of the corresponding gallium hydrides [Dipp¹] $\text{Ga}(\text{R})\text{H}$.^{23,57} Typically these reactions occur readily under ambient conditions and elevated temperatures are required only when the gallium centre is particularly sterically encumbered. By contrast, the extension of this method to the synthesis of β -diketiminato-ligated aluminium hydrides is under-explored. In 2006, an attempt to synthesise [Dipp¹] $\text{Al}(\text{Me})\text{H}$ from the reaction of [Dipp¹] $\text{Al}(\text{Me})\text{Cl}$ with $\text{Li}[\text{HBEt}_3]$ was reported to yield an intractable and uncharacterisable mixture of products, and no further exploration of this chemistry was reported.⁵⁷

The synthesis of the aluminium hydrides [Dipp¹] $\text{Al}(\text{R})\text{H}$ ($\text{R} = \text{Me}, \text{Et}$) was attempted *via* the addition of excess $\text{K}[\text{HBEt}_3]$ (5 equiv.) to solutions of the corresponding chlorides [Dipp¹] $\text{Al}(\text{R})\text{Cl}$ (**3.2^{Me}**, **3.2^{Et}**) in benzene-d₆. No reactivity was observed after 48 h at room temperature and the solutions were subsequently heated to 80°C. Regular monitoring of the solutions by ¹H NMR spectroscopy showed the slow consumption of aluminium chloride complexes over the course of 14 d. In both cases, a broad downfield resonance grew in (**3.2^{Me}**: $\delta_{\text{H}} = 4.64$ ppm; **3.2^{Et}**: $\delta_{\text{H}} = 4.57$ ppm) characteristic of an aluminium hydride (²⁷Al I = 5/2).²⁵ However, the reactions were not selective and in both cases a side product was formed in *ca.* 25% yield. The side product could not be identified, nor could it be separated from the major species, even upon increasing the yield of the reaction and repeated recrystallisations. The stronger nature of the Al-Cl bond,

compared to that of gallium (reported E-Cl bond strengths: E = Al 426 kJ mol⁻¹, E = Ga 363 kJ mol⁻¹), presumably leads to the markedly different conditions required to bring about reactivity of the complexes $[\text{Dipp}\mathbf{1}]\text{M}(\text{Me})\text{Cl}$ (M = Al, Ga) with $\text{K}[\text{HBEt}_3]$.^{57,67}

In order to improve both the rate of reaction and its selectivity, the weaker nature of the Al-I bond was exploited, and $[\text{Dipp}\mathbf{1}]\text{Al}(\text{Me})\text{I}$ (**3.1**) treated with a slight excess of $\text{K}[\text{HBEt}_3]$ (1.2 equiv). As observed by ¹H NMR spectroscopy, **3.1** was completely consumed after 48 h at room temperature or within 2h with heating at 80°C, to yield a product with the same ¹H NMR spectroscopic signatures as those previously attributed to the aluminium hydride $[\text{Dipp}\mathbf{1}]\text{Al}(\text{Me})\text{H}$ (**3.4^{Me}**). However, the selectivity of the reaction was not improved, and the desired product could not be isolated cleanly.



Scheme 3.5: Synthesis of novel aluminium hydrides $[\text{Dipp}\mathbf{1}]\text{Al}(\text{R})\text{H}$ (**3.4^{Me}**, Et, Cl).

The use of an alternative (more reactive) hydride source yields significantly more success. The treatment of the aluminium halide complexes $[\text{Dipp}\mathbf{1}]\text{Al}(\text{R})\text{X}$ (R = Me, X = Cl, I; R = Et, X = Cl; R = X = Cl) with one equivalent of LiAlH_4 at -78°C cleanly yields the Nacnac-ligated aluminium hydride complexes $[\text{Dipp}\mathbf{1}]\text{Al}(\text{R})\text{H}$ (R = Me, **3.4^{Me}**; R = Et, **3.4^{Et}**; R = Cl, **3.4^{Cl}**), with elimination of lithium chloride and AlH_3 . The aluminium hydrides are readily soluble in both pentane and *n*-hexane but may be recrystallised from *n*-hexane at low temperatures (6°C to -30°C). Each can be isolated in high yield (**3.4^{Me}** 65%, **3.4^{Et}** 79%, **3.4^{Cl}** 77%), and has been fully characterised by standard spectroscopic and

analytical techniques; their molecular structures have also been elucidated by X-ray crystallography (Figure 3.7).

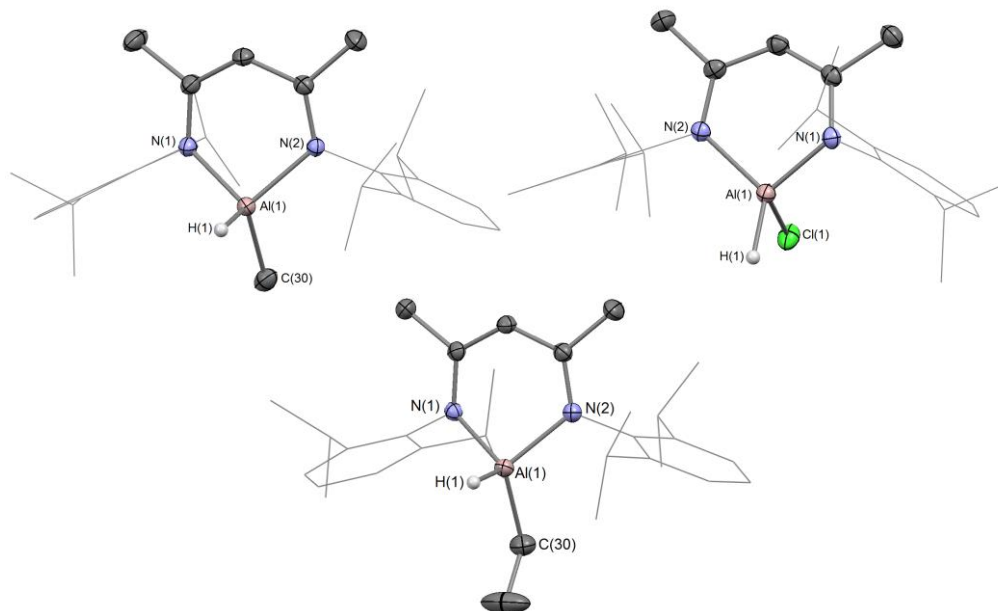


Figure 3.7: Molecular structures of [Dipp¹]Al(Me)H (**3.4^{Me}**, top left), [Dipp¹]Al(Cl)H (**3.4^{Cl}**, top right) and [Dipp¹]Al(Et)H (**3.4^{Et}**, bottom). Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Al-H located in the difference Fourier map and refined isotropically. Key bond lengths (Å) and angles (°): **3.4^{Me}** Al(1)-N(1) 1.9081(13), Al(1)-N(2) 1.9123(12), Al(1)-C(30) 1.9998(18), Al(1)-H(1) 1.576(10), N(1)-Al(1)-N(2) 96.09(5); **3.4^{Cl}** Al(1)-H(1) 1.5403(10), Al(1)-N(1) 1.8755(16), Al(1)-N(2) 1.8906(16), Al(1)-Cl(1) 2.1366(9), N(1)-Al(1)-N(2) 98.44(7); **3.4^{Et}** Al(1)-N(1) 1.9151(13), Al(1)-N(2) 1.9170(13), Al(1)-C(30) 1.9605(18), Al(1)-H(1) 1.67(4), N(1)-Al(1)-N(2) 95.10(5).

Crystallographic studies of these novel hydrides reveal that they are monomeric in the solid state. This is consistent with the previously reported behaviour of Nacnac-ligated alanes, in which both the coordinatively saturated nature of the metal centre, and the high degree of steric protection provided by the ligand inhibit oligomerisation.⁶⁸ In each case, the aluminium hydrides were located in the difference Fourier map and the Al-H

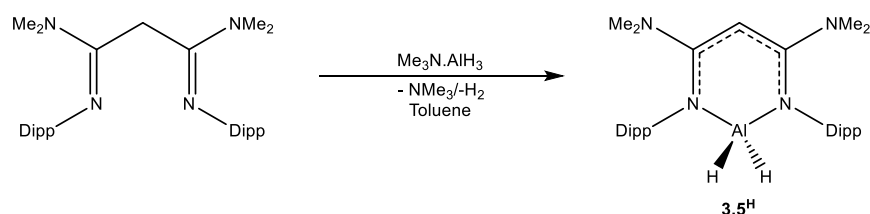
distances (Figure 3.7) are consistent with those reported in the literature for related complexes.^{50,69}

The characterisation of these hydrides by standard spectroscopic techniques and X-ray crystallography (See Section 3.4.1.5/6) is consistent with their formulation as aluminium monohydrides of the type [Dipp¹Al(R)H. In light of the highly reactive nature of LiAlH₄ in both hydride transfer and transmetallation reactions, the selectivity of this route to form monohydrides, especially in the case of **3.4^{Cl}**, is surprising and represents an unprecedented route to systems of this type.^{69,70}

3.4.1.4 Synthesis of novel β -diketiminato-ligated aluminium hydrides: the use of electronically-modified ligands

Modification of β -diketimate ligands can occur in two different positions: variation of the N-bound substituents and of the backbone C-bound groups. The steric demands of these groups can readily be tuned to modulate access to the metal centre. Modification of the N-bound substituents has been extensively employed in the synthesis of β -diketimate aluminium hydrides, and a variety of systems of the type [R¹AlH₂ have been reported, where R varies from a methyl to a Dipp substituent.^{31,46,48,68} Variation of the electronic properties of the Nacnac ligand have been explored to a lesser extent. One method utilised to achieve this is the installation of electronically-modifying substituents within the N-aryl groups. The use of ligands of this type within group 13 chemistry is relatively limited; a number of aluminium complexes bearing the [C⁶F⁵1] ligand have been reported but these are solely limited to alkyl and halide complexes.^{62,71} A different method used to modulate the electronic properties of the β -diketimate ligand is to modify the nature of the backbone C-bound groups. Examples of this

approach involve the use of trifluoromethyl and electron-withdrawing aryl substituents and, more recently, electron-donating amino substituents.⁶¹ The application of these ligands towards group 13 chemistry is largely unexplored.



Scheme 3.6: Synthesis of [Dipp₂]AlH₂ (**3.5^H**) from deprotonation of the protio-ligand with Me₃N·AlH₃.

A particularly successful route for the synthesis of Nacnac-ligated aluminium dihydrides is the reaction of Me₃N·AlH₃ with the corresponding protio-ligand. This method can be extended to the recently reported Me₂N-functionalised Nacnac ligand. Thus, addition of [Dipp₂]H to a solution of Me₃N·AlH₃ in toluene at 0°C leads to the rapid evolution of gas (H₂ and NMe₃) and selectively yields [Dipp₂]AlH₂ (**3.5^H**) in 64% yield. The synthesis of **3.5^H** *via* this protolysis route is successful, despite the existence of the protio-ligand [Dipp₂]H in the diamine form, with the acidic proton being situated on the backbone of the ligand rather than being nitrogen-bound. Similar reactivity is observed during the reaction of [Dipp₂]H with AlMe₃ to yield [Dipp₂]AlMe₂ and methane. One of the only other reportedly stable N-nacnac-ligated metal hydride species is [Dipp₂]SnH, which decomposes at 25°C in benzene-d₆ solution over the course of 12 h and in the solid state after several days.⁶¹ By contrast, **3.5^H** shows significant thermal stability and no decomposition is observed in the solid state after several months or in solution at 25°C after several weeks. This can be attributed to both the greater strength of the Al-H bond, compared to the Sn-H bond of [Dipp₁]SnH, and the coordinatively saturated nature of the metal centre for [Dipp₂]AlH₂.

Single crystals of **3.5^H** suitable for X-ray diffraction were obtained from hexane at -30°C ; **3.5^H** was fully characterised by standard spectroscopic and analytical techniques, in addition to X-ray crystallography. The molecular structure is shown in Figure 3.8. X-ray crystallography reveals the molecular structure of **3.5^H** to be consistent with the desired monomeric product.

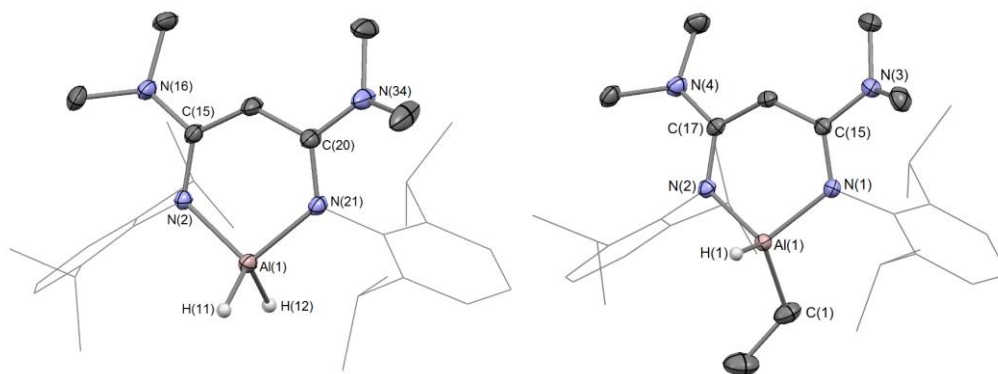


Figure 3.8: Molecular structures of $[\text{Dipp}2]\text{AlH}_2$ (**3.5^H**) (left) and $[\text{Dipp}2]\text{Al}(\text{Et})\text{H}$ (**3.5^{Et}**) (right).

Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Al-H located in the Fourier difference map and refined isotropically. Key bond lengths ($\text{\AA}$) and angles ($^\circ$): **3.5^H**: Al(1)-N(2) 1.8963(12), Al(1)-N(21) 1.8897(13), Al(1)-H(12) 1.55(2), Al(1)-H(11) 1.54(2), C(15)-N(2) 1.3496(18), C(20)-N(21) 1.3537(19), C(15)-N(16) 1.3787(19), C(20)-N(34) 1.375(2), N(2)-Al(1)-N(21) 100.09(5); **3.5^{Et}**: Al(1)-N(1) 1.8946(10), Al(1)-N(2) 1.9222(10), Al(1)-C(1) 1.9803(14), Al(1)-H(1) 1.52(3), N(1)-C(15) 1.3551(15), N(2)-C(17) 1.3431(15), N(3)-C(15) 1.3887(15), N(4)-C(17) 1.3693(16), N(1)-Al(1)-N(2) 99.36(4).

The scope of the coordination chemistry of this ligand within group 13 hydride chemistry may be further extended. Careful addition of a slight excess of LiAlH_4 to an ethereal solution of the mixed ethyl/chloro system **3.3** at -78°C yields $[\text{Dipp}2]\text{Al}(\text{Et})\text{H}$ (**3.5^{Et}**) in 52% yield. **3.5^{Et}** was also characterised by standard spectroscopic and analytical techniques and its molecular structure elucidated by X-ray crystallography

(Figure 3.8). The molecular structure of **3.5^{Et}** is shown in Figure 3.8 and confirms its identity to be that of a monomeric aluminium hydride. The hydride was located in the difference Fourier map and refined isotropically; the measured Al-H distance (1.52(3) Å) is consistent with literature precedent.^{50,69}

3.4.1.5 Structural analysis of novel β -diketiminato-ligated aluminium complexes

	Distance of Al from C ₃ N ₂ plane (Å)	<i>d</i> (Al-N) (Å)	<i>d</i> (Al-R) (Å)	<i>d</i> (Al-H) (Å)	N-Al-N angle (°)
[^{Dipp} 1]Al(Me)I (3.1^{Me})	0.572	1.891(2) 1.896(2)	2.023(3)	-	99.01(8)
[^{Dipp} 1]Al(Me)Cl ⁵⁷	0.664	1.906(2) 1.887(2)	1.905(5)	-	97.6(1)
[^{Dipp} 1]Al(Et)Cl (3.2^{Et})	0.693	1.8978(13) 1.8845(13)	1.9555(18)	-	96.85(6)
[^{Dipp} 1]AlCl ₂ ⁷²	0.525	1.8843(9) 1.8663(9)	2.1185(4) 2.1344(4)	-	99.36(4)
[^{Dipp} 2]Al(Et)Cl (3.3)	0.667	1.8917(9) 1.8866(9)	1.9703(11)	-	101.73(4)
[^{Dipp} 1]Al(Me)H (3.4^{Me})	0.614	1.9081(13) 1.9123(12)	1.9998(18)	1.576(10)	96.09(5)
[^{Dipp} 1]Al(Et)H (3.4^{Et})	0.663	1.9151(13) 1.9170(13)	1.9605(18)	1.67(4)	95.10(5)
[^{Dipp} 1]Al(Cl)H (3.4^{Cl})	0.467	1.8755(16) 1.8906(16)	2.1366(9)	1.5403(10)	98.44(7)
[^{Dipp} 1]AlH ₂ ⁶⁹	0.006	1.8989(12)	-	1.51(2) 1.518(19)	96.41(5)
[^{Me} 1]AlH ₂ ⁷³	0.001	1.8775(13) 1.8822(14)	-	-	97.44(5)
[^{iPr} 1]AlH ₂ ⁷³	0.501	1.898(2) 1.900(2)	-	-	97.87(9)
[^{m-Xyl} 1]AlH ₂ ⁷⁴	0.00	1.8867(15)	-	-	96.71(9)
[^{Mes} 1]AlH ₂ ⁴⁷	-	1.893(1) 1.887(2)	-	-	96.4(1)
[^{Dipp} 2]AlH ₂ (3.5^H)	0.094	1.8963(12) 1.8897(13)	-	1.572 1.564	100.09(5)
[^{Dipp} 2]Al(Et)H (3.5^{Et})	0.464	1.8946(10) 1.9222(10)	1.9803(14)	1.52(3)	99.36(4)

Table 3.1: Comparison of key structural parameters of (N)-Nacnac aluminium hydrides.

Each of the novel Nacnac hydrides, [Dipp $\mathbf{1}$]Al(R)H (R = Me, Et, Cl), features a distorted tetrahedral aluminium centre which is projected out of the plane of the Nacnac ligand (Table 3.1). These deviations of the ring from planarity, arising from disrotary realignment of the N-M contacts, is a common feature of β -diketimate-ligated metal complexes and is typically accompanied by a narrowing of the N-M-N angle. Typically, the installation of more sterically encumbering substituents at the aluminium centre (or sterically hindering N-bound substituents) can cause unfavourable interactions between the N-bound aryl substituents and the metal, pushing it out of the plane of the Nacnac ligand.⁷⁵ Folding of the ring reduces sterically unfavourable interactions between the Dipp and metal-bound substituents. Increased planarity is therefore associated with smaller substituents, such as hydrides and this is illustrated in the distance of the aluminium centre from the least-squares C₃N₂ plane for the aluminium dihydride derivatives e.g. [Dipp $\mathbf{1}$]AlH₂ (0.006 Å).⁶⁹ A pronounced increase in the degree of ring folding is observed upon increasing the size of the aluminium-bound R substituent. As such, the degree of ring folding observed for the unsymmetrically substituted aluminium hydride complexes (**3.4^{Me}**/**3.4^{Et}**/**3.4^{Cl}** and **3.5^{Et}**) lies between that observed for the aluminium dihydride derivatives and their precursor halide complexes, reflecting the steric environment surrounding the aluminium centres. Consistently, greater distortion is observed on increasing the size of the R substituent from hydride to chloride to ethyl. This effect is also accompanied by a marked narrowing of the N-Al-N angle as the aluminium centre is displaced further from the C₃N₂ plane.

Conversely, an increase in size of the β -C substituents can lead to steric conflict between these substituents and those bound to nitrogen. This typically pushes the N-aryl ring closer to the metal centre, causing the metal centre to move deeper into the Nacnac

binding pocket.⁷⁵ This structural feature is observed for the N-nacnac ligated complexes where the installation of the bulkier NMe₂ substituents at the β -position cause the aluminium centre to lie closer to the least-squares C₃N₂ plane of the ligand than is observed in the traditional Nacnac-ligated counterparts (e.g. 0.693 Å (**3.2^{Et}**), 0.667 Å (**3.3**); 0.663 Å (**3.4^{Et}**), 0.464 Å (**3.5^{Et}**)).

The non-planar C₃N₂Al skeleton renders the sites occupied by the two aluminium-bound substituents inequivalent, resulting in distinct “axial” and “equatorial” positions. Typically, the larger substituent occupies the less sterically hindered “equatorial” position; in all of these molecular structures the alkyl substituent occupies this position. In the case of **3.1**, the methyl substituent occupies the equatorial position, and the iodide the axial position. This contrasts to that observed for the molecular structure obtained for [Dipp**1**]Al(Me)Cl, in which the methyl and chloride substituents are disordered over the two positions, due to their similarity in size, reducing the degree of positional preference.⁵⁷ This effect is also observed in the molecular structure of **3.4^{Cl}**; the chloride and hydride substituents are disordered across both positions.

For these complexes, the contacts surrounding the aluminium centres reveal information regarding its electronic and steric environment, imparted by the ligand and substituents. The Al-N bonds of **3.1** ($d(\text{Al}(1)\text{-N}(4))$ 1.891(2), $d(\text{Al}(1)\text{-N}(3))$ 1.896(2) Å) lie between those of [Dipp**1**]AlMe₂ ($d(\text{Al-N})$ 1.922(2), 1.935(2) Å) and [Dipp**1**]AlI₂ ($d(\text{Al-N})$ 1.872(2), 1.893(3) Å), presumably reflecting the impact of the presence of both an alkyl and halide substituent on the Lewis acidity of the aluminium centre.^{64,72} This effect is also observed in the molecular structures of the unsymmetrically substituted aluminium hydrides (**3.4^{Me}**/**3.4^{Et}**/**3.4^{Cl}**/**3.5^{Et}**), where the Al-N contacts and the Al-C/Al-Cl distances are lengthened compared to their precursor halides (Table 3.1). This is presumably due

to a reduction in the Lewis acidity of the aluminium centre on replacement of an electronegative halide substituent with a σ -donating hydride moiety. Similar features are observed when comparing the structural metrics of the hydrides [Dipp¹Al(R)H (R = Me, Et, H, Cl); a lengthening of the Al-N distances is observed upon replacement of an electronegative halide substituent with a σ -donating, but simultaneously more sterically encumbering, alkyl group. The Al-N distances of **3.5^{Et}** are longer than those of **3.5^H**; the closer approach is presumably enabled by the presence of two small hydride substituents, leading to a reduction in steric bulk surrounding the aluminium centre.

Crystallographic characterisation of the N-nacnac derivatives **3.3**, **3.5^H** and **3.5^{Et}** reveals structural features which are in line with their “regular” Nacnac-ligated counterparts. Thus, the aluminium centre in **3.5^H** lies only marginally (0.094 Å) out of the least-squares C₃N₂ plane, as is also found with [Dipp¹AlH₂].⁶⁹ Ethyl/hydride complexes **3.4^{Et}** and **3.5^{Et}** feature only minimal differences in the Al-N and Al-C distances, although the metal lies noticeably closer to the least-squares C₃N₂ plane in the N-nacnac compound (0.464 vs. 0.663 Å) and, as a result, widening of the N-Al-N angle is observed (99.4(1)° vs. 95.1(1)°).

In each of these molecular structures, the degree of planarity of the ring of causes the N-aryl groups to lie closer to the NC₃N plane, resulting in increased steric congestion. This forces the *exo*-cyclic NMe₂ groups to rotate out of the plane, a common feature of all N-nacnac ligated metal complexes; in the case of **3.3** the torsion angles between the NC₃N chelate and NC₂ amino planes are 31.8 and 34.2°. ⁶¹ For **3.5^{Et}** and **3.5^H**, these torsion angles are 22.8/40.3° and 31.8/34.2°, respectively. While this implies less efficient π -conjugation into the chelate ring for these complexes, the C-N distances between the β -carbon and its adjacent nitrogens are comparable in distance (e.g. **3.3**:

$d(\text{C}(16)\text{-N}(3)/\text{N}(17))$ 1.3561(14)/1.3651(13), $d(\text{C}(21)\text{-N}(22)/\text{N}(35))$ 1.3611(14)/1.3684(14) Å). This is suggestive of some degree of delocalisation of the Me₂N lone pair into the ligand system, as these bonds lie between reported double and single C-N bond distances.⁷⁶

3.4.1.6 Spectroscopic analysis of novel β -diketiminato-ligated aluminium hydride complexes

The ¹H NMR spectra of the new unsymmetrically substituted hydride complexes feature four doublets for the Dipp CH₃ groups and two septets for the Dipp CH groups, consistent with Nacnac systems that lack C₂ symmetry, arising from unsymmetrical substitution of the aluminium centre. By contrast, the ¹H NMR spectrum for **3.5^H**, a complex which retains C₂ symmetry, features two doublets and one septet for these substituents. The ¹H NMR spectra show resonances for the aluminium-bound hydrogens that are typical of those reported for aluminium hydrides, and are broadened significantly due to the highly quadrupolar nature of ²⁷Al.^{25,68} In the case of the alkyl-substituted alanes, the resonances corresponding to the alkyl functionalities are shifted considerably upfield relative to those of their precursor halide complexes (**3.1** δ_{H} = -0.31 ppm; **3.2^{Et}** δ_{H} = 0.80, -0.04 ppm; **3.3** δ_{H} = 0.71, 0.09 ppm). Presumably, this reflects the increase in shielding arising from the highly σ -donating character of the aluminium-bound hydride. As is reported for other systems of this type, the resonances that corresponds to the N-nacnac backbone γ -H of **3.5^{Et}** and **3.5^H** (Table 3.2) are considerably more upfield than that of their “regular” Nacnac analogues [^{Dipp}**1**]AlH₂ (δ_{H} = 4.86 ppm), a phenomenon thought to arise from π -electron delocalisation from the NMe₂ groups into the ligand backbone.⁶¹

	3.4^{Me}	3.4^{Et}	3.4^{Cl}	3.5^{Et}	3.5^H
δ_{H} (Al-H) (ppm)	4.64	4.57	4.55	4.90	4.52
δ_{H} (γ -H) (ppm)	4.93	4.92	4.88	3.68	3.84
δ_{H} (Al-R) (ppm)	-0.74	0.79, -0.13	-	0.72, -0.27	-
$\nu_{\text{Al-H}}$ (cm ⁻¹)	1767	1776	1865, 1842	1788	1840, 1793

Table 3.2: Comparison of key spectroscopic parameters of (N)-Nacnac alanes.

While Al-H bond metrics are not easily established from X-ray crystallography, the stretching frequencies measured by IR for the hydride derivatives do provide a potentially informative probe of the nature of the Al-H bond. Strong absorptions are exhibited in the IR spectra of these complexes in the region typical for Al-H stretches. The stretching frequencies are highly dependent on the aluminium-bound substituent and the electronic character it imparts on the metal centre, and consequently the Al-H bond. This may be illustrated through comparison with reported species of the type [Dipp¹]Al(R)H.^{50,68}

In the case of **3.4^{Cl}** two Al-H stretching bands are observed at 1865 cm⁻¹ and 1842 cm⁻¹, arising from the disordered nature of the Cl and H substituents in the axial/equatorial positions in the solid state. These data are comparable to those measured for related species bearing electron-withdrawing groups (e.g. 1854, 1824 cm⁻¹ for R = NHPH, OⁱPr).⁵⁰ By contrast, the Al-H stretches measured for **3.4^{Me}** (1767 cm⁻¹) and **3.4^{Et}** (1776 cm⁻¹) are considerably red-shifted, and represent some of the lowest Al-H stretching frequencies measured for complexes of this type.⁵⁰ The IR spectrum of **3.5^H** shows two strong bands at $\nu_{\text{Al-H}}$ 1841 and 1793 cm⁻¹ which are associated with the antisymmetric and symmetric stretches of the Al-H bonds, respectively. The influence of the Nacnac backbone substituents on the Al-H stretching frequencies is much less pronounced: the mean Al-H stretching frequency measured for **3.5^H** (1817 cm⁻¹) is

essentially identical to that of [Dipp¹] AlH_2 (1814 cm⁻¹), and that measured for **3.5^{Et}** (1788 cm⁻¹) is marginally (12 cm⁻¹) higher than that of its “regular” Nacnac analogue.

A degree of correlation of the Al-H stretching frequency with electronic character of the aluminium-bound substituent is apparent.⁵⁰ It is suggested that the installation of electron-withdrawing substituents leads to a lowering of the aluminium-centred orbitals and more effective overlap with those of the hydrogen atom, leading to a stronger bond and a higher stretching frequency.⁷⁷

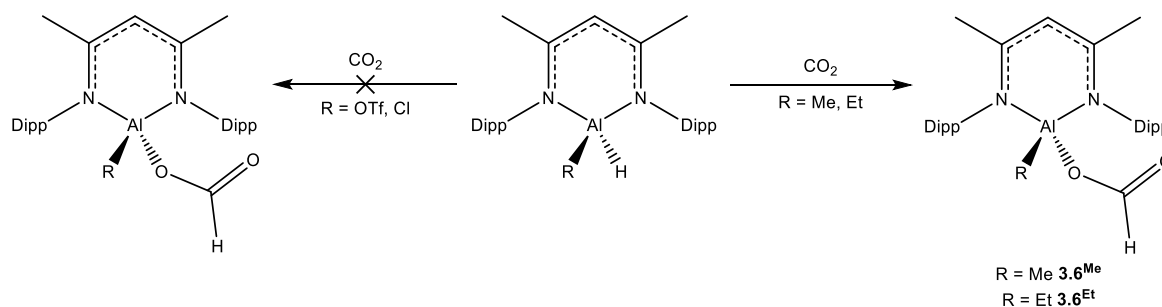
A comparison of the structural and spectroscopic features of the N-nacnac ligated group 13 hydride complexes with their “regular” Nacnac-ligated counterparts reveals the extent to which the use of this ligand affects the electronic character of the aluminium centres in these complexes. The structural and spectroscopic data associated with these complexes (notably NMR and X-ray crystallographic data) are indicative of π -donation from the NMe₂ groups into the ligand backbone. However, IR data for the two series of compounds imply that the electronic differences between the compounds are relatively small; the Al-H stretches for the N-nacnac compounds are very similar to their Nacnac analogues. Whilst the differences are small, these Al-H stretches are found at slightly *higher* wavenumber than their Nacnac analogues. Given that the presence of electron-withdrawing aluminium-bound substituents generally leads to higher stretching frequencies, this may suggest that, for these complexes, the primary effect of the backbone amino groups of the N-nacnac ligand is as a σ -electron-withdrawing group. Whilst the π -framework of the ligand is indeed more electron rich, the extent to which this influences these complexes appears to be minimal due to the four-coordinate nature of the aluminium centres and the σ -withdrawing nature of the backbone amino substituents dominates.

3.4.2 Reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂

3.4.2.1 Reactivity of “conventional” β -diketiminato-ligated aluminium hydrides towards CO₂

There are a number of reported examples of the reactivity of aluminium hydrides with CO₂, in which one of the C=O bonds undergoes insertion into the Al-H bond to yield an aluminium formate.^{26–28} However while a range of well-defined Nacnac-ligated aluminium hydrides is available, the reactivity of these systems towards CO₂ has not been reported. A recent paper, however, describes a Nacnac-ligated aluminium hydride that is capable of catalytically hydroborating carbonyl functionalities *via* insertion of the C=O unit into the Al-H bond.³⁷ With this in mind, the reactivity of our novel systems (and related alanes) towards CO₂ was targeted with the aims of (i) defining potential modes of reactivity; and (ii) understanding the factors controlling the relative rates of reaction.

In light of the ready insertion of benzaldehyde into the Al-H bond of [Dipp $\mathbf{1}$]Al(OTf)H (**3.4^{OTf}**), a solution of **3.4^{OTf}** in benzene-d₆ was degassed by three freeze-pump-thaw cycles and placed under *ca.* 1 bar of CO₂.³⁷ Monitoring of the solution by ¹H NMR spectroscopy revealed that no reaction occurred at room temperature after 24 h. The solution was subsequently heated at 80°C for several days; the resulting ¹H NMR spectrum contained resonances that correspond to protonated forms of the ligand, *viz* [Dipp $\mathbf{1}$]H and [Dipp $\mathbf{1}$]H₂⁺[OTf][–] together with unreacted **3.4^{OTf}**. It is apparent that insertion of CO₂ into the Al-H bond of **3.4^{OTf}** is not facile. A similar lack of reactivity towards CO₂ was observed for **3.4^{Cl}**.



Scheme 3.7: Reactivity of the aluminum monohydrides $[\text{Dipp}1]\text{Al}(\text{R})\text{H}$ (**3.4^{OTf}**, **3.4^{Cl}**, **3.4^{Me}** and **3.4^{Et}**) towards CO_2 .

By contrast, solutions of the alkylaluminium hydrides **3.4^{Me}** and **3.4^{Et}** react readily under ambient pressures of CO_2 at room temperature to selectively yield the aluminium formates, **3.6^{Me}** and **3.6^{Et}**. The insertion of CO_2 is signalled by the loss of the Al-H resonance in the respective ^1H NMR spectra ($\delta_{\text{H}} = 4.64$ ppm for **3.4^{Me}**; $\delta_{\text{H}} = 4.57$ ppm for **3.4^{Et}**) and the appearance of a sharp downfield resonance diagnostic of a formate functionality ($\delta_{\text{H}} = 8.46$ ppm for **3.6^{Me}**; $\delta_{\text{H}} = 8.49$ ppm for **3.6^{Et}**). This is supported by the observation of downfield singlet resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at $\delta_{\text{C}} = 162.4$ ppm (**3.6^{Me}**), 162.7 ppm (**3.6^{Et}**).²³ The resonances for the aluminium-bound alkyl substituents are retained and shifted marginally upfield, relative to those of their respective hydrides.

^1H NMR spectroscopy reveals these transformations to be quantitative and **3.6^{Me}**/**3.6^{Et}** can be isolated in the solid state in 65% and 90% yields, respectively, following workup and recrystallisation from *n*-hexane. Both complexes have been characterised by standard analytical and spectroscopic techniques, in addition to X-ray crystallography; their molecular structures are shown in Figure 3.9.

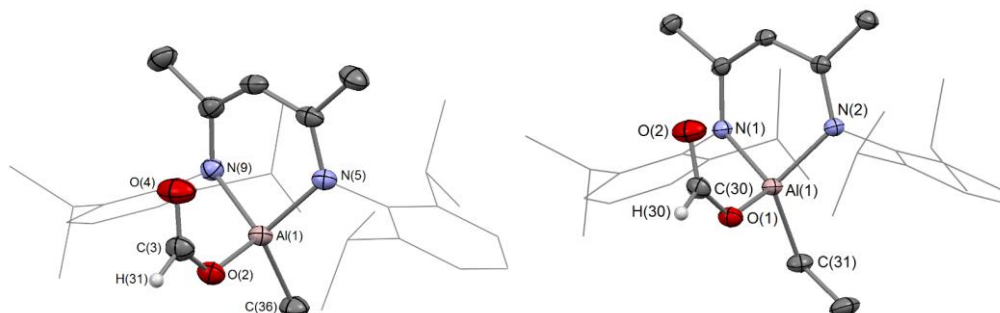


Figure 3.9: Molecular structures of [Dipp1]Al(Me)(OC(O)H) (**3.6^{Me}**) (left) and [Dipp1]Al(Et)(OC(O)H) (**3.6^{Et}**) (right). Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°): **3.6^{Me}**: Al(1)-O(2) 1.780(2), Al(1)-N(5) 1.891(3), Al(1)-N(9) 1.890(3), Al(1)-C(36) 1.935(3), O(2)-C(3) 1.294(4), C(3)-O(4) 1.205(4), N(5)-Al(1)-N(9) 97.14(11), O(2)-C(3)-O(4) 126.5(3). **3.6^{Et}**: Al(1)-O(1) 1.7832(8), Al(1)-N(1) 1.8855(9), Al(1)-N(2) 1.8914(9), Al(1)-C(31) 1.9605(11), O(1)-C(30) 1.2988(14), O(2)-C(30) 1.2039(15), N(1)-Al(1)-N(2) 97.43(4), O(2)-C(30)-O(1) 125.84(11).

	[Dipp1]Al(Me)(OC(O)H)	[Dipp1]Al(Me)H	[Dipp1]Al(Et)(OC(O)H)	[Dipp1]Al(Et)H
Distance of Al from C ₃ N ₂ plane (Å)	0.548	0.614	0.488	0.663
<i>d</i> (Al-N) (Å)	1.891(3), 1.890(3)	1.9081(13), 1.9123(12)	1.8855(9), 1.8914(9)	1.9151(13), 1.9170(13)
<i>d</i> (Al-C) (Å)	1.935(3)	1.9998(18)	1.9605(11)	1.9605(18)

Table 3.3: A comparison of some of the structural metrics of aluminium formate complexes **3.6^{Me}** and **3.6^{Et}** with their precursor alanes.

3.6^{Me} and **3.6^{Et}** represent rare structurally characterised molecular aluminium formate complexes, where the formate acts as a monodentate ligand. The molecular structures display the expected molecular connectivity around the tetrahedral aluminium centre. The aluminium centres are found at distances of 0.548 Å (**3.6^{Me}**) and 0.488 Å (**3.6^{Et}**) from the least-squares C₃N₂ plane, i.e. closer than the corresponding hydrides (0.614 Å **3.4^{Me}**; 0.663 Å **3.4^{Et}**). While this might not be predicted based on steric grounds, it may

be rationalised based on the position the formate substituent occupies. For both **3.6^{Me}** and **3.6^{Et}**, the formate substituent occupies the axial position, where it lies in close proximity to the *i*Pr groups of the Dipp substituents. These interactions may be somewhat reduced by lowering the Al centres closer to the C₃N₂ plane.

Many of the structural features of **3.6^{Me}** and **3.6^{Et}** are comparable, including the N-Al and Al-O bond lengths. The formate functionality is bonded to the aluminium centre *via* a single aluminium-oxygen bond, the lengths of which are consistent with literature precedent.^{58,60} The molecular structures feature two distinct C-O bond lengths, consistent with single and double C-O bonds, and a trigonal planar environment around the formate carbon.⁷⁶ Such features are present in the reported molecular structure of the ketiminatoaluminium formate complex Al(OC(O)H)(OCMeCHCMeNAr)₂ (Ar = Dipp) (*d*(Al-O) 1.798(2), *d*(C-O) 1.213(3), 1.296(3) Å).²⁶ A comparison of the bond metrics of the formates with their precursor hydrides (Table 3.3) reveals a shortening of the N-Al and Al-C bonds, upon insertion of CO₂ into the Al-H bond. This presumably reflects the increase in Lewis acidity of the aluminium centre by virtue of the presence of the more electronegative aluminium-bound oxygen in the formate product. The IR spectra of **3.6^{Me}** and **3.6^{Et}** feature a strong band at 1673 cm⁻¹ and 1680 cm⁻¹, respectively, for the C=O stretching band of the formate ester functionality.

Complexes **3.6^{Me}** and **3.6^{Et}** are thermally stable and remain unchanged even when heated at 60°C under vacuum for several hours, indicating that the insertion of CO₂ is irreversible. The formation of these complexes is selective and, whilst there is literature precedent for insertion of CO₂ into aluminium-alkyl bonds, this is not evident in these systems.⁷⁸

In order to further quantify this reactivity, solutions of **3.4^{Me}** and **3.4^{Et}** in benzene-d₆ were placed under 1 bar of CO₂ and monitored by ¹H NMR spectroscopy (Figure 3.10). This shows that the reactions reach > 90% completion after *ca.* 40 minutes for **3.4^{Me}** and 60 minutes for **3.4^{Et}**. Both reactions show *pseudo*-first order kinetics with respect to the concentration of alane and rate constants (k_{obs}) of $7.16 \times 10^{-4} \text{ s}^{-1}$ and $6.16 \times 10^{-4} \text{ s}^{-1}$ for **3.4^{Me}** and **3.4^{Et}**, respectively, can be calculated. As such, the half-lives of the aluminium hydrides can be shown to be 16.1 min for **3.4^{Me}** and 18.8 minutes for **3.4^{Et}**; the reactivity of these complexes towards CO₂ is therefore clearly comparable.

Calculated mechanisms for CO₂ reduction typically involve initial nucleophilic attack of a metal hydride at the C-centre of CO₂ or dual-site Lewis acid/Lewis base activation of CO₂.⁷⁹ In this case, due to the coordinatively saturated nature of the aluminium centre and the observed first-order reaction kinetics, it is unlikely that the second mode of reactivity is operative. In the case of single site chemistry, it has been suggested that the interaction of the metal hydride with the carbon centre of CO₂ plays a significant role in determining the rate of reactivity.⁷⁹ The observed differences in the rates of reactivity of these aluminium hydrides compared to that observed for [Dipp¹]**1**Ga(^tBu)H (time for 100% conversion > 12h; Chapter 4) are consistent with this notion, given that Al-H bonds are known to be significantly more hydridic than their gallium counterparts.

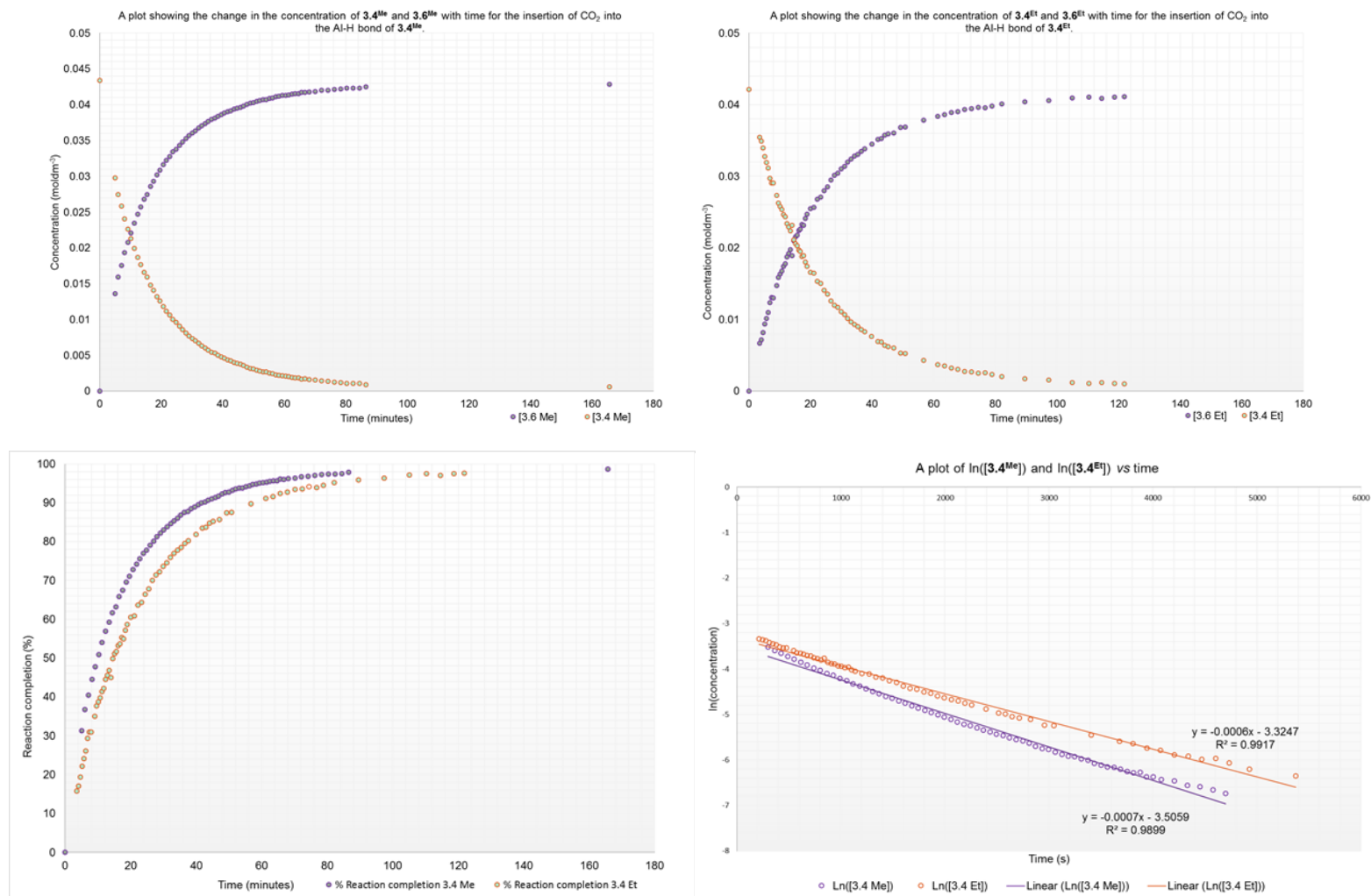


Figure 3.10: Plots to show the change in concentration with time for the insertion of CO₂ into the Al-H bond of 3.4^{Me} (top, left) and 3.4^{Et} (top, right), the percentage completion of these reactions with time (bottom, left) and a plot of ln[alane] against time (bottom, right).

Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂ and boranes

With this in mind, similar effects are observed as a function of the second aluminium-bound substituent, R. The presence of an electron-withdrawing R substituent - such as Cl or OTf - reduces the hydridic character of the Al-H bond and consequently its reactivity towards CO₂: unlike **3.4^{Me}** and **3.4^{Et}**, **3.4^{Cl}** and **3.4^{OTf}** are unreactive towards CO₂. Moreover, this behaviour correlates with the measured Al-H stretching frequencies: (1854 cm⁻¹ (mean)/1905 cm⁻¹ for R = Cl/OTf and 1767/1776 cm⁻¹ for R = Me/Et) with stronger bonds proving unreactive towards CO₂.

Whilst the reactivity of the Nacnac-ligated aluminium monohydrides towards CO₂ is selective, an investigation of the reactivity of [^{Dipp}**1**]₂AlH₂ (**3.4^H**) with CO₂ reveals that the presence of a second aluminium-bound hydride leads to more complex chemistry. Placing a solution of **3.4^H** in benzene-d₆ under CO₂ leads to relatively rapid consumption of the hydride, as monitored by ¹H NMR spectroscopy. After 20 min, *ca.* 40% of **3.4^H** has been consumed and the major product species is suggested to be [^{Dipp}**1**]₂Al(H)(OC(O)H), as signalled by a sharp downfield singlet, integrating to 1H, at $\delta_{\text{H}} = 8.11$ ppm. This reactivity, however, is not selective and an additional three singlets are present in the $\delta_{\text{H}} = 4.78 - 5.13$ ppm region, indicative of the formation of additional Nacnac-ligated species. After 45 minutes, 60% of **3.4^H** has been consumed and, while the putative mono-formate remains the major species, other species are also evident, including a second formate-containing species, signalled by the appearance of a singlet at $\delta_{\text{H}} = 8.21$ ppm. **3.4^H** is consumed over the course of several hours, leading to a mixture of several species which could not be separated. The resonance observed at $\delta_{\text{H}} = 8.21$ ppm is possibly due to insertion of CO₂ into the second Al-H bond, which is likely to be slower than into the first, due to the presence of an electron-withdrawing formate substituent at aluminium. The lack of selectivity in the reaction of **3.4^H** with CO₂ is further signified

by the appearance of a singlet at $\delta_{\text{H}} = 3.89$ ppm, this chemical shift being typical of a methoxide resonance, and potentially indicating further reduction of the formate functionality. There is some literature precedent for p-block metal formate complexes undergoing reactivity with the corresponding hydrides to yield acetal metal complexes.²²

In the presence of a deficit of CO₂, the same major formate signal at $\delta_{\text{H}} = 8.11$ ppm is observed, although again the reaction is not selective. In this case, crystals suitable for X-ray diffraction could be obtained from the reaction mixture after several days, and shown to contain the dimeric dialuminium-acetal complex, $\{[\text{Dipp}\mathbf{1}]\text{Al}(\text{OCH}_2\text{O})\}_2$ (**3.7**) (Figure 3.11), a binuclear aluminium complex with a $(\text{AlOCH}_2\text{O})_2$ core structure, which has previously been reported to be formed in the reaction of a germanium formate complex with **3.4**^H.²¹

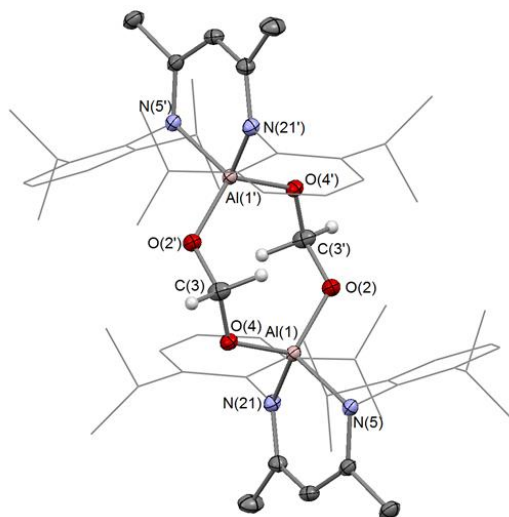
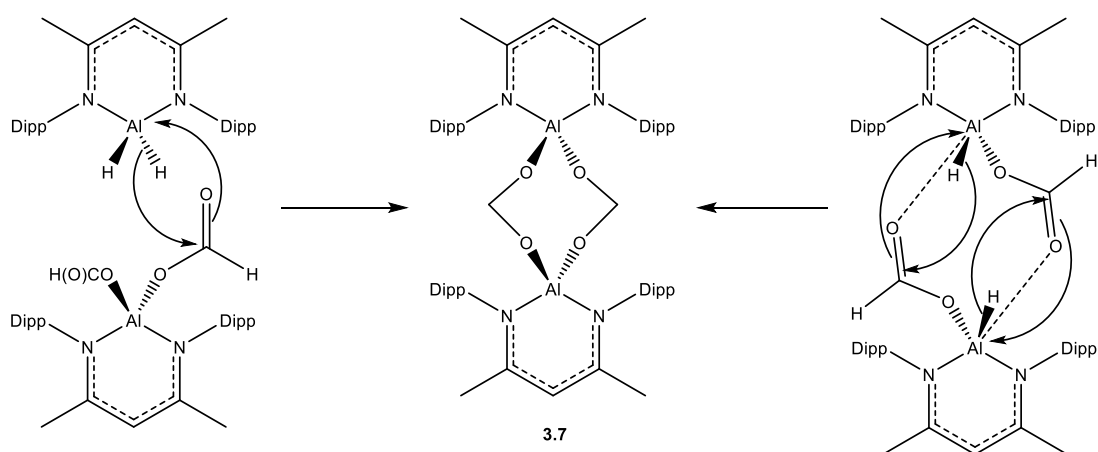


Figure 3.11: Molecular structure of $\{[\text{Dipp}\mathbf{1}]\text{Al}(\text{OCH}_2\text{O})\}_2$ (**3.7**). Thermal ellipsoids set at the 40% probability level. Select hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths ($\text{\AA}$) and angles ($^\circ$): Al(1)-O(4) 1.7231(9), Al(1)-O(2) 1.7161(9), Al(1)-N(5) 1.8977(10), Al(1)-N(21) 1.8919(10), O(2)-C(3) 1.3950(15), C(3)-O(4) 1.3965(15), O(4)-Al(1)-O(2) 114.01(4), N(5)-Al(1)-N(21) 97.55(4), O(2)-C(3)-O(4) 112.78(10).

In our case, it is postulated that **3.7** may be formed either *via* insertion of both formate functionalities of [Dipp₂Al(OC(O)H)₂] into the Al-H bonds of unreacted **3.4^H** or from [Dipp₂Al(H)(OC(O)H)] *via* intermolecular (bimolecular) hydro-alumination of the formate function. The fact that it is only when a solution of **3.4^H** is exposed to sub-stoichiometric CO₂ that significant quantities of **3.7** are formed may be indicative that the second pathway dominates in its formation. Similar chemistry is observed with reactive B-H bonds (see below) and the deficit of CO₂ presumably promotes this reaction pathway over CO₂ insertion into the second Al-H bond.



Scheme 3.8: Proposed routes for the formation of **3.7**.

3.4.2.2 Reactivity of “electronically modified” β -diketiminato-ligated aluminium hydrides towards CO₂

Examination of the features of β -diketiminato-ligated aluminium hydrides that favour rapid and selective reactivity towards CO₂ reveals the apparent advantage of an aluminium-bound alkyl substituent. It is observed that the alanes which exhibit reduced stretching frequencies effect the hydroalumination of CO₂ most readily. Therefore, the marginally higher Al-H IR stretching frequencies observed for the N-nacnac ligated

aluminium hydrides may suggest that they should undergo slower reactivity with CO₂.

This hypothesis was therefore investigated.

Placing a solution of **3.5^{Et}** in benzene-d₆ under 1 bar of CO₂ leads to the *instantaneous* insertion of CO₂ into the Al-H bond, leading to quantitative formation of [Dipp₂]Al(Et)(OC(O)H) (**3.8^{Et}**). The formation of **3.8^{Et}** is signalled by the disappearance of the Al-H resonance at $\delta_{\text{H}} = 4.90$ ppm, and the appearance of a sharp downfield resonance at $\delta_{\text{H}} = 8.76$ ppm, diagnostic of a formate functionality. The aluminium-bound ethyl substituent is retained, and ¹H NMR resonances for this are observed at $\delta_{\text{H}} = 0.63$ and -0.24 ppm for the methyl and methylene groups, respectively. By increasing the scale of the reaction and recrystallising from toluene at -30°C , **3.8^{Et}** could be isolated in 62% yield and characterised by standard spectroscopic/analytical techniques, and X-ray crystallography. The observation of a strong C=O absorption at 1678 cm^{-1} in the IR spectrum is consistent with the presence of a formate functionality. The molecular structure of **3.8^{Et}** is shown in Figure 3.12.

The molecular structure of **3.8^{Et}** displays the expected molecular connectivity. There are few notable distinctions between the solid state structure of **3.8^{Et}** and that of its Nacnac counterpart **3.6^{Et}**; nominal differences are observed in the Al-N, Al-O and Al-C bond distances (Table 3.4). The bond lengths and angles associated with the carbon of the formate functionality are consistent with those observed for **3.6^{Me}** and **3.6^{Et}** and two distinctly different C-O bond lengths are observed, consistent with the presence of both single and double bonds. As observed for the Nacnac complexes, shortening of the Al-N and Al-C bonds is observed upon insertion of CO₂ into the Al-H bond, consistent with an increase in Lewis acidity of the metal centre.

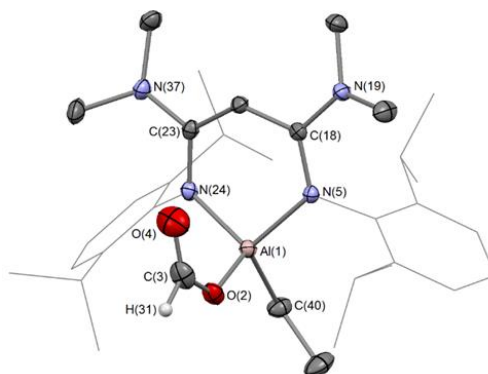
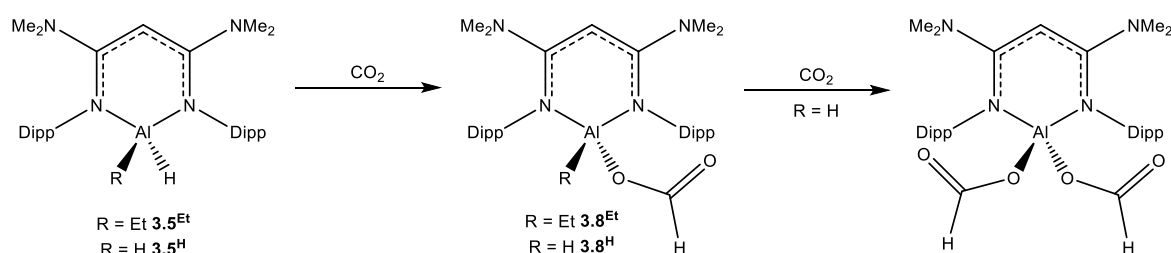


Figure 3.12: Molecular structure of [Dipp₂]Al(Et)(OC(O)H) (**3.8^{Et}**). Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°): Al(1)-O(2) 1.7819(11), Al(1)-N(5) 1.8872(11), Al(1)-N(24) 1.8809(11), Al(1)-C(40) 1.9613(14), O(2)-C(3) 1.297(2), C(3)-O(4) 1.195(2), N(5)-C(18) 1.3570(16), C(23)-N(24) 1.3565(16), C(18)-N(19) 1.3684(16), C(23)-N(37) 1.3734(16), N(5)Al(1)-N(24) 101.96(5), O(2)-C(3)-O(4) 126.95(16).

Compound	[Dipp ₂]Al(Et)(OC(O)H)	[Dipp ₁]Al(Et)(OC(O)H)	[Dipp ₂]Al(Et)H
Distance of Al from C ₃ N ₂ plane (Å)	0.355	0.488	0.464
<i>d</i> (Al-N) (Å)	1.8872(11), 1.8809(11)	1.8855(9), 1.8914(9)	1.8946(10), 1.9222(10)
<i>d</i> (Al-O) (Å)	1.7819(11)	1.7832(8)	-
<i>d</i> (Al-C) (Å)	1.9613(14)	1.9605(11)	1.9803(14)
<i>d</i> (C-O) (Å)	1.297(2), 1.195(2)	1.2988(14), 1.2039(15)	-
N-Al-N (°)	101.96(5)	97.43(4)	99.36(4)

Table 3.4: A comparison of some of key structural features of **3.8^{Et}**, **3.6^{Et}** and **3.5^{Et}**.



Scheme 3.9: Insertion of CO₂ into the Al-H bonds of N-nacnac-ligated aluminium hydrides.

The rate of insertion of CO₂ into the Al-H bonds of **3.4^{Et}** and **3.5^{Et}** shows a vast enhancement arising from the use of the N-nacnac ligand. This is also reflected in the

reactivity of **3.5^H** with CO₂. A solution of **3.5^H** in benzene-d₆ in an NMR tube fitted with a J. Young's tap, was pressurised with CO₂ (*ca.* 1 bar). Monitoring of the course of the reaction by ¹H NMR spectroscopy shows instant consumption of **3.5^H** and the selective formation of a novel species, proposed to be [Dipp²]Al(H)(OC(O)H) (**3.8^H**). This is signalled by the appearance of a sharp downfield singlet at $\delta_{\text{H}} = 8.31$ ppm, integrating to one hydrogen, and the shifting of the broad Al-H resonance from $\delta_{\text{H}} = 4.52$ ppm to $\delta_{\text{H}} = 5.22$ ppm. Moreover, the ¹H NMR spectrum features four doublets and two septets in the aliphatic region, corresponding to the Dipp ⁱPr groups of a N-nacnac species that lacks C₂ symmetry and contains an unsymmetrically substituted aluminium centre. Many attempts were made to isolate **3.8^H** in the solid state but intractable mixtures of products were consistently obtained. To probe the ability of **3.8^H** to dimerise and form a dialumyl-acetal such as **3.7**, its stability in benzene-d₆ was assessed. No reactivity was observed at room temperature over the course of several days and after heating at 60°C for 1 week decomposition was observed, no spectroscopic signals were observed in the typical region for acetal functionalities ($\delta_{\text{H}} = 4.5 - 6.0$ ppm). It is suggested that the formation of **3.7** *via* intermolecular insertion of the formate functionality of [Dipp¹]Al(H)(OC(O)H) into an Al-H bond may require activation of the formate by its coordination to the Lewis acidic aluminium centre. In the case of **3.8^H**, the coordination of the electron-rich N-nacnac ligand to the aluminium centre may significantly lower its Lewis acidity, hence minimising the propensity of **3.8^H** to dimerise. When a solution of **3.8^H** in benzene-d₆ is pressurised with CO₂ (*ca.* 1 bar) insertion into the second Al-H bond occurs over the course of 12 hours, to yield [Dipp²]Al(OC(O)H)₂ (with *ca.* 40% protio-ligand). The formation of [Dipp²]Al(OC(O)H)₂ is signalled by the loss in the ¹H NMR spectrum of the Al-H resonance at $\delta_{\text{H}} = 5.22$ ppm and the resonance at $\delta_{\text{H}} = 8.30$ ppm, and the appearance of a resonance at $\delta_{\text{H}} = 8.06$ ppm, integrating to two hydrogens.

In addition, the resonances observed for the Dipp ⁱPr groups (one septet and two doublets) correspond to those of a symmetrically substituted aluminium centre, consistent with insertion into both Al-H bonds.

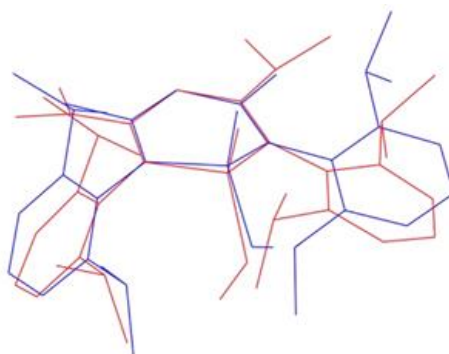


Figure 3.13: Overlay of the molecular structures of [Dipp1]Al(Et)H (blue) and [Dipp2]Al(Et)H (red) as determined by X-ray crystallography.

It is apparent that the N-nacnac ligated species **3.5^H** and **3.5^{Et}** react significantly faster than their [Dipp1] counterparts with CO₂. IR data for the two series of compounds imply that the electronic differences between the two compounds are rather small. Notably the Al-H stretches for the N-nacnac compounds are very similar to (or even at slightly *higher* wavenumber than) their Nacnac analogues. This in turn would imply comparable or (if anything) slower reactivity towards CO₂. We hypothesise that the differences between the two sets of compounds are largely steric in origin, with more open access to the reactive Al-H bond being possible in the N-nacnac compounds. This reflects the steric effects of the backbone NMe₂ groups which exert a pronounced steric repulsion on the N-bound Dipp substituents, causing them to be bent down significantly out of the C₃N₂ plane. Since the hydride ligand occupies the axial position in both **3.4^{Et}** and **3.5^{Et}**, and is projected out of the C₃N₂ plane in the opposite sense, this renders the Al-H bond less sterically protected in the N-nacnac system. As evidence for the difference in steric profiles, we note that the centroid-Al-centroid angle relating to the two flanking Dipp

rings is somewhat more acute in **3.5^{Et}** than **3.4^{Et}** (140.0 vs. 146.7°). Moreover, the extent to which the aluminium centre is projected out of the β -diketimate C₃N₄ plane is known to be related to steric pressures at aluminium, and it is of note therefore that in **3.5^{Et}**, the metal lies significantly closer to the respective plane (0.464 vs 0.663 Å; Figure 3.13).

3.4.3 Can aluminium hydrides act as catalysts for the reduction of CO₂ by boranes?

The observed reactivity of β -diketimate-ligated aluminium alkyl hydrides **3.4^{Me}**, **3.4^{Et}** and **3.5^{Et}** towards CO₂ is both selective and rapid, especially in the case of **3.5^{Et}**. Until recently, the most efficient single-site main group catalyst for the reduction of CO₂ was [Dipp¹]₂Ga(^{*t*}Bu)H.²³ This catalyst operates by insertion of CO₂ into the Ga-H bond, followed by reduction of the corresponding formate complex with pinacolborane (HBpin), and operates with a TOF value of 2.5 h⁻¹ (10 mol%, 60°C). In light of the parallels between these systems, and the observed reactivity of β -diketimate aluminium hydrides towards CO₂, it was hypothesised that they might be capable of functioning as active catalysts for the reduction of CO₂. With this in mind, we decided to probe the reactions of our newly synthesised aluminium formate complexes with boranes, with the aim of establishing whether this could lead to Al-H bond formation, and thereby demonstrate the viability of aluminium hydride catalysts for the reduction of CO₂ by boranes.

3.4.3.1 Catalytic and stoichiometric studies: pinacolborane as the reductant

A benzene solution of HBpin containing 10 mol% of **3.4^{Et}** was pressurised with CO₂ (ca. 2 bar) and the reaction monitored by ¹H and ¹¹B NMR spectroscopy. Analysis of the

solution after 24 h at room temperature showed conversion of **3.4^{Et}** only as far as its formate **3.6^{Et}**, and no consumption of HBpin. The solution was subsequently heated to 60°C for 36 h, and ¹H and ¹¹B NMR spectra measured again. These showed only the resonances for **3.6^{Et}** and unreacted HBpin, and no signals corresponding to any of the typical products reported to be formed in the reduction of CO₂ by HBpin (e.g. MeOBpin and O(Bpin)₂).^{6,16,80} In order to confirm this behaviour, an isolated sample of **3.6^{Et}** was treated with an excess of HBpin (10 equiv.) in benzene-d₆ and heated to 80°C for 48 h. The ¹H and ¹¹B NMR spectra of the resulting solution again show no reactivity of **3.6^{Et}** towards HBpin. A similar lack of reactivity characterises the behaviour of both **3.6^{Me}** and **3.8^{Et}** towards HBpin. It is proposed that catalytic reduction of CO₂ by a metal hydride proceeds by insertion of CO₂ into the M-H bond to yield a metal formate. This is followed by reaction of the formate species with a borane to regenerate the hydride and yield a boryl formate ester or to form a metal borylacetal complex *via* formal hydroboration of the formate C=O bond. It is suggested that the regeneration of the metal hydride occurs *via* a formal σ -bond metathesis across the M-O bond with the B-H bond of the borane.^{16,22} In a similar fashion, the catalytic hydroboration of aldehydes and ketones by [Dipp¹Al(OTf)H is also proposed to turnover *via* σ -bond metathesis between the Al-O bond of the aluminium alkoxide and the B-H bond of HBpin.^{35,37,38} It is apparent, however, that HBpin does not possess the requisite reactivity to effect σ -bond metathesis across the Al-O bond of **3.6^{Et}** to regenerate **3.4^{Et}**. In the absence of an alternative reaction pathway, regeneration of the aluminium hydride **3.4^{Et}** is prevented and **3.4^{Et}** cannot function in a catalytic manner for the reduction of CO₂ when used in conjunction with HBpin.

3.4.3.2 Catalytic studies: catecholborane as the reductant

Catecholborane (HBcat) is also a commonly employed reductant in the metal-hydride-catalysed reduction of CO₂, and frequently shows enhanced reactivity compared to HBpin due to the greater Lewis acidity of the boron centre.⁸¹ This is illustrated by the group 14 metal-hydride catalysed reduction of CO₂, in which turnover frequencies are orders of magnitude larger when HBcat is employed as the reductant, as compared to HBpin (1 mol% $\{({}^i\text{Pr}_3\text{Si})(\text{Ar}^*)\text{N}\}\text{SnH}$ ($\text{Ar}^* = \text{C}_6\text{H}_2{}^i\text{Pr}-4\text{-}\{\text{C}(\text{H})\text{Ph}_2\}_2\text{-2,6}$); HBpin TOF = 14.5 h⁻¹; HBcat TOF = 1188 h⁻¹).²²

Hence, the possibility for catalytic turnover in the reduction of CO₂ by **3.4^{Et}** was investigated utilising HBcat as the reductant. A benzene solution of HBcat with 10 mol% of **3.4^{Et}** as a catalyst was pressurised with CO₂ (*ca.* 2 bar) and monitored by ¹H and ¹¹B NMR spectroscopy. After 24 h at room temperature, ¹¹B NMR spectroscopy showed no significant consumption of HBcat. The resulting ¹H NMR spectrum however featured resonances that did not correspond to those of **3.6^{Et}** or **3.4^{Et}** but signalled the formation of a Nacnac-ligated species that contains neither a formate or Al-H functionality. The solution was heated to 60°C for 36 h, but analysis of the solution by both ¹H and ¹¹B NMR spectroscopy revealed no further consumption of HBcat, and no apparent catalytic turnover. Further investigation therefore focussed on a series of stoichiometric reactivity studies.

3.4.3.3 Stoichiometric studies: catecholborane as the reductant

The addition of excess HBcat (3 equiv.) to a solution of **3.6^{Et}** in benzene-d₆ yields a single Nacnac-ligated species (**3.9^{Et}**) over the course of 6 h at room temperature, as determined by ¹H NMR spectroscopy. The appearance of a singlet at $\delta_{\text{H}} = 3.36$ ppm

signals the formation of a trace amount of MeOBcat.⁶ The aluminium-bound ethyl functionality is retained, although the resonances observed for this moiety are shifted downfield relative to those of **3.6**^{Et} (**3.9**^{Et}: $\delta_{\text{H}} = 0.91, -0.06$ ppm; **3.6**^{Et}: $\delta_{\text{H}} = 0.74, -0.15$ ppm). The ¹¹B NMR spectrum shows a broad resonance at $\delta_{\text{B}} = 21.5$ ppm, consistent with a tri-coordinate boron centre surrounded by 3 oxygen atoms.⁸² A small number of single crystals suitable for X-ray crystallography were obtained from diethyl ether at -30°C ; the molecular structure is shown in Figure 3.14.

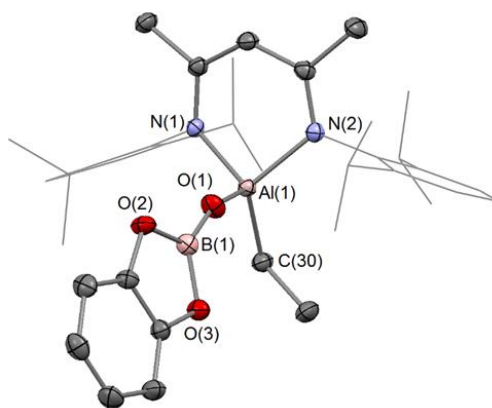


Figure 3.14: Molecular structure of [Dipp¹Al(Et)(OBcat) (3.9^{Et}). Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°): Al(1)-O(1) 1.7387(10), Al(1)-N(1) 1.8859(11), Al(1)-N(2) 1.9016(11), Al(1)-C(30) 1.9532(13), O(2)-C(32) 1.3749(16), O(2)-B(1) 1.4086(17), O(3)-B(1) 1.4055(18), O(1)-B(1) 1.3081(18), N(1)-Al(1)-N(2) 96.97(5), Al(1)-O(1)-B(1) 153.66(10), O(1)-B(1)-O(3) 126.51(13), O(1)-B(1)-O(2) 123.70(13), O(3)-B(1)-O(2) 109.78(11). Distance from least-squares C₃N₂ plane: 0.555 Å.

The molecular structure revealed the product of the reaction to be [Dipp¹]Al(Et)(OBcat) (**3.9^{Et}**), a Nacnac-ligated aluminium boryloxy complex. The Al-O bond of **3.9^{Et}** ($d(\text{Al}(1)\text{-O}(1) 1.7387(10) \text{ \AA})$) lies within the expected range for Al-O bonds. Typically, the Al-O bond of complexes featuring a boryloxide ligand are longer than those featuring alkoxide or hydroxide ligands due to the weaker π -donor properties of the oxygen atom.

Despite this, the Al-O bond of **3.15** lies close in length to that of [Dipp**1**]Al(Et)(OH) ($d(\text{Al}-\text{O})$ 1.7409(17) Å).⁶⁰ A wide Al(1)-O(1)-B(1) angle (153.66(10)°) is observed for **3.9^{Et}**, presumed to arise from the minimisation of unfavourable steric interactions rather than electronic factors and the B(1) centre is found to be in a trigonal planar environment (distance of B from least-squares O₃ plane 0.002 Å; $\Sigma(\text{O}-\text{Al}-\text{O}) = 359.99^\circ$).⁸²

The only reported example of an aluminium complex bearing an Al-O-B unit and the Bcat fragment is Al(κ^2 -O,O-(MeO)₂BCat)₃, a decomposition product which features a 6-coordinate aluminium centre and 4-coordinate boron centres.⁴⁰ These coordination numbers are reflected in its longer Al-O ($d(\text{Al}-\text{O})$ 1.8593(14) – 1.8842(13) Å) and B-O ($d(\text{B}-\text{O})$ 1.442(3) – 1.498(2) Å) bonds. Synthetic methods for the preparation of aluminium boron complexes that bear Al-O-B units are typically restricted to protonolysis reactions between a boronic acid and an aluminium alkyl or hydride compound.^{83–86} The number of examples of molecular compounds featuring this linkage are relatively restricted.^{87–91} Most of the reported complexes feature two Al-O-B linkages and are cyclic e.g. [Dipp**1**]Al(OBPh)₂(μ -O), [Dipp**1**]Al[OB(2-PhC₆H₄)(OH)]₂, [Dipp**1**]Al[OB(*o*-CH₂O)(C₆H₄)]₂.^{84,85} The complex that is most similar to **3.9^{Et}** is the monometallic aluminium borate ester [Mes**1**]Al(OH)(OBpin).⁸³ This complex was not crystallographically characterised due to its tendency to dimerise to form [[Mes**1**]Al(OBpin)]₂(μ -OH)₂, which features a 5-coordinate aluminium centre.⁸³

The reactivity of [Dipp**1**]Al(Me)(OC(O)H) (**3.6^{Me}**) with HBcat is similar to that observed for **3.6^{Et}**. ¹H NMR spectroscopy shows the consumption of **3.6^{Me}** over the course of several hours and the formation of a single novel species. This species was characterised by NMR spectroscopy and, based on its spectroscopic similarities to **3.9^{Et}**, is postulated to be [Dipp**1**]Al(Me)(OBcat) (**3.9^{Me}**) (Table 3.5).

Compound	δ_B (ppm)	δ_H (Al-Me) (ppm)	δ_H (γ -H) (ppm)	δ_H (Bcat) (ppm)	δ_C (Bcat) (ppm)
[^{Dipp} 1]Al(Et)(OBcat)	21.5	-	4.98	6.74 – 6.77 (m)	111.7, 121.7, 149.6
[^{Dipp} 1]Al(Me)(OBcat)	21.6	-0.67	5.00	6.75 – 6.77 (m)	111.7, 121.7, 149.6

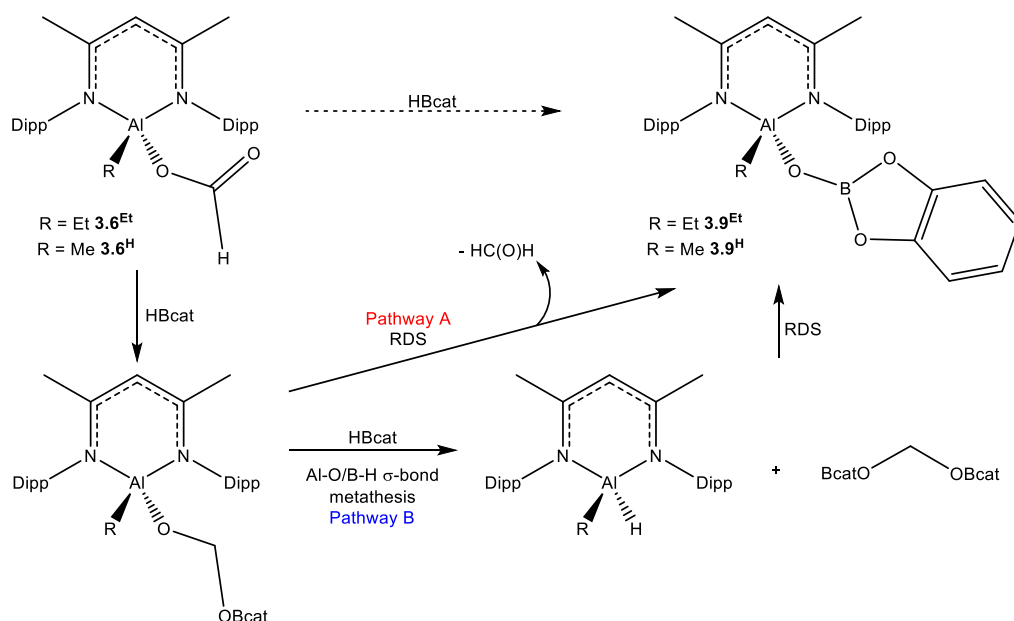
Table 3.5: Some of the key spectroscopic features of **3.9^{Me}** and **3.9^{Et}**.

Metallo-borate esters such as **3.9^{Me}** and **3.9^{Et}** have been implicated as intermediates in the borane-mediated catalytic reduction of CO₂. There are very few structurally authenticated examples of such compounds that feature main group elements. Recently, crystallographically characterised examples of group 14 metal(II) borate esters $\{(i\text{Pr}_3\text{Si})(\text{Ar}^*)\text{N}\}\text{M}(\text{OBpin})$ (M = Ge, Sn; Ar* = C₆H₂^{*i*}Pr-4-{C(H)Ph₂}_{2-2,6}) were reported to be formed on addition of one equivalent of HBpin to the corresponding formate complexes.²² A closely related complex is $\{[\text{Dipp}\mathbf{1}]\text{Mg}(\text{OBpin})\}_2$, formed from the magnesium-hydride catalysed hydrodeoxygenation of isocyanates.⁹²

Recently, the mechanism for the reduction of CO₂ with HBpin, catalysed by LGeH (L = -N(Ar)(Si^{*i*}Pr₃), Ar = C₆H₂Pr-4-^{*i*}{C(H)Ph₂}_{2-2,6}), has been computationally assessed and offers a hint as to potential mechanistic routes for the formation of **3.9^{Me}**/**3.9^{Et}**.²² It is suggested that the metal formate reacts with HBpin to yield a germa-bora-acetal intermediate, $\{(i\text{Pr}_3\text{Si})(\text{Ar}^*)\text{N}\}\text{Ge}(\text{OCH}_2\text{OBpin})$, that can react onwards *via* two potential pathways which have very similar activation energies.

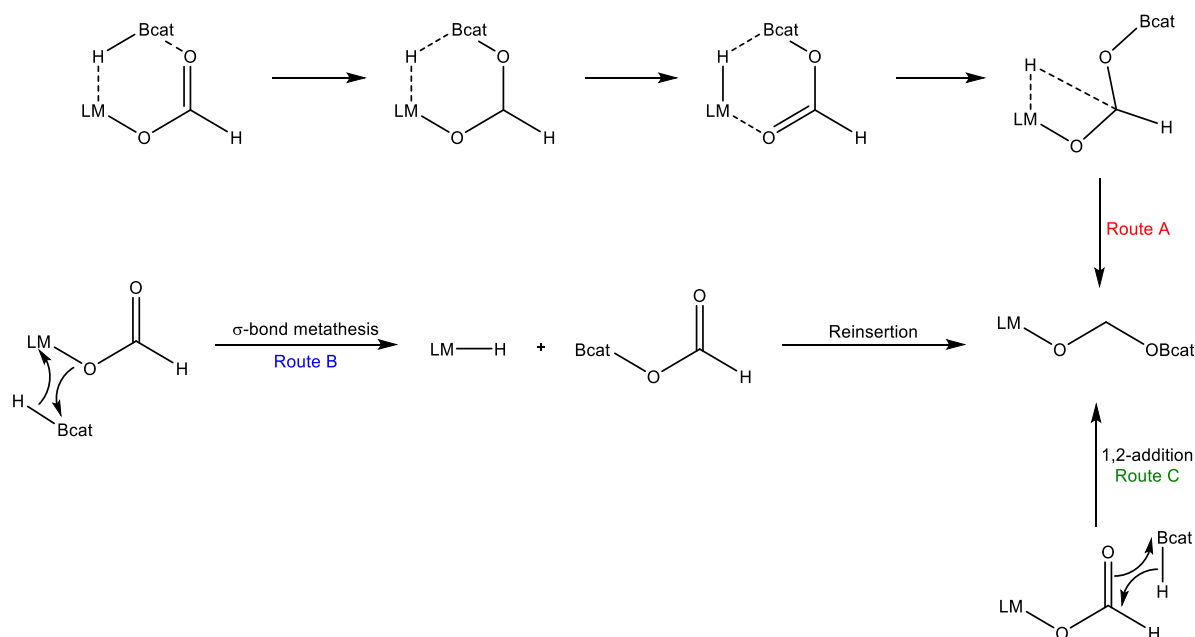
In the first route, Ge-O/B-H σ -bond metathesis with HBpin regenerates the Ge(II) hydride and (pinBO)₂CH₂. These two species recombine in the rate determining step ($\Delta H^\ddagger = 150.6 \text{ kJ mol}^{-1}$), yielding MeOBpin and $\{(i\text{Pr}_3\text{Si})(\text{Ar}^*)\text{N}\}\text{Ge}(\text{OBpin})$. The latter then reacts readily with HBpin to regenerate the catalyst and give the diboroxane product (pinB)₂O. The proposed alternative route involves the direct extrusion of formaldehyde

from $\{[i\text{Pr}_3\text{Si}](\text{Ar}^*)\text{N}\}\text{Ge}(\text{OCH}_2\text{OBpin})$, as the rate-determining step, *via* a cyclic GeOCO four-membered transition state.^{14,22} The barrier for this process ($\Delta H^\ddagger = 153.6 \text{ kJ mol}^{-1}$) is only marginally higher than that observed in the first route. Similar routes have been proposed and computationally assessed using HBcat as the reductant.¹⁵



Scheme 3.10: The preparation of $[\text{Dipp}^1]\text{Al}(\text{R})(\text{OBcat})$ (**3.9**^{Me, Et}) from the addition of HBcat to $[\text{Dipp}^1]\text{Al}(\text{R})(\text{OC(O)H})$ (**3.6**^{Me, Et}) and the routes by which the reactivity is proposed to proceed.

With this in mind, we wanted to probe possible pathways for the formation of **3.9**^{Et} from **3.6**^{Et} (Scheme 3.10). In the first instance, a solution of **3.6**^{Et} in benzene- d_6 was treated with one equivalent of HBcat. The reaction proceeds to completion, generating exclusively **3.9**^{Et} after 48 h at room temperature; no intermediates were detected. The completion of this reaction under these conditions is suggestive of the formation of **3.9**^{Et} *via* the intermediate aluma-bora-acetal $[\text{Dipp}^1]\text{Al}(\text{Et})(\text{OCH}_2\text{OBcat})$, a transient species which readily eliminates formaldehyde to give the product. Although the formaldehyde generated was not detected, this pathway is consistent with the completion of the reaction in the presence of only a single equivalent of HBcat.



Scheme 3.11: Computationally assessed routes for the formation of metallo-bora-acetal complexes from the reaction of boranes with metal formate complexes.

Whilst no reactivity of **3.6^{Et}** with HBpin is observed at elevated temperatures, it reacts with HBcat at room temperature and is proposed to form [Dipp¹]Al(Et)(OCH₂OBcat) as an intermediate. This suggests that there is a pathway for the formation of [Dipp¹]Al(Et)(OCH₂OBX₂) that is accessible for HBcat (and related Lewis acidic boranes – see section 3.4.3.6) but not HBpin. Three pathways for the formation of the related intermediate {(iPr₃Si)(Ar*)N}Ge(OCH₂OBpin) from {(iPr₃Si)(Ar*)N}Ge(OC(O)H) and HBpin were computationally assessed.²² The first proceeds by a cycloaddition reaction involving the formate with HBpin across one Ge-O bond to give a 6-membered transition state, which yields an intermediate which is described as an adduct of pinBOC(O)H with LGeH. Hydrogen migration from LGeH then occurs to the electrophilic carbon of the formate functionality (Route A). This route was determined to be the most likely to operate under catalytic conditions. An alternative mechanism that was considered to lead to a reaction dead-end was a formal σ -bond metathesis across the Ge-O bond of LGe(OC(O)H) which yields the hydride and free pinBOC(O)H which react together to

give the acetal (Route B). A third route considered was the 1,2-addition reaction of HBpin across one CO bond of LGe(OC(O)H) which was found to be kinetically less accessible ($\Delta H^\ddagger$ 122.2 kJ mol⁻¹) (Route C).²²

The reported E-H/E-O bond strengths for E = B, Al (E-H: 377, 282 kJ mol⁻¹; E-O: 559, 585 kJ mol⁻¹) suggest that Al-O/B-H metathesis is highly thermodynamically unfavourable. This in turn suggests that the formation of [Dipp¹]Al(Et)(OCH₂OBcat) proceeds *via* a mechanistic route that avoids cleavage of the Al-O bond, for example direct hydroboration of the formate functionality. This pathway may be accessible due the absence of alternative metathetical pathways and the greater Lewis acidity of the boron centre of HBcat which may allow precoordination of the borane to the formate functionality.

Independent assessment of the lability of [Dipp¹]Al(R)(OBcat) (R = Me, Et) in the presence of excess HBcat (10 equiv.) shows no conversion to [Dipp¹]Al(R)H and O(Bcat)₂, even after 48 h at 80°C in benzene-d₆. The inability of HBcat to regenerate the corresponding hydrides accounts for observed lack of catalytic reduction of CO₂. It is apparent that Al-O/B-H σ -bond metathesis to regenerate the aluminium hydride is not possible under the conditions employed here.

3.4.3.4 Catalytic studies: {H(9-BBN)}₂ as the reductant

9-Borabicyclo[3.3.1]nonane {H(9-BBN)}₂ is another commonly employed reductant for metal-hydride-catalysed reduction of CO₂, and typically yields higher TOFs than other boranes due to the highly electrophilic nature of the boron centre.^{13,79} The ability of **3.4**^{Et} to catalyse the reduction of CO₂ utilising {H(9-BBN)}₂ as the reductant was therefore investigated. It was observed by ¹H and ¹¹B NMR spectroscopy that the generation of a

benzene solution of {H(9-BBN)}₂ with 10 mol% of **3.4**^{Et} as a catalyst leads to the formation of a novel species, prior to the addition of CO₂. The ¹¹B NMR spectrum shows resonances at $\delta_B = 27.9$ ppm (for {H(9-BBN)}₂) and $\delta_B = -15.6$ ppm (Figure 3.15). This solution was then pressurised with CO₂ (*ca.* 2 bar) and the reaction progress monitored by ¹H and ¹¹B NMR spectroscopy. The ¹H NMR spectrum showed a mixture of species, and the ¹¹B NMR spectrum was characterized by the disappearance of the resonance at $\delta_B = -15.7$ ppm and the appearance of a broad resonance at $\delta_B = 56.0$ ppm over the course of 24 h at room temperature, but no significant consumption of {H(9-BBN)}₂. The solution was heated to 60°C for 24 h but no further consumption of {H(9-BBN)}₂, and hence no catalysis, was observed. A series of stoichiometric reactivity studies were undertaken to understand this reactivity.

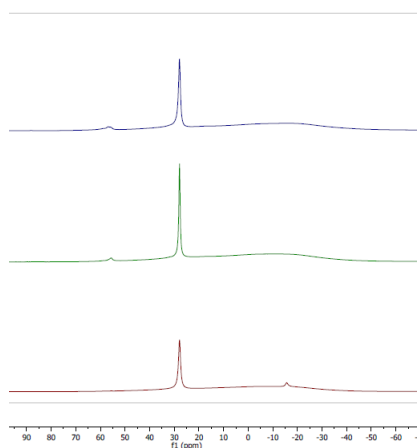


Figure 3.15: The ¹¹B NMR spectra of the attempted catalytic reaction: prior to the addition of CO₂ (bottom), after 24 h at room temperature under *ca.* 2 bar CO₂ (middle), after 24 h of heating at 60°C (top).

3.4.3.5 Stoichiometric studies: the formation of dialkylborohydride complexes

The addition of 0.5 equivalents of {H(9-BBN)}₂ to a solution of **3.4^{Et}** in toluene leads to the immediate formation of a novel product. Following workup and recrystallisation at low temperature, this product could be isolated in 71% yield as single crystals suitable for X-ray crystallography. The molecular structure is shown in Figure 3.16 and reveals the formation of a complex between **3.4^{Et}** and the electrophilic borane and its constitution as the dialkylborohydride complex [Dipp**1**]Al(Et)(κ^2 -H₂(9-BBN)) (**3.10^{Et}**). This observed reactivity is in stark contrast to that observed for **3.4^{Et}** with HBpin/HBcat, for which no such complex is formed. This difference in reactivity presumably arises from the increased Lewis acidity of the boron centre in {H(9-BBN)}₂, arising from the absence of π -donating boron-bound oxygen groups.

The molecular structure features the coordination at aluminium atom of a [H₂(BBN)]⁻ ligand *via* two 3c-2e Al-H-B bonds. There are several compounds featuring this bonding mode reported in the literature, the formation of which exploits the hydridic nature of the M-H bonds and the Lewis acidic nature of the metal centre. Many of the reported complexes feature the nominal coordination of BH₃ (*i.e.* the borohydride ligand, [BH₄]⁻), and the mostly closely related example of this to **3.10^{Et}** is [Dipp**1**]Al{ κ^2 -H₂(BH₂)}₂, formed from the nucleophilic substitution of DippNH₂ from (DippNH₂)·BH₃ by [Dipp**1**]AlH₂.⁹³ There are comparatively fewer examples where the boron centre bears substituents other than hydrides; those reported however include B(C₆F₅)₂ and, more pertinent to this study, 9-BBN fragments.^{43,94–96}

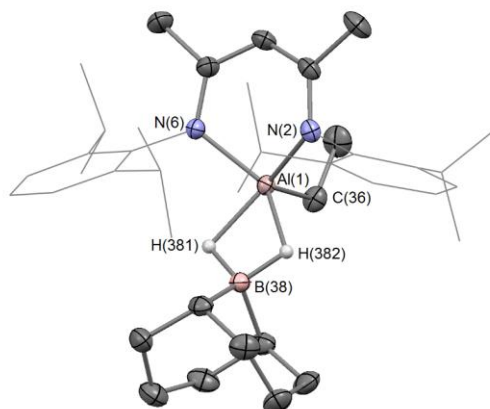


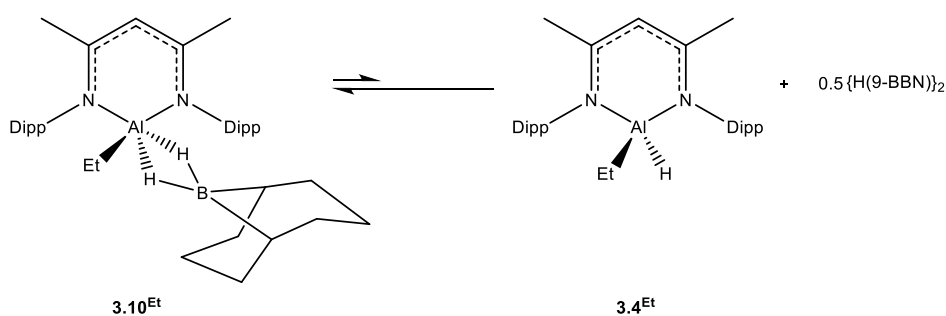
Figure 3.16: Molecular structure of [^{Dipp}1]Al(Et)(κ^2 -H₂(9-BBN)) (**3.10^{Et}**). Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Al-H-B located in the difference Fourier map and refined isotropically. Key bond lengths (Å) and angles (°): Al(1)-N(2) 1.9189(10), Al(1)-N(6) 1.9182(10), Al(1)-C(36) 1.9686(12), Al(1)-B(38) 2.2510(13), Al(1)-H(382) 1.819, Al(1)-H(381) 1.768, B(38)-C(39) 1.6078(17), B(38)-C(43) 1.6009(18), B(38)-H(382) 1.216, B(38)-H(381) 1.236, N(2)-Al(1)-N(6) 95.11(4), C(36)-Al(1)-B(38) 105.60(5).

Geometrically, the core of the structure consists of a 4-membered AlH₂B ring, with the [H₂(9-BBN)] fragment based around a tetrahedral boron centre. The aluminium centre has a coordination number of five, a fairly common feature for aluminium hydride species.⁹⁷⁻¹⁰¹ The aluminium coordination geometry is close to square pyramidal ($\tau = 0.036$), with the two β -diketiminate nitrogen donors and the bridging hydrogens constituting the basal plane and the Et substituent occupying the apical position. The bridging hydrogens were located in the difference Fourier map and refined isotropically. The aluminium atom is projected out of the plane of the supporting Nacnac backbone by 0.790 Å, markedly more than that of **3.4^{Et}** (0.663 Å), presumably reflecting the increase in steric congestion surrounding the metal centre. The Et substituent occupies the axial position and the [H₂(9-BBN)] fragment the less sterically hindered equatorial position.

The Al-B distance ($d(\text{Al}(1)\text{-B}(38))$ 2.2510(13) Å) is only marginally longer than the sum of their covalent radii ($1.21 + 0.84 = 2.05$ Å) and is in accordance with a 3-centre-2-electron bonding interaction.^{96, 102} This distance is marginally longer than those reported for borohydride complexes bearing the $[\text{BH}_4]^-$ ligand (e.g. $[\text{Dipp}1]\text{Al}(\kappa^2\text{-H}_2\text{BH}_2)_2$ 2.219(5) Å, $\text{Al}(\text{BH}_4)_3$ 2.12(2) Å) and lies closer to that of $\text{Al}(\text{tmp})_2(\text{H}_2(9\text{-BBN}))$ (2.223(7) Å).^{93,95,103} Comparison of the Al-B distances of complexes bearing the $[\text{BH}_4]^-$ and $[\text{H}_2(9\text{-BBN})]^-$ fragments implies that the binding of the borohydride ligand is marginally weaker in the case of $[\text{H}_2(9\text{-BBN})]^-$. The coordination of the borane to **3.4^{Et}** has very little impact on the bond lengths of aluminium-bound substituents; the Al-N and Al-C contacts of **3.10^{Et}** and **3.4^{Et}** show marginal differences (**3.4^{Et}**: $d(\text{Al-N})$ 1.9151(13), 1.9170(13), $d(\text{Al-C})$ 1.9605(18) Å).

3.10^{Et} was characterised by standard spectroscopic and analytical techniques. The IR spectrum features two broad absorptions at 2066 and 2026 cm⁻¹, characteristic of the symmetric and antisymmetric stretching frequencies typically observed for Al-H-B bridges.¹⁰⁴ The stretching frequencies are comparable to that observed for $\text{Al}(\text{tmp})_2(\text{H}_2(9\text{-BBN}))$ ($\nu_{\text{Al-H-B}}$ 2057 cm⁻¹).⁹⁵ The observation of these broad stretches, and the absence of any stretches in the region typical for terminal B-H stretches, supports the κ^2 -ligation mode. The ¹H NMR chemical shifts for the resonances associated with the aluminium-bound ethyl substituent are considerably downfield relative to those of **3.4^{Et}** (**3.10^{Et}** $\delta_{\text{H}} = 0.52$ ppm; **3.4^{Et}** $\delta_{\text{H}} = -0.13, 0.79$ ppm). This is suggestive that the coordination of the borane reduces the σ -donating ability of the aluminium-bound hydride towards the metal centre, hence reducing the shielding of the aluminium-bound alkyl group. The resonance for the bridging Al-H-B protons has been reportedly observed at $\delta_{\text{H}} = 1.61$ ppm for related complexes.⁹⁶ In this case, this resonance is not

observed in the ^1H or $^1\text{H}\{^{11}\text{B}\}$ NMR spectra, presumably it is both obscured by the resonances for the 9-BBN and Dipp ^iPr substituents and broadened due to the quadrupolar ^{27}Al nucleus ($I = 5/2$). The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum shows a broad, unresolved signal which narrows upon ^1H decoupling from $\Delta\omega_{1/2}$ 285 Hz to 212 Hz. The chemical shift ($\delta_{\text{B}} = -15.6$ ppm) is consistent with a 4-coordinate boron centre of the type $[\text{R}_2\text{BH}_2]^-$ ($\text{R} = \text{alkyl}$).^{105–107} The ^{11}B chemical shift measured for **3.10**^{Et} is considerably more upfield compared to that of $\text{Al}(\text{tmp})_2(\text{H}_2(9\text{-BBN}))$ ($\delta_{\text{B}} = -3.0$ ppm) and lies closer to that observed for $\text{K}[\text{H}_2(9\text{-BBN})]$ ($\delta_{\text{B}} = -16.4$ ppm).^{95,108}



Scheme 3.12: Partial dissociation of the borohydride complex **3.10**^{Et} in solution.

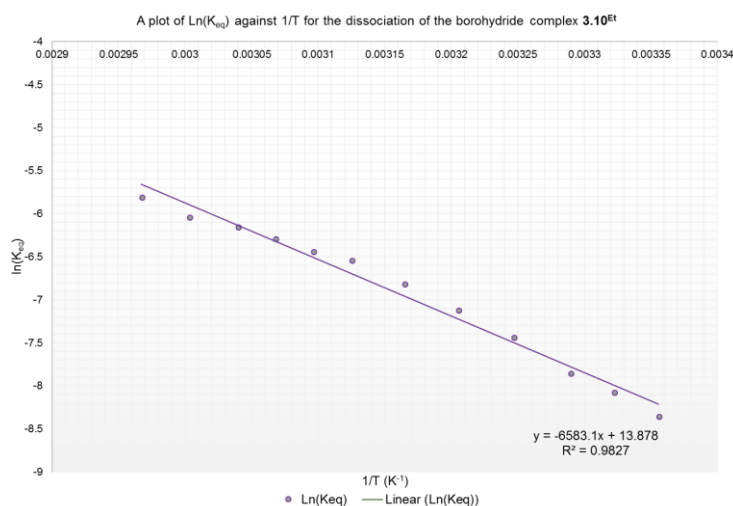


Figure 3.17: The van't Hoff plot for the equilibrium of the borohydride complex **3.10**^{Et} with the aluminium hydride **3.4**^{Et} and $\{ \text{H}(9\text{-BBN}) \}_2$.

In solution, **3.10^{Et}** exists in equilibrium with **3.4^{Et}** and the free borane, signalled by a resonance in the ¹¹B NMR spectrum at $\delta_B = 27.9$ ppm. The availability of isolated samples of **3.10^{Et}** allowed the thermodynamic parameters associated with the borane/borohydride equilibrium to be investigated. Thus, re-dissolving a crystalline sample of **3.10^{Et}** in toluene-d₈ leads to the formation of a mixture containing a 7:1 mixture of **3.10^{Et}**:**3.4^{Et}** at room temperature. The effects of temperature on this equilibrium allow for the calculation of ΔH° (54.7 kJ mol⁻¹) and ΔS° (115.4 J mol⁻¹ K⁻¹) for borane dissociation through a van't Hoff analysis. This relatively facile dissociation of the borane is a feature that is, to the best of our knowledge, unreported for aluminium borohydride complexes, even those which feature the [H₂(9-BBN)]⁻ fragment.^{95,96} In the case of **3.10^{Et}**, the coordinatively-saturated nature of the aluminium centre presumably reduces its Lewis acidity, leading to a diminished interaction with the B-H bond and a weaker interaction. This may also be affected by the steric bulk surrounding both the aluminium and boron centres.

The observed dissociation of the borane from **3.10^{Et}** is novel and therefore we sought to investigate this by preparing a range of related systems. The addition of 0.5 equivalents of {H(9-BBN)}₂ to a range of Nacnac-ligated aluminium hydrides leads to the formation of the respective dialkylborohydride complexes. These could also be characterised in the solid state by X-ray crystallography and their molecular structures are shown in Figure 3.18. In the case of dihydride complexes **3.10^H** and **3.11^H**, the addition of excess of {H(9-BBN)}₂ does not lead to coordination of the second Al-H bond, as is observed in the formation of [Dipp¹]**1**Al(BH₄)₂.⁹³ This is likely to arise from the increased steric bulk of {H(9-BBN)}₂ relative to BH₃.

Geometrically, these complexes feature molecular structures closely related to that of **3.10^{Et}**. In all cases, the aluminium centre lies in an approximately square pyramidal geometry (τ see Table 3.6). In the cases of **3.10^H** and **3.11^H**, the terminal aluminium-bound hydride was located in the difference Fourier map and refined isotropically; each lies at a distance consistent with those reported for terminal Al-H bonds (Table 3.6).⁶⁹ A comparison of the Al-B distances between the N-nacnac aluminium borohydrides and those featuring the Nacnac ligand reveals a marginal lengthening and this may be indicative that binding of the borohydride ligand is weaker in the case **3.11^{Et}**/**3.11^H**.

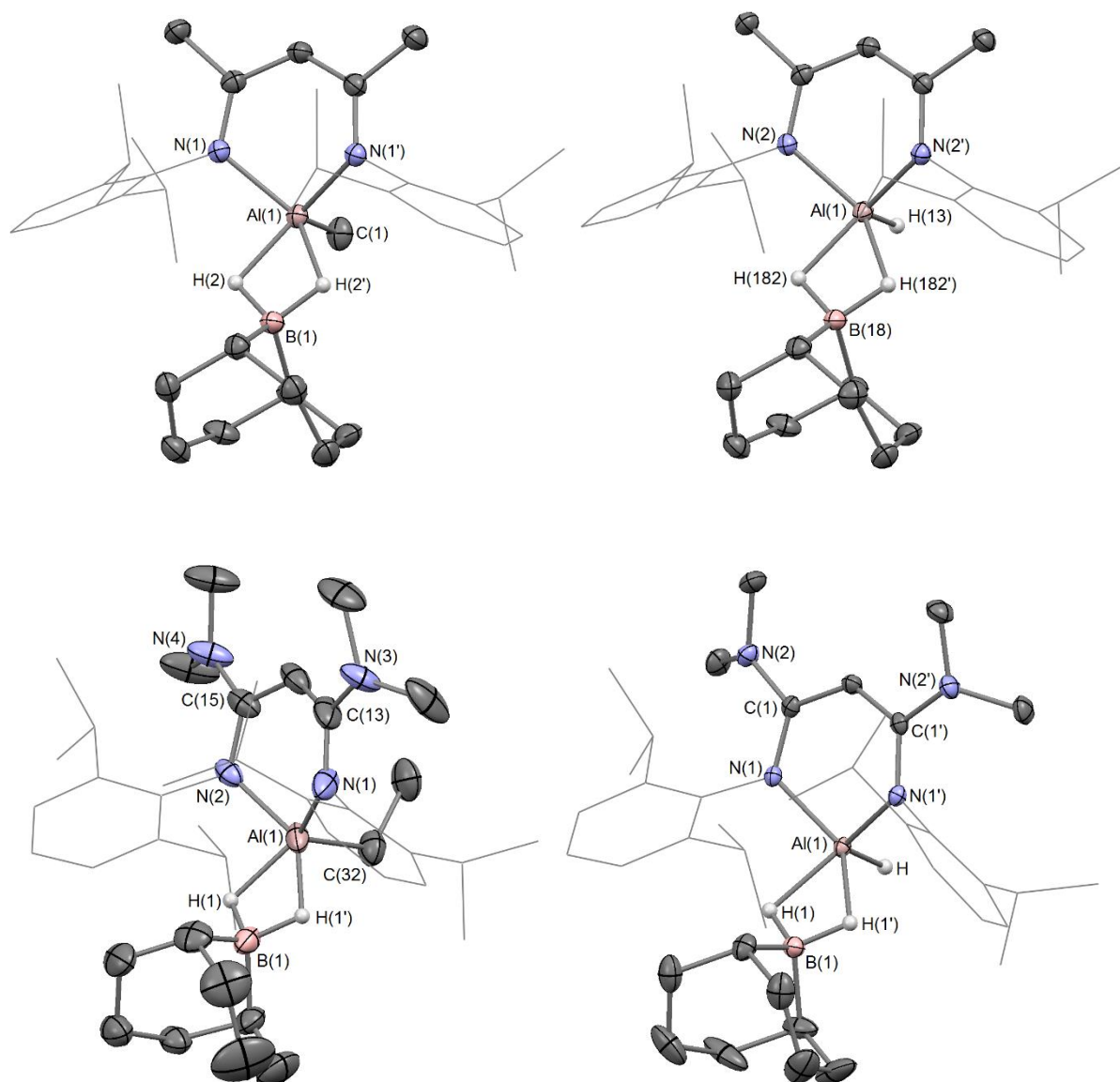


Figure 3.18: Molecular structures of $[\text{Dipp}^1]\text{Al}(\text{Me})(\kappa^2\text{-H}_2(9\text{-BBN}))$ (**3.10^{Me}**) (top left), $[\text{Dipp}^1]\text{Al}(\text{H})(\kappa^2\text{-H}_2(9\text{-BBN}))$ (**3.10^H**) (top right), $[\text{Dipp}^2]\text{Al}(\text{Et})(\kappa^2\text{-H}_2(9\text{-BBN}))$ (**3.11^{Et}**) (bottom left) and $[\text{Dipp}^2]\text{Al}(\text{H})(\kappa^2\text{-H}_2(9\text{-BBN}))$ (**3.11^H**) (bottom right). Thermal ellipsoids set at the 40% probability level. Al-H, Al-H-B located in the difference Fourier map and refined isotropically. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. H atoms located in the difference Fourier map and refined isotropically.

	Distance of Al from C ₃ N ₂ plane (Å)	τ	$d(\text{Al-N})$ (Å)	$d(\text{Al-C})$ (Å)	$d(\text{Al-H})$ (Å)	$d(\text{B-H})$ (Å)	$d(\text{Al-B})$ (Å)	N-Al-N (°)	$d(\text{C-N/N})$ (Å)	Torsion angle between NC ₃ N chelate and NC ₂ amino plane (°)
3.10^{Et}	0.790	0.036	1.9189(10) 1.9182(10)	1.9686(12)	-	-	2.2510(13)	95.11(4)	-	-
3.4^{Me}	0.614	-	1.9081(13) 1.9123(12)	1.9998(18)	1.576(10)	-	-	96.09(5)	-	-
3.10^{Me}	0.760	0	1.9123(11) 1.9124(13)	1.933(12)	1.724(17)	1.192(17)	2.234(3)	95.44(8)	-	-
3.4^H	0.006	-	1.8989(12)	-	1.51(2) 1.518(19)	-	-	-	-	-
3.10^H	0.730	0	1.8997(10)	-	1.746 1.522	1.205	2.228(2)	94.75(6)	-	-
3.5^{Et}	0.464	-	1.8946(10) 1.9222(10)	1.9803(14)	1.52(3)	-	-	99.36(4)	1.3551(15)/ 1.3887(15) 1.3431(15)/ 1.3693(16)	22.8 40.3
3.11^{Et}	0.737	0.15	1.921(2) 1.924(2)	2.039(5)	-	-	2.268(3)	98.93(8)	1.359(4)/ 1.440(7) 1.352(3)/ 1.361(3)	25.74 27.0
3.5^H	0.094	-	1.8963(12) 1.8897(13)	-	1.572 1.564	-	-	100.09(5)	1.3496(18)/ 1.3787(19) 1.3537(19)/ 1.375(2)	31.8 34.2
3.11^H	0.546	0	1.9069(9)	-	1.49(2) 1.816(14)	1.178(14)	2.2679(18)	98.77(6)	1.3563(14)/ 1.3734(14)	33.39

Table 3.6: Some of the key structural features of novel aluminium borohydride complexes and a comparison with their precursor hydrides.

Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂ and boranes

Compound	3.4^{Et}	3.10^{Et}	3.4^{Me}	3.10^{Me}	3.4^H	3.10^H
Yield	-	71%	-	55%	-	91%
IR ($\nu_{\text{Al-H}}/\nu_{\text{Al-H-B}}$) (cm ⁻¹)	1776	2066, 2026	1767	2065, 2030	1796, 1832	1846, 2065, 2034
δ_{H} (Al-R) (ppm)	-0.13, 0.79	0.52	-0.74	-0.10	-	-
δ_{H} (Al-H) (ppm)	4.57	-	4.64	-	4.49	4.58
δ_{H} (γ -H) (ppm)	4.92	4.83	4.93	4.91	4.87	4.90
δ_{B} (ppm)	-	-15.6	-	-15.2	-	-15.7
$\Delta\omega_{1/2}$	-	285.0, 212.2	-	604.1, 420.3	-	585.4, 390.5

Compound	3.5^{Et}	3.11^{Et}	3.5^H	3.11^H
Yield	-	47%	-	66%
IR ($\nu_{\text{Al-H}}/\nu_{\text{Al-H-B}}$) (cm ⁻¹)	1788	2104	1793, 1840	1850, 2103
δ_{H} (Al-R) (ppm)	-0.24, 0.74	0.78, 0.97	-	-
δ_{H} (Al-H) (ppm)	4.57	-	4.52	4.58
δ_{H} (γ -H) (ppm)	3.67	3.67	3.84	3.61
δ_{B} (ppm)	-	-17.4	-	-17.4
$\Delta\omega_{1/2}$	-	332.9, 253.4	-	320.0, 199.5

Table 3.7: A comparison of some of the spectroscopic features of the aluminium borohydride complexes with their aluminium hydride precursors.

These borohydrides may be isolated in moderate yields and their investigation by standard spectroscopic techniques reveals many similar features to those of **3.10^{Et}**. In the case of the hydrides **3.10^H** and **3.11^H**, broad resonances for the terminal Al-Hs are observed in the ¹H NMR spectra and this suggests that exchange between the hydrides *via* disassociation and reassociation of the borane does not occur in solution. These complexes display broad upfield resonances in the ¹¹B{¹H} NMR spectra which narrow upon ¹H decoupling.

The availability of isolated samples of **3.10^{Me}**, **3.10^H**, **3.11^{Et}** and **3.11^H** allowed for the thermodynamic parameters associated with the borane/borohydride equilibrium to be investigated through VT-NMR. In the case of **3.10^H** and **3.11^H**, the ¹¹B NMR spectra revealed the liberation of only a trace amount of borane (signalled by a resonance at δ_{B} =

27.9 ppm) even at elevated temperatures (>365 K for **3.10^H**; >350 K for **3.11^H**). Above these temperatures, the ¹H NMR spectra were very broad and did not allow for a reliable van't Hoff calculation of ΔH° and ΔS° . Qualitatively, however, these observations suggest relatively tight binding to the aluminium hydride in these complexes – they display no hint of dissociation at room temperature. On the other hand, thermodynamic parameters could be definitively established for **3.10^{Me}** (ΔH° 38.7 kJ mol⁻¹, ΔS° 53.6 J mol⁻¹ K⁻¹) and **3.11^{Et}** (ΔH° 43.5 kJ mol⁻¹, ΔS° 98.9 J mol⁻¹ K⁻¹) (Figure 3.19) and these are consistent with those calculated for **3.10^{Et}** (ΔH° 54.7 kJ mol⁻¹, ΔS° 115.4 J mol⁻¹ K⁻¹). Moreover, these parameters are consistent with the notion that breakage of the bridging Al-H-B bonds can be accomplished with relatively minor energetic changes to the system. The interaction of the aluminium centre with the borane in these complexes may be viewed in two ways: interaction of a [H₂(9-BBN)]⁻ ligand with the cationic aluminium fragment, or a neutral system in which the hydridic Al-H bond acts as a donor towards the boron centre and the B-H bond to the aluminium centre. In the latter description, the electronic character of the R substituent affects this interaction in conflicting ways. The presence of an electron-withdrawing substituent (i) reduces the hydridic character of the Al-H bond, thereby reducing its donor capabilities towards the boron centre, but (ii) increases the interaction of the boron hydride by increasing the Lewis acidity of the aluminium centre.

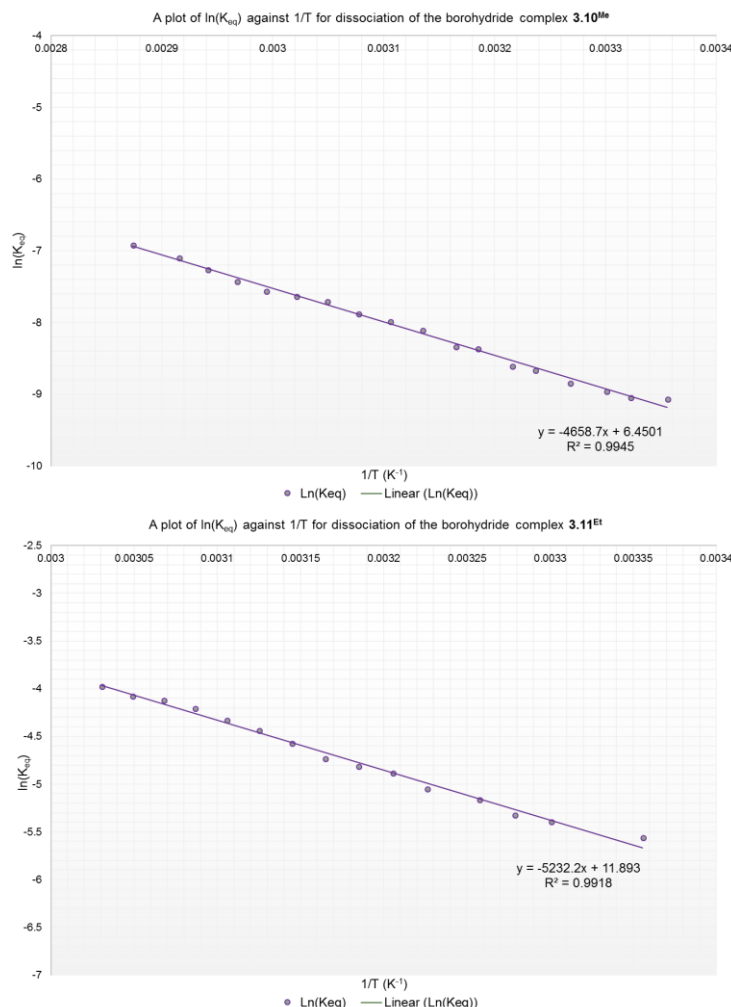


Figure 3.19: The van't Hoff plot for the equilibrium of the borohydride complexes **3.10^{Me}** (above) and **3.11^{Et}** (below) with their aluminium hydride **3.4^{Me}** and **3.5^{Et}** and {H(9-BBN)}₂.

A comparison of the ΔH°_{diss} values (**3.10^{Et}** 54.7 kJ mol⁻¹, **3.11^{Et}** 43.5 kJ mol⁻¹) and solid state Al-B distances (**3.10^{Et}** 2.2510(13) Å, **3.11^{Et}** 2.268(3) Å) of **3.10^{Et}** and **3.11^{Et}** indicate that binding of the borane may be marginally weaker in the case of **3.11^{Et}**. In light of the view that the hydrides that bear the N-nacnac ligand are less hydridic due to the σ -withdrawing ligand backbone amino functionalities, this suggests that the bonding within the borohydrides is dominated by the interaction of the aluminium hydride with the boron centre. The interaction of the boron hydride with the aluminium centre might be expected to play less of a role within the interaction due to the coordinatively saturated nature of the aluminium centre.

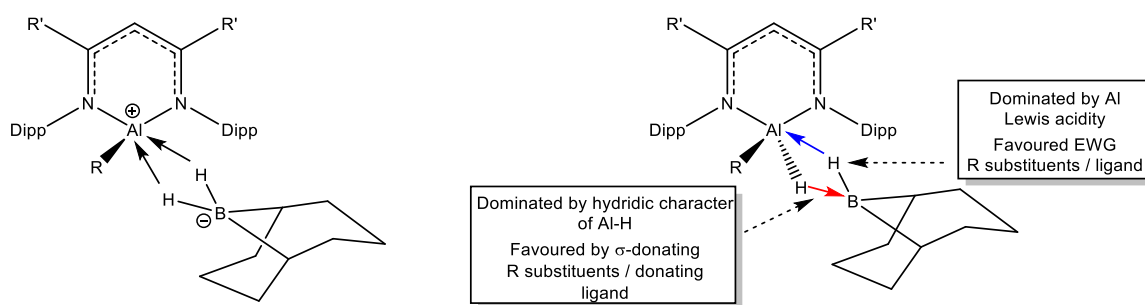


Figure 3.20: Two descriptions of the interaction between the aluminium hydride and borane in the aluminium borohydride complexes.

The addition of one equivalent of DMAP to solutions of these borohydride complexes (**3.10** – **3.11**) in benzene-d₆ at room temperature causes the immediate dissociation of the complex, regenerating the aluminium hydride and forming (DMAP)·(H(9-BBN)). The ¹H NMR spectra of the resulting mixtures show resonances for the aluminium hydrides and the adduct, consistent with those reported in the literature.¹⁰⁹ The ¹¹B NMR spectra all show a broad signal at $\delta_B = -2.6$ ppm.

3.4.3.6 Stoichiometric studies: the reactivity of aluminium formates towards {H(9-BBN)}₂

A solution of **3.10**^{Et} in benzene-d₆ was placed under *ca.* 1 bar of CO₂ and monitored by ¹H and ¹¹B NMR spectroscopy. After 3 h at room temperature complete consumption of **3.10**^{Et} occurs, signalled by the absence of a resonance at $\delta_B = -15.6$ ppm, and the resulting reaction mixture contains formate complex **3.6**^{Et}, {H(9-BBN)}₂ and an additional Nacnac-ligated species. The reactivity of **3.10**^{Et} towards CO₂ is slower than that observed for **3.4**^{Et} (> 90% reaction completion in 60 min). We postulate that CO₂ does not directly react with **3.10**^{Et}, but rather with hydride complex **3.4**^{Et}, present in low concentration in solution *via* dissociation of the borane. This phenomenon is also observed in the reactivity of nickel borohydride complexes with CO₂.⁷

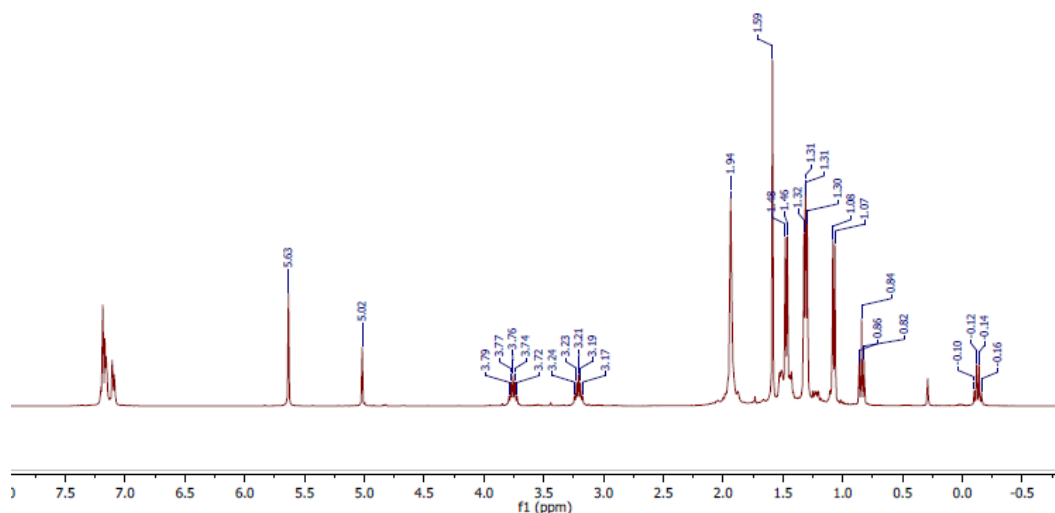


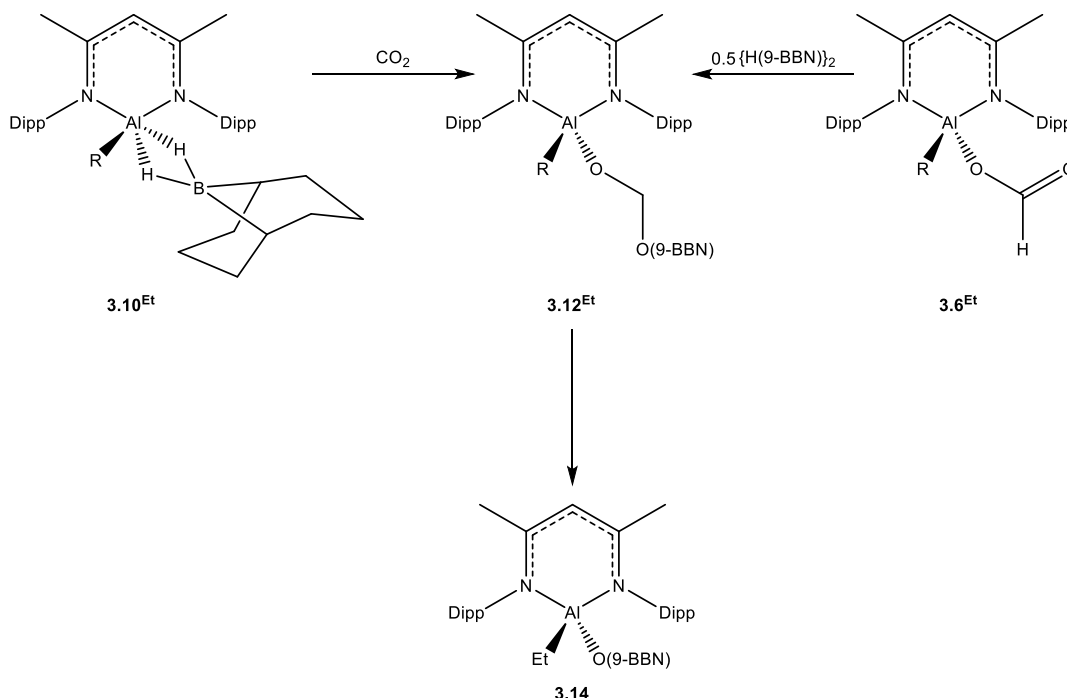
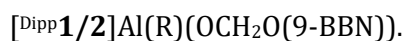
Figure 3.21: The ¹H NMR spectrum of [Dipp¹]Al(Et)(OCH₂O(9-BBN)) (**3.12^{Et}**).

After *ca.* 6 h all **3.6^{Et}** is consumed, yielding a single novel Nacnac-ligated species, proposed to be formed from the reaction of **3.6^{Et}** with {H(9-BBN)}₂. Indeed, this could be corroborated by the reaction of **3.6^{Et}** with 0.5 equivalents of {H(9-BBN)}₂, which reaches >95% completion after 6 h at room temperature and selectively yields the same product. This novel species has been characterised by NMR spectroscopy as an aluma-bora-acetal [Dipp¹]Al(Et)(OCH₂O(9-BBN)) (**3.12^{Et}**). Its ¹¹B NMR spectrum features a single broad resonance at $\delta_B = 56.0$ ppm, the chemical shift of which is consistent with a 3-coordinate boron environment of the nature R₂BOR' (e.g. MeO(9-BBN) $\delta_B = 52.0$ ppm, O(9-BBN)₂ $\delta_B = 58.2$ ppm).^{110,111} In addition, the ¹H NMR spectrum features a singlet at $\delta_H = 5.63$, integrating to two hydrogens (and correlating to a secondary carbon resonance at $\delta_C = 87.6$ ppm). This resonance was assigned to the acetal functionality of the (OCH₂O(9-BBN)) substituent; its chemical shift is consistent with those reported for related compounds (e.g. CH₂(O(9-BBN))₂ $\delta_H = 5.34$ ppm, CH₂(OBpin)₂ $\delta_H = 5.49$ ppm).^{12,112} The corresponding systems [Dipp¹]Al(Me)(OCH₂O(9-BBN)) (**3.12^{Me}**) and [Dipp²]Al(Et)(OCH₂O(9-BBN)) (**3.13^{Et}**) can be synthesised using analogous methods and characterised by NMR spectroscopy. The diagnostic ¹H, ¹¹B and ¹³C resonances

associated with the (OCH₂O(9-BBN)) function appear at essentially identical chemical shifts for all three compounds (Table 3.8).

Compound	3.12^{Et}	3.12^{Me}	3.13^{Et}
δ_B (ppm)	56.0	56.6	57.3
δ_H (γ -H) (ppm)	5.02	5.00	3.77
δ_H (Al-R) (ppm)	-0.13, 0.84	-0.76	-0.18, 0.66
δ_H (OCH ₂ O) (ppm)	5.63	5.53	5.84
δ_C (OCH ₂ O) (ppm)	87.6	87.4	87.8

Table 3.8: Some key spectroscopic features of the acetal complexes



Scheme 3.13: The two routes for the preparation of the complexes

[^{Dipp}1/2]Al(R)(OCH₂O(9-BBN)) and the isolation of [^{Dipp}1]Al(Et)(O(9-BBN)) (**3.14**).

No significant differences are observed in the rate of reactivity of the aluminium formates (**3.6^{Et}**, **3.6^{Me}** and **3.8^{Et}**) with 0.5 equivalents of {H(9-BBN)}₂ to yield the acetal complexes. Placing a solution of the N-nacnac system [^{Dipp}2]Al(Et)(κ^2 -H₂(9-BBN)) (**3.11^{Et}**) under CO₂, however, leads to a significantly greater rate of consumption of **3.11^{Et}**, relative to that observed for **3.10^{Me}**/**3.10^{Et}**, such that the consumption of **3.11^{Et}** was

complete by the time ¹H NMR spectra could be obtained (< 5 min). This presumably reflects both the greater dissociation of the borane from **3.11^{Et}** in solution, and the greater reactivity of **3.5^{Et}** towards CO₂.

Acetal complexes of this nature have frequently been implicated as intermediates within the borane-mediated catalytic reduction of CO₂, and the formation of [Dipp¹]Al(Et)(OBcat) is hypothesised to proceed *via* the closely related intermediate [Dipp¹]Al(Et)(OCH₂O(Bcat)). However, acetals are rarely observed experimentally; typically, such species are not persistent in solution due to their propensity to undergo further σ -bond metathesis reactions across the M-O bond or to eliminate formaldehyde to yield a metal borate ester. Whilst these mechanistic steps have not been computationally assessed for the use of {H(9-BBN)}₂, it is likely that this borane mimics the reactivity of HBpin/HBcat.^{15,22} It is suggested that, as for HBcat, the greater Lewis acidity of the boron centre allows for the direct hydroboration of the C=O bond of the formate functionality. If a competing Lewis base, such as DMAP, is added to {H(9-BBN)}₂ prior to the addition of **3.6^{Et}**, the adduct (DMAP)·H(9-BBN) does not react at all with **3.6^{Et}**, even when heated to 80°C overnight.

Accordingly, attempts were made to isolate **3.12^{Et}** in the solid state for crystallographic characterisation. Single crystals were obtained from the storage of an ethereal solution of **3.12^{Et}** at -30°C for one week. The molecular structure revealed, however, that the species was not **3.12^{Et}** but the product of formaldehyde loss from **3.12^{Et}**, i.e. [Dipp¹]Al(Et)(O(9-BBN)) (**3.14**) (Figure 3.22). Repeated attempts were made to crystallise **3.12^{Et}** from a range of solvents, at different temperatures and in the presence of a base for stabilisation, but **3.14** was consistently isolated instead.

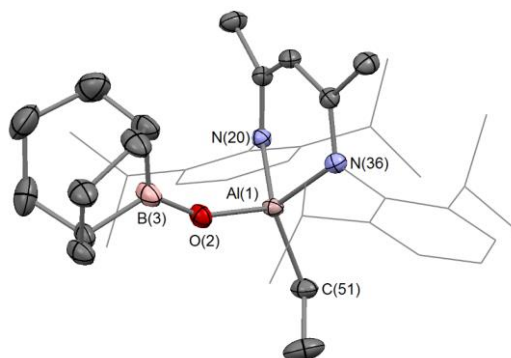


Figure 3.22: Molecular structure of [Dipp1]Al(Et)(O(9-BBN)) (**3.14**). Thermal ellipsoids set at the 40% probability level. Hydrogen atoms omitted and Dipp groups shown in wireframe for clarity.

Key bond lengths and angles are given in **Table 3.9**:

Compound	[Dipp1]Al(Et)(O(9-BBN))	[Dipp1]Al(Et)(OBcat)
Distance of Al from C ₃ N ₂ plane (Å)	0.720	0.555
<i>d</i> (Al-N) (Å)	1.9017(13), 1.9071(14)	1.8859(11), 1.9016(11)
<i>d</i> (Al-C) (Å)	1.9508(17)	1.9532(13)
<i>d</i> (Al-O) (Å)	1.7306(12)	1.7387(10)
<i>d</i> (O-B) (Å)	1.3246(19)	1.3081(18)
N-Al-N (°)	96.47(6)	96.97(5)
Al-O-B (°)	154.90(12)	153.66(10)
Distance of B from C ₂ O/O ₃ plane (Å)	0.002	0.054
δ_H (Al-Et) (ppm)	0.02, 1.02	-0.05, 0.92
δ_H (γ -H) (ppm)	4.99	4.98
δ_H (BBN-H) (ppm)	1.56, 2.04	-
δ_B (ppm)	55.0	21.5

Geometrically, the molecular structure of **3.14** closely resembles that of the related complex [Dipp1]Al(Et)(OBcat), with only minor differences in the geometry at the aluminium centre (Table 3.9). The Al-O bond lengths correlate inversely with those of the B-O bonds; a shortening of the B-O bond due to increased π -bonding should result in elongation of the Al-O bond. The B-O bond of **3.14** is longer than that of **3.9^{Et}**, and the Al-O bond shorter.⁸⁸ This observation is the opposite to that predicted based on the typical Lewis acidities observed for the boron centres. It is apparent that, in this case, the oxygen substituents of the Bcat fragment might function primarily as σ -withdrawing

groups rather than π -donating, hence leading to a greater Lewis acidity than the boron centre of the 9-BBN fragment.

There are relatively few reported examples of complexes that feature the 9-BBN fragment and an Al-O-B linkage. The only reported examples take the form $[(\mu\text{-O(9-BBN))AlR}_2]_2$ (R = Me, Br, Cl), of which two examples have been crystallographically characterised.^{88,111} A comparison of the Al-O and B-O bond lengths of **3.14** with reported data for these complexes reveal shorter bonds in the case of **3.14** (R = Me: average $d(\text{Al-O})$ 1.861 Å, $d(\text{B-O})$ 1.375(4) Å; R = Br, average $d(\text{Al-O})$ 1.827 Å, $d(\text{B-O})$ 1.392(8) Å). This is consistent with reported observations of shorter terminal Al-O-B contacts. Moreover, the boron centre of **3.14** is 3-coordinate rather than 4, which should lead to a shorter B-O bond.

Analysis of **3.14** by NMR spectroscopy supports its formulation as an aluminium-borate ester. The ¹¹B NMR spectrum shows a single broad resonance at $\delta_{\text{B}} = 55.0$ ppm, the chemical shift of which is consistent with a three-coordinate boron centre of the formulation RBOR' (R = alkyl) (e.g. MeO(9-BBN) $\delta_{\text{B}} = 52.0$ ppm, O(9-BBN)₂ $\delta_{\text{B}} = 58.2$ ppm).^{110,111} The ¹H NMR spectrum shows a pronounced downfield shift of both the resonances for the ethyl substituent ($\delta_{\text{H}} = 0.02$ ppm for the methylene protons, $\delta_{\text{H}} 1.02 =$ ppm for the methyl protons) and the 9-BBN protons ($\delta_{\text{H}} = 1.56, 2.04$ ppm). This is consistent with the presence of an aluminium- and boron-bound electron-withdrawing group, in this case the oxide linkage. Most significantly, the observed pattern of resonances is clearly distinct from that observed for **3.12^{Et}** and there are no resonances in the region typical of acetal functionalities.

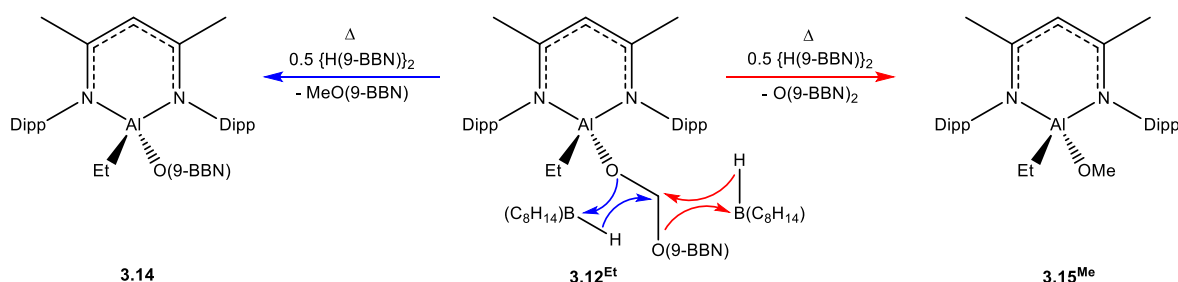
The persistent isolation of **3.14** in the solid state from the attempted crystallisations of **3.12^{Et}** illustrates the predisposition of such complexes to undergo elimination of

formaldehyde, consistent with literature precedent.¹⁴ Placing **3.12^{Et}** under vacuum (*ca.* 10⁻² mbar) for several hours shows that **3.12^{Et}** is stable to the elimination of formaldehyde in the solid state under these conditions. **3.12^{Et}** is stable in solution at room temperature for up to 32 h but over longer periods (*ca.* 2 weeks) a significant level of degradation is observed resulting in the formation of **3.14**, although this is not selective. The ¹¹B NMR spectrum shows a sharp resonance at $\delta_B = 87.6$ ppm, indicating that some of the degradation arises from elimination of Et(9-BBN).¹¹⁰ **3.12^{Et}** is stable in solution for three hours at 50°C but heating to 60°C leads to its consumption over the course of *ca.* 12 h, leading to the formation of **3.14**, amongst other products. The observation of a resonance in the ¹¹B NMR spectrum at $\delta_B = 87.6$ ppm is suggestive of the elimination of Et(9-BBN).¹¹⁰ The elevated temperature required to bring about reactivity of **3.12^{Et}**, is consistent with the relatively high barrier for the elimination of formaldehyde that has been computationally assessed for related systems.²² **3.12^{Me}** and **3.13^{Et}** are somewhat less stable than **3.12^{Et}** at room temperature and degrade over the course of several days, evolving Me(9-BBN) and Et(9-BBN), respectively. The corresponding borate ester complexes were not observed.

In the case of [Dipp¹Al(Et)(OCH₂O(9-BBN))], the difference in stability compared to its putative Bcat analogue [Dipp¹Al(Et)(OCH₂O(Bcat))] is striking. While the latter cannot even be detected as an intermediate on the pathway to [Dipp¹Al(Et)(OBcat)], its 9-BBN counterpart undergoes the analogous loss of formaldehyde very slowly. The elimination of HC(O)H from species of the type [Dipp¹Al(Et)(OCH₂O(BX₂))] necessarily involves the cleavage of either the Al-O or B-O bond. The very different stabilities of the 9-BBN and Bcat systems of this type implies that the boron-bound substituents play a significant role in modulating lability, and we therefore favour a mechanism involving B-O bond

breakage. The much longer-lived nature of the 9-BBN derivative would then be in line with the stronger B-O bond expected in association with a dialkyl BX₂ function.

In the presence of excess {H(9-BBN)}₂ **3.12^{Et}** exhibits minimal onward reactivity over several days at room temperature. Complete conversion does occur when the reaction mixture is heated to 80°C for 4 d. The ¹H NMR spectrum of the product mixture is consistent with the presence of two major Nacnac-ligated species. One of these is identified as **3.14**, the formation of which is accompanied by the generation of the known compound MeO(9-BBN) (singlet at δ_{H} = 3.45 ppm).^{13,110} The other major species gives rise to a singlet at δ_{H} = 3.85 ppm which integrates to three protons, the chemical shift being consistent with a methoxide resonance. The identity of this methoxide-ligated species was subsequently confirmed as [Dipp₂Al(Et)(OMe)] (**3.15**) through independent synthesis (see below). Importantly, no evidence is observed for the formation of any Al-H containing species, nor for the presence of CH₂(O(9-BBN))₂, suggesting that σ -bond metathesis does not occur across the Al-O bond.



Scheme 3.14: Proposed routes for formation of the observed Nacnac-containing products in the reaction of **3.12^{Et}** with excess {H(9-BBN)}₂ at 80°C.

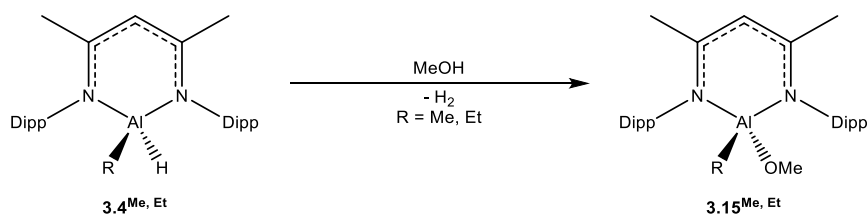
We propose that the observed product profile arises from B-H/C-O σ -bond metathesis across either C-O bond of the (OCH₂O(9-BBN)) functionality of **3.12^{Et}**, yielding either **3.14** and MeO(9-BBN) or **3.15** and O(9-BBN)₂ (Scheme 3.14). These pathways are apparently feasible in the absence of accessible M-O/B-H metathetical pathways, but

presumably incur relatively high activation barriers, consistent with the high temperature and long reaction times required to bring about consumption of **3.12^{Et}**.

The independent synthesis of **3.15** was accomplished through the addition of one equivalent of methanol to **3.4^{Et}** at room temperature, leading to the rapid evolution of dihydrogen. The basic nature and polarity of the Al-H bond of alanes have previously been shown to underpin their ability to deprotonate a range of protic functional groups, such as alcohols, thiols, amines, boronic acids and alkynes.^{31,85,86} Accordingly, this property has been heavily exploited in both the synthesis of complexes of the type [Dipp**1**]AlR₂ derived from the dihydride [Dipp**1**]AlH₂, and the alane-catalysed dehydrocoupling of boranes with phenols, amines and thiols.³¹

Monitoring of the reaction by ¹H NMR spectroscopy shows that the formation of **3.15** is both rapid and quantitative and is signalled by the loss of the hydride resonance of **3.4^{Et}** at $\delta_{\text{H}} = 4.57$ ppm and the appearance of a singlet at $\delta_{\text{H}} = 3.85$ ppm, integrating to three hydrogens. This singlet is assigned to the methoxide protons of **3.15**; the chemical shift is consistent with those observed for related complexes (e.g. [Dipp**1**]AlH(OMe) $\delta_{\text{H}} = 3.35$ ppm, [Dipp**1**]Al(OMe)₂ $\delta_{\text{H}} = 3.54$ ppm) and correlates to a resonance at $\delta_{\text{C}} = 51.8$ ppm in the ¹³C NMR spectrum.⁵² The observation of a triplet resonance at $\delta_{\text{H}} = 0.82$ ppm and a quartet resonance $\delta_{\text{H}} = -0.18$ ppm and 4 doublets and 2 septets in the aliphatic region of the ¹H NMR spectrum for the Dipp ⁱPr substituents is highly indicative of an unsymmetrically substituted aluminium centre, and hence retention of the ethyl substituent in the presence of methanol. **3.15^{Et}** could be isolated in the solid state in 61% yield as large colourless crystals which are suitable for X-ray crystallography. The molecular structure of **3.15^{Et}** is shown in Figure 3.23 and displays the expected molecular connectivity.

3.14 and **3.15^{Et}** were both treated with excess {H(9-BBN)}₂ in benzene-d₆ and heated to 80°C. The resulting ¹H NMR spectra showed no reactivity after several days and are consistent with the non-viability of Al-O/B-H metathetical reactivity.



Scheme 3.15: The synthesis of [Dipp₂Al(R)(OMe)] (**3.15^{Me, Et}**) from the addition of methanol to the corresponding aluminium hydrides **3.4^{Me, Et}**.

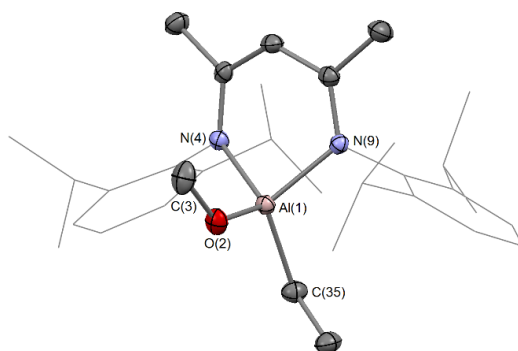


Figure 3.23: Molecular structure of [Dipp₁Al(Et)(OMe)] (**3.15^{Et}**). Thermal ellipsoids set at the 40% probability level. Select hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°): Al(1)-O(2) 1.7169(13), Al(1)-N(4) 1.9074(15), Al(1)-N(9) 1.9073(14), Al(1)-C(35) 1.9530(19), N(4)-Al(1)-N(9) 95.43(6), Al(1)-O(2)-C(3) 131.52(13).

3.4.3.7 Catalytic studies: Me₂S·BH₃ as the reductant

Whilst BH₃-containing reagents have commonly been used in the hydroboration of unsaturated carbon-element bonds, they have been much less widely employed in the catalytic reduction of CO₂.^{113,114} The first reported deployment of Me₂S·BH₃ as a reductant was in the reduction of CO₂ catalysed by the borane/phosphine FLP, 1-Bcat-2-PPh₂-C₆H₄, for which a TON of 853 h⁻¹ was obtained at 0.003 mol% loading and

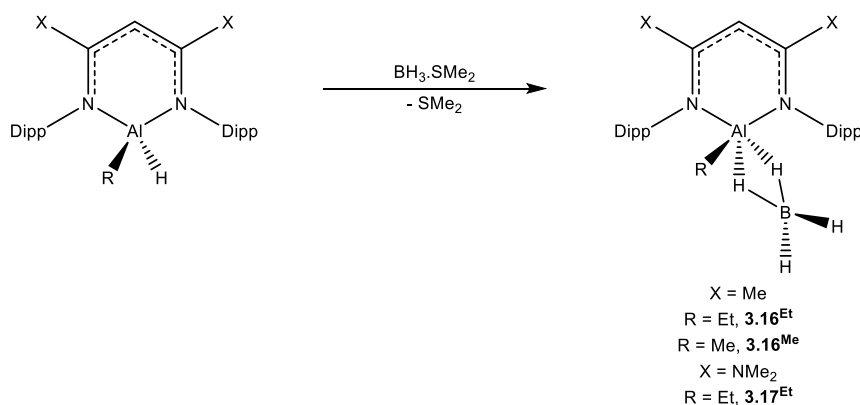
70°C.^{80,115} The successful use R·BH₃ (R = OTf, SMe₂) in conjunction with metal hydrides for the reduction of CO₂ has, to our knowledge, not been reported, despite potential merits relating to its inexpensive nature, enhanced reactivity and high hydrogen content, relative to other boranes. Typically, the product yielded from this reaction is (MeOBO)₃ or, less commonly, B(OMe)₃, both of which may be hydrolysed to methanol.^{116–123}

The ability of **3.4^{Et}** to catalyse the reduction of CO₂, utilising Me₂S·BH₃ as the reductant, was therefore investigated. It was observed by ¹H and ¹¹B NMR spectroscopy that the generation of a benzene solution of Me₂S·BH₃ with 10 mol% of **3.4^{Et}** as a catalyst leads to the formation of a novel species, prior to the addition of CO₂. The ¹¹B{¹H} NMR spectrum shows resonances at $\delta_B = -19.4$ ppm (for Me₂S·BH₃) and $\delta_B = -36.6$ ppm. This solution was pressurised with CO₂ (*ca.* 2 bar) and the progression of the any catalysis monitored by ¹H and ¹¹B NMR spectroscopy. After 24 h at room temperature, the ¹H NMR and ¹¹B NMR spectra showed very few changes. The solution was heated to 60°C for 24 h but no consumption of Me₂S·BH₃, and hence no catalysis, was observed. A series of stoichiometric reactivity studies was undertaken to understand this reactivity.

3.4.3.8 Stoichiometric studies: the formation of borohydride complexes

The addition of one equivalent of Me₂S·BH₃ to a solution of **3.4^{Et}** in toluene leads to the immediate formation of a single novel species. This species could be recrystallised from toluene at -30°C in 65% yield; the molecular structure is shown in Figure 3.24. The molecular structure reveals the constitution of **3.16^{Et}** to be a monomeric aluminium borohydride complex, in which the aluminium centre is chelated by the Nacnac ligand

and a κ^2 -[BH₄]⁻ fragment. The bidentate mode of binding of the borohydride ligand at the metal centre *via* 3 centre-2 electron bonds is fairly common for aluminium and is observed in complexes such as [Dipp₂Al(BH₄)₂], Al(BH₄)₃ and Me₂Al(BH₄).^{103,124} It is apparent that **3.16**^{Et} is formed from the nucleophilic displacement of SMe₂ from Me₂S·BH₃ by the aluminium hydride. Such reactivity is commonly observed for masked boranes of the nature X·BH₃ (X = SMe₂, THF), illustrated in the reactivity of AlH₃ with THF·BH₃, yielding a range of AlH_{3-n}(BH₄)_n species.⁹³ **3.16**^{Et} is thermally stable both in isolation and under dynamic vacuum; no loss of BH₃ is observed when **3.16**^{Et} is exposed to a dynamic vacuum for several hours.



Scheme 3.16: Syntheses of the borohydride complexes **3.16**^{Et}, **3.16**^{Me} and **3.17**^{Et} from the addition of Me₂S·BH₃ to the corresponding hydrides.

Geometrically, **3.16**^{Et} features a closely related molecular structure to that of **3.10**^{Et}, with the [BH₄]⁻ fragment based around a tetrahedral boron centre and two hydrogens bridging to the aluminium atom. These hydrogens, and the terminal boron hydrides were located in the difference Fourier map and refined isotropically; the terminal B-H distances are consistent with literature precedent.¹²⁵ The aluminium coordination geometry is distorted square pyramidal ($\tau = 0.22$), with the two Nacnac nitrogen donors and the bridging hydrides constituting the basal plane and the Et substituent occupying

the apical position. The aluminium atom is projected out of the plane of the supporting Nacnac backbone by 0.504 Å. In contrast to the distortion from planarity observed for **3.10^{Et}**, which is larger than that of the aluminium hydride **3.4^{Et}**, the aluminium atom of **3.16^{Et}** lies closer to the plane of the Nacnac backbone. This may be because the [BH₄]⁻ ligand occupies the axial position; a marginal flattening of the ring reduces sterically unfavourable interactions between this substituent and the Dipp ⁱPr groups.

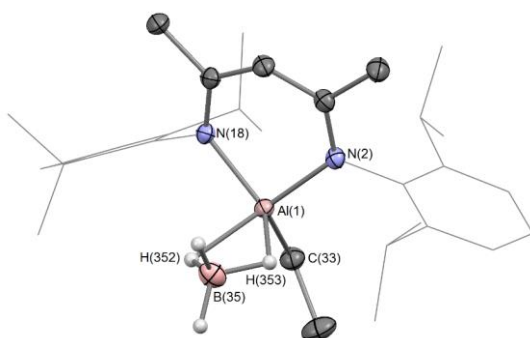


Figure 3.24: Molecular structure of [Dipp1]Al(Et)(H₂(BH₂)) (**3.16^{Et}**). Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. B-H and Al-H-B located in the difference Fourier map and refined isotropically. Key bond lengths (Å) and angles (°): Al(1)-N(2) 1.9104(13), Al(1)-N(18) 1.9171(13), Al(1)-C(33) 1.9698(16), Al(1)-B(35) 2.2333(19), Al(1)-H(352) 1.842, Al(1)-H(353) 1.779, B(35)-H(352) 1.130, B(35)-H(353) 1.168, B(35)-H(351) 1.081, B(35)-H(354) 1.098, N(2)-Al(1)-N(18) 96.11(6).

Compound	3.4^{Et}	3.10^{Et}	3.16^{Et}	[Dipp1]Al(BH ₄) ₂
Distance of Al from C ₃ N ₂ plane (Å)	0.663	0.790	0.504	-
<i>d</i> (Al-N) Å	1.9151(13) 1.9170(13)	1.9189(10) 1.9182(10)	1.9104(13) 1.9171(13)	1.898(3)
<i>d</i> (Al-C) Å	1.9605(18)	1.9686(12)	1.9698(16)	-
<i>d</i> (Al-B) Å	-	2.2510(13)	2.2333(19)	2.207(4) 2.231(6)

Table 3.10: A comparison of some of the structural metrics of **3.16^{Et}** with related complexes.

The Al-B distance ($d(\text{Al}(1)\text{-B}(35))$ 2.2333(19) Å) is marginally longer than the sum of the respective covalent radii ($1.25 + 0.88 = 2.13$ Å) and lies between those reported for Al(BH₄)₃ ($d(\text{Al-B})$ 2.12(2) Å) and Me₂Al(BH₄) ($d(\text{Al-B})$ 2.411(6) Å).¹⁰³ The Al-B distance is also comparable to the mean Al-B distance of the closely related complex [Dipp¹]Al(BH₄)₂ ($d(\text{Al-B})$ 2.219(5) Å) and is shorter than that observed for **3.10**^{Et}. This is indicative of tighter binding of the [BH₄]⁻ borohydride ligand, as compared to [H₂(9-BBN)]⁻, which may arise due to its reduced steric bulk.

3.16^{Et} was characterised by a range of spectroscopic and standard analytical techniques. The ¹H NMR spectrum features a broad resonance in the region $\delta_{\text{H}} = 0.71 - 1.20$ ppm which overlaps with the doublets of the Dipp ⁱPr substituents and which potentially corresponds to the boron-bound hydrogens – presumably broadened significantly due to the quadrupolar nature of both ²⁷Al ($I = 5/2$) and ¹¹B ($I = 3/2$). A chemical shift in a similar region of the spectrum is reported for the [BH₄]⁻ ligands of [Dipp¹]Al(BH₄)₂ ($\delta_{\text{H}} = 1.06$ ppm).⁹³ The observation of a single signal for the boron-bound hydrogens is indicative of an intramolecular exchange process between the bridging and terminal hydrogens, a common feature for metal borohydride complexes, which is only inhibited in the case of very strong metal-ligand interactions.^{104,126} The ¹¹B NMR spectrum of **3.16**^{Et} shows an upfield quintet at $\delta_{\text{B}} = -36.6$ ppm, showing coupling of the boron to the 4 hydrogens bound to it ($^1J_{\text{BH}} = 83.7$ Hz). Both the chemical shift and coupling constant of this resonance are consistent with those reported for borohydride complexes (e.g. LiBH₄ $\delta_{\text{B}} = -38.2$ ppm ($^1J_{\text{BH}} = 75.0$ Hz), $\delta_{\text{B}} = \text{NaBH}_4 -38.7$ ppm ($^1J_{\text{BH}} = 82.0$ Hz), [Dipp¹]Al(BH₄)₂ $\delta_{\text{B}} = -36.6$ ppm ($^1J_{\text{BH}} = 85.3$ Hz)).^{93,127}

The IR spectrum of **3.16**^{Et} shows two bands at 2450 and 2400 cm⁻¹, which are attributed to the symmetric and antisymmetric stretches of the terminal BH₂ unit, and which lie

within the typical range for metal borohydride complexes (2400 – 2600 cm⁻¹).¹⁰⁴ The bridging B-H stretching band is broad and observed at 2201 cm⁻¹, signalling a κ^2 -ligation mode.¹⁰⁴ No band is observed that may be attributed to the BH₂ deformation mode; this is most likely obscured by the bands associated with the ligand framework.

When **3.10^{Et}** is dissolved in benzene-d₆, partial dissociation of the borane occurs to generate the free hydride in an equilibrium mixture. By contrast, the ¹H and ¹¹B NMR spectra of **3.16^{Et}** show no evidence for dissociation of the borane in solution at room temperature. A crystalline sample of **3.16^{Et}** was dissolved in toluene-d₈ and ¹H and ¹¹B of the resulting solution were obtained at elevated temperatures. At 375 K, the ¹H and ¹¹B NMR spectra showed no dissociation of the borane. This difference in behaviour of **3.10^{Et}** and **3.16^{Et}** illustrates the weaker binding of the [H₂(9BBN)]⁻ fragment to the aluminium centre, consistent with the longer Al-B distance measured for **3.10^{Et}**. Furthermore, the addition of one equivalent of DMAP to a solution of **3.16^{Et}** in benzene-d₆ at room temperature does not lead to the immediate displacement of the aluminium hydride from the borane. Complete dissociation of the borane from **3.16^{Et}** was only brought about by heating the solution to 80°C for 5 h, yielding **3.4^{Et}** and (DMAP)·BH₃ as the sole products.¹²⁸ The observed difference in reactivity of **3.10^{Et}** and **3.16^{Et}** towards DMAP further illustrates the difference in the binding strength of the boranes.

In related fashion, the addition of one equivalent of Me₂S·BH₃ to solutions of **3.4^{Me}** and **3.5^{Et}** in benzene-d₆ at room temperature leads to the immediate formation of the respective borohydride complexes [Dipp¹]AlMe(H₂(BH₂)) (**3.16^{Me}**) and [Dipp²]Al(Et)(H₂(BH₂)) (**3.17^{Et}**) respectively. These complexes were characterised by NMR spectroscopy and their identities assigned based on their spectroscopic similarities

to **3.16^{Et}** (Table 3.11). These complexes also show no apparent dissociation of the borane in solution.

Compound	3.16^{Et}	3.4^{Me}	3.16^{Me}	3.5^{Et}	3.17^{Et}
$\delta_{\text{H}}(\text{Al-R})$ (ppm)	-0.02, 0.81	-0.74	-0.48	-0.24, 0.74	0.28, 0.94
$\delta_{\text{H}}(\text{Al-H})$ (ppm)	-	4.64	-	4.90	
$\delta_{\text{H}}\gamma\text{-H}$ (ppm)	4.91	4.93	4.90	3.67	3.82
δ_{B} (ppm)	-36.6	-	-36.4	-	-39.2
$^1J_{\text{BH}}$ (Hz)	83.7	-	82.8	-	82.5

Table 3.11: Some of the spectroscopic features of the borohydride complexes and their precursor hydrides.

3.4.3.9 Stoichiometric studies: Me₂S·BH₃ as the reductant

In light of the formation of borohydride complex **3.16^{Et}** from **3.4^{Et}** and Me₂S·BH₃, its reactivity towards CO₂ was probed. Accordingly, a solution of **3.16^{Et}** in benzene-d₆ was degassed and placed under *ca.* 1 bar of CO₂ in an NMR tube fitted with a J. Young's valve. The solution was monitored by ¹H and ¹¹B NMR spectroscopy; after 24 h at room temperature, these revealed that only a trace quantity of **3.16^{Et}** was consumed. This is in stark contrast to the reactivity observed for **3.4^{Et}** with CO₂, which proceeds selectively and rapidly under such conditions. In the case of dialkyl borohydride complex **3.10^{Et}** it was proposed that the observed reactivity with CO₂ proceeds by initial dissociation of the borane, followed by insertion of CO₂ into the Al-H bond of **3.4^{Et}**. This would be consistent with the observed lack of reactivity of **3.16^{Et}** towards CO₂ at room temperature, under which conditions no dissociation of the borane occurs. Similar features have been reported in nickel-hydride-catalysed reduction of CO₂.⁷ The pincer-ligated nickel hydride [2,6-(R₂PO)₂C₆H₃]NiH (R = ^tBu, ⁱPr) forms nickel borohydride complexes in the presence of H₃B·THF, {H(9-BBN)}₂ and HBcat. The latter two complexes exist in equilibrium with the nickel hydride and the borane at room

temperature and catalyse the reduction of CO₂ to methanol derivatives with maximum TOFs of 100 h⁻¹. By contrast, the complexes [2,6-(R₂PO)₂C₆H₃]Ni(BH₄) (R = ^tBu, ⁱPr) show no dissociation of the borane and no catalytic activity.⁷

The solution was heated at 80°C to induce reactivity of the complex with CO₂. Whilst the consumption of **3.16**^{Et} was observed, this was not complete in 7 days, nor did it proceed in a selective manner. The ¹H NMR spectrum of the resulting product mixture showed the formation of *ca.* six Nacnac-ligated species and featured a series of singlet resonances with chemical shifts in the range $\delta_{\text{H}} = 3.37 - 3.84$ ppm, typical of methoxide ligands. From this spectroscopic data the formation of **3.15**^{Et}, B(OMe)₃ ($\delta_{\text{H}} = 3.43$ ppm) and (CH₃OBO)₃ ($\delta_{\text{H}} = 3.37$ ppm) could be deduced, but the two major species could not be identified. The ¹¹B NMR spectrum showed a series of broad resonances from $\delta_{\text{B}} = 16.8 - 32.0$ ppm.

To understand the observed reactivity, the formate complex **3.6**^{Et} was reacted with an excess of Me₂S·BH₃ (3 equiv.) at room temperature; this reaction proceeds to >95% consumption after 3 h. The resulting ¹H NMR spectrum is indicative of the presence of one major and two minor Nacnac-ligated species (in approximate ratio 5:1:1); one of these minor species was shown to be **3.16**^{Et}. The ¹¹B{¹H} NMR spectrum showed resonances at $\delta_{\text{B}} = -36.6$ ppm (for **3.16**^{Et}), -19.4 ppm (for Me₂S·BH₃), 25.1 ppm and 28.1 ppm. Despite the presence of excess Me₂S·BH₃, no further production of **3.16**^{Et} was observed over the course of several hours at room temperature. The major product of the reaction could be crystallised from *n*-hexane at 6°C and its structure determined by X-ray crystallography. This allows it to be identified as [^{Dipp}**1**]Al(Et)(OBH(OMe)) (**3.18**^{Et}), as shown in Figure 3.25.

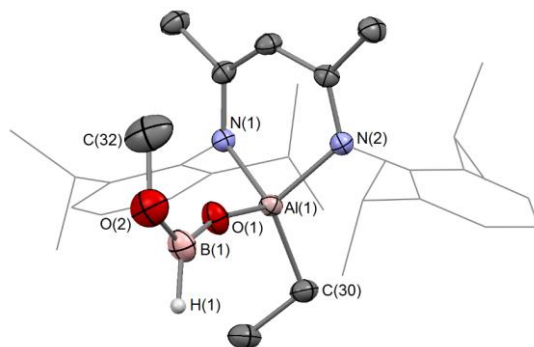


Figure 3.25: Molecular structure of [Dipp1]Al(Et)(OBH(OMe)) (**3.18^{Et}**). Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. B-H located in difference Fourier map and refined isotropically. Key bond lengths (Å) and angles (°): Al(1)-O(1) 1.7253(13), Al(1)-N(2) 1.8960(13), Al(1)-N(1) 1.9036(13), Al(1)-C(30) 1.9600(18), O(1)-B(1) 1.318(2), O(2)-B(1) 1.357(3), O(2)-C(32) 1.427(4), B(1)-H(1) 1.16(3), N(2)-Al(1)-N(1) 96.85(6), B(1)-O(1)-Al(1) 163.24(17), O(1)-B(1)-O(2) 124.3(2), O(1)-B(1)-H(1) 121.9(14), O(2)-B(1)-H(1) 113.8(14), O(1)-B(1)-C(32) 119.32(18).

The molecular structure of **3.18^{Et}** features a tetra-coordinate aluminium centre, ligated by Nacnac and ethyl donors and an unusual borate ligand [OB(OMe)H], featuring a trigonal boron centre and pendant H/OMe substituents. The B-H hydrogen was located in the difference Fourier map and refined isotropically; the B-H distance is consistent with those reported in the literature.¹²⁵ The aluminium centre is projected 0.637 Å from the least-squares C₃N₂ plane and the [OB(OMe)H] substituent occupies the more sterically hindered axial position. The Al-N and Al-C bond lengths lie close in value to the closely related complexes **3.9^{Et}** and **3.14**, reflecting the similar electronic environments of the aluminium centres. Both the Al-O and O-B bond lengths lie between those observed for **3.9^{Et}** and **3.14**. The respective B-O bond lengths suggest that the Lewis acidity of the respective boron centres increases with more oxygen-substituents, rather than decreases due to their π -donor capabilities. The B-O-C angle (119.32(18)°)

significantly narrower than the Al-O-C angle of **3.15^{Et}** (131.52(13)°), presumably due to the lower steric bulk in the (OBH(OMe)) fragment.

Compound	[Dipp 1]Al(Et)(OBH(OMe))	[Dipp 1]Al(Et)(O(9-BBN))	[Dipp 1]Al(Et)(OBcat)
Distance of Al from C ₃ N ₂ plane (Å)	0.637	0.720	0.555
<i>d</i> (Al-N) (Å)	1.8960(17), 1.9036(13)	1.9017(13), 1.9071(14)	1.8859(11), 1.9016(11)
<i>d</i> (Al-C) (Å)	1.9600(18)	1.9508(17)	1.9532(13)
<i>d</i> (Al-O) (Å)	1.7253(13)	1.7306(12)	1.7387(10)
<i>d</i> (O-B) (Å)	1.318(2), 1.357(3)	1.3246(19)	1.3081(18)
N-Al-N (°)	96.85(6)	96.47(6)	96.97(5)
Al-O-B (°)	163.24(17)	154.90(12)	153.66(10)

Table 3.12: A comparison of some of the structural metrics of the aluminium borate ester complexes reported in this chapter.

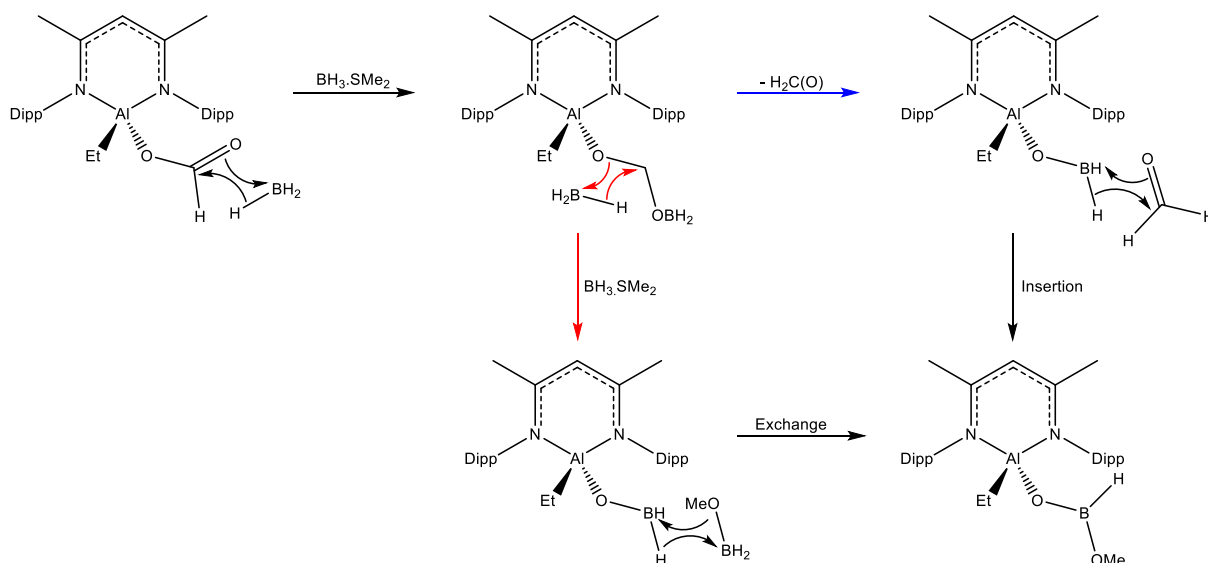
Spectroscopically, the OMe substituent is characterized by a ¹H NMR singlet at $\delta_{\text{H}} = 3.63$ ppm, integrating to three protons and correlating to a primary carbon resonance at $\delta_{\text{C}} = 50.0$ ppm. The chemical shifts observed are consistent with those reported for methoxide substituents and lies between those observed for **3.15^{Et}** ($\delta_{\text{H}} = 3.85$ ppm) and B(OMe)₃ ($\delta_{\text{H}} = 3.43$ ppm). A broad resonance is observed in the ¹H{¹¹B} NMR spectrum at $\delta_{\text{H}} = 4.77$ ppm, supporting the presence of the boron-bound hydrogen. The ¹¹B NMR spectrum shows a broad resonance at $\delta_{\text{B}} = 25.1$ ppm which narrows markedly upon ¹H decoupling from $\Delta\omega_{1/2}$ 1102 Hz to $\Delta\omega_{1/2}$ 458 Hz. The chemical shift of this resonance is consistent with those reported for three-coordinate boron centres of the form BH(OR)₂, such as (MeO)₂BH ($\delta_{\text{B}} = 26.1$ ppm) and HBcat ($\delta_{\text{B}} = 28.3$ ppm).^{127,129} In addition, the IR spectrum features a B-H stretch at 2434 cm⁻¹ consistent with the presence of a terminal B-H bond.¹³⁰

The formation of **3.18^{Et}** from **3.6^{Et}** uses all B-H bonds of one equivalent of BH₃; the mechanism by which this reaction proceeds is clearly of some interest. To ascertain how

3.18^{Et} might be formed, one equivalent of Me₂S·BH₃ was added to a solution of **3.6^{Et}** in benzene-d₆ and monitored by ¹H and ¹¹B NMR spectroscopy. The consumption of **3.6^{Et}** occurs more slowly in the presence of one equivalent of Me₂S·BH₃ and only reaches completion after 24 h. A number of intermediate species were observed including [Dipp¹]Al(Et)(OMe), B(OMe)₃ and presumably an acetal-containing species, as signalled by a series of singlets in the $\delta_H = 5.55 - 5.75$ ppm region. These intermediates were formed in small quantities and were not present upon reaction completion.

Based on the observed reactivity of **3.6^{Et}** towards HBcat and {H(9-BBN)}₂, we postulate that this reaction proceeds initially *via* the formation of an acetal derivative, [Dipp¹]Al(Et)(OCH₂OBH₂) (possibly with SMe₂ coordinated at boron), which extrudes formaldehyde to give the corresponding borate species, [Dipp¹]Al(Et)(OBH₂), featuring the Al-O-B linkage present in the final product (Scheme 3.17). In contrast to the analogous products, [Dipp¹]Al(Et)(OX) (X = Bcat, 9-BBN), obtained in the reaction with HBcat or {H(9-BBN)}₂, this putative species would contain reactive B-H bonds, and the recapture of HC(O)H *via* a net hydroboration process would then generate the observed BOMe unit. Alternatively, [Dipp¹]Al(Et)(OCH₂OBH₂) may undergo further reactivity with BH₃ across the O-C bond (Scheme 3.17) to produce [Dipp¹]Al(Et)(OBH₂) and (MeO)BH₂; exchange of the methoxide group would then lead to product **3.18^{Et}**. However, the energetic barriers associated with C-O/B-H metathesis, as evidenced in the reactivity of [Dipp¹]Al(Et)(OCH₂O(9-BBN)) with further {H(9-BBN)}₂ at 80°C, suggests that the first pathway is more likely to operate at room temperature.

Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂ and boranes



Scheme 3.17: The proposed routes for the formation of **3.18^{Et}** from the reaction of **3.6^{Et}** with Me₂S·BH₃.

The behaviour of **3.6^{Me}** towards Me₂S·BH₃ is consistent with that observed for **3.6^{Et}**; the resulting product could be characterised *in situ* by NMR spectroscopy, based on its spectroscopic similarities to **3.18^{Et}** (Table 3.13).

	δ_{H} (Al-R) (ppm)	δ_{H} (B-OMe) (ppm)	δ_{H} (B-H) (ppm)	δ_{H} (γ -H) (ppm)	δ_{C} (B-OMe) (ppm)	δ_{B} (ppm)
3.18^{Et}	-0.12, 0.83	3.63	4.77	4.96	50.0	25.1
3.18^{Me}	-0.78	3.58	4.70	4.98	50.2	25.5

Table 3.13: A comparison of some of the key spectroscopic features of **3.18^{Et}** and **3.18^{Me}**.

Solutions of **3.18^{Et}** and **3.18^{Me}** in benzene-d₆ were treated with excess Me₂S·BH₃ (>10 equiv.) and their reactivity monitored by ¹H and ¹¹B NMR spectroscopy. After 24 h at room temperature, no reactivity was observed. When the complexes **3.18^{Et}** and **3.18^{Me}** were heated to 80°C in the presence of Me₂S·BH₃ for 12 h, a complicated product mixture was obtained with a series of resonances observed in the region from δ_{B} = -6.5 to -41.6 ppm in the ¹¹B NMR spectrum. Further heating of the reaction mixtures at 80°C yielded the same major product in both cases, with a γ -H proton at δ_{H} = 4.96 and a

resonance integrating to three protons at $\delta_{\text{H}} = 3.53$, and no observable resonances for the aluminium-bound alkyl groups. In this case, it is suggested that the major product is [Dipp¹Al(BH₄)(OBH(OMe))], formed from the exchange of the alkyl group of **3.18^{Et, Me}** for a hydride, and subsequent coordination of the borane. This is consistent with the resonances observed in the ¹¹B NMR spectrum, in the region typical for borohydride complexes and complexes of the type Me₂S·RBH₂ (e.g. Me₂S·BMeH₂ $\delta_{\text{B}} = -10.3$ ppm).¹³¹ As such, release of the [OB(H)OMe] unit *via* Al-H bond formation does not appear feasible, and the possibility for catalytic conversion in the Me₂S·BH₃/CO₂ system using **3.4^{Et}** is ruled out.

3.4.3.10 Stoichiometric studies: regeneration of aluminium hydrides?

Whilst several interesting complexes were isolated from the reactions of aluminium formate complexes with boranes, no net Al-O bond cleavage was observed. It has been shown that, under the conditions employed in this work (and in contrast to the chemistry reported by Roesky),³⁷ no regeneration of aluminium hydride complexes could be brought about by an Al-O/B-H σ -bond metathesis process. A series of alternative hydride sources was therefore employed in an attempt to break the Al-O bond in formate complex **3.6^{Et}** and regenerate the aluminium hydride **3.4^{Et}**.

A solution of **3.6^{Et}** in benzene-d₆ was treated with an excess of Et₃SiH (10 equiv.) and the reaction monitored by ¹H NMR spectroscopy. No reactivity was observed after the solution was heated to 80°C for 48 h. A similar treatment of **3.6^{Et}** with excess CaH₂ in THF also yielded no regeneration of the hydride.

The use of aluminium hydride sources, however, was more promising. The addition of excess Me₃N·AlH₃ (3 equiv.) to a benzene-d₆ solution of **3.6^{Et}** at room temperature leads

to the immediate regeneration of **3.4^{Et}**; the formate-containing products could not be identified. The use of LiAlH₄ also leads to the formation of **3.4^{Et}** from **3.6^{Et}**. It has been demonstrated that the germylene formate [Dipp₃Ge(OC(O)H)] readily reacts with Me₃N·AlH₃ to afford deuterated methanol upon hydrolysis with D₂O.²¹ This was proposed to proceed *via* formation of the germa-bora-acetal complex [Dipp₃Ge(OCH₂OAlH₂·NMe₃)], which can undergo further reaction with Me₃N·AlH₃ to regenerate the hydridogermylene LGeH and form (NMe₃H₂AlO)₂CH₂. This is then suggested to react with Me₃N·AlH₃ to form MeO(AlH₂·NMe₃) and O(AlH₂·NMe₃)₂. These intermediates/products were not identified in the reaction of **3.6^{Et}** with an excess or a deficiency of Me₃N·AlH₃. When **3.6^{Et}** is reacted with a deficiency of Me₃N·AlH₃, the formate is mostly converted to hydride and a trace amount of **3.15^{Et}** is observed, suggesting that the reaction might proceed *via* a different mechanism to that suggested by Driess *et al.*²¹

This work demonstrates that regeneration of the aluminium hydride **3.4^{Et}** from **3.6^{Et}** is possible in the presence of a hydride source of sufficient reactivity and where Al-O/E-H σ -bond metathesis is thermodynamically favourable. The employment of Me₃N·AlH₃ as a reductant in the catalytic reduction of CO₂ is not however practically feasible due to the propensity of alane itself to react with CO₂.

3.5 Conclusions and suggestions for further work

The work in this chapter demonstrates unprecedented synthetic routes for the preparation of Nacnac-ligated aluminium hydrides and a range of novel aluminium hydrides of the type (Nacnac)Al(R)H has been synthesised, offering variation in the auxiliary R substituent and in the Nacnac backbone itself. These show significant

Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂ and boranes

variation in the nature of the Al-H bond, as signalled by wide variation in their measured IR stretching frequencies. A comparison of the hydrides which bear the novel amino-functionalised Nacnac ligand with their more traditional Nacnac counterparts revealed (small) differences in the Al-H stretching frequencies which suggest that the amino-groups of this ligand might function primarily as σ -electron withdrawing substituents in this case.

The reactivity of a range of Nacnac-ligated aluminium hydride complexes [Dipp¹/2]Al(R)H towards CO₂ has subsequently been investigated. These complexes show markedly increased rates of reactivity compared to their gallium counterparts, consistent with the greater polarity of the Al-H bond. In addition to this, significant variation in the reactivity of these alanes towards CO₂ is observed. This correlates with the electronic character of the aluminium-bound R substituent; electron-donating R groups give rise to weaker (and presumably more hydridic) Al-H bonds, leading to enhanced rates of reactivity towards CO₂ whilst electron-withdrawing substituents inhibit hydroalumination of CO₂. The alanes which bear the electronically-modified N-nacnac ligand exhibit significantly enhanced reactivity towards CO₂; this is proposed to arise on steric, rather than electronic grounds.

A series of catalytic and stoichiometric reactivity studies reveal reactivity which is in line with the properties typically associated with aluminium: high Lewis acidity, polarised Al-H bonds and extremely strong Al-O bonds. The combination of the aluminium hydrides reported in this chapter with boranes which feature more Lewis acidic boron centres led to the isolation of a range of novel borohydride complexes. The formation of such complexes is consistent with behaviour typical of aluminium hydrides and a number of similar complexes have been reported in the literature.

Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂ and boranes

With a view to probing the viability of the steps needed for catalytic turnover in the reduction of CO₂, the reactions of [Dipp¹/2]Al(R)(OC(O)H) with a range of boranes have been investigated. In the case of pinacolborane, no reactivity is observed even under forcing conditions. The reactivity of these complexes with a range of more Lewis acidic boranes was shown to be typically governed by the formation of the maximum number of Al-O and B-O bonds and no overall Al-O bond breakage *via* an Al-O/B-H metathesis step. The use of HBcat and {H(9-BBN)}₂ ultimately yields products of the type [Dipp¹]Al(Et)(OBX₂) involving cleavage of one of the C-O bonds in CO₂. In the {H(9-BBN)}₂ case, this chemistry can be shown explicitly to proceed *via* an acetal intermediate of the type [Dipp¹]Al(Et)(OCH₂O(9-BBN)). Under forcing conditions in the presence of excess {H(9-BBN)}₂, this species is cleaved to give products ([Dipp¹]Al(Et)(O(9-BBN)) and [Dipp¹]Al(Et)(OMe) - in which the Al-O bond is invariably retained. In the case of Me₂S·BH₃, the major product, [Dipp¹]Al(Et)(OB(H)OMe), also features an Al-O-B unit. This study allowed for the isolation of a series of complexes which have been previously alluded to as intermediates within the borane-mediated catalytic reduction of CO₂ but have rarely been observed spectroscopically. This provides further mechanistic insight into how such systems may operate under catalytic conditions.

The inability of boranes to regenerate the aluminium hydrides from Al-O/B-H metathetical pathways is consistent with literature-tabulated E-H/E-O bond strengths for E = B and Al (E-H: 377, 282 kJ mol⁻¹; E-O: 559, 585 kJ mol⁻¹) which imply that Al-O/B-H metathesis is likely to be thermodynamically unfavourable (> +120 kJ mol⁻¹).^{67,125} Additionally, the inability of these hydrides to act as catalysts for this process suggests that no viable alternative mechanistic pathway operates under catalytic conditions. Therefore, in our hands, the non-viability of Al-O/B-H metathesis pathways that are key

to catalytic turnover suggests that the potential of aluminium hydrides to act as catalysts for processes which involve this pathway is very limited.

This observation has led to two further fields of work. It has been shown that gallium hydride complexes can bring about the catalytic reduction of CO₂, albeit with relatively low turnover frequencies. Mechanistically, the viability of both the CO₂ insertion and Ga-O/B-H metathesis steps key to catalytic turnover were demonstrated *via* independent stoichiometric reactions.²³ This is consistent with reported E-H/E-O bond strengths for E = B and Ga (E-H: 377, 260 kJ mol⁻¹; E-O: 559, 430 kJ mol⁻¹) which imply that (unlike the corresponding aluminum chemistry) Ga-O/B-H metathesis should be thermodynamically favourable (albeit marginally so).^{67,125} Improvement of the reported catalysis might arise from an understanding of how this catalyst, and related gallium hydrides operate in the key turnover steps (Chapter 4).

Additionally, reports of the catalytic hydroboration of benzaldehyde (and related carbonyl functionalities) by aluminium hydrides invoke catalytic turnover *via* an Al-O/B-H metathesis process of a type superficially similar to those which were demonstrated in this chapter to be unfeasible.^{35,37-39} In-depth study of these systems might allow for an understanding of the differences inherent in Roesky's system which apparently allow for Al-O/B-H metathesis (Chapter 6).

3.6 References

- (1) Huang, K.; Sun, C.-L.; Shi, Z.-J. *Chem. Soc. Rev.* **2011**, 40 (5), 2435–2452.
- (2) Schneider, J.; Jia, H.; Muckerman, J. T.; Fujita, E. *Chem. Soc. Rev.* **2012**, 41 (6), 2036–2051.
- (3) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *Nature Communications*. 6, **2015**, 5933–5948.
- (4) Murphy, L. J.; Robertson, K. N.; Kemp, R. A.; Tuononen, H. M.; Clyburne, J. A. C. *Chem. Commun.* **2015**, 51 (19), 3942–3956.
- (5) Tlili, A.; Blondiaux, E.; Frogneux, X.; Cantat, T. *Green Chem.* **2015**, 17 (1), 157–168.
- (6) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. *J. Am. Chem. Soc.* **2010**, 132 (26), 8872–8873.
- (7) Chakraborty, S.; Zhang, J.; Patel, Y. J.; Krause, J. A.; Guan, H. *Inorg. Chem.* **2013**, 52 (1), 37–47.
- (8) Shintani, R.; Nozaki, K. *Organometallics* **2013**, 32 (8), 2459–2462.

Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂ and boranes

- (9) Suh, H.-W.; Guard, L. M.; Hazari, N. *Chem. Sci.* **2014**, 5 (10), 3859–3872.
- (10) Berkefeld, A.; Piers, W. E.; Parvez, M.; Castro, L.; Maron, L.; Eisenstein, O. *Chem. Sci.* **2013**, 4 (5), 2152–2162.
- (11) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2014**, 136 (11), 4419–4425.
- (12) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2012**, 51 (7), 1671–1674.
- (13) Jin, G.; Werncke, C. G.; Escudié, Y.; Sabo-Etienne, S.; Bontemps, S. *J. Am. Chem. Soc.* **2015**, 137 (30), 9563–9566.
- (14) Bontemps, S.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2013**, 52 (39), 10253–10255.
- (15) Huang, F.; Zhang, C.; Jiang, J.; Wang, Z. X.; Guan, H. *Inorg. Chem.* **2011**, 50 (8), 3816–3825.
- (16) Anker, M. D.; Arrowsmith, M.; Bellham, P.; Hill, M. S.; Kociok-Köhn, G.; Liptrot, D. J.; Mahon, M. F.; Weetman, C. *Chem. Sci.* **2014**, 5 (7), 2826–2830.
- (17) Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. *Chem. Commun.* **2016**, 52 (89), 13155–13158.
- (18) Mukherjee, D.; Osseili, H.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2016**, 138 (34), 10790–10793.
- (19) Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. *J. Am. Chem. Soc.* **2009**, 131 (3), 1288–1293.
- (20) Jana, A.; Roesky, H. W.; Schulzke, C.; Döring, A. *Angew. Chem. Int. Ed.* **2009**, 48 (6), 1106–1109.
- (21) Tan, G.; Wang, W.; Blom, B.; Driess, M. *Dalton Trans.* **2014**, 43 (16), 6006–6011.
- (22) Hadlington, T. J.; Kefalidis, C. E.; Maron, L.; Jones, C. *ACS Catal.* **2017**, 7 (3), 1853–1859.
- (23) Abdalla, J. A. B.; Riddlestone, I. M.; Tirfoin, R.; Aldridge, S. *Angew. Chem. Int. Ed.* **2015**, 54 (17), 5098–5102.
- (24) Jana, A.; Tavčar, G.; Roesky, H. W.; John, M. *Dalton Trans.* **2010**, 39 (40), 9487–9489.
- (25) Aldridge, S.; Downs, A. J. *Chem. Rev.* **2001**, 101 (11), 3305–3365.
- (26) Kuo, P. C.; Chen, I. C.; Chang, J. C.; Lee, M. T.; Hu, C. H.; Hung, C. H.; Lee, H. M.; Huang, J. H. *Eur. J. Inorg. Chem.* **2004**, (24), 4898–4906.
- (27) Myers, T. W.; Berben, L. A. *Chem. Sci.* **2014**, 5 (7), 2771–2777.
- (28) A. E. Finholt, E. C. J. *J. Am. Chem. Soc.* **1952**, 74 (15), 3943–3944.
- (29) Li, W.; Ma, X.; Walawalkar, M. G.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2017**, 350, 14–29.
- (30) Nikonov, G. I. *ACS Catal.* **2017**, 7 (10), 7257–7266.
- (31) Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H. W. *J. Am. Chem. Soc.* **2016**, 138 (8), 2548–2551.
- (32) Romero, E. A.; Peltier, J. L.; Jazzar, R.; Bertrand, G. *Chem. Commun.* **2016**, 52 (69), 10563–10565.
- (33) Bismuto, A.; Thomas, S. P.; Cowley, M. J. *Angew. Chem. Int. Ed.* **2016**, 55 (49), 15356–15359.
- (34) Bismuto, A.; Cowley, M. J.; Thomas, S. P. *ACS Catal.* **2018**, 8 (3), 2001–2005.
- (35) Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S. Z. *Anorg. Allg. Chem.* **2016**, 642 (22), 1245–1250.
- (36) Jakobsson, K.; Chu, T.; Nikonov, G. I. *ACS Catal.* **2016**, 6 (11), 7350–7356.
- (37) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, 54 (35), 10225–10229.
- (38) Jakhar, V. K.; Barman, M. K.; Nembenna, S. *Org. Lett.* **2016**, 18 (18), 4710–4713.
- (39) Pollard, V. A.; Orr, S. A.; McLellan, R.; Kennedy, A. R.; Hevia, E.; Mulvey, R. E. *Chem. Commun.* **2018**, 54 (10), 1233–1236.
- (40) Courtemanche, M. A.; Larouche, J.; Légaré, M. A.; Bi, W.; Maron, L.; Fontaine, F. G. *Organometallics* **2013**, 32 (22), 6804–6811.
- (41) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, 132 (6), 1796–1797.
- (42) Ménard, G.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2011**, 50 (36), 8396–8399.
- (43) Ménard, G.; Stephan, D. W. *Dalton Trans.* **2013**, 42 (15), 5447–5453.
- (44) Boudreau, J.; Courtemanche, M.-A.; Fontaine, F. G. *Chem. Commun.* **2011**, 47 (39), 11131–11133.
- (45) Saleh, M.; Powell, D. R.; Wehmschulte, R. J. *Organometallics* **2017**, 36 (24), 4810–4815.
- (46) Kuhn, N.; Fuchs, S.; Steimann, M. Z. *Anorg. Allg. Chemie* **2000**, 626 (6), 1387–1392.
- (47) González-Gallardo, S.; Jancik, V.; Cea-Olivares, R.; Toscano, R. A.; Moya-Cabrera, M. *Angew. Chem. Int. Ed.* **2007**, 46 (16), 2895–2898.
- (48) Jana, B.; Uhl, W. *Inorganica Chim. Acta* **2017**, 455 (1), 61–69.
- (49) Nako, A. E.; Gates, S. J.; White, A. J. P.; Crimmin, M. R. *Dalton Trans.* **2013**, (42), 15199–15206.
- (50) Chu, T.; Korobkov, I.; Nikonov, G. I. *J. Am. Chem. Soc.* **2014**, 136 (25), 9195–9202.
- (51) Yang, Y.; Li, H.; Wang, C.; Roesky, H. W. *Inorg. Chem.* **2012**, 51 (4), 2204–2211.
- (52) Hao, H.; Mou, Z.; Zhuang, J.; Wan, P.; Li, H. *Faming Zhuanhi Shiqing* **2014**.
- (53) Chu, C.; Yang, Y.; Zhu, H. *Sci. China Chem.* **2010**, 53 (9), 1970–1977.
- (54) Zhu, H.; Yang, Z.; Magull, J.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **2005**, 24 (26), 6420–6425.

Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂ and boranes

- (55) Nako, A. E.; Gates, S. J.; Schädel, N.; White, A. J. P.; Crimmin, M. R. *Chem. Commun.* **2014**, 50 (67), 9536–9538.
- (56) Uhl, W.; Jana, B. J. *Organomet. Chem.* **2009**, 694 (7–8), 1101–1106.
- (57) Singh, S.; Ahn, H.-J.; Stasch, A.; Jancik, V.; Roesky, H. W.; Pal, A.; Biadene, M.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H. G. *Inorg. Chem.* **2006**, 45 (4), 1853–1860.
- (58) Zhu, H.; Chai, J.; He, C.; Bai, G.; Roesky, H. W.; Jancik, V.; Schmidt, H. G.; Noltemeyer, M. *Organometallics* **2005**, 24 (3), 380–384.
- (59) Yang, Y.; Schulz, T.; John, M.; Yang, Z.; Jimenez-Perez, V. M.; Roesky, H. W.; Gurubasavaraj, P. M.; Stalke, D.; Ye, H. *Organometallics* **2008**, 27 (4), 769–777.
- (60) Yang, Y.; Gurubasavaraj, P. M.; Ye, H.; Zhang, Z.; Roesky, H. W.; Jones, P. G. *J. Organomet. Chem.* **2008**, 693 (8–9), 1455–1461.
- (61) Do, D. C. H.; Keyser, A.; Protchenko, A. V.; Maitland, B.; Pernik, I.; Niu, H.; Kolychev, E. L.; Rit, A.; Vidovic, D.; Stasch, A.; Jones, C.; Aldridge, S. *Chem. Eur. J.* **2017**, 23 (24), 5830–5841.
Do, D. C. H.; Protchenko, A. V.; Vasko, P.; Campos, J.; Kolychev, E.; Aldridge, S. *Z. Anorg. Allg. Chemie.* **2018**, DOI:10.1002/zaac.201800259
- (62) Yang, Z.; Zhu, H.; Ma, X.; Chai, J.; Roesky, H. W.; He, C.; Magull, J.; Schmidt, H. G.; Noltemeyer, M. *Inorg. Chem.* **2006**, 45 (4), 1823–1827.
- (63) Cui, C.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem. Int. Ed.* **2000**, 39 (23), 4274–4276.
- (64) Qian, B.; Ward, D. L.; Smith, M. R. *Organometallics* **1998**, 17 (14), 3070–3076.
- (65) Gong, S.; Ma, H. *Dalton Trans.* **2008**, (25), 3345–3357.
- (66) Martin Badertscher; Philippe Bühlmann; Ernö Pretsch. *Structure Determination of Organic Compounds*; Springer, Heidelberg, Berlin, Germany.
- (67) Downs, A. J.; Himmel, H. J. in *The Group 13 Metals Aluminium, Gallium, Indium and Thallium; Chemical Patterns and Peculiarities* (Eds.: S. Aldridge, A.J. Downs) Wiley, Chichester, UK.
- (68) Cui, C.; Roesky, H. W.; Hao, H.; Schmidt, H. G.; Noltemeyer, M. *Angew. Chem. Int. Ed.* **2000**, 39 (10), 1815–1817.
- (69) Twamley, B.; Hardman, N. J.; Power, P. P. *Acta Crystallogr. E* **2001**, 57 (6), 227–228.
- (70) Cowley, A. H.; Isom, H. S.; Decken, A. *Organometallics* **1995**, 14 (5), 2589–2592.
- (71) Vidovic, D.; Jones, J. N.; Moore, J. A.; Cowley, A. H. *Z. Anorg. Allg. Chem.* **2005**, 631 (13–14), 2888–2892.
- (72) Stender, M.; Eichler, B. E.; Hardman, N. J.; Power, P. P.; Prust, J.; Noltemeyer, M.; Roesky, H. W. *Inorg. Chem.* **2001**, 40 (12), 2794–2799.
- (73) Kuhn, N.; Fuchs, S.; Steimann, M. *Z. Anorg. Allg. Chem.* **2000**, 626 (6), 1387–1392.
- (74) Yang, Y.; Li, H.; Wang, C.; Roesky, H. W. *Inorg. Chem.* **2012**, 51 (4), 2204–2211.
- (75) Chen, C.; Bellows, S. M.; Holland, P. L. *Dalton Trans.* **2015**, 44 (38), 16654–16670.
- (76) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc. Perkin Trans.* **1987**, (12), S1.
- (77) Badger, R. M. *J. Chem. Phys.* **1934**, 2 (3), 128–131.
- (78) Ziegler, K.; Krupp, F.; Weyer, K.; Larbig, W. *Justus Liebigs Ann. Chem.* **1960**, 629 (1), 251–256.
- (79) Chong, C. C.; Kinjo, R. *ACS Catal.* **2015**, 5 (6), 3238–3259.
- (80) Courtemanche, M. A.; Légaré, M. A.; Maron, L.; Fontaine, F. G. *J. Am. Chem. Soc.* **2014**, 136 (30), 10708–10717.
- (81) Pereira, S.; Srebnik, M. *Organometallics* **1995**, 14 (7), 3127–3128.
- (82) Kyri, A. W.; Kunzmann, R.; Schnakenburg, G.; Qu, Z.-W.; Grimme, S.; Streubel, R. *Chem. Commun.* **2016**, 52 (91), 13361–13364.
- (83) Bernabé-Pablo, E.; Jancik, V.; Martínez-Otero, D.; Barroso-Flores, J.; Moya-Cabrera, M. *Inorg. Chem.* **2017**, 56 (14), 7890–7899.
- (84) Yang, Z.; Ma, X.; Oswald, R. B.; Roesky, H. W.; Noltemeyer, M. *J. Am. Chem. Soc.* **2006**, 128 (38), 12406–12407.
- (85) Ma, X.; Yang, Z.; Wang, X.; Roesky, H. W.; Wu, F.; Zhu, H. *Inorg. Chem.* **2011**, 50 (5), 2010–2014.
- (86) Yang, Z.; Hao, P.; Liu, Z.; Ma, X.; Roesky, H. W.; Li, J. *J. Organomet. Chem.* **2014**, 751, 788–791.
- (87) Jaśkowska, E.; Justyniak, I.; Cyrański, M. K.; Adamczyk-Woźniak, A.; Sporyński, A.; Zygałło-Monikowska, E.; Ziemkowska, W. *J. Organomet. Chem.* **2013**, 732, 8–14.
- (88) Anulewicz-ostrowska, R.; Lulin, S.; Serwatowski, J. *Inorg. Chem.* **1999**, 38 (17), 3796–3800.
- (89) Anulewicz-Ostrowska, R.; Luliński, S.; Serwatowski, J.; Suwińska, K. *Inorg. Chem.* **2000**, 39 (25), 5763–5767.
- (90) Synoradzki, L.; Boleśławski, M.; Lewiński, J. *J. Organomet. Chem.* **1985**, 284 (1), 1–4.
- (91) Gibson, V. C.; Mastroianni, S.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2001**, 40 (5), 826–827.

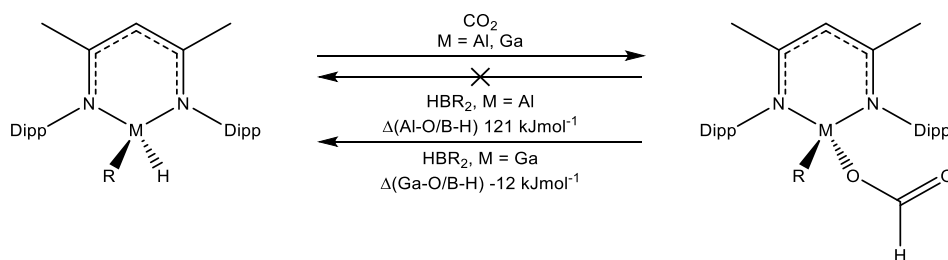
Chapter III: Investigation of the reactivity of β -diketiminato-ligated aluminium hydrides towards CO₂ and boranes

- (92) Yang, Y.; Anker, M. D.; Fang, J.; Mahon, M. F.; Maron, L.; Weetman, C.; Hill, M. S. *Chem. Sci.* **2017**, *8* (5), 3529–3537.
- (93) Harder, S.; Spielmann, J. *Chem. Commun.* **2011**, 47 (43), 11945–11947.
- (94) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123* (34), 8291–8309.
- (95) Knabel, K.; Krossing, I.; Noeth, H.; Schwenk-Kircher, H.; Schmidt-Amelunxen, M.; Seifert, T. *Eur. J. Inorg. Chem.* **1998**, (8), 1095–1114.
- (96) Erdmann, M.; Rösener, C.; Holtrichter-Rößmann, T.; Daniliuc, C. G.; Fröhlich, R.; Uhl, W.; Würthwein, E.-U.; Kehr, G.; Erker, G. *Dalton Trans.* **2013**, 42 (3), 709–718.
- (97) Burlakov, V. V.; Kaleta, K.; Beweries, T.; Arndt, P.; Baumann, W.; Spannenberg, A.; Shur, V. B.; Rosenthal, U. *Organometallics* **2011**, *30* (5), 1157–1161.
- (98) Hecht, E. *Appl. Organomet. Chem.* **2005**, *19* (3), 390–390.
- (99) Dümichen, U.; Gelbrich, T.; Sieler, J. *Z. Anorg. Allg. Chem.* **2001**, 627 (8), 1915–1920.
- (100) Sizov, A. I.; Molodnitskaya, I. V.; Bulychev, B. M.; Evdokimova, E. V.; Soloveichik, G. L.; Gusev, A. I.; Chuklanova, E. B.; Andrianov, V. I. *J. Organomet. Chem.* **1987**, 335 (3), 323–330.
- (101) Cui, C.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G. *Organometallics*, **1999**, *18* (24), 5120–5123.
- (102) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, (21), 2832–2838.
- (103) Aldridge, S.; Blake, A. J.; Downs, A. J.; Gould, R. O.; Parsons, S.; Pulham, C. R. *J. Chem. Soc. Trans.* **1997**, (6), 1007–1012.
- (104) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77* (2), 263–293.
- (105) Hubbard, J. L.; Kramer, G. W. *J. Organomet. Chem.* **1978**, 156 (1), 81–94.
- (106) Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A. *Organometallics* **2007**, *26* (16), 4076–4079.
- (107) Spielmann, J.; Harder, S. *Chem. Eur. J.* **2007**, *13* (32), 8928–8938.
- (108) Hubbard, J. L. P. D. T. Doctoral Thesis, Purdue University, 1977.
- (109) Chu, J.; Han, X.; Kefalidis, C. E.; Zhou, J.; Maron, L.; Leng, X.; Chen, Y. *J. Am. Chem. Soc.* **2014**, *136* (31), 10894–10897.
- (110) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73* (1), 1–15.
- (111) Köster, R.; Tsay, Y.-H.; Krüger, C.; Serwatowski, J. *Chem. Ber.* **1986**, *119* (4), 1174–1188.
- (112) Das Neves Gomes, C.; Blondiaux, E.; Thuéry, P.; Cantat, T. *Chem. Eur. J.* **2014**, *20* (23), 7098–7106.
- (113) Geier, S. J.; Vogels, C. M.; Westcott, S. A. In *ACS Symposium Series*. **2016**, *1236*, 209–225.
- (114) *Boron Reagents in Synthesis* (Ed.: A. Coca), *ACS Symposium Series*, **2016**, Vol. 1236.
- (115) Courtemanche, M. A.; Légaré, M. A.; Maron, L.; Fontaine, F. G. *J. Am. Chem. Soc.* **2013**, *135* (25), 9326–9329.
- (116) Wang, T.; Stephan, D. W. *Chem. Eur. J.* **2014**, *20* (11), 3036–3039.
- (117) Yang, Y.; Xu, M.; Song, D. *Chem. Commun.* **2015**, 51 (56), 11293–11296.
- (118) Fujiwara, K.; Yasuda, S.; Mizuta, T. *Organometallics* **2014**, *33* (22), 6692–6695.
- (119) Ho, S. Y.-F.; So, C.-W.; Saffon-Merceron, N.; Mézailles, N. *Chem. Commun.* **2015**, 51 (11), 2107–2110.
- (120) Sau, S. C.; Bhattacharjee, R.; Vardhanapu, P. K.; Vijaykumar, G.; Datta, A.; Mandal, S. K. *Angew. Chem. Int. Ed.* **2016**, *55* (48), 15147–15151.
- (121) Lafage, M.; Pujol, A.; Saffon-Merceron, N.; Mézailles, N. *ACS Catal.* **2016**, *6* (5), 3030–3035.
- (122) Légaré, M.-A.; Courtemanche, M. A.; Fontaine, F. G. *Chem. Commun.* **2014**, 50 (77), 11362–11365.
- (123) Ramos, A.; Antiñolo, A.; Carrillo-Hermosilla, F.; Fernandez-Galan, R.; Rodríguez Diéguez, A.; García-Vivó, D. G. *Chem. Commun.* **2018**, 4700 (54), 4700–4703.
- (124) Harder, S.; Spielmann, J. *Chem. Commun.* **2011**, 47 (43), 11945–11947.
- (125) Glockler, G. *Trans. Faraday Soc.* **1963**, *59*, 1080–1085.
- (126) Empsall, H. D.; Mentzer, E.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1975**, (21), 861–862.
- (127) Onak, T. P.; Landesman, H.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *63* (9), 1533–1535.
- (128) Lesley, M. J. G.; Woodward, A.; Taylor, N. J.; Marder, T. B.; Cazenobe, I.; Ledoux, I.; Zyss, J.; Thornton, A.; Bruce, D. W.; Kakkar, A. K. *Chem. Mater.* **1998**, *10* (5), 1355–1365.
- (129) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97* (18), 5249–5255.
- (130) M. Diem, in *Modern Vibrational Spectroscopy and Micro-Spectroscopy*, Wiley, Chichester, **2015**, 397–398.
- (131) Brown, H. C.; Cole, T. E.; Srebnik, M.; Kim Richard, K.-W. B. *J. Org. Chem.* **1986**, *51*, 4925–4930.

4. Synthesis of novel gallium hydrides and their potential as catalysts for the borane-mediated reduction of CO₂

4.1 Introduction

The work in this chapter builds on that outlined in Chapter 3 which focused on the development of novel Nacnac-ligated aluminium hydrides and an investigation of their ability to function as catalysts for the borane-mediated catalytic reduction of CO₂. It was demonstrated that a number of these aluminium hydrides react readily with CO₂ to yield the corresponding formate complexes but do not possess the capacity to reduce CO₂ in a catalytic manner. The reactivity of these aluminium formate complexes with a range of boranes is dominated by maximising the number of strong Al-O and B-O bonds. However, no Al-O/B-H metathesis and no overall Al-O bond breakage was observed; the inability of the boranes employed to regenerate the aluminium hydrides accounts for their inability to function as catalysts. A comparison of reported E-H/E-O bond strengths for E = B and Ga (E-H: 377, 260 kJ mol⁻¹; E-O: 559, 430 kJ mol⁻¹) suggests that Ga-O/B-H metathesis should be thermodynamically favourable and that gallium hydrides might be better suited for use as catalysts for processes which feature M-O/B-H metathetical steps.¹



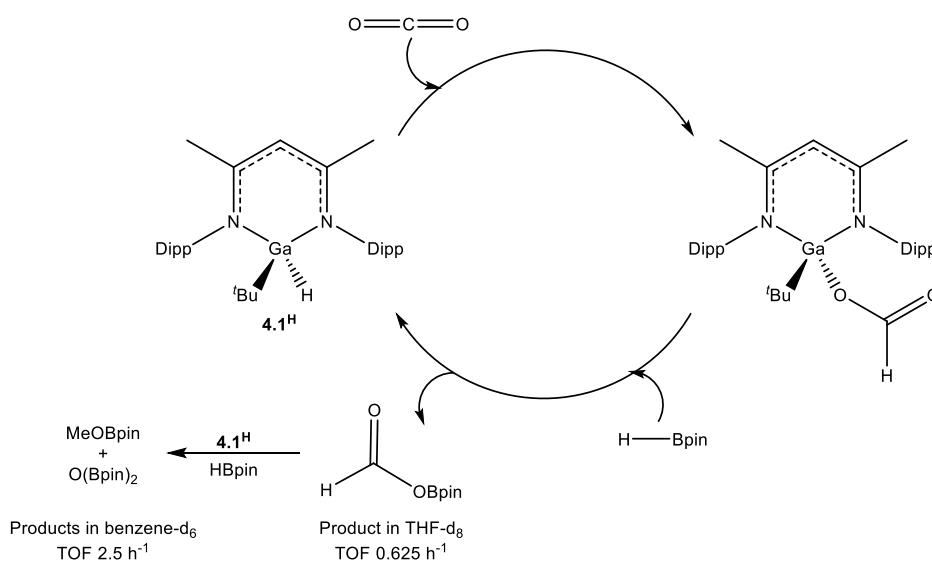
Scheme 4.1: The two steps which are key to catalytic turnover for the reduction of CO₂, employing a single-site metal-centred catalyst.

One of the dominant modes of reactivity of gallium hydrides is hydrogallation of unsaturated C=E bonds. There are many reported examples of the insertion of Ga-H bonds into alkenes and alkynes,²⁻⁸ and examples of the hydrogallation of C=N bonds have also been described.^{9,10} There is much less literature precedent for the insertion of Ga-H bonds into C=O bonds; and most of those reported only involve the stoichiometric reduction of these functionalities.¹¹ Key examples include reactions towards α,β -unsaturated ketones, where insertion into the C=C and C=O bonds compete,¹² and CO₂. There are two reported examples of gallium hydrides which react with CO₂ *via* insertion of the Ga-H bond to yield a gallium formate complex.^{13,14} These include a Nacnac-ligated monohydride, [Dipp $\mathbf{1}$] $\text{Ga}(t\text{Bu})\text{H}$ (**4.1^{tBu}**) (Scheme 4.2), and a gallium hydride stabilised by an amino donor, $(\text{CH}_3)\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{GaH}$.

Despite the proclivity of gallium hydrides for hydrometallation of unsaturated functionalities, there are very few reports of the exploitation of this reactivity catalytically. In 2000, LiGaH_4 was used in combination with the S,O-chelate 2-hydroxy-2'-mercapto-1,1'-binaphthyl (MTBH₂), to form an active catalyst for the asymmetric reduction of prochiral ketones, with catecholborane as the hydride source.¹⁵

In 2015, it was shown by our group that **4.1^{tBu}** may catalytically reduce carbon dioxide selectively to either methanol or formic acid equivalents, when HBpin is used as the

hydrogen source.¹⁴ Placing of a 10 mol% solution of **4.1^{tBu}** and HBpin in benzene-d₆ under CO₂ (*ca.* 2 bar) selectively yields the methanol derivative MeOBpin and the diboroxane O(Bpin)₂ with a turnover frequency of 2.5 h⁻¹ when heated to 60°C. If the reaction is carried out in THF-d₈, the reaction proceeds more slowly and yields HC(O)OBpin as the major product with a TOF of 0.625 h⁻¹. Both of these product profiles are consistent with those previously reported for catalytic CO₂ reduction where HBpin/HBcat is used as the reductant.^{16–18} **4.1^{tBu}** represents one of the few examples of main group metal hydride catalysts for this process, together with the Nacnac-ligated alkaline earth metal hydrides [Dipp**1**]MH (M = Mg, Ca) reported by Hill *et al.* (which use B(C₆F₅)₃ as a co-catalyst) and group 14 M(II) hydrides ligated by bulky amido ligands (L = N(Si(*i*Pr)₃Ar) (Ar = C₆H₂Pr^{*i*}-{C(H)Ph₂}_{2-4,2,6})) reported by the group of Jones.^{16,17} The latter catalysts operate under ambient conditions and yield turnover frequencies which rival those reported for transition metal hydride catalysts (1 mol% (Ar(*i*Pr₃Si)N)SnH (Ar = C₆H₂Pr^{*i*}-{C(H)Ph₂}_{2-4,2,6}), 298 K; HBpin TOF = 14.5 h⁻¹; HBcat TOF = 1188 h⁻¹).¹⁷



Scheme 4.2: An example of a gallium hydride which effects the hydrogallation of CO₂ and the proposed catalytic cycle for the reduction of CO₂ by **4.1^{tBu}**.¹⁴

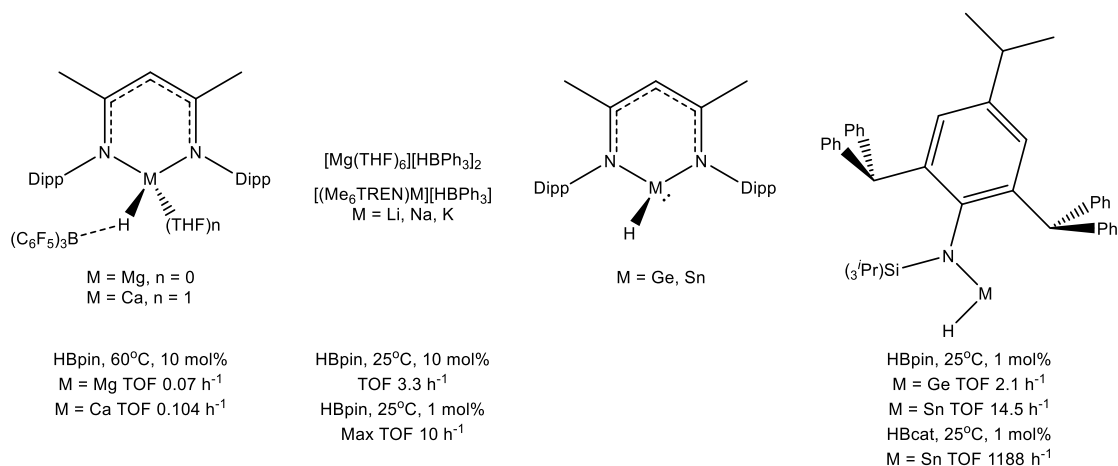
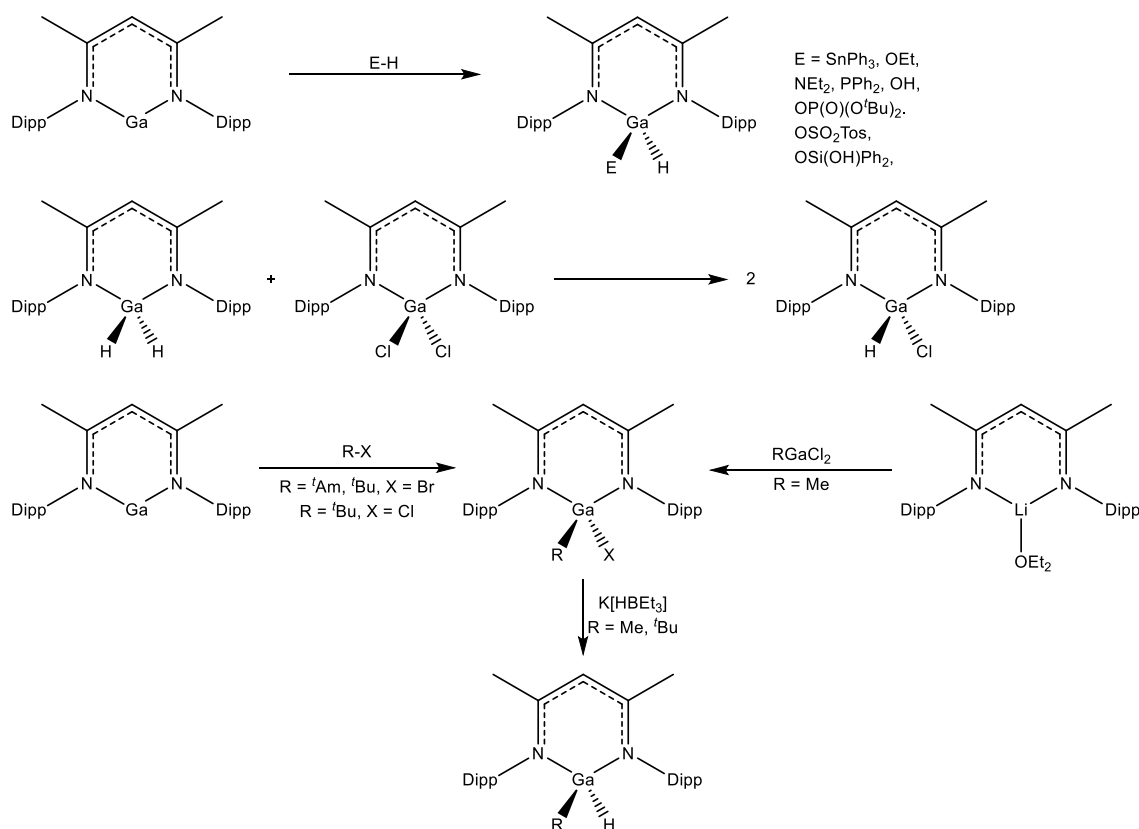


Figure 4.1: Examples of main group metal hydride complexes which catalyse the reduction of CO₂ using boranes as a reductant.^{14,16,17,19–22}

Only rudimentary investigation of how **4.1^{tBu}** operates as a catalyst was undertaken. It was suggested that the catalysis proceeds by insertion of CO₂ into the Ga-H bond, followed by a series of Ga-O/B-H σ-bond metathesis and reinsertion steps, in a similar manner to the mechanistic routes which have been computationally assessed for related systems.¹⁷ The two steps critical to turnover in this catalytic process - insertion of CO₂ into the Ga-H bond and metathesis with HBpin to generate a formate ester, were independently verified *via* stoichiometric reactions. The work in Chapter 3 showed significant variation in the lability of aluminium hydrides of the form [DippX]Al(R)H towards CO₂ as a function of the electronic properties of the R group and the ligand. An exploration of the factors that favour insertion of CO₂ into the Ga-H bond of related complexes may lead to the enhancement of the catalytic activity of gallane systems.

The library of reported Nacnac-ligated gallium hydrides is significantly less well developed than for aluminium and most of their established chemistry is derived from the gallium dihydride complexes [R¹]GaH₂ (R = Ph, Mes, Dipp).^{24–26} There has been no reported use of electronically-modified Nacnac ligands in gallium hydride chemistry and variation of these complexes by modification of the ligand is limited to that of the

N-bound Aryl groups $[\text{R}^1]\text{GaH}_2$ ($\text{R} = \text{Ph}, \text{Mes}, \text{Dipp}$).^{24–26} These complexes may be synthesised by deprotonation of the corresponding protio-ligand by $\text{EtMe}_2\text{N}\cdot\text{GaH}_3$ or LiGaH_4 (for $\text{R} = \text{Ph}$) or by treatment of $[\text{Dipp}^1]\text{GaX}_2$ ($\text{X} = \text{I}, \text{Cl}$) or $([\text{Mes}^1]\text{GaCl})_2(\mu\text{-O})$ with $\text{M}[\text{HBEt}_3]$ ($\text{M} = \text{Li}, \text{K}$) or $\text{Me}_3\text{N}\cdot\text{AlH}_3$, respectively.^{24–26} Unsymmetrically substituted complexes of the form $[\text{Dipp}^1]\text{Ga}(\text{R})\text{H}$ can potentially be synthesised *via* three different routes (Scheme 4.3).^{14,23,24,27,28} These involve activation of a polarised E-H bond at the Ga(I) centre of $[\text{Dipp}^1]\text{Ga}$, intermolecular H/Cl exchange, or metathesis of a gallium halide with a borohydride, such as $\text{K}[\text{HBEt}_3]$. The latter method is employed to synthesise alkyl-substituted $[\text{Dipp}^1]\text{Ga}(\text{R})\text{H}$ complexes; their precursor halide complexes may be prepared from the activation of the C-X bond of a haloalkane by $[\text{Dipp}^1]\text{Ga}$ or a metathetical reaction of $[\text{Dipp}^1]\text{Li}(\text{OEt})_2$ with RGaCl_2 sources.^{14,24,29}



Scheme 4.3: The synthetic routes reported in the literature for the synthesis of unsymmetrically substituted Nacnac-ligated gallium hydride complexes.^{14,23,24}

4.2 Project aims

It has been demonstrated that gallium hydrides have the potential to catalyse the selective reduction of CO₂ into methanol derivatives using HBpin as a hydrogen source, albeit with relatively low turnover frequencies and under forcing conditions. The proposed rate determining step, insertion of CO₂ into the Ga-H bond, is relatively slow in the case of **4.1**^{tBu}. The development of related aluminium systems (Chapter 3) showed marked improvement of this insertion chemistry by virtue of the greater polarity of the M-H bond. This study showed the importance of the hydricity of the M-H bond in its interaction with the electrophilic carbon centre of CO₂ and hence its ability to undergo hydrometallation with CO₂. These systems could not function in a catalytic manner, however, due to prohibitive factors associated with Al-O/B-H metathesis processes and hence regeneration of the aluminium hydride.

Enhancement of the catalytic activity of the related gallium systems may arise from the determination of the factors which favour insertion of CO₂ into the Ga-H bond. This may be achieved through modification of these systems by variation of the gallium-bound R substituent. The initial aim of this work was to explore different synthetic routes for the formation of unsymmetrically substituted Nacnac-ligated gallium hydrides. The reactivity towards CO₂ of novel hydrides, together with those reported in the literature, was then to be probed to investigate the impact that the electronic and steric characteristics of the gallium-bound substituents have on such reactivity.

There is little experimental data on the mechanism by which the reported catalysis proceeds, although it is proposed to follow a similar mechanism to those calculated for related systems.¹⁷ Accordingly, this will be studied by examining the reactions of gallium formate complexes with a range of boranes (HBpin, HBcat, {H(9-BBN)}₂, Me₂S·BH₃)

under stoichiometric conditions. These studies will also probe the influence that the gallium-bound R substituent has on the borane-mediated regeneration of the gallium hydride and provide a useful comparison with the reactivity of the aluminium formate complexes reported in Chapter 3. The catalytic activity of promising systems will be investigated.

4.3 Experimental details

Preparation of {HC(MeCNDipp)₂}Ga(OTf)H – [Dipp1]Ga(OTf)H (4.1^{OTf})

Method A: MeOTf (0.30 g, 2.04 mmol) was added dropwise to a solution of [Dipp1]GaH₂ (1.0 g, 2.04 mmol) in toluene (15 mL) at 0°C. The colourless reaction mixture was allowed to warm to room temperature and stirred for 72 h, followed by removal of volatiles *in vacuo*. The resulting white solid residue was re-extracted into minimal toluene, filtered and stored at –30°C, yielding large colourless single crystals of the toluene solvate overnight. Yield: 0.71 g, 55%.

Method B: MeOTf (0.067 g, 0.45 mmol) was added to a solution of [Dipp1]Ga(H)(OC(O)H) (0.22 g, 0.41 mmol) in toluene (5 mL) at room temperature and stirred for 15 h. The removal of volatiles *in vacuo* yielded a spectroscopically pure, crystalline sample of 4.1^{OTf}. Yield: 0.18, 69%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 1.04, 1.11, 1.27, 1.49 (6H, s, CH₃ of β-diketiminato backbone), 1.52 (6H, d, ³J_{HH} = 6.9 Hz, CH₃ of Dipp ⁱPr), 2.99 (2H, sept, ³J_{HH} = 6.9 Hz, CH of Dipp ⁱPr), 3.25 (2H, sept, ³J_{HH} = 6.9 Hz, CH of Dipp ⁱPr), 4.76 (1H, s, γ-CH), 5.62 (1H, br s, GaH), 6.96 – 7.20 (6H, m, aromatic CH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_C 23.1 (CH₃ of β-diketiminato backbone), 24.4, 24.8, 24.9, 25.0 (CH₃ of Dipp ⁱPr), 28.6, 28.7 (CH of Dipp ⁱPr), 96.7 (γ-CH), 124.9, 125.2, 128.5,

137.7, 143.5, 144.4 (ArC of Dipp), 171.2 (NC). Resonance for CF₃ not observed. **¹⁹F NMR** (376 MHz, benzene-d₆, 298 K): δ_F -77.5.

¹H NMR (400 MHz, tetrahydrofuran-d₈, 298 K): δ_H 1.21, 1.29 (12H, d, $^3J_{HH}$ = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.92 (6H, s, CH₃ of β -diketiminato backbone), 3.11 (4H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ⁱPr), 5.30 (1H, br s, GaH), 5.37 (1H, s, γ -CH), 7.05 – 7.35 (6H, m, aromatic CH).

¹³C{¹H} NMR (126 MHz, tetrahydrofuran-d₈, 298 K): δ_C 23.6 (CH₃ of β -diketiminato backbone), 24.8, 25.2 (CH₃ of Dipp ⁱPr), 29.2 (CH of Dipp ⁱPr), 97.6 (γ -CH), 125.5, 128.8, 138.5, 144.7 (ArC of Dipp), 172.2 (NC). **¹⁹F NMR** (376 MHz, tetrahydrofuran-d₈, 298 K): δ_F - 78.66. **EI-MS**: m/z calc for C₃₀H₄₂N₂GaF₃O₃S ([M]⁺) 636.2119, meas. 636.214 (4%).

IR (nujol/cm⁻¹): ν_{Ga-H} 1994 (s). **Elemental microanalysis**: calc. for C₃₀H₄₂N₂GaO₃F₃S: C 56.53% H 6.64% N 4.39% meas. C 56.63% H 6.76% N 4.48%.

Preparation of [{HC(MeCNDipp)₂}Ga(DMAP)H][OTf] - [[^{Dipp}1]Ga(DMAP)H][OTf] (4.2)

To a solution of [^{Dipp}1]Ga(OTf)H (0.39 g, 0.612 mmol) in toluene (2 mL) was added at room temperature a solution of DMAP (0.08 g, 0.654 mmol) also in toluene (1 mL), and the reaction mixture stirred for 2 h. The reaction mixture was concentrated to the point of incipient crystallisation, filtered and layered with *n*-hexane. Over the course of 3 d, large colourless block-like crystals (of the toluene hemi-solvate), suitable for X-ray crystallography, were formed. Yield: 0.38 g, 84%.

Spectroscopic data: **¹H NMR** (400 MHz, benzene-d₆, 298 K): δ_H 0.40, 1.01, 1.29, 1.33 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.79 (6H, s, CH₃ of β -diketiminato backbone), 2.40 (6H, s, N(CH₃)₂ of DMAP), 2.96 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ⁱPr), 3.14 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ⁱPr), 4.92 (1H, br s, GaH), 5.51 (1H, s, γ -CH), 6.72 (2H, br s, *m*-CH

of DMAP), 6.96 – 7.13 (6H, m, aromatic CH), 7.82 (2H, br s, *o*-CH of DMAP). **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_C 23.5 (CH₃ of β-diketiminato backbone), 24.2, 24.4, 24.5, 24.8 (CH₃ of Dipp ⁱPr), 28.3, 29.3 (CH of Dipp ⁱPr), 38.9 (N(CH₃)₂ of DMAP), 99.7 (γ-CH), 108.7 (br, *m*-CH of DMAP), 124.5, 125.5, 129.3, 139.4, 142.9, 145.9 (ArC of Dipp), 146.7 (br, *o*-CH of DMAP), 156.9 (*p*-C of DMAP), 172.7 (NC). Resonance for CF₃ not observed. **¹⁹F NMR** (376 MHz, benzene-d₆, 298 K): δ_F –77.5. **MS(ESI):** *m/z* calc for C₂₉H₄₂GaN₂ ([M-DMAP-OTf]⁺) 487.2604, meas. 487.2570 (100%), calc for C₃₀H₄₂F₃GaN₂O₃S ([M-DMAP]⁺) 636.2124, meas. 636.2152 (20%). **IR (nujol/cm⁻¹):** ν_{Ga-H} 1972 (s). **Elemental microanalysis:** calc. for C₃₇H₅₂N₄GaO₃F₃S: C 58.50% H 6.90% N 7.38% meas. C 58.34% H 6.79% N 7.45%.

Variable temperature NMR data: **¹H NMR** (400 MHz, toluene-d₈, 298 K): δ_H 0.37, 1.03, 1.24, 1.32 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.80 (6H, s, CH₃ of β-diketiminato backbone), 2.67 (6H, s, N(CH₃)₂ of DMAP), 2.89 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.12 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.86 (1H, br s, GaH), 5.49 (1H, s, γ-CH), 6.81 (2H, br s, *m*-CH of DMAP), 6.94 – 7.09 (6H, m, aromatic CH), 7.80 (2H, br s, *o*-CH of DMAP).

¹H NMR (400 MHz, toluene-d₈, 378 K): δ_H 0.86 (12H, br m, 2 x overlapping CH₃ of Dipp ⁱPr), 1.13 (12H, d, ³J_{HH} = 6.7 Hz, CH₃ of Dipp ⁱPr), 1.84 (6H, s, CH₃ of β-diketiminato backbone), 2.68 (6H, s, N(CH₃)₂ of DMAP), 2.99 (4H, br multiplet, CH of Dipp ⁱPr), 4.90 (1H, br s, GaH), 5.54 (1H, s, γ-CH), 6.78 (2H, br d, ³J_{HH} = 6.5 Hz, *m*-CH of DMAP), 6.93 – 7.09 (6H, m, aromatic CH), 7.95 (2H, br d, ³J_{HH} = 6.5 Hz, *o*-CH of DMAP).

Preparation of {HC(MeCNDipp)₂}Ga(Ph)Cl – [Dipp¹]Ga(Ph)Cl (4.3)

A solution of PhLi (0.56 g, 6.6 mmol) in diethyl ether (15 mL) was added dropwise to a rapidly stirred solution of GaCl₃ (0.89 g, 5.08 mmol) in toluene (15 mL) at –78°C. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight, producing a white precipitate. The reaction mixture was cooled again to –78°C and a solution of [Dipp¹]Li·OEt₂ (2.3 g, 4.62 mmol) in toluene (20 mL) added dropwise. The reaction mixture was again allowed to warm to room temperature and stirred overnight before removing the volatiles *in vacuo*. The product was extracted into toluene (30 mL), filtered and concentrated to the point of incipient crystallisation. Storage of the solution at –30°C yielded a colourless crystalline solid. Further concentration of the supernatant solution and storage at –30°C produced a second crop of crystalline material. Yield: 2.22 g, 80%. Repeated attempts to obtain single crystals suitable for X-ray crystallography from a range of compatible hydrocarbon solvents were unsuccessful.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): 0.82, 1.03, 1.21, 1.49 (6H, d, ³J_{HH} = 6.9 Hz, CH₃ of Dipp ⁱPr), 1.62 (6H, s, CH₃ of β-diketiminato backbone), 3.13 (2H, sept, ³J_{HH} = 6.9 Hz, CH of Dipp ⁱPr), 3.93 (2H, sept, ³J_{HH} = 6.9 Hz, CH of Dipp ⁱPr), 4.97 (1H, s, γ-CH), 6.84 – 7.19 (11H, m, aromatic CH of GaPh and Dipp). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_C 23.5 (CH₃ of Dipp ⁱPr), 23.7 (CH₃ of β-diketiminato backbone), 24.5, 24.8, 26.6 (CH₃ of Dipp ⁱPr), 28.5, 29.1 (CH of Dipp ⁱPr), 97.8 (γ-CH), 124.2, 125.4, 127.7 (ArC of Dipp), 127.7, 128.7, 136.4 (*m*-, *p*-, *o*-ArC of GaPh), 140.9 (ArC of Dipp), 141.1 (*ipso*-ArC of GaPh), 143.6, 145.6 (ArC of Dipp), 170.1 (NC). **EI-MS:** *m/z* calc for C₃₅H₄₆N₂GaCl ([M]⁺) 598.2605, meas. 598.2587 (5%), calc. for C₃₅H₄₆N₂Ga ([M-Cl]⁺)

563.2917, meas. 563.2874 (30%). **Elemental microanalysis:** calc. for C₃₅H₄₆N₂GaCl: C 70.07% H 7.73% N 4.67% meas. C 70.16% H 7.57% N 4.55%.

Preparation of {HC(MeCNDipp)₂}Ga(ⁱPr)Br – [Dipp¹]Ga(ⁱPr)Br (4.4^{iPr})

To a solution of [Dipp¹]Ga (0.500 g, 1.03 mmol) in diethyl ether (5 mL) was added dropwise 2-bromopropane (125 µL, 1.33 mmol). The yellow solution decolourised within minutes and a colourless precipitate was formed. After stirring at room temperature for 1 h, removal of volatiles *in vacuo* yielded a spectroscopically pure powder. Yield: 0.46 g, 73%. Crystals suitable for X-ray crystallography could be obtained from a concentrated solution in toluene at –30°C.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 0.70 (6H, d, ³J_{HH} = 7.4 Hz, CH₃ of GaⁱPr), 1.02, 1.20, 1.30, 1.51 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.57 (6H, s, CH₃ of β-diketiminato backbone), 3.26 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.90 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.90 (1H, s, γ-CH), 7.02 – 7.14 (6H, m, aromatic CH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_C 15.9 (CH of GaⁱPr), 20.1 (CH₃ of Ga ⁱPr), 23.4 (CH₃ of β-diketiminato backbone), 23.8, 24.7, 25.1, 27.4 (CH₃ of Dipp ⁱPr), 28.1, 29.3 (CH of Dipp ⁱPr), 97.6 (γ-CH), 123.7, 125.7, 127.7, 141.4, 142.9, 146.1 (ArC of Dipp), 169.3 (NC). **EI-MS:** *m/z* calc for C₃₂H₄₈N₂Ga ([M-Br]⁺) 529.3073, meas. 529.3093 (25%). **Elemental microanalysis:** calc. for C₃₂H₄₈N₂GaBr: C 62.97% H 7.93% N 4.59% meas. C 63.04% H 8.08% N 4.67%.

Preparation of {HC(MeCNDipp)₂}Ga(Ph)Br – [Dipp¹]Ga(Ph)Br (4.4^{Ph})

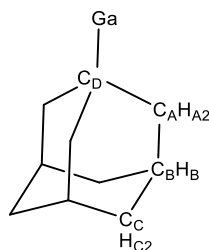
To a solution of [Dipp¹]Ga (0.328 g, 0.674 mmol) in toluene (5 mL) was added bromobenzene (0.70 mL, 6.74 mmol), and the resulting solution heated at 80°C for 4 d. Following removal of volatiles *in vacuo*, the resulting solid was extracted into *n*-hexane,

yielding a pale-yellow solution, which was filtered, concentrated to the point of incipient crystallisation and cooled to -30°C. Storage of this solution for several days yielded a crystalline material which was isolated and dried *in vacuo*. Yield: 0.18 g, 41%. Repeated attempts to isolate crystals suitable for X-ray diffraction from a range of compatible hydrocarbon solvents were unsuccessful.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 0.79, 1.02, 1.21, 1.50 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.62 (6H, s, CH₃ of β-diketiminato backbone), 3.11 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.92 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.98 (1H, s, γ-CH), 6.88 - 7.18 (11H, CH of GaPh and aromatic CH of Dipp). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_C 23.7 (CH₃ of β-diketiminato backbone), 23.8, 24.6, 24.7, 26.8 (CH₃ of Dipp ⁱPr), 28.7, 29.0 (CH of Dipp ⁱPr), 98.0 (γ-CH), 124.3, 125.3, 127.7 (ArC of Dipp), 128.4, 128.7, 136.4 (*m*-, *p*-, *o*-ArC of Ph), 140.8 (ArC of Dipp), 142.7 (*ipso*-ArC of Ph), 143.9, 145.4 (ArC of Dipp), 170.3 (NC).

Preparation of {HC(MeCNDipp)₂}Ga(Ad)Br – [Dipp¹]Ga(Ad)Br (4.4^{Ad})

[Dipp¹]Ga (1.07 g, 2.20 mmol) was dissolved in toluene (10 mL) and a solution of AdBr (0.52 g, 2.41 mmol), also in toluene (5 mL), added at room temperature. The resulting solution was heated to 80°C for 4 h, during which time the yellow solution decolourised. The solution was filtered while hot and allowed to attain room temperature. Storage of this solution at -30°C overnight yielded large colourless crystals, which were isolated and dried *in vacuo*. Yield: 1.1 g, 73%. Crystals of the bis(benzene) solvate suitable for X-ray diffraction were obtained from a concentrated solution in benzene at room temperature.



Labelling system applied to complexes featuring the 1-adamantyl (Ad) substituent

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 1.01, 1.18, 1.40 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.51 – 1.59 (9H, m, CH_B/CH_{C2} of Ad), 1.54 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.61 (6H, s, CH₃ of β-diketiminato backbone), 1.82 (6H, br m, CH_{A2} of Ad), 3.35 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.02 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 5.01 (1H, s, γ-CH), 7.06 – 7.13 (6H, m, aromatic CH). ¹³C{¹H} NMR (101, MHz, benzene-d₆, 298 K): δ_C 21.4, (C_D of Ad), 23.7 (CH₃ of β-diketiminato backbone), 23.8, 25.0, 25.1, 26.5 (CH₃ of Dipp ⁱPr), 28.3 (CH of Dipp ⁱPr), 29.0 (C_B of Ad), 29.8 (CH of Dipp ⁱPr), 38.0 (C_C of Ad), 41.8 (C_A of Ad), 98.7 (γ-CH), 123.6, 125.8, 127.6, 142.6, 142.9, 146.1 (ArC of Dipp), 169.9 (NC). **EI-MS:** *m/z* calc for C₃₉H₅₆N₂Ga ([M-Br]⁺) 621.3699, meas. 621.3620 (5%), calc for C₃₉H₅₇N₂GaBr ([M+H]⁺) 701.2883, meas. 701.2752 (5%). **Elemental microanalysis:** calc. for C₃₉H₅₆N₂GaBr: C 66.68% H 9.21% N 3.99% meas. C 66.56% H 8.17% N 4.04%.

Preparation of {HC(MeCNDipp)₂}Ga(Me)H – [Dipp1]Ga(Me)H (4.1^{Me})

A solution of methyllithium (1.6 M in hexane, 1.74 mL, 2.8 mmol) was added dropwise *via* syringe to a rapidly stirred solution of [Dipp1]Ga(Cl)H (1.464 g, 2.80 mmol) in diethyl ether (25 mL) at –78°C. The solution was stirred at –78°C for 1 h before being allowed to warm to room temperature, and stirred for a further 24 h. During this time the solution developed a yellow colour and produced a colourless precipitate. The reaction mixture was filtered, concentrated to the point of incipient crystallisation and cooled to –30°C.

Storage of the ethereal solution at this temperature for 48 h produced colourless crystals which were isolated and dried *in vacuo*. Yield: 1.17 g, 83%. ¹H NMR data were consistent with those reported in the literature.²⁴

Preparation of {HC(MeCNDipp)₂}Ga(Ph)H – [Dipp¹]Ga(Ph)H (4.1^{Ph})

Method A: [Dipp¹]Ga(Cl)H (1.37 g, 2.61 mmol) was dissolved in diethyl ether (20 mL) and cooled to –78°C. To this solution was added dropwise a solution of PhLi (0.24 g, 2.86 mmol), also in diethyl ether (10 mL) and allowed to warm to room temperature. The reaction mixture was stirred for 5 h at room temperature, over which time a white precipitate was produced. After filtration and the removal of volatiles *in vacuo*, the resulting white solid was extracted into minimal *n*-hexane (*ca.* 3 mL) and filtered. Storage of the supernatant solution at –30°C for one week yielded large, colourless, single crystals suitable for X-ray crystallography. Isolated yield of single crystals: 1.43 g, 96%. Analysis of the isolated crystals by ¹H NMR spectroscopy revealed contamination of the sample with trace quantities of [Dipp¹]Ga(Ph)Cl; the product could not be separated from this impurity despite multiple recrystallisation attempts.

Method B: K[HBet₃] (1.0 M in THF, 1.03 mL, 1.03 mmol) was added to a solution of [Dipp¹]Ga(Ph)Cl (0.57 g, 0.94 mmol) in toluene (15 mL) in an ampoule fitted with a J. Young's valve. The reaction mixture was heated to 75°C overnight, followed by filtration of the resulting yellow solution and removal of solvent *in vacuo*. The resulting yellow solid was extracted into *n*-hexane (*ca.* 5 mL), filtered, concentrated to the point of incipient crystallisation and left to stand at room temperature, yielding large, colourless single crystals. A second crop of crystals was produced on further concentration of the supernatant solution and storage at –30°C. Yield: 0.44 g, 82%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): 0.57, 1.11, 1.21, 1.41 (6H, d, ³J_{HH} = 6.9 Hz, CH₃ of Dipp ⁱPr), 1.63 (6H, s, CH₃ of β-diketiminato backbone), 3.19 (2H, sept, ³J_{HH} = 6.9 Hz, CH of Dipp ⁱPr), 3.59 (2H, sept, ³J_{HH} = 6.9 Hz, CH of Dipp ⁱPr), 4.83 (1H, s, γ-CH), 5.43 (1H, br s, GaH), 6.99 – 7.30 (11H, m, aromatic CH of GaPh and Dipp). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_C 23.2 (CH₃ of β-diketiminato backbone), 24.1, 24.6, 24.8, 25.4 (CH₃ of Dipp ⁱPr), 28.5, 28.7 (CH of Dipp ⁱPr), 95.6 (γ-CH), 124.6 (2 overlapping ArC of Dipp), 127.2 (ArC of Dipp), 127.4, 137.3 (*m*-, *o*- ArC of GaPh), 141.8, 143.9, 144.6 (ArC of Dipp), 147.8 (*ipso*-ArC of GaPh), 168.8 (NC). Resonance for *p*-ArC of GaPh obscured by solvent. **EI-MS:** *m/z* calc for C₃₅H₄₆N₂Ga ([M-H]⁺) 563.2911, meas. 563.2899 (100%), calc. for C₂₉H₄₂N₂Ga ([M-Ph]⁺) 487.2604, meas. 487.2596 (25%). **IR (nujol/cm⁻¹):** ν_{Ga-H} 1909 (s) **Elemental microanalysis:** calc. for C₃₅H₄₇N₂Ga: C 74.34% H 8.38% N 4.95% meas. C 74.52% H 8.49% N 5.24%.

Preparation of {HC(MeCNDipp)₂}Ga(^tAm)H – [^{Dipp}1]Ga(^tAm)H (4.1^tAm)

[^{Dipp}1]Ga(^tAm)Br (0.83 g, 1.30 mmol) was dissolved in toluene (7 mL) in an ampoule fitted with a J. Young's valve. To this solution was added K[HBET₃] (1.0 M in THF, 1.44 mL, 1.44 mmol), with stirring. The solution was heated to 75°C, producing a colourless precipitate over the course of 15 h, after which time the reaction mixture was allowed to cool to room temperature and filtered. The precipitate was washed with a further portion of toluene (*ca.* 5 mL) and the filtrate and washings combined. Volatiles were removed *in vacuo* to yield a colourless solid which was then extracted into *n*-hexane, filtered and concentrated to the point of incipient crystallisation. The solid was redissolved by gentle warming, and the solution stored at –30°C for several days, during which time single colourless crystals suitable for X-ray crystallography were produced. Isolated yield of single crystals: 0.39 g, 53%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 0.74 (6H, s, CH₃ of ^tAm Me), 0.78 (3H, t, ³J_{HH} = 7.4 Hz, CH₃ of ^tAm Et), 1.13, 1.16 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.29 (2H, q, ³J_{HH} = 7.4 Hz, CH₂ of ^tAm Et), 1.39 (12H, d, 2 overlapping signals, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.63 (6H, s, CH₃ of β-diketiminato backbone), 3.43 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.51 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.87 (1H, s, γ-CH), 5.53 (1H, br s, GaH), 7.02 – 7.14 (6H, m, aromatic CH). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_C 7.7 (CH₃ of ^tAm Et), 23.6 (CH₃ of β-diketiminato backbone), 23.7, 24.9, 25.0, 25.1 (CH₃ of Dipp ⁱPr), 25.9 (C(CH₃)₂(CH₂CH₃) of ^tAm), 26.8 (CH₃ of ^tAm Me), 28.4, 29.2 (CH of Dipp ⁱPr), 35.7 (CH₂ of ^tAm Et), 96.1 (γ-CH), 123.9, 124.8, 126.9, 143.1, 144.0, 144.6 (ArC of Dipp), 168.9 (NC). **EI-MS:** *m/z* calc. for C₂₉H₄₂N₂Ga ([M-^tAm]⁺) 487.2604, meas. 487.2602 (100%), calc. for C₃₄H₅₂N₂Ga ([M-H]⁺) 557.3381, meas. 557.3362 (15%). **IR (nujol/cm⁻¹):** ν_{Ga-H} 1797 (s). **Elemental microanalysis:** calc. for C₃₄H₅₃N₂Ga: C 72.98% H 9.55% N 5.01% meas. C 72.90% H 9.56% N 5.02%.

Preparation of {HC(MeCNDipp)₂}Ga(Ad)H – [^{Dipp}1]Ga(Ad)H (4.1^{Ad})

An ampoule fitted with a J. Young's valve was charged with [^{Dipp}1]Ga(Ad)(Br) (0.95 g, 1.35 mmol) and K[HB(Et)₃] (0.206 g, 1.49 mmol) and toluene (10 mL) added. The reaction mixture was heated to 75°C overnight, the solution developing a bright yellow colour and producing a white precipitate. The reaction mixture was subsequently filtered, and the precipitate washed with a further portion of toluene; the filtrate and washing were combined, and volatiles removed *in vacuo*. The resulting yellow solid was extracted into minimal toluene, filtered and cooled to -30°C, yielding colourless single crystals, suitable for X-ray diffraction, overnight. Yield: 0.59 g, 69%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 1.14, 1.16, 1.43, 1.46 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.59 (6H, s, CH₃ of β-diketiminato backbone), 1.56

– 1.67 (15H, m, CH/CH₂ of Ad), 3.40 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 3.53 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 4.85 (1H, s, γ -CH), 5.29 (1H, br s, GaH), 7.09 – 7.16 (6H, m, aromatic CH). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101, MHz, benzene-d₆, 298 K): δ_{C} 23.3 (CH₃ of β -diketiminato backbone), 23.7, 24.9, 25.0, 25.4 (CH₃ of Dipp ⁱPr), 28.3 (CH of Dipp ⁱPr), 29.1 (C_B of Ad), 29.4 (CH of Dipp ⁱPr), 29.5 (C_D of Ad), 38.4 (C_C of Ad), 42.4 (C_A of Ad), 95.9 (γ -CH), 123.8, 124.9, 126.8, 143.0, 143.8, 144.6 (ArC of Dipp), 168.8 (NC). **EI-MS**: m/z calc for C₃₉H₅₆N₂Ga ([M-H]⁺) 621.3694, meas. 621.3668 (5%), calc. for C₂₉H₄₂N₂Ga 487.2604, meas. 487.2580 (50%). **IR (nujol/cm⁻¹)**: $\nu_{\text{Ga-H}}$ 1802 (s). **Elemental microanalysis**: calc. for C₃₉H₅₇N₂Ga: C 75.11% H 9.21% N 4.49% meas. C 74.95% H 9.31% N 4.60%.

Preparation of {HC(MeCNDipp)₂}Ga(H)(OC(O)H) – [Dipp¹]Ga(H)(OC(O)H) (4.5^H)

[Dipp¹]GaH₂ (0.737 g, 1.51 mmol) was dissolved in toluene (3 mL) in an ampoule fitted with a J. Young's valve and degassed by three freeze-pump-thaw cycles. The ampoule was then back-filled with carbon dioxide (*ca.* 1 bar) at room temperature. The solution was heated to 60°C for 14 d, by which time complete conversion had occurred. The solution was filtered and concentrated to the point of incipient crystallisation. Storage of the solution for 48 h at –30°C yielded colourless acicular crystals of the toluene solvate suitable for X-ray crystallography. Yield: 0.49 g, 61%.

Spectroscopic data: **^1H NMR** (400 MHz, benzene-d₆, 298 K): δ_{H} 1.09, 1.15, 1.29, 1.31 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ⁱPr), 1.55 (6H, s, CH₃ of β -diketiminato backbone), 3.19 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 3.44 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 4.91 (1H, s, γ -CH), 5.33 (1H, s, GaH), 7.04 – 7.14 (6H, m, aromatic CH), 8.36 (1H, d, $^4J_{\text{HH}} = 2.4$ Hz, Ga(OC(O)H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, benzene-d₆, 298 K): 23.4 (CH₃ of β -diketiminato backbone), 24.6, 24.7, 24.9, 25.5 (CH₃ of Dipp ⁱPr), 27.7, 28.8 (CH of Dipp

ⁱPr), 97.5 (γ-CH), 124.5, 124.9, 127.9, 140.1, 143.4, 145.2 (ArC of Dipp), 164.9 (Ga(OC(O)H)), 169.9 (NC). **EI-MS**: *m/z* calc for C₃₀H₄₂N₂GaO₂ ([M-H]⁺) 531.2497, meas. 531.2491 (2%). **IR (nujol, cm⁻¹)**: ν_{C=O} 1659 (s) ν_{Ga-H} 1996 (s). **Elemental microanalysis**: calc. for C₃₀H₄₃N₂GaO₂: C 67.55% H 8.13% N 5.25% meas. C 67.67% H 8.01% N 5.24%.

Preparation of {HC(MeCNDipp)₂}Ga(Ph)(OC(O)H) – [Dipp1]Ga(Ph)(OC(O)H) (4.5^{Ph})

[Dipp1]Ga(Ph)H (0.55 g, 0.97 mmol) was dissolved in toluene (5 mL) in an ampoule fitted with a J. Young's valve and degassed by three freeze-pump-thaw cycles. The ampoule was then backfilled with carbon dioxide (*ca.* 1 bar) at room temperature and heated at 60°C for 14 d. The resulting solution was filtered and concentrated until significant quantities of solid product was suspended in solution. The suspension was heated until the solid redissolved, and the resulting solution was allowed to cool slowly to room temperature, and then cooled to –30°C. Storage of this solution overnight yielded colourless crystals, suitable for X-ray crystallography. Yield: 0.40 g, 67%.

Spectroscopic data: **¹H NMR** (400 MHz, benzene-d₆, 298 K): 0.85, 1.04, 1.20, 1.34 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.63 (6H, s, CH₃ of β-diketiminato backbone), 3.10 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.61 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 5.15 (1H, s, γ-CH), 6.71 – 7.18 (11H, m, aromatic CH of GaPh and Dipp), 8.65 (1H, d, ³J_{HH} = 2.4 Hz), Ga(OC(O)H). **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_C 23.5 (CH₃ of β-diketiminato backbone), 23.6, 24.5, 24.7, 25.9 (CH₃ of Dipp ⁱPr), 27.7, 29.1 (CH of Dipp ⁱPr), 99.3 (γ-CH), 124.3, 125.2, 127.6 (ArC of Dipp), 127.6, 128.6, 136.7 (*m*-, *p*-, *o*-ArC of Ga-Ph), 139.2 (*ipso*-ArC of GaPh), 141.2, 143.7, 145.4 (ArC of Dipp), 164.4 (Ga(OC(O)H), 170.4 (NC). **EI-MS**: *m/z* calc for C₃₆H₄₆N₂GaO₂ ([M-H]⁺) 607.2893, meas. 607.2925 (2%), calc for C₂₉H₄₂N₂Ga ([M-Ph-CO₂]⁺) 487.2604, meas. 487.2535 (80%), calc for C₃₅H₄₆N₂Ga

([M-OC(O)H]⁺) 563.2917, meas 563.2938 (100%). **IR (nujol/cm⁻¹):** $\nu_{C=O}$ 1659 (s).

Elemental microanalysis: calc. for C₃₆H₄₇N₂GaO₂: C 70.94% H 7.77% N 4.60% meas. C 70.89% H 7.86% N 9.39%.

Preparation of {HC(MeCNDipp)₂}Ga(Me)(OC(O)H) – [Dipp¹]Ga(Me)(OC(O)H) (4.5^{Me})

A solution of [Dipp¹]Ga(Me)H (1.20 g, 2.39 mmol) in toluene (10 mL) in an ampoule fitted with a J. Young's valve was degassed by three freeze-pump-thaw cycles and backfilled with CO₂ (ca. 1 bar) at room temperature. The solution was subsequently heated to 60°C for 36 h, filtered and concentrated to the point of incipient crystallisation. The storage of this solution at –30°C for 5 d led to the production of fine, acicular crystals, suitable for X-ray diffraction. Yield: 0.99 g, 76%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H –0.31 (3H, s, CH₃ GaMe), 1.04, 1.19, 1.23, 1.31 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.57 (6H, s, CH₃ of β -diketiminato backbone), 3.12 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.53 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 5.03 (1H, s, γ -CH), 7.03 – 7.15 (6H, m, aromatic CH), 8.67 (1H, s, Ga(OC(O)H)). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_C – 12.1 (br, CH₃ of GaMe), 23.5 (CH₃ of β -diketiminato backbone), 24.0, 24.3, 24.8, 26.4 (CH₃ of Dipp ⁱPr), 27.5, 29.0 (CH of Dipp ⁱPr), 98.60 (γ -CH), 124.0, 125.1, 127.6, 140.6, 143.0, 145.7 (ArC of Dipp), 164.6 (Ga(OC(O)H)), 169.7 (NC). **EI-MS:** *m/z* calc for C₃₁H₅₄₄N₂Ga ([M-H]⁺) 545.2737, meas. 545.2660 (10%). **IR (nujol/cm⁻¹):** $\nu_{C=O}$ 1661 (s). **Elemental microanalysis:** calc. for C₃₁H₄₅N₂GaO₂: C 68.02% H 8.29% N 5.12% meas. C 67.91% H 8.16% N 5.21%.

Preparation of {HC(MeCNDipp)₂}Ga(^tAm)(OC(O)H) – [Dipp¹]Ga(^tAm)(OC(O)H) (4.5^tAm)

A solution of [Dipp¹]Ga(^tAm)H (0.073 g, 0.130 mmol) in toluene (3 mL) in an ampoule fitted with a J. Young's valve was degassed by three freeze-pump-thaw cycles. The ampoule was backfilled with carbon dioxide (*ca.* 1 bar) and stirred for 24 h at room temperature. Volatiles were subsequently removed *in vacuo* and the resulting colourless solid extracted into minimal *n*-hexane. The *n*-hexane solution was filtered, concentrated and stored at –30°C for 48 h, during which time large colourless crystals suitable for X-ray crystallography were obtained. Yield: 0.057 g, 72%.

Spectroscopic data: ¹H NMR (500 MHz, benzene-d₆, 298 K): δ_H 0.53 (3H, t, ³J_{HH} = 7.4 Hz, CH₃ of ^tAm Et), 0.83 (6H, s, CH₃ of ^tAm Me), 1.03, 1.18, 1.32 (6H, d, ³J_{HH} = 6.7 Hz, CH₃ of Dipp ⁱPr), 1.37 (2H, q, ³J_{HH} = 7.4 Hz, CH₂ of ^tAm Et), 1.42 (6H, d, ³J_{HH} = 6.7 Hz, CH₃ of Dipp ⁱPr), 1.60 (6H, s, CH₃ of β-diketiminato backbone), 3.25 (2H, sept, ³J_{HH} = 6.7 Hz, CH of Dipp ⁱPr), 3.51 (2H, sept, ³J_{HH} = 6.7 Hz, CH of Dipp ⁱPr), 5.08 (1H, s, γ-CH), 7.03 – 7.15 (6H, m, aromatic CH), 8.86 (1H, s, Ga(OC(O)H)). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_C 5.99 (CH₃ of ^tAm Et), 23.6 (CH₃ of β-diketiminato backbone), 23.9 (CH₃ of Dipp ⁱPr), 24.5 (C(CH₃)₂(CH₂CH₃) of ^tAm), 24.7, 25.0, 25.1 (CH₃ of Dipp ⁱPr), 25.4 (CH₃ of ^tAm Me), 27.6, 29.6 (CH of Dipp ⁱPr), 33.4 (CH₂ of ^tAm Et), 99.6 (γ-CH), 123.8, 125.3, 127.7, 142.7, 142.9, 145.5 (ArC of Dipp), 164.7 (Ga(OC(O)H)), 170.0 (NC). **EI-MS:** *m/z* calc for C₃₀H₄₂N₂GaO₂ ([M-^tAm]⁺) 531.2502, meas. 531.2501 (10%), calc for C₃₄H₅₂N₂Ga ([M-OC(O)H]⁺) 557.3386, meas. 557.3374 (5%). **IR (nujol/cm⁻¹):** ν_{C=O} 1677 (s). **Elemental microanalysis:** calc. for C₃₅H₅₃N₂GaO₂: C 69.65% H 8.85% N 4.64% meas. C 69.53% H 8.76% N 4.58%.

Preparation of {HC(MeCNDipp)₂}Ga(Ad)(OC(O)H) – [Dipp¹]Ga(Ad)(OC(O)H) (4.5^{Ad})

[Dipp¹]Ga(Ad)H (0.30 g, 0.481 mmol) was dissolved in toluene (3 mL) in an ampoule fitted with a J. Young's valve and degassed by three freeze-pump-thaw cycles. The ampoule was backfilled with carbon dioxide (*ca.* 1 bar) at room temperature and stirred overnight. The solution was subsequently filtered, concentrated to the point of incipient crystallisation and stored at –30°C overnight, yielding colourless crystals suitable for X-ray diffraction. Yield: 0.25 g, 77%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} 1.04, 1.18, 1.39, 1.45 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH₃ of Dipp ⁱPr), 1.55 – 1.63 (9H, m, CH_B/CH_{C2} of Ad), 1.60 (6H, s, CH₃ of β -diketiminato backbone), 1.80 (6H, br s, CH_{A2} of Ad), 3.28 (2H, sept, $^3J_{\text{HH}} = 6.7$ Hz, CH of Dipp ⁱPr), 3.50 (2H, sept, $^3J_{\text{HH}} = 6.7$ Hz, CH of Dipp ⁱPr), 5.07 (1H, s, γ -CH), 7.07 – 7.16 (6H, m, aromatic CH), 8.88 (1H, s, Ga(OC(O)H)). ¹³C{¹H} NMR (101, MHz, benzene-d₆, 298 K): δ_{C} 23.7 (CH₃ of β -diketiminato backbone), 23.7, (CH₃ of Dipp ⁱPr), 24.9 (2 overlapping signals, 2 x CH₃ of Dipp ⁱPr), 25.0 (CH₃ of Dipp ⁱPr), 27.6 (CH of Dipp ⁱPr), 28.8 (C_B of Ad), 29.7 (CH of Dipp ⁱPr), 31.6 (C_D of Ad), 38.1 (C_C of Ad), 41.4 (C_A of Ad), 99.5 (γ -CH), 123.8, 125.4, 127.6, 142.7, 142.9, 145.4 (ArC of Dipp), 164.2 (Ga(OC(O)H)), 170.0 (NC). **EI-MS:** *m/z* calc for C₃₀H₄₂N₂GaO₂ ([M-Ad]⁺) 531.2502, meas. 531.2523 (100%), calc for C₃₉H₅₆N₂Ga ([M-OC(O)H]⁺) 621.3699, meas. 621.3786 (10%), calc for C₄₀H₅₆N₂GaO₂ ([M-H]⁺) 665.3676, meas. 665.3705 (2%). **IR (nujol/cm⁻¹):** $\nu_{\text{C=O}}$ 1679 (s). **Elemental microanalysis:** calc. for C₄₀H₅₇N₂GaO₂: C 71.96% H 8.61% N 4.20% meas. C 71.73% H 8.46% N 4.15%.

General procedure for assessing rates of insertion of CO₂ into Ga-H bonds

An NMR tube fitted with a J. Young's valve was charged with [Dipp¹]₂Ga(R)H (R = OTf, Cl, H, Me, Ph, Ad, ^tBu, ^tAm) (0.020 mmol) and benzene-d₆ (0.5 mL) and degassed by three freeze-pump-thaw cycles. The tube was subsequently back-filled with 1 bar of CO₂, shaken vigorously and the progress of the reaction monitored by ¹H NMR spectroscopy.

General procedure for assessing the reactivity of gallium formate complexes with pinacolborane (HBpin)

An NMR tube fitted with a J. Young's valve was charged with [Dipp¹]₂Ga(R)(OC(O)H) (0.0511 mmol), HBpin (30 μL, 0.205 mmol) and benzene-d₆. The resulting solution was monitored by ¹H and ¹¹B NMR spectroscopy for 4 d. In the event of no reactivity, the solution was heated to 80°C and the progress of the reaction monitored by ¹H and ¹¹B NMR spectroscopy.

General procedure for assessing the reactivity of gallium formate complexes with catecholborane (HBcat)

An NMR tube fitted with a J. Young's valve was charged with [Dipp¹]₂Ga(R)(OC(O)H) (0.0365 mmol) (R = H, Me, Ph, ^tBu, ^tAm, Ad), HBcat (14 μL, 0.113 mmol) and benzene-d₆ (0.5 mL). The solution was shaken vigorously, and the progress of the reaction monitored by ¹H and ¹¹B NMR spectroscopy.

General procedure for assessing the reactivity of gallium formate complexes with 9-borabicyclo[3.3.1]nonane

An NMR tube fitted with a J. Young's valve was charged with [Dipp¹]₂Ga(R)(OC(O)H) (0.0365 mmol) (R = H, Me, Ph, ^tBu, ^tAm, Ad), {H(9-BBN)}₂ (5 mg, 0.0205 mmol) and

benzene-d₆ (0.5 mL). The solution was shaken vigorously, and the progress of the reaction monitored by ¹H and ¹¹B NMR spectroscopy. These reactions were also undertaken employing 1.5 equivalents of {H(9-BBN)}₂ (14 mg, 0.0574 mmol); identical conditions were otherwise employed.

Procedure for studies of the reactivity of [Dipp¹]Ga(^tBu)(OC(O)H) with Me₂S·BH₃

An NMR tube fitted with a J. Young's valve was charged with [Dipp¹]Ga(^tBu)(OC(O)H) (20 mg, 0.0339 mmol), benzene-d₆ (0.5 mL) and Me₂S·BH₃ (4 μL, 0.0422 mmol). The progress of the reaction was monitored by ¹H and ¹¹B NMR spectroscopy.

Preparation of {HC(MeCNDipp₂)Ga(Ph)(OMe) – [Dipp¹]Ga(Ph)(OMe) (4.6^{Ph})

To a solution of [Dipp¹]Ga(Ph)H (0.410 g, 0.726 mmol) in toluene (5 mL) was added excess methanol (147 μL, 3.63 mmol), and the resulting solution heated to 80°C for 3 d. Volatiles were then removed *in vacuo* and the resulting white solid extracted with *n*-hexane, leaving a colourless residue. Filtration, concentration to the point of incipient crystallisation and storage at 6°C for several days led to the formation of large colourless crystals suitable for X-ray diffraction. A second crop of crystals could be obtained from further concentration and cooling of the supernatant. Yield: 0.38 g, 87%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): 0.85, 1.07, 1.28, 1.49 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.63 (6H, s, CH₃ of β-diketiminato backbone), 3.13 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.90 (3H, s, CH₃ of Ga-OMe), 3.92 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.87 (1H, s, γ-CH), 6.77 – 7.22 (11H, m, aromatic CH of GaPh and Dipp). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_c 23.3 (CH₃ of β-diketiminato backbone), 23.8, 24.7, 24.8, 25.6 (CH₃ of Dipp ⁱPr), 28.0, 28.9 (CH of Dipp ⁱPr), 54.6 (CH₃ of Ga-OMe), 97.1 (γ-CH), 124.2, 125.0, 127.5 (ArC of Dipp), 127.6, 128.2, 137.0 (*m*-, *p*-,

o-ArC of GaPh), 140.1 (*ipso*-C of GaPh), 141.9, 143.6, 145.3 (ArC of Dipp), 169.6 (NC).

MS(ESI): *m/z* calc for C₃₅H₄₆GaN₂ ([M-OMe]⁺) 563.2917, meas. 563.2902 (20%).

Elemental microanalysis: calc. for C₃₆H₄₉N₂GaO: C 72.61% H 8.29% N 4.70% meas. C 72.50% H 8.27% N 4.68%.

Methods used for the NMR experiments described in section 4.4.4

General method for attempted catalytic studies

In a high pressure NMR tube equipped with a J. Young's tap, [Dipp¹]Ga(R)H (R = ^tBu, Me, Ad) (0.009 mmol, 10 mol%) and HBpin (0.012 g, 0.091 mmol) were dissolved in benzene-d₆ (0.5 mL). The solution was subject to three freeze-pump-thaw cycles and then backfilled with CO₂ (1.5 bar) at -60°C. The solution was allowed to warm to room temperature, generating a pressure of *ca.* 2.4 bar. The resulting solutions were heated to 60°C and ¹H and ¹¹B NMR spectra were measured at regular intervals.

General method for comparative insertion of CO₂ into Ga-H bonds of 4.1^{tBu} and 4.1^{Me}

In a high pressure NMR tube equipped with a J. Young's valve, [Dipp¹]Ga(R)H (R = ^tBu or Me) (0.009 mmol) was dissolved in benzene-d₆ (0.5 mL). The solution was subject to three freeze-pump-thaw cycles and then backfilled with CO₂ (1.5 bar) at -60°C. The solution was allowed to warm to room temperature, generating a pressure of *ca.* 2.4 bar. ¹H NMR spectra were measured at 60°C at regular intervals until > 90% of the gallium hydride had been consumed.

General method for comparative reactivity of 4.5^{tBu} and 4.5^{Me} with excess HBpin

To an NMR tube fitted with a J. Young's valve was added [Dipp¹]Ga(R)OC(O)H (0.009 mmol) and 0.5 mL of a stock solution (in benzene-d₆) containing 10 equivalents of HBpin and 0.5 equivalents of O(SiMe₃)₂, used as an internal standard. The resulting solutions were heated to 60°C and monitored by ¹H NMR spectroscopy until all of the respective formate complexes had been consumed.

General method for comparative reactivity of 4.5^{tBu} and 4.1^{tBu} with excess HBpin and CO₂ under “catalytic conditions”

In a high pressure NMR tube equipped with a J. Young's tap, [Dipp¹]Ga(^tBu)H or [Dipp¹]Ga(^tBu)OC(O)H (0.009 mmol) was dissolved in 0.5 mL of a stock solution containing 10 equivalents of HBpin and 0.5 equivalents of O(SiMe₃)₂, used as an internal standard, in benzene-d₆. The solution was subject to three freeze-pump-thaw cycles and then backfilled with CO₂ (1.5 bar) at -60°C. The solution was allowed to warm to room temperature, generating a pressure of *ca.* 2.4 bar. ¹H NMR spectra were measured at 60°C at regular intervals for *ca.* 12 hours. An analogous method was utilised for [Dipp¹]Ga(^tBu)OC(O)H using 3 equivalents of HBpin in benzene-d₆.

4.4 Results and discussion

4.4.1 Synthesis of novel β-diketiminato-ligated gallium hydrides

A commonly utilised method for the synthesis of unsymmetrically substituted Nacnac-ligated aluminium hydrides involves the dehydrocoupling of one Al-H bond of [Dipp¹]AlH₂ with an alcohol or alkyne, to yield complexes of the type [Dipp¹]Al(R)H (R = C≡CPh, OR' (R' = Me, Et, ⁱPr, ^tBu)).³⁰ In similar fashion, the addition of methyl

trifluoromethanesulfonate (MeOTf) to [Dipp $\mathbf{1}$]AlH₂ leads to the formation of [Dipp $\mathbf{1}$]Al(OTf)H, with evolution of methane.³¹ By contrast, the use of such methods in the synthesis of unsymmetrically substituted gallium hydrides is unexplored, presumably due to their reduced basicity.

Accordingly, the addition of one equivalent of MeOTf to a solution of [Dipp $\mathbf{1}$]GaH₂ in toluene at 0°C was examined and shown to selectively yield the unsymmetrically substituted gallium hydride [Dipp $\mathbf{1}$]Ga(OTf)H (**4.1^{OTf}**), after stirring at room temperature for 72 h. The formation of **4.1^{OTf}** following this method takes significantly longer (< 12 h) to reach completion than the corresponding aluminium system [Dipp $\mathbf{1}$]Al(OTf)H; this is presumably due to the reduced basicity of the M-H bond.¹ The formation of **4.1^{OTf}** is signalled by the appearance of four doublets and two septets in the aliphatic region of the ¹H NMR spectrum, corresponding to the ⁱPr substituents of the Dipp groups of **4.1^{OTf}**. This pattern of resonances is consistent with a Nacnac-ligated species that lacks C₂ symmetry, and features an unsymmetrically substituted gallium centre. The gallium hydride resonance is observed at $\delta_{\text{H}} = 5.62$ ppm, integrating to one hydrogen, and broadened due to the presence of the quadrupolar ^{69/71}Ga nucleus (*I* = 3/2). The chemical shift of this resonance is shifted considerably downfield relative to that observed for [Dipp $\mathbf{1}$]GaH₂ ($\delta_{\text{H}} = 5.19$ ppm); this may signify a significant reduction of the hydridic character of the Ga-H arising from the presence of the highly electron-withdrawing triflate substituent.²⁴ A single signal was observed in the ¹⁹F NMR spectrum at $\delta_{\text{F}} = -77.5$ ppm for the triflate CF₃ group; this is consistent with that observed for [Dipp $\mathbf{1}$]Ga(Cl)(OTf) ($\delta_{\text{F}} = -75.5$ ppm).³² **4.1^{OTf}** could be isolated as colourless crystals in 55% yield from toluene solution. The molecular structure in the solid state was elucidated by X-ray crystallography and is shown in Figure 4.2.

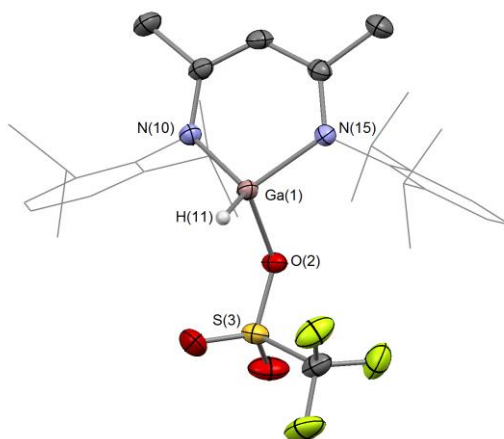
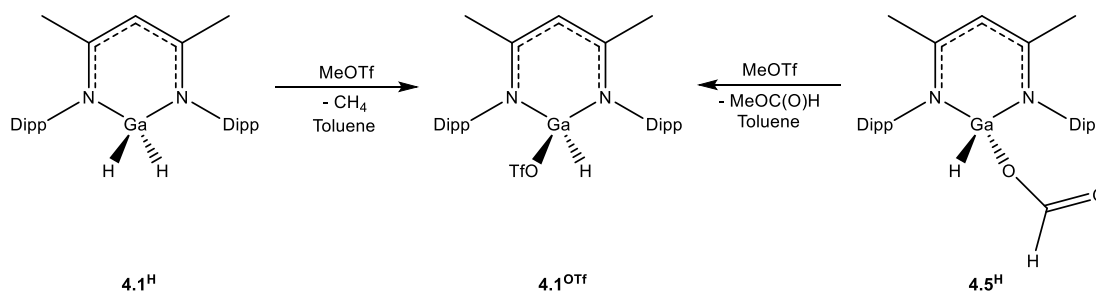


Figure 4.2: Molecular structure of [Dipp1]Ga(OTf)H (**4.1^{OTf}**). Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Gallium hydride located in the difference Fourier map and refined isotropically. Key bond lengths (Å) and angles (°): Ga(1)-O(2) 1.9459(16), Ga(1)-N(10) 1.9075(19), Ga(1)-N(15) 1.9189(19), O(2)-S(3) 1.4898(16), N(10)-Ga(1)-N(15) 97.77(8).

As expected, the molecular structure of **4.1^{OTf}** features a four-coordinate gallium centre in an approximately tetrahedral geometry. Ga(1) is found 0.532 Å from the least-squares C₃N₂ plane, representing a significantly greater distortion than that observed for [Dipp1]GaH₂ (0.031 Å), due to the steric impact of the triflate substituent. The Ga-N bond lengths of **4.1^{OTf}** are considerably shorter than those of [Dipp1]GaH₂ ($d(\text{Ga-N})$ 1.960(1), 1.963(1) Å) (**4.1^H**) and are closer in length to those of the related complex [Dipp1]Ga(OTs)H ($d(\text{Ga-N})$ 1.921(1), 1.933(1) Å), presumably reflecting a significant increase in Lewis acidity of the gallium centre upon installation of the highly electron-withdrawing triflate substituent.²⁸ The Ga-O bond length is significantly longer than the Al-O bond in [Dipp1]Al(OTf)H ($d(\text{Al-O})$ 1.8038(15) Å), despite the very similar covalent radii of aluminium and gallium (Al: 1.21(4) Å, Ga: 1.22(3) Å), underlining the more Lewis acidic nature of aluminium.³³ The Ga-O bond of **4.1^{OTf}** is also significantly longer than that of [Dipp1]Ga(OEt)H ($d(\text{Ga-O})$ 1.792(3) Å) and [Dipp1]Ga(OTs)H ($d(\text{Ga-O})$ 1.888(1) Å).^{27,28} This weakening of the Ga-O bond is accompanied by an increase in

strength of the Ga-H bond, as evidenced by IR spectroscopy ($\nu_{\text{Ga-H}}$: [Dipp¹]Ga(OEt)H 1901 cm⁻¹, [Dipp¹]Ga(OTs)H 1977 cm⁻¹, **4.1**^{OTf} 1994 cm⁻¹). The Ga-H stretching frequency of **4.1**^{OTf} is significantly blue shifted compared to that of **4.1**^H ($\nu_{\text{Ga-H sym/asym}}$ 1893, 1860 cm⁻¹) and represents, to the best of our knowledge, the highest value for any Nacnac-ligated gallium hydride.²⁴



Scheme 4.4: The two synthetic routes for the preparation of [Dipp¹]Ga(OTf)H (**4.1**^{OTf}).

4.1^{OTf} can also be formed *via* methylation of the formate/alkoxide substituents of [Dipp¹]GaH(OC(O)H)/[Dipp¹]GaH(OCH₂Ph) using one equivalent of MeOTf, generating methyl formate (δ_{H} = 7.51, 3.19 ppm) or MeOCH₂Ph (δ_{H} = 4.23, 3.11 ppm) as the co-product. These reactions proceed selectively and more rapidly at room temperature, such that the reactions reach completion in under 15 h.

The ¹H NMR spectrum of **4.1**^{OTf} shows somewhat broadened resonances for the ⁱPr groups of the Dipp substituents; the feature is also reportedly observed for the related complex [Dipp¹]Ga(Me)(OTf).³⁴ This, in addition to the relatively long Ga-O bond length, might suggest the possibility of a fluxional process brought about by dissociation of the triflate substituent from the gallium centre of **4.1**^{OTf}. When **4.1**^{OTf} is dissolved in d₈-THF the resulting ¹H NMR spectrum features only one septet and two doublets for the Dipp ⁱPr substituents, and the γ -H and Ga-H resonances are observed at δ_{H} = 5.36 and 5.30 ppm, respectively; this pattern of signals is indicative of a Nacnac complex with C₂ symmetry (Figure 4.3). This might arise from dissociation of the triflate substituent in

the more polar solvent to yield either the separate cation/anion pair featuring a trigonal planar gallium centre, or a fluxional system in which the triflate substituent dissociates and reassociates on the opposite face, forming a symmetrical species on the NMR timescale. Additionally, this pattern of resonances may arise from the formation of $[[^{\text{Dipp}}\mathbf{1}]\text{Ga}(\text{H})(\text{THF})][\text{OTf}]$, in which THF is coordinated to the cationic gallium centre but undergoes exchange rapidly on the NMR timescale.

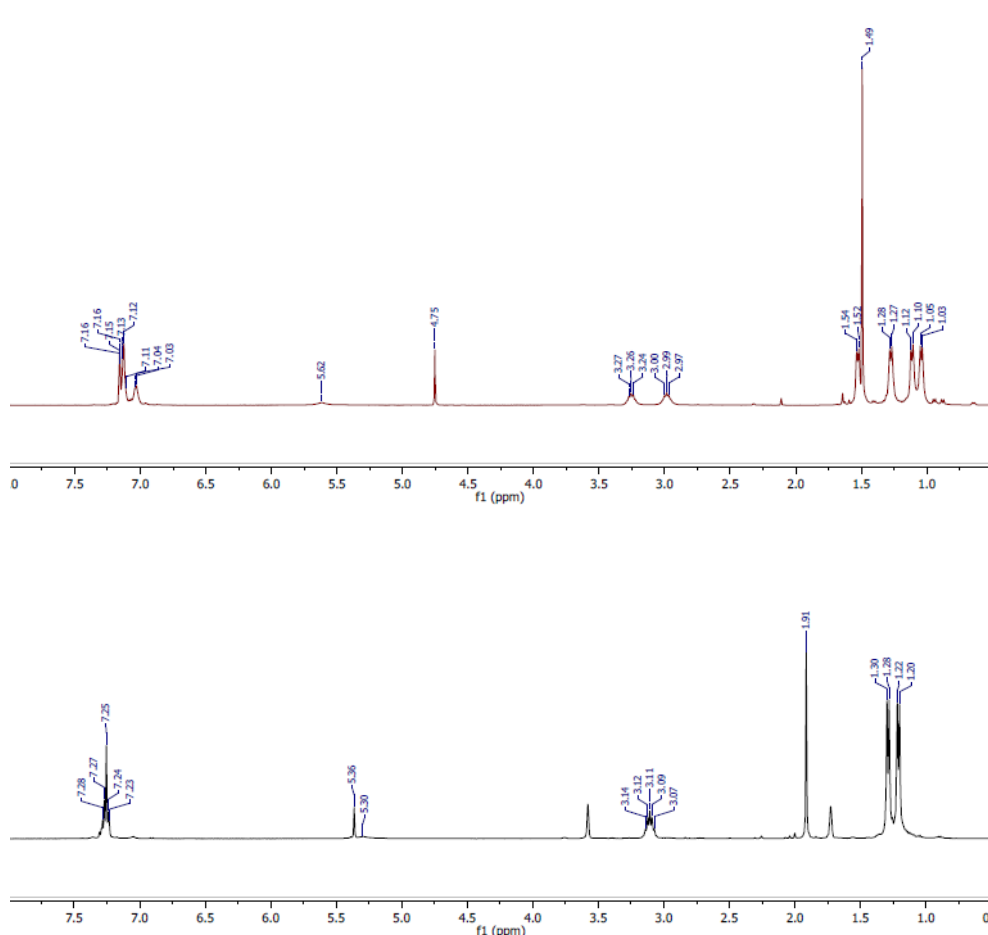
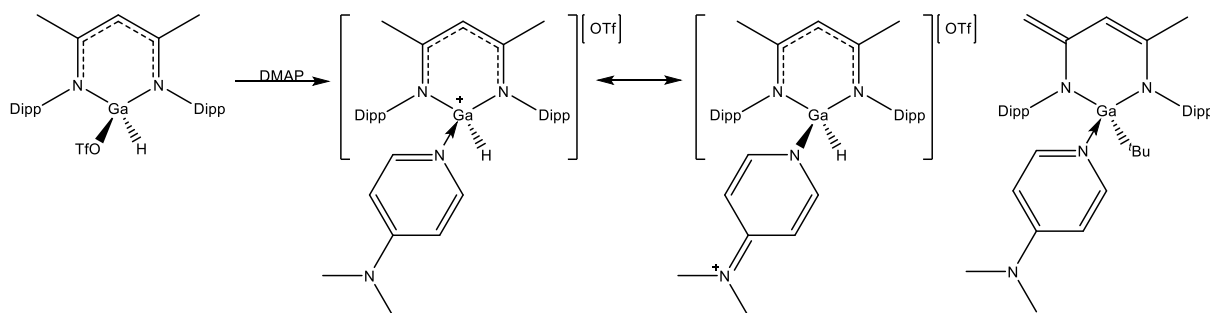


Figure 4.3: The ¹H NMR spectrum of **4.1**^{OTf} in benzene-d₆ (above) and THF-d₈ (below).

The dissociative ability of the triflate substituent is further illustrated by the reaction of **4.1**^{OTf} with DMAP, which yields the complex $[[^{\text{Dipp}}\mathbf{1}]\text{GaH}(\text{DMAP})][\text{OTf}]$ (**4.2**). **4.2** represents a rare example of a base-stabilised cationic gallium hydride and is presumably formed from by substitution of the triflate substituent by DMAP at gallium. **4.2** may be crystallised as large colourless blocks from a toluene/hexane layering at

room temperature and isolated in 84% yield. The molecular structure of **4.2**, determined crystallographically, is shown in Figure 4.4.



Scheme 4.5: Synthesis of $[[\text{Dipp}1]\text{Ga}(\text{DMAP})(\text{H})][\text{OTf}]$ (**4.2**) from the addition of DMAP to **4.1**^{OTf} and the related complex $[\text{Dipp}1']\text{Ga}(\text{DMAP})(\text{tBu})$ (right).

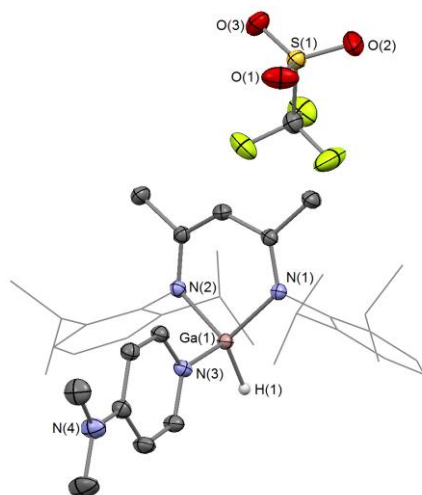


Figure 4.4: Molecular structure of $[[\text{Dipp}1]\text{Ga}(\text{DMAP})(\text{H})][\text{OTf}]$ (**4.2**) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Gallium hydride located in the difference Fourier map and refined isotropically. Key bond lengths (Å) and angles (°): Ga(1)-N(2) 1.9141(12), Ga(1)-N(1) 1.9210(12), Ga(1)-N(3) 1.9671(13), Ga(1)-H(1) 1.42(3), S(1)-O(1) 1.4356, S(1)-O(2) 1.4351(15), S(1)-O(3) 1.4319(14), N(2)-Ga(1)-N(1) 99.46(5), N(3)-Ga(1)-H(1) 107.4(13).

The molecular structure of **4.2** clearly shows the dissociation of the triflate group from the gallium centre in the solid state; the average Ga-O distance (6.79 Å) is outside the

sum of the respective Van der Waals radii. The gallium centre is found in an approximately tetrahedral environment and is projected out of the least squares C₃N₂ plane by 0.289 Å. This is significantly less than observed for **4.1**^{OTf}, consistent with the replacement of the triflate substituent with the planar DMAP ligand. The Ga-N_{DMAP} bond length (1.9671(13) Å) is significantly longer than the endocyclic Ga-N bonds (*d*(Ga-N 1.9141(12), 1.9210(12) Å), consistent with the assertion that this is a donor-acceptor interaction rather than a formal covalent bond. The Ga-N_{DMAP} bond length of **4.2** is significantly shorter than that of the related complex [Dipp¹']Ga(*t*Bu)(DMAP) (*d*(Ga-N) 2.0793(15) Å).¹⁴ Both complexes feature 4-coordinate gallium centres; the shorter Ga-N_{DMAP} bond length found in **4.2** presumably arises from the formally cationic, and therefore highly Lewis acidic, nature of the gallium centre. This shorter distance may also arise, in part, due to the presence of the hydride rather than *tert*-butyl ligand at the gallium centre, thus reducing the steric bulk.

The IR spectrum of **4.2** features an absorption at $\nu_{\text{Ga-H}}$ 1972 cm⁻¹ for the Ga-H stretching frequency. This stretching frequency is consistent with the formally cationic nature of the gallium centre which presumably brings about a lowering in energy of the gallium-centred orbitals and more effective overlap with those of the hydrogen atom, leading to a stronger bond and a higher stretching frequency.³⁵ Despite this, the stretching frequency associated with the Ga-H of **4.2** is *lower* than that of **4.1**^{OTf} (1994 cm⁻¹). This may arise as a result of the relative donor abilities of the DMAP and OTf⁻ substituents or a significant contribution of a resonance form of **4.2**, in which the positive charge is based on the nitrogen of the DMAP substituent, rather than the gallium centre (Scheme 4.5).

The ¹H NMR resonances measured for **4.2** are consistent with retention of its molecular structure in solution. Four doublets and two septets are observed for the ⁱPr groups of the Dipp substituents, consistent with a Nacnac complex that lacks C₂ symmetry, and the Ga-H resonance is observed at δ_H = 4.92 ppm. The resonance for the γ-H undergoes a pronounced downfield shift from δ_H = 4.76 ppm (for **4.1^{OTf}**) to δ_H = 5.51 ppm for **4.2**. Such downfield shifts are commonly observed for cationic Nacnac-ligated species (e.g. [^{Dipp}**1**]AlMe₂ δ_H (γ-H) = 4.91 ppm; [[^{Dipp}**1**]AlMe][B(C₆F₅)₄] δ_H (γ-H) = 5.31 ppm).³⁶ The resonances for the protons of the DMAP ligand are very broad at 298 K, which suggests the molecule displays dynamic behaviour on the NMR timescale at this temperature. Variable temperature NMR experiments were carried out to investigate this process. At 298 K, the *o*-CH and *m*-CH protons of the DMAP ligand give rise to broad singlets at δ_H = 6.81 and 7.80 ppm, respectively. Upon cooling, the *o*-CH proton signals split into two broad signals at δ_H = 7.79 and 8.68 ppm, with coalescence observed around 234 K. In a similar manner the *m*-CH protons split into two broad signals at δ_H = 5.88 and 6.51 ppm, with coalescence observed around 231 K. Despite cooling to 183 K, these resonances do not sharpen to form doublet resonances. These observations suggest that rotation around the Ga-N_{DMAP} bond is relatively facile but may be slowed at low temperatures. The coalescence behaviour allowed for estimation of the barrier associated with this process (ΔG[‡] = 44 kJ mol⁻¹).

At higher temperatures, a second dynamic process evidently occurs. At 298 K, two septets and four doublets are observed for the Dipp ⁱPr groups, indicative of a lack of C₂ symmetry in the molecule; at high temperatures (378 K), one septet and two doublets are observed, although the resonances are broad. This suggests that the DMAP ligand is labile: at high temperatures DMAP has been shown to dissociate from the gallium centre

of the related complex $[\text{Dipp}\mathbf{1}']\text{Ga}(\text{tBu})(\text{DMAP})$ and reattach from either face.¹⁴ It is likely that, at high temperatures, the behaviour of the DMAP ligand of **4.2** is similar. If this process is rapid on the NMR timescale, the molecule should appear to possess C_2 symmetry and display only one septet and two doublets in the ^1H NMR spectrum. Coalescence of the septets for the methine protons is observed around 345 K and this enables the calculation of an approximate barrier of $\Delta G^\ddagger = 70 \text{ kJ mol}^{-1}$ for this process. The barrier for this process is higher than that reported for $[\text{Dipp}\mathbf{1}']\text{Ga}(\text{tBu})(\text{DMAP})$ ($\Delta G^\ddagger = 61.5 \text{ kJ mol}^{-1}$), consistent with the tighter binding of the DMAP ligand to the cationic gallium centre.¹⁴

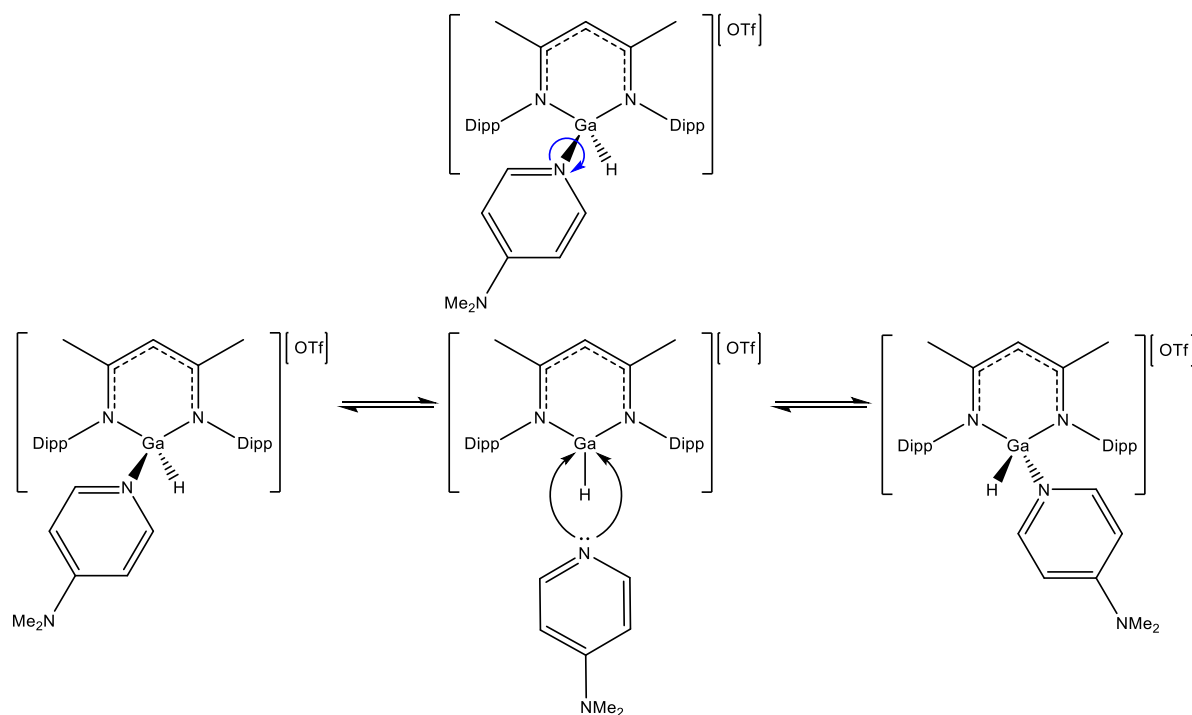
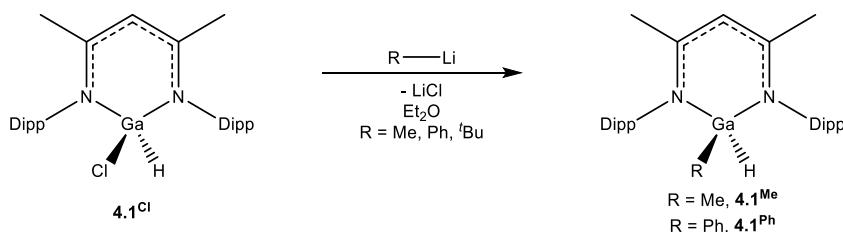


Figure 4.5: Fluxional processes occurring in **4.2**: rotation about the Ga-N bond (top), dissociation DMAP and reassociation to either face of the gallium centre (bottom).

Another potential route for the synthesis of Nacnac-ligated gallium hydrides of the form $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{R})\text{H}$ ($\text{R} = \text{alkyl}$) is salt metathesis between $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{Cl})\text{H}$ (**4.1^{Cl}**) and alkyllithium reagents. The careful addition of one equivalent of methyllithium (MeLi) to a solution of **4.1^{Cl}** in diethyl ether at -78°C leads to the selective formation of

[^{Dipp}1]Ga(Me)H (**4.1^{Me}**), with elimination of LiCl, after stirring at -78°C for 1 h and room temperature for 24 h. The product of the reaction could be isolated in an 83% yield after recrystallisation from diethyl ether, and the ¹H NMR data obtained were consistent with those reported in the literature.²⁴



Scheme 4.6: Attempted synthesis of [^{Dipp}1]Ga(R)H complexes from the addition of alkyllithium reagents to **4.1^{Cl}**.

In light of the promising selectivity of this route, its extension to other gallium hydrides was investigated. The employment of this method using PhLi led to the consumption of **4.1^{Cl}** and the formation of a mixture of two novel species. The major species is suggested to be [^{Dipp}1]Ga(Ph)H (**4.1^{Ph}**), based on its ¹H NMR spectroscopic signatures. The ¹H NMR spectrum shows a broad resonance at $\delta_{\text{H}} = 5.43$ ppm for the gallium-bound hydride, and the multiplet observed for the aromatic protons for both the Dipp and Ph substituents integrates to 11 protons, rather than 6 (as is typical for most ^{Dipp}Nacnac-ligated species). The pattern of two septets and four doublets for the Dipp ⁱPr groups is consistent with unsymmetrical substitution at the gallium centre. The side product formed was later identified as [^{Dipp}1]Ga(Ph)(Cl) (**4.3**), presumably formed from the elimination of LiH during the course of the reaction. **4.1^{Ph}** could not be isolated cleanly, despite multiple recrystallisation attempts and an alternative synthetic route to this compound was sought. The use of *tert*-butyllithium (^tBuLi) yielded no greater selectivity. The ¹H NMR spectrum of the resulting product mixture showed unreacted **4.1^{Cl}**, a trace quantity (<10%) of [^{Dipp}1]Ga(^tBu)H (**4.1^{tBu}**) and **4.1^H** as the major product. It has been previously

demonstrated that *t*BuLi may act as a hydride donor *via* β-hydrogen elimination to yield 2-methylpropene. This method is utilised to synthesise the gallium hydride complex Mes*₂GaH (Mes* = 2,4,6-*t*Bu₃C₆H₂) from the reaction of Mes*₂GaCl with *t*BuLi.³⁷ The scope of the method outlined in Scheme 4.6 to selectively synthesise alkyl-substituted gallium hydrides is relatively limited.

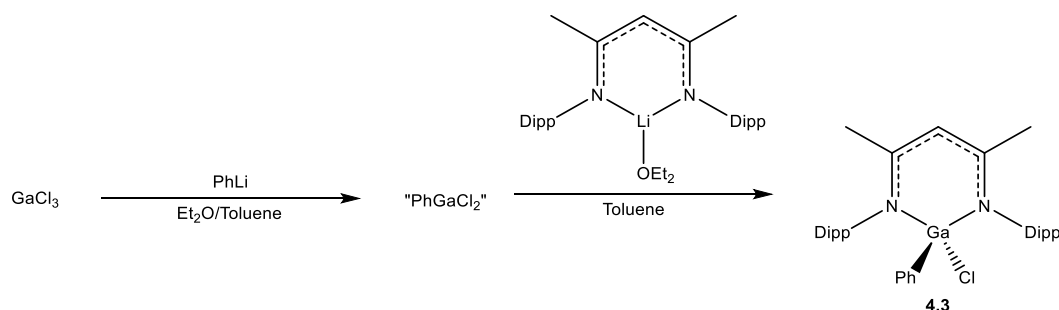
The two most commonly utilised methodologies for the synthesis of substituted Nacnac gallium hydrides are the oxidative addition of an E-H bond at the gallium centre of [Dipp₁]Ga and hydride-for-halide exchange of a Nacnac gallium halide complex using hydride sources.^{14,24,27,28} However, only the use of the second method may be used for the formation of alkyl-substituted Nacnac gallium hydrides, due to the difficulties associated with alkane C-H activation. The number of reported examples of halide complexes of the form [Dipp₁]Ga(R)X is however relatively limited. Complexes of this type may be synthesised from the oxidative addition of the C-X bond of a haloalkane across the gallium(I) centre of [Dipp₁]Ga, as illustrated by the syntheses of [Dipp₁]Ga(R)Br (R = *t*Bu, *t*Am {*t*Am = -CMe₂Et}) and [Dipp₁]Ga(*t*Bu)Cl.^{14,29} Alternatively, such complexes may be formed from salt-metathesis reactions between [Dipp₁]Li(OEt₂) and reagents of the type RGaCl₂, as demonstrated by the formation of [Dipp₁]Ga(Me)Cl from the reaction of [Dipp₁]Li(OEt)₂ with MeGaCl₂.²⁴

Typically, the metathetical reactions of [Dipp₁]Li(OEt₂) with sources of RMCl₂ selectively yield complexes of the form [Dipp₁]M(R)Cl (M = Al, Ga, In). [Dipp₁]Al(Ph)Cl cannot be synthesised *via* the reaction of [Dipp₁]AlCl₂ with PhLi, but may instead be accessed *via* the addition of [Dipp₁]Li to a toluene solution of PhAlCl₂ (itself generated *in-situ* from PhLi and AlCl₃).³⁸ This reactivity is relatively well-established for the synthesis of aluminium complexes due to the commercial availability of RAlCl₂ reagents. By contrast,

RGaCl₂ reagents must be independently synthesised, typically from the trialkylgallium complex and GaCl₃.³⁹

Notwithstanding this, a synthetic route from RGaCl₂ was investigated for the preparation of complexes of the type [Dipp¹]Ga(R)Cl. The dropwise addition of a solution of PhLi in diethyl ether to a solution of GaCl₃ in toluene at -78°C leads to the immediate precipitation of LiCl upon warming to room temperature. The resulting solution of "PhGaCl₂" was subsequently cooled to -78°C whereupon a solution of [Dipp¹]Li(OEt₂) was added dropwise. Following stirring overnight at room temperature and workup, [Dipp¹]Ga(Ph)Cl (**4.3**) was isolated as a microcrystalline material in 80% yield. Repeated attempts to grow crystals suitable for X-ray diffraction from a range of hydrocarbon solvents and at a range of temperatures were unsuccessful. The formation of **4.3** is signalled by the presence of four doublets and two septets in the aliphatic region of the ¹H NMR spectrum for the Dipp ⁱPr substituents. This pattern of resonances is consistent with the Nacnac-ligated complex that lacks C₂ symmetry and is indicative of the formation of an unsymmetrically substituted gallium complex. Moreover, a complex overlapping multiplet is observed at δ_H = 6.84 – 7.19 ppm, integrating to 11 protons, for the aromatic protons of the Dipp groups (6H) and gallium-bound phenyl substituent (5H). In the ¹³C NMR spectrum a broad resonance is observed at δ_C = 141.1 ppm for the *ipso*-carbon of the phenyl substituent; the broadening presumably arises from the proximity to the quadrupolar ^{69/71}Ga nucleus (I = 3/2). The formation of **4.3** strongly suggests that the addition of one equivalent of PhLi to GaCl₃ leads to the selective formation of PhGaCl₂, a compound previously reported to be synthesised from GaPh₃ and two equivalents of hydrochloric acid.⁴⁰ An analogous method was employed for the synthesis of [Dipp¹]Ga(^tBu)Cl, using ^tBuLi/GaCl₃. In this case, analysis of the resulting

product mixture by ¹H NMR spectroscopy revealed the chemistry to be less selective and [Dipp₁]Ga(^tBu)Cl was formed as *ca.* 15% of the product mixture, together with [Dipp₁]GaCl₂ and protio-ligand.

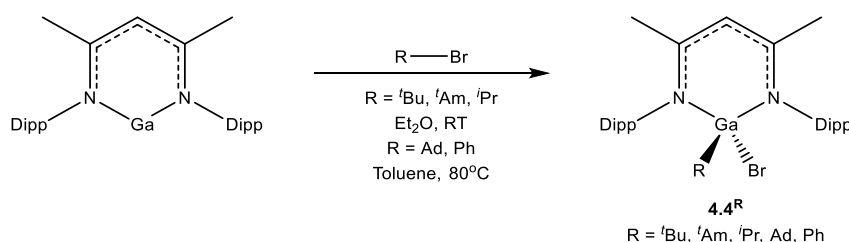


Scheme 4.7: Synthesis of [Dipp₁]Ga(Ph)Cl (**4.3**).

Oxidative addition of E-X bonds at the gallium(I) centre of [Dipp₁]Ga has extensive literature precedent.^{27–29} This method has been used, for example, to synthesise alkyl-substituted gallium halide complexes [Dipp₁]Ga(R)X (R = ^tBu, ^tAm, X = Br; R = ^tBu, X = Cl).^{14,29} The established synthetic route to [Dipp₁]Ga itself exploits the reaction of [Dipp₁]Li(OEt₂) with 'GaI', and relies on fractional crystallisation to separate [Dipp₁]Ga from the side product [Dipp₁]GaI₂.⁴¹ However, during the course of this study it was found that [Dipp₁]GaI₂ can be prepared independently *via* the reaction of [Dipp₁]Li(OEt)₂ with GaI₃, and that reduction of [Dipp₁]GaI₂ offers a better yielding synthetic route to [Dipp₁]Ga. The use of alkali metal mirrors (M = Na, K) in a range of solvents typically leads to overreduction, and the use of alkali metal chunks (M = Na, K, Mg) yields no reduced product at all. The employment of the soluble reducing agent ([^{Mes}₁]Mg)₂, however, selectively leads to the isolation of [Dipp₁]Ga in 72% yield.⁴²

With a reliable route to [Dipp₁]Ga in hand, the literature synthesis of [Dipp₁]Ga(R)Br (R = ^tBu, ^tAm) was adapted to produce the analogous complexes [Dipp₁]Ga(R)Br (R = ⁱPr (**4.4ⁱPr**), Ad (**4.4^{Ad}**), Ph (**4.4^{Ph}**)) *via* the oxidative addition of the C-Br bonds of

2-bromopropane, 1-bromoadamantane and bromobenzene, respectively. The conditions required to bring about activation of the C-X bonds at [Dipp₂1]Ga strongly relate to both the bond strength and steric environment of the haloalkane. The oxidative addition of *t*BuCl, for example, requires heating at 60°C, while the weaker C-Br bond of *t*BuBr is cleaved readily at room temperature over the course of several hours.^{14,29} The oxidative addition of *i*PrBr is complete within minutes at room temperature, whereas only a trace of reactivity with AdBr is observed after stirring at room temperature overnight. The latter reaction requires heating to 80°C for 4 h to bring about oxidative addition of the highly sterically encumbered C-Br bond. The formation of **4.4^{Ph}** is only complete after heating at 80°C for 4 d: elevated reaction temperatures and long reaction times are required to activate the stronger sp²-hybridised C-Br bond.



Scheme 4.8: Synthesis of unsymmetrically substituted complexes [Dipp₂1]Ga(R)(Br) (**4.4^R**).

4.4^{iPr}, **4.4^{Ad}** and **4.4^{Ph}** could be isolated in moderate yields after recrystallisation and have been characterised in each case by spectroscopic and analytical techniques. Each displays four doublets and two septets in the ¹H NMR spectrum for the *i*Pr groups of the Dipp substituent, consistent with an unsymmetrically substituted gallium centre. The identities of these complexes were further supported by EI mass spectrometry and elemental analysis. Single crystals of **4.4^{iPr}** were obtained by cooling a concentrated toluene solution to −30°C; single crystals of **4.4^{Ad}** were obtained from a benzene solution at room temperature. Repeated attempts to obtain single crystals of **4.4^{Ph}** suitable for

X-ray crystallography, however, were unsuccessful. The molecular structures of **4.4^{iPr}** and **4.4^{Ad}** are shown in Figure 4.6.

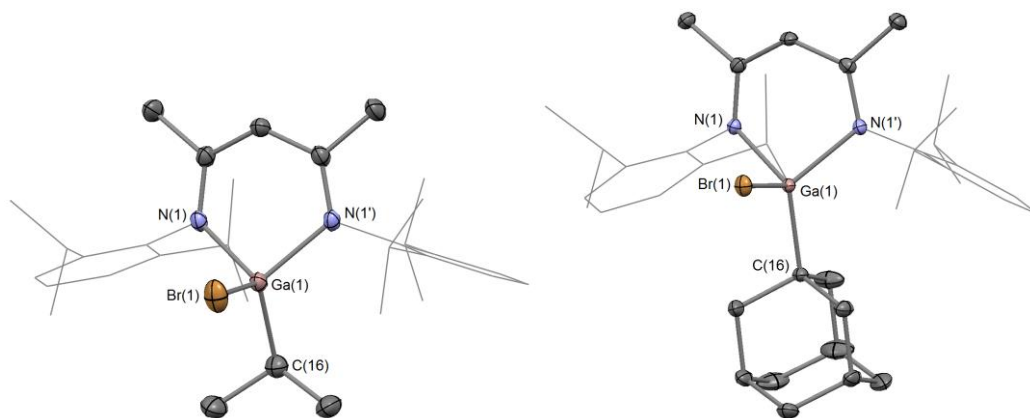
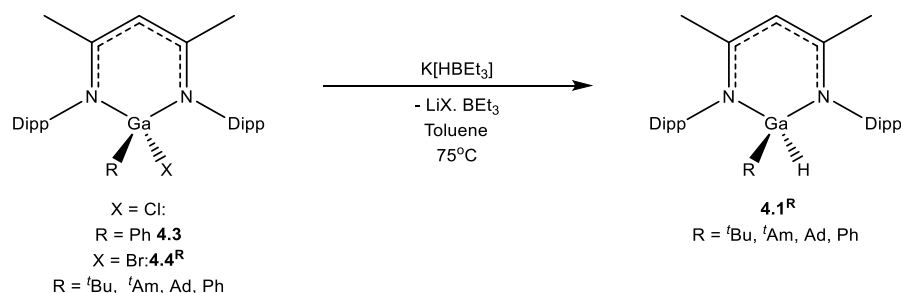


Figure 4.6: Molecular structures of [Dipp1]Ga(*i*Pr)Br (**4.4^{iPr}**) (left) and [Dipp1]Ga(Ad)Br (**4.4^{Ad}**) (right) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°): **4.4^{iPr}**: Br(1)-Ga(1) 2.3578(4), Ga(1)-N(1) 1.9576(14), Ga(1)-C(16) 1.970(3), N(1)-Ga(1)-N(1) 96.34(8), C(16)-Ga(1)-Br(1) 112.71(10). **4.4^{Ad}**: Br(1)-Ga(1) 2.3907(3), Ga(1)-N(1) 1.9621(12), Ga(1)-N(1') 1.9621(11), Ga(1)-C(16) 1.9948(19), N(1)-Ga(1)-N(1') 95.56(7), C(16)-Ga(1)-Br(1) 108.69(6).

Geometrically, the molecular structures of **4.4^{iPr}** and **4.4^{Ad}** closely resemble that reported for [Dipp1]Ga(*t*Bu)Br. In each case, the gallium atom is found in a distorted tetrahedral environment and located significantly out of the plane of the C₃N₂ plane of the Nacnac ligand (**4.4^{iPr}** 0.533 Å; **4.4^{Ad}** 0.701 Å); a greater distortion from planarity arises for larger alkyl substituents. For all three complexes, the bromide substituent occupies the axial position and the alkyl group the less sterically hindered equatorial position. The Ga-N, Ga-Br and Ga-C bond lengths of **4.4^{Ad}** lie close in value to those of [Dipp1]Ga(*t*Bu)Br (*d*(Ga-N) 1.9528(17), 1.9596(17) Å, *d*(Ga-Br) 2.3997(3) Å, *d*(Ga-C) 1.9970(16) Å). By contrast, the Ga-C and Ga-Br bonds of **4.4^{iPr}** are significantly shorter;

this may arise due to the reduced steric bulk or reduced σ -donating properties of the gallium-bound isopropyl substituent.



Scheme 4.9: Synthesis of unsymmetrically substituted hydride complexes **4.1^R**.

Taking inspiration from the reported synthesis of $[\text{Dipp}\mathbf{1}]\text{Ga}({}^t\text{Bu})\text{H}$, solutions of the gallium(III) halide complexes $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{R})\text{X}$ ($\text{R} = {}^i\text{Pr, } {}^t\text{Am, Ad, Ph, X} = \text{Br}$; $\text{R} = \text{Ph, X} = \text{Cl}$) in toluene were treated with a slight excess of $\text{K}[\text{HBET}_3]$ and heated to 75°C overnight.¹⁴ The use of this method selectively yields the novel gallium hydride complexes $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{R})\text{H}$ ($\text{R} = {}^t\text{Am}$ (**4.1^{tAm}**), **Ad** (**4.1^{Ad}**), **Ph** (**4.1^{Ph}**). Uniquely, in the case of $\text{R} = {}^i\text{Pr}$, an intractable mixture of species is formed and the synthesis of $[\text{Dipp}\mathbf{1}]\text{Ga}({}^i\text{Pr})\text{H}$ was not explored further. The other hydrides were obtained in good yields (**4.1^{tAm}**: 53%; **4.1^{Ad}**: 69%; **4.1^{Ph}**: 82%) and were characterised by standard spectroscopic and analytical techniques.

A singlet is observed in the ${}^1\text{H}$ NMR spectrum for the Nacnac backbone γ -H in each case, in the region typical for Nacnac-ligated gallium hydrides.^{6,24,27,28} A singlet resonance integrating to 1H is observed for the gallium hydride, broadened due to the presence of the quadrupolar ${}^{69/71}\text{Ga}$ nucleus. The chemical shifts for these resonances (Table 4.1) are in the region typical of Nacnac-ligated gallium hydrides, although a mutual comparison reveals no significant correlation with the electronic character of the gallium-bound substituent. The formulation of these complexes as gallium monohydrides is further supported by elemental analysis, EI mass spectrometry (which shows a strong signal for

the [M-H]⁺ ion in each case) and infra-red spectroscopy (which shows a single strong absorption in the region typical for Ga-H stretches). As observed for aluminium hydride complexes (Chapter 3), the Ga-H stretching frequency is strongly influenced by the gallium-bound substituent. The presence of a strongly electron-withdrawing substituent leads to significantly higher stretching frequencies (Table 4.1). The molecular structures of **4.1^{iPr}**, **4.1^{Ad}** and **4.1^{Ph}** were determined by X-ray crystallography (Figure 4.7).

[^{Dipp} 1]Ga(R)H	δ_H (γ -H) (ppm)	δ_H (Ga-H) (ppm)	IR $\nu_{\text{Ga-H}}$ (cm ⁻¹)
^t Am	4.87	5.53	1797
Ad	4.85	5.29	1802
Ph	4.83	5.43	1909
^t Bu	4.87	5.45	1798
H	4.76	5.19	1893, 1861
Me	4.81	5.49	1825
OTf	4.76	5.62	1994
Cl	4.79	5.47	1910, 1941

Table 4.1: A comparison of spectroscopic features of **4.1^{tAm}**/**4.1^{Ad}**/**4.1^{Ph}** with other gallium hydrides [^{Dipp}1]Ga(R)H reported in the literature.^{14,23,24}

The molecular structures of **4.1^{iPr}**, **4.1^{Ad}** and **4.1^{Ph}** all display the expected connectivity, and are closely related to those reported for related unsymmetrically substituted [^{Dipp}1]Ga(R)H complexes.^{14,23,24} The gallium centres are found in an approximately tetrahedral environment and lie significantly out of the plane of the Nacnac ligand (distance from least squares C₃N₂ plane: **4.1^{tAm}** 0.829 Å, **4.1^{Ad}** 0.791 Å, **4.1^{Ph}** 0.473 Å). The distance of the Ga centre from the least-squares C₃N₂ plane correlates to the steric bulk of the gallium-bound substituents, such that the gallium centre of [^{Dipp}1]GaH₂ almost lies in the plane of the Nacnac ligand (distance 0.031 Å). The extent of distortion of the ring observed for **4.1^{tAm}** and **4.1^{Ad}** is similar, and significantly greater than that observed for **4.1^{Ph}**. Presumably, the planar nature of the phenyl substituent leads to reduced steric interactions. The gallium hydrides were located in the difference Fourier

map and refined isotropically; the gallium hydride invariably occupies the more sterically hindered axial position; consistent with previous observations for other unsymmetrically substituted Nacnac complexes.

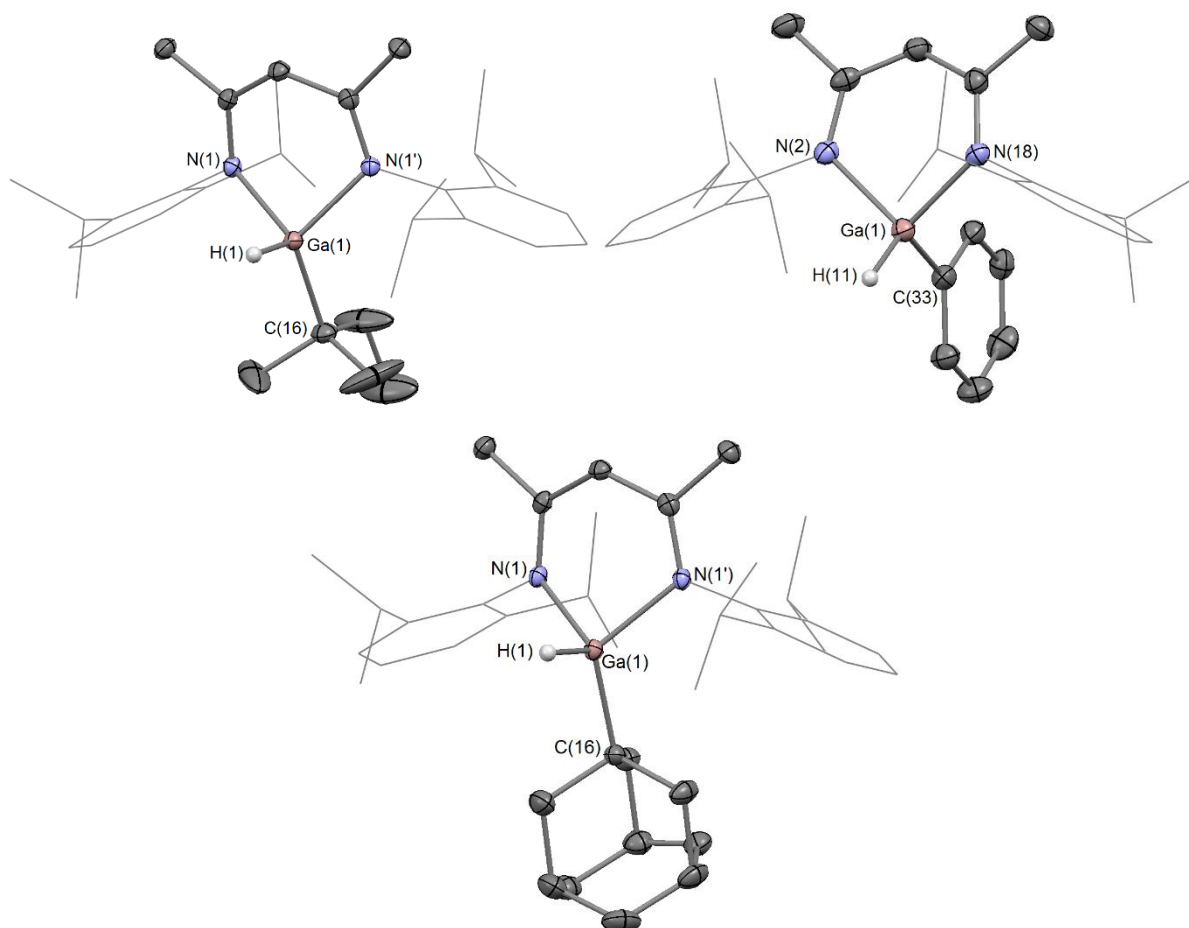


Figure 4.7: Molecular structures of [Dipp¹]₂Ga(*t*Am)H (**4.1^{tAm}**) (top left), [Dipp¹]₂Ga(Ph)H (**4.1^{Ph}**) (top right) and [Dipp¹]₂Ga(Ad)H (**4.1^{Ad}**) (below) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Gallium hydride located in the difference Fourier map and refined isotropically. Key bond lengths (Å) and angles (°): **4.1^{tAm}**: Ga(1)-N(1) 1.9876(10), Ga(1)-C(16) 2.0157(19), Ga(1)-H(1) 1.49(3), N(1)-Ga(1)-N(1) 92.52(6). **4.1^{Ph}**: Ga(1)-N(2) 1.974(4), Ga(1)-N(18) 1.972(4), Ga(1)-C(33) 1.969(5), Ga(1)-H(11) 1.553, N(2)-Ga(1)-N(18) 95.00(16). **4.1^{Ad}**: Ga(1)-N(1) 1.9913(10), Ga(1)-C(16) 2.0115(18), Ga(1)-H 1.65(3), N(1)-Ga(1)-N(1) 92.53(6).

4.1^R	^t Am	Ad	^t Bu	H	Ph	Cl	OTf
<i>d</i> (Ga-N)	1.9876(10)	1.9913(10)	1.9873(10) 2.013(2)	1.960(1) 1.963(1)	1.974(4) 1.972(4)	1.938(2) 1.921(1)	1.9075(19) 1.9189(19)
<i>d</i> (Ga-H)	1.49(3)	1.65(3)	1.495	1.54(2) 1.52(2)	1.553	1.47	1.468
$\nu_{\text{Ga-H}}$ (cm ⁻¹)	1797	1802	1798	1893, 1861	1909	1910, 1941	1994

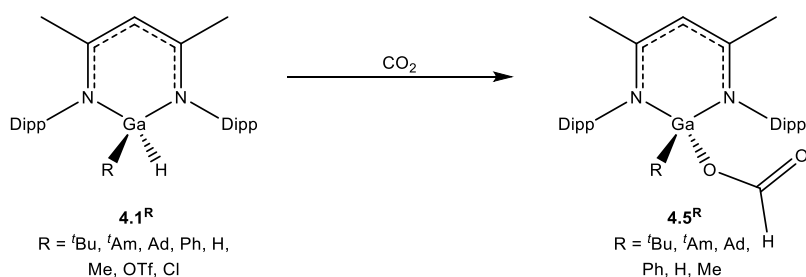
Table 4.2: A comparison of the Ga-N and Ga-H distances for **4.1^{tAm}**, **4.1^{Ad}**, **4.1^{Ph}** and **4.1^{OTf}** with those reported in the literature.^{14,23,24}

A comparison of the molecular structures of **4.4^{Ad}** and **4.1^{Ad}** reveals that bromide-for-hydride exchange leads to a pronounced lengthening of the Ga-N contacts (**4.4^{Ad}** *d*(Ga-N) 1.9621(12), 1.9621(11) Å; **4.1^{Ad}** *d*(Ga-N) 1.9913(10) Å). This arises from the reduction in Lewis acidity of the gallium centre on replacing an electronegative halide substituent with a strongly σ -donating hydride substituent. This effect is also observed for the complexes **4.4^{tBu}** (*d*(Ga-N) 1.9528(17), 1.9596(17) Å) and **4.1^{tBu}** (*d*(Ga-N) 1.9873(10) Å).¹⁴ A comparison of the Ga-N distances of these hydrides with those reported in the literature reflect the impact that the electronic character of the gallium-bound substituent has on the Lewis acidity of the metal centre (Table 4.2). The complexes that bear electron-withdrawing substituents (Cl, OTf) typically feature comparatively short Ga-N contacts arising from increased Lewis acidity of the gallium centre; these are significantly lengthened upon the replacement of these substituents with strongly σ -donating alkyl groups (^tBu, ^tAm, Ad). Potentially, the influence on the Lewis acidity at gallium of the R substituent (and the associated changes in Ga-N distances) is also reflected in the corresponding Ga-H bond strengths. Thus, electron-withdrawing R substituents should bring about a lowering in energy of gallium-centred orbitals which would then better match those of hydrogen, producing a shorter, stronger Ga-H bond.³⁵ The use of Ga-H distances, determined

crystallographically, to gauge this is an unreliable tool; the trend in the observed Ga-N distances does however correlate with the trend in Ga-H stretching frequencies.

4.4.2 Reactivity of gallium hydrides towards CO₂

The synthesis of these novel hydrides allows for the investigation of the impact of the gallium-bound R substituent on the reactivity of the gallium-hydrides towards substrates containing unsaturated C=X bonds. The reduction of CO₂, catalysed by [Dipp₁]Ga(^tBu)H, proceeds *via* insertion of CO₂ into the Ga-H bond and an enhancement of the rate of this process might be achieved through an understanding of the impact of the R substituent.¹⁴ With this in mind, the reactivity of our novel Nacnac-ligated gallium hydrides (and related systems) towards CO₂ was probed.



Scheme 4.10: Insertion of CO₂ into the Ga-H bonds of **4.1^R** to yield the corresponding formate complexes **4.5^R**.

The gallium hydrides [Dipp₁]Ga(R)H (R = H, Me, Ph, ^tAm, Ad) all react with CO₂ in similar fashion to [Dipp₁]Ga(^tBu)H. Insertion of CO₂ into the Ga-H bond to yield gallium formate complexes of the type [Dipp₁]Ga(R)(OC(O)H) is signalled by the loss of the broad resonance in the region $\delta_{\text{H}} = 5.19 - 5.53$ ppm associated with the gallium hydride, and the appearance of a sharp downfield resonance in the region $\delta_{\text{H}} = 8.36 - 8.88$ ppm, diagnostic of a formate functionality. In each case, the resonance associated with the backbone γ -H is shifted downfield relative to that observed for the corresponding

gallium hydride. Moreover, the respective IR spectra show strong absorptions in the region 1659 – 1679 cm⁻¹ corresponding to the C=O stretching band of the formate substituent (Table 4.3).

[^{Dipp} 1]Ga(R)(OC(O)H)	H	Me	Ph	^t Am	Ad	^t Bu
Yield	61%	76%	67%	72%	77%	-
δ_{H} (γ -H) (ppm)	4.91	5.03	5.15	5.08	5.07	5.09
δ_{H} (Ga-H) (ppm)	5.33	-	-	-	-	-
δ_{H} (OC(O)H) (ppm)	8.36	8.67	8.65	8.86	8.88	8.84
δ_{C} (OC(O)H) (ppm)	164.9	164.6	164.4	164.7	164.2	164.4
IR (C=O) (cm ⁻¹)	1659	1661	1659	1677	1679	1679
IR (Ga-H) (cm ⁻¹)	1996	-	-	-	-	-

Table 4.3: Some key spectroscopic features observed for the novel gallium formate complexes reported in this chapter.¹⁴

For **4.1^H**, insertion into only one of the gallium hydride bonds is observed. The ¹H NMR spectrum of the product is consistent with the formulation of the product as [^{Dipp}1]Ga(H)(OC(O)H) (**4.5^H**). The pattern of four doublets and two septets observed, conforms to that observed for unsymmetrically substituted Nacnac complexes. Moreover, the resonance for the formate functionality at δ_{H} = 8.36 ppm integrates to one proton and appears as a doublet (⁴J_{HH} = 2.4 Hz), presumably due to coupling of the formate proton to the gallium hydride. A broad resonance is observed at δ_{H} = 5.33 ppm for the remaining gallium-bound hydride. The IR spectrum of **4.5^H** features a strong absorption at 1996 cm⁻¹ for the Ga-H stretch. This is significantly blue-shifted relative to those observed for [^{Dipp}1]GaH₂ ($\nu_{\text{Ga-H}}$ 1893, 1861 cm⁻¹) and lies closer in value to the stretching frequencies measured for complexes that bear electron-withdrawing substituents ($\nu_{\text{Ga-H}}$: **4.1^{OTf}**: 1994 cm⁻¹, **4.1^{Cl}** 1910, 1941 cm⁻¹). The presence of the electron-withdrawing formate functionality of **4.5^H** leads to a reduction in the hydridic character of the remaining gallium hydride, with the consequence that formation of **4.5^H** is selective, and no insertion of CO₂ into the second Ga-H bond is observed, despite

heating to 80°C for 48 h. Moreover, unlike the reactivity observed for [Dipp¹]AlH₂ with CO₂, no dimerisation of **4.5^H** to form a species analogous to ([Dipp¹]AlOCH₂O)₂ is observed at room temperature or on heating at 80°C for 72 h. This contrasting behaviour is consistent with the reduced Lewis acidity of gallium and reduced hydridity of the Ga-H bond, which prevents the formate functionality of one molecule of **4.5^H** being attacked by the Ga-H bond of another.

Complexes **4.5^H**, **4.5^{Me}**, **4.5^{Ph}**, **4.5^{tAm}** and **4.5^{Ad}** could be isolated as single crystals in high yields and their molecular structures in the solid state elucidated by X-ray crystallography (Figure 4.8).

Geometrically, these molecular structures are closely related to that of [Dipp¹]Ga(^tBu)(OC(O)H).¹⁴ The gallium centre is found in a distorted tetrahedral environment in each case, and lies significantly out of the plane of the Nacnac ligand. The complexes with larger R substituents exhibit a greater degree of ring folding, and consequently a narrower N-Al-N angle. Typically, the formate complexes exhibit a reduced degree of ring folding compared to the corresponding hydrides, despite the increased steric bulk of the formate substituent and the shorter N-Ga contacts. The exception to this is **4.1^H** and **4.5^H**, where the gallium centre of the dihydride lies almost planar with the least-squares C₃N₂ plane. In each case, the formate substituent occupies the axial position; this positioning may cause a slight flattening of the ring to minimise sterically unfavourable interactions with the Dipp ⁱPr groups.

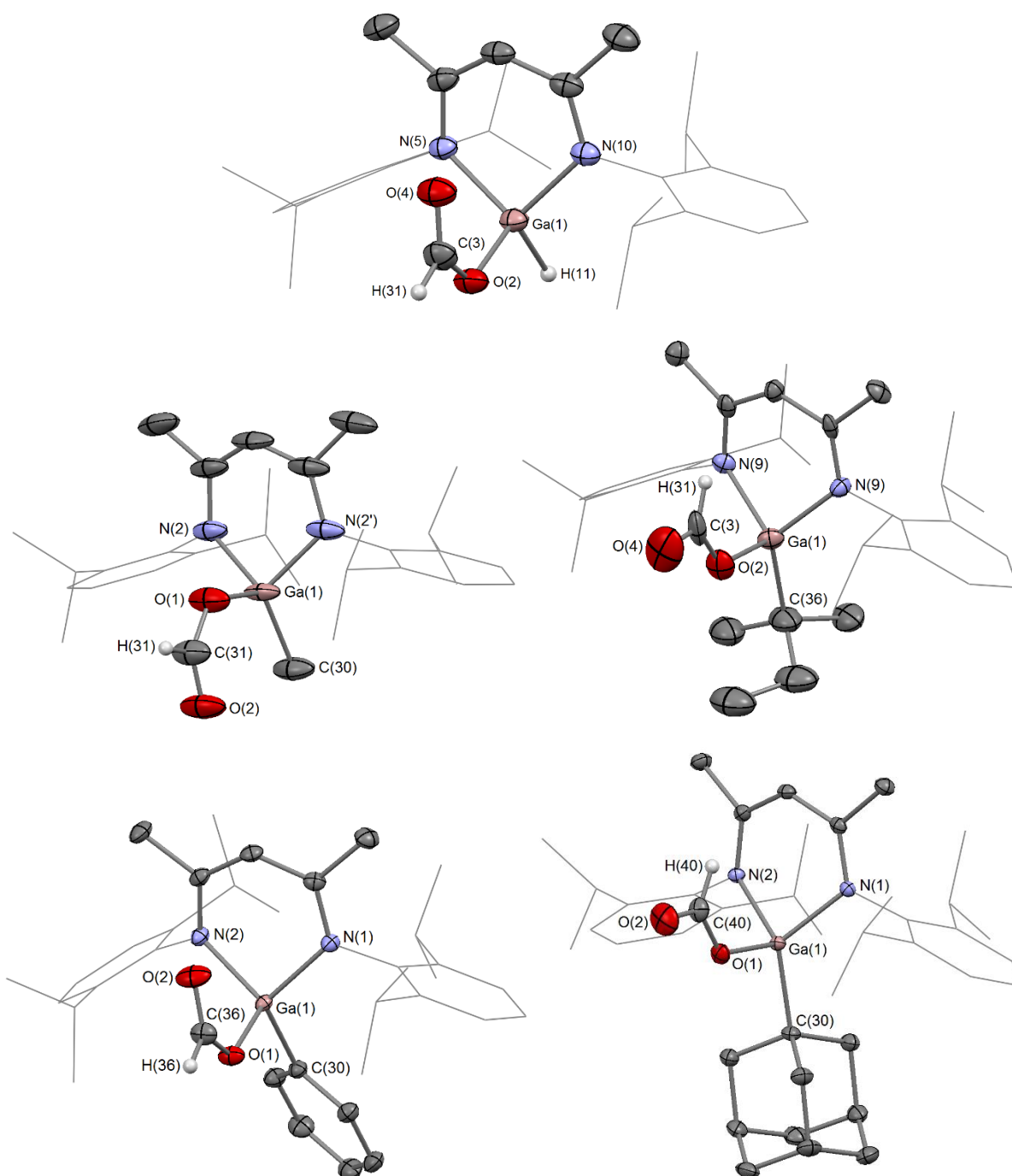


Figure 4.8: Molecular structures of **4.5^H** (top), **4.5^{Me}**, **4.5^{tAm}** (middle left, right), **4.5^{Ph}**, **4.5^{Ad}** (bottom left, right) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Gallium hydride of **4.5^H** located in the difference Fourier map and refined isotropically.

Key bond lengths (Å) and angles (°) are given in **Table 4.4**.

	$d(\text{Ga-O})$ (Å)	$d(\text{Ga-N})$ (Å)	$d(\text{Ga-C})$ (Å)	$d(\text{Ga-H})$ (Å)	$d(\text{C-O})$ (Å)	$d(\text{C=O})$ (Å)	N-Ga-N (°)	O-C-O (°)	O-Ga-R (°)	Distance of Ga from C ₃ N ₂ plane (Å)
4.5^H	1.884(2)	1.921(2) 1.919(2)	-	1.558	1.304(4)	1.203(4)	98.01(10)	126.4(3)	105.7	0.418
4.5^{Me}	1.905(3)	1.938(3) 1.938(3)	1.935(6)	-	1.269(6)	1.184(7)	96.62(18)	128.8(5)	120.23(19)	0.538
4.5^{tAm}	1.886(6)	1.951(6) 1.958(6)	1.983(9)	-	1.304(13)	1.201(12)	94.9(3)	122.8(11)	105.7(3)	0.596
4.5^{Ph}	1.8934(10)	1.9256(12) 1.9345(11)	1.9595(14)	-	1.2955(19)	1.205(2)	97.29(5)	126.62(15)	102.63(5)	0.465
4.5^{Ad}	1.8966(11)	1.9483(12) 1.9586(11)	1.9865(14)	-	1.293(2)	1.182(2)	95.65(5)	125.77(18)	103.48(5)	0.592
4.5^{tBu}	1.9073(13)	1.9431(14) 1.9477(14)	1.9963(17)	-	1.281(2)	1.126(3)	95.85(6)	128.5(2)	100.31(7)	0.568

Table 4.4: Key bond lengths (Å) and angles (°) of of **4.5^R** (R = H, Me, ^tAm, Ph, Ad, ^tBu) (above) and a comparison of some of the structural features of their precursor hydrides (below).

	H	Me	^t Am	Ph	Ad	^t Bu
Distance of Ga from C ₃ N ₂ plane (Å)	0.031	-	0.829	0.473	0.791	-
$d(\text{Ga-N})$ (Å)	1.960(1) 1.963(1)	1.968(2) 1.976(2)	1.9876(10)	1.974(4) 1.972(4)	1.9913(10)	1.9873(10)

A comparison of the Ga-O bonds of these complexes shows only nominal differences within three standard deviations. The Ga-O bonds are shorter than that of (CH₃)N(CH₂CH₂CH₂)₂Ga(OC(O)H) (*d*(Ga-O) 1.951 Å) but significantly longer than the Nacnac-ligated gallium hydroxide and alkoxide complexes [Dipp¹]₂Ga(Me)(OH) (*d*(Ga-O) 1.831(1) Å) and [Dipp¹]₂Ga(H)(OEt) (*d*(Ga-O) 1.792(3) Å).^{13,27,43} This is likely to arise due to the reduced π-donor abilities of the formate ligand compared to hydroxide/alkoxide ligands. The Ga-N bond lengths are significantly shorter than the corresponding hydrides, consistent with an increase in Lewis acidity of the gallium centre upon insertion of CO₂ into the Ga-H bond.

The Ga-O bond of **4.5^{Me}** (*d*(Ga-O) 1.905(3) Å) is significantly longer than that of [Dipp¹]₂Al(Me)(OC(O)H) (*d*(Al-O) 1.780(2) Å), despite the very similar covalent radii of aluminium and gallium (Al: 1.21(4) Å, Ga: 1.22(3) Å), underlining the greater Lewis acidity of aluminium.³³ This presumably also reflects the weaker nature of the Ga-O bond compared to that of aluminium, a feature which may be exploited in the employment of gallium hydrides as catalysts for the borane-mediated catalytic reduction of carbon dioxide.

Benzene-d₆ solutions of the Nacnac-ligated gallium hydrides [Dipp¹]₂Ga(R)H (R = H, Me, Ph, ^tAm, ^tBu, Ad, OTf, Cl) were placed under CO₂ (1 bar) and their reactivity monitored as a function of time in order to establish the kinetic effect(s) that the R substituents might have. As with their aluminium counterparts, gallium hydrides which bear electron-withdrawing substituents [Dipp¹]₂Ga(R)H (R = Cl, OTf, OC(O)H) are unreactive towards CO₂. Placing solutions of **4.1^{OTf}**, **4.1^{Cl}** or **4.5^H** in benzene-d₆ under CO₂ (1 bar) leads to no insertion of CO₂ into the Ga-H bonds even under forcing conditions (80°C, 7 d). This is consistent with the assertion that the presence of the electron-withdrawing

R substituents leads both to a significant reduction in the hydridic character of the Ga-H bond and an increase in its strength, arising from a lowering in energy of the gallium-centred orbitals. Consistently, the Ga-H stretching frequencies associated with these gallanes are 1994 cm⁻¹ (R = OTf), 1941, 1910 cm⁻¹ (R = Cl) and 1996 cm⁻¹ (R = OC(O)H).³⁵.

The hydrides **4.1^H** and **4.1^{Ph}** exhibit no reactivity with CO₂ after 24 h at room temperature. The solutions were heated to 60°C and reaction progress monitored by ¹H NMR spectroscopy for 17 days (heating at 80°C resulted in significant decomposition of the hydrides to protio-ligand). At 60°C, hydrogallation of CO₂ occurs to yield the corresponding formate complexes **4.5^H** and **4.5^{Ph}**, although this is clearly a very slow reaction with these two complexes. ¹H NMR spectroscopy shows the reactions to be 60% and 70% complete after 17 days for **4.1^H** and **4.1^{Ph}**, respectively. On a preparative scale, at higher concentrations and with vigorous stirring, both reactions are complete within 2 weeks.

By contrast, the hydrides that bear alkyl substituents (R = Me, ^tBu, ^tAm, Ad) react with CO₂ at room temperature. For **4.1^{Me}** this occurs relatively slowly and only 12% conversion to the formate complex is observed after *ca.* 16 h at room temperature. The reaction is 80% complete after 10 days at room temperature and complete within two weeks. If the solution is heated at 60°C, the reaction is complete after approximately 24 h. The presence of a more σ -donating hydride leads to significantly increased reactivity with CO₂ and the progression of these reactions was monitored by ¹H NMR spectroscopy for **4.1^{tBu}**, **4.1^{tAm}** and **4.1^{Ad}** (Figure 4.9).

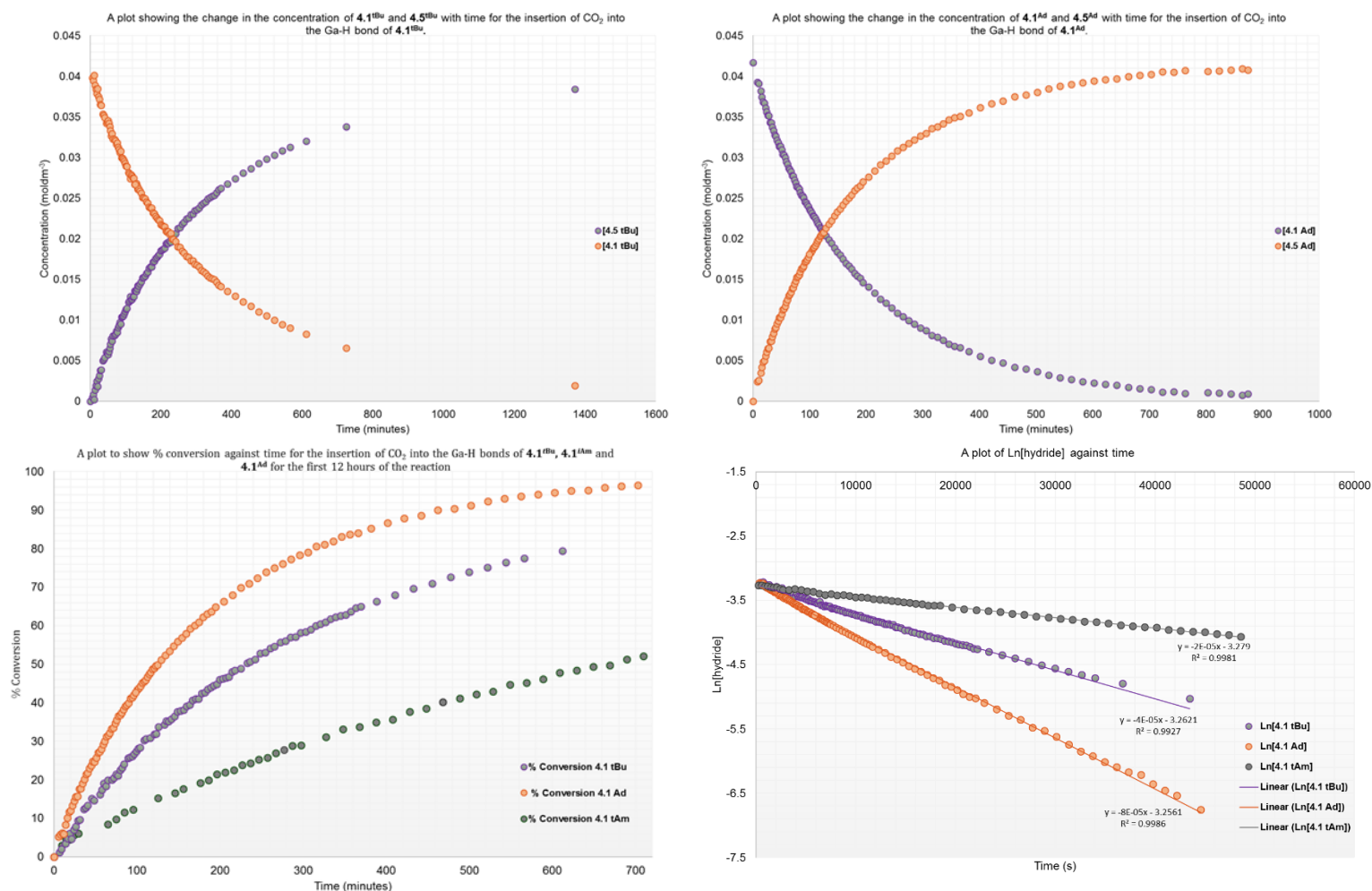


Figure 4.9: Top: A plot of concentration vs. time for the insertion of CO₂ into the Ga-H bonds of **4.1^{tBu}** (left) and **4.1^{Ad}** (right), T = 298 K, P_{CO₂} ~ 1 bar. Bottom: Left: A plot of % conversion vs. time for the first 12 h of these reactions. Right: A plot of ln[**4.1^R**] vs. time. Rate constants determined by linear regression.

Insertion of CO₂ into the Ga-H bonds of these complexes occurs selectively and in a relatively facile manner, with reaction completion times varying from 14 – 30 h. The rate of hydride consumption in all three cases follows *pseudo*-first order reaction kinetics and the *pseudo*-first-order rate constants are shown in Table 4.5.

	4.1^{tBu}	4.1^{tAm}	4.1^{Ad}
% conversion after 12 h	84%	52%	97%
Rate constant, k_{obs} (s ⁻¹)	4×10^{-5}	2×10^{-5}	8×10^{-5}
Half life ($t_{1/2}$, s)	289	578	144

Table 4.5: The rate constants and half-lives for the insertion of CO₂ into the Ga-H bonds of **4.1^{tBu}/4.1^{tAm}/4.1^{Ad}**.

R	OC(O)H	OTf	Cl	Ph	H	Me	Ad	^t Bu	^t Am
$\nu_{\text{Ga-H}}$ (cm ⁻¹)	1996	1994	1910 1941	1909	1893 1861	1825	1802	1798	1797
Conditions	-	-	-	60°C weeks	60°C weeks	RT weeks	RT	RT	RT

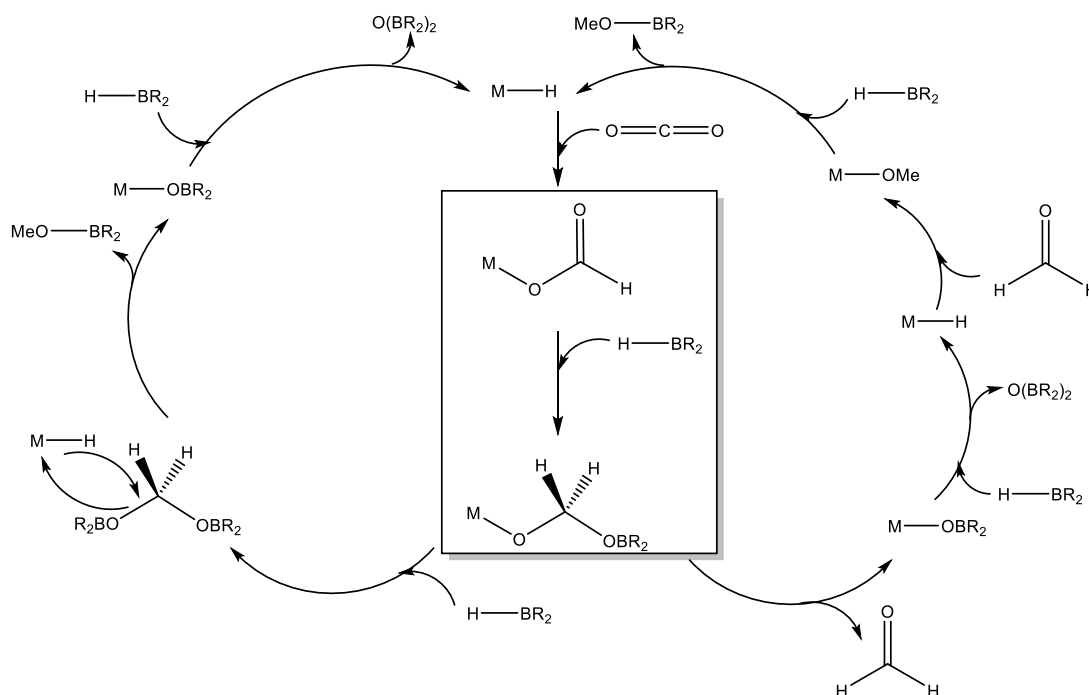
Table 4.6: A comparison of the Ga-H IR stretching frequencies and the conditions required to insert CO₂ into the respective Ga-H bond.

This study emphasises the differing conditions required to bring about insertion of CO₂ into the Ga-H bond. Firstly, it is of note that these gallium hydrides react significantly more slowly with CO₂ than the aluminium systems reported in Chapter 3; this is consistent with the reduced polarity of the Ga-H bonds. Consistent with the aluminium hydride systems is the impact that the gallium-bound R substituent has on the hydridic character of the Ga-H bond, and hence its interaction with the electrophilic C-centre of CO₂. The propensity of the hydrides to insert CO₂ correlates strongly (and inversely) with the Ga-H stretching frequencies; high stretching frequencies are typically associated with reduced (or no) reactivity with CO₂. Conversely, the hydrides with lower Ga-H stretching frequencies exhibit the greatest proclivity for hydrogallation of

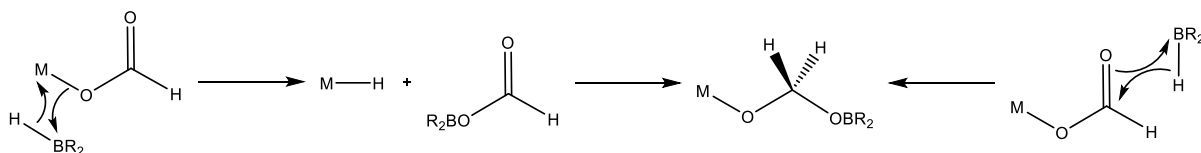
CO₂ (Table 4.6). On the other hand, a comparison of the reactivity of **4.1^{Me}**, **4.1^{tBu}** and **4.1^{Ad}** with CO₂ reveals that the effect of the steric bulk of the R substituent is minimal.

4.4.3 Stoichiometric reactivity studies of gallium formate complexes with boranes

When **4.1^{tBu}** was initially reported, it was the most active single-site main group catalyst for the borane-mediated reduction of CO₂. However, with the exception of demonstrating the viability of the CO₂ insertion and borane metathesis steps in stoichiometric reactions, little investigation of how this system operates mechanistically was undertaken. It was reported that **4.5^{tBu}** readily reacts “with an excess of HBpin at room temperature over the course of several hours in benzene-d₆” to yield MeOBpin and the diboroxane O(Bpin)₂.¹⁴ Having established that the nature of the auxiliary gallium-bound substituent has a significant impact on the propensity of the corresponding hydride to hydrogallate CO₂, the impact of these substituents on the reduction of the gallium formate complexes by boranes may also be crucial. Accordingly, these complexes were reacted with a range of boranes with the aim of probing this issue, and providing a comparison with the reactivity of aluminium formate complexes reported in Chapter 3.



Scheme 4.11: The proposed generic catalytic cycle for the metal hydride-catalysed reduction of CO₂, when a borane is employed as the reductant. This mechanism shows the reduction of CO₂ through to a methanol derivative, with concomitant formation of diboroxane.^{17,44}



Scheme 4.12: Two routes have been proposed for the formation of metallo-bora-acetal intermediates from the reaction of metal formate complexes with boranes.^{17,44}

4.4.3.1 Stoichiometric reactivity studies of gallium formate complexes with HBpin

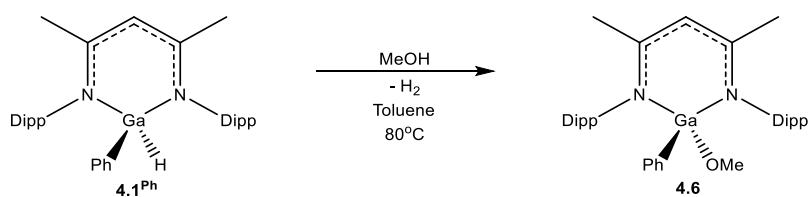
Excess HBpin (4 equiv.) was added to benzene-d₆ solutions of [Dipp¹]₂Ga(R)(OC(O)H) (R = H, Me, Ph, ^tAm, ^tBu, Ad) (**4.5^R**) and the progress of the respective reactions at room temperature monitored by ¹H and ¹¹B NMR spectroscopy. It became apparent, however, after leaving the solutions at room temperature for 4 days, that under the conditions employed none of the complexes regenerate the corresponding hydride in 100% yield.

In each case, a product can be identified which is characterised by singlet resonances at $\delta_{\text{H}} = 8.12$ ppm (1H) and $\delta_{\text{H}} = 0.92$ ppm (12H). The identity of this species is postulated to be (pinBO)C(O)H, presumably formed *via* Ga-O/B-H metathesis between [Dipp¹]**4.5**Ga(R)(OC(O)H) and HBpin - a step that would be favoured by a less sterically hindered and more electron-deficient gallium centre.⁴⁵ This is consistent with the observation that the complexes **4.5^{tBu}**, **4.5^{tAm}** and **4.5^{Ad}** react significantly more slowly with HBpin than their counterparts which bear smaller substituents (**4.5^H**, **4.5^{Me}**, **4.5^{Ph}**). The formate ester (pinBO)C(O)H is considered to be a transient intermediate in the HBpin-mediated catalytic reduction of CO₂.^{17,44,45} It is suggested to be consumed by reinsertion into the M-H bond of the catalyst, followed by a series of metathetical steps (Scheme 4.11).^{17,44,45} It seems likely that the propensity of gallium hydrides to reinsert (pinBO)C(O)H correlates with their relative reactivities towards CO₂, as illustrated by the persistence of (pinBO)C(O)H in the presence of the (less reactive) gallium hydrides **4.1^H**/**4.1^{Me}**/**4.1^{Ph}**. In every case, a small singlet is observed at $\delta_{\text{H}} = 5.49$ ppm, which corresponds to the acetal functionality of (pinBO)₂CH₂, another key intermediate in the postulated catalytic cycle (Scheme 4.11).⁴⁵

Complete regeneration of the gallium hydride species is brought about only when the reaction mixtures are heated. For **4.5^{tBu}**, **4.5^{tAm}** and **4.5^{Ad}**, the ¹H NMR spectra show complete consumption of the formate, and regeneration of the hydride (with accompanying formation of MeOBpin and O(Bpin)₂), when the reaction mixtures are heated at 80°C for one hour. By contrast, **4.5^H**, **4.5^{Me}** and **4.5^{Ph}** require heating to 80°C for extended periods (*ca.* 12 h) to bring about complete regeneration of the corresponding hydride species. This is consistent with a higher energetic barrier for reinsertion of (pinBO)C(O)H into these Ga-H bonds.

It is suggested that the transformation of (pinBO)C(O)H to MeOBpin/O(Bpin)₂ proceeds *via* intermediates of the form LM(OBpin) and LM(OMe) (Scheme 4.11).^{16,17,44} The attempted isolation of the complexes [Dipp₁]₂Ga(R)(OBpin) from the addition of one equivalent of HBpin to solutions of [Dipp₁]₂Ga(R)(OC(O)H) in toluene was unsuccessful; the reactions proceed straight to the hydride and leave unreacted formate complexes.

Alternatively, the preparation of gallium methoxide complexes, [Dipp₁]₂Ga(R)(OMe), was targeted in order to assay their potential to operate as intermediates within the borane-mediated catalytic reduction of CO₂. The work reported in Chapter 3 shows that the addition of methanol to the aluminium hydrides [Dipp₁]₂Al(R)H (R = Me, Et) leads to the rapid formation of the methoxide complexes [Dipp₁]₂Al(R)(OMe). The use of this method to generate the corresponding gallium alkoxide complexes met with limited success. The addition of excess MeOH (> 10 equiv.) to a solution of **4.1^{tBu}** or **4.1^{tAm}** in benzene-d₆ leads to no deprotonation of the alcohol by the gallium hydride, even when heated to 80°C for 48 h. Whilst surprising that these complexes display such stability under these conditions, the contrasting behaviour of these group 13 hydrides towards methanol is consistent with their relative basicities.



Scheme 4.12: The formation of [Dipp₁]₂Ga(Ph)(OMe) (**4.6**) from the deprotonation of methanol by the gallium hydride complex **4.1^{Ph}**.

[Dipp₁]₂Ga(Ph)(OMe) (**4.6**) may be formed from the addition of 5 equivalents of MeOH to a solution of **4.1^{Ph}** in toluene, followed by heating to 80°C for 3 days, and could be isolated in 87% yield as small, colourless crystals. **4.6** was characterised by standard

spectroscopic and analytical techniques, in addition to X-ray crystallography. Its formation is signalled spectroscopically by the loss of the broad resonance for the gallium hydride at $\delta_{\text{H}} = 4.83$ ppm in the ¹H NMR spectrum and the appearance of a sharp singlet integrating to 3H at $\delta_{\text{H}} = 3.90$ ppm for the methoxide substituent (cf. [Dipp¹]Al(Et)(OMe) $\delta_{\text{H}} = 3.84$ ppm).

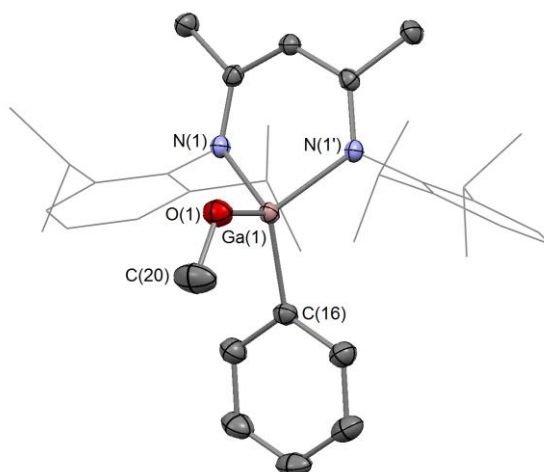
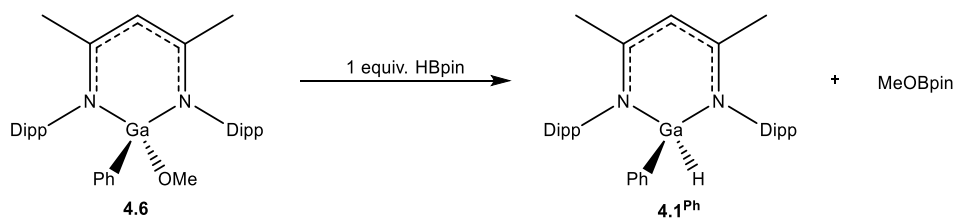


Figure 4.10: Molecular structure of [Dipp¹]Ga(Ph)(OMe) (**4.6**). Thermal ellipsoids set at the 40% probability level. Hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°): Ga(1)-O(1) 1.8179(18), Ga(1)-N(1) 1.9591(12), Ga(1)-C(16) 1.975(2), N(1)-Ga(1)-N(1) 95.31(7).

The molecular structure of **4.6** (Figure 4.10) displays the expected molecular connectivity. The Ga-O distance ($d(\text{Ga}(1)\text{-O}(1))$ 1.8179(18) Å) is somewhat shorter than both the sum of the covalent radii (1.22(3) + 0.66(2) = 1.88 Å) and the Ga-O bond length of **4.5^{Ph}** ($d(\text{Ga-O})$ 1.8934(10) Å).³³ This may arise due to the ability of the methoxide ligand to act as a better π -donor than the formate ligand. This in turn is reflected in increased lengths of the other bonds to gallium in **4.6** ($d(\text{Ga}(1)\text{-N}(1))$ 1.9591(12), $d(\text{Ga}(1)\text{-C}(16))$ 1.975(2) Å) relative to those of **4.5^{Ph}** ($d(\text{Ga-N})$ 1.9256(12), 1.9354(11) Å, $d(\text{Ga-C})$ 1.9595(14) Å). There are relatively few examples of Nacnac-ligated gallium complexes that bear terminal alkoxide ligands; those reported include [Dipp¹]Ga(OEt)H,

synthesised through the activation of ethanol by [Dipp¹Ga], and [Dipp¹Ga(OEt)₂]/[Dipp¹Ga(Cl)(OEt)] produced by the deprotonation of ethanol by the gallium amide complexes [Dipp¹Ga(NHEt)₂] and [Dipp¹Ga(Cl)(NH^tBu)], respectively.^{27,46} The Ga-O bond length of **4.6** is comparable to those observed for these complexes ([Dipp¹GaH(OEt)] *d*(Ga-O) 1.792(3) Å, [Dipp¹Ga(OEt)₂] *d*(Ga-O) 1.812(1), 1.802(1) Å).

The Ga-O bond length is markedly longer than the Al-O bond of [Dipp¹Al(Et)(OMe)] (*d*(Al-O) 1.7169(13) Å) despite the very similar covalent radii of Al (1.21(4) Å) and Ga (1.22(3) Å).³³ This presumably reflects the increased Lewis acidity of aluminium over gallium, and signals the greater strength of the Al-O bond. This in turn has a profound impact on the relative reactivities of these complexes towards HBpin. [Dipp¹Al(Et)(OMe)] is unreactive towards HBpin (and more reactive boranes), even when treated with large excesses at elevated temperatures. By contrast, the addition of one equivalent of HBpin to **4.6** leads to the regeneration of **4.1^{Ph}**, with concomitant formation of MeOBpin in a timeframe shorter than that taken to obtain a ¹H NMR spectrum of the reaction mixture. The reactivity of **4.6** towards HBpin reflects the potential of complexes of this nature to participate as (albeit unobserved) intermediates within the catalytic cycle for the reduction of CO₂.



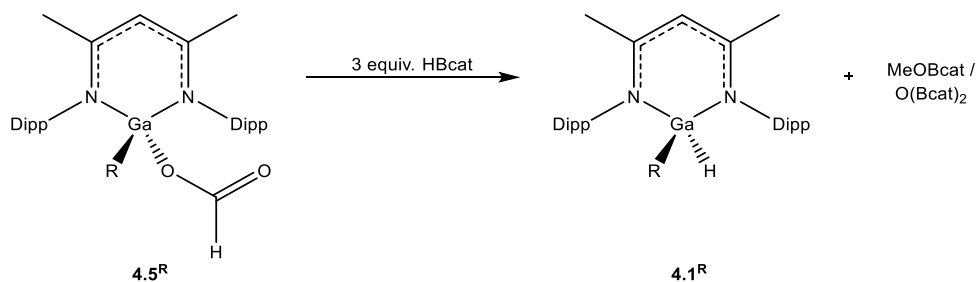
Scheme 4.13: The addition of one equivalent of HBpin to a solution of **4.6**, leading to the immediate regeneration of **4.1^{Ph}** and MeOBpin.

It is clear from these studies that the reactivity of the formate complexes with HBpin is significantly more complicated than initially considered.¹⁴ Further study of this

reactivity, and its impact on the ability of these hydrides to function as catalysts for the reduction of CO₂ when used in conjunction with HBpin is discussed in Section 4.4.4.

4.4.3.2 Stoichiometric reactivity studies of gallium formate complexes with HBcat

In contrast to the behaviour observed with HBpin, the addition of excess HBcat (3 equiv.) to benzene-d₆ solutions of the gallium formate complexes [Dipp¹]**1**Ga(R)(OC(O)H) (R = H, Me, Ph, ^tBu, ^tAm, Ad) leads to the rapid regeneration of the corresponding hydrides at room temperature. These reactions are complete within 20 min; no obvious trends in the rates of reactivity as a function of the gallium-bound R substituents are discernible. The regeneration of the hydrides is accompanied by the formation of the methanol derivative MeOBcat and the diboroxane O(Bcat)₂ as the formate-derived products (as evidenced by sharp resonances at δ_B = 23.4 and 22.4 ppm, respectively, in the ¹¹B NMR spectrum). This is accompanied by the appearance of a singlet resonance at δ_H = 3.36 ppm for the methoxy protons of MeOBcat.^{47,48} No intermediates could be detected by ¹H or ¹¹B NMR spectroscopy; it is presumed that the reaction proceeds by similar mechanistic routes to those proposed in the literature for the catecholborane-mediated catalytic reduction of CO₂.⁴⁴ The significantly increased reactivity of the gallium formate complexes towards HBcat as compared to HBpin is consistent with the greater Lewis acidity of the boron centre.^{17,49}



Scheme 4.14: The reactivity of [Dipp¹]**1**Ga(R)(OC(O)H) with excess HBcat.

4.4.3.3 Stoichiometric reactivity studies of gallium formate complexes with {H(9-BBN)}₂

The gallium formate complexes [^{Dipp}1]Ga(R)(OC(O)H) (R = H, Me, Ph, ^tBu, ^tAm, Ad) were treated with excess {H(9-BBN)}₂ (1.5 equivalents) in benzene-d₆ and the progress of the reactions monitored by ¹H and ¹¹B NMR spectroscopy. In each case, the regeneration of the corresponding gallium hydride complex occurs significantly faster than for HBpin. In contrast to the behaviour observed for the aluminium hydrides (Chapter 3), the gallium hydrides do not form borohydride complexes when in the presence of excess {H(9-BBN)}₂. This may be rationalised on the basis of the reduced Lewis acidity at gallium and the reduced hydridic character of Ga-H bonds. In this case, dimerisation of H(9-BBN) to form {H(9-BBN)}₂ is evidently preferential to the formation of a gallium borohydride complex. The reaction yields MeO(9-BBN) and O(9-BBN)₂, signalled by the observation of a singlet resonance at $\delta_{\text{H}} = 3.45$ ppm in the ¹H NMR spectrum and two resonances at $\delta_{\text{B}} = 56.9, 58.8$ ppm in the ¹¹B NMR spectrum; these chemical shifts are consistent with those reported in the literature.^{50–52}

The reactivity of the gallium formate complexes towards {H(9-BBN)}₂ shows significant differences arising from the gallium-bound R substituents. Those that feature smaller/less σ -donating substituents (R = H, Me, Ph) undergo complete conversion in the presence of {H(9-BBN)}₂ within two hours at room temperature to form the corresponding hydride and the *bis*(boryl)acetal complex {(9-BBN)O}₂CH₂ ($\delta_{\text{H}} = 5.35$ ppm, $\delta_{\text{B}} = 58.9$ ppm) as the sole formate-derived species. *Bis*(boryl)acetal complexes such as {(9-BBN)O}₂CH₂ have been hypothesised as intermediates within the borane-mediated catalytic reduction of CO₂ (Scheme 4.11).^{17,52} In this case, it is likely that {(9-BBN)O}₂CH₂ is formed in the reaction of [^{Dipp}1]Ga(R)(OCH₂O(9-BBN)) with

$\{H(9\text{-BBN})\}_2$ *via* B-H/Ga-O metathesis. $\{(9\text{-BBN})O\}_2CH_2$ is relatively long-lived in solution due to the increased strength of the B-O bond, arising from the Lewis acidity of the boron centre, relative to the corresponding species $\{(X_2B)O\}_2CH_2$ ($X_2 = \text{pin, cat}$). Species of this nature are proposed to be consumed by their reaction with a metal hydride (*via* M-H/C-O metathesis) to produce $MeO(9\text{-BBN})$ and a metalborate ester (which typically rapidly undergo further M-O/B-H metathesis with a borane).¹⁷ This step has been calculated to be the rate-determining step for the reduction of CO₂ with HBpin, catalysed by LGeH ($L = -N(\text{Ar})Si(i\text{Pr})_3$, $\text{Ar} = \text{C}_6\text{H}_2\text{Pr}^i\{\text{C}(\text{H})\text{Ph}_2\}_{2-4,2,6}$) and this is evident in this case by the persistence of $\{(9\text{-BBN})O\}_2CH_2$ in solution. $\{(9\text{-BBN})O\}_2CH_2$ is consumed within 2 further hours by **4.1^H** or **4.1^{Me}** and after significantly longer for **4.1^{Ph}** (> 8 h); this may be dominated by steric factors.

By contrast, the gallium formate complexes that bear larger/more σ -donating R groups undergo significantly faster reactivity with $\{H(9\text{-BBN})\}_2$; in these cases the formate is typically consumed within one hour. The ¹H NMR spectra of the resulting product mixtures show only a trace quantity of the corresponding hydrides and $\{(9\text{-BBN})O\}_2CH_2$; the resonances for the major species are tentatively assigned to $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{R})(\text{OCH}_2\text{O}(9\text{-BBN}))$, based on their spectroscopic similarities to complexes of the form $[\text{Dipp}\mathbf{1}]\text{Al}(\text{R})(\text{OCH}_2\text{O}(9\text{-BBN}))$ (Chapter 3; $\text{R} = \text{Me}$, $\delta_{\text{H}} = 5.53$ ppm; $\text{R} = \text{Et}$, $\delta_{\text{H}} = 5.63$ ppm) (Table 4.7). The persistence of these complexes and the formation of only trace quantities of $\{(9\text{-BBN})O\}_2CH_2$ are consistent with Ga-O/B-H σ -bond metathesis processes which are less favoured for systems which feature more sterically hindered/electron-rich metal centres. In turn, this hypothesis suggests that relatively rapid formation of these galla-bora-acetal species from the corresponding formate

complexes occurs *via* a process that avoids Ga-O/B-H σ -bond metathesis - such as direct hydroboration of the C=O functionality of the formate substituent.

R	^t Bu	^t Am	Ad
$\delta_{\text{H}}(\gamma\text{-H})$ (ppm)	4.88	4.81	4.81
$\delta_{\text{H}}(\text{OCH}_2\text{O})$ (ppm)	5.82	5.82	5.84

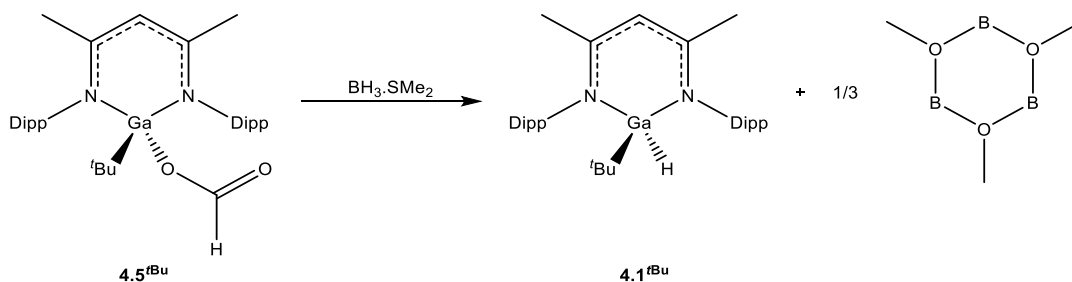
Table 4.7: Some of the spectroscopic signatures of the intermediates, proposed to be the acetal complexes $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{R})(\text{OCH}_2\text{O}(9\text{-BBN}))$.

These galla-bora-acetal complexes ($[\text{Dipp}\mathbf{1}]\text{Ga}(\text{R})(\text{OCH}_2\text{O}(9\text{-BBN}))$) (R = ^tBu, ^tAm, Ad) react slowly with $\{\text{H}(9\text{-BBN})\}_2$ to regenerate the corresponding gallium hydrides and form $\{(9\text{-BBN})\text{O}\}\text{CH}_2$ (e.g. for R = ^tBu, complete consumption of $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{^tBu})(\text{OCH}_2\text{O}(9\text{-BBN}))$ occurs after *ca.* 3 h). $\{(9\text{-BBN})\text{O}\}\text{CH}_2$ is consumed slowly *via* its reaction with **4.1^R** to eventually produce $\text{MeO}(9\text{-BBN})/\text{O}(9\text{-BBN})_2$ (e.g. after 32 h for R = ^tBu). This is consistent with the notion that σ -bond metathesis processes (in this case Ga-H/O-C metathesis) are less favoured for systems which feature more sterically hindered/electron-rich metal centres.

4.4.3.4 Stoichiometric reactivity studies of gallium formate complexes with $\text{Me}_2\text{S}\cdot\text{BH}_3$

$[\text{Dipp}\mathbf{1}]\text{Ga}(\text{^tBu})(\text{OC(O)H})$ (**4.5^{tBu}**) was treated with a slight excess of $\text{Me}_2\text{S}\cdot\text{BH}_3$ (1.1 equiv.) in benzene- d_6 at room temperature and the progress of the reaction monitored at regular intervals by ^1H and ^{11}B NMR spectroscopy. This reaction leads to the complete regeneration of the gallium hydride **4.1^{tBu}** within an hour, with no formation of a gallium borohydride complex observed. The reaction yields $(\text{CH}_3\text{OB})_3$ as the sole formate-derived product, signalled by the observation of a singlet resonance, integrating to 9H, at $\delta_{\text{H}} = 3.37$ ppm for the methoxy-protons. The ^{11}B NMR spectrum features a

broad resonance at $\delta_B = 19.1$ ppm for (CH₃OBO)₃; these chemical shifts are consistent with those reported in the literature.^{53–56} The use of Me₂S·BH₃ leads to the formation of (CH₃OBO)₃ *via* reduction of one molecule of CO₂ by all three B–H bonds of one equivalent of BH₃. A similar process has been previously demonstrated in the borane/phosphine FLP (1-Bcat-2-PPh₂-C₆H₄) catalysed reduction of CO₂, where maximum turnovers of 853 h^{–1} were obtained (0.003 mol%, 70°C).⁵⁷ The successful use L·BH₃ (L = THF, SMe₂) in conjunction with metal hydrides for the catalytic reduction of CO₂ is, to date, unreported but the observed reactivity between **4.5^{tBu}** and Me₂S·BH₃ suggests that its use could be feasible.



Scheme 4.15: The reaction of Me₂S·BH₃ with [Dipp**1**]**Ga**(^tBu)(OC(O)H).

The ¹H NMR spectrum of the reaction of **4.5^{tBu}** with Me₂S·BH₃ features a series of four singlets in the region typical for aldehyde resonances ($\delta_H = 8.43, 8.67, 8.72, 8.80$ ppm). These are proposed to correspond to complexes of the form (HC(O)O)_nBH_(3–n), produced *via* metathesis reactions across the Ga–O bond of **4.5^{tBu}** with Me₂S·BH₃. The resonances associated with these postulated intermediates disappear over the course of *ca.* 2 h and it is presumed that they undergo further reactivity with **4.1^{tBu}** to eventually form (CH₃OBO)₃, although the exact manner in which this proceeds is unclear. This reactivity is in stark contrast to that observed for the aluminium formate complex [Dipp**1**]**Al**(Et)(OC(O)H), whose reactivity is dominated by the avoidance of

thermodynamically unfavourable Al-O/B-H metathesis, and is proposed to undergo direct 1,2-addition across the C=O bond of the formate substituent.

4.4.4 Exploring the catalytic potential of these systems

The work described thus far in this chapter has demonstrated the viability *via* independent stoichiometric reactions of both the CO₂ insertion and Ga-O/B-H metathesis steps which are mechanistically key to catalytic turnover. In addition, this work has shown that the insertion of CO₂ into the Ga-H bond is favoured by complexes which bear σ -donating R substituents, while Ga-O/B-H metathesis is disfavoured by the presence of such substituents.

The contrasting impact of such substituents on the two steps key to catalytic turnover was then investigated under catalytic conditions. Benzene-d₆ solutions of HBpin containing 10 mol% of **4.1^{Me}** or **4.1^{Ad}** as the catalyst were pressurised with *ca.* 2 bar CO₂ and heated to 60°C. The progress of the reaction was monitored by both ¹H and ¹¹B NMR spectroscopy. Somewhat surprisingly, the chemistry in both cases is significantly slower and less selective than that reported for **4.1^{tBu}**, despite obvious parallels with these systems. In the case of **4.1^{Me}**, after heating to 60°C for 20 h, the ¹H NMR spectrum shows the consumption of only *ca.* 20% of the HBpin. The ¹H NMR spectrum shows a mixture of pinBOC(O)H, MeOBpin and (pinB)₂O as the CO₂ reduction products.⁴⁵ The use of **4.1^{Ad}** leads to the complete consumption of HBpin after heating to 60°C for 36 h. Whilst MeOBpin and (pinB)₂O are the major products of the reaction, the formic ester pinBOC(O)H is also formed in *ca.* 15% yield. Despite the similar rates of reaction of **4.1^{Ad}** and **4.1^{tBu}** towards CO₂, the propensity of **4.1^{Ad}** to function as a catalyst for this process contrasts significantly with the performance reported for **4.1^{tBu}** (complete consumption of HBpin within 4 h to yielding MeOBpin and (pinB)₂O).¹⁴ In my hands, the use of **4.1^{tBu}**

as a catalyst also shows markedly reduced activity; only *ca.* 20% of the reductant HBpin is consumed after 4 h and the product mixture contains a significant quantity of (pinBO)C(O)H.¹⁴

4.4.4.1 Investigating the mechanistic steps key to catalytic turnover

Efforts were undertaken to understand the contrasting catalytic reactivity of these systems to that reported previously. A series of stoichiometric studies was undertaken to elucidate the impact of the gallium-bound R substituents on the individual steps key to catalytic turnover *under conditions similar to the catalytic runs*.

Solutions of **4.1^{tBu}** and **4.1^{Me}** in benzene-d₆, at the same concentrations as utilised in the catalytic runs, were placed under *ca.* 2 bar CO₂, heated to 60°C and the reaction monitored by ¹H NMR spectroscopy. The speciation profiles as a function time are shown in Figure 4.11. It is demonstrated that, as expected, the reactions reach near-completion significantly faster at elevated temperatures and under a higher pressure of CO₂ than when operated under ambient conditions. Additionally, as observed at room temperature, **4.1^{tBu}** undergoes hydrogallation of CO₂ significantly more quickly than **4.1^{Me}**. This study further shows that the insertion process follows *pseudo*-first order kinetics, and rate constants (and half-lives) for the two gallium hydrides could therefore be calculated (**4.1^{tBu}**: $k_{obs} = 3.0 \times 10^{-4} \text{ s}^{-1}$, $t_{1/2} = 38 \text{ min}$; **4.1^{Me}**: $k_{obs} = 3.7 \times 10^{-5} \text{ s}^{-1}$, $t_{1/2} = 315 \text{ min}$). The relative reactivities of the gallium hydrides towards CO₂ suggest that, if hydrogallation of CO₂ is the rate determining step of the reaction, **4.1^{tBu}** should function as a superior catalyst compared to **4.1^{Me}**.

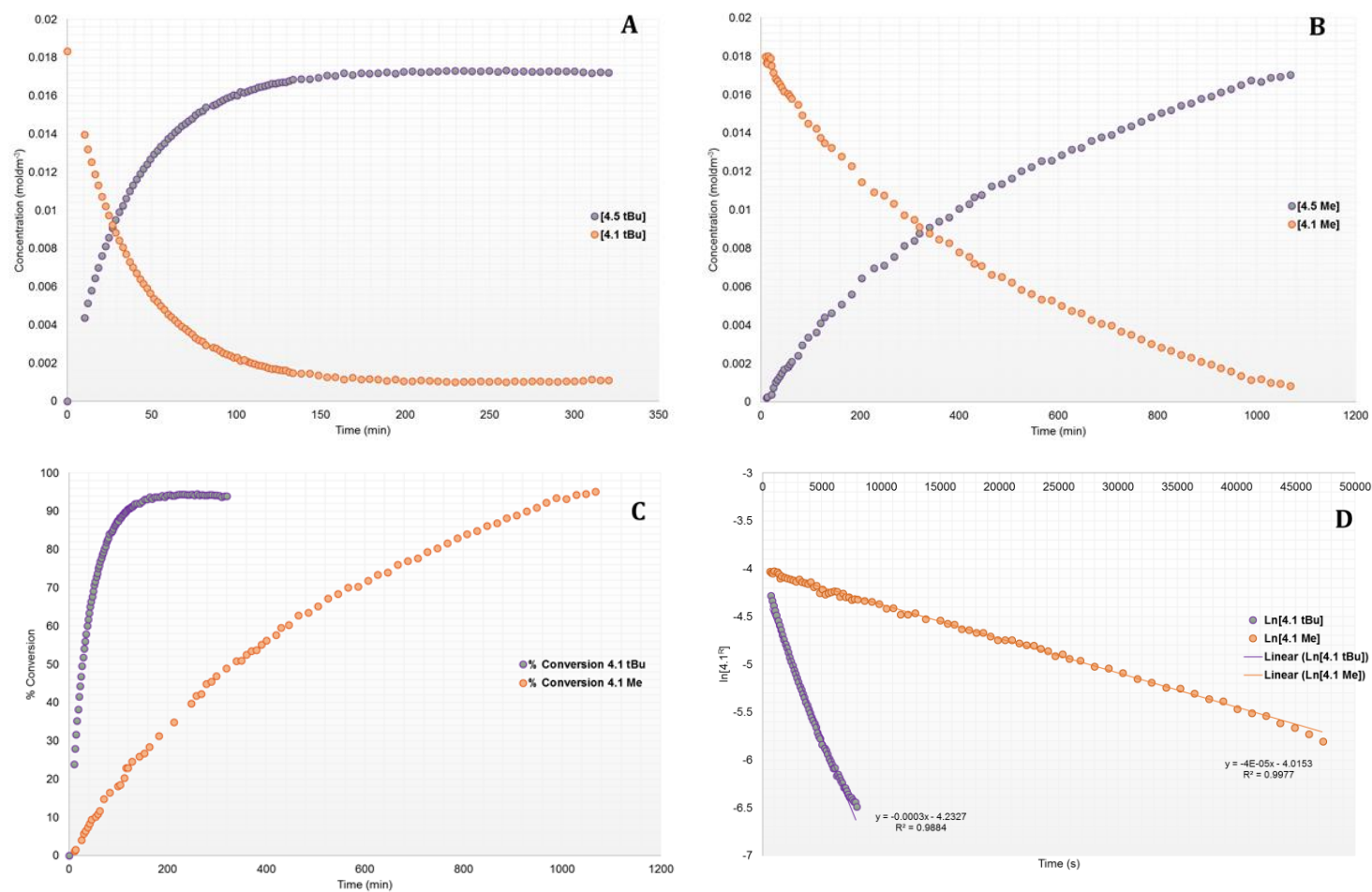


Figure 4.11: Top: A plot of concentration vs. time as monitored by ¹H NMR spectroscopy in benzene-d₆ for the insertion of CO₂ into the Ga-H bonds of **4.1^tBu** (A) and **4.1^{Me}** (B), T = 333 K, P_{CO₂} ~ 2 bar. Bottom: A plot of % conversion vs. time for these reactions, based on formation of the formate complex (C); a plot of $\ln[4.1^R]$ vs. time for these reactions (D).

To assess the impact of the gallium-bound R substituent on the regeneration of the gallium hydride complex under conditions similar to the catalytic runs, gallium formate complexes **4.5^{tBu}** and **4.5^{Me}** were reacted with 10 equivalents of HBpin and heated to 60°C. These reactions were monitored by ¹H NMR spectroscopy and the resulting temporal profiles are shown in Figure 4.12. It is clear from these profiles that the regeneration of **4.1^{tBu}** from **4.5^{tBu}** when reacted with HBpin is neither as rapid nor as simple as reported previously.¹⁴

It is apparent that (at short reaction times) these complexes undergo relatively facile reactivity with HBpin to generate the corresponding hydride complex and pinBOC(O)H. In both cases, this initial period of reactivity follows *pseudo*-first order reaction kinetics (Figure 4.12) and a plot of ln[**4.5^R**] against time allows calculation of the respective rate constants (*k_{obs}*) of 5.5 x 10⁻⁵ s⁻¹ (R = ^tBu) and 2.45 x 10⁻⁴ s⁻¹ (R = Me). Initial consumption of the formate complex occurs more readily in the case of **4.5^{Me}**, consistent with the assertion that Ga-O/B-H σ-bond metathesis should occur more readily for systems which bear smaller/less σ-donating auxiliary R substituents at the gallium centre.

However, in both cases, after consumption of *ca.* 50% of the gallium formate complex **4.5^R** (R = ^tBu, Me), the rate of reaction (and by implication, the rate of regeneration of the corresponding gallium hydride) reduces dramatically. This occurs after *ca.* 70 min for **4.5^{Me}** and *ca.* 220 min for **4.5^{tBu}**. Following this, the consumption of **4.5^R** (R = ^tBu, Me) by HBpin remains slow, until the concentration of pinBOC(O)H reduces substantially (*ca.* 1800 min for **4.5^{Me}** and *ca.* 950 min for **4.5^{tBu}**) whereupon the reaction of **4.5^R** with HBpin resumes at a faster rate. At the end of the reaction, the product mixture contains **4.1^R**, MeOBpin and O(Bpin)₂.

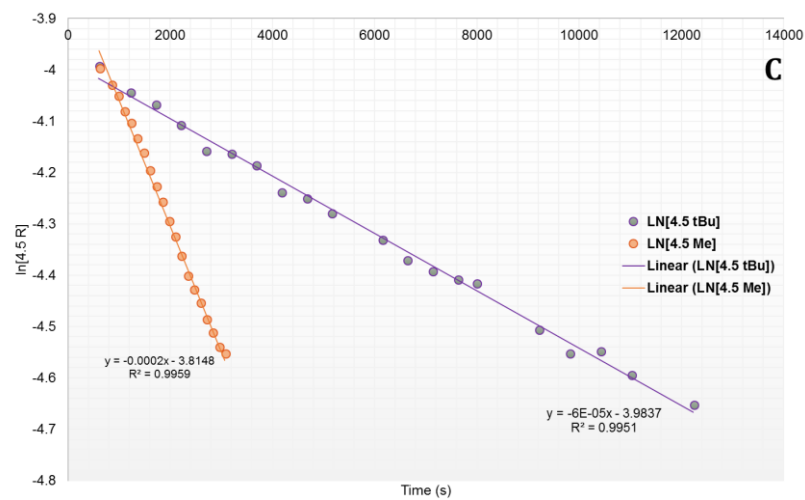
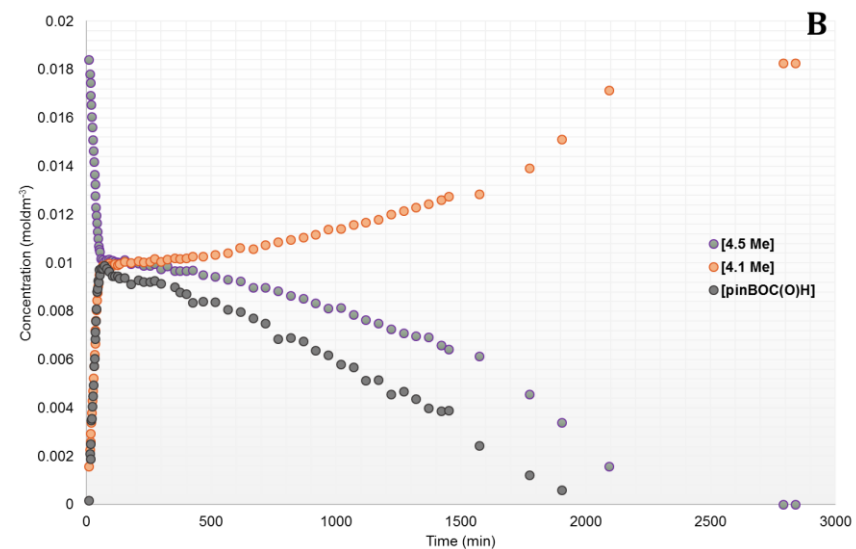
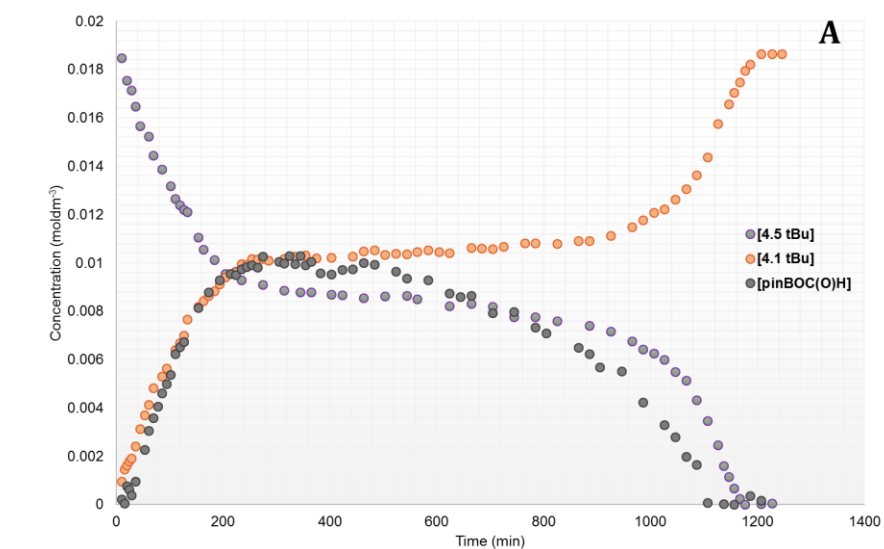


Figure 4.12: A plot of concentration vs. time as monitored by ^1H NMR spectroscopy in benzene- d_6 for the reactions of **4.5^{tBu}** (A) and **4.5^{Me}** (B) with excess HBpin (10 equiv.), $T = 333$ K. A plot of $\ln[4.5^R]$ vs. time for the initial period of reactivity for these reactions (C).

It is suggested that pinBOC(O)H is consumed by reinsertion into the Ga-H bond of **4.1^R**. This is consistent with computationally-assessed mechanisms for the borane-mediated catalytic reduction of CO₂ where formic acid derivatives of the form R₂BOC(O)H are considered to be transient intermediates within the catalytic cycle.^{17,44,45} The propensity of the gallium hydrides to undergo reinsertion of pinBOC(O)H strongly correlates to their relative reactivities towards CO₂, consistent with the significantly slower consumption of pinBOC(O)H by **4.1^{Me}**, as compared to **4.1^{tBu}** (Figure 4.12). In addition to this, gallium hydrides **4.1^{Me}** and **4.1^{tBu}** appear to be far less reactive towards pinBOC(O)H compared to CO₂. This might be predicted based on the relative steric environments and electrophilicities of the carbon centres of the substrates. However, the rapid reduction in reactivity of **4.5^{Me}** and **4.5^{tBu}** towards HBpin when their consumption reaches 50% (and subsequent resumption of reactivity upon the consumption of pinBOC(O)H) suggests that pinBOC(O)H inhibits the Ga-O/B-H metathesis reactivity of **4.5^{Me}** and **4.1^{tBu}** with HBpin. The exact manner in which this proceeds is unclear and no evidence for the coordination of pinBOC(O)H to **4.5^{Me}** or **4.5^{tBu}** could be found. This impact of this inhibition on (i) the ability of **4.1^{tBu}** to catalyse the reduction of CO₂ and (ii) the selectivity of this process was investigated in greater depth.

4.4.4.2 Further investigation of the system under catalytic conditions

Benzene-d₆ solutions of HBpin containing 10 mol% of **4.1^{tBu}** and **4.5^{tBu}** were pressurised with CO₂ (*ca.* 2 bar) and the reactions heated to 60°C and monitored by ¹H NMR spectroscopy for *ca.* 10 h (Figure 4.13). Both **4.1^{tBu}** and **4.5^{tBu}** catalyse this process, with comparable (albeit low) activity, operating with fewer than two turnovers in 10 h. Consistent with the slow consumption of pinBOC(O)H under stoichiometric conditions,

this formic acid derivative is formed selectively under catalytic conditions. This process is *pseudo*-first order with respect to the concentration of HBpin, with a k_{obs} of $9 \times 10^{-6} \text{ s}^{-1}$. Regardless of whether **4.1^{tBu}** or **4.5^{tBu}** is employed as the catalyst, it can be shown by *in situ* NMR monitoring that both **4.1^{tBu}** and **4.5^{tBu}** are present throughout the course of the catalysis. This suggests that (while in both cases **4.5^{tBu}** is present as the major species), the rates of insertion of CO₂ into the Ga-H bond and of Ga-O/B-H σ -bond metathesis are comparable (and relatively slow).

4.5 Conclusions and suggestions for further work

A significant amount of the work reported in this chapter details attempts made to establish novel routes for the preparation of unsymmetrically substituted Nacnac-ligated gallium hydrides (and their halide precursors). In doing so, a range of novel gallium hydrides of the type [^{Dipp}**1**]₂Ga(R)H has been prepared, offering variation in the gallium-bound R substituent. As observed for their aluminium counterparts, a wide variation in the Ga-H stretching frequencies is observed, indicative of considerable variation in the nature of the Ga-H bond.

The ability of a range of Nacnac-ligated gallium hydride complexes [^{Dipp}**1**]₂Ga(R)H to hydrogallate CO₂ was investigated, revealing significant variation in their rates of reactivity. As observed for the reactions of Nacnac-ligated aluminium hydrides with CO₂ (Chapter 3), the lability of the gallium hydrides correlates with the electronic character of the auxiliary R substituent. Electron-donating R groups give rise to weaker (and presumably more hydridic) Ga-H bonds, leading to enhanced rates of reactivity towards CO₂.

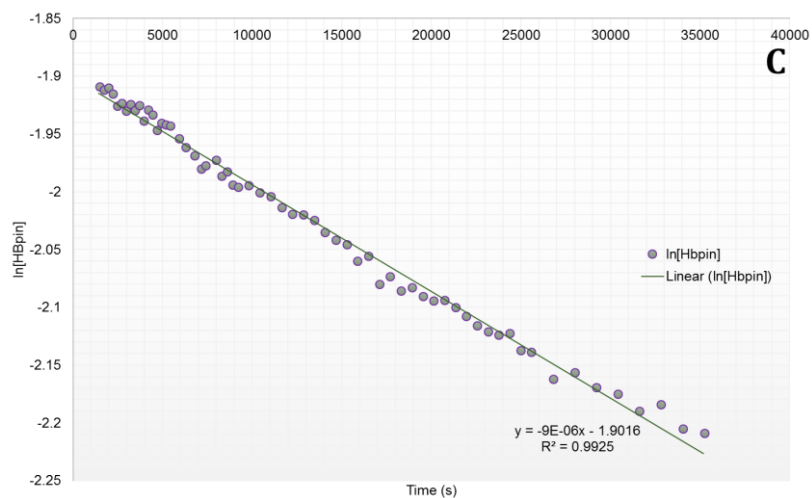
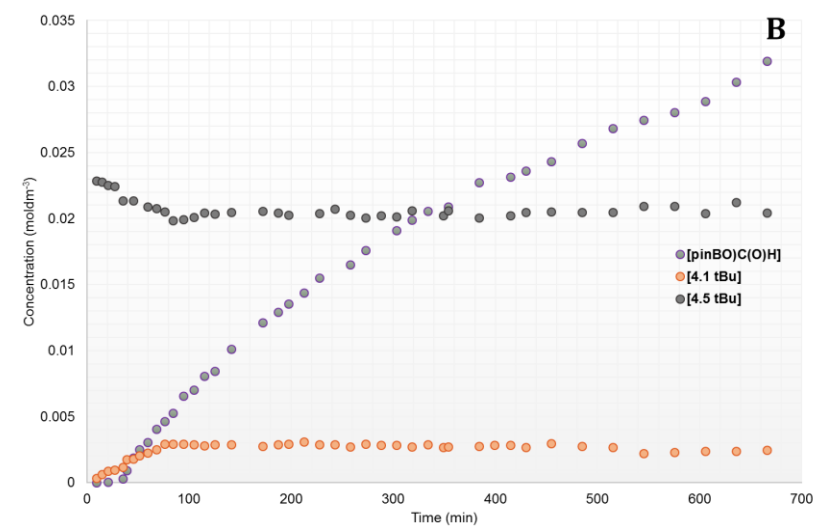
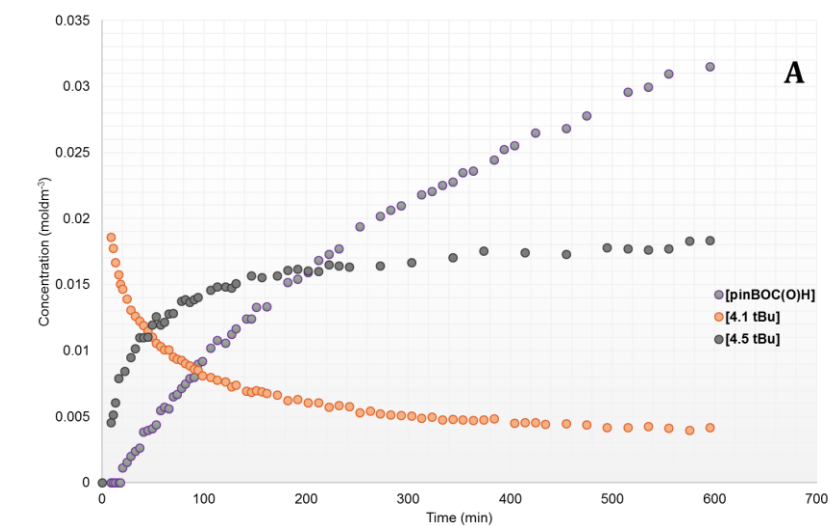


Figure 4.13: Top: A plot of concentration vs. time for the reduction of CO₂ (at T = 333 K, P_{CO2} ~ 2 bar), catalysed by: **A:** 4.1 tBu (10 mol%) and **B:** 4.5 tBu (10 mol%) for the first ca. 10 h of the reaction. **C:** A plot of ln[HBpin] vs. time for this process, catalysed by 4.1 tBu.

By appropriate choice of the R group, a number of gallium hydrides can be targeted which effect the hydrogallation of CO₂ under ambient conditions. This behaviour hints at an ability to effect (under mild conditions) the first step in catalytic turnover in the borane-mediated reduction of CO₂.

The second step key to catalytic turnover – regeneration of the hydride catalyst – has been investigated stoichiometrically through the treatment of metal formate complexes of the type [Dipp¹]₂Ga(R)(OC(O)H) (R = H, Me, Ph, ^tAm, ^tBu, Ad) with a variety of boranes. The use of more reactive boranes (HBcat, {H(9-BBN)}₂, Me₂S·BH₃) leads to the complete regeneration of the gallium hydride at room temperature, with concomitant formation of methanol derivatives of the types MeOBR₂ or (MeOBO)₃. Notably, the reactions of complexes [Dipp¹]₂Ga(R)(OC(O)H) with {H(9-BBN)}₂ reveal that Ga-O/B-H metathesis is favoured by complexes which bear smaller/less σ-donating R substituents.

However, a series of stoichiometric reactivity studies, under conditions similar to the catalytic runs, reveals that the reactivity of gallium formate complexes [Dipp¹]₂Ga(R)(OC(O)H) towards HBpin is not as simple. While the generation of the corresponding hydrides proceeds in a facile manner at short reaction times, the formate ester product, pinBOC(O)H, appears to inhibit the reaction of the gallium formate complexes with HBpin as it builds up a significant concentration. Moreover, further reduction of pinBOC(O)H (presumably *via* reinsertion into the Ga-H bond) requires elevated temperatures and long reaction times. Thus, under catalytic conditions [Dipp¹]₂Ga(^tBu)H, for example, effects the reduction of CO₂ very slowly, yielding (pinBO)C(O)H selectively.

The ability of these gallium hydrides to effect hydrogallation of unsaturated substrates has led us to consider their use for the catalytic hydrosilylation of CO₂ (Chapter 5) and

hydroboration of aldehydes/ketones (Chapter 6), where the ability of gallium alkoxide complexes to undergo rapid Ga-O/B-H metathesis reactions with mild borane reagents may be utilised.

4.6 References

- (1) A.J. Downs, H.-J. Himmel in *The Group 13 Metals Aluminium, Gallium, Indium and Thallium; Chemical Patterns and Peculiarities* (Eds.: S. Aldridge, A.J. Downs) Wiley, Chichester, UK.
- (2) Pulham, C. R.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Am. Chem. Soc.* **1991**, *113* (14), 5149–5162.
- (3) Uhl, W.; Claesener, M. *Inorg. Chem.* **2008**, *47* (2), 729–735.
- (4) Uhl, W.; Claesener, M. *Inorg. Chem.* **2008**, *47* (11), 4463–4470.
- (5) Uhl, W. *Coord. Chem. Rev.* **2008**, *252* (15–17), 1540–1563.
- (6) Aldridge, S.; Downs, A. J. *Chem. Rev.* **2001**, *101* (11), 3305–3365.
- (7) Uhl, W.; Hentschel, A.; Kovert, D.; Kösters, J.; Layh, M. *Eur. J. Inorg. Chem.* **2015**, *2015* (14), 2486–2496.
- (8) Zaidlewicz, M.; Wolan, A.; Budny, B. In *Comprehensive Organic Synthesis: Second Edition* Elsevier.
- (9) J. L. Atwood; S. G. Bott; C. Jones; C. L. Raston. *Inorg. Chem.* **1991**, *30* (25), 4868–4870.
- (10) Uhl, W.; Molter, J.; Neumüller, B. *J. Organomet. Chem.* **2001**, *634* (2), 193–197.
- (11) Raston, C. L.; Siu, A. F. H.; Tranter, C. J.; Young, D. J. *Tetrahedron Lett.* **1994**, *35* (32), 5915–5918.
- (12) Ohshita, J.; Schmidbaur, H. *J. Organomet. Chem.* **1993**, *453* (1), 7–12.
- (13) Schumann, H.; Just, O.; Seuß, T. D.; Weimann, R. *J. Organomet. Chem.* **1994**, *472* (1–2), 15–25.
- (14) Abdalla, J. A. B.; Riddlestone, I. M.; Tirfoin, R.; Aldridge, S. *Angew. Chem. Int. Ed.* **2015**, *54* (17), 5098–5102.
- (15) Blake, A. J.; Cunningham, A.; Ford, A.; Teat, S. J.; Woodward, S. *Chem. Eur. J.* **2000**, *6* (19), 3586–3594.
- (16) Anker, M. D.; Arrowsmith, M.; Bellham, P.; Hill, M. S.; Kociok-Köhn, G.; Liptrot, D. J.; Mahon, M. F.; Weetman, C. *Chem. Sci.* **2014**, *5* (7), 2826–2830.
- (17) Hadlington, T. J.; Kefalidis, C. E.; Maron, L.; Jones, C. *ACS Catal.* **2017**, *7* (3), 1853–1859.
- (18) Chakraborty, S.; Patel, Y. J.; Krause, J. A.; Guan, H. *Polyhedron* **2012**, *32* (1), 30–34.
- (19) Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. *Chem. Commun.* **2016**, *52* (89), 13155–13158.
- (20) Mukherjee, D.; Osseili, H.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2016**, *138* (34), 10790–10793.
- (21) Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. *J. Am. Chem. Soc.* **2009**, *131* (3), 1288–1293.
- (22) Jana, A.; Roesky, H. W.; Schulzke, C.; Döring, A. *Angew. Chem. Int. Ed.* **2009**, *48* (6), 1106–1109.
- (23) Turner, J.; Abdalla, J. A. B.; Bates, J. I.; Tirfoin, R.; Kelly, M. J.; Phillips, N.; Aldridge, S. *Chem. Sci.* **2013**, *4* (11), 4245–4250.
- (24) Singh, S.; Ahn, H.-J.; Stasch, A.; Jancik, V.; Roesky, H. W.; Pal, A.; Biadene, M.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2006**, *45* (4), 1853–1860.
- (25) Jana, B.; Uhl, W. *Inorg. Chim. Acta* **2017**, *455* (1), 61–69.
- (26) Bernabé-Pablo, E.; Jancik, V.; Moya-Cabrera, M. *Inorg. Chem.* **2013**, *52* (12), 6944–6950.
- (27) Seifert, A.; Scheid, D.; Linti, G.; Zessin, T. *Chem. Eur. J.* **2009**, *15* (44), 12114–12120.
- (28) Herappe-Mejía, E.; Trujillo-Hernández, K.; Carlos Garduño-Jiménez, J.; Cortés-Guzmán, F.; Martínez-Otero, D.; Jancik, V. *Dalton Trans.* **2015**, *44* (38), 16894–16902.
- (29) Kempter, A.; Gemel, C.; Fischer, R. A. *Inorg. Chem.* **2008**, *47* (16), 7279–7285.
- (30) Chu, C.; Yang, Y.; Zhu, H. *Sci. China Chem.* **2010**, *53*, 1970–1977.
- (31) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, *54* (35), 10225–10229.
- (32) Chisholm, M. H.; Navarro-Llobet, D.; Gallucci, J. *Inorg. Chem.* **2001**, *40* (25), 6506–6508.
- (33) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, (21), 2832–2838.
- (34) Doddi, A.; Gemel, C.; Seidel, R. W.; Winter, M.; Fischer, R. A. *J. Organomet. Chem.* **2011**, *696* (13),

- 2635–2640.
- (35) Badger, R. M. *J. Chem. Phys.* **1934**, *2* (3), 128–131.
- (36) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121* (37), 8673–8674.
- (37) Wehmschulte, R. J.; Ellison, J. J.; Ruhlandtsenge, K.; Power, P. P. *Inorg. Chem.* **1994**, *33* (26), 6300–6306.
- (38) Yang, Y.; Schulz, T.; John, M.; Yang, Z.; Jimenez-Perez, V. M.; Roesky, H. W.; Gurubasavaraj, P. M.; Stalke, D.; Ye, H. *Organometallics* **2008**, *27* (4), 769–777.
- (39) Beachley, O.; Rosenblum, D.; MacRae, D. *Organometallics* **2001**, *20* (5), 945–949.
- (40) Perkins, P. G.; Twentyman, M. E. *J. Chem. Soc.* **1965**, *0*, 1038–1044.
- (41) Hardman, N. J.; Eichler, B. E.; Power, P. P. *Chem. Commun.* **2000**, *53* (20), 1991–1992.
- (42) Green, S. P.; Jones, C.; Stasch, A. *Science* **2007**, *318* (5857), 1754–1757.
- (43) Singh, S.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Inorg. Chem.* **2006**, *45* (3), 949–951.
- (44) Huang, F.; Zhang, C.; Jiang, J.; Wang, Z. X.; Guan, H. *Inorg. Chem.* **2011**, *50* (8), 3816–3825.
- (45) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2012**, *51* (7), 1671–1674.
- (46) Solis-Ibarra, D.; Gómora-Figueroa, A. P.; Zavala-Segovia, N.; Jancik, V. *Eur. J. Inorg. Chem.* **2009**, *2009* (29–30), 4564–4571.
- (47) Povie, G.; Villa, G.; Ford, L.; Pozzi, D.; Schiesser, C. H.; Renaud, P. *Chem. Commun.* **2010**, *46* (5), 803–805.
- (48) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. **2010**, *2* (2), 8872–8873.
- (49) Pereira, S.; Srebnik, M. *Organometallics* **1995**, *14* (7), 3127–3128.
- (50) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73* (1), 1–15.
- (51) Köster, R.; Tsay, Y.-H.; Krüger, C.; Serwatowski, J. *Chem. Ber.* **1986**, *119* (4), 1174–1188.
- (52) Jin, G.; Werncke, C. G.; Escudié, Y.; Sabo-Etienne, S.; Bontemps, S. *J. Am. Chem. Soc.* **2015**, *137* (30), 9563–9566.
- (53) Wang, T.; Stephan, D. W. *Chem. Commun.* **2014**, *50* (53), 7007–7010.
- (54) Yang, Y.; Xu, M.; Song, D. *Chem. Commun.* **2015**, *51* (56), 11293–11296.
- (55) Fujiwara, K.; Yasuda, S.; Mizuta, T. *Organometallics* **2014**, *33* (22), 6692–6695.
- (56) Ho, S. Y.-F.; So, C.-W.; Saffon-Merceron, N.; Mézailles, N. *Chem. Commun.* **2015**, *51* (11), 2107–2110.
- (57) Courtemanche, M. A.; Légaré, M. A.; Maron, L.; Fontaine, F. G. *J. Am. Chem. Soc.* **2013**, *135* (25), 9326–9329.

5. β -diketiminato complexes of group 13 elements as catalysts for the hydrosilylation of CO_2

5.1 Introduction

The use of CO_2 as a renewable C_1 feedstock for the synthesis of value-added organic chemicals and fuels represents a desirable process but is somewhat challenging due to its thermodynamic stability and kinetic resistance to many transformations.¹ A widely pursued strategy to activate CO_2 exploits its propensity for insertion into reactive metal-hydrogen bonds. Moreover it was demonstrated in Chapters 3 and 4 that group 13 hydrides ($\text{M} = \text{Al}, \text{Ga}$) may be employed in this manner.^{2,3} However, utilising this strategy, the challenge of breaking thermodynamically strong element-oxygen bonds during the catalytic cycle often emerges. In contrast to the behaviour observed for aluminium complexes, it was demonstrated that the regeneration of Ga-H bonds from Ga-O bonds is sufficiently thermodynamically favourable when treated with a highly energetic, oxophilic transmetallating co-reagent such as a borane.⁴⁻⁶

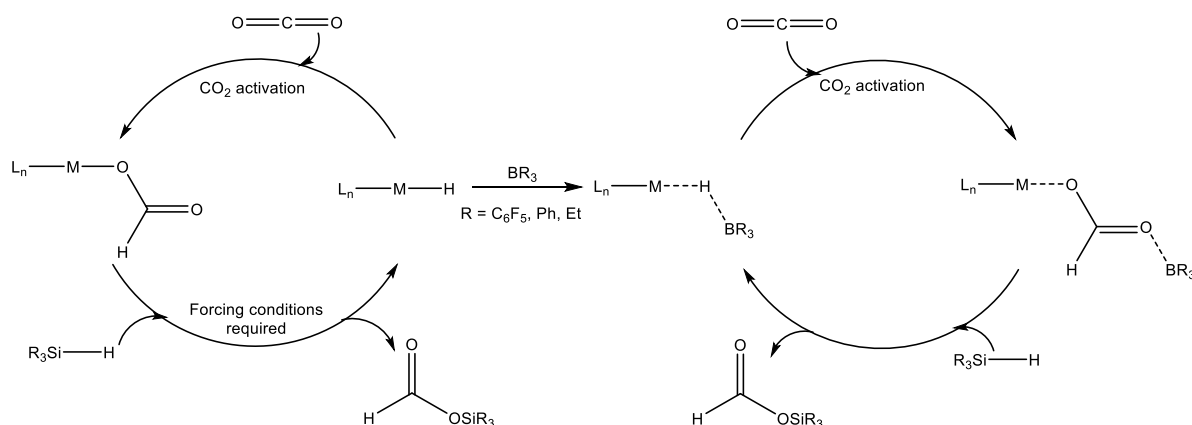
An alternative approach to effect the functionalisation of CO_2 focuses on hydrosilylation, a process which has several advantages. The addition of an Si-H bond to CO_2 is more thermodynamically favourable than the addition of, for example, the H-H bond. Additionally, a range of inexpensive and environmentally benign hydrosilanes are readily available, and the hydrosilylation of CO_2 may proceed in a stepwise manner,

allowing for the targeting of products with different carbon oxidation levels, including silyl formates, silyl acetals, methoxysilanes and methane (which is formed in conjunction with bis(silyl)ethers).⁷

A variety catalysts have been developed which effect the hydrosilylation of CO₂, including complexes of precious metals such as Pd/Pt,^{8,9} Rh,¹⁰ Re,^{11,12} Ru,¹³⁻¹⁷ and Ir.^{7,18-21} Additionally, catalysts based on cheaper and more abundant metals such as Co,²² Zr,²³ Cu,²⁴⁻²⁷ Ni,^{28,29} Sc,^{30,31} Zn,³²⁻³⁵ and Mg³⁶ have been reported. Strategies based on Lewis acid catalysts,³⁷⁻⁴¹ frustrated Lewis pairs (FLPs),⁴²⁻⁴⁴ organocatalysts,^{40,45-48} alkali metal carbonates,⁴⁹ diazaphospholenes,⁵⁰ metal salts of borohydride complexes,⁵¹ and even polar solvents such as DMF have all shown promise.⁴⁵

Many of these metal-based catalytic systems feature reactive metal hydride or alkyl moieties, which effect the initial activation of CO₂. Systems which operate in the absence of a Lewis acid co-catalyst typically require elevated temperatures and pressures of CO₂ to bring about catalytic hydrosilylation of CO₂, but do tend to exhibit more selective reactivity, typically yielding silylformate products.^{15-17,32-34} Copper hydride complexes, such as the carbene-stabilised copper hydride (IPr)Cu(H), will selectively hydrosilylate CO₂ to silylformate complexes, but under ambient CO₂ pressures (1 atm) and comparably low temperatures (60 – 100°C), rendering them some of the most active catalysts to selectively yield this product (e.g. TON 8100).^{24,25} These primary products of the hydrosilylation of CO₂, silyl formates, are precursors for formic acid, formamides, formates, and many other valuable chemicals. While more reactive metal hydride systems have been reported, operating at room temperature and under lower CO₂ pressures, these tend to be less selective in the product distributions yielded. For instance, the pincer-ligated cobalt hydride, (*t*BuPNP)CoH (*t*BuPNP =

2,6-bis(di-*tert*-butylphosphinomethyl)pyridine), reduces CO_2 at room temperature when a primary silane, PhSiH_3 , is employed but yields oligomers which feature silyl formate, bis(silyl)acetal and silyl ether subunits.^{19–22}

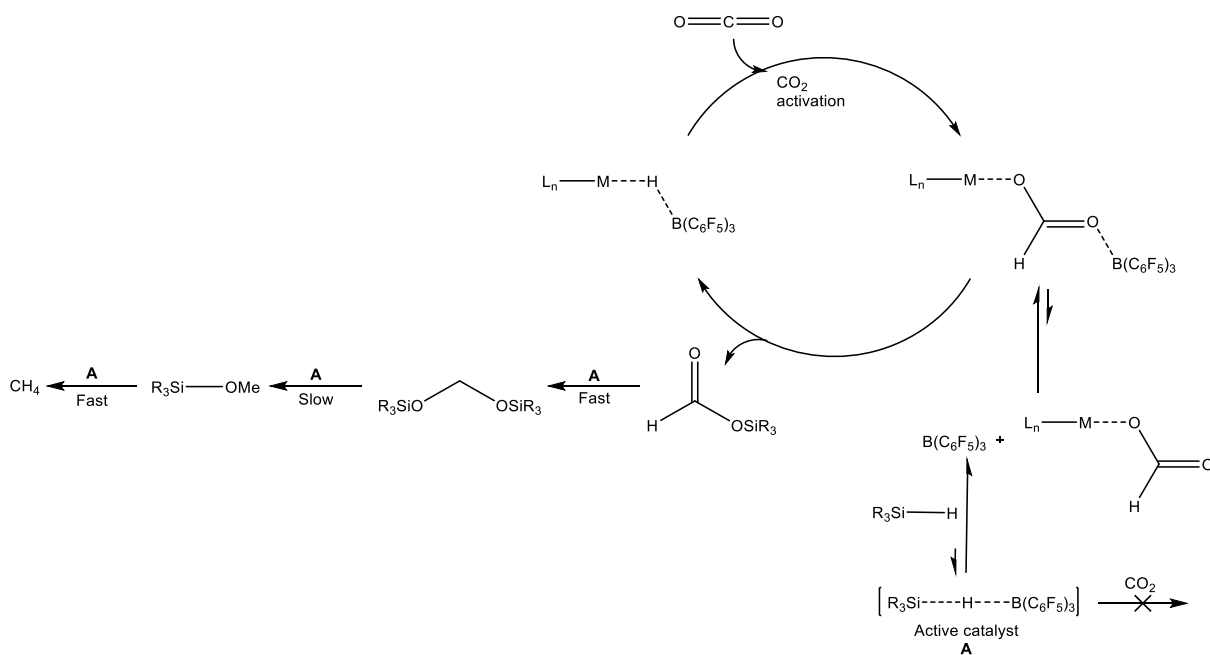


Scheme 5.1: The two catalytic cycles for metal hydride mediated catalytic hydrosilylation of CO_2 , with and without a borane Lewis acid co-catalyst.

An emerging approach to enhance catalytic performance in reductive hydrosilylation systems is to add a strong organo-Lewis acid; such as BET_3 ,²⁹ BPh_3 ,^{8,40} or, more commonly, $\text{B}(\text{C}_6\text{F}_5)_3$.⁵² $\text{B}(\text{C}_6\text{F}_5)_3$ is a known co-catalyst in hydrosilylation reactions in the reduction of carbonyl or alcohol functions,^{53–55} in which it was demonstrated that the borane activates the silane through the formation of the “adduct” $\text{R}_3\text{Si-H-B}(\text{C}_6\text{F}_5)_3$.^{56–59} This silane-borane complex cannot hydrosilylate CO_2 on its own due to its inability to effect the first step, i.e. the initial activation of CO_2 to a formate adduct.^{23,60} However, in the presence of an additional catalyst, $\text{B}(\text{C}_6\text{F}_5)_3$ is involved in tandem catalysis for the hydrosilylation of CO_2 .

A number of metal complexes have been reported to function as catalysts for the hydrosilylation of CO_2 when used in conjunction with $\text{B}(\text{C}_6\text{F}_5)_3$. Typically, these metal complexes are based on reactive M-H moieties^{8,28,30,36,43} or cationic metal centres.²³ Generally, the metal component of the catalytic system activates CO_2 *via* either insertion

into the M-H bond, to typically yield a $\text{B}(\text{C}_6\text{F}_5)_3$ -activated metal formate complex, or its fixation in a “frustrated Lewis pair” manner. The $\text{B}(\text{C}_6\text{F}_5)_3$ activated silane then transfers a $[\text{SiR}_3]^+$ silylium ion to the formate functionality, or activated CO_2 , forming a silyl formate and regenerating the metal hydride or metal complex.^{28,30} Silyl formate intermediates are rarely observed due to their propensity to be further reduced by $[\text{R}_3\text{Si-H-B}(\text{C}_6\text{F}_5)_3]$ to bis(silyl)acetal complexes - intermediates which typically accumulate in tandem catalytic systems.³¹ The activated silane may also reduce bis(silyl)acetal species further to methane, *via* methoxy silane intermediates, although this is typically a relatively slow transformation.



Scheme 5.2: The general catalytic cycle proposed when metal hydrides are used in tandem with $\text{B}(\text{C}_6\text{F}_5)_3$ for catalytic hydrosilylation of CO_2 .

Stepwise reduction of CO_2 using silanes typically yields products including silyl formates,^{9,21,33} silyl acetals,^{8,12,13,19,23,28,31,36,37} methoxy silanes,^{13,20,46} and methane.^{6–8,19,23,30,37,38,61–64} Metal-hydride catalysed transformation of CO_2 employing boranes as reductants typically results in the selective isolation of methoxyborane (with a

bis(boryl)ether complex) from three subsequent hydroboration reactions, and there are very few complexes which selectively yield formoxyborane or bis(boryl)acetal species.⁶ Formoxyborane species, representing reduction of CO_2 to the formic acid oxidation level, are observed in most catalytic hydroboration systems but very few complexes allow for its selective formation; those that do include copper and palladium hydride catalysts and, within main group chemistry, alkali metal borohydrides $[(\text{Me}_6\text{TREN})\text{M}][(\text{HBPh}_3)]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$).^{65–67} Examples of catalysts which allow for the selective reduction of CO_2 to the formaldehyde oxidation level are even rarer (despite the demonstration of the ability of bis(boryl)acetal complexes to function as methylene transfer agents with a wide range of substrates) and there are no reported main group catalysts which convert CO_2 selectively to this oxidation level.^{68–71}

While it has been demonstrated that the use of $\text{B}(\text{C}_6\text{F}_5)_3$ as a co-catalyst commonly leads to enhancement of catalytic activity, the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ -activated silanes often leads to over-reduction of the formic acid, formaldehyde and methanol derivatives to methane (Scheme 5.2). As such, when $\text{B}(\text{C}_6\text{F}_5)_3$ is employed, silyl formate species are rarely observed as intermediates and methoxysilanes are rarely isolated in significant quantities due to their propensity to undergo subsequent reduction with the activated silane adducts. There have been a number of strategies developed, however, that allow for control of the reductive hydrosilylation of CO_2 , even in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$.

The quantity of $\text{B}(\text{C}_6\text{F}_5)_3$ available for activation of the silane has been demonstrated to play a key role in the determination of the product distribution obtained.³⁰ The use of a sub-stoichiometric quantity of $\text{B}(\text{C}_6\text{F}_5)_3$, relative to the catalyst, typically leads to reduced catalytic activity but greater concentrations of bis(silyl)acetal species in the product distribution.²³ Additionally, a number of catalytic systems have been reported,

based on metals such as Ni, Re and Sc which, when employed with one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$, selectively yield bis(silyl)acetal products.^{28,31,43,72} It is proposed in these cases that the $\text{B}(\text{C}_6\text{F}_5)_3$ remains sequestered by the catalyst during the course of the reaction, inhibiting the formation of the activated silane in sufficient quantities to reduce the bis(silyl)acetal species further.

Whilst the use of boron-based reagents as (co-)catalysts for the hydrosilylation of CO_2 is widespread, the employment of heavier group 13 metals ($\text{M} = \text{Al}, \text{Ga}$) as either a Lewis acidic or metal hydride component for this process is much less well established. The highly Lewis acidic cationic aluminium complex $[\text{Et}_2\text{Al}][\text{CB}_{11}\text{H}_6\text{I}_6]$ catalyses the hydrosilylation of CO_2 , under relatively forcing conditions (10 mol%, 80°C) with low turnover frequencies (0.16 h^{-1}) utilising Et_3SiH as the reductant.^{38,73} Methane, toluene and diphenylmethane are the major products, the latter two species arising from alkylation of the solvent. More recently, it was reported that $\text{Al}(\text{C}_6\text{F}_5)_3$, when used in tandem with $\text{B}(\text{C}_6\text{F}_5)_3$, effects the catalytic hydrosilylation of CO_2 , selectively yielding methane and the bis(silyl)ether, $\text{H}_2\text{C}(\text{OSiEt}_3)_2$.³⁷ This system operates at 80°C , with 5 mol% each of $\text{M}(\text{C}_6\text{F}_5)_3$ ($\text{M} = \text{Al}, \text{B}$), producing moderate TOF values (4 h^{-1}). The oxophilic and highly Lewis acidic aluminium component is proposed to be sufficiently potent to bring about CO_2 fixation into silylformate, whilst $\text{B}(\text{C}_6\text{F}_5)_3$ reduces this species further to methane. Hydrosilylation is by far the most intensely studied reaction catalysed by aluminium and Lewis acidic aluminium complexes, in particular aluminium cations, have been shown to effect the hydrosilylation of a range of unsaturated substrates.^{74–76} In these cases, the aluminium catalysts act as Lewis acids, even in reactions with relatively non-polar substrates, such as the hydrosilylation of olefins, catalysed by $[[\text{Dipp}]\text{Al}(\text{H})][\text{BAR}^f_4]$.⁷⁵ While it was demonstrated that insertion of an alkene into the

Al-H bond of $[(^{\text{Dipp}}\mathbf{1})\text{Al}(\text{H})][\text{BAr}^f_4]$ occurs readily, the catalysis proceeds by Lewis acid activation of the silane.⁷⁵ There is considerably less literature describing the use of gallium catalysts that effect the hydrosilylation of unsaturated functionalities, presumably due to the inherently reduced Lewis acidity of gallium compared to aluminium.⁷⁷ In spite of this, two cationic gallium complexes ($[\text{Et}_2\text{Ga}][\text{CHB}_{11}\text{Cl}_{11}]$ and $[(2,6\text{-Dipp}_2\text{C}_6\text{H}_3)\text{Ga}(\text{Et})][\text{CHB}_{11}\text{Cl}_{11}]$) have recently been reported to effect catalytic hydrosilylation of CO₂.³⁹ While relatively forcing conditions are required (80°C), the latter catalyst effects this process in 8 h, yielding a mixture of Et₃SiOMe and CH₄.

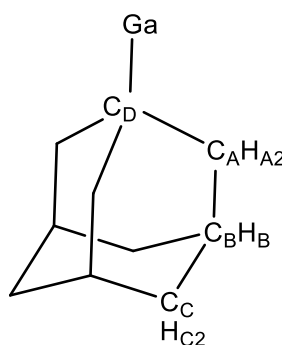
5.2 Project aims

There are many systems reported which effect the catalytic hydrosilylation of CO₂, transforming a relatively inert gas into a range of products representing different carbon oxidation levels. Despite this, extension of this reactivity to main group metal hydrides is relatively unexplored, despite their lower cost, toxicity and greater abundance. Reported examples of such systems include a magnesium hydride which, when used in tandem with excess B(C₆F₅)₃ (5 equiv.), catalytically reduces CO₂ at room temperature to either methane (PhSiH₃, TOF 38.7 h⁻¹) or H₂C(OSiPh₃)₂ (Ph₃SiH, TOF 1.2 h⁻¹).³⁶ The use of the heavier group 13 elements (Al, Ga) is relatively limited and all examples function as Lewis acid catalysts.³⁷⁻³⁹ Within metal-hydride catalysed hydrosilylation of CO₂, the primary role of the hydride is in the initial activation of the unsaturated substrate, typically *via* insertion into the M-H bond, to yield the corresponding metal formate complex. The work reported in Chapters 3 and 4 demonstrates the ability of aluminium and gallium hydrides to effect the hydrometallation of CO₂ under ambient conditions, a feature which was then exploited in an attempt to develop their use as catalysts for the reduction of CO₂, employing boranes as reductants.³ The isolation of a range of these

group 13 metal formate intermediates allows for the investigation of the M-O/E-H metathesis steps essential to catalytic turnover, *via* independent stoichiometric reactions, using a range of oxophilic transmetallating reagents. At the outset, the main focus of this Chapter was to probe the possibility for extending the catalytic reactivity of group 13 hydride complexes, into the catalytic hydrosilylation of CO_2 . While it was demonstrated (in Chapter 3) that the aluminium formate complex $[\text{Dipp}^1]\text{Al}(\text{Et})(\text{OC}(\text{O})\text{H})$ is unreactive towards Et_3SiH , the related gallium formate complexes may be more amenable to Ga-O/Si-H metathetical reactivity, to regenerate the gallium hydride, based on the reduced strength of Ga-O bonds.⁷⁸ The metathesis of Ga-X bonds with silanes is a well-established route to Ga-H bonds.⁷⁹

Many catalytic systems based on metal hydrides do not operate catalytically under ambient conditions in the absence of a Lewis acid co-catalyst, where M-O/Si-H metathesis is presumably not feasible. In the event that the metal formate complexes are unreactive towards silanes, the use of a Lewis acid co-catalyst, such as $\text{B}(\text{C}_6\text{F}_5)_3$, was to be investigated.

5.3 Experimental details



Labelling system applied to complexes featuring the 1-adamantyl (Ad) substituent

Preparation of {HC(MeCNDipp)₂}Ga(Ad)(HC(O)OB(C₆F₅)₃) –

[^{Dipp}1]Ga(Ad)(HC(O)OB(C₆F₅)₃) (5.1)

To a solution of [^{Dipp}1]Ga(Ad)(OC(O)H) (0.50 g, 0.75 mmol) in toluene (5 mL) was added a solution of B(C₆F₅)₃ (0.422 g, 0.82 mmol), also in toluene (5 mL). The solution was stirred overnight and volatiles were removed *in vacuo*, producing a colourless oil. This oil was extracted into minimal hot *n*-hexane, filtered (whilst hot) and allowed to warm slowly to room temperature. Storage of this solution at 6°C for 48 h yielded large colourless crystals of **5.1** as the *n*-hexane solvate. Yield: 0.645 g, 73%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} 0.85, 0.93, 1.21 (6H, d, ³J_{HH} = 6.7 Hz, CH₃ of Dipp ⁱPr), 1.32 (6H, s, CH₃ of β -diketiminato backbone), 1.37 (9H, br m, CH_B/CH_{C2} of Ad), 1.45 (6H, d, ³J_{HH} = 6.7 Hz, CH₃ of Dipp ⁱPr), 1.58 (6H, br s, CH_{A2} of Ad), 2.73 (2H, sept, ³J_{HH} = 6.7 Hz, CH of Dipp ⁱPr), 2.86 (2H, sept, ³J_{HH} = 6.7 Hz, CH of Dipp ⁱPr), 4.74 (1H, s, γ -CH), 6.92 – 7.08 (6H, m, aromatic CH), 8.31 (1H, s, Ga(OC(O)H)). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_{C} 23.1 (CH₃ of β -diketiminato backbone), 24.5, 24.1, 24.0, 23.8 (CH₃ of Dipp ⁱPr), 28.4 (C_B of Ad), 28.4, 28.4 (CH of Dipp ⁱPr), 33.6 (br, C_D of Ad), 37.4 (C_C of Ad), 41.4 (C_A of Ad), 97.7 (γ -CH), 118.8 (*ipso*-C of C₆F₅), 124.3, 125.7, 128.7 (ArC of Dipp), 137.7 (dm, ¹J_{CF} = 254.5 Hz, CF), 140.5 (ArC of Dipp), 140.6 (dm, ¹J_{CF} = 252.5, 142.3, 144.4 (ArC of Dipp), 148.5 (d of multiplet, ¹J_{CF} = 247.0 Hz, CF), 171.4 (NC), 172.9 (OC(O)H). ¹¹B NMR (128 MHz, benzene-d₆, 298 K): δ_{B} 0.6 ($\Delta\omega_{1/2}$ 380 Hz ¹H decoupled; $\Delta\omega_{1/2}$ 660 Hz ¹H coupled). ¹⁹F NMR (376 MHz, benzene-d₆, 298 K): δ_{F} –132.8 (d, ²J_{FF} = 24.0 Hz, *ortho*-F), –157.2 (t, ³J_{FF} = 20.7 Hz, *para*-F), –163.6 (m, *meta*-F). **EI-MS:** *m/z* calc for C₃₉H₅₆N₂Ga ([M-(CO₂H·BCF)]⁺) 621.3699, meas. 621.3756 (2%). **IR (nujol/cm⁻¹)** $\nu_{\text{C=O}}$: 1618, 1644 (s). **Elemental microanalysis:** calc. for C₅₈H₅₇N₂GaBF₁₅O₂: C 59.06% H 4.87% N 2.37% meas. C 59.29% H 5.03% N 2.25%.

Preparation of $\{[HC(MeCNDipp)_2]Ga(Ad)\}[H\{B(C_6F_5)_3\}]$ –

$[^{Dipp}1]Ga(Ad)[H\{B(C_6F_5)_3\}]$ (5.2)

To a solution of $[^{Dipp}1]Ga(Ad)H$ (0.20 g, 0.32 mmol) in 1,2-difluorobenzene (3 mL) was added a solution of $B(C_6F_5)_3$ (0.18 g, 0.35 mmol), also in 1,2-difluorobenzene (2 mL). The reaction mixture was stirred at room temperature for 1 h before being concentrated to ca. 1.5 mL, filtered and layered with *n*-hexane, yielding large colourless crystals after several days. Yield: 0.20 g, 55%.

Spectroscopic data: ^1H NMR (400 MHz, benzene-*d*₆, 298 K): δ_H 0.94, 1.10 (12H, d, $^3J_{HH}$ = 6.7 Hz, CH₃ of Dipp ^{*i*}Pr), 1.30 (9H, br m, CH_B/CH_{C2} of Ad), 1.50 (6H, br m, CH_{A2} of Ad), 1.65 (6H, s, CH₃ of β -diketiminato backbone), 2.53 (4H, sept, $^3J_{HH}$ = 6.7 Hz, CH of Dipp ^{*i*}Pr), 4.39 (q, $^1J_{BH}$ = 117 Hz, $\{H\{B(C_6F_5)_3\}^-\}$), 5.68 (1H, s, γ -CH), 6.94 – 8.01 (6H, m, aromatic CH). $^{13}C\{^1H\}$ NMR (126 MHz, benzene-*d*₆, 298 K): δ_C 23.2 (CH₃ of β -diketiminato backbone), 23.7 (2 overlapping CH₃ of Dipp ^{*i*}Pr), 28.7 (C_B of Ad), 29.7 (CH of Dipp ^{*i*}Pr), 36.7 (C_C of Ad), 41.3 (C_A of Ad), 45.3 (C_D of Ad), 103.8 (γ -CH), 125.3, 130.0 (ArC of Dipp), 137.3 (dm, $^1J_{CF}$ = 254.5 Hz, CF), 138.4 (ArC of Dipp), 138.5 (dm, $^1J_{CF}$ = 253.3 Hz, CF), 142.5 (ArC of Dipp), 149.2 (d of multiplet, $^1J_{CF}$ = 224.3 Hz, CF), 174.5 (NC). ^{11}B NMR (128 MHz, benzene-*d*₆, 298 K): δ_B –25.0 (d, $^1J_{BH}$ = 76.8 Hz, BH). ^{19}F NMR (376 MHz, benzene-*d*₆, 298 K): δ_F –132.5 (d, $^2J_{FF}$ = 24.4 Hz, ortho-F), –163.9 (t, $^3J_{FF}$ = 20.5 Hz, para-F), –166.8 (m, meta-F). IR (nujol/cm^{–1}) ν_{B-H} : 2404 (w). Elemental microanalysis: calc. for C₅₇H₅₇N₂GaBF₁₅: C 60.29% H 5.06% N 2.47% meas. C 60.39% H 4.79% N 2.56%.

Preparation of $\{[HC(MeCNDipp)_2]Ga(Ad)\}[BAr^f_4]$ – $[^{Dipp}1]Ga(Ad)[BAr^f_4]$ (5.3)

A Schlenk tube was charged with both $[^{Dipp}1]Ga(Ad)Br$ (0.11 g, 0.15 mmol), Na[BAr^f₄] (0.15 g, 0.16 mmol) and dichloromethane (3 mL). The reaction mixture was stirred

overnight, over which time a colourless solid precipitated from solution. The resulting yellow solution was filtered from the precipitate, concentrated (to *ca.* 1.0 mL) and layered with *n*-hexane. Large crystals suitable for X-ray crystallography were obtained after 7 days. Yield: 0.077 g, 35%.

Spectroscopic data: ^1H NMR (400 MHz, dichloromethane- d_2 , 298 K): δ_{H} 1.24, 1.34 (12H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ^iPr), 1.48 – 1.60 (m, CH/CH₂ of Ad), 2.13 (6H, s, CH₃ of β -diketiminato backbone), 2.72 (4H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ^iPr), 5.98 (1H, s, γ -CH), 7.37 – 7.52 (6H, m, aromatic CH), 7.56 (4H, s, *p*-CH of [BAr^f₄][−]), 7.72 (8H, s, *o*-CH of [BAr^f₄][−]). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, dichloromethane- d_2 , 298 K): δ_{C} 24.3 (CH₃ of β -diketiminato backbone), 24.3 (CH₃ of Dipp ^iPr), 29.1 (C_B of Ad), 30.2 (CH of Dipp ^iPr), 37.0 (C_C of Ad), 41.7 (C_A of Ad), 103.4 (γ -CH), 118.0 (m, *p*-CH of [BAr^f₄][−]), 125.2 (q, $^1J_{\text{CF}} = 272.2$ Hz, CF₃ of [BAr^f₄][−]), 126.0 (ArC of Dipp), 129.4 (q, $^2J_{\text{CF}} = 34.0$ Hz, *m*-CH of [BAr^f₄][−]), 130.6 (ArC of Dipp), 135.4 (*o*-CH of [BAr^f₄][−]), 138.6, 142.6 (ArC of Dipp), 162.3 (q, $^1J_{\text{CB}} = 49.9$ Hz, *ipso*-C of [BAr^f₄][−]), 174.7 (NC). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, benzene- d_6 , 298 K): $\delta_{\text{B}} -6.6$. ^{19}F NMR (376 MHz, dichloromethane- d_2 , 298 K): $\delta_{\text{F}} -62.9$.

Preparation of [{HC(MeCNDipp)₂}(Ad)GaO₂CH][HB(C₆F₅)₃] –

[{^{Dipp}1}(Ad)GaO₂CH][HB(C₆F₅)₃] (5.4)

A Schlenk was charged with [^{Dipp}1]Ga(Ad)H (0.047 g, 0.075 mmol) and B(C₆F₅)₃ (0.039 g, 0.076 g), and fluorobenzene (3 mL) added. The resulting solution was stirred for 1 h at room temperature before a solution of [^{Dipp}1]Ga(Ad)(OC(O)H) (0.050 g, 0.075 mmol) in fluorobenzene (1 mL) was added. The reaction mixture was stirred for 1 h before being concentrated, filtered and layered with *n*-hexane. Large, colourless crystals were yielded within hours and were isolated and dried *in vacuo*. Yield: 0.067 g, 49%. Single crystals of

the (bis)benzene solvate suitable for X-ray crystallography could be obtained from a concentrated solution of **5.4** in C₆D₆ at room temperature.

Spectroscopic data: ¹H NMR (500 MHz, bromobenzene-d₅, 298 K): δ_{H} 0.94, 0.96, 1.01, 1.09, 1.14, 1.20, 1.24, 1.25 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.37 – 1.48 (30H, m, CH/CH₂ of Ad), 1.67 (12H, s, CH₃ of β -diketiminato backbone), 2.82 (6H, sept, 3 overlapping signals, ³J_{HH} = 6.8 Hz, 3 CH of Dipp ⁱPr), 2.92 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.32 (q, ¹J_{BH} = 93.4 Hz, {H(B(C₆F₅)₃)⁻}, 5.22 (2H, s, γ -CH), 6.76 – 7.19 (6H, m, aromatic CH), 8.52 (1H, s, OC(O)H). ¹³C{¹H} NMR (126 MHz, bromobenzene-d₅, 298 K): δ_{C} 23.6 (CH₃ of β -diketiminato backbone), 24.0, 24.1, 24.3, 24.5, 24.9 (CH₃ of Dipp ⁱPr), 27.7, 28.0 (CH of Dipp ⁱPr), 28.2 (C_B of Ad), 29.6, 29.8 (CH of Dipp ⁱPr) 37.3 (C_C of Ad), 41.3 (C_A of Ad), 99.8 (γ -CH), 124.2, 124.3, 124.8, 125.1, 125.3, 129.0 (ArC of Dipp), 136.9 (dm, ¹J_{CF} = 249.5 Hz, CF), 138.1 (dm, ¹J_{CF} = 243.2 Hz, CF), 140.4 (*ipso*-C of Dipp), 142.5, 142.7, 143.2, 143.8 (*o*-C of Dipp), 148.9 (d of multiplet, ¹J_{CF} = 231.6 Hz, CF), ¹¹B NMR (160 MHz, bromobenzene-d₅, 298 K): δ_{B} -24.5 (d, ¹J_{BH} = 93.4 Hz). ¹⁹F NMR (470 MHz, bromobenzene-d₅, 298 K): δ_{F} -131.9 (d, ²J_{FF} = 25.0 Hz, ortho-F), -163.4 (t, ³J_{FF} = 21.0 Hz, para-F), -166.1 (m, meta-F). IR (nujol/cm⁻¹) $\nu_{\text{C=O}}$: 1640 (s), $\nu_{\text{B-H}}$: 2383 (w). **Elemental microanalysis:** calc. for C₉₆H₁₁₁N₄Ga₂BF₁₅O₂: C 64.48% H 6.26% N 3.13% meas. C 64.63% H 6.35% N 3.04%.

General procedure for Gutmann-Beckett Assay of Lewis acidity

Gutmann-Beckett tests were performed on **5.6**, B(C₆F₅)₃ and [Dipp¹']Ga(^tBu) by mixing the two equivalents of the compound with Et₃PO in CD₂Cl₂. A single resonance was observed in the ³¹P NMR spectrum in each case. The acceptor number was calculated using the relationship $\text{AN} = \{(\delta_{\text{complex}} - \delta(1)) / (\delta(2) - \delta(1))\} \times 100$, where $\delta(1)$ and $\delta(2)$

are the ^{31}P NMR chemical shifts of Et_3PO in hexane (41.0 ppm) and in SbCl_5 (86.1 ppm) respectively.

General procedure for catalytic studies

In a high pressure NMR tube equipped with a J. Young's valve $[[^{\text{Dipp}}\text{1}]\text{Ga}(\text{Ad})][\text{H}(\text{B}(\text{C}_6\text{F}_5)_3)]$ (0.011 mg, 0.01 mmol, 10 mol%) was dissolved in a stock solution of Et_3SiH (0.1 mmol) in benzene- d_6 (0.5 mL). The solution was subject to three freeze-pump-thaw cycles and then backfilled with CO_2 (1.5 bar) at -60°C . The solution was allowed to warm to room temperature, generating a pressure of *ca.* 2.4 bar. The resulting solution was heated to 60°C , and ^1H and ^{11}B NMR spectra were measured at regular intervals. When the catalysis was undertaken in the presence of excess $\text{B}(\text{C}_6\text{F}_5)_3$, the identical procedure was utilised, adding additional equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ in each case.

Spectroscopic data for $\text{H}_2\text{C}(\text{OSiEt}_3)_2$: ^1H NMR (400 MHz, benzene- d_6 , 298 K): δ_{H} 0.66 (12H, q, $^3J_{\text{HH}} = 8.0$ Hz, CH_2 of SiEt), 1.03 (9 H, t, $^3J_{\text{HH}} = 8.0$ Hz, CH_3 of SiEt), 5.06 (2H, s, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene- d_6 , 298 K): δ_{C} 5.3, 7.0 (SiEt), 84.6 (CH_2 of $(\text{Et}_3\text{SiO})_2\text{CH}_2$). ^{29}Si NMR (80 MHz, benzene- d_6 , 298 K): δ_{Si} 18.37.

NMR data for the common organic products of hydrosilylation of CO_2 , using Et_3SiH , are reported in benzene- d_6 ²³ and bromobenzene- d_5 .³⁷

Preparation of $\{\text{HC}(\text{MeCNDipp})_2\}\text{Al}(\text{Et})(\text{HC}(\text{O})\text{OB}(\text{C}_6\text{F}_5)_3) -$

$[\text{Dipp}^1]\text{Al}(\text{Et})(\text{HC}(\text{O})\text{OB}(\text{C}_6\text{F}_5)_3)$ (5.5)

To a schlenk containing $[\text{Dipp}^1]\text{Al}(\text{Et})(\text{OC}(\text{O})\text{H})$ (0.240 g, 0.463 mmol) in toluene (5 mL) at -78°C was added dropwise a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.250 g, 0.488 mmol), also in toluene (2 mL). The reaction mixture was allowed to warm to room temperature and

stirred overnight, over which time the solution developed a pale-yellow colour. A yellow oily solid was isolated, following the removal of volatiles in vacuo, which was extracted into hot hexane, filtered and concentrated until the point of incipient crystallisation. Storage of this solution at 6°C for 2 d yielded colourless crystals of the hexane solvate, suitable for X-ray crystallography. A second crop of crystals could be obtained from further concentration and cooling of the supernatant solution. Yield: 0.363 g, 73%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} -0.26 (2H, q, ³J_{HH} = 8.2 Hz, CH₃CH₂Al), 0.47 (3H, t, ³J_{HH} = 8.2 Hz, CH₃CH₂Al), 0.89, 1.00 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of DippⁱPr), 1.14 (12H, 2 x overlapping d, ³J_{HH} = 6.8 Hz, 2 x CH₃ of DippⁱPr), 1.41 (6H, s, CH₃ of β -diketiminato backbone), 2.80 (4H, 2 x overlapping sept, ³J_{HH} = 6.8 Hz, 2 x CH of DippⁱPr), 4.97 (1H, s, γ -CH), 6.95 – 7.08 (6H, m, aromatic CH), 8.35 (1H, s, Al(OC(O)H)). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_{C} -4.9 (br, CH₃CH₂Al), 7.6 (CH₃CH₂Al), 23.0 (CH₃ of β -diketiminato backbone), 23.4, 24.3, 24.5, 25.1 (CH₃ of DippⁱPr), 28.2, 29.2 (CH of DippⁱPr), 99.4 (γ -CH), 117.7 (*ipso*-C of C₆F₅), 124.6, 125.3, 128.4 (ArC of Dipp), 137.7 (dm, ¹J_{CF} = 252 Hz, *m*-CF), 138.2 (ArC of Dipp), 140.8 (d of t, ¹J_{CF} = 251.8 Hz, ²J_{CF} = 14.0 Hz, CF), 142.9, 144.5 (ArC of Dipp), 148.6 (d of multiplet, ¹J_{CF} = 242.3 Hz, CF), 172.2 (OC(O)H), 173.0 (NC). ¹¹B NMR (128 MHz, benzene-d₆, 298 K): δ_{B} 0.6 ($\Delta\omega_{1/2}$ 497 Hz ¹H decoupled, $\Delta\omega_{1/2}$ 661 Hz ¹H coupled). ¹⁹F NMR (376 MHz, benzene-d₆, 298 K): δ_{F} -132.8 (d, ²J_{FF} = 24.0 Hz, *ortho*-F), -156.1 (t, ³J_{FF} = 20.9 Hz, *para*-F), -163.3 (m, *meta*-F). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **EI-MS:** *m/z* calc for C₃₀H₄₂N₂AlO₂ ([M-(Et-BCF)]⁺) 489.3062, meas. 489.3071 (15%). **IR (nujol/cm⁻¹)** $\nu_{\text{C=O}}$: 1625, 1644 (s). **Elemental microanalysis:** calc. for C₅₀H₄₇N₂AlBF₁₅O₂: C 58.27% H 4.60% N 2.72% meas. C 58.10% H 4.76% N 2.63%.

Preparation of $[\{\text{HC}(\text{MeCNDipp})_2\}\text{Al}(\text{Et})][\text{HB}(\text{C}_6\text{F}_5)_3]$ – $[\text{Dipp1}]\text{Al}(\text{Et})[\text{HB}(\text{C}_6\text{F}_5)_3]$ (5.6) and isolation of $[\text{Dipp1}]\text{Al}(\text{Et})(\kappa^2\text{-H}_2\text{B}(\text{C}_6\text{F}_5)_2)$ (5.7)

To an NMR tube fitted with a J. Young's valve was added $[\text{Dipp1}]\text{Al}(\text{Et})\text{H}$ (0.010 g, 0.021 mmol), $\text{B}(\text{C}_6\text{F}_5)_3$ (0.011 g, 0.021 mmol) and benzene- d_6 . The solution was shaken vigorously, and the reaction mixture analysed by NMR spectroscopy. ^1H NMR showed the conversion to be quantitative to a single Nanac-containing species. Attempts were made to isolate **5.6** in the solid state on a preparative scale. To a solution of $[\text{Dipp1}]\text{Al}(\text{Et})\text{H}$ (0.075 g, 0.16 mmol) in toluene (3 mL) at -78°C was added dropwise a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.082, 0.16 mmol), also in toluene (1 mL). The resulting solution was allowed to warm to room temperature and stirred for one hour. Subsequently the solution was concentrated, filtered and layered with *n*-hexane. A small number of crystals suitable for X-ray crystallography were produced after 1 week. These crystals were identified by single crystal X-ray diffraction as $[\text{Dipp1}]\text{Al}(\text{Et})(\kappa^2\text{-H}_2\text{B}(\text{C}_6\text{F}_5)_2)$.

Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298 K): δ_{H} -0.06 (2H, q, $^3J_{\text{HH}} = 8.1$ Hz, $\text{CH}_3\text{CH}_2\text{Al}$), 0.25 (3H, t, $^3J_{\text{HH}} = 8.1$ Hz, $\text{CH}_3\text{CH}_2\text{Al}$), 0.95 (24H, 2 x overlapping d, $^3J_{\text{HH}} = 6.8$ Hz, 4 x CH_3 of Dipp ^iPr), 1.11 (6H, s, CH_3 of β -diketiminato backbone), 2.57 (4H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ^iPr), 4.26 (1H, br q, HB of $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$), 5.48 (1H, s, $\gamma\text{-CH}$), 6.92 – 7.08 (6H, m, aromatic CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene- d_6 , 298 K): δ_{C} -3.7 (br, $\text{CH}_3\text{CH}_2\text{Al}$), 6.4 ($\text{CH}_3\text{CH}_2\text{Al}$), 23.1 (CH_3 of β -diketiminato backbone), 23.7 , 24.3 , (CH_3 of Dipp ^iPr), 29.3 (CH of Dipp ^iPr), 104.4 ($\gamma\text{-CH}$), 125.4 (ArC of Dipp), 125.8 (*ipso*-C of C_6F_5), 129.7 (ArC of Dipp), 135.4 (ArC of Dipp), 137.5 (d of multiplet, $^1J_{\text{CF}} = 257.6$ Hz, *m*-CF), 138.7 (d of multiplet, $^1J_{\text{CF}} = 250.5$ Hz, CF), 143.4 (ArC of Dipp), 149.5 (d of multiplet, $^1J_{\text{CF}} = 238.8$ Hz, CF), 176.4 (NC). ^{11}B NMR (128 MHz, benzene- d_6 , 298 K): δ_{B} -25.1 ($\Delta\omega_{1/2}$ 279 Hz ^1H decoupled, $\Delta\omega_{1/2}$ 195 Hz ^1H coupled). ^{19}F NMR (377 MHz, benzene- d_6 , 298 K): δ_{F}

–132.2 (br s, *ortho*-F), –162.6 (br s, *para*-F), –164.2 (br s, *meta*-F). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K: δ_{Al} not observed.

Preparation of [HC(MeCNDipp)₂]Al(Et)(OBpin) – [Dipp1]Al(Et)(OBpin) (5.8)

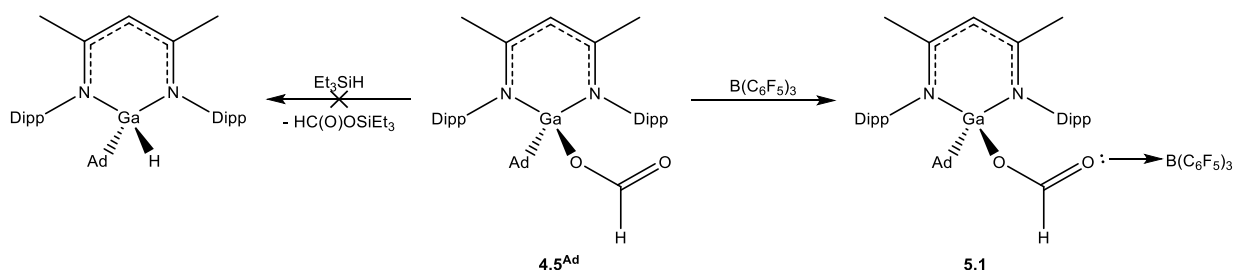
To a solution of HBpin (81 μ L, 0.56 mmol) in benzene (1 mL) was added dropwise H₂O (5 μ L, 0.27 mmol). The reaction mixture was stirred vigorously overnight until gas evolution ceased and then added to a solution of [Dipp1]Al(Et)H (0.13 g, 0.27 mmol) in benzene (2 mL). The resulting mixture was stirred for 6 h after which volatiles were removed *in vacuo*, yielding a colourless oil. This oil was extracted into hexamethyldisiloxane, filtered and concentrated. Storage at –30°C for several days yielded a colourless crystalline solid. Yield: 0.07 g, 43%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} –0.14 (2H, q, ³J_{HH} = 8.1 Hz, CH₃CH₂Al), 0.84 (3H, t, ³J_{HH} = 8.1 Hz, CH₃CH₂Al), 1.07 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.17 (12H, s, CH₃ of Bpin), 1.33, 1.35, 1.53 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.60 (6H, s, CH₃ of β -diketiminato backbone), 3.23 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.76 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 5.03 (1H, s, γ -CH), 7.08 – 7.22 (6H, m, aromatic CH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_{C} –2.9 (br, CH₃CH₂Al), 8,9 (CH₃CH₂Al), 23.3 (CH₃ of β -diketiminato backbone), 24.4, 24.5, 24.9 (CH₃ of Dipp ⁱPr), 25.4 (CH₃ of OBpin), 26.6 (CH₃ of Dipp ⁱPr), 27.8, 29.0 (CH of Dipp ⁱPr), 80.1 (C(CH₃)₂ of OBpin), 99.1 (γ -CH), 125.1, 127.3, 128.4, 141.0, 143.4, 145.7 (ArC of Dipp), 169.9 (NC). ¹¹B NMR (128 MHz, benzene-d₆, 298 K): δ_{B} 20.7. ²⁷Al NMR (104 MHz, benzene-d₆, 298 K: δ_{Al} not observed.

5.4 Results and discussion

5.4.1 Gallium formate complexes: amenable to Ga-O/Si-H σ -bond metathesis?

The availability of isolated samples of the gallium formate complexes of the type $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{R})(\text{OC}(\text{O})\text{H})$ (Chapter 4) allows for the investigation of the Ga-O/Si-H metathesis step which is key to catalytic turnover in the gallium hydride catalysed hydrosilylation of CO_2 . The treatment of $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{Ad})(\text{OC}(\text{O})\text{H})$ (**4.5^{Ad}**) with excess triethylsilane (Et_3SiH) (10 equiv.) in benzene- d_6 reveals markedly different reactivity to that observed with boranes (Chapter 4). Whilst **4.5^{Ad}** reacts readily under ambient conditions with a variety of boranes *via* Ga-O/B-H metathesis, **4.5^{Ad}** is resolutely unreactive towards Et_3SiH , even at elevated temperatures over extended reaction times (80°C, 48 h). The electronegativity differences for Si-H and B-H bonds suggest that the B-H bond is less polar than the Si-H bond.^{80,81} The contrary reactivity of **4.5^{Ad}** towards HBpin and Et_3SiH therefore suggests that the Lewis acidity of the borane significantly contributes to the M-O/B-H metathesis pathway. There are relatively few reported systems based on metal hydrides which effect the catalytic hydrosilylation of CO_2 under ambient conditions, in the absence of a strong Lewis acid co-catalyst.⁶



Scheme 5.3: The addition of one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ to **4.5^{Ad}** leads to its coordination to the formate oxygen and the formation of **5.1**.

There are many examples of systems which combine the potent Lewis acid *tris*(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$) and metal complexes, which have been reported to catalyse the hydrosilylation of CO_2 .^{6,7} The addition of one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ to **4.5^{Ad}** leads to the immediate formation of the borate complex, [^{Dipp}**1**] $\text{Ga}(\text{Ad})(\text{HC}(\text{O})\text{OB}(\text{C}_6\text{F}_5)_3)$ (**5.1**), in which the $\text{B}(\text{C}_6\text{F}_5)_3$ moiety is coordinated to the $\text{C}=\text{O}$ functionality through the Lewis basic oxygen atom. **5.1** was characterised by standard spectroscopic and analytical techniques and its molecular structure was elucidated by X-ray crystallography (Figure 5.1).

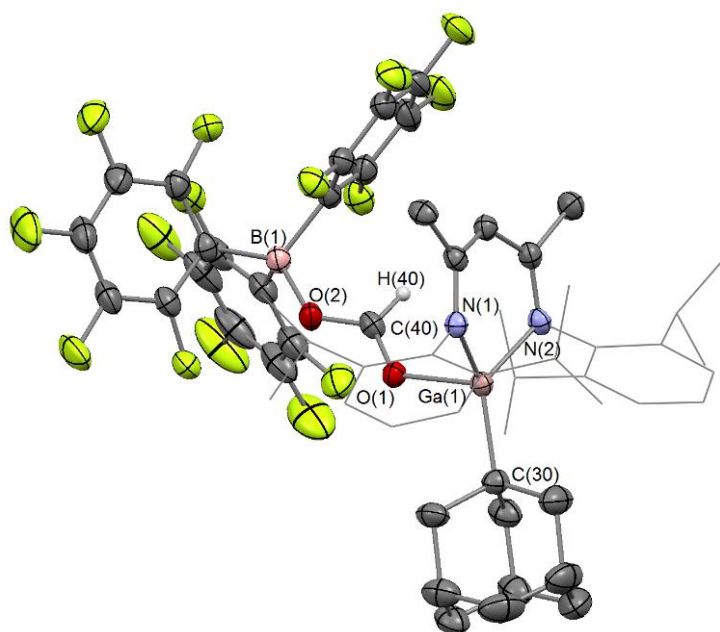
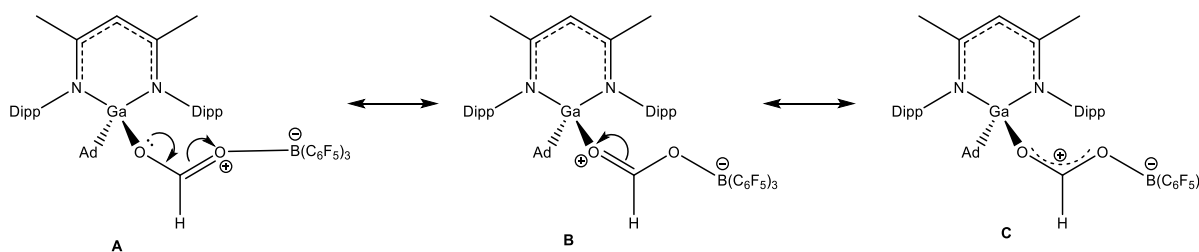


Figure 5.1: Molecular structure of [^{Dipp}**1**] $\text{Ga}(\text{Ad})(\text{HC}(\text{O})\text{OB}(\text{C}_6\text{F}_5)_3)$ (**5.1**) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths ($\text{\AA}$) and angles ($^\circ$) are given in **Table 5.1**.

	$[\text{Dipp}^1]\text{Ga}(\text{Ad})(\text{HCO}_2\text{B}(\text{C}_6\text{F}_5)_3)$ (5.1)	$[\text{Dipp}^1]\text{Ga}(\text{Ad})(\text{OC}(\text{O})\text{H})$ (4.5^{Ad})
Distance of Ga from least-squares C_3N_2 plane ($\text{\AA}$)	0.551	0.592
$d(\text{Ga}-\text{N})$ ($\text{\AA}$)	1.925(3), 1.938(3)	1.9483(12), 1.9586(11)
$d(\text{Ga}-\text{C})$ ($\text{\AA}$)	1.970(4)	1.9865(14)
$d(\text{Ga}-\text{O})$ ($\text{\AA}$)	1.992(3)	1.8966(11)
$d(\text{C}-\text{O})$ ($\text{\AA}$)	O(1)-C(40) 1.249(5) O(2)-C(40) 1.246(5)	1.182(2) 1.293(2)
$d(\text{O}-\text{B})$ ($\text{\AA}$)	1.552(6)	-
N-Ga-N ($^\circ$)	97.22(14)	95.65
C-Ga-O ($^\circ$)	104.49(14)	103.48(5)
C(40)-O(2)-B(1) ($^\circ$)	125.5(3)	-
O-C-O ($^\circ$)	121.6(3)	125.77(18)

Table 5.1: A comparison of some of the structural features of **5.1** and **4.5^{Ad}**.**Figure 5.2:** The resonance forms possible for **5.1**.

The molecular structure of **5.1** displays the expected connectivity and shows clear pyramidalisation of the boron centre of $\text{B}(\text{C}_6\text{F}_5)_3$ upon coordination to the formate fragment. The gallium centre is found in an approximately tetrahedral geometry at 0.551 $\text{\AA}$ from the least-squares C_3N_2 plane. The adamantyl substituent occupies the equatorial position and the $\{\text{OC}(\text{H})\text{O}(\text{B}(\text{C}_6\text{F}_5)_3)\}$ fragment the axial position. The coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ to the formate substituent of **4.5^{Ad}** leads to a pronounced lengthening of the $\text{Ga}(1)-\text{O}(1)$ distance and slight shortening of the remaining contacts surrounding the gallium centre (Table 5.1). This may arise due to a prominent contribution of the resonance form **B** (Figure 5.2), which features a formally cationic gallium centre and dative O-Ga interaction. However, the bond distances in the $\text{Ga}(1)-\text{O}(1)-\text{C}(40)-\text{O}(2)-\text{B}(1)$ fragment suggest that the structure lies closer to a neutral resonance structure in which the $\text{C}=\text{O}$ bond coordinates to the $\text{B}(\text{C}_6\text{F}_5)_3$ substituent and delocalisation across the $\text{O}(1)-\text{C}(40)-\text{O}(2)$ fragment occurs, rather than a charge-separated species such as

$[[\text{Dipp}^1]\text{Ga}(\text{Ad})][\text{HC}(\text{O})\text{O}(\text{B}(\text{C}_6\text{F}_5)_3)]$ (Figure 5.3). The $\text{C}(40)\text{-O}(1)/\text{O}(2)$ distances (1.249(5), 1.246(5) Å, respectively) lie very close in magnitude, in contrast to the two distinct bond distances observed for **4.5^{Ad}**, which signal the presence of both a single and double bond (1.293(2), 1.182(2) Å, respectively). Whilst the $\text{Ga}(1)\text{-O}(1)$ distance of **5.1** is somewhat lengthened compared to that of **4.5^{Ad}**, the $\text{B}(1)\text{-O}(2)$ distance (1.552(6) Å) lies in the range typically observed for datively bonded carbonyl adducts of $\text{B}(\text{C}_6\text{F}_5)_3$, within three standard deviations (e.g. $\text{PhC}(\text{O})\text{Me}$ $d(\text{B-O})$ 1.576(5) Å, $\text{PhC}(\text{O})\text{OEt}$ $d(\text{B-O})$ 1.594(6) Å, $\text{PhC}(\text{O})\text{NPr}_2$ $d(\text{B-O})$ 1.52(1) Å).⁸² The metrics are therefore more consistent with the delocalised bonding found in the more symmetrical anion $[\text{HCO}_2\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$, in which the observed bond distances are 1.586(3) and 1.583(3) Å for the B-O bonds, and 1.255(3) and 1.268(5) Å for the C-O bonds.⁴² This behaviour deviates from that commonly observed for previously reported $\text{B}(\text{C}_6\text{F}_5)_3$ adducts of metal formate complexes, which are identified as intermediates within the catalytic hydrosilylation of CO_2 and are typically zwitterionic species. Such complexes generally feature two distinct C-O bond distances, signalling the presence of the $[\text{HC}(\text{O})\text{O}(\text{B}(\text{C}_6\text{F}_5)_3)]^-$ anion, in which the carbonyl oxygen is typically coordinated to the cationic metal centre e.g. $[\text{Cp}^*_2\text{Sc}][\text{HCO}_2\{\text{B}(\text{C}_6\text{F}_5)_3\}]$ ($d(\text{C-O})$ 1.236(5), 1.272(5) Å).³⁰ These bond lengths lie close in magnitude to those observed for the anionic component of $[\text{TMPH}][\text{HC}(\text{O})\text{O}(\text{B}(\text{C}_6\text{F}_5)_3)]$, which is not coordinated to a metal centre ($d(\text{C-O})$ 1.236(3), 1.288(3) Å).⁸³

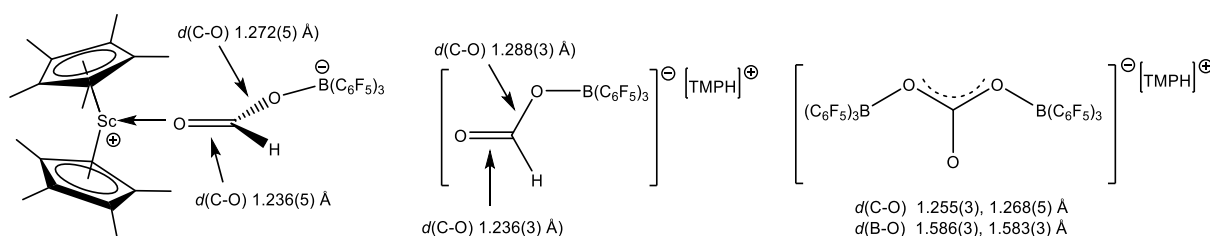
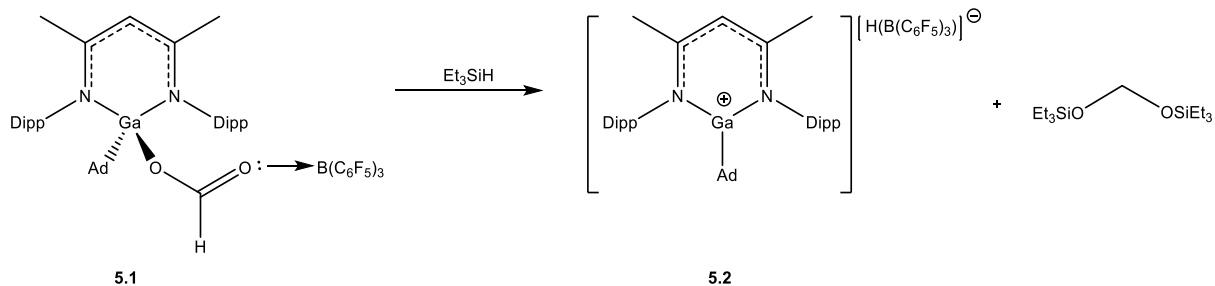


Figure 5.3: Examples of $\text{B}(\text{C}_6\text{F}_5)_3$ adducts of metal formate complexes, which are identified as zwitterionic species.

The formation of **5.1** is signalled by a shift in the formate resonance in the ¹H NMR spectrum (from $\delta_{\text{H}} = 8.88$ ppm for **4.5^{Ad}** to 8.31 ppm for **5.1**). In addition, coordination of B(C₆F₅)₃ to the formate moiety is signalled by a downfield shift in the ¹³C resonance for the carbonyl carbon from $\delta_{\text{C}} = 164.2$ ppm (for **4.5^{Ad}**) to $\delta_{\text{C}} = 172.9$ ppm (for **5.1**); this reflects increased deshielding on coordination of the Lewis acid due to polarisation of the C=O bond.⁸² A broad resonance ($\nu_{1/2} \sim 660$ Hz) is observed at $\delta_{\text{B}} = 0.60$ ppm in the ¹¹B NMR spectrum. The upfield nature of this chemical shift, relative to uncoordinated B(C₆F₅)₃ ($\delta_{\text{B}} = 60.0$ ppm), is characteristic of a neutral four-coordinate boron compound of the type [LB(C₆F₅)₃].^{82,84} Additionally, the coordination of B(C₆F₅)₃ is signalled by a reduction in the separation between the ¹⁹F chemical shifts of the *meta*- and *para*- fluorines ($\delta_{\text{F}} = -157.2$ ppm (*para*-F), -163.6 ppm (*meta*-F), a feature which is typically observed upon pyramidalisation of the boron centre of B(C₆F₅)₃.⁵² This $\Delta\delta_{\text{F}_{m-p}}$ value (6.4 ppm) is in accordance with those reported for B(C₆F₅)₃ adducts of metal formate complexes, such as [Cp*₂Sc][HCO₂B(C₆F₅)₃] ($\Delta\delta_{\text{F}_{m-p}}$ 6.8 ppm), [TMPH][HCO₂B(C₆F₅)₃] ($\Delta\delta_{\text{F}_{m-p}}$ 6.2 ppm) and [TMPH][HCO₂{B(C₆F₅)₃}₂] ($\Delta\delta_{\text{F}_{m-p}}$ 6.9 ppm).^{30,42,83} A comparison of the IR spectra of **4.5^{Ad}** and **5.1** reveals that the C=O stretching frequencies observed for **5.1** ($\nu_{\text{C=O}}$ 1618, 1644 cm⁻¹) are red-shifted compared to that of the free formate ($\nu_{\text{C=O}}$ 1679 cm⁻¹). This is consistent with the reduced order of the C=O bond upon activation by B(C₆F₅)₃. In light of the fairly symmetrical nature of the C-O bonding across the O₂CH fragment, the two absorptions at 1618 and 1644 cm⁻¹ are assigned to the symmetric and anti-symmetric C-O stretches of this fragment.

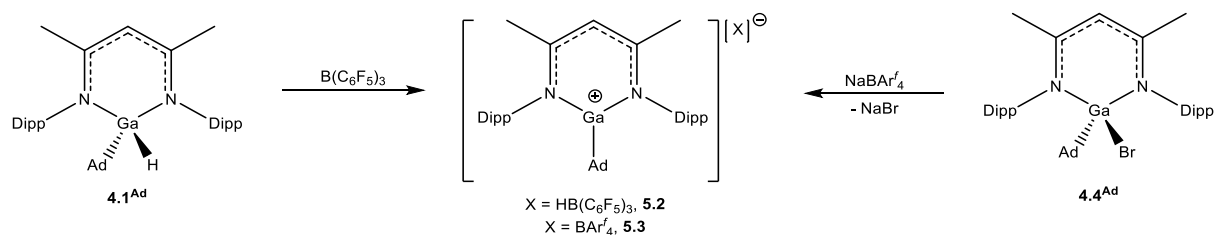
The addition of excess Et₃SiH (10 equiv.) to a solution of **5.1** in benzene-d₆ leads to no discernible reactivity after 24 hours at room temperature. However, over the course of 5 days at room temperature, **5.1** reacts with Et₃SiH to selectively yield H₂C(OSiEt₃)₂, and a

single novel Nacnac-ligated species. The formation of $\text{H}_2\text{C}(\text{OSiEt}_3)_2$, a common organic product in the silane-mediated reduction of CO_2 , is signalled by a new resonance at $\delta_{\text{H}} = 5.06$ ppm, corresponding to the protons of the acetal functionality, and a singlet at $\delta_{\text{Si}} = 18.3$ ppm in the ^{29}Si NMR spectrum; the ^1H , ^{13}C and ^{29}Si NMR data obtained for this species are in accordance to those reported in the literature.^{30,31,42}



Scheme 5.4: The addition of excess Et_3SiH to **5.1** leads to the evolution of a novel three-coordinate cationic gallium species (**5.2**) and $\text{H}_2\text{C}(\text{OSiEt}_3)_2$.

The Nacnac-ligated product, $[[\text{Dipp}^1]\text{Ga}(\text{Ad})][\text{H}(\text{B}(\text{C}_6\text{F}_5)_3)]$ (**5.2**), is proposed to be generated from the reaction of $[\text{Dipp}^1]\text{Ga}(\text{Ad})\text{H}$ (**4.1^{Ad}**) (itself formed *via* metathesis between **5.1** with Et_3SiH) and $\text{B}(\text{C}_6\text{F}_5)_3$. This species can be synthesised independently by the addition of one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ to a solution of **4.1^{Ad}** in toluene at room temperature. The formation of **5.2** is shown to be quantitative by ^1H NMR spectroscopy, and it may be isolated in the solid state as large, colourless crystals in 55% yield. **5.2** was characterised by standard spectroscopic and analytical techniques and X-ray crystallography; the molecular structure is shown in Figure 5.4. A related complex, containing the essentially non-coordinating tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate anion, $[\text{BAr}^f_4]^-$, may be prepared *via* the reaction of $[\text{Dipp}^1]\text{Ga}(\text{Ad})\text{Br}$ (**4.4^{Ad}**) with $\text{Na}[\text{BAr}^f_4]$. **5.3** was characterised by standard spectroscopic and analytical techniques and its molecular structure elucidated by X-ray crystallography (Figure 5.4).



Scheme 5.5: The two routes for the preparation of **5.2/5.3**, which feature a 3-coordinate cationic gallium centre.

Recently, there has been a mounting interest in the development of cationic complexes of group 13 metals,^{85,86} primarily due to their enhanced Lewis acidity in comparison with their neutral counterparts. Much of this literature features aluminium complexes (rather than gallium) due to their greater Lewis acidity, and consequent ability to activate a wide range of substrates and participate in polymerisation processes.⁸⁶ Cationic complexes of gallium have been prepared by employing either highly sterically encumbering ligands, as in the isolation of the two-coordinate complex $[\text{Ar}_2\text{Ga}][\text{Li}\{\text{Al}(\text{OCH}(\text{CF}_3)_2)_4\}_2]$ ($\text{Ar} = \text{C}_6\text{H}_3-2,6\text{-Mes}_2$),⁸⁷⁻⁸⁹ or ligands which feature an intramolecularly coordinating substituent.^{86,90-98} The use of chelating Nacnac ligands has allowed for the isolation of stable three-coordinate aluminium cations of the form $[[^{\text{Dipp}}\mathbf{1}]\text{Al}(\text{R})][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{Me}, i\text{Bu}$).⁹⁹ To the best of our knowledge, the use of Nacnac ligands to stabilise three-coordinate gallium cations has not been reported and the synthesis of **5.2** represents the first reported examples of such a complex.

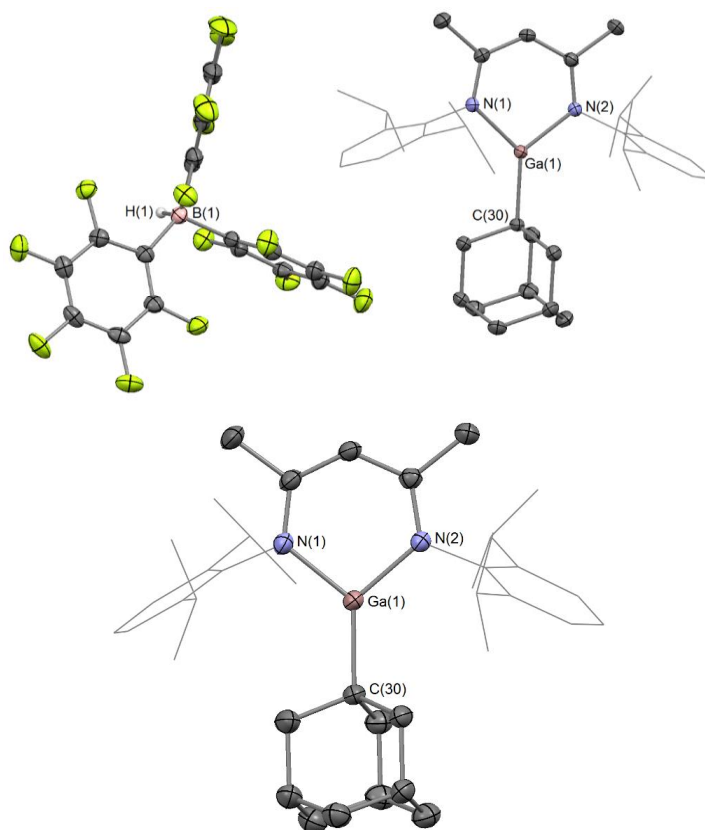


Figure 5.4: Molecular structure of $[[\text{Dipp}1]\text{Ga}(\text{Ad})][\text{H}(\text{B}(\text{C}_6\text{F}_5)_3)]$ (**5.2**) (above) and the cationic component of $[[\text{Dipp}1]\text{Ga}(\text{Ad})][\text{BARf}_4]$ (**5.3**) (below) as determined by X-ray crystallography.

Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. For **5.3** anion omitted for clarity. B-H of **5.2** located in the difference Fourier map and refined isotropically. Key bond lengths ($\text{\AA}$) and angles ($^\circ$) are listed in **Table 5.2**.

	$[\text{Dipp}1]\text{Ga}(\text{Ad})\text{H}$	$[[\text{Dipp}1]\text{Ga}(\text{Ad})][\text{X}]$ $\text{X} = \text{H}(\text{B}(\text{C}_6\text{F}_5)_3)$	$[[\text{Dipp}1]\text{Ga}(\text{Ad})][\text{X}]$ $\text{X} = \text{BARf}_4$
Distance of Ga from least-squares C_3N_2 plane ($\text{\AA}$)	0.791	0.027	0.031
$d(\text{Ga}-\text{N})$ ($\text{\AA}$)	1.9913(10)	1.8790(17) 1.8872(17)	1.8812(19) 1.8843(19)
$d(\text{Ga}-\text{C})$ ($\text{\AA}$)	2.0115(18)	1.973(2)	1.969(2)
$d(\text{B}-\text{H})$ ($\text{\AA}$)	-	1.20(2)	-
N-Ga-N ($^\circ$)	92.53(6)	100.01(7)	99.76(8)
N(1)-Ga(1)-C(30)	-	131.68(8)	129.43(9)
N(2)-Ga(1)-C(30)	-	128.12(8)	130.73(9)

The molecular structures of **5.2** and **5.3** confirm the presence of the cationic gallium component $[[\text{Dipp}1]\text{Ga}(\text{Ad})]^+$, in both cases. The cations, which are essentially identical in

these two salts, feature a three-coordinate gallium centre, and result from either abstraction of the hydride substituent from **4.1^{Ad}** by B(C₆F₅)₃, or elimination of NaBr from **4.4^{Ad}**. In both systems, the gallium atom is found in the plane of the Nacnac ligand in a trigonal planar environment, with the sum of the angles at gallium being 359.8° (in **5.2**) and 359.9° (in **5.3**). This leads to a marked widening of the N-Ga-N angle for **5.2** (100.01(7)°) and **5.3** (99.76(8)°), as compared to the four-coordinate gallium centres in **4.1^{Ad}** (92.53(6)°) and **4.4^{Ad}** (95.56(7)°), which are projected significantly out of the least-squares C₃N₂ plane. The Ga-N and Ga-C contacts in **5.2** ($d(\text{Ga-N})$ 1.8790(17), 1.8872(17) Å, $d(\text{Ga-C})$ 1.973(2) Å) and **5.3** ($d(\text{Ga-N})$ 1.8812(19), 1.8843(19) Å, $d(\text{Ga-C})$ 1.969(2) Å) are significantly shorter than those of the precursor hydride ($d(\text{Ga-N})$ 1.9913(10) Å, $d(\text{Ga-C})$ 2.0115(18) Å) and bromide complexes (**4.4^{Ad}** $d(\text{Ga-N})$ 1.9621(12), 1.9948(19) Å, $d(\text{Ga-C})$ 1.9948(19) Å). These distances lie closer to those found in [Dipp^{1'}]*Ga*(^{*t*}Bu) ($d(\text{Ga-N})$ 1.854(2), 1.849(2) Å), in which the ligand is considered to be a dianionic diamide, rather than the classical chelating amido/imino Nacnac ligand.^{3,100} A similar effect is observed in the cationic aluminium complex [[Dipp¹]*Al*(Me)][B(C₆F₅)₄].^{99,101} This shortening of the N-M distance is proposed to arise from increased ionic interactions between the ligand and metal or from N-M π -bonding.

There are no obvious close contacts between the ion pair of **5.2** in the solid state and the nonbonded Ga(1)-H(1) distance of 10.3 Å clearly shows that the cationic gallium centre does not interact with the hydride of the hydroborate anion. A common feature of complexes which feature cationic Lewis acidic metal centres and anions which bear fluoroarene substituents are interactions of the cation and anion *via* bridging M-F-C interactions.^{102,103,99} This type of interaction is not evident in the solid state structure of

5.2; the closest Ga-F contact ($d(\text{Ga-F}) = 5.90 \text{ \AA}$) is significantly longer than the sum of the respective van der Waals radii.

The ¹H NMR spectra of both **5.2** and **5.3** feature two doublets and one septet in the aliphatic region, for the CH₃ and CH of the ⁱPr groups of the Dipp substituents, respectively. This is consistent with a C_{2v} symmetry Nacnac complex and suggests that the cationic components of **5.2** and **5.3** retain their three-coordinate nature in solution. The resonances associated with the γ -CH in the respective ¹H and ¹³C NMR spectra (e.g. **5.2**: $\delta_{\text{H}} = 5.68$, $\delta_{\text{C}} = 103.8 \text{ ppm}$) are shifted considerably downfield compared to their neutral precursor complexes (e.g. **4.1^{Ad}**: $\delta_{\text{H}} = 4.85$, $\delta_{\text{C}} = 95.9 \text{ ppm}$), consistent with both a reduction in the electron density of the ligand by withdrawal by the strongly electrophilic gallium centre and an increase in the formal aromatic character of the complex. The abstraction of the hydride moiety of **4.1^{Ad}** by B(C₆F₅)₃ to yield **5.2** is signalled by both the reduction in the number of resonances for the Dipp ⁱPr substituents and the loss of the broad resonance at $\delta_{\text{H}} 5.29 \text{ ppm}$ for the gallium hydride of **4.1^{Ad}**. Analysis of **5.2** by ¹¹B, ¹⁹F and ¹H NMR spectroscopy is consistent with the presence of the [H(B(C₆F₅)₃)⁻ anion in solution.^{103–105}

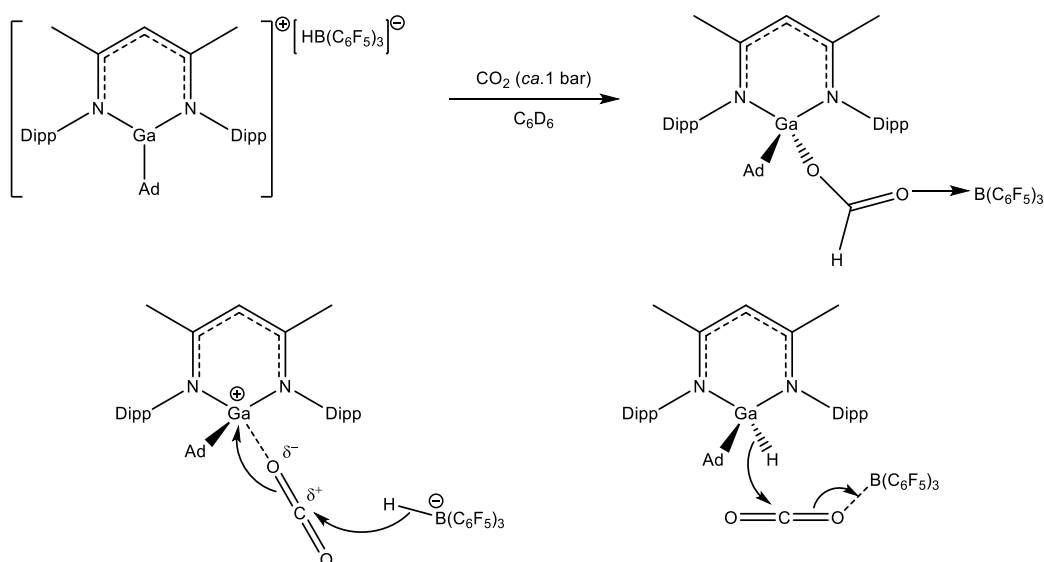
Quantitative comparison of the Lewis acidity of **5.3** with related systems was carried out using the modified version of the Gutmann method reported by Adamczyk-Wozniak *et al.*¹⁰⁶ Thus, using Et₃PO as the Lewis basic probe, an acceptor number (AN) of 69.8 can be calculated for **5.3**, based on the chemical shift ($\delta_{\text{P}} = +72.5 \text{ ppm}$) measured for the phosphine oxide in the presence of two equivalents of the gallium cation **5.3**. The corresponding value obtained for B(C₆F₅)₃ using the same method is 79.6, implying that **5.3** is a weaker Lewis acid, in accordance with the relative electronegativities of boron and gallium.⁷⁸ By contrast, analysis of the Lewis acidity of the zwitterionic gallium

system [Dipp¹']Ga(^tBu) (AN = 67.1) shows that **5.3** is a slightly stronger Lewis acid, consistent its cationic nature.¹⁰⁰

The stability of **5.3**, which features the non-coordinating BAr^f₄ anion, is proposed to arise from the coordination of the sterically demanding and chelating Nacnac ligand which assists to saturate the coordination sphere of the metal centre in order to avoid both decomposition reactions and the formation of aggregates.⁸⁶ The steric bulk of the adamantyl substituent presumably also helps to achieve this. Despite the propensity of the highly reactive [HB(C₆F₅)₃]⁻ anion to undergo fluoroarene/alkyl ligand scrambling in the presence of highly Lewis acidic group 13 metal cations, this is not observed in the case of **5.2**. It is evident that the steric bulk of the Nacnac ligand and the adamantyl substituent (and chelating nature of the former), inhibit interactions of the cation and hydroborate anion in both the solid and solution states, thus limiting possible decomposition routes.

5.4.2 Investigation of the two steps key to catalytic turnover

The viability of both the CO₂ insertion and Ga-O/Si-H metathesis steps key to catalytic turnover were investigated in further detail. Placing a solution of **5.2** in benzene-d₆ under CO₂ (*ca.* 1 bar) leads to the immediate formation of formate complex **5.1**. This reactivity contrasts greatly with that of gallium hydride **4.1^{Ad}**, which requires *ca.* 12 h for the insertion of CO₂ into the Ga-H bond to form **4.5^{Ad}** to reach > 90% completion (Chapter 4). The enhanced reactivity of **5.2** towards CO₂ is indicative of some degree of Lewis acid-assisted activation of CO₂; this can proceed in two different ways: hydride transfer to CO₂ may occur from either the hydroborate anion (with or without participation of the counter-cation) or from the metal hydride complex with the assistance of a borane.¹⁰⁷



Scheme 5.6: The reactivity of **5.2** with CO_2 yields **5.1** immediately; there are two ways proposed in which $\text{B}(\text{C}_6\text{F}_5)_3$ may activate the system.

Insertion of CO_2 into a hydroborate B-H bond has previously been observed for main group systems involving FLPs but can require significantly elevated temperatures.^{42,83} Studies have shown that insertion into the B-H bond of $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ can be challenging due to its relatively low hydricity.^{6,67,108,109} Significantly increased reactivity may occur in the presence of a strongly Lewis acidic cation which activates CO_2 towards hydride transfer. It is conceivable that for **5.2**, the steric bulk of the ligand and adamantyl substituent inhibits association of the $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ counterion with the gallium centre, but that the smaller CO_2 molecule can be activated at the metal thereby facilitating hydride transfer. A similar reaction mechanism has been proposed in the reaction of $[\text{Cp}^*_2\text{Sc}][\text{HB}(\text{C}_6\text{F}_5)_3]$ with CO_2 to yield the formatoborate complex $[\text{Cp}^*_2][\text{HC}(\text{O})\text{OB}(\text{C}_6\text{F}_5)_3]$,³⁰ *i.e.* coordination of CO_2 to scandium, followed by hydride transfer to the electrophilic carbon centre and formation of a Sc-O bond.³⁰ The second route involves the activation of CO_2 by $\text{B}(\text{C}_6\text{F}_5)_3$, to facilitate hydride transfer from the gallium hydride. The operation of this pathway would require equilibration of **5.2** in solution in the presence of CO_2 to liberate $\text{B}(\text{C}_6\text{F}_5)_3$ for its activation of CO_2 . No

significant dissociation of $\text{B}(\text{C}_6\text{F}_5)_3$ from **5.2** is observed by ^1H , ^{11}B and ^{19}F NMR spectroscopy and it is highly unlikely that the second route is operative.

Having established that CO_2 reacts with **5.2** to give the gallium formate species **5.1**, stoichiometric processes were probed with a view to regenerating **5.2**, e.g. *via* the reaction of **5.1** with silanes. Accordingly, **5.1** was treated with excess Et_3SiH (10 equiv.) in benzene- d_6 at 60°C , and the progress of the reaction monitored by ^1H NMR spectroscopy (Figure 5.5).

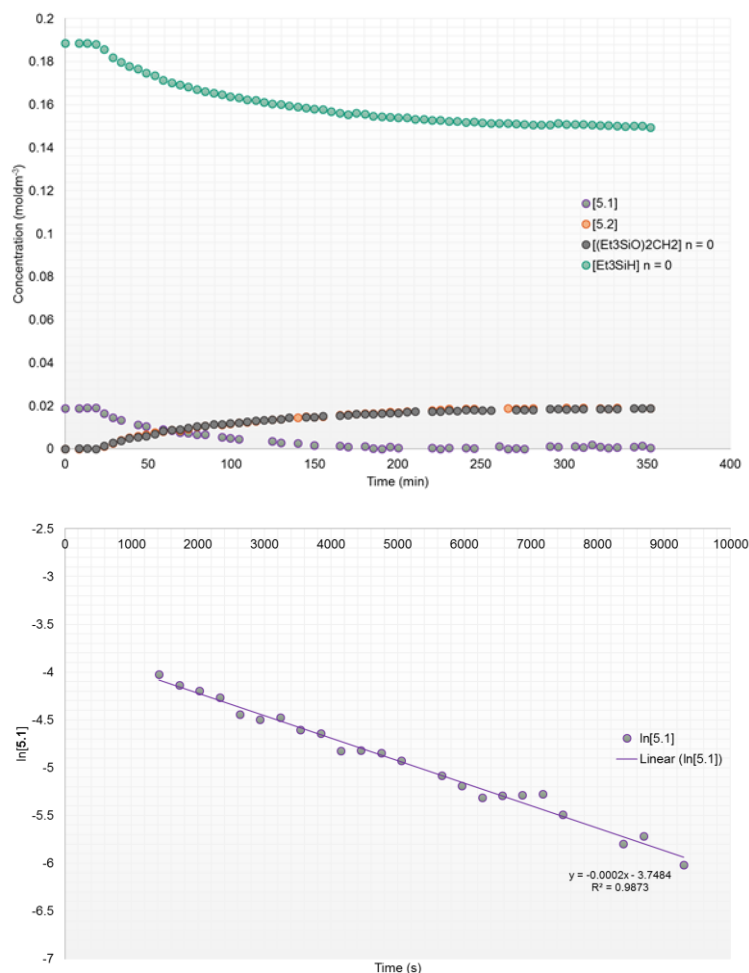


Figure 5.5: Top: A plot of reactant and product concentrations vs. time for the reaction of **5.1** with Et_3SiH (10 equiv.), as monitored by ^1H NMR spectroscopy (benzene- d_6 solution, $T = 333\text{ K}$, no additional $\text{B}(\text{C}_6\text{F}_5)_3$ added). Below: A plot of $\ln[\mathbf{5.1}]$ vs. time for this reaction, rate constant determined by linear regression.

The formation of **5.2** in the reaction of **5.1** with Et₃SiH occurs very slowly at room temperature (*ca.* 5 days) and requires heating to 60°C for *ca.* 4 h to go to completion. Typically, metal hydride systems which can effect catalytic hydrosilylation of CO₂ under ambient conditions are operated under conditions which ensure the presence of a statistical quantity of B(C₆F₅)₃.^{28,30,31} Reports in the literature indicate that one of the primary roles of B(C₆F₅)₃ in hydrosilylation chemistry is to activate the silicon centre of Et₃SiH towards nucleophilic attack *via* the formation of an incipient adduct [Et₃Si-H-B(C₆F₅)₃].^{53,54} After initial activation of CO₂ by a metal hydride complex, it is typically considered that catalytic turnover proceeds by release of the silylformate, HC(O)OSiEt₃, with concomitant regeneration of metal hydride catalyst, *via* attack of a formate oxygen atom at the silicon centre of the *activated* silane. Therefore, the conditions required to bring about the reaction of **5.1** with Et₃SiH indicate that B(C₆F₅)₃ coordinates strongly to the formate ligand of **5.1** but may possess the capacity to dissociate to a small extent at elevated temperatures. Attempts to establish this by high temperature NMR spectroscopic analysis of a toluene-d₈ solution of **5.1** yielded little information.

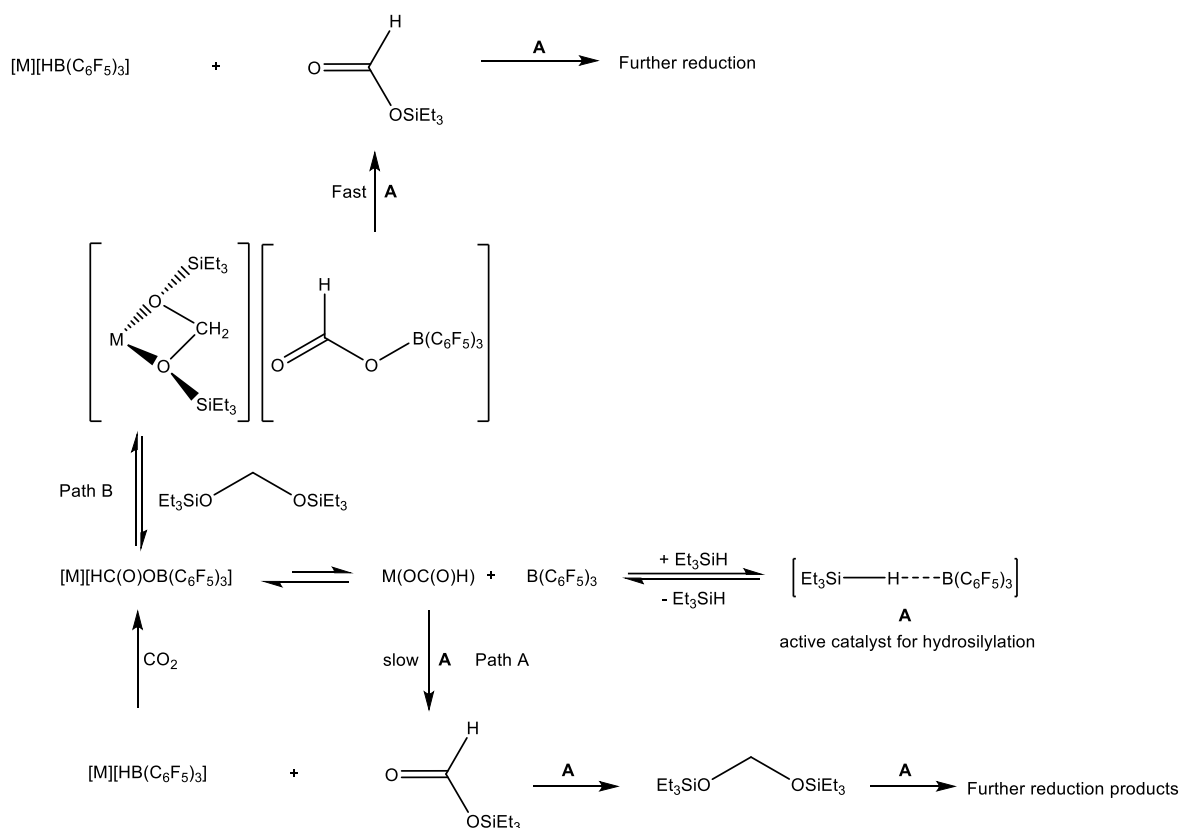
It is also noteworthy that the sole formate-derived species produced in this reaction is the acetal, H₂C(OSiEt₃)₂, which represents reduction of CO₂ to the formaldehyde oxidation level. The formation of such a species is proposed to occur through the rapid hydrosilylation of the highly reactive intermediate HC(O)OSiEt₃ with [Et₃Si-H-B(C₆F₅)₃]. Whilst this adduct does not react with CO₂ itself, the ability of [Et₃Si-H-B(C₆F₅)₃] to achieve sequential reduction of H₂C(OSiEt₃)₂ to methane *via* a methoxy silane intermediate, (CH₃O)SiEt₃, is also precedented.^{23,30,37,61} However, this typically occurs relatively slowly and allows for the accumulation of the acetal species within the

product distribution of catalytic systems.³¹ H₂C(OSiEt₃)₂ does not undergo further reduction in the presence of **5.2** and excess Et₃SiH, even when heated to 60°C for greater than 48 h. This suggests that H₂C(OSiEt₃)₂ does not react with **5.2** *via* any metathetical reaction pathways and that **4.1^{Ad}** has the ability to sequester free B(C₆F₅)₃, and thereby prevents it from mediating any further hydrosilylation reactivity.³¹ The addition of excess B(C₆F₅)₃ to a reaction mixture containing **5.2**, H₂C(OSiEt₃)₂ and excess Et₃SiH, on the other hand, leads to the transformation of H₂C(OSiEt₃)₂ into methane, with the accompanying formation of (Et₃Si)₂O (section 5.4.4).

The speciation profile vs. time for the reaction of **5.1** with excess Et₃SiH is shown in Figure 5.5. The rate of consumption of **5.1** shows a *pseudo*-first order dependence in [**5.1**], and a rate constant, k_{obs} , of $2.35 \times 10^{-4} \text{ s}^{-1}$ could be calculated. However, careful examination of the profile suggests that there is a short induction period of *ca.* 19 minutes, where consumption of the reagents is slower. This may indicate that the formation of one of the products of the reaction, **5.2** or H₂C(OSiEt₃)₂, leads to an acceleration in the rate of reactivity of **5.1** with Et₃SiH.

A similar induction period was shown for the [Cp*₂Sc][HB(C₆F₅)₃] catalysed hydrosilylation of CO₂. The induction period is shown to relate to the time taken to generate sufficient quantities of H₂C(OSiEt₃)₂ to convert [Cp*₂Sc][HC(O)OB(C₆F₅)₃] into a separated ion pair in which H₂C(OSiEt₃)₂ serves as a chelating ligand to the [Cp*₂Sc]⁺ cation. The formatoborate anion of this ion pair is much more susceptible to hydrosilylation by [Et₃Si-H-B(C₆F₅)₃], which constitutes Path B (Scheme 5.7).³⁰ The propensity for formatoborate anion dissociation from **5.1** was investigated employing formaldehyde dimethyl acetal as a model acetal. However, the analysis of a reaction mixture containing **5.1** and H₂C(OMe)₂ (>10 equiv.) by NMR spectroscopy revealed no

obvious formation of a separated ion pair at either room temperature or 333 K, consistent with the retention of the strong Ga-O bond.



Scheme 5.7: The two pathways proposed to occur in the hydrosilylation of CO_2 , catalysed by a cationic scandium complex ($\text{M} = [\text{Cp}^*_2\text{Sc}]^+$).³⁰

Alternatively, it was investigated whether the induction period observed relates to the regeneration of $[[^{\text{Dipp}}\mathbf{1}]\text{Ga}(\text{Ad})][\text{H}(\text{B}(\text{C}_6\text{F}_5)_3)]$, **5.2**. The addition of *ca.* 0.2 equivalents of **5.2** to the reaction mixture containing **5.1** and Et_3SiH leads to the formation of trace quantities of $\text{H}_2\text{C}(\text{OSiEt}_3)_2$ before NMR spectra could be acquired and hence loss of this observed induction period (Figure 5.6).

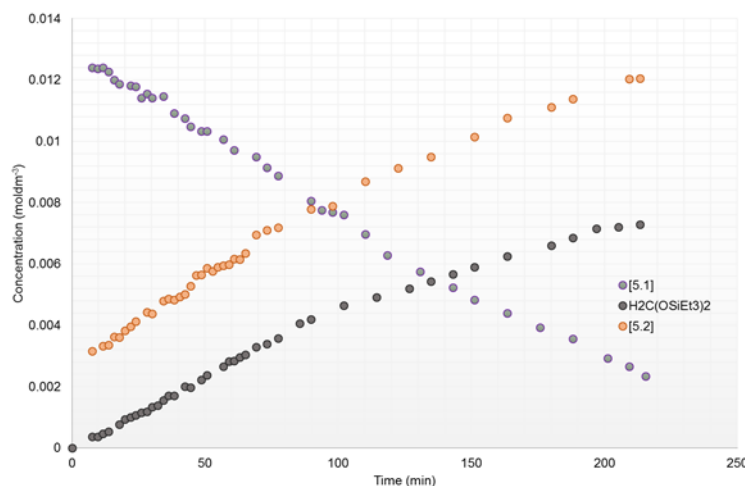
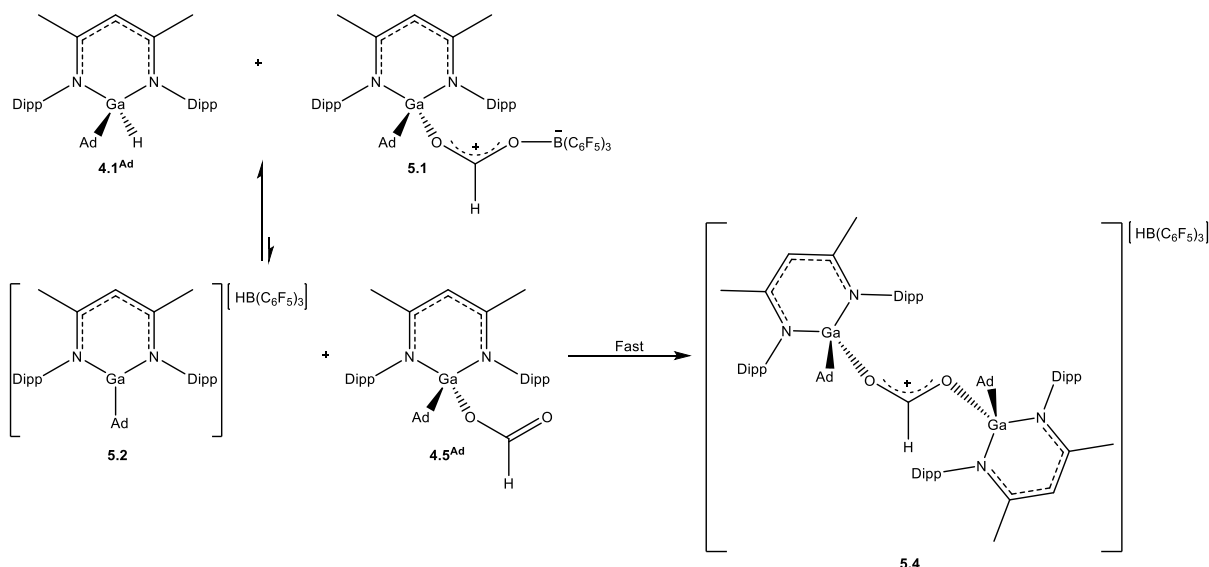


Figure 5.6: A speciation profile vs. time for the reaction of **5.1** with excess Et_3SiH in the presence of *ca.* 20% **5.2**, as monitored by ^1H NMR spectroscopy (benzene- d_6 solution, $T = 333\text{ K}$, no additional $\text{B}(\text{C}_6\text{F}_5)_3$ added).

A series of studies were undertaken to elucidate the role that **5.2** may perform in accelerating the reaction of gallium formate complex **5.1** with Et_3SiH . Analysis of a reaction mixture containing an equimolar mixture of **5.1** and **5.2** by NMR spectroscopy reveals that they exhibit no evident reactivity with each other. However, the addition of one equivalent of **5.2** to a solution of $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{Ad})(\text{OC}(\text{O})\text{H})$ (**4.5^{Ad}**) in benzene- d_6 leads to the *immediate* formation of a novel species, $[[\text{Dipp}\mathbf{1}]\text{Ga}(\text{Ad})\text{O}-\text{C}(\text{H})-\text{O}(\text{Ad})\text{Ga}[\text{Dipp}\mathbf{1}]][\text{H}(\text{B}(\text{C}_6\text{F}_5)_3)]$ (**5.4**), at room temperature. Single crystals of **5.4** were yielded from this benzene solution and analysis by single crystal X-ray diffraction showed this compound to be a charge-separated species in which the cationic component features a formate ligand bridging between two gallium centres. The reaction of **5.1** with $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{Ad})\text{H}$ (**4.1^{Ad}**) also leads to the formation of **5.4**, although this occurs significantly more slowly, requiring *ca.* 3 h to reach completion. It is proposed that, in this case, the $\text{B}(\text{C}_6\text{F}_5)_3$ group dissociates slowly from the formate oxygen of **5.1**, yielding **4.5^{Ad}** and then immediately forms **5.2** by abstracting the

gallium-bound hydride from **4.1^{Ad}**, **4.5^{Ad}** and **5.2** then react together immediately to form **5.4** (Scheme 5.8).



Scheme 5.8: The routes suggested for the formation of **5.4**.

The addition of one further equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ to a solution of **5.4** leads to the immediate formation of a 1:1 mixture of **5.1** and **5.2**, arising from the displacement of the gallium centre coordinated to the formate substituent by $\text{B}(\text{C}_6\text{F}_5)_3$. This is consistent with the fact that $\text{B}(\text{C}_6\text{F}_5)_3$ (A.N 79.6) is a better Lewis acid than **5.2** (A.N 69.8), and would suggest that **5.4** does not form in the presence of sufficient quantities of $\text{B}(\text{C}_6\text{F}_5)_3$.

To assess the potential of **5.4** to function as an intermediate in the catalytic hydrosilylation of CO_2 , its reactivity towards both CO_2 and Et_3SiH was investigated. **5.4** does react with CO_2 to yield a 1:1 mixture of **4.5^{Ad}** and **5.1**, although this occurs slowly and requires heating to 60°C for 15 h to reach > 90% completion. The reactivity of **5.4** towards CO_2 contrasts greatly to that observed for **5.2**, despite the fact that insertion into the B-H bond of $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ formally occurs for both. Due to the low hydricity of $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$, insertion of CO_2 into the B-H bond is demonstrated to require elevated temperatures when operated in the absence of a Lewis acidic cation which may facilitate

initial activation of CO₂ (e.g. [TMPH][HB(C₆F₅)₃], 100°C).^{6,109,110} The behaviour of **5.4** towards CO₂ is consistent with this, where there is no significant concentration of Lewis acid present to activate the CO₂. Similarly, **5.4** is relatively unreactive towards Et₃SiH and, when heated to 80°C for 4 days in the presence of a large excess of Et₃SiH (10 equiv.), only reaches *ca.* 50% completion, yielding H₂C(OSiEt₃)₂. In part, the conditions required to bring about the consumption of **5.4** may arise from the absence of free B(C₆F₅)₃. The unreactive nature of **5.4** towards Et₃SiH (and in light of the fact that **5.4** does not form in the presence of sufficient quantities of B(C₆F₅)₃) suggests that it plays no role in accelerating the reactivity of **5.1** towards Et₃SiH.

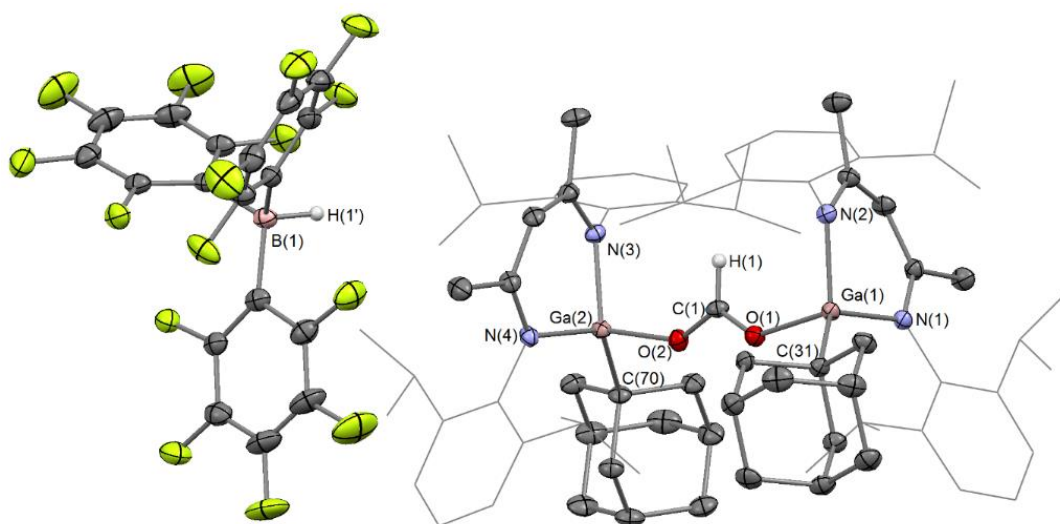


Figure 5.7: Molecular structure of $[(\text{Dipp})\text{Ga}(\text{Ad})\text{O})_2\text{CH}][\text{H}(\text{B}(\text{C}_6\text{F}_5)_3)]$ (**5.4**) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°): Ga(1)-N(1) 1.931(3), Ga(1)-N(2) 1.936(2), Ga(1)-C(31) 1.972(3), Ga(1)-O(1) 2.000(2), Ga(2)-N(4) 1.934(3), Ga(2)-N(3) 1.935(2), Ga(2)-C(70) 1.976(3), Ga(2)-O(2) 1.987(2), O(1)-C(1) 1.246(4), O(2)-C(1) 1.245(5), C(1)-H(1) 0.9500, B(1)-H(1) 1.12(5), N(1)-Ga(1)-N(2) 98.44(12), C(31)-Ga(1)-O(1) 106.00(12), N(4)-Ga(2)-N(3) 97.98(12), C(70)-Ga(2)-O(2) 104.18(12), C(1)-O(1)-Ga(1) 138.9(2), C(1)-O(2)-Ga(2) 143.2(2), O(2)-C(1)-O(1) 123.8(2), O(2)-C(1)-H(1) 118.1, O(1)-C(1)-H(1) 118.1.

The molecular structure of **5.4** features the $[[\text{Dipp1}]\text{Ga}(\text{Ad})\text{O}]_2\text{CH}]^+$ cation and $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ as the anionic component, and is closely related to that of the associated complex $[[\text{Dipp1}]\text{Al}(\text{Me})\text{O}]_2\text{CH}][\text{B}(\text{C}_6\text{F}_5)_4]$, formed from the reaction of $[[\text{Dipp1}]\text{Al}(\text{Me})(\text{OC}(\text{O})\text{PPh}_3)][\text{B}(\text{C}_6\text{F}_5)_4]$ with Et_3SiH .¹¹¹ Both gallium centres of **5.4** are found in an approximately tetrahedral environment at distances of 0.526 Å (Ga(1)) and 0.509 Å (Ga(2)) from the least-squares C₃N₂ planes of the ligand. These distances lie closer to that observed for **5.1** (0.551 Å); the pronounced distortion from the planarity observed for **5.2** is consistent coordination of the [O₂CH] fragment to both gallium centres. The Ga-N distances (Figure 5.7) are in accordance with those observed for **5.1** ($d(\text{Ga-N})$ 1.925(3), 1.938(3) Å) and somewhat longer than those observed for **5.2** ($d(\text{Ga-N})$ 1.8790(17), 1.8872(17) Å). These observations are consistent with a resonance form which comprises of two equal Ga-O interactions, rather than one single Ga-O bond and an O-Ga dative interaction, with one formally cationic gallium centre. This is also reflected in the two Ga-O distances ($d(\text{Ga(1)-O(1)})$ 2.000(2), $d(\text{Ga(2)-O(2)})$ 1.987(2) Å) which are, within three standard deviations, almost equidistant. The Ga-O distances are longer than that observed for **4.5^{Ad}** ($d(\text{Ga-O})$ 1.8966(11) Å) and lie close to that observed for **5.1** ($d(\text{Ga-O})$ 1.992(3) Å), consistent with a similar bonding situation in which the Lewis acidic B(C₆F₅)₃ moiety is replaced by $[[\text{Dipp1}]\text{Ga}(\text{Ad})]^+$. The symmetrical binding of the [O₂CH] fragment to both $[\text{Dipp1}]\text{Ga}(\text{Ad})$ fragments leads to the observed equidistant C-O bond lengths ($d(\text{O(1)-C(1)})$ 1.246(4), $d(\text{O(2)-C(1)})$ 1.245(5) Å). These bond lengths are comparable to those observed for **5.1** ($d(\text{C-O})$ 1.249(5), 1.246(5) Å) and lie between the C-O distances observed for **4.5^{Ad}** ($d(\text{C-O})$ 1.293(2), 1.182(2) Å) which may be classified as a formal double and single bond, respectively.

The ¹H NMR spectrum of **5.4** shows a resonance for the formate proton at $\delta_{\text{H}} = 8.52$ ppm which integrates 1:2 relative to the resonance associated with the γ -H at $\delta_{\text{H}} = 5.22$ ppm. A quartet resonance is observed at $\delta_{\text{H}} = 4.32$ ppm, which collapses to a broad singlet ($\Delta\omega_{1/2}$ 17.9 Hz) upon ¹¹B decoupling, for the hydride of the [HB(C₆F₅)₃]⁻ anion. Analysis of **5.4** by ¹¹B, ¹⁹F and ¹H NMR spectroscopy is consistent with the presence of the [H(B(C₆F₅)₃)]⁻ anion.¹⁰³⁻¹⁰⁵ The IR spectrum of **5.4** features a broad absorption at 2383 cm⁻¹ for the B-H stretch of the [HB(C₆F₅)₃]⁻ anion and an absorption at 1640 cm⁻¹ for the C=O stretch. This lies between those observed for **4.5^{Ad}** ($\nu_{\text{C=O}}$ 1679 cm⁻¹) and **5.1** ($\nu_{\text{C=O, av}}$ 1631 cm⁻¹) and reflects the reduction in bond order associated with the coordination of this formate functionality to a Lewis acid.

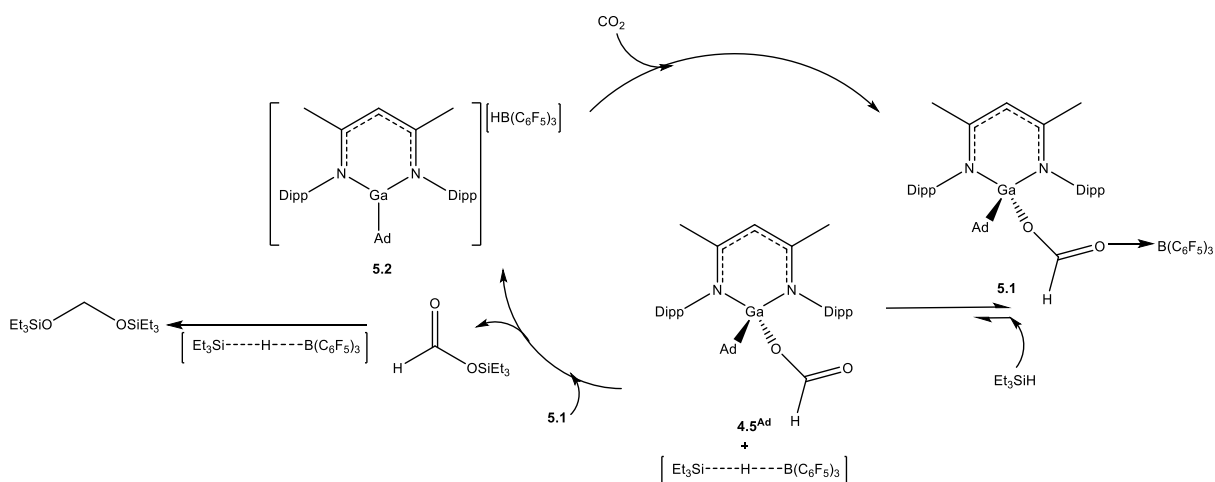
We propose that the induction period observed in the reaction of **5.1** with Et₃SiH (Figure 5.5), relates to the time taken to regenerate **5.2**. During this period, the reaction of **5.1** with Et₃SiH is very slow due to a low concentration of [Et₃Si-H-B(C₆F₅)₃]. However, upon the regeneration of a sufficient quantity of **5.2**, we propose that a greater amount of [Et₃Si-H-B(C₆F₅)₃] may be generated through more facile dissociation of B(C₆F₅)₃ from **5.2** as compared to **5.1**. Therefore, the formation of a larger amount of the reactive adduct [Et₃Si-H-B(C₆F₅)₃] leads to its greater reactivity with **5.1** (and therefore faster consumption). This is supported further by the observation that when **5.1** is reacted with excess Et₃SiH in the presence of an additional equivalent of B(C₆F₅)₃, no induction period is observed (Section 5.4.4).

5.4.3 Catalytic hydrosilylation of CO₂ using stoichiometric B(C₆F₅)₃

Having demonstrated the viability of the two steps key to catalytic turnover for the hydrosilylation of CO₂, it appeared that **5.1** could be an active catalyst for the hydrosilylation of CO₂, albeit at elevated temperatures. When a solution of Et₃SiH in

benzene-d₆ with 10 mol% of **5.1** as a catalyst is pressurised with *ca.* 2 bar CO₂ and heated 60°C, catalytic turnover proceeds and completely selective conversion to CH₂(OSiEt₃)₂ reaches *ca.* 85% completion after 58 hours. The highly selective formation of CH₂(OSiEt₃)₂ suggests that, as observed in the stoichiometric reactivity of **5.2** with Et₃SiH, B(C₆F₅)₃ remains primarily sequestered by the gallium catalyst during the course of the catalysis.³¹

The derived turnover frequency (TOF 0.16 h⁻¹) is very low and the catalysis requires extended reaction times to reach near-completion. Examination of the catalytic mixture by ¹H NMR spectroscopy reveals that the concentration of **5.1** remains essentially constant throughout the catalysis, due to the rapid reaction of **5.2** with CO₂ (Figure 5.8). As such, the concentration of **5.2** remains close to zero. The rate of silane consumption shows a first order dependence and the plot of ln[Et₃SiH] vs. time gives a rate constant of 9 x 10⁻⁶ s⁻¹ (t_{1/2} = 1283 min). This suggests that the rate-determining step of the catalysis is regeneration of **5.2** from the reaction of **5.1** with Et₃SiH (*via* the formation of the reactive silane-borane adduct), consistent with the relative rates observed for the two individual steps measured stoichiometrically.³⁰



Scheme 5.9: The proposed catalytic cycle for the hydrosilylation of CO₂ by **5.2**.

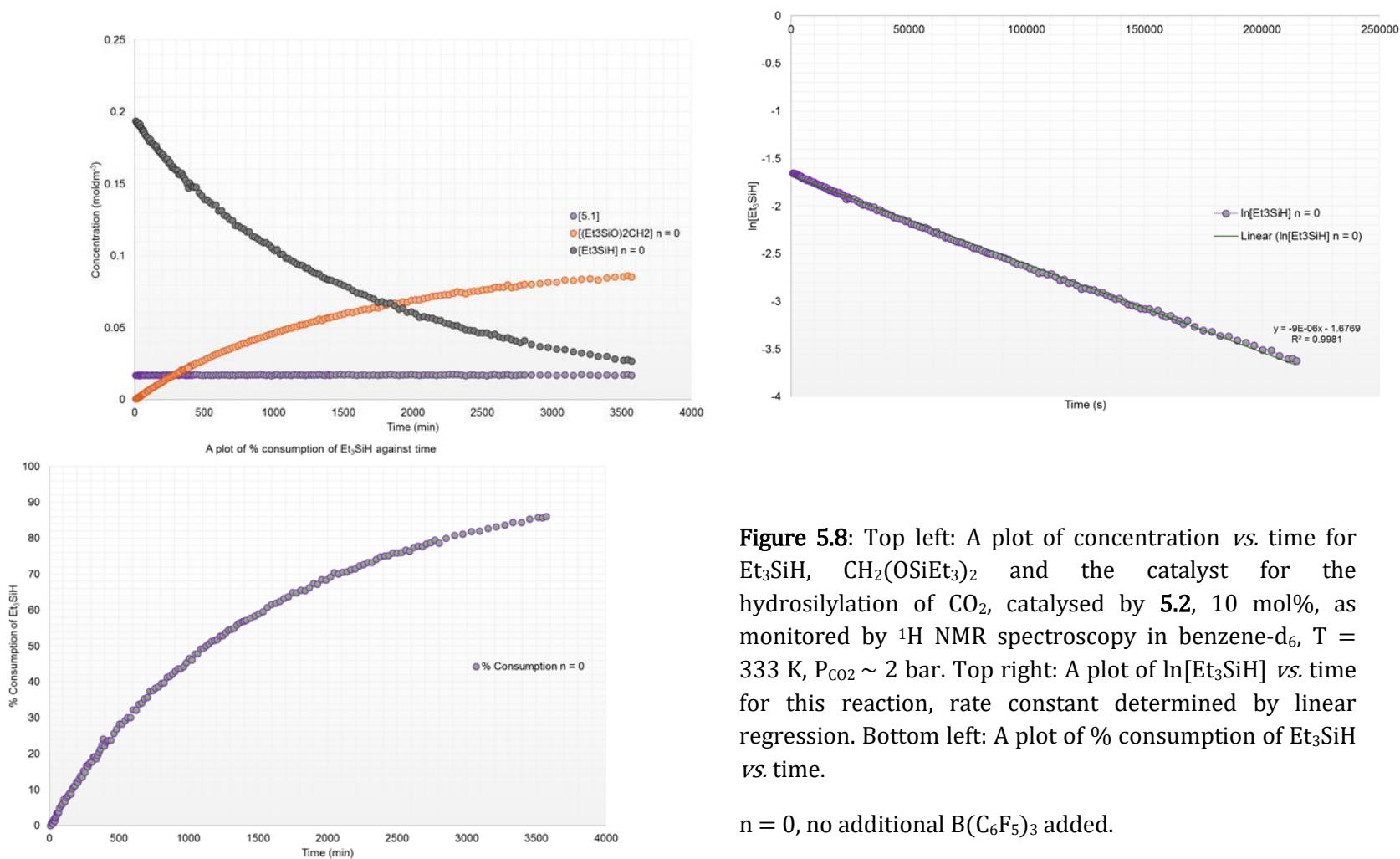


Figure 5.8: Top left: A plot of concentration *vs.* time for Et_3SiH , $\text{CH}_2(\text{OSiEt}_3)_2$ and the catalyst for the hydrosilylation of CO_2 , catalysed by **5.2**, 10 mol%, as monitored by ^1H NMR spectroscopy in benzene- d_6 , $T = 333 \text{ K}$, $P_{\text{CO}_2} \sim 2 \text{ bar}$. Top right: A plot of $\ln[\text{Et}_3\text{SiH}]$ *vs.* time for this reaction, rate constant determined by linear regression. Bottom left: A plot of % consumption of Et_3SiH *vs.* time.

$n = 0$, no additional $\text{B}(\text{C}_6\text{F}_5)_3$ added.

The importance of the role of the metal centre in facilitating nucleophilic attack upon CO₂ in the first step of the conversion is highlighted by the observation that the reaction of the 2,2,6,6-tetramethylpiperidine derivative, [TPMH][HB(C₆F₅)₃], and CO₂ to form [TPMH][HCO₂B(C₆F₅)₃] does not occur at room temperature and requires heating to 56°C to reach completion.^{6,61,110} In this case, elevated temperatures are required to bring about the reaction of **5.1** with Et₃SiH. In part, the slow progression of the reaction and the incomplete reduction of the CO₂ is likely due to the low concentration of free B(C₆F₅)₃, which is necessary to effect hydrosilylation at reasonable rates.³⁰ In addition to this, the sluggish reactivity may arise due to the strength of the binding of the formatoborate anion [HC(O)O(B(C₆F₅)₃)⁻ to the gallium centre of [[^{Dipp}**1**]Ga(Ad)]⁺, illustrated in the molecular structure of **5.1**. It is demonstrated that the reaction of Et₃SiH with [TPMH][HC(O)O(B(C₆F₅)₃)] (in which the anion interacts minimally with the [TPMH]⁺ cation) instantly affords [TPMH][HB(C₆F₅)₃]⁻ and CH₂(OSiEt₃)₂, when in the presence of one additional equivalent of B(C₆F₅)₃ at room temperature.^{61,110} It is proposed that the anionic component of [TPMH][HC(O)O(B(C₆F₅)₃)] reacts with the silylium ion, Et₃Si⁺, generated from the activation of Et₃SiH by B(C₆F₅)₃.⁴² For **5.1**, the formatoborate anion is strongly bound to the cationic gallium centre of [[^{Dipp}**1**]Ga(Ad)]⁺ and therefore transfer of the silylium ion to the formate moiety of **5.1** is less Coulombically favoured than that for a charge-separated formatoborate anion.^{42,83} Therefore, the silylium ion transfer necessary to facilitate regeneration of **5.2** from **5.1** occurs under somewhat harsher conditions than are required for metal formatoborate complexes which are formally identified as charge-separated complexes. Therefore, enhancement of the ability of **5.2** to catalyse the hydrosilylation of CO₂ is relatively limited but may be achieved through the use of additional equivalents of B(C₆F₅)₃.

5.4.4 The use of excess B(C₆F₅)₃: impact on rate and selectivity

Typically, catalytic systems which effect hydrosilylation of CO₂ and operate in the presence of *excess* B(C₆F₅)₃ yield significant quantities of methane in the product distribution. Generally, this is attributed to the formation of the reactive silane adduct [R₃Si-H-B(C₆F₅)₃], which has been demonstrated to reduce a range of C=O and C-O functionalities.^{53,54,61} Accordingly, the addition of further equivalents of B(C₆F₅)₃ to a reaction mixture containing **5.2**, H₂C(OSiEt₃)₂ and excess Et₃SiH leads to the complete consumption of the acetal species at 60°C. H₂C(OSiEt₃)₂ is converted into methane ($\delta_{\text{H}} = 0.17$ ppm) and O(SiEt₃)₂, *via* a methoxysilane intermediate, Me(OSiEt₃) ($\delta_{\text{H}} = 3.32$ ppm), although the latter is observed only in trace quantities. Under these conditions, the consumption of H₂C(OSiEt₃)₂ occurs relatively slowly, requiring between 5 – 16 h to reach completion (Figure 5.9). This is consistent with reports which show that (among the hydrosilylation products of CO₂) H₂C(OSiEt₃)₂ is the least reactive substrate with respect to [Et₃Si-H-B(C₆F₅)₃], primarily due to the necessity to break a C-O bond to effect the transformation.⁶¹ The use of more equivalents of B(C₆F₅)₃ leads to the generation of higher concentrations of [Et₃Si-H-B(C₆F₅)₃] and hence faster consumption of H₂C(OSiEt₃)₂. The use of either one or three equivalents of B(C₆F₅)₃ leads to kinetic plots which are first order with respect to the concentration of H₂C(OSiEt₃)₂, and from these data, rate constants ($n = 1$, $k_{\text{obs}} = 7.17 \times 10^{-5} \text{ s}^{-1}$; $n = 3$, $k_{\text{obs}} = 1.92 \times 10^{-4} \text{ s}^{-1}$) and half-lives ($n = 1$, $t_{1/2} = 161 \text{ min}$; $n = 3$, $t_{1/2} = 60 \text{ min}$) could be calculated for the consumption of the acetal.

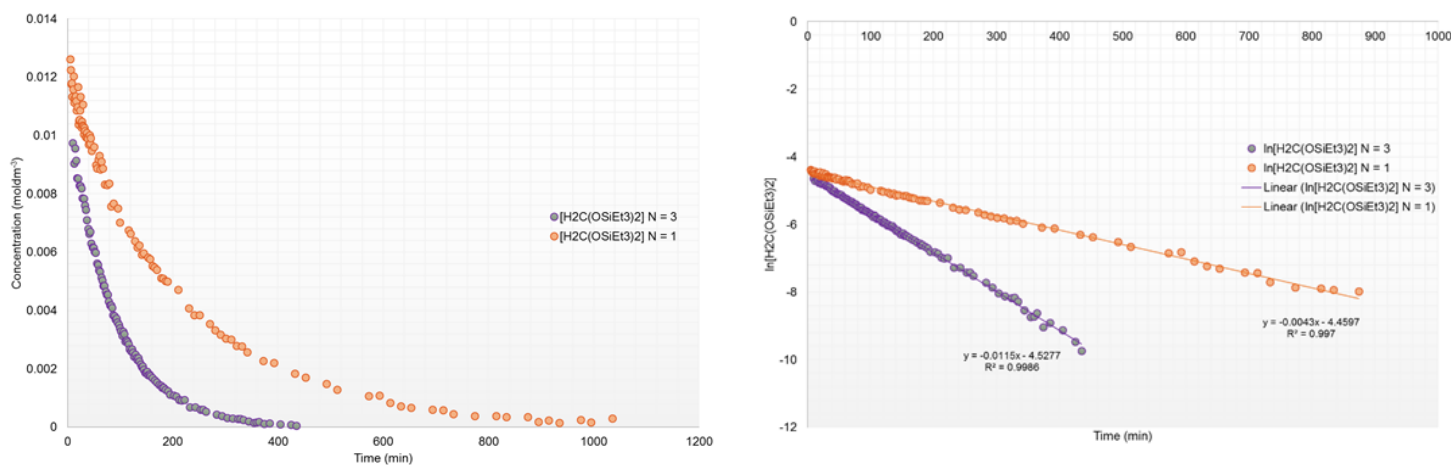


Figure 5.9: Left: A plot of $[\text{H}_2\text{C}(\text{OSiEt}_3)_2]$ against time, when one and three additional equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ are added (benzene- d_6 , $T = 333 \text{ K}$); right: A plot of $\ln[\text{H}_2\text{C}(\text{OSiEt}_3)_2]$ against time for these reactions.

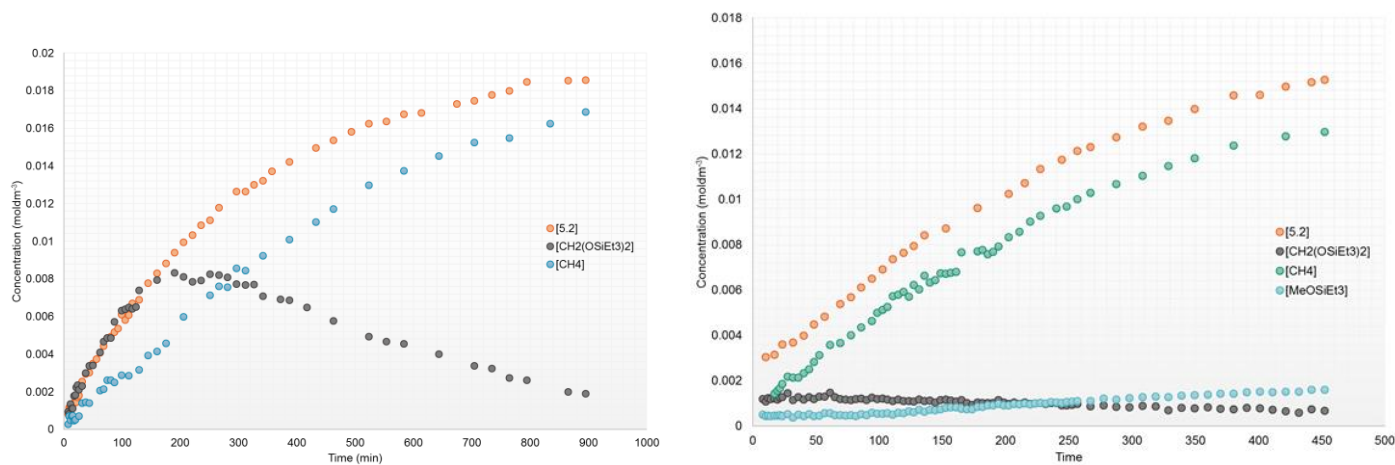


Figure 5.10: A speciation plot for the reaction of **5.1** with excess Et_3SiH (10 equiv.) at 333 K in the presence of one (left) and nine (right) additional equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$.

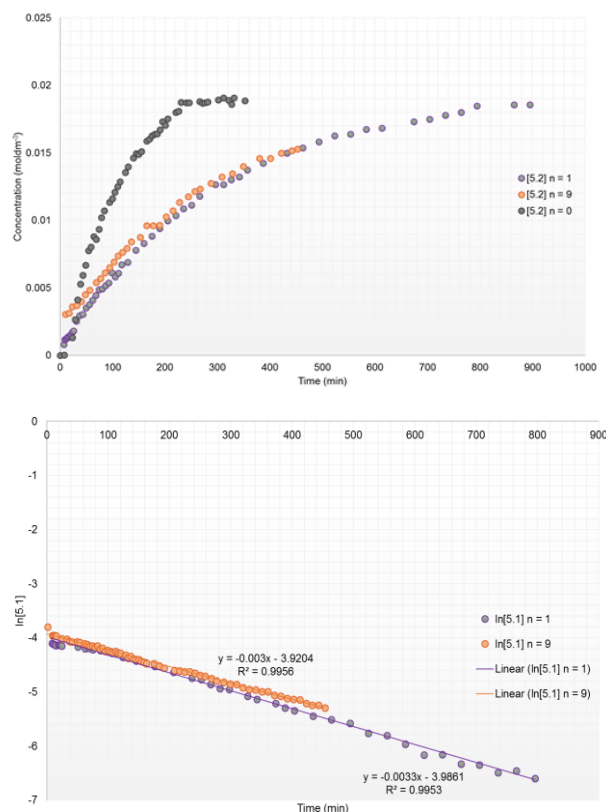


Figure 5.11: Above: A plot of [5.2] against time for the reaction of 5.1 with excess Et_3SiH (10 equiv.) at 333K, in the presence of 0, 1 and 9 additional equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$. Below: A plot of $\ln[5.1]$ against time for this reaction.

To assess the impact of excess $\text{B}(\text{C}_6\text{F}_5)_3$ on the regeneration of 5.2 from 5.1, 5.1 was reacted with excess Et_3SiH at 60°C in the presence of one and nine additional equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$. The progress of these reactions was monitored by ^1H NMR spectroscopy and the speciation plots are shown in Figure 5.10. As expected, the use of additional $\text{B}(\text{C}_6\text{F}_5)_3$ leads to reduced selectivity in the formate-derived products such that a mixture of $\text{CH}_2(\text{OSiEt}_3)_2$, CH_4 and $\text{O}(\text{SiEt}_3)_2$ is yielded, with trace quantities of MeOSiEt_3 . In the presence of large excesses of $\text{B}(\text{C}_6\text{F}_5)_3$ (e.g. $n = 9$), $\text{H}_2\text{C}(\text{OSiEt}_3)_2$ accumulates in lower concentrations than in the presence of fewer equivalents ($n = 1$). In addition, the use of additional equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ leads to initially greater consumption of 5.1 (and subsequent regeneration of 5.2) (Figure 5.11), such that no

induction period is observed. This is presumably due to the presence of a greater concentration of [Et₃Si-H-B(C₆F₅)₃] at the beginning of the reaction, although this effect appears to be minimal beyond the addition of 1 additional equivalent of B(C₆F₅)₃. However, the overall regeneration of **5.2** occurs significantly more slowly in the presence of excess B(C₆F₅)₃. In both cases, the reactions are first order with respect to the concentration of **5.1** (Figure 5.11) and from this, an average rate constant of $5.3 \times 10^{-5} \text{ s}^{-1}$ and half-life of 210 minutes could be calculated.

5.4.5 Catalytic hydrosilylation of CO₂ using excess B(C₆F₅)₃

In light of the unimpressive turnover frequencies obtained (TOF 0.16 h⁻¹) when **5.2** was employed as a catalyst for the hydrosilylation of CO₂, we sought to investigate whether the use of **5.2** in conjunction with additional equivalents of B(C₆F₅)₃ might yield improved catalytic performance. Indeed, the exposure of a solution of Et₃SiH in benzene-d₆ containing 10 mol% of **5.2** and one additional equivalent of B(C₆F₅)₃ to CO₂ at 2 bar pressure leads to an improvement of the catalytic turnover frequency to 2.44 h⁻¹ at 60°C. As observed in the stoichiometric reactivity, a mixture of H₂C(OSiEt₃)₂, CH₄ and O(SiEt₃)₂ is yielded (Table 5.3). Additionally, this system operates at room temperature, albeit somewhat more slowly (TOF 0.86 h⁻¹). By contrast, the magnesium hydride complex, [Tism^{PriBenz}]MgH, catalyses the hydrosilylation of CO₂ with turnover frequencies of 1.2, 2.9 and 38.7 h⁻¹ when Ph₃SiH, Et₃SiH and PhSiH₃, respectively are employed as reductants.³⁶ It is noteworthy that, in contrast to many other catalysts for this transformation, this system operates at room temperature, with a low catalyst loading (0.5 mol%, with 2.5 mol% B(C₆F₅)₃). The related zinc hydride, [Tism^{PriBenz}]ZnH, also catalyses this process, albeit with lower activity (maximum TOF 0.8 h⁻¹, PhSiH₃) and at higher catalyst loadings (2.5 mol%, with 5 mol% B(C₆F₅)₃).

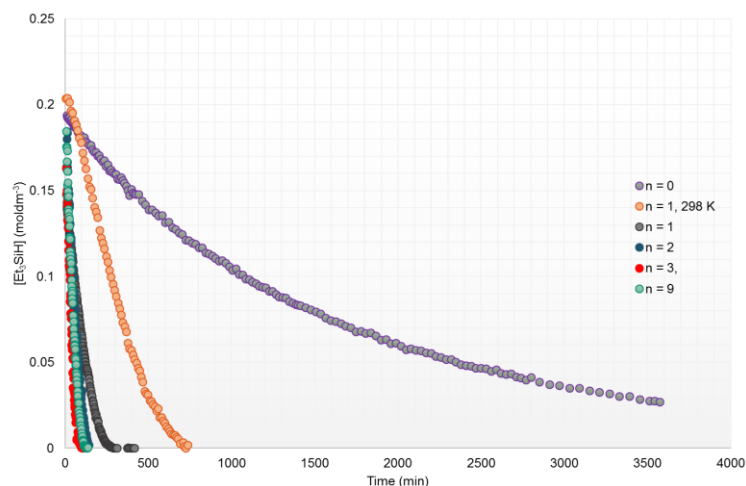


Figure 5.12: A comparative plot of the concentration of Et_3SiH vs. time for the catalytic hydrosilylation of CO_2 , catalysed by **5.2**, 10 mol%, as monitored by ^1H NMR spectroscopy in benzene- d_6 , $P_{\text{CO}_2} \sim 2$ bar, with n additional equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$.

	TOF (h^{-1})	% $\text{H}_2\text{C}(\text{OSiEt}_3)_2$	% $\text{Me}(\text{OSiEt}_3)$	% $\text{CH}_4/\text{O}(\text{SiEt}_3)_2$
$n = 0$, 333 K	0.16	100	0	0
$n = 1$, 298 K	0.86	20	< 0.5	80
$n = 1$, 333 K	2.44	65	< 0.5	35
$n = 2$, 333 K	4.20	60	< 0.5	40
$n = 3$, 333 K	5.50	59	< 0.5	41
$n = 7$, 333 K	-	56	< 0.5	44
$n = 9$, 333 K	5.34	29	< 1	70

Table 5.3: The turnover frequencies and product distributions for the hydrosilylation of CO_2 catalysed by **5.2** and n additional equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$.

Carrying out catalysis in the presence of further additional equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ (up to nine) leads to only a nominal increase in TOF values, especially beyond the addition of two additional equivalents. However, the use of a greater number of equivalents does lead to a shift in product distribution towards CH_4 and $\text{O}(\text{SiEt}_3)_2$. This is a feature that has been previously reported for related systems and is consistent with the formation of greater concentrations of the reductant $[\text{Et}_3\text{Si-H-B}(\text{C}_6\text{F}_5)_3]$.³⁰

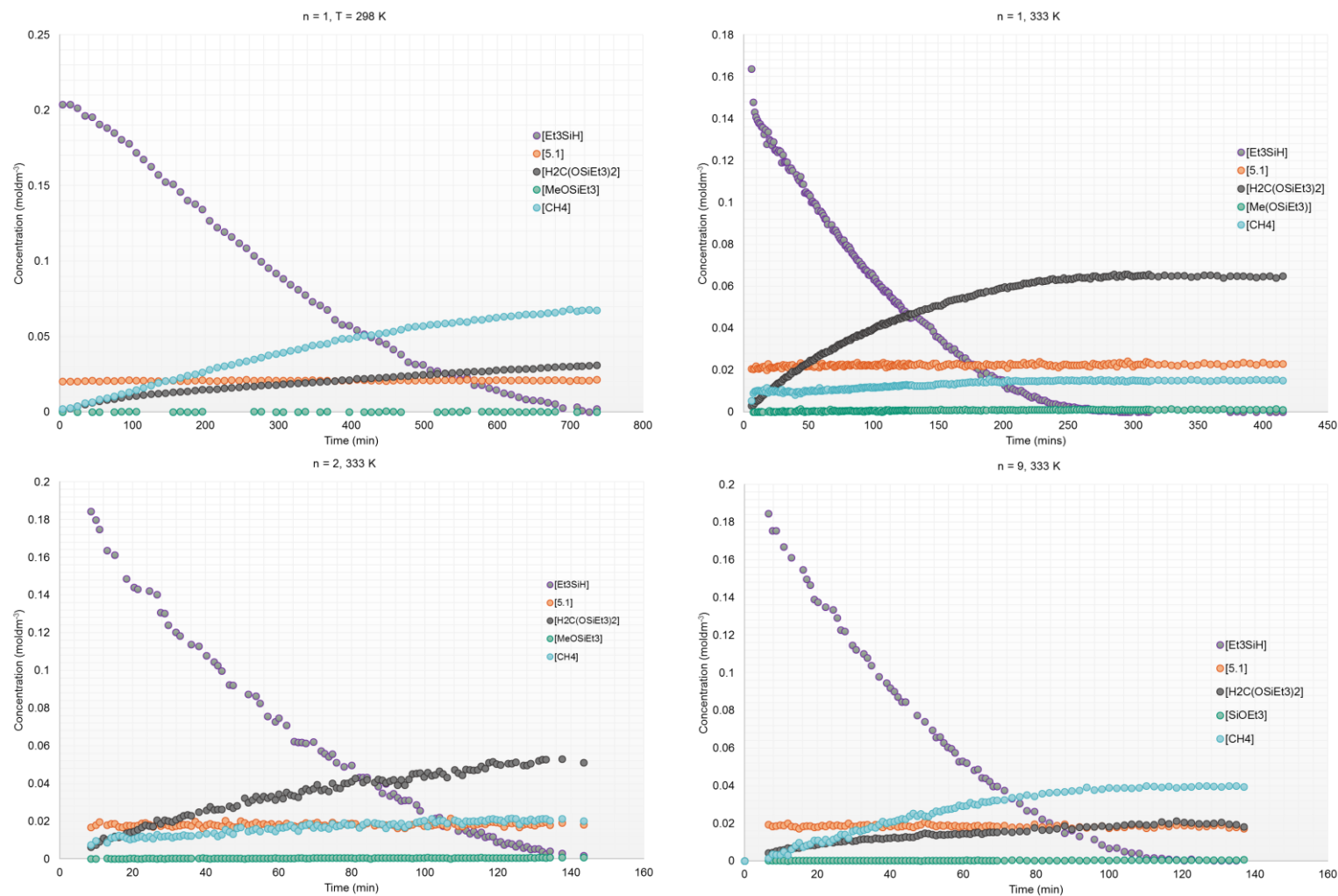


Figure 5.13: Plots of concentration vs. time for the catalytic hydrosilylation of CO₂, catalysed by **5.2**, 10 mol%, as monitored by ¹H NMR spectroscopy in benzene-d₆, P_{CO₂} ~ 2 bar, with n additional equivalents of B(C₆F₅)₃ added. Top left: n = 1, 298 K; top right: n = 1, 333 K; bottom left: n = 2, 333 K; bottom right: n = 9, 333 K.

5.4.6 Can B(C₆F₅)₃ activate aluminium complexes towards Al-O/E-H σ -bond metathesis?

The work in Chapter 3 demonstrated that aluminium formate complexes, [Dipp¹Al(R)(OC(O)H) (R = Me, Et; **3.6^R**), generated in the reactions of the corresponding aluminium hydrides with CO₂, are unreactive to Al-O/E-H metathesis, such that they do not react at all with HBpin or Et₃SiH. In light of the activation of **4.5^{Ad}** towards Ga-O/Si-H metathesis by the use of B(C₆F₅)₃, we considered that this might also be possible for the related aluminium systems.

As in the formation of **5.1**, the addition of one equivalent of B(C₆F₅)₃ to **3.6^{Et}** leads to its coordination to the formate substituent and the formation of [Dipp¹Al(Et)(HC(O)OB(C₆F₅)₃) (**5.5**). This may be demonstrated using a range of spectroscopic and analytical techniques; many of the spectroscopic features observed are analogous to those observed for **5.1**. ¹H NMR spectroscopy shows the formation of **5.5** to be quantitative and completely selective; despite the propensity of B(C₆F₅)₃ for the abstraction of alkyl substituents, this is not evident in the formation of **5.5**. The coordination of B(C₆F₅)₃ to the formate moiety of **3.6^{Et}** is demonstrated in both the ¹¹B and ¹⁹F NMR spectra. The ¹¹B NMR spectrum shows a broad resonance at $\delta_B = 0.6$ ppm, which is consistent with the chemical shift observed for **5.1** ($\delta_B = 0.6$ ppm). Additionally, the difference in chemical shifts of the *para*- and *meta*-fluorines ($\Delta\delta_{p-m}$ 7.2 ppm), is consistent with that observed for **5.1** ($\Delta\delta_{p-m}$ 6.4 ppm).⁵² The IR spectrum of **5.5** shows two absorptions at 1625 and 1644 cm⁻¹, for the symmetric and antisymmetric C=O stretches, which are red-shifted compared to **3.6^{Et}** (1673 cm⁻¹) consistent with a reduction in the bond order. Single crystals of **5.5** could be obtained from *n*-hexane at

6°C; the molecular structure of **5.5**, as elucidated by single crystal X-ray crystallography is shown in Figure 5.14.

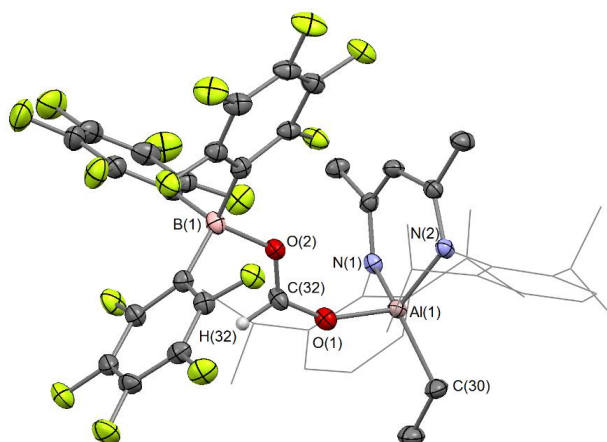


Figure 5.14: Molecular structure of [Dipp**1**]Al(Et)(HC(O)OB(C₆F₅)₃) (**5.5**) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°) are listed in **Table 5.4**:

	5.5	3.6^{Et}
Distance of Al from C ₃ N ₂ plane (°)	0.536	0.488
$d(\text{Al-O})$ (Å)	1.837(3)	1.7832(8)
$d(\text{Al-N})$ (Å)	1.875(3), 1.877(3)	1.8855(9), 1.8914(9)
$d(\text{Al-C})$ (Å)	1.945(4)	1.9605(11)
$d(\text{O-C})$ (Å)	1.243(5), 1.243(5)	1.2988(14), 1.2039(15)
$d(\text{O-B})$ (Å)	1.574(6)	-
N-Al-N (°)	98.35(14)	97.43(4)

The molecular structure of **5.5** displays the expected molecular connectivity and features similar structural features to **5.1**. The coordination of B(C₆F₅)₃ to the formate functionality causes a lengthening of the Al-O bond, although to a lesser extent than is observed for **5.1** ($\Delta(d(\text{Al-O})) = 0.0538$ Å; $\Delta(d(\text{Ga-O})) = 0.0954$ Å). Hence, the Ga-O bond of **5.1** is longer than **5.5**, despite the very similar covalent radii of aluminium and gallium (Al: 1.21(4) Å, Ga: 1.22(3) Å); this is consistent with reported data for M-O (M = Al, Ga) bonds which typically show that Al-O bonds are stronger and therefore

shorter.^{78,112} The O-B distances of **5.1** and **5.5** are comparable within three standard deviations (**5.1**: $d(\text{O-B})$ 1.552(6) Å, **5.5**: $d(\text{O-B})$ 1.574(6) Å). In contrast to the C-O bond lengths of **3.6^{Et}**, which are clearly indicative of the presence of a single and double bond, the C-O bonds of **5.5** are equidistant and lie between typical single and double C-O bond lengths. This is a feature that is also present in **5.1** and is indicative of delocalisation of the metal-bound oxygen lone pair across both C-O bonds. The structural metrics of **5.5** indicate the the Al-O single bond is retained and that **5.5** does not exist as the zwitterionic species $[[^{\text{Dipp}}\mathbf{1}]\text{Al}(\text{Et})][\text{HCO}_2\text{B}(\text{C}_6\text{F}_5)_3]$, featuring a cationic aluminium centre. This is consistent with the behaviour observed for **5.1** and with the chemical properties typical of aluminium, namely high Lewis acidity and strong Al-O bonds.⁷⁸

Whilst **3.6^{Et}** is unreactive towards Et₃SiH, treatment of **5.5** with excess Et₃SiH (10 equiv.) leads to its complete consumption over the course of 1 h at room temperature. However, a mixture of products is formed (as observed by ¹H, ¹¹B and ¹⁹F spectroscopy) and none of the spectroscopic signatures are present for the organic products expected from the cleavage of the formate functionality. No change in the product distribution is observed with heating to 60°C for 3 d.

In order to probe the identity of the resulting Nacnac-ligated species, the reaction of $[[^{\text{Dipp}}\mathbf{1}]\text{Al}(\text{Et})\text{H}$ (**3.4^{Et}**) was investigated, since this compound could potentially be formed *via* cleavage of the Al-O bond of **3.6^{Et}**, with Et₃SiH. Accordingly, the addition of one equivalent of B(C₆F₅)₃ to **3.4^{Et}** leads to the selective formation of a novel species, proposed to be $[[^{\text{Dipp}}\mathbf{1}]\text{Al}(\text{Et})][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**5.6**). **5.6** could be characterised by *in-situ* NMR spectroscopy and many of the spectral features are comparable to those of the closely related complexes **5.2** and $[[^{\text{Dipp}}\mathbf{1}]\text{Al}(\text{Me})][\text{B}(\text{C}_6\text{F}_5)_4]$.⁹⁹ These spectral features (Table 5.5) are consistent with the presence of a cationic, three-coordinate aluminium

centre and hydroborate anion. However, the resonances associated with the anion in the ¹⁹F and ¹¹B NMR spectra are unresolved, which may be indicative of some Al-F interaction in solution. Similar interactions have been previously reported for the closely related complex $[\text{Dipp}\mathbf{1}]\text{Al}(\text{Me})[\text{B}(\text{C}_6\text{F}_5)_4]$, which exhibits very high Lewis acidity (A.N 89.7).^{99,111}

	5.6	5.2
$\delta_{\text{H}}(\gamma\text{-H})$ (ppm)	5.48	5.68
$\delta_{\text{C}}(\gamma\text{-H})$ (ppm)	104.4	103.8
$\delta_{\text{H}}(\text{B-H})$ (ppm)	4.26	4.39
δ_{B} (ppm)	-25.1	-25.0
$\Delta\delta_{\text{F-}p\text{-}m}$ (ppm)	1.6	2.9

Table 5.5: A comparison of some of the features of the NMR spectra of **5.6** and **5.2**.

Whilst **5.6** is stable in solution at room temperature over the course of several days, repeated attempts to isolate **5.6** in the solid state were unsuccessful and a small number of single crystals of a decomposition product were obtained. The analysis of these crystals by single crystal X-ray diffraction revealed the molecular structure to be that of the dialkylborohydride complex $[\text{Dipp}\mathbf{1}]\text{Al}(\text{Et})(\kappa^2\text{-H}_2\text{B}(\text{C}_6\text{F}_5)_2)$ (**5.7**). It is proposed that **5.7** forms from decomposition of **5.6** *via* abstraction of a -C₆F₅ ligand by the cation, producing $[\text{Dipp}\mathbf{1}]\text{Al}(\text{Et})(\text{C}_6\text{F}_5)$ and $\text{HB}(\text{C}_6\text{F}_5)_2$. This may then undergo further reactivity with a further equivalent of **3.4**^{Et} to yield **5.7**. There is precedent for the exchange of fluoroaryl substituents in reactive $[\text{RB}(\text{C}_6\text{F}_5)_3]^-$ (R = H, Me) anions with Lewis acidic aluminium centres, and the decomposition of **5.6** in this manner may also reflect some degree of interaction of the cation with a fluoroaryl substituent of the anion in solution.¹¹³

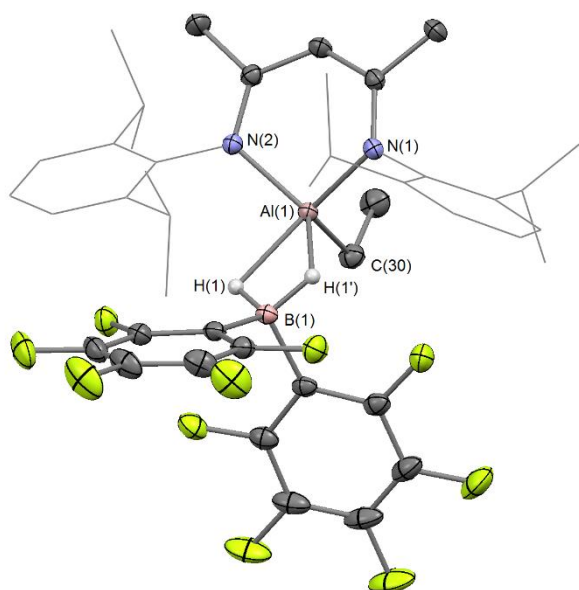
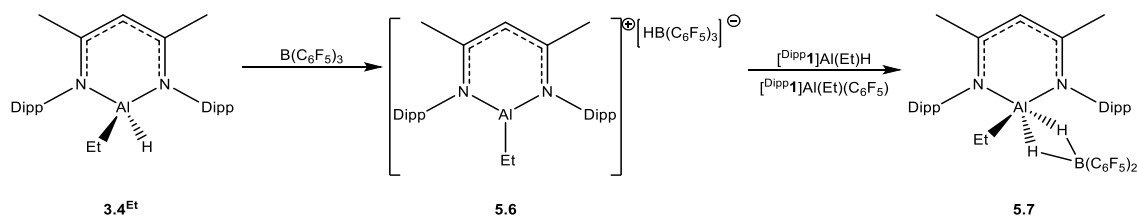


Figure 5.15: Molecular structure of $[\text{Dipp1}]\text{Al}(\text{Et})(\kappa^2\text{-H}_2\text{B}(\text{C}_6\text{F}_5)_2)$ (**5.7**) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°): Al(1)-N(2) 1.8871(12), Al(1)-N(1) 1.9124(12), Al(1)-C(30) 1.9685(16), Al(1)-B(1) 2.3146(15), Al(1)-H(1) 1.86(2), Al(1)-H(1') 1.949(19), B(1)-H(1) 1.15(2), B(1)-H(1') 1.10(2), N(2)-Al(1)-N(1) 97.01(5).



Scheme 5.10: The preparation of **5.6** and the proposed route for its decomposition.

While the reaction of **5.5** with Et₃SiH generates a number of different products, no evidence for the formation of the alane **3.4^{Et}**, the cation **5.6** or the borohydride **5.7** could be obtained. On the other hand, **5.5** reacts cleanly with HBpin over the course of 48 h at 60°C, yielding MeOBpin and $[\text{Dipp1}]\text{Al}(\text{Et})(\text{OBpin})$ (**5.8**) as the major Nacnac-ligated product. **5.8** was synthesised independently and characterised based its spectroscopic similarities to the aluminium borate ester complexes synthesised in Chapter 3.

Consistent with the reactivity reported in Chapter 3, however, no Al-O cleavage is observed.

5.5 Conclusions and suggestions for further work

The work in this chapter demonstrates that $\text{B}(\text{C}_6\text{F}_5)_3$ may be used as a co-catalyst with a Nacnac-ligated gallium hydride complex, $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{Ad})\text{H}$ to effect the catalytic hydrosilylation of CO_2 . The presence of the $\text{B}(\text{C}_6\text{F}_5)_3$ leads to the activation of the gallium complexes towards both of the processes key to catalytic turnover. The addition of an equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ to $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{Ad})\text{H}$ leads to the formation of a tractable 3-coordinate cationic gallium complex, coupled with a hydroborate anion, $[[\text{Dipp}\mathbf{1}]\text{Ga}(\text{Ad})][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**5.2**). This complex shows significantly enhanced reactivity towards CO_2 as compared to its neutral counterpart, yielding $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{Ad})(\text{HC}(\text{O})\text{OB}(\text{C}_6\text{F}_5)_3)$ (**5.1**) rapidly and selectively. The enhanced reactivity is proposed to arise from Lewis acid activation of CO_2 (by the gallium cation), followed by its reduction by the hydroborate anion. Whilst the neutral gallium formate complex is unreactive towards Et_3SiH , its $\text{B}(\text{C}_6\text{F}_5)_3$ adduct reacts, regenerating **5.2** and forming $\text{H}_2\text{C}(\text{OSiEt}_3)_2$, albeit only at appreciable rates at elevated temperatures (60°C). This represents formal reduction of CO_2 to the formaldehyde oxidation level, in a stoichiometric manner. This transformation may also be effected in catalytic fashion, again selectively yielding $\text{H}_2\text{C}(\text{OSiEt}_3)_2$, with a turnover frequency of 0.16 h^{-1} . It is proposed that both the selectivity and inefficiency of this catalysis arises, in part, from the absence of unbound $\text{B}(\text{C}_6\text{F}_5)_3$ throughout the course of the catalysis.

When the catalysis is undertaken in the presence of excess $\text{B}(\text{C}_6\text{F}_5)_3$, an appreciable enhancement in activity of the system is observed (max TOF 5.5 h^{-1}), with a simultaneous reduction in selectivity, yielding a product distribution including

H₂C(OSiEt₃)₂, CH₄ and O(SiEt₃)₂. Consistent with literature precedent, it is proposed that the presence of excess B(C₆F₅)₃ leads to the greater extent of formation of [Et₃Si-H-B(C₆F₅)₃], the species responsible for both cleavage of the formate functionality from gallium to yield HC(O)OSiEt₃ and its further reduction to methane.

Whilst the use of **5.2** to catalyse the hydrosilylation of CO₂ represents a rare example of the use of a main group hydride as a catalyst for this process, the TOF values obtained are poor. Typically, in B(C₆F₅)₃-mediated reactivity, it is considered that the interaction between [Et₃Si-H-B(C₆F₅)₃] (*i.e.* effectively the silylium cation) and the formatoborate anion species determines the efficiency of the catalysis. As such, in the case of **5.1**, in which the formato-borate anion remains strongly bound to the gallium centre, the Coulombic interaction of the silylium cation and formatoborate anion is reduced.

Nevertheless, we were able to demonstrate some selectivity in the products obtained, dependent on both the number of equivalents of B(C₆F₅)₃ utilised and temperature. It has been demonstrated, utilising a magnesium hydride catalyst, that the product distribution may also be controlled by the silane reductant utilised.^{23,36} Therefore, even greater product selectivity may be obtained through an investigation of the catalytic hydrosilylation by **5.2**, employing a variety of different silanes.

Additionally, it was shown that B(C₆F₅)₃ activates the aluminium complex [Dipp¹Al(Et)(OC(O)H)] towards substrates such as Et₃SiH and HBpin (to which the formate itself is unreactive). In these cases, however, no obvious Al-O/E-H metathesis reactivity was observed and the way in which B(C₆F₅)₃ activates this complex is a subject of ongoing investigation.

5.6 References

- (1) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *Nature Communications*, **2015**, 6, 5933–5948.
- (2) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E. *Angew. Chem. Int. Ed.*, **2011**, 50 (37), 8510–8537.
- (3) Abdalla, J. A. B.; Riddlestone, I. M.; Tirfoin, R.; Aldridge, S. *Angew. Chem. Int. Ed.* **2015**, 54 (17), 5098–5102.
- (4) Zhang, Y.; Riduan, S. N. *Angew. Chem. Int. Ed.* **2011**, 50 (28), 6210–6212.
- (5) Correa, A.; Martín, R. *Angew. Chem. Int. Ed.* **2009**, 48 (34), 6201–6204.
- (6) Bontemps, S. *Coord. Chem. Rev.* **2016**, 308 (2), 117–130.
- (7) Fernández-Alvarez, F. J.; Aitani, A. M.; Oro, L. A. *Catal. Sci. Technol.* **2014**, 4 (3), 611–624.
- (8) Mitton, S. J.; Turculet, L. *Chem. Eur. J.* **2012**, 18 (48), 15258–15262.
- (9) Rios, P.; Diez, J.; Lopez-Serrano, J.; Rodriguez, A.; Conejero, S. *Chem. Eur. J.* **2016**, 22 (47), 16791–16795.
- (10) Huckaba, A. J.; Hollis, T. K.; Reilly, S. W. *Organometallics* **2013**, 32 (21), 6248–6256.
- (11) Morris, D. S.; Weetman, C.; Wennmacher, J. T. C.; Cokoja, M.; Drees, M.; Kühn, F. E.; Love, J. B. *Catal. Sci. Technol.* **2017**, 7 (13), 2838–2845.
- (12) Jiang, Y.; Blacque, O.; Fox, T.; Berke, H. *J. Am. Chem. Soc.* **2013**, 135 (20), 7751–7760.
- (13) Metsänen, T. T.; Oestreich, M. *Organometallics* **2015**, 34 (3), 543–546.
- (14) Deglmann, P.; Ember, E.; Hofmann, P.; Pitter, S.; Walter, O. *Chem. Eur. J.* **2007**, 13 (10), 2864–2879.
- (15) Jansen, A.; Pitter, S. *J. Mol. Catal. A Chem.* **2004**, 217 (1–2), 41–45.
- (16) Jansen, A.; Görls, H.; Pitter, S. *Organometallics* **2000**, 19 (2), 135–138.
- (17) Koinuma, H.; Kawakami, F.; Kato, H.; Hirai, H. *J. Chem. Soc. Chem. Commun.* **1981**, (1), 213–214.
- (18) Julián, A.; Jaseer, E. A.; Garcés, K.; Fernández-Alvarez, F. J.; García-Orduña, P.; Lahoz, F. J.; Oro, L. A. *Catal. Sci. Technol.* **2016**, 6 (12), 4410–4417.
- (19) Park, S.; Bézier, D.; Brookhart, M. *J. Am. Chem. Soc.* **2012**, 134 (28), 11404–11407.
- (20) Eisenschmid, T. C.; Eisenberg, R. *Organometallics* **1989**, 8 (7), 1822–1824.
- (21) Lalrempuia, R.; Iglesias, M.; Polo, V.; Sanz Miguel, P. J.; Fernández-Alvarez, F. J.; Pérez-Torrente, J. J.; Oro, L. A. *Angew. Chem. Int. Ed.* **2012**, 51 (51), 12824–12827.
- (22) Scheuermann, M. L.; Semproni, S. P.; Pappas, I.; Chirik, P. J. *Inorg. Chem.* **2014**, 53 (18), 9463–9465.
- (23) Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2006**, 128 (38), 12362–12363.
- (24) Zhang, L.; Cheng, J.; Hou, Z. *Chem. Commun.* **2013**, 49 (42), 4782–4784.
- (25) Motokura, K.; Kashiwame, D.; Miyaji, A.; Baba, T. *Org. Lett.* **2012**, 14 (10), 2642–2645.
- (26) Motokura, K.; Kashiwame, D.; Takahashi, N.; Miyaji, A.; Baba, T. *Chem. Eur. J.* **2013**, 19 (30), 10030–10037.
- (27) Tani, Y.; Kuga, K.; Fujihara, T.; Terao, J.; Tsuji, Y. *Chem. Commun.* **2015**, 51 (65), 13020–13023.
- (28) Rios, P.; Curado, N.; Lopez-Serrano, J.; Rodriguez, A. *Chem. Commun.* **2016**, 52 (10), 2114–2117.
- (29) González-Sebastián, L.; Flores-Alamo, M.; García, J. J. *Organometallics* **2013**, 32 (23), 7186–7194.
- (30) Berkefeld, A.; Piers, W. E.; Parvez, M.; Castro, L.; Maron, L.; Eisenstein, O. *Chem. Sci.* **2013**, 4 (5), 2152–2162.
- (31) Leblanc, F. A.; Piers, W. E.; Parvez, M. *Angew. Chem. Int. Ed.* **2014**, 53 (3), 789–792.
- (32) Rit, A.; Zanardi, A.; Spaniol, T. P.; Maron, L.; Okuda, J. *Angew. Chem. Int. Ed.* **2014**, 53 (48), 13273–13277.
- (33) Sattler, W.; Parkin, G. *J. Am. Chem. Soc.* **2012**, 134 (42), 17462–17465.
- (34) Specklin, D.; Fliedel, C.; Gurlaouen, C.; Bruyere, J. C.; Avilés, T.; Boudon, C.; Ruhlmann, L.; Dagorne, S. *Chem. Eur. J.* **2017**, 23 (23), 5509–5519.
- (35) Deshmukh, M. M.; Sakaki, S. *Inorg. Chem.* **2014**, 53 (16), 8485–8493.
- (36) Rauch, M.; Parkin, G. *J. Am. Chem. Soc.* **2017**, 139 (50), 18162–18165.
- (37) Chen, J.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2016**, 138 (16), 5321–5333.
- (38) Khandelwal, M.; Wehmschulte, R. *J. Angew. Chem. Int. Ed.* **2012**, 51 (29), 7323–7326.
- (39) Saleh, M.; Powell, D. R.; Wehmschulte, R. *J. Organometallics* **2017**, 36 (24), 4810–4815.
- (40) Mukherjee, D.; Sauer, D. F.; Zanardi, A.; Okuda, J. *Chem. Eur. J.* **2016**, 22 (23), 7730–7733.
- (41) Schäfer, A.; Saak, W.; Haase, D.; Müller, T. *Angew. Chemie Int. Ed.* **2012**, 51 (12), 2981–2984.
- (42) Berkefeld, A.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2010**, 132 (31), 10660–10661.
- (43) Jiang, Y.; Blacque, O.; Fox, T.; Berke, H. *J. Am. Chem. Soc.* **2013**, 135 (20), 7751–7760.
- (44) Del Rio, N.; Lopez-Reyes, M.; Baceiredo, A.; Saffon-Merceron, N.; Lutters, D.; Müller, T.; Kato, T.

- Angew. Chem. Int. Ed.* **2017**, 56 (5), 1365–1370.
- (45) Courtemanche, M.-A.; Pulis, A. P.; Rochette, É.; Légaré, M.-A.; Stephan, D. W.; Fontaine, F.-G. *Chem. Commun.* **2015**, 51 (48), 9797–9800.
- (46) Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem. Int. Ed.* **2009**, 48 (18), 3322–3325.
- (47) Janes, T.; Yang, Y.; Song, D. *Chem. Commun.* **2017**, 53 (83), 11390–11398.
- (48) Frogneux, X.; Blondiaux, E.; Thuéry, P.; Cantat, T. *ACS Catal.* **2015**, 5 (7), 3983–3987.
- (49) Fang, C.; Lu, C.; Liu, M.; Zhu, Y.; Fu, Y.; Lin, B.-L. *ACS Catal.* **2016**, 6 (11), 7876–7881.
- (50) Chong, C. C.; Kinjo, R. *Angew. Chem. Int. Ed.* **2015**, 54 (41), 12116–12120.
- (51) Lu, Z.; Hausmann, H.; Becker, S.; Wegner, H. A. *J. Am. Chem. Soc.* **2015**, 137 (16), 5332–5335.
- (52) Piers, W. E. *Advances in Organometallic Chemistry*. **2004**, 52, 1–76.
- (53) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, 65 (10), 3090–3098.
- (54) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, 118 (39), 9440–9441.
- (55) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J. X.; Yamamoto, Y. *J. Org. Chem.* **2000**, 65 (19), 6179–6186.
- (56) Houghton, A. Y.; Hurmalainen, J.; Mansikkamäki, A.; Piers, W. E.; Tuononen, H. M. *Nat. Chem.* **2014**, 6 (11), 983–988.
- (57) Hog, D. T.; Oestreich, M. *Eur. J. Org. Chem.* **2009**, (29), 5047–5056.
- (58) Oestreich, M.; Hermeke, J.; Mohr, J. *Chem. Soc. Rev.* **2015**, 44 (8), 2202–2220.
- (59) Rendler, S.; Oestreich, M. *Angew. Chem. Int. Ed.* **2008**, 47 (32), 5997–6000.
- (60) von Wolff, N.; Lefèvre, G.; Berthet, J.-C.; Thuéry, P.; Cantat, T. *ACS Catal.* **2016**, 6 (7), 4526–4535.
- (61) Berkefeld, A.; Piers, W. E.; Parvez, M. J. *J. Am. Chem. Soc.* **2010**, 132 (31), 10660–10661.
- (62) Lawrence, N. J.; Drew, M. D.; Bushell, S. M. *J. Chem. Soc. Perkin Trans.* **1999**, (23), 3381–3391.
- (63) Fernandez-Alvarez, F. J.; Iglesias, M.; Oro, L. A.; Polo, V. *ChemCatChem*. **2013**, 5 (12), 3481–3494.
- (64) Liu, M.; Qin, T.; Zhang, Q.; Fang, C.; Fu, Y.; Lin, B. L. *Sci. China Chem.* **2015**, 58 (10), 1524–1531.
- (65) Shintani, R.; Nozaki, K. *Organometallics* **2013**, 32 (8), 2459–2462.
- (66) Suh, H.-W.; Guard, L. M.; Hazari, N. *Chem. Sci.* **2014**, 5 (10), 3859–3872.
- (67) Mukherjee, D.; Osseili, H.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2016**, 138 (34), 10790–10793.
- (68) Jin, G.; Wernicke, C. G.; Escudie, Y.; Sabo-Etienne, S.; Bontemps, S. *J. Am. Chem. Soc.* **2015**, 137 (30), 9563–9566.
- (69) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2014**, 136 (11), 4419–4425.
- (70) Bontemps, S.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2013**, 52 (39), 10253–10255.
- (71) Murphy, L. J.; Hollenhorst, H.; McDonald, R.; Ferguson, M.; Lumsden, M. D.; Turculet, L. *Organometallics* **2017**, 36 (19), 3709–3720.
- (72) Ríos, P.; Rodríguez, A.; López-Serrano, J. *ACS Catal.* **2016**, 6 (9), 5715–5723.
- (73) Wehmschulte, R. J.; Saleh, M.; Powell, D. R. *Organometallics* **2013**, 32 (22), 6812–6819.
- (74) Nikonov, G. I. *ACS Catal.* **2017**, 7 (10), 7257–7266.
- (75) Jakobsson, K.; Chu, T.; Nikonov, G. I. *ACS Catal.* **2016**, 6 (11), 7350–7356.
- (76) Koller, J.; Bergman, R. G. *Organometallics* **2012**, 31 (7), 2530–2533.
- (77) Revunova, K.; Nikonov, G. I. *Dalton Trans.* **2015**, 44 (3), 840–866.
- (78) Downs, A. J.; Himmel, H. J. in *The Group 13 Metals Aluminium, Gallium, Indium and Thallium; Chemical Patterns and Peculiarities* (Eds.: S. Aldridge, A. J. Downs) Wiley, Chichester, UK.
- (79) Aldridge, S.; Downs, A. J. *Chem. Rev.* **2001**, 101 (11), 3305–3365.
- (80) Allen, L. C. *J. Am. Chem. Soc.* **1989**, 111 (25), 9003–9014.
- (81) Mukherjee, D.; Ellern, A.; Sadow, A. D. *Chem. Sci.* **2014**, 5 (3), 959–964.
- (82) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, 17 (7), 1369–1377.
- (83) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem. Int. Ed.* **2009**, 48 (52), 9839–9843.
- (84) Bavarian, N.; Baird, M. C. *Dalton Trans.* **2004**, (24), 4089–4091.
- (85) Atwood, D. A. *Coord. Chem. Rev.* **1998**, 176 (1), 407–430.
- (86) Dagorne, S.; Atwood, D. A. *Chem. Rev.* **2008**, 108 (10), 4037–4071.
- (87) Wehmschulte, R. J.; Steele, J. M.; Young, J. D.; Khan, M. A. *J. Am. Chem. Soc.* **2003**, 125 (6), 1470–1471.
- (88) Young, J. D.; Khan, M. A.; Powell, D. R.; Wehmschulte, R. J. *Eur. J. Inorg. Chem.* **2007**, (12), 1671–1681.
- (89) Wehmschulte, R. J.; Steele, J. M.; Khan, M. A. *Organometallics* **2003**, 22 (23), 4678–4684.
- (90) Atwood, D. A.; Jones, R. A.; Cowley, A. H.; Bott, S. G.; Atwood, J. L. *J. Organomet. Chem.* **1992**, 425 (1–2), C1–C3.
- (91) Iravani, E.; Neumüller, B. Z. *Anorg. Allg. Chem.* **2003**, 629 (14), 2509–2515.
- (92) Clyburne, J. a. C.; Culp, R. D.; Kamepalli, S.; Cowley, A. H.; Decken, A. *Inorg. Chem.* **1996**, 35 (23),

- 6651–6655.
- (93) Cowley, A. H.; Gabbai, F. P.; Atwood, D. A.; Carrano, C. J.; Mokry, L. M.; Bond, M. R. *J. Am. Chem. Soc.* **1994**, *116* (4), 1559–1560.
- (94) Schnee, G.; Bolley, A.; Gourlaouen, C.; Welter, R.; Dagorne, S. *J. Organomet. Chem.* **2016**, *820*, 8–13.
- (95) Tang, S.; Monot, J.; El-Hellani, A.; Michelet, B.; Guillot, R.; Bour, C.; Gandon, V. *Chem. Eur. J.* **2012**, *18* (33), 10239–10243.
- (96) Dąbrowska, A. M.; Hurko, A.; Dranka, M.; Varga, V.; Urbańczyk, M.; Horeglad, P. *J. Organomet. Chem.* **2017**, *840*, 63–69.
- (97) Korolev, A. V.; Delpech, F.; Dagorne, S.; Guzei, I. A.; Jordan, R. F. *Organometallics* **2001**, *20* (16), 3367–3369.
- (98) Masuda, J. D.; Walsh, D. M.; Wei, P.; Stephan, D. W. *Organometallics* **2004**, *23* (8), 1819–1824.
- (99) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121* (37), 8673–8674.
- (100) Abdalla, J. A. B.; Tirfoin, R. C.; Niu, H.; Aldridge, S. *Chem. Commun.* **2017**, *53* (44), 5981–5984.
- (101) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120* (36), 9384–9385.
- (102) Anker, M. D.; Arrowsmith, M.; Bellham, P.; Hill, M. S.; Kociok-Köhn, G.; Liptrot, D. J.; Mahon, M. F.; Weetman, C. *Chem. Sci.* **2014**, *5* (7), 2826–2830.
- (103) Berkefeld, A.; Piers, W. E.; Parvez, M.; Castro, L.; Maron, L.; Eisenstein, O. *J. Am. Chem. Soc.* **2012**, *134* (26), 10843–10851.
- (104) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129* (7), 1880–1881.
- (105) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2* (7), 3921–3923.
- (106) Adamczyk-Woźniak, A.; Jakubczyk, M.; Sporzyński, A.; Zukowska, G. *Inorg. Chem. Commun.* **2011**, *14* (11), 1753–1755.
- (107) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2012**, *51* (7), 1671–1674.
- (108) Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. *Chem. Commun.* **2016**, *52* (89), 13155–13158.
- (109) Heiden, Z. M.; Lathem, A. P. *Organometallics* **2015**, *34* (10), 1818–1827.
- (110) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem. Int. Ed.* **2009**, *48* (52), 9839–9843.
- (111) Stennett, T. E.; Pahl, J.; Zijlstra, H. S.; Seidel, F. W.; Harder, S. *Organometallics* **2016**, *35* (2), 207–217.
- (112) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, (21), 2832–2838.
- (113) Qian, B.; Ward, D. L.; Smith, M. R. *Organometallics* **1998**, *17* (14), 3070–3076.

6. Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms

6.1 Introduction

The reduction of compounds featuring unsaturated functionalities such as C=X bonds (X = N, O, S) are some of the most significant conversions in organic synthesis. In particular, the reduction of aldehydes and ketones to alcohols is one of the most widely used chemical transformations.¹⁻³ Traditionally, the reduction of carbonyl compounds is achieved by the employment of metal hydrides or transition metal-catalysed hydrogenation.^{4,5} The catalytic hydroboration of carbonyl compounds has, however, gained interest due to the mild reaction conditions required, and the avoidance of highly flammable dihydrogen gas. Typically, hydroboration involves the equimolar addition of a borane reagent to a carbonyl compound to form a borate ester, which in turn can readily be hydrolysed to an alcohol. Until recently, the scope of catalysts employed in the hydroboration of carbonyl compounds was limited to complexes based on transition metals such as Ru,⁶ Mo,⁷ and Ti.⁸⁻¹³

A range of main group metal hydride catalysts have been developed which display impressive performance in the reduction of carbonyl compounds, based on alkaline earth metals, or on Group 13, Group 14 and Group 15 elements (Figure 6.1).^{12,14-24}

Typically the catalytic species contains a reactive E-H bond. Thus, for example, the magnesium alkyl $[\text{Dipp}\mathbf{1}]\text{Mg}(^n\text{Bu})$ has been employed as a precatalyst for carbonyl hydroboration, with the active catalyst being shown to be the dimeric hydride complex, $\{[\text{Dipp}\mathbf{1}]\text{Mg}(\mu\text{-H})\}_2$.¹⁴ In most cases, these metal hydrides effect the hydroboration of a wide range of aldehydes and ketones at room temperature, generating the borate ester product in >90% yield.

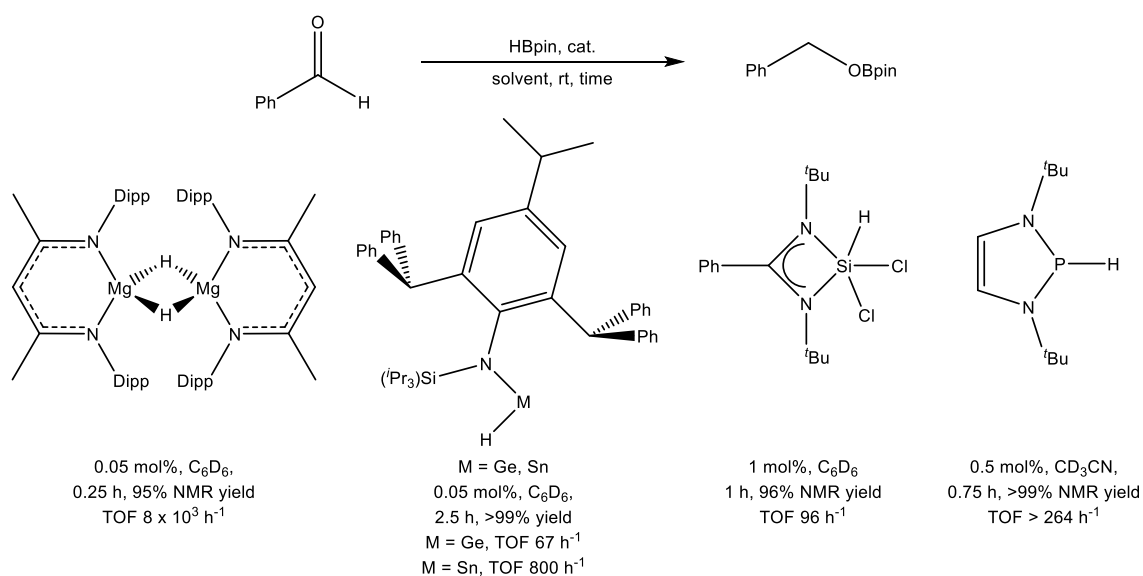


Figure 6.1: Examples of single site main group hydride catalysts for this process and the conditions required for each to bring about the hydroboration of benzaldehyde.^{14,18,20,22,24}

In 2014, the use of low valent Ge(II) and Sn(II) hydrides as catalysts for the hydroboration of a wide range of aldehyde and ketone substrates was reported (Figure 6.1).²² The Sn(II) hydride catalyst effects the hydroboration of aldehydes with TOF values between 400 and $>13\,300 \text{ h}^{-1}$ at 0.05 mol% catalyst loading. The hydroboration of ketones requires higher catalyst loadings (0.5 – 5 mol%) to effect moderate TOF values ($0.47 - 1330 \text{ h}^{-1}$). These systems are typically more efficient catalysts for this process than previously reported transition metal systems employing HBpin as the reductant.^{14,20}

The mechanism by which these catalytic processes proceed has been investigated in some depth.¹² It is generally considered that hydrometallation of the carbonyl functionality is the initial step. In certain cases this has been validated experimentally, e.g. by the isolation of the intermediate metal alkoxide complexes from the reaction of the group 14 hydrides LMH ($L = N(\text{Ar})(\text{Si}^i\text{Pr}_3)$; $\text{Ar} = \text{C}_6\text{H}_2\{\text{C}(\text{H})\text{Ph}_2\}_2$ - ^iPr -2,6,4; $M = \text{Ge}, \text{Sn}$) with bulky carbonyl substrates, ($^i\text{Pr}_2\text{C}(\text{O})$ or ($p\text{-MeOPh})\text{C}(\text{O})\text{H}$)).²² The corresponding hydrides can easily be regenerated from these metal alkoxide complexes by a M-O/B-H σ -bond metathesis, yielding the pinacolborate ester.²²

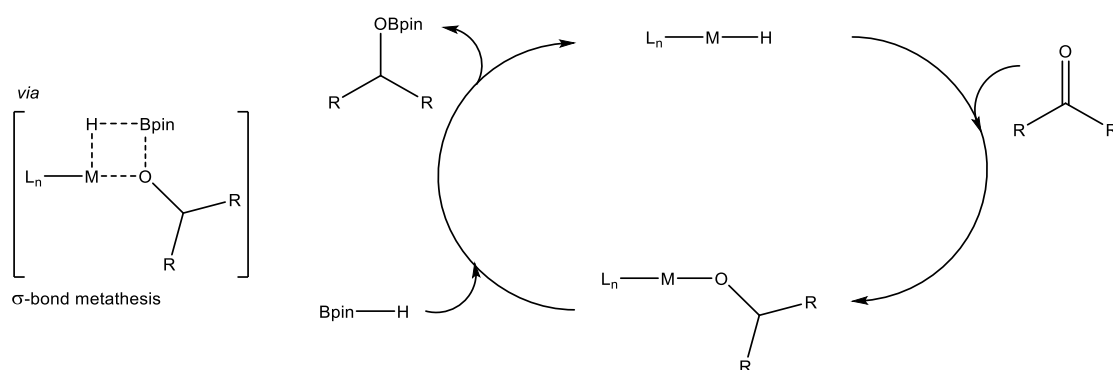


Figure 6.2: The general mechanism proposed for this reactivity.

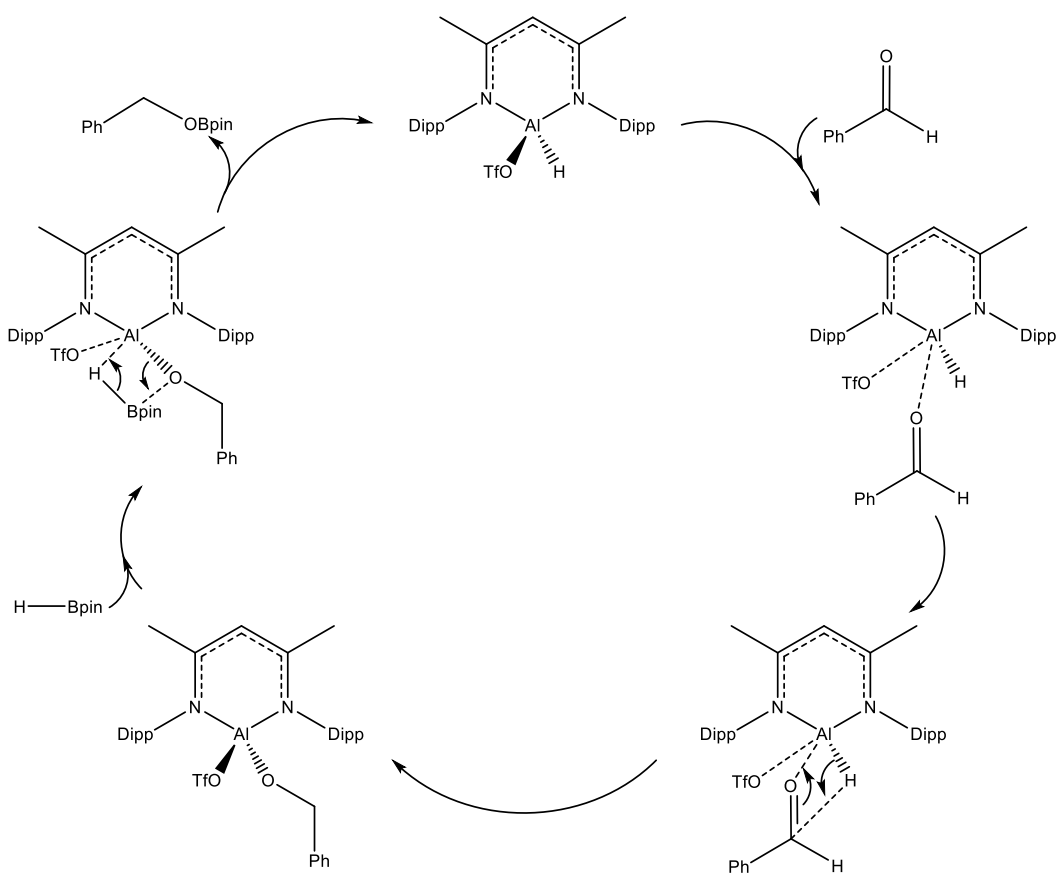
Moreover, a first-order dependence of the reaction in both HBpin and catalyst, and a zero-order dependence in the ketone were confirmed for this system.²² This suggests that the metal alkoxide intermediates are resting states of the catalytic cycles and that the rate-determining step is the σ -bond metathesis step.

Existing literature describing the use of aluminium hydrides to reduce a range of unsaturated substrates in stoichiometric fashion (including aldehydes and ketones) is diverse.²⁵ However, the use of aluminium hydride species as *catalysts* for the hydroboration of carbonyl functionalities has only recently been reported.²⁶

In 2015 a Nacnac-ligated aluminum monohydride, $[\text{Dipp}^1]\text{Al}(\text{OTf})\text{H}$ (**3.4^{OTf}**), was reported to effect the catalytic hydroboration of a range of aldehydes and ketones at room

temperature, employing low catalyst loadings (1 mol%) and HBpin as the reductant.²⁶

For this system, the electron-withdrawing triflate aluminium-bound substituent is proposed to enhance the catalytic activity by opening the coordination site for substrate binding and activation. The triflate substituent confers a higher positive charge to the aluminium centre, enhancing the Lewis acidity of the aluminium centre, whilst retaining the hydridic character of the Al-H bond.²⁶



Scheme 6.1: The proposed catalytic cycle for the reduction of benzaldehyde, catalysed by

3.4OTf.26

It was proposed that the catalytic cycle proceeds *via* initial insertion of the aldehyde/ketone into the Al-H bond, yielding an aluminium alkoxide complex. This intermediate then reacts with HBpin *via* Al-O/B-H metathesis to form the borate ester product and regenerate the metal hydride. This mechanism was backed up by quantum

mechanical calculations which imply that the overall rate-determining step of the hydroboration reaction is the formation of the aluminium alkoxide complex by insertion of the aldehyde into the Al-H bond *via* a four-membered transition state ($\Delta G^\ddagger = 99.6$ kJ mol⁻¹). **3.4^{OTf}** catalyses the hydroboration of a wide range of aliphatic and aromatic aldehydes, with high yields (99%), with a maximum TOF of 100 h⁻¹. The borate esters so generated can be hydrolysed to form the corresponding alcohols in good yields (86 – 96%).²⁷

The use of Nacnac-ligated aluminium complexes in the catalytic hydroboration of aldehydes and ketones has recently been explored in more depth. Very recently, it was shown that, under stoichiometric conditions, benzaldehyde will insert into the Al-H bonds of [Dipp¹]AlH₂ (**3.4^H**), to form [Dipp¹]Al(H)(OCH₂Ph) and [Dipp¹]Al(OCH₂Ph)₂.²⁸ However, in contrast to the reported behaviour of [Dipp¹]Al(OTf)(OCH₂Ph), the reaction of [Dipp¹]Al(H)(OCH₂Ph) and HBpin under stoichiometric reaction conditions, produces a mixture of products with no evident formation of PhCH₂OBpin or regeneration of **3.4^H**. Whilst this system was not investigated under catalytic conditions, this study may highlight the importance of the triflate substituent when complexes of the form [Dipp¹]Al(R)H are employed as catalysts.

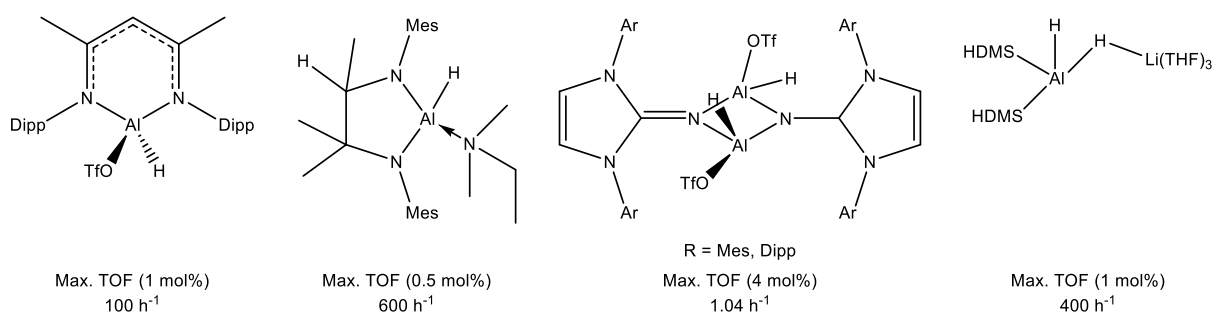


Figure 6.3: Examples of aluminium hydride catalysts for the hydroboration of aldehydes and ketones.

Following the initial report of this reactivity by Yang *et al.*, a number of catalytic systems based on both neutral aluminium hydrides and anionic aluminates have since been reported to effect this transformation (Figure 6.3).^{27,29-32} Employing these systems, the catalytic hydroboration of a wide range of aldehydes (including aromatic systems, ArC(O)H , featuring either electron-donating or -withdrawing substituents), was demonstrated to be possible under ambient conditions, at low catalyst loadings. These systems also effect the catalytic hydroboration of ketones, but at higher catalyst loadings and employing either longer reaction times or elevated temperatures.^{26,27} This lower reactivity is thought to be due to the reduced electrophilicity and more sterically encumbered nature of the carbonyl carbon which disfavours both insertion and σ -bond metathesis steps. Furthermore, it was demonstrated that the N-donor-stabilised aluminum monohydride $\text{LAlH(NMe}_2\text{Et)}$ ($\text{L} = [(\text{Mes})\text{NC(Me)}]_2(\text{Me})(\text{H})$) catalyses both inter- and intramolecular chemoselective hydroboration of aldehydes over ketones.²⁷ The reaction of equimolar amounts of benzaldehyde, acetophenone, and HBpin with 1 mol% of this catalyst at room temperature produced the borate ester derived from the hydroboration of benzaldehyde with 98% conversion. In addition, the chemoselectivity in the hydroboration step was further emphasised by the corresponding reaction with 4-(2-oxo-2-phenylethoxy)-benzaldehyde, which features both a ketone and an aldehyde functionality. In this case, selective hydroboration of the aldehyde was observed with 98% conversion, and the corresponding alcohol could be isolated in 85% yield after hydrolysis.^{25,27}

All of these catalytic systems are thought to operate by the mechanism proposed by Yang *et al.*, based on a sequence of insertion and Al-O/B-H metathesis steps.²⁶ In cases other than the original report, however, minimal experimental or computational

evidence was given to supported this.^{27,29,30} A proposed intermediate in the hydroboration of benzaldehyde catalysed by the lithium diamidodihydridoaluminate, $(\text{HMDS})_2\text{AlH}(\mu\text{-H})\text{Li}(\text{THF})_3$ ($\text{HMDS} = (\text{Me}_3\text{Si})_2\text{N}^-$), was isolated *via* the addition of two equivalents of benzaldehyde to the hydride and characterised crystallographically.³⁰ The use of this species, $(\text{HMDS})_2\text{Al}(\mu\text{-OCH}_2\text{Ph})_2\text{Li}(\text{THF})_2$, as the catalyst for the hydroboration of benzaldehyde using HBpin yields the same borate ester product. This suggests that the hydrometallated product has the potential to function as an intermediate within this catalytic cycle, although the exact details have not been reported.³⁰

Other Nacnac-ligated aluminium complexes have been reported to catalyse the hydroboration of aldehydes and ketones. Of particular note are $[\text{Mes}\mathbf{1}]\text{Al}(\text{SCH}_2\text{Ph})_2$ and $[\text{Ar}\mathbf{1}]\text{AlCl}_2$ ($\text{Ar} = 2\text{-}^i\text{Pr-C}_6\text{H}_4$) *i.e.* catalysts which *do not* bear hydride functionalities.³³ These complexes catalyse these processes with comparable activity to that of $\mathbf{3.4}^{\text{OTf}}$ (1 mol%, 25°C, max TOF = 100 h⁻¹). The mechanism by which these catalysts effect this process is not clear.

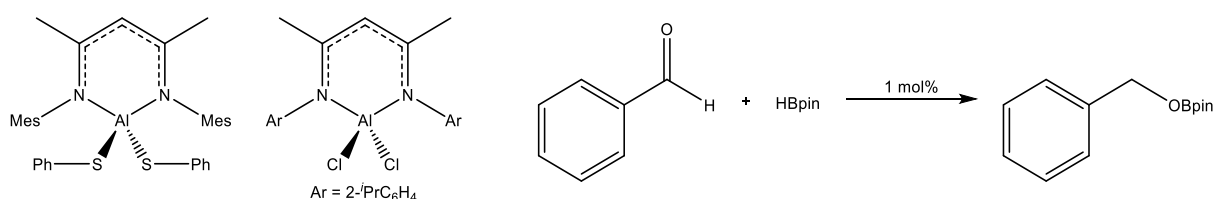


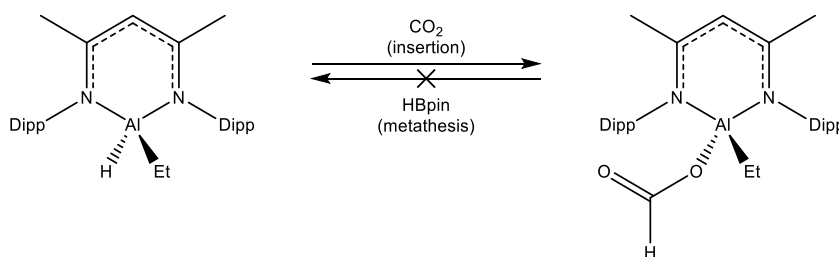
Figure 6.4: Examples of aluminium catalysts which *do not* bear hydride functionalities that bring about the catalytic hydroboration of carbonyl functionalities.³³

Despite the demonstration of the ability of gallium hydrides to effect the catalytic reduction of CO_2 , to the best of our knowledge, there are very few reports of the use of well-defined gallium hydrides as catalysts for the hydroboration of other carbonyl functionalities.³⁴ The enantioselective hydroboration of ketones catalysed by chiral

gallium complexes generated *in situ* has, however, been examined.²¹ The catalyst in this case is generated *in situ* by combining LiGaH_4 with the chiral protio-ligands, 1,1'-(bi-2-naphthol), 2-hydroxy-2'-mercapto-1,1'-binaphthyl (MTBH_2), or 2,2'-dimercapto-1,1'-binaphthyl; HBcat is employed as the reductant. Mechanistic studies suggest that the resting state of the catalyst is the dimeric (non-hydride containing) species $[\text{Li}_2(\text{MTB})][\text{Ga}_2(\text{MTB})_3]$, although the nature of the active catalyst is not clear.²¹

6.2 Project aims

The work outlined in Chapter 4 demonstrates that a range of Nacnac-ligated gallium hydride complexes, $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{R})\text{H}$, are competent in the catalytic reduction of CO_2 , albeit with low turnover frequencies.³⁴ Mechanistically, the viability of both the CO_2 insertion and Ga-O/B-H metathesis steps key to catalytic turnover (Scheme 6.3) could be demonstrated *via* independent stoichiometric reactions, enabled by the isolation of the formate intermediates $[\text{Dipp}\mathbf{1}]\text{Ga}(\text{R})(\text{OC}(\text{O})\text{H})$ ($\text{R} = {}^t\text{Bu}, {}^t\text{Am}, \text{Ad}, \text{Ph}, \text{Me}, \text{H}$).

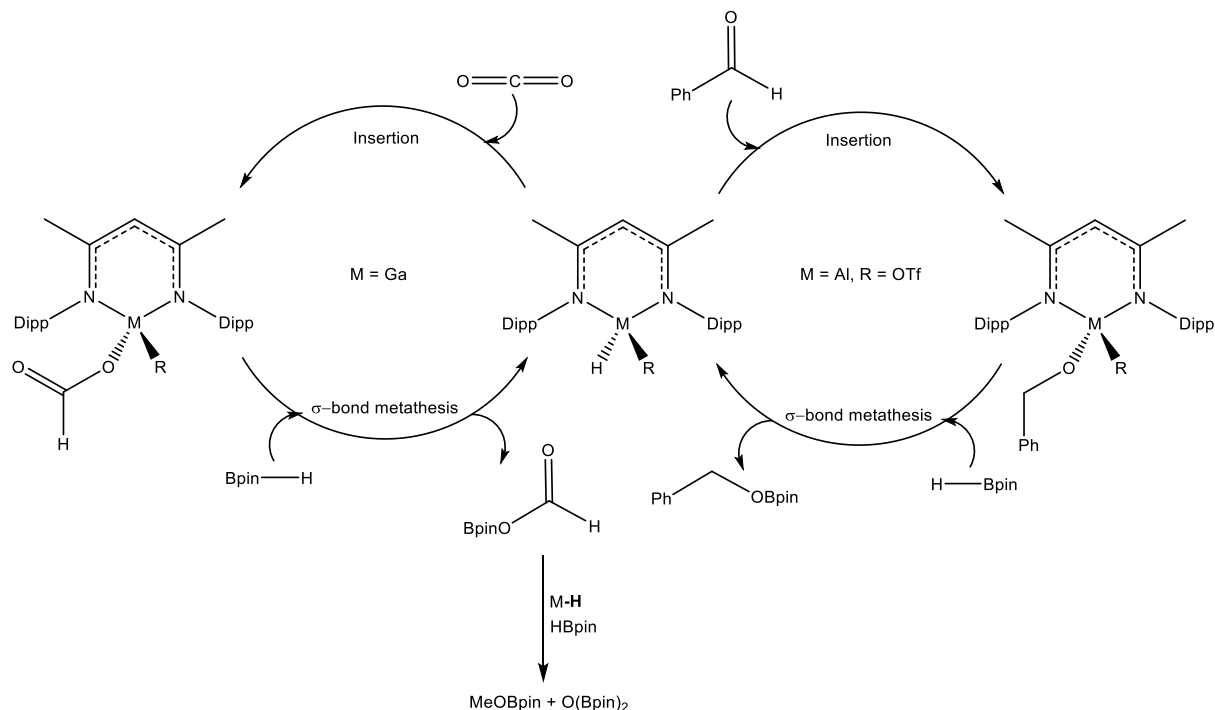


Scheme 6.2: CO_2 insertion into the Al-H bond of $[\text{Dipp}\mathbf{1}]\text{Al}(\text{Et})\text{H}$ to give $[\text{Dipp}\mathbf{1}]\text{Al}(\text{Et})(\text{OC}(\text{O})\text{H})$, and subsequent lack of reactivity of this formate complex towards HBpin .

The relative cost/terrestrial abundance of gallium and aluminium led us to consider related processes based on the lighter group 13 metal (Chapter 3). However, attempts to extend the scope of this chemistry to aluminium-based catalysts were unsuccessful. While systems such as $[\text{Dipp}\mathbf{1}]\text{Al}(\text{R})\text{H}$ (**3.4^R**; $\text{R} = \text{H}, \text{Me}, \text{Et}$) are amenable to rapid CO_2

Chapter VI: Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms

insertion into the Al-H bonds, the resulting formate derivatives are resolutely unreactive to Al-O/B-H metathesis, and catalytic turnover cannot be achieved (Scheme 6.2).³⁵



Scheme 6.3: Reported mechanisms for the reduction by HBpin of CO₂ catalysed by [Dipp $\mathbf{1}$]Ga(R)H, and of benzaldehyde catalysed by **3.4**^{OTf}. In both cases turnover is proposed *via* carbonyl insertion and M-O/B-H metathesis steps.

This reactivity contrasts greatly with the reports of the catalytic hydroboration of benzaldehyde (and related aldehydes) by [Dipp $\mathbf{1}$]Al(OTf)H, for which a superficially similar Al-O/B-H metathesis process was reported to be a key step in the catalytic cycle (Scheme 6.3). In this report, it was asserted that the alkoxide intermediate [Dipp $\mathbf{1}$]Al(OTf)(OCH₂Ph), formed by the insertion of PhC(O)H into the Al-H bond of **3.4**^{OTf}, reacts with one equivalent of HBpin at room temperature to regenerate **3.4**^{OTf}, and release the product PhCH₂OBpin.²⁶ The apparent advantages conferred by the triflate substituent in this chemistry prompted us to consider its use in a range of reduction processes.

6.3 Experimental details

Spectroscopic data for {HC(MeCNDipp)₂}Al(OTf)H – [Dipp¹]Al(OTf)H (3.4^{OTf})

The preparation of [Dipp¹]Al(OTf)H followed the method reported by Yang *et al.*²⁶ However, some of the spectroscopic data obtained for 3.4^{OTf} contrast with those reported in the literature and are therefore reported below.

¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 1.05, 1.06, 1.36 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.47 (6H, s, CH₃ of β-diketiminato backbone), 1.51 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 3.12 (4H, sept, 2 overlapping signals, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.48 (1H, br s, Al-H), 4.82 (1H, s, γ-CH), 7.06 – 7.15 (6H, m, aromatic CH). **¹H NMR** (400 MHz, THF-d₈, 298 K): δ_H 1.20 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.29 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.91 (6H, s, CH₃ of β-diketiminato backbone), 3.09 (4H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.00 (1H, br s, Al-H), 5.48 (1H, s, γ-CH), 7.24 – 7.31 (6H, m, aromatic CH). **¹³C{¹H} NMR** (126 MHz, benzene-d₆, 298 K): δ_C 23.4 (CH₃ of β-diketiminato backbone), 25.2 (CH₃ of Dipp ⁱPr, 2 overlapping signals), 28.4, 28.6 (CH of Dipp ⁱPr), 98.7 (γ-CH), 125.5, 128.9, 137.5, 144.9 (*m*-, *p*-, *ipso*-, *o*-ArC of Dipp) 173.5 (NC). **¹⁹F NMR** (376 MHz, THF-d₈, 298 K): δ_F –78.7. **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **IR** (nujol/cm^{–1}): ν_{Al-H} 1905 (s).

Preparation of {HC(MeCNDipp)₂}Al(OTf)(OCH₂Ph) – [Dipp¹]Al(OTf)(OCH₂Ph) (6.1^{OTf})

[Dipp¹]Al(OTf)H (0.50 g, 0.84 mmol) was dissolved in toluene (5 mL) and PhC(O)H (98 μL, 0.967 mmol) added dropwise, with stirring. The reaction mixture was stirred overnight, and volatiles then removed *in vacuo* from the resulting yellow solution to yield a yellow oil. The oil was extracted into *n*-hexane, and volatiles were again removed

in vacuo to yield a yellow powder. The powder was extracted into *n*-hexane, filtered and concentrated to the point of incipient crystallisation. Storage of this solution at -30°C for several days yielded large yellow crystals, which were isolated and dried *in vacuo*. Yield: 0.36 g, 61%. Crystals suitable for X-ray crystallography could be obtained from the storage of a concentrated solution of **6.1**^{OTf} in pentane at -30°C for several days.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} 0.99 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ⁱPr), 1.12 (12H, apparent t, $^3J_{\text{HH}} = 6.8$ Hz, 2 overlapping CH₃ of Dipp ⁱPr), 1.44 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH₃ of Dipp ⁱPr), 1.51 (6H, s, CH₃ of β -diketiminato backbone), 3.24 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 3.28 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 5.00 (1H, s, γ -CH), 5.06 (2H, s, CH₂ of OCH₂Ph), 7.02 – 7.20 (11H, m, aromatic CH of Dipp and OCH₂Ph). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_{C} 23.5 (CH₃ of β -diketiminato backbone), 24.5, 24.6, 24.8, 24.9 (CH₃ of Dipp ⁱPr), 28.5, 28.7 (CH of Dipp ⁱPr), 65.3 (CH₂ of OCH₂Ph), 99.1 (γ -CH), 124.9 (*m*-CH of Dipp, 2 overlapping signals), 125.1 (*o*-ArC of OCH₂Ph), 126.4 (*p*-ArC of OCH₂Ph), 127.4 (*p*-ArC of Dipp), 128.3 (*m*-ArC of OCH₂Ph), 138.3 (*ipso*-ArC of Dipp), 144.3, 144.7 (*o*-ArC of Dipp), 144.2 (*ipso*-ArC of OCH₂Ph), 173.5 (NC). ¹⁹F NMR (376 MHz, benzene-d₆, 298 K): δ_{F} -77.4. ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **EI-MS:** *m/z* calc for C₃₇H₄₈N₂AlF₃O₄S ([M]⁺) 700.3097, meas. 700.3075 (5%), calc for ([M-OCH₂Ph]⁺) 593.2605, meas. 593.2557 (2%). **Elemental microanalysis:** calc. for C₃₇H₄₈N₂AlF₃O₄S: C 63.41% H 6.90% N 4.00% meas. C 63.36% H 6.63% N 4.21%.

Preparation of {HC(MeCNDipp)₂}Al(Et)(OCH₂Ph) – [Dipp¹]Al(Et)(OCH₂Ph) (6.1**^{Et})**

[Dipp¹]Al(Et)H (0.30 g, 0.63 mmol) was dissolved in toluene (10 mL) and benzylalcohol (98 μL , 0.95 mmol) added dropwise at room temperature, leading to the evolution of hydrogen. The reaction mixture was stirred for 3 h, over which time evolution of gas

ceased; volatiles were then removed *in vacuo* to yield a colourless oil. The oil was extracted into *n*-hexane, concentrated until the volume reached *ca.* 0.5 mL, and cooled to -30°C . Storage of the solution at this temperature overnight yielded large single crystals, suitable for X-ray crystallography. Yield: 0.31 g, 85%.

Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298 K): δ_{H} -0.08 (2H, q, $^3J_{\text{HH}} = 8.2$ Hz, $\text{CH}_3\text{CH}_2\text{Al}$), 0.96 (3H, t, $^3J_{\text{HH}} = 8.2$ Hz, $\text{CH}_3\text{CH}_2\text{Al}$), 1.09 , 1.10 , 1.19 , 1.30 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH_3 of Dipp $i\text{Pr}$), 1.60 (6H, s, CH_3 of β -diketiminato backbone), 3.20 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp $i\text{Pr}$), 3.54 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp $i\text{Pr}$), 5.02 (1H, s, $\gamma\text{-CH}$), 5.13 (2H, s, CH_2 of OCH_2Ph), $7.07 - 7.16$ (7H, m, aromatic CH of Dipp and $p\text{-CH}$ of OCH_2Ph), 7.27 (2H, apparent t, $^3J_{\text{HH}} = 7.5$ Hz, $m\text{-CH}$ of OCH_2Ph), 7.58 (2H, dm, $^3J_{\text{HH}} = 7.8$ Hz, $o\text{-CH}$ of OCH_2Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene- d_6 , 298 K): δ_{C} -3.4 (br, $\text{CH}_3\text{CH}_2\text{Al}$), 9.4 ($\text{CH}_3\text{CH}_2\text{Al}$), 23.3 (CH_3 of β -diketiminato backbone), 24.4 , 24.6 , 24.8 , 25.6 (CH_3 of Dipp $i\text{Pr}$), 28.0 , 28.9 (CH of Dipp $i\text{Pr}$), 65.5 (CH_2 of OCH_2Ph), 98.1 ($\gamma\text{-CH}$), 124.1 , 124.9 ($m\text{-ArC}$ of Dipp), 125.7 ($o\text{-ArC}$ of OCH_2Ph), 126.1 ($p\text{-ArC}$ of OCH_2Ph), 127.4 ($p\text{-ArC}$ of Dipp), 128.2 ($m\text{-ArC}$ of OCH_2Ph), 141.0 ($ipso\text{-ArC}$ of Dipp), 143.4 , 145.4 ($o\text{-ArC}$ of Dipp), 146.3 ($ipso\text{-ArC}$ of OCH_2Ph), 170.0 (NC). ^{27}Al NMR (104 MHz, benzene- d_6 , 298 K): δ_{Al} 111 . **EI-MS:** m/z calc for $\text{C}_{36}\text{H}_{48}\text{N}_2\text{AlO}$ ($[\text{M}-\text{CH}_2\text{CH}_3]^+$) 551.3582 , meas. 551.3589 (50%).

Preparation of $\{\text{HC}(\text{MeCNDipp})_2\}\text{Al}(\text{Cl})(\text{OCH}_2\text{Ph}) - [\text{Dipp}^1]\text{Al}(\text{Cl})(\text{OCH}_2\text{Ph})$ (6.1^{Cl})

To a solution of $[\text{Dipp}^1]\text{Al}(\text{Cl})\text{H}$ (0.375 g, 0.78 mmol) in toluene (10 mL) was added dropwise benzaldehyde (88 μL , 0.86 mmol) at room temperature. The resulting solution was stirred overnight at room temperature and volatiles then removed *in vacuo*, yielding an orange oil. This oil was extracted into minimal toluene, filtered and concentrated to the point of incipient crystallisation. Storage of this solution at -30°C for one week yielded colourless crystals suitable for X-ray diffraction. Yield: 0.35 g, 77%.

Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298 K): δ_{H} 1.06, 1.17, 1.29, 1.44 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH_3 of Dipp $i\text{Pr}$), 1.54 (6H, s, CH_3 of β -diketiminato backbone), 3.38 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp $i\text{Pr}$), 3.55 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp $i\text{Pr}$), 4.64 (2H, s, CH_2 of OCH_2Ph), 4.89 (1H, s, γ -CH), 6.71 (2H, m, aromatic CH of OCH_2Ph), 6.97 – 7.22 (9H, m, aromatic CH of Dipp and OCH_2Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene- d_6 , 298 K): δ_{C} 23.4 (CH_3 of β -diketiminato backbone), 24.3, 24.9, 25.0, 26.4 (CH_3 of Dipp $i\text{Pr}$), 28.3, 29.1 (CH of Dipp $i\text{Pr}$), 65.4 (CH_2 of OCH_2Ph), 98.0 (γ -CH), 124.5, 125.2 (m -ArC of Dipp), 125.9 (p -ArC of OCH_2Ph), 126.1 (o -ArC of OCH_2Ph), 127.9 (p -ArC of Dipp), 128.0 (m -ArC of OCH_2Ph), 139.0 ($ipso$ -ArC of Dipp), 144.5 ($ipso$ -ArC of OCH_2Ph), 144.6, 145.4 (o -ArC of Dipp), 171.6 (NC). ^{27}Al NMR (104 MHz, benzene- d_6 , 298 K): δ_{Al} 101. **EI-MS:** m/z calc for $\text{C}_{36}\text{H}_{48}\text{AlClN}_2\text{O}$ ($[\text{M}]^+$) 586.3265, meas. 586.3277 (100%).

Preparation of $\{\text{HC}(\text{MeCNDipp})_2\}\text{Al}(\text{Me})(\text{OCH}_2\text{Ph}) - [\text{Dipp1}]\text{Al}(\text{Me})(\text{OCH}_2\text{Ph})$ (6.1^{Me})

To a solution of $[\text{Dipp1}]\text{Al}(\text{Me})\text{H}$ (0.015 g, 0.033 mmol) in benzene- d_6 was added benzylalcohol (5 μL , 0.048 mmol) and H_2 gas was evolved. Following this, volatiles were removed *in vacuo* and the resulting solid redissolved into C_6D_6 .

In-situ spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298 K): $-\text{0.73}$ (3H, s, CH_3 of AlMe), 1.11 (12H, d, $^3J_{\text{HH}} = 6.8$ Hz, 2 x overlapping CH_3 of Dipp $i\text{Pr}$), 1.20, 1.28 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, CH_3 of Dipp $i\text{Pr}$), 1.60 (6H, s, CH_3 of β -diketiminato backbone), 3.21 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp $i\text{Pr}$), 3.57 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp $i\text{Pr}$), 5.00 (2H, s, CH_2 of OCH_2Ph), 5.01 (1H, s, γ -CH), 6.95 – 7.42 (11H, m, aromatic CH of Dipp and OCH_2Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene- d_6 , 298 K): δ_{C} $-\text{14.6}$ (CH_3 of AlMe), 23.4 (CH_3 of β -diketiminato backbone), 24.4, 24.8, 24.9, 25.6 (CH_3 of Dipp $i\text{Pr}$), 28.1, 28.7 (CH of Dipp $i\text{Pr}$), 65.6 (CH_2 of OCH_2Ph), 98.1 (γ -CH), 124.2, 124.9 (m -ArC of Dipp), 125.9 (p -ArC of OCH_2Ph), 126.1 (o -ArC of OCH_2Ph), 127.4 (p -ArC of Dipp), 128.1 (m -ArC of OCH_2Ph),

140.8 (*ipso*-ArC of Dipp), 143.6, 145.5 (*o*-ArC of Dipp), 146.1 (*ipso*-ArC of OCH₂Ph), 170.0 (NC). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} 111.

It is of note that the preparation of [Dipp¹Al(H)(OCH₂Ph)] and [Dipp¹Al(OCH₂Ph)₂] from the reaction of [Dipp¹AlH₂] with benzaldehyde were reported during the course of this study; the spectroscopic data for **6.1^H** and **6.1^{OCH₂Ph}** are consistent with those reported in the literature.²⁸

Preparation of {HC(MeCNDipp)₂}Al(H)(OCH₂Ph) – [Dipp¹Al(H)(OCH₂Ph)] (6.1^H**)**

Benzaldehyde (76 μ L, 0.74 mmol) was added to a solution of [Dipp¹AlH₂] (0.30 g, 0.67 mmol) in toluene (5 mL). at room temperature and the reaction mixture was stirred for 2 h. **6.1^H** was isolated as a colourless oil following the removal of volatiles from the reaction mixture *in vacuo*. The residue was extracted into *n*-hexane, volatiles removed *in vacuo* to yield a foam, which was re-extracted into minimal hexane. The resulting solution was stored at 6°C for several days, producing colourless acicular crystals, suitable for X-ray crystallography. Yield: 0.31 g, 85%.

Spectroscopic data: **¹H NMR** (400 MHz, benzene-d₆, 298 K): δ_{H} 1.12, 1.15, 1.31, 1.37 (6H, d, $^3J_{\text{HH}}$ = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.57 (6H, s, CH₃ of β -diketiminato backbone), 3.40 (4H, 2 x overlapping sept, $^3J_{\text{HH}}$ = 6.8 Hz, 2 x CH of Dipp ⁱPr), 4.56 (2H, s, CH₂ of OCH₂Ph), 4.89 (1H, s, γ -CH), 6.63 – 6.68 (2H, m, aromatic CH of OCH₂Ph), 6.96 – 7.22 (9H, m, aromatic CH of Dipp and OCH₂Ph). **¹³C{¹H} NMR** (126 MHz, benzene-d₆, 298 K): δ_{C} 23.0 (CH₃ of β -diketiminato backbone), 24.5, 24.6, 24.8, 25.9 (CH₃ of Dipp ⁱPr), 28.4, 28.8 (CH of Dipp ⁱPr), 65.0 (CH₂ of OCH₂Ph), 96.6 (γ -CH), 124.6, 124.7 (*m*-ArC of Dipp), 125.7 (*p*-ArC of OCH₂Ph), 126.0 (*o*-ArC of OCH₂Ph), 127.6 (*p*-ArC of Dipp), 128.3 (*m*-ArC of OCH₂Ph), 139.5 (*ipso*-ArC of Dipp), 144.5, 145.0 (*o*-ArC of Dipp), 145.4 (*ipso*-ArC of

OCH₂Ph), 170.3 (NC). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} 103. **IR (nujol/cm⁻¹):** ν_{Al-H} 1823 (s). **EI-MS:** *m/z* calc for C₃₆H₄₈AlN₂O ([M-H]⁺) 551.3577, meas. 551.3553 (5%). **Elemental microanalysis:** calc. for C₃₆H₄₉AlN₂O: C 78.22% H 8.94% N 5.07% meas. C 78.08% H 9.09% N 5.18%.

Preparation of {HC(MeCNDipp)₂}Al(OCH₂Ph)₂ – [Dipp¹]Al(OCH₂Ph)₂ (6.1^{OCH₂Ph})

Benzylalcohol (0.15 mL, 1.48 mmol) was added dropwise to a solution of [Dipp¹]AlH₂ (0.30 g, 0.67 mmol) in toluene (10 mL) at room temperature. The reaction mixture was stirred for 2h, followed by removal of volatiles *in vacuo*. The resulting white solid was re-extracted into toluene, filtered, concentrated until the point of incipient crystallisation and stored at –30°C, yielding single crystals overnight. Yield: 0.35 g, 78%.

Spectroscopic data: **¹H NMR** (400 MHz, benzene-d₆, 298 K): 1.12, 1.20 (12H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.59 (6H, s, CH₃ of β-diketiminato backbone), 3.46 (4H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.82 (4H, s, CH₂ of OCH₂Ph), 4.96 (1H, s, γ-CH), 7.02 – 7.20 (16H, m, aromatic CH of Dipp and OCH₂Ph). **¹³C{¹H} NMR** (126 MHz, benzene-d₆, 298 K): δ_C 23.4 (CH₃ of β-diketiminato backbone), 24.6, 25.0, (CH₃ of Dipp ⁱPr), 28.5 (CH of Dipp ⁱPr), 65.2 (CH₂ of OCH₂Ph), 97.4 (γ-CH), 124.6 (*m*-ArC of Dipp), 125.5 (*o*-ArC of OCH₂Ph), 125.9 (*p*-ArC of OCH₂Ph), 127.5 (*p*-ArC of Dipp), 128.4 (*m*-ArC of OCH₂Ph), 140.4 (*ipso*-ArC of Dipp), 144.8 (*o*-ArC of Dipp), 145.7 (*ipso*-ArC of OCH₂Ph), 171.0 (NC). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **EI-MS:** *m/z* calc for C₄₃H₅₅N₂AlO₂ ([M]⁺), 658.4073 meas. 658.4055 (3%). **Elemental microanalysis:** calc. for C₄₃H₅₅AlN₂O₂: C 78.38% H 8.41% N 4.25% meas. C 78.24% H 8.31% N 4.22%.

Preparation of {HC(Me₂NCNDipp)₂}Al(Et)(OCH₂Ph) – [Dipp₂]Al(Et)(OCH₂Ph) (6.2^{Et})

To a stirred solution of [Dipp₂]Al(Et)H (0.317 g, 0.59 mmol) in toluene (10 mL) was added dropwise benzaldehyde (74 μ L, 0.73 mmol). The reaction mixture was stirred for 6 h at room temperature after which volatiles were removed *in vacuo* to yield a white solid. Extraction into hexane, filtration, concentration of the filtrate and cooling to –30°C yielded colourless crystals, suitable for X-ray crystallography. The supernatant yielded a second crop of crystals upon concentration and storage at –30°C. Yield: 0.14 g, 38%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): –0.11 (q, ³J_{HH} = 8.2 Hz, CH₃CH₂Al), 0.73 (3H, t, ³J_{HH} = 8.2 Hz, CH₃CH₂Al), 1.09, 1.15, 1.30, 1.50 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 2.26 (6H, s, CH₃ of (CH₃)₂N), 3.06 (4H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.83 (1H, s, γ -CH), 4.01 (4H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 5.22 (2H, s, CH₂ of OCH₂Ph), 7.09 – 7.15 (7H, m, aromatic CH of Dipp and OCH₂Ph), 7.29 (2H, t, *m*-CH of OCH₂Ph), 7.67 (2H, d, *o*-CH of OCH₂Ph). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_c –1.3 (br, CH₃CH₂Al), 9.5 (CH₃CH₂Al), 24.5, 26.3, 26.8, 27.9 (CH₃ of Dipp ⁱPr), 28.3, 32.0 (CH of Dipp ⁱPr), 41.2 (CH₃ of (CH₃)₂N), 65.9 (CH₂ of OCH₂Ph), 76.1 (γ -CH), 124.5, 125.2 (ArC of Dipp), 126.0 (*p*-ArC of OCH₂Ph), 126.8 (*p*-ArC of OCH₂Ph), 127.9 (ArC of Dipp), 128.1 (*m*-ArC of OCH₂Ph), 142.1, 144.1, 145.5 (ArC of Dipp), 146.4 (*ipso*-ArC of OCH₂Ph), 167.2 (NC). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed.

Preparation of [{HC(MeCNDipp)₂}Al(DMAP)(H)][OTf] – [[Dipp₁]Al(DMAP)(H)][OTf] (6.3)

DMAP (0.04 g, 0.319 mmol) was dissolved in toluene (5 mL) and added to a solution of [Dipp₁]Al(OTf)H (0.15 g, 0.252 mmol) in toluene (5 mL). The reaction mixture was stirred for 1 h, filtered, concentrated until the point of incipient crystallisation and layered with

n-hexane. Storage of this solution for several days yielded large, colourless crystals suitable for X-ray crystallography. Yield: 0.14 g, 76%.

Spectroscopic data: ^1H NMR (400 MHz, benzene- d_6 , 298 K): δ_{H} 0.35 – 1.62 (24H, d, br multiplet, CH_3 of Dipp ^iPr), 1.77 (6H, s, CH_3 of β -diketiminato backbone), 2.44 (6H, s, $\text{N}(\text{CH}_3)_2$ of DMAP), 3.08 (4H, br sept, CH of Dipp ^iPr), 4.09 (1H, br s, Al-H), 5.57 (1H, s, γ -CH), 6.63 (2H, br s, *m*-CH of DMAP), 7.02 – 7.13 (6H, m, aromatic CH), 7.95 (2H, br s, *o*--CH of DMAP). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, benzene- d_6 , 298 K): δ_{C} 23.5 (CH_3 of β -diketiminato backbone), 24.3, 24.7 (br, CH_3 of Dipp ^iPr), 28.9 (br, CH of Dipp ^iPr), 39.0 ($((\text{CH}_3)_2\text{N}$ of DMAP), 101.1 (γ -CH), 108.5 (br, *m*-CH of DMAP), 125.1 (br, *m*-ArC of Dipp), 128.5 (*p*-ArC of Dipp), 137.9 (*ipso*-ArC of Dipp), 144.9 (br, *o*-ArC of Dipp), 146.4 (*o*-ArC of DMAP), 157.0 (*p*-ArC of DMAP), 174.0 (NC). ^{19}F NMR (376 MHz, benzene- d_6 , 298 K): δ_{F} –77.5. ^{27}Al NMR (104 MHz, benzene- d_6 , 298 K): δ_{Al} not observed. IR (nujol/ cm^{-1}): $\nu_{\text{Al-H}}$ 1894 (s). **Elemental microanalysis:** calc. for $\text{C}_{37}\text{H}_{52}\text{N}_4\text{AlBF}_3\text{O}_3\text{S}$: C 61.99% H 7.31% N 7.82% meas. C 61.63% H 7.18% N 7.71%.

Variable temperature NMR data: ^1H NMR (400 MHz, toluene- d_8 , 244 K): δ_{H} 0.37, 1.03, 1.27, 1.40 (6H, d, $^3J_{\text{HH}} = 6.6$ Hz, CH_3 of Dipp ^iPr), 1.76 (6H, s, CH_3 of β -diketiminato backbone), 2.71 (6H, br s, $(\text{CH}_3)_2\text{N}$ of DMAP), 2.87 (2H, sept, $^3J_{\text{HH}} = 6.6$ Hz, CH of Dipp ^iPr), 3.22 (2H, sept, $^3J_{\text{HH}} = 6.6$ Hz, CH of Dipp ^iPr), 4.02 (1H, br s, Al-H), 5.54 (1H, s, γ -CH), 6.77 (2H, br s, *m*-CH of DMAP), 6.92 – 7.12 (6H, m, aromatic CH), 7.81 (2H, br s, *o*-CH of DMAP). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, toluene- d_8 , 244 K): δ_{C} 23.2 (CH_3 of β -diketiminato backbone), 23.9, 24.2, 24.4, 24.8 (CH_3 of Dipp ^iPr), 28.1, 29.5 (CH of Dipp ^iPr), 39.2 ($((\text{CH}_3)_2\text{N}$ of DMAP), 100.7 (γ -CH), 108.4 (br, *m*-ArC of DMAP), 124.4, 125.4 (*m*-ArC of Dipp), 128.3 (*p*-ArC of Dipp), 137.6 (*ipso*-ArC of Dipp), 143.0, 145.6 (*o*-ArC of Dipp), 145.6 (*o*-ArC of DMAP), 157.0 (*p*-ArC of DMAP), 173.6 (NC). ^{19}F NMR (377 MHz,

Chapter VI: Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms

toluene-d₈, 244 K): δ_F -77.6. **²⁷Al NMR** (104 MHz, toluene-d₈, 244 K): δ_{Al} not observed.

¹H NMR (500 MHz, toluene-d₈, 378 K): δ_H 1.12 (24H, d, $^3J_{HH}$ = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.73 (6H, s, CH₃ of β -diketiminato backbone), 2.54 (6H, s, (CH₃)₂N of DMAP), 3.08 (4H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ⁱPr), 5.33 (1H, s, γ -CH), 6.46 (2H, d, $^3J_{HH}$ = 6.2 Hz, *m*-CH of DMAP), 6.96 – 7.09 (6H, m, aromatic CH), 8.16 (2H, d, $^3J_{HH}$ = 6.2 Hz, *o*-CH of DMAP).

**Preparation of {HC(MeCNDipp)₂}Al(Et)(OCH₂(C₆H₄NMe₂-4) –
[^{Dipp}1]Al(Et)(OCH₂(C₆H₄NMe₂-4))**

To an NMR tube fitted with a J. Young's valve was added [^{Dipp}1]Al(Et)H (0.03 g, 0.063 mmol), (*p*-Me₂NC₆H₄)C(O)H (0.01 g, 0.067 mmol) and benzene-d₆ (0.5 mL). The progress of the reaction was monitored by ¹H NMR spectroscopy until completion. The product of the reaction was characterised by *in situ* NMR spectroscopy.

Spectroscopic data: **¹H NMR** (400 MHz, benzene-d₆, 298 K): δ_H -0.07 (2H, q, $^3J_{HH}$ = 8.1 Hz, CH₃CH₂Al), 0.99 (3H, t, $^3J_{HH}$ = 8.1 Hz, CH₃CH₂Al), 1.10, 1.17, 1.28, 1.32 (6H, d, $^3J_{HH}$ = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.62 (6H, s, CH₃ of β -diketiminato backbone), 2.59 (6H, s, CH₃ of Me₂N), 3.22 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ⁱPr), 3.63 (2H, sept, $^3J_{HH}$ = 6.8 Hz, CH of Dipp ⁱPr), 5.05 (1H, s, γ -CH), 5.15 (2H, s, CH₂ of OCH₂Ar), 6.75 (2H, d, $^3J_{HH}$ = 8.2 Hz, aromatic CH of *p*-Me₂NC₆H₄), 7.09 – 7.16 (6H, m, aromatic CH of Dipp), 7.54 (2H, d, $^3J_{HH}$ = 8.2 Hz, aromatic CH of *p*-Me₂NC₆H₄). **¹³C{¹H} NMR** (101 MHz, benzene-d₆, 298 K): δ_C -3.0 (br, CH₃CH₂Al), 9.5 (CH₃CH₂Al), 23.3 (CH₃ of β -diketiminato backbone), 24.6, 24.7, 24.8, 25.7 (CH₃ of Dipp ⁱPr), 28.0, 28.9 (CH of Dipp ⁱPr), 40.8 (CH₃ of Me₂N), 65.4 (CH₂ of OCH₂Ar), 98.1 (γ -CH), 113.2 (ArC of *p*-Me₂NC₆H₄), 124.1, 124.9 (ArC of Dipp), 126.6 (ArC of *p*-Me₂NC₆H₄), 127.3 (ArC of Dipp), 134.7 (ArC of *p*-Me₂NC₆H₄), 141.0, 143.3, 145.6 (ArC of Dipp), 149.7 (ArC of *p*-Me₂NC₆H₄), 169.9 (NC). **²⁷Al NMR** (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed.

Preparation of {HC(MeCNDipp)₂}Ga(H)(OCH₂Ph) – [Dipp¹]Ga(H)(OCH₂Ph) (6.4)

[Dipp¹]GaH₂ (0.70 g, 1.43 mmol) was dissolved in toluene (5 mL) in an ampoule fitted with a J. Young's valve and PhC(O)H (163 μ L, 1.58 mmol) added. The reaction mixture was heated at 80°C for three weeks. Volatiles were then removed *in vacuo* and the resulting oil extracted into *n*-hexane. Filtration, concentration and storage of the resultant solution at –30°C yielded colourless crystals, suitable for X-ray diffraction, over the period of one week. Yield: 0.26 g, 31%. Monitoring of the reaction mixture by ¹H NMR spectroscopy indicated that conversion to product reached >95% after three weeks; the low isolated yield of **6.4** reflects its high solubility in compatible alkane solvents.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} 1.11, 1.18, 1.23, 1.43 (6H, d, ³J_{HH} = 6.7 Hz, CH₃ of Dipp ⁱPr), 1.58 (6H, s, CH₃ of β -diketiminato backbone), 3.25 (2H, sept, ³J_{HH} = 6.7 Hz, CH of Dipp ⁱPr), 3.54 (2H, sept, ³J_{HH} = 6.7 Hz, CH of Dipp ⁱPr), 4.60 (2H, s, CH₂ of OCH₂Ph), 4.78 (1H, s, γ -CH), 5.28 (1H, br s, GaH), 6.76 (2H, m, aromatic CH of OCH₂Ph), 6.99 – 7.18 (9H, m, aromatic CH of OCH₂Ph and Dipp). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_{C} 23.1 (CH₃ of β -diketiminato backbone), 24.6, 24.7, 24.9, 25.7 (CH₃ of Dipp ⁱPr), 28.3, 28.8 (CH of Dipp ⁱPr), 68.0 (CH₂ of OCH₂Ph), 95.1 (γ -CH), 124.5, 124.7 (*m*-ArC of Dipp), 125.7 (*p*-ArC of OCH₂Ph), 126.1 (*o*-ArC of OCH₂Ph), 127.4 (*p*-ArC of Dipp), 128.0 (*m*-ArC of OCH₂Ph), 140.4 (*ipso*-ArC of Dipp), 143.7, 145.1 (*o*-ArC of Dipp), 146.1 (*ipso*-ArC of OCH₂Ph), 169.0 (NC). **IR (nujol/cm⁻¹):** $\nu_{\text{Ga-H}}$ 1933 (s). **EI-MS:** *m/z* calc for C₃₆H₄₈N₂GaO ([M-H]⁺) 593.3017, meas. 593.2992 (10%).

Preparation of {HC(MeCNDipp)}₂Al(OTf)(κ^2 -H₂(9-BBN)) –

[^{Dipp}1]Al(OTf)(κ^2 -H₂(9-BBN)) (6.5)

To a solution of [^{Dipp}1]Al(OTf)H (0.80 g, 1.35 mmol) in toluene (6 mL) was added a solution of {H(9-BBN)}₂ (0.18 g, 0.74 mmol), also in toluene (5 mL), at room temperature. The solution was stirred overnight, filtered and concentrated to the point of incipient crystallisation. Storage of this solution at –30°C for 48 h produced colourless crystals of the toluene bis-solvate, suitable for X-ray diffraction. Yield: 0.86 g, 89%.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} 0.93, 1.25, 1.32, 1.47 (6H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH₃ of Dipp ⁱPr), 1.59 (6H, s, CH₃ of β -diketiminato backbone), 1.02 – 1.96 (14H, m, CH/CH₂ of 9-BBN), 2.95 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 3.65 (2H, sept, $^3J_{\text{HH}} = 6.8$ Hz, CH of Dipp ⁱPr), 5.20 (1H, s, γ -CH), 7.09 – 7.19 (6H, m, aromatic CH of Dipp and OCH₂Ph). ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_{C} 15.9 (br, B-CH), 24.1 (CH₃ of β -diketiminato backbone), 24.3, 24.6 (CH₃ of Dipp ⁱPr), 24.8 (B-CHCH₂CH₂-), 24.9, 25.4 (CH₃ of Dipp ⁱPr), 27.7, 29.3 (CH of Dipp ⁱPr), 33.2 (B-CHCH₂CH₂-), 101.0 (γ -CH), 124.4, 125.7, 139.1, 143.2, 146.6 (ArC of Dipp), 174.5 (NC). Resonance for CF₃ of OSO₂CF₃ not observed. ¹⁹F NMR (376 MHz, benzene-d₆, 298 K): δ_{F} –76.9. ¹¹B{¹H} NMR (128 MHz, benzene-d₆, 298 K): δ_{B} –17.5 (s, $\Delta\omega_{1/2}$ 222 Hz (¹H decoupled), $\Delta\omega_{1/2}$ 300 Hz (¹H coupled). ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **IR (nujol/cm⁻¹):** $\nu_{\text{Al-H-B}}$ 2021 (br). **EI-MS:** m/z calc for C₃₀H₄₁N₂AlF₃O₃S ([M-(H₂{9-BBN})])⁺ 593.2605, meas. 593.2637 (12%). **Elemental microanalysis:** calc. for C₃₈H₅₇AlBF₃N₂O₃S: C 63.68% H 8.02% N 3.91%, meas. C 63.60% H 7.84% N 3.95%.

Preparation of [HC(MeCNDipp)₂]Al(DMAP)(OCH₂Ph)][OTf] –

[[^{Dipp}1]Al(DMAP)(OCH₂Ph)][OTf] (6.6)

A Schlenk was charged with [^{Dipp}1]Al(OTf)(OCH₂Ph) (0.110 g, 0.157 mmol) and DMAP (0.022 g, 0.180 mmol). Upon addition of toluene (5 mL), a colourless solution was formed, followed by precipitation of a white solid within 5 min. The solution was heated gently until the solid redissolved and the resulting solution was filtered (while warm) and cooled to –30°C. Small acicular crystals were grown over the course of several hours; these crystals were isolated and dried *in vacuo*. Yield: 0.06 g, 48%. Crystals of the benzene solvate suitable for X-ray crystallography were obtained from a concentrated solution of **6.6** in benzene on standing for 48 h.

Spectroscopic data: ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_H 0.46, 0.99, 1.25, 1.29 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr) 1.85 (6H, s, CH₃ of β-diketiminato backbone), 2.08 – 2.74 (6H, br m, (CH₃)₂N of DMAP), 2.81 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.33 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.51 (2H, s, CH₂ of OCH₂Ph), 5.76 (1H, s, γ-CH), 5.43 (1H, br s, *m*-CH of DMAP), 6.48 – 7.12 (11H, m, aromatic CH of OCH₂Ph and Dipp), 7.93 (1H, br s, *o*-CH of DMAP), 8.88 (1H, br s, *o*-CH of DMAP). *m*-CH of DMAP obscured by aromatic resonances. ¹³C{¹H} NMR (101 MHz, benzene-d₆, 298 K): δ_C 23.6 (CH₃ of β-diketiminato backbone), 23.9, 24.4, 24.6, 24.8 (CH₃ of Dipp ⁱPr), 28.6, 29.6 (CH of Dipp ⁱPr), 38.8 (br, (CH₃)₂N of DMAP), 66.0 (CH₂ of OCH₂Ph), 101.4 (γ-CH), 109.9 (br, *m*-ArC of DMAP), 124.4, 125.3 (*m*-ArC of Dipp), 126.0 (*p*-ArC of OCH₂Ph), 126.1 (*o*-ArC of OCH₂Ph), 127.1 (*p*-ArC of Dipp), 128.6 (*m*-ArC of OCH₂Ph), 138.3 (*ipso*-ArC of Dipp), 142.9 (*ipso*-ArC of OCH₂Ph), 142.9 (br, *o*-ArC of DMAP), 145.7, 144.0 (*o*-ArC of Dipp), 157.2 (*p*-ArC of DMAP), 175.1 (NC). ¹⁹F NMR (376 MHz, benzene-d₆, 298 K): δ_F –77.5. ²⁷Al NMR (104 MHz, benzene-d₆, 298 K): δ_{Al} not observed. **MS(ESI):** *m/z* calc for

$C_{37}H_{48}AlF_3N_2O_4S$ ([M-DMAP]⁺) 700.3102, meas. 700.3178 (100%). **Elemental microanalysis:** calc. for $C_{44}H_{58}N_4AlF_3O_4S$: C 64.21% H 7.10% N 6.81% meas. C 64.0% H 7.29% N 6.72%.

Variable temperature NMR data: ¹H NMR (400 MHz, toluene-d₈, 233 K): δ_H 0.45, 0.97, 1.26, 1.30 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr) 1.80 (6H, s, CH₃ of β-diketiminato backbone), 2.24, (3H, s, (CH₃)₂N of DMAP), 2.81 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 2.93 (3H, s, (CH₃)₂N of DMAP), 3.33 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 4.49 (2H, s, CH₂ of OCH₂Ph), 5.42 (1H, d, ³J_{HH} = 8.0 Hz *m*-CH of DMAP), 5.65 (1H, s, γ-CH), 6.34 (1H, d, ³J_{HH} = 8.0 Hz *m*-CH of DMAP), 6.95 – 7.14 (11H, m, aromatic CH of Dipp and OCH₂Ph), 7.93 (1H, d, ³J_{HH} = 8.0 Hz, *o*-CH of DMAP), 8.79 (1H, d, ³J_{HH} = 8.0 Hz, *o*-CH of DMAP). ¹H NMR (400 MHz, toluene-d₈, 380 K): δ_H 1.09 – 1.22 (24H, m, CH₃ of Dipp ⁱPr) 1.72 (6H, s, CH₃ of β-diketiminato backbone), 2.44 (6H, s, (CH₃)₂N of DMAP), 3.17 (4H, br sept, CH of Dipp ⁱPr), 4.74 (2H, s, CH₂ of OCH₂Ph), 5.39 (1H, s, γ-CH), 6.32 (2H, br s, *m*-CH of DMAP), 6.88 – 7.12 (11H, m, aromatic CH of Dipp and OCH₂Ph), 8.16 (2H, br s, *o*-CH of DMAP).

General procedure for assessing the rate of insertion of benzaldehyde into Al-H bonds

To an NMR tube fitted with a J. Young's valve was added [^{Dipp}**1**]Al(R)H (0.063 mmol), benzene-d₆ (0.5 mL) and benzaldehyde (7 μL, 0.069 mmol). The progress of the reaction was monitored by ¹H NMR spectroscopy. For [^{Dipp}**1**]Al(Et)H, this experiment was repeated using 10 equivalents of benzaldehyde (64 μL, 0.63 mmol).

Reaction of $[\text{Dipp1/2}]\text{Al}(\text{R})(\text{OCH}_2\text{Ph})$ ($\text{R} = \text{OTf, Et, Cl, H, OCH}_2\text{Ph}$) with HBpin

To an NMR tube fitted with a J. Young's valve was added $[\text{Dipp1/2}]\text{Al}(\text{R})(\text{OCH}_2\text{Ph})$ (0.021 mmol), benzene- d_6 (0.5 mL) and HBpin (15 μL , 0.10 mmol). The reaction was monitored by ^1H and ^{11}B NMR spectroscopy for 5 d at room temperature and for 48 h at 60°C.

Reaction of $[\text{Dipp1/2}]\text{Al}(\text{R})(\text{OCH}_2\text{Ph})$ ($\text{R} = \text{OTf, Et, Cl, H, OCH}_2\text{Ph}$) with $\{\text{H}(9\text{-BBN})\}_2$

To an NMR tube fitted with a J. Young's valve was added $[\text{Dipp1/2}]\text{Al}(\text{R})(\text{OCH}_2\text{Ph})$ (0.021 mmol), benzene- d_6 (0.5 mL) and $\{\text{H}(9\text{-BBN})\}_2$ (13 mg, 0.053 mmol). The reaction was monitored by ^1H and ^{11}B NMR spectroscopy for 5 d at 60°C.

Reaction of $[\text{Dipp1}]\text{Ga}(\text{H})(\text{OCH}_2\text{Ph})$ with HBpin

To an NMR tube fitted with a J. Young's valve was added $[\text{Dipp1}]\text{Ga}(\text{H})(\text{OCH}_2\text{Ph})$ (0.03 g, 0.05 mmol), benzene- d_6 (0.5 mL) and HBpin (8 μL , 0.055 mmol). The progress of the reaction was monitored by ^1H and ^{11}B NMR spectroscopy.

Reaction of $[\text{Dipp1}]\text{Al}(\text{R})\text{H}$ with $\text{PhCH}_2\text{OBpin}$

To a solution of HBpin (220 μL , 1.52 mmol) in benzene- d_6 (6 mL) was added dropwise benzylalcohol (235 μL , 2.26 mmol). The resulting solution was stirred for 90 min and subsequently added to solid KH (0.033 g, 0.82 mmol), and stirred rapidly for 1 h. Following this, the solution was filtered and the concentration of $\text{PhCH}_2\text{OBpin}$ calculated against a toluene standard. To 0.5 mL of this solution was added $[\text{Dipp1}]\text{Al}(\text{R})\text{H}$ ($\text{R} = \text{OTf, Et, H, Me, Cl}$) (0.019 mmol), and the progress of the reaction monitored by ^1H NMR spectroscopy.

General procedure for the catalytic transformation of benzaldehyde to benzylbenzoate

To a solution of $[\text{Dipp}\mathbf{1}]\text{Al}(\text{R})(\text{OCH}_2\text{Ph})$ ($\text{R} = \text{OTf}, \text{Et}, \text{H}, \text{OCH}_2\text{Ph}$) (0.021 mmol, 2 mol%) in benzene- d_6 (0.6 mL) was added benzaldehyde (107 μL , 1.05 mmol). The progress of the reaction was monitored by ^1H NMR spectroscopy. The use of $[\text{Dipp}\mathbf{1}]\text{Al}(\text{DMAP})(\text{OCH}_2\text{Ph})[\text{OTf}]$ (17 mg, 0.021 mmol, 2 mol%) and a mixture of $[\text{Dipp}\mathbf{1}]\text{Al}(\text{Et})(\text{OCH}_2\text{Ph})$ (12 mg, 0.021 mmol, 2 mol%) and DMAP (3 mg, 0.025 mmol) as the catalyst was also explored using this method.

6.4 Results and discussion

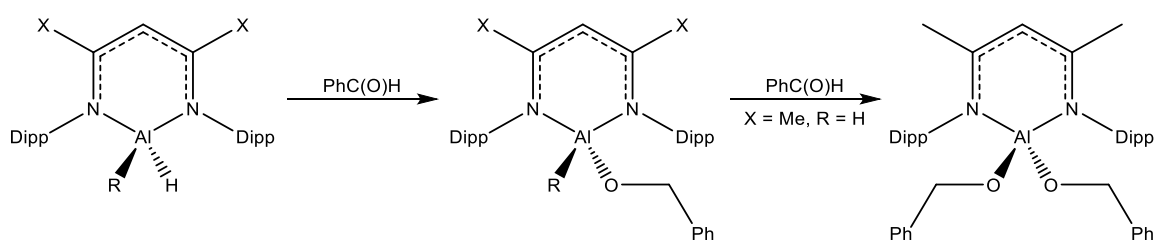
6.4.1 Activation of aldehydes by group 13 hydrides

6.4.1.1 Reactivity of β -diketiminato-ligated aluminium hydrides towards aldehydes

As a starting point for the study, we first sought to obtain isolated samples of the insertion product $[\text{Dipp}\mathbf{1}]\text{Al}(\text{OTf})(\text{OCH}_2\text{Ph})$ (**6.1^{OTf}**), with a view to probing its chemical competence as an intermediate in the formation of $\text{PhCH}_2\text{OBpin}$ *via* the route outlined in Scheme 6.3. Consistent with the report of Yang *et al.*, it was found that the reaction of **3.4^{OTf}** with benzaldehyde leads to very rapid formation of **6.1^{OTf}**, with the reaction being complete at room temperature before acquisition of NMR spectra could be achieved. In the absence of any previously reported characterising data for **6.1^{OTf}**, homogenous samples of this material were obtained in order to identify its spectroscopic signatures. **6.1^{OTf}** could be crystallised from pentane at -30°C and characterised by standard

spectroscopic/analytical techniques together with single crystal X-ray diffraction (Figure 6.5).

Additionally, the broader scope of this insertion process could be demonstrated: in our hands benzaldehyde will also insert into the corresponding Al-H bonds of $[\text{Dipp1}] \text{Al}(\text{R})\text{H}$ (**3.4^R**, where R = Et, Cl, Me, H, OCH_2Ph) and $[\text{Dipp2}] \text{Al}(\text{Et})\text{H}$ (**3.5^{Et}**), albeit at significantly slower rates, to generate the corresponding alkoxides $[\text{Dipp1/2}] \text{Al}(\text{R})(\text{OCH}_2\text{Ph})$ (**6.1^R**/**6.2^{Et}**). An alternative route for the preparation of these alkoxide complexes involves the reaction of benzylalcohol with the respective aluminium hydrides. During the course of this work, the syntheses of $[\text{Dipp1}] \text{Al}(\text{H})(\text{OCH}_2\text{Ph})$ and $[\text{Dipp1}] \text{Al}(\text{OCH}_2\text{Ph})_2$, *via* the reaction of $[\text{Dipp1}] \text{AlH}_2$ with benzaldehyde, were reported by Masuda *et al.*, together with the solid-state structures of these compounds.²⁸



Scheme 6.4: Insertion of benzaldehyde into the Al-H bond of a range of Nacnac-ligated aluminium hydrides is demonstrated to be possible, including insertion into both Al-H bonds of $[\text{Dipp1}] \text{AlH}_2$.

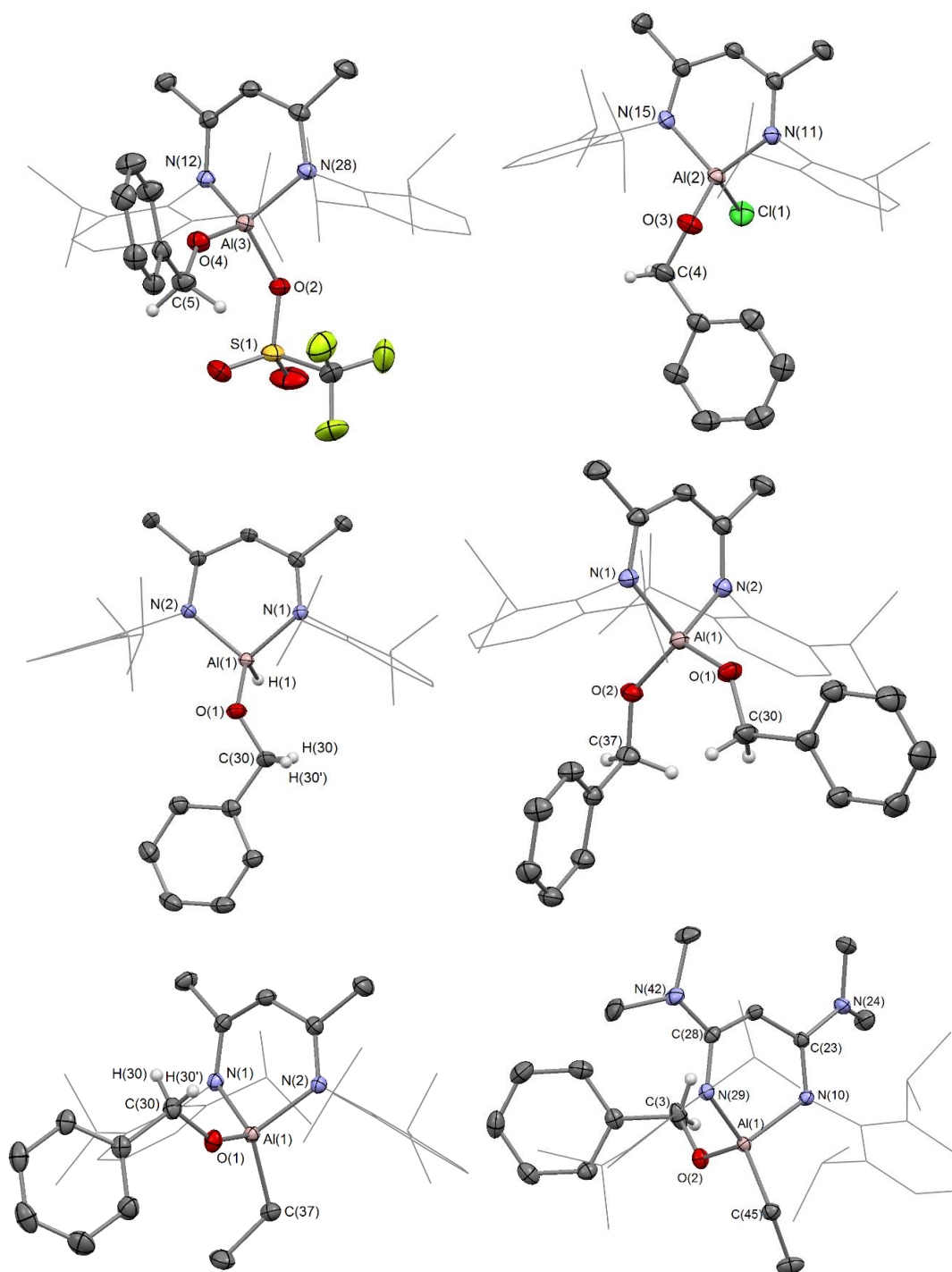


Figure 6.5: Molecular structures of $[\text{Dipp1}]\text{Al}(\text{R})(\text{OCH}_2\text{Ph})$ (**6.1^R**) ($\text{R} = \text{OTf}, \text{Cl}, \text{Et}, \text{H}, \text{OCH}_2\text{Ph}$) and $[\text{Dipp2}]\text{Al}(\text{Et})(\text{OCH}_2\text{Ph})$ (**6.2^{Et}**) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Al-H located in the difference Fourier map and refined isotropically. Key bond lengths ($\text{\AA}$) and angles ($^\circ$) are shown in **Table 6.1**.

	$d(\text{Al-O})$ (Å)	$d(\text{Al-N})$ (Å)	$d(\text{Al-R})$ (Å)	$d(\text{O-C})$ (Å)	N-Al-N (°)	Al-O-C (°)	R-Al-O (°)	$d(\text{C-N})$ (Å)	Distance of Al from C ₃ N ₂ plane	OCH ₂ Ph position
6.1^{OTf}	1.6766(10)	1.8594(11) 1.8718(11)	1.7924(10)	1.3993(17)	98.99(5)	147.76(10)	112.52(5)	-	0.573	Axial
6.1^{Cl}	1.7041(13)	1.8671(12) 1.8748(14)	2.1239(6)	1.398(2)	99.23(6)	126.55(12)	110.10(5)	-	0.391	Equatorial
6.1^H	1.7172(14)	1.8806(17) 1.8916(17)	1.63(4)	1.400(3)	97.10(7)	123.79(14).	114.6(13)	-	0.546	Equatorial
6.1^{OCH₂Ph}	1.7033(9) 1.7175(10)	1.8880(11) 1.8894(11)	-	1.3897(17) 1.3929(16)	97.29(5)	130.03(9) 140.90(9)	115.76(5)	-	0.276	Both
6.1^{Et}	1.7200(9)	1.9063(10) 1.9107(10)	1.9513(13)	1.3936(15)	96.14(4)	138.69(9)	111.84(5)	-	0.614	Axial
6.2^{Et}	1.7323(13)	1.9086(15) 1.9033(14)	1.9658(18)	1.406(2)	100.09(6)		115.98(7)	1.353(2)/ 1.373(2) 1.360(2)/ 1.371(2)	0.519	Axial

Table 6.1: Some of the structural features associated with aluminium alkoxide complexes **6.1^R** and **6.2^{Et}** (above) and their precursor hydrides (below).

	3.4^{OTf}	3.4^{Cl}	3.4^H	3.4^{Et}	3.5^{Et}
Distance of Al from least-squares C ₃ N ₂ plane (Å)	-	0.467	0.006	0.663	0.464
$d(\text{Al-N})$ (Å)	1.8674(10)	1.8755(16) 1.8906(16)	1.8989(12)	1.9151(13) 1.9170(13)	1.8946(10) 1.9222(10)
$d(\text{Al-R})$ (Å)	1.8038(15)	2.1366(9)	1.51(2) 1.518(19)	1.9605(18)	1.9803(14)

Chapter VI: Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms

In the molecular structures of each of these alkoxide complexes the aluminium centre is found in an approximately tetrahedral environment and is projected out of the least-squares C₃N₂ plane of the ligand, typically to an extent greater than in the precursor hydride. Further comparison with the respective hydrides reveals a marginal shortening of the Al-N distances, presumably arising from an increase in the Lewis acidity of the metal centre (Table 6.1). The Al-N distances and N-Al-N angles of these alkoxide complexes are near-identical but the Al-O distance associated with the OCH₂Ph group is marginally shorter for the complexes with more electron withdrawing aluminium-bound substituents, for example **6.1**^{OTf} (1.6766(10) Å) and **6.1**^{Et} (1.7200(9) Å), consistent with the stronger Al-O bond expected for a more electrophilic aluminium centre.

R	[Dipp 1]Al(R)H		[Dipp 1]Al(R)(OCH ₂ Ph)	
	δ _H (γ-H) (ppm)	δ _H (Al-H) (ppm)	δ _H (γ-H) (ppm)	δ _H (OCH ₂ Ph) (ppm)
1 : OTf	4.82	4.48	5.00	5.06
1 : Cl	4.88	4.55	4.89	4.64
1 : H	4.87	4.48	4.89	4.56
1 : OCH ₂ Ph	-	-	4.96	4.82
1 : Et	4.92	4.57	5.02	5.13

Table 6.2: Spectroscopic data associated with aluminium alkoxide complexes **6.1**^R and their precursor hydrides.

Insertion of benzaldehyde into the aluminium hydride bond of [Dipp**1/2**]Al(R)H (R = OTf, Cl, H, OCH₂Ph, Et) is signalled by the loss of the broad resonance associated with the aluminium hydride in the ¹H NMR spectrum and the appearance of a sharp resonance, integrating to two protons (relative to the ligand γ-H signal), in the region δ_H = 4.56 – 5.22 ppm corresponding to the methylene group of the OCH₂Ph substituent (Table 6.2). Typically, the resonance for the γ-CH of the alkoxide complex is shifted downfield compared to that of its parent hydride compound. The formation of **6.1**^H by insertion of

benzaldehyde into one of the two Al-H bonds of **3.4^H**, is characterised by the appearance of two septets and four doublets in the aliphatic region of the ^1H NMR spectrum for the Dipp CH and CH_3 substituents, respectively. These observations are consistent with the absence of C_2 symmetry in **6.1^H**, due to the presence of an unsymmetrically substituted aluminium centre. Additionally, the IR spectrum of **6.1^H** features a single Al-H stretching band at 1823 cm^{-1} ; this is greater than the mean Al-H stretching frequency reported for the aluminium dihydride (1814 cm^{-1}), consistent with the installation of an electron-withdrawing alkoxide substituent.³⁶ Insertion of benzaldehyde into the second Al-H bond is signalled by a reduction in the number of resonances associated with the Dipp ^iPr substituents, consistent with an increase in the symmetry of the product, **6.1^{OCH₂Ph}**; the resonance for the CH_2 group of the OCH_2Ph substituents at $\delta_{\text{H}} = 4.82\text{ ppm}$ integrates to four protons.

6.4.1.2 Investigation of the factors which influence aldehyde insertion

The reaction of **3.4^{OTf}** with benzaldehyde proceeds to completion before a ^1H NMR spectrum can be obtained. The work reported in Chapter 3, however, highlights significant differences in the reactivity of aluminium hydrides of the type $[\text{Dipp}\mathbf{1}]\text{Al}(\text{R})\text{H}$ ($\text{R} = \text{Me}, \text{Et}, \text{H}, \text{Cl}, \text{OTf}$) with respect to the insertion of CO_2 , which arise from variation in the auxiliary substituent, R. With a view to assessing the impact of R on the corresponding rate of insertion of benzaldehyde, hydrides $[\text{Dipp}\mathbf{1}]\text{Al}(\text{R})\text{H}$ ($\text{R} = \text{Et}, \text{Me}, \text{H}, \text{Cl}, \text{OCH}_2\text{Ph}$) were treated with a slight excess (1.1 equiv.) of PhCHO and the reaction monitored by ^1H NMR spectroscopy (Figure 6.6).

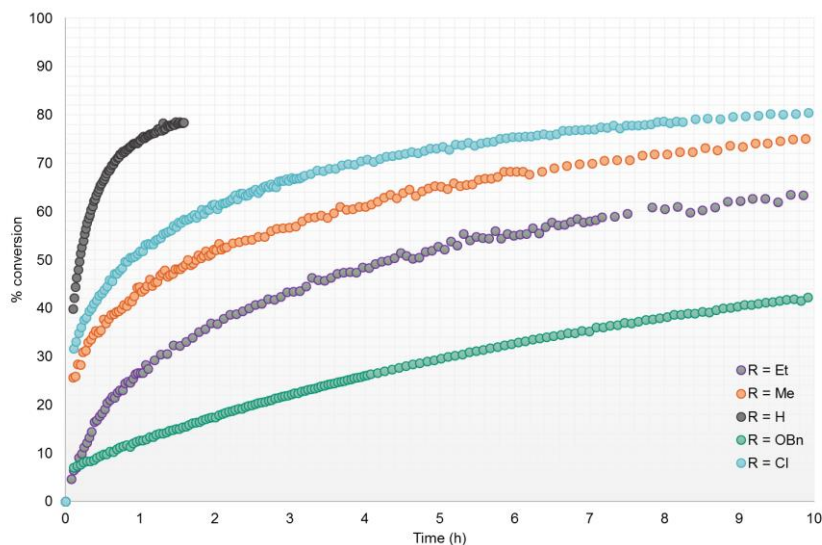


Figure 6.6: A plot of % conversion vs. time for the insertion of benzaldehyde into the Al-H bond of **3.4^R** (R = Et, Me, H, OCH₂Ph, Cl) at room temperature, for the first 10 h of the reaction.

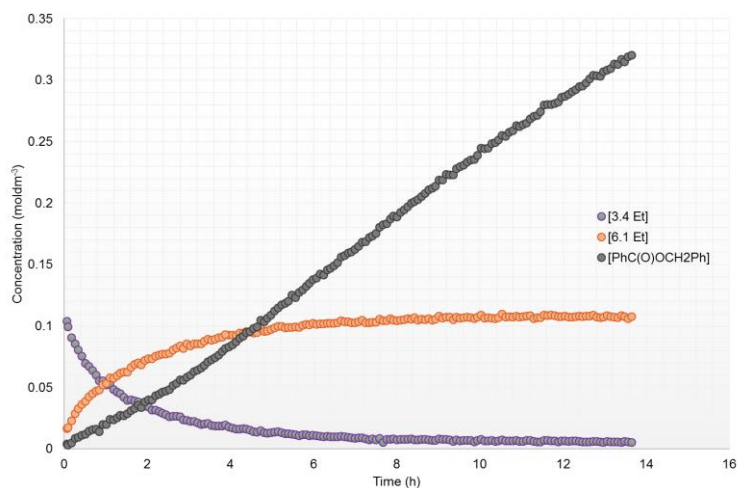


Figure 6.7: A plot of concentration against time for the reaction of **3.4^{Et}** with excess benzaldehyde (10 equiv.).

In examining these data, it is apparent that the hydrides featuring R = Et, Me or H insert benzaldehyde significantly more slowly than they do CO₂. This is consistent with the relatively electrophilicities of the carbon centres of these unsaturated substrates. However, whilst **3.4^{OTf}**/**3.4^{Cl}** are unreactive towards CO₂, they do react with benzaldehyde over the course of several hours. The work reported in Chapters 3 and 4

shows that the rate of insertion of CO₂ is strongly influenced by the hydridic character of the M-H bond (M = Al, Ga), and that sterics play a minimal role. In the case of benzaldehyde, not only is the carbonyl substrate larger, but it is also more basic, meaning that activation of the substrate by pre-coordination to the Lewis acidic aluminium centre may play a role. On this basis, aluminium hydrides which bear an electron-withdrawing substituent (and hence possess a more Lewis acidic aluminium centre) might be expected to activate the substrate faster. On the other hand, the hydridic character of the Al-H bond will likely be reduced by electron-withdrawing R groups, decreasing their propensity to undergo insertion of the C=O bond.

The data shown in Figure 6.6 show that the rates of hydroalumination of benzaldehyde fall in the order R = OTf >>> H > Cl > Me > Et > OCH₂Ph. On this basis, it is difficult to discern an overall trend based on the electronic character of the R substituent, although systems featuring a more sterically hindered aluminium centre do appear to react more slowly. In terms of the aldehyde itself, the hydroalumination of *p*-Me₂NPhC(O)H by **3.4^{Et}** occurs significantly more slowly than that of benzaldehyde: only 9% consumption of **3.4^{Et}** occurs after 12 h at room temperature, and 90% after one month. It seems likely that, while the greater basicity of *p*-Me₂NPhC(O)H allows for increased pre-coordination to the aluminium centre, the reduced electrophilicity of the carbonyl carbon renders the overall reactivity slower.

Additionally, the prerequisite for coordination of the aldehyde prior to insertion can be demonstrated in the presence of a competing Lewis base. Thus, while the ¹H NMR spectrum of the reaction mixture containing **3.4^{Et}** and DMAP (1 equiv.) suggests that there exists no obvious interaction between the hydride and base, the presence of this Lewis base significantly reduces the reactivity of **3.4^{Et}** towards benzaldehyde. The

reaction of **3.4^{Et}** with benzaldehyde in the absence of DMAP reaches 50% completion after *ca.* 6 h, while the presence of DMAP reduces the reactivity such that 50% completion is only observed after 4 days.

The significantly increased reactivity of **3.4^{OTf}** towards benzaldehyde, relative to that observed for other Nacnac-ligated aluminium hydrides, may be indicative of the potential of the triflate substituent to dissociate from the aluminium centre to facilitate coordination of benzaldehyde. Indeed, the addition of one equivalent of DMAP to **3.4^{OTf}** results in dissociation of the triflate substituent and coordination of DMAP at aluminium, yielding the base-stabilised cationic aluminium hydride, $[[^{\text{Dipp}}\mathbf{1}]\text{AlH}(\text{DMAP})][\text{OTf}]$ (**6.3**). Comparable behaviour is observed for the corresponding gallium hydride complex $[[^{\text{Dipp}}\mathbf{1}]\text{Ga}(\text{OTf})\text{H}$ (Chapter 4). **6.3** could be crystallised from a toluene/*n*-hexane layering at room temperature and characterised by standard spectroscopic/analytical techniques together with single crystal X-ray diffraction (Figure 6.8).

The molecular structure of **6.3** displays the dissociation of the triflate substituent from the aluminium centre in the solid state and N-coordination of the DMAP substituent. The Al-N_{DMAP} bond length (1.9098(13) Å) is longer than the endocyclic Al-N bonds (*d*(Al-N 1.8718(12), 1.8772(12) Å), consistent with the assertion that this is a donor-acceptor interaction rather than a formal covalent bond. It is, however, markedly shorter than that found in its gallium analogue, $[[^{\text{Dipp}}\mathbf{1}]\text{GaH}(\text{DMAP})][\text{OTf}]$, (1.9671(13) Å), despite the very similar covalent radii of aluminium and gallium (Al: 1.21(4) Å, Ga: 1.22(3) Å).³⁷ This is presumably due to the tighter binding of DMAP to the more Lewis acidic aluminium centre.

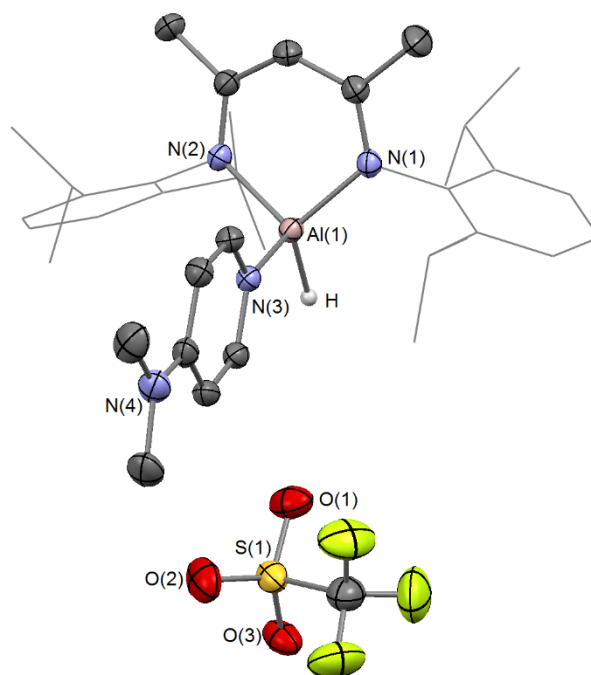


Figure 6.8: Molecular structure of $[[^{\text{Dipp}}\mathbf{1}]\text{AlH}(\text{DMAP})][\text{OTf}]$ (**6.3**) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Aluminium hydride located in the difference Fourier map and refined isotropically. Key bond lengths ($\text{\AA}$) and angles ($^\circ$): Al(1)-N(1) 1.8718(12), Al(1)-N(2) 1.8772(12), Al(1)-N(3) 1.9098(13), Al(1)-H 1.539(17), N(1)-Al(1)-N(2) 99.06(5), N(3)-Al(1)-H 103.0(6). Distance of Al(1) from least-squares C_3N_2 plane: 0.325 $\text{\AA}$.

The ^1H NMR resonances for **6.3** are consistent with the retention of its molecular structure in benzene- d_6 . The Al-H resonance is observed at $\delta_{\text{H}} = 4.09$ ppm and the resonance for the γ -H undergoes a pronounced downfield shift from $\delta_{\text{H}} = 4.82$ ppm (for **3.4^{OTf}**) to $\delta_{\text{H}} = 5.57$ ppm for **6.3**. A similar downfield shift is observed for $[[^{\text{Dipp}}\mathbf{1}]\text{GaH}(\text{DMAP})][\text{OTf}]$ and is consistent with the formally cationic nature of the metal centre. Both the resonances associated with the $i\text{Pr}$ groups of the Dipp substituents and the DMAP ligand are broad at 298 K, which suggests the molecule displays dynamic behaviour on the NMR timescale at this temperature. Variable temperature NMR

experiments were carried out and it was revealed that (as for $[[^{\text{Dipp}}\mathbf{1}]\text{GaH}(\text{DMAP})][\text{OTf}]$) two dynamic processes are in operation. At room temperature, rotation around the Al-N_{DMAP} bond occurs in a relatively facile manner; this rotation can be slowed at low temperatures ($T = 183\text{ K}$), but not completely frozen out. Upon cooling, the resonance associated with the *o*-CH protons splits into two broad signals (at $\delta_{\text{H}} = 7.69$ and 8.60 ppm), with coalescence observed at 218 K ; similarly, the *m*-CH protons split into two broad signals at $\delta_{\text{H}} = 5.86$ and 6.72 ppm, which coalesce at 216 K . The coalescence behaviour allows for the calculation of an approximate barrier of $\Delta G^{\ddagger} = 40.6\text{ kJ mol}^{-1}$ for this process.

The second fluxional process is based on the lability of the DMAP ligand; DMAP dissociates from the aluminium centre of **6.3** and reattaches on the opposite face.³⁴ If this process is rapid on the NMR timescale, the molecule will appear to possess C_2 symmetry and display only one septet and two doublets in the ^1H NMR spectrum (Figure 6.9). Coalescence of the septets for the methine protons is observed around 292 K and this enables the calculation of an approximate barrier of $\Delta G^{\ddagger} = 57.7\text{ kJ mol}^{-1}$ for this process.

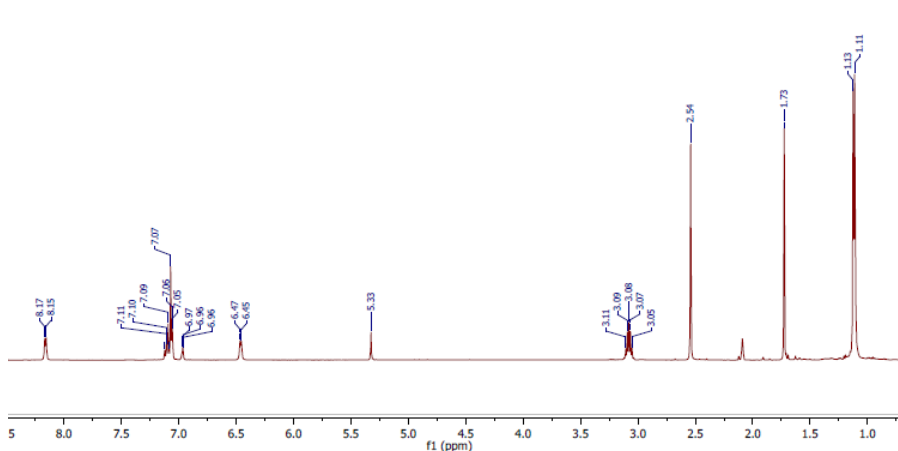


Figure 6.9: The ^1H NMR spectrum of **6.3** in toluene-d_8 above 350 K .

Chapter VI: Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms

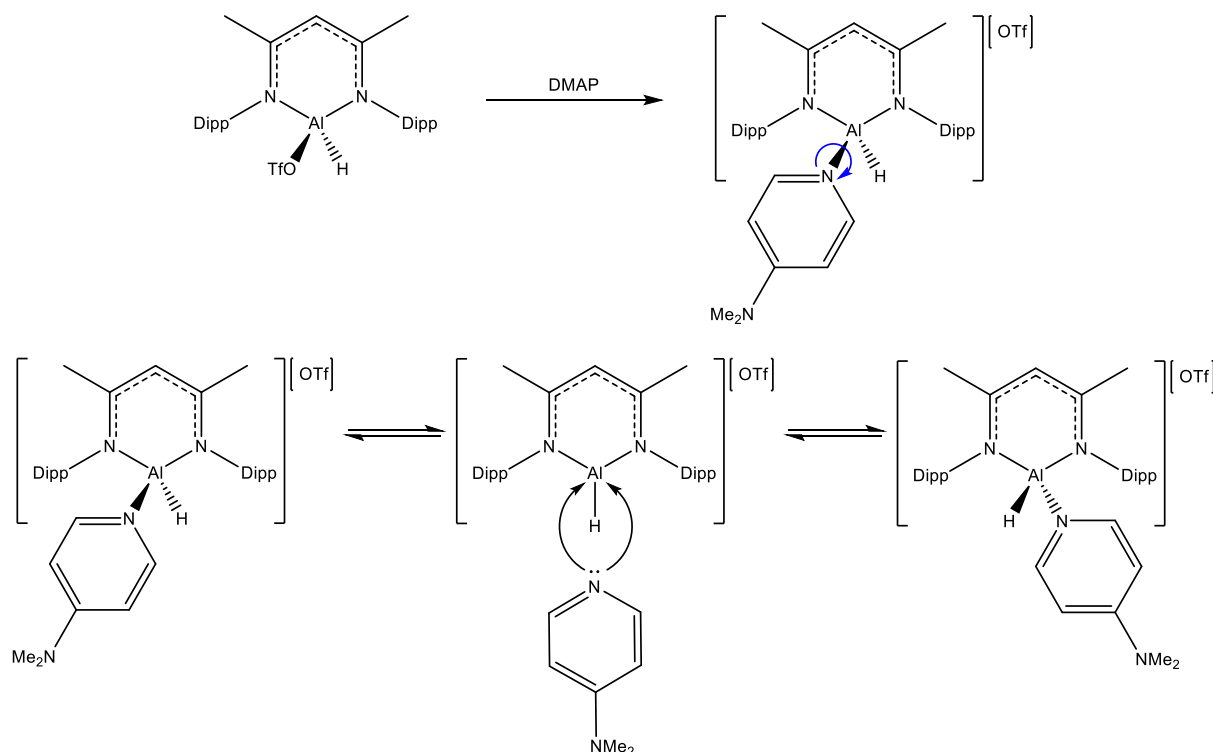
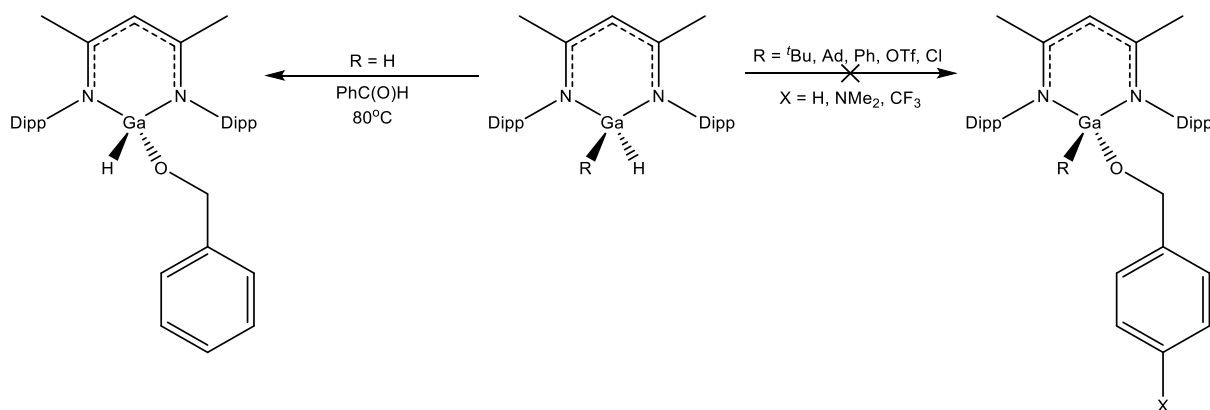


Figure 6.10: Fluxional processes occurring in **6.3**: rotation about the Al-N bond (top), dissociation DMAP and reassociation to either face of the aluminium centre (bottom).

6.4.1.3 Can β -diketiminato-ligated gallium hydrides hydrogallate aldehydes?

In light of the ability of Nacnac-ligated gallium hydrides to insert CO_2 (Chapter 4), it was hypothesised that they might be able to react in a similar fashion towards other carbonyl functionalities.³⁴ With this in mind, the gallium hydrides that show the greatest propensity for CO_2 insertion, $[\text{Dipp}1]\text{Ga}(\text{R})\text{H}$ (**4.1^R**; $\text{R} = \text{tBu, Ad}$), were reacted with benzaldehyde. Surprisingly, these complexes are completely unreactive towards the aldehyde, despite the use of a large excess (>10 equiv.) and elevated temperatures (80°C , >24h). The use of other gallium monohydrides also led to no reaction, either with benzaldehyde or with other aromatic aldehydes of varying electronic character (Scheme 6.5).

Chapter VI: Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms



Scheme 6.5: Benzaldehyde undergoes insertion into the Ga-H bond of [Dipp¹]GaH₂ to form the gallium *mono*-alkoxide complex [Dipp¹]Ga(H)(OCH₂Ph) (**6.4**), whereas related gallium monohydrides are unreactive towards a range of aldehydes under analogous conditions.

The gallium dihydride [Dipp¹]GaH₂ (**4.1^H**) does, however, react with benzaldehyde to yield the corresponding alkoxide [Dipp¹]GaH(OCH₂Ph) (**6.4**), albeit very slowly, requiring heating to 80°C for greater than three weeks to bring about completion. Insertion into the first Ga-H bond is selective, and no subsequent reactivity of **6.4** with benzaldehyde is observed. **6.4** may be crystallised from *n*-hexane at -30°C and characterised by standard spectroscopic/analytical techniques and single crystal X-ray crystallography (Figure 6.11).

The molecular structure of **6.4** displays the expected molecular connectivity.^{34,38} The Ga-O distance ($d(\text{Ga-O})$ 1.8240(19) Å) lies close in magnitude to the hydroxide [Dipp¹]Ga(Me)(OH) and methoxide complexes [Dipp¹]Ga(Ph)(OMe) ($d(\text{Ga-O})$ 1.831(1), 1.8179(18) Å, respectively).³⁹ This Ga-O bond is notably longer than the Al-O bond of **6.1^H** ($d(\text{Al-O})$ 1.7172(14) Å), despite the very similar covalent radii of aluminium and gallium (Al: 1.21(4) Å, Ga: 1.22(3) Å), underlining the greater Lewis acidity of aluminium.³⁷

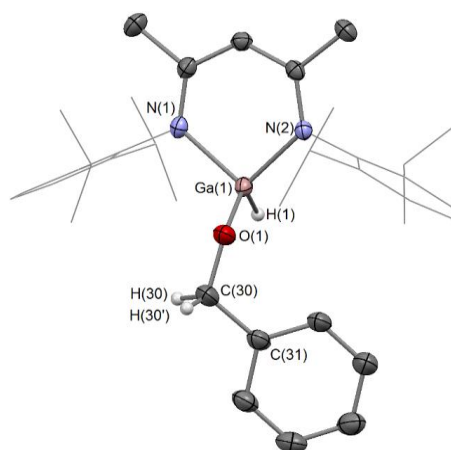


Figure 6.11: Molecular structure of [Dipp1]Ga(H)OCH₂Ph (**6.4**) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Selected hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Gallium hydride located in the difference Fourier map and refined isotropically. Key bond lengths (Å) and angles (°): Ga(1)-O(1) 1.8240(19), Ga(1)-N(1) 1.9444(16), Ga(1)-N(2) 1.9519(16), Ga(1)-H(1) 1.43(5), O(1)-C(30) 1.397(3), N(1)-Ga(1)-N(2) 96.34(7), C(30)-O(1)-Ga(1) 123.3(2). Distance of Ga(1) from least-squares C₃N₂ plane: 0.176 Å.

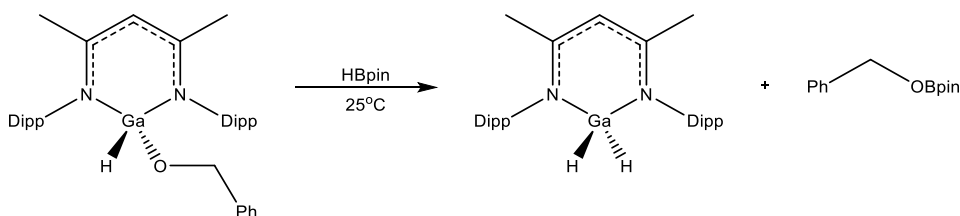
Insertion of benzaldehyde into only one of the Ga-H bonds is consistent with the ¹H NMR spectrum of **6.4**, which shows four doublet and two septet resonances for the ⁱPr groups of the Dipp substituents, signalling a loss of C₂ symmetry. Moreover, the broad resonance associated with the gallium-bound hydride shifts from δ_H = 5.19 ppm (for **4.1^H**) to δ_H = 5.28 ppm (for **6.4**) and is halved in intensity. A new resonance, integrating to two protons, is observed at δ_H = 4.60 ppm, for the CH₂ group of the OCH₂Ph substituent. The Ga-H stretch of **6.4** measured by IR (1933 cm⁻¹) is somewhat higher than the mean value measured for the precursor (1877 cm⁻¹), consistent with the formation of the electron-withdrawing alkoxide substituent.⁴⁰

Whilst Nacnac-ligated gallium hydrides can effect the hydrogallation of CO₂ under ambient conditions (Chapter 4), their reactivity towards aldehydes is significantly more

limited. This is consistent with the reduced electrophilicity of the carbon centre of the carbonyl substrate. It was demonstrated that activation of aldehydes by aluminium hydrides requires both sufficient Lewis acidity of the aluminium centre to pre-coordinate and therefore activate the aldehyde, and sufficient hydridicity of the M-H bond. The reduced Lewis acidity and hydridicity of these coordinatively-saturated gallium hydrides (arising from the greater electronegativity of gallium) presumably leads to their significantly more limited reactivity towards aldehydes, relative to their alane counterparts.

6.4.2 Regenerating the metal hydride: exploring M-O/B-H σ -bond metathesis (M = Al, Ga)

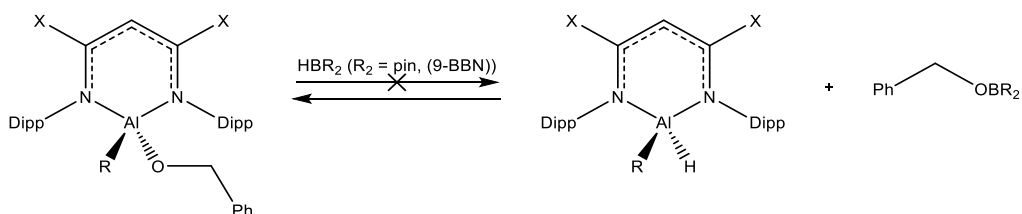
Consistent with the facile Ga-O/B-H metathesis reported in Chapter 4, the addition of one equivalent of HBpin to a solution of gallium alkoxide complex **6.4** in benzene- d_6 leads to regeneration of the corresponding hydride **4.1^H**, with accompanying formation of one equivalent of PhCH₂OBpin. The rate of this reaction is so fast that it is complete even before a ¹H NMR spectrum could be obtained. This is consistent with the reactivity observed for [Dipp¹]₂Ga(Ph)(OMe) towards HBpin, in which the regeneration of the corresponding gallium hydride also occurs very rapidly (Chapter 4).



Scheme 6.6: The reaction of **6.4** with HBpin leads to the rapid regeneration of **4.1^H**.

The reactivity of [Dipp¹]₂Al(OTf)(OCH₂Ph) (**6.10^{Tf}**), and related aluminium systems towards B-H bonds was then investigated. This step was thought to be of particular

interest, given the proposal by Yang and co-workers that it is intrinsic to turnover in the hydroboration of benzaldehyde catalysed by **3.4^{OTf}**. However, rather than confirming that the reaction of **6.1^{OTf}** with HBpin takes place readily 'at room temperature in C₆D₆,'²⁶ it is found that no conversion of **6.1^{OTf}**/HBpin into **3.4^{OTf}** and PhCH₂OBpin occurs over the course of 5 days under such conditions. Given that the catalytic hydroboration of benzaldehyde by HBpin is reported to take place at room temperature, this caused us to question whether **6.1^{OTf}** is chemically competent as an intermediate in this process. Moreover, in order to test the viability of Al-O/B-H metathesis in a broader range of systems of this sort, the reactivity of related systems [Dipp₂Al(R)(OCH₂Ph)] (**6.1^R**; R = Et, Cl, H, OCH₂Ph) and [Dipp₂Al(Et)(OCH₂Ph)] (**6.2**) towards both HBpin and the more reactive borane {H(9-BBN)}₂ was examined. In none of these cases was any appreciable conversion to the respective Al-H containing compounds observed either at room temperature or at 60°C over a period of 5 days.



Scheme 6.7: Aluminium alkoxide complexes **6.1^R** (X = Me, R = OTf, Et, Cl, H, OCH₂Ph) and **6.2^{Et}** (X = NMe₂) are unreactive towards boranes (with respect to Al-O/B-H metathesis), and in fact can themselves be generated by the reverse reaction between the corresponding aluminium hydride and PhCH₂OBpin.

Hypothesising that the lack of reactivity of the aluminium alkoxide complexes **6.1^R** (R = OTf, Et, Cl, H, OCH₂Ph) towards HBpin might be due either to a prohibitive kinetic barrier under the conditions employed, or to more fundamental thermodynamic factors, we sought to examine the viability of the reverse reaction. Thus, the alkoxyborane PhCH₂OBpin was prepared independently from benzyl alcohol and HBpin, and its

reactivity towards hydride complex **3.4^{OTf}** examined under the conditions employed in the catalytic chemistry reported by Yang (C_6D_6 , room temperature). Informatively, this reaction proceeds spontaneously in the presence of only a slight excess of $PhCH_2OBpin$ (*ca.* 1.3 equiv.), leading to quantitative generation to **6.1^{OTf}** and H_{Bpin} over a period of *ca.* 3 h (Figure 6.12). Moreover, the fact that the reverse B-O/Al-H metathesis process is spontaneous for a wide range of examples can be demonstrated by the reactions of **3.4^R** ($R = Et, Me, Cl, H$) with $PhCH_2OBpin$, which also proceed at room temperature to yield the corresponding alkoxide **6.1^R**.⁴¹ The reaction completion times vary from 30 min ($R = H, Me$) to greater than 7 h ($R = Et$); this variation in reaction times as a function of the auxiliary R substituent may be steric in origin.

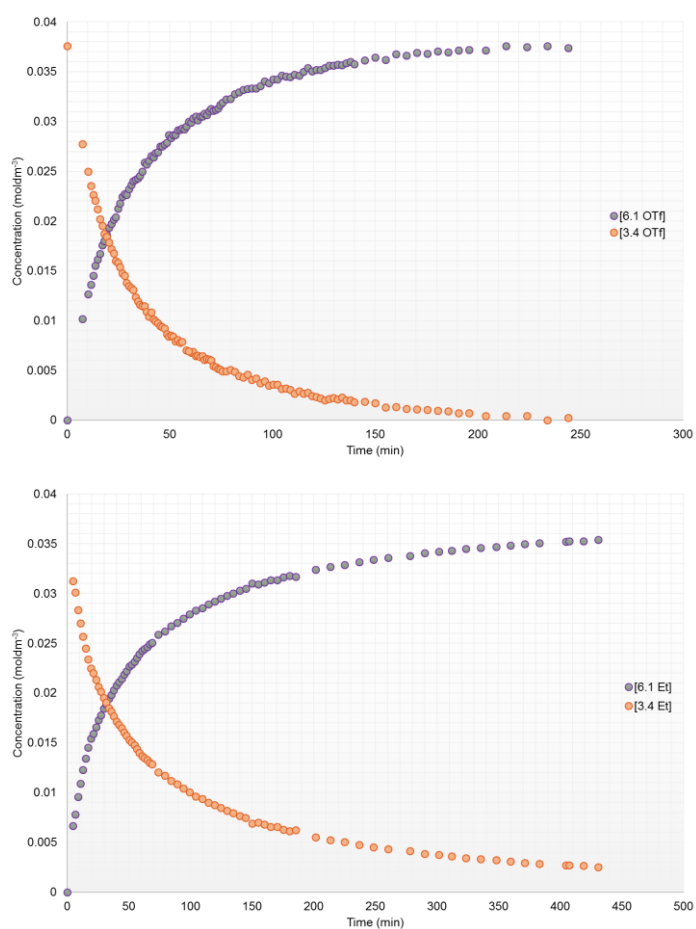


Figure 6.12: Speciation plots as a function of time for the reaction of hydrides **3.4^{OTf}** (top) and **3.4^{Et}** (bottom) with $PhCH_2OBpin$ at room temperature.

As such, not only could no evidence be found from our experiments for the key Al-O/B-H metathesis step proposed by Yang *et al.* (Scheme 6.3), but its underlying thermodynamic basis is found to be unfavorable under conditions of temperature and solvent comparable to those used in catalytic runs.

6.4.3 Consideration of alternative mechanisms

In the absence of accessible Al-O/B-H metathesis to bring about regeneration of the metal hydride, alternative mechanisms by which catalytic turnover could proceed were considered, including activation of the borane by the alane, catalysis of the process by **6.1^{OTf}** and the involvement of Tishchenko type chemistry.

6.4.3.1 Activation of the borane

One possibility considered was that catalytic turnover does not involve the formation of the catalytically non-productive aldehyde insertion product, **6.1^{OTf}**. It was therefore investigated whether the productive catalytic cycle proceeds through a mechanism that avoids the deep thermodynamic well associated with Al-O bond formation.³⁵

It was hypothesised that the observed hydroboration chemistry might proceed *via* an alternative mechanism involving initial activation of the borane by **3.4^{OTf}**. A similar activation mechanism has been demonstrated for the B(C₆F₅)₃-catalysed hydrosilylation of ketones.⁴² Consistent with this assertion, it can be demonstrated that pre-mixing **3.4^{OTf}** and an excess of either borane (HBpin or {H(9-BBN)}₂) prior to addition of excess benzaldehyde does indeed lead to the formation of the hydroboration product (*i.e.* PhCH₂OBpin or PhCH₂O(9-BBN)). The species formed by the interaction of **3.4^{OTf}** with HBpin and {H(9-BBN)}₂ were thus thought to be of some interest mechanistically. In the former case, investigation by multinuclear NMR of a 1:1 mixture of **3.4^{OTf}** and HBpin

shows that it features exclusively signals due to the unreacted alane and borane. However, it could not be ruled out that in the presence of a large excess of the borane (*i.e.* under conditions which more closely resemble the catalytic system containing 1 mol% of **3.4^{OTf}**), an interaction between the alane and borane may be present, although this could not be observed spectroscopically.

The use of the more electrophilic borane, {H(9-BBN)}₂, on the other hand yields the dialkylborohydride complex [Dipp**1**]Al(OTf)(κ^2 -H₂(9-BBN)) (**6.5**). This behaviour is in line with that reported in Chapter 3, where it was demonstrated that a range of Nacnac-ligated aluminium hydrides form complexes of this nature with electrophilic boranes such as {H(9-BBN)}₂ and BH₃. **6.5** may be crystallized from toluene and its identity confirmed by single crystal X-ray diffraction (Figure 6.13). Reactivity-wise, it can be demonstrated that **6.5**, and the closely related complex [Dipp**1**]Al(Et)(κ^2 -H₂(9-BBN)), react with benzaldehyde to produce PhCH₂O(9-BBN).

Geometrically, **6.5** features a molecular structure closely related to systems of the type [Dipp**1**]Al(R)(κ^2 -H₂(9-BBN)) (R = Me, Et, H) (Chapter 3), with the [H₂(9-BBN)] fragment centred around a tetrahedral boron centre, and featuring two hydrogens bridging to the aluminium atom. The metal coordination geometry is close to square pyramidal ($\tau = 0$), with the two β -diketiminato nitrogen donors and the bridging hydrogens constituting the basal plane and the OTf substituent occupying the apical position. The aluminium atom is projected out of the plane of the supporting Nacnac backbone by 0.766 Å. Comparison of the Al...B distances of **6.5** and [Dipp**1**]Al(Et)(κ^2 -H₂(9-BBN)) (2.166(3) and 2.2510(13) Å, respectively) reveals that binding of the borohydride ligand is tighter in the case of **6.5**, presumably reflecting the differing electronic effects of the OTf and Et substituents at the aluminium centre.

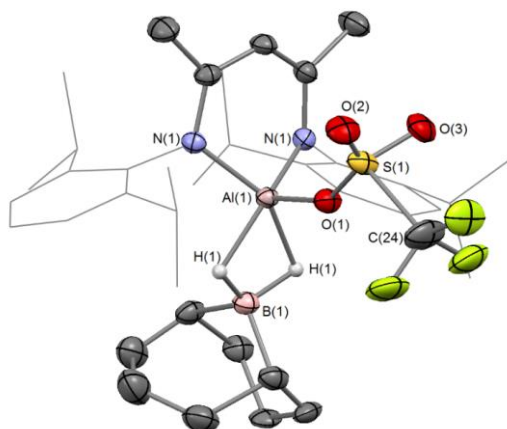


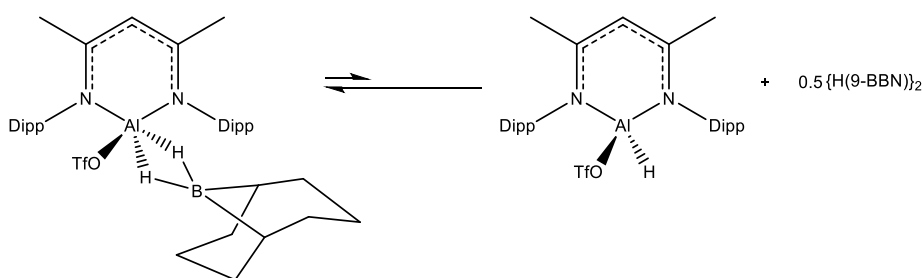
Figure 6.13: Molecular structure of $[\text{Dipp}1]\text{Al}(\text{OTf})(\kappa^2\text{-H}_2(9\text{-BBN}))$ (**6.5**) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°): Al(1)-O(1) 1.8025(19), Al(1)-N(1) 1.8711(16), Al(1)-N(1') 1.8712(16), Al(1)-B(1) 2.166(3), S(1)-O(2) 1.418(11), S(1)-O(2') 1.422(12), S(1)-O(1) 1.509(2).

The IR spectrum of **6.5** features a broad absorption at 2021 cm^{-1} , characteristic of the stretching frequencies typically observed for Al-H-B bridges. The stretching frequencies observed for related complexes vary from 2020 to 2100 cm^{-1} (Chapter 3).⁴³ The ^{11}B NMR spectrum shows a broad, unresolved signal which narrows upon ^1H decoupling from $\Delta\omega_{1/2}$ 300 Hz to 222 Hz . The chemical shift ($\delta_{\text{B}} = -17.5\text{ ppm}$) is consistent with a 4-coordinate boron centre of the type $[\text{R}_2\text{BH}_2]^-$ ($\text{R} = \text{alkyl}$).⁴⁴⁻⁴⁶

The availability of isolated samples of **6.5** also allowed for the thermodynamic parameters associated with the borane/borohydride equilibrium (Scheme 6.8) to be investigated. Thus, re-dissolving a crystalline sample of **6.5** in toluene- d_8 leads to the formation of an equilibrium mixture containing a 1:0.4 ratio of **6.5**:**3.4^{OTf}**; the effects of temperature on this equilibrium allow for the calculation of ΔH° (27.9 kJ mol^{-1}) and ΔS° ($64.9\text{ J mol}^{-1}\text{ K}^{-1}$) for borane dissociation through a van't Hoff analysis (Figure 6.14). The work described in Chapter 3 indicates that the interaction in these borohydride

Chapter VI: Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms

complexes is dominated by donation of electron density from the Al-H bond into the empty orbital of the borane. Hence, the presence of an aluminium-bound electron withdrawing substituent reduces the hydricity of the aluminium hydride and weakens the interaction with the borane. A comparison of the ΔH° values determined for borane dissociation from **6.5** (27.9 kJ mol^{-1}) and $[\text{Dipp}^1]\text{Al}(\text{Et})(\kappa^2\text{-H}_2(9\text{-BBN}))$ (54.7 kJ mol^{-1}) are consistent with this notion. In the context of potential mechanisms for the reaction of PhCHO with **6.5**, such data are consistent with the notion that the formation and breakage of Al-H-B bonds can be accomplished with minor energetic changes to the system.



Scheme 6.8: Dialkylborohydride complex **6.5** is in equilibrium with the alane **3.4^{OTf}** and $\{\text{H}(9\text{-BBN})\}_2$ in solution.

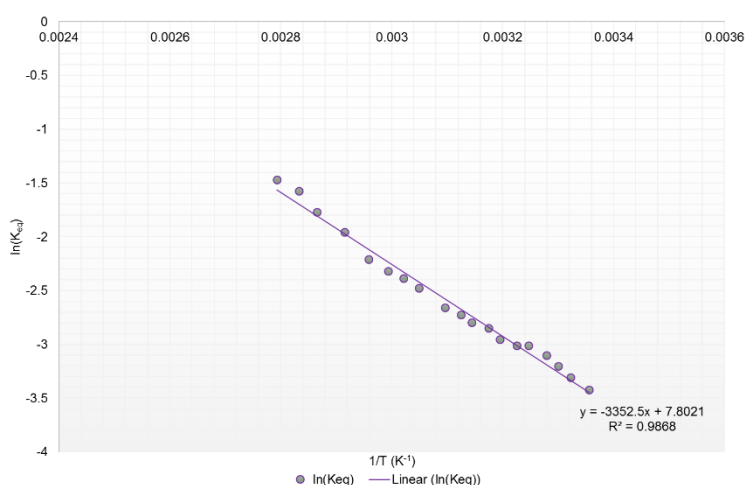


Figure 6.14: Van't Hoff plot for the equilibrium of the borohydride complex **6.5** with the aluminium hydride **3.4^{OTf}** and $\{\text{H}(9\text{-BBN})\}_2$.

Whilst we were able to demonstrate the propensity of these Nacnac-ligated aluminium hydrides to form borohydride complexes with more electrophilic boranes, no spectroscopic or computational evidence could be obtained for the formation of the analogous complex derived from HBpin, *i.e.* $[\text{Dipp}\mathbf{1}]\text{Al}(\text{OTf})(\kappa^2\text{-H}_2\text{Bpin})$. This is consistent with the proposition that the interaction within these borohydride complexes is dominated by alane donation to the borane. Presumably, the reduced Lewis acidity of HBpin precludes the formation of such complexes and, to the best of our knowledge, there are no reported examples of aluminium borohydride complexes featuring the HBpin fragment. A number of complexes of this nature have been reported that feature transition metals such as Os,⁴⁷ Ru,^{48–50} Cu,⁵¹ Ir,^{52,53} and Fe,⁵⁴ but it has been proposed that the boron centre of HBpin is not Lewis acidic enough to stabilise a symmetrical dihydridoborate coordination mode. Interestingly, a pinacolborane complex of a magnesium hydride has recently been reported.¹⁵ The slow addition of a benzene solution of $(\text{TO}^{\text{M}})\text{MgMe}$ (TO^{M} = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) to 15 equiv. of HBpin at ambient temperature generates $(\text{TO}^{\text{M}})\text{Mg}(\text{H}_2\text{Bpin})$. The molecular structure reveals that the pinacolborate unit is coordinated to the Mg centre through one of the oxygen atoms, and the two hydrogens are bonded to boron.¹⁵ As such, $\text{TO}^{\text{M}}\text{Mg}(\text{H}_2\text{Bpin})$ is not considered to be a borohydride complex.

Metal borohydride complexes have been utilised within the catalytic hydroboration of CO_2 but are typically considered to be resting states for the catalyst.^{55,56} This was also demonstrated in the reactivity of the aluminium borohydride complexes $[\text{Dipp}\mathbf{1}]\text{Al}(\text{R})(\kappa^2\text{-H}_2(9\text{-BBN}))$ ($\text{R} = \text{Me}, \text{Et}$) with CO_2 (Chapter 3), where it was shown that the borane dissociates, liberating the aluminium hydride which reacts with CO_2 . In light

of this, and the absence of evidence for a complex of the constitution $[\text{Dipp}\mathbf{1}]\text{Al}(\text{OTf})(\kappa^2\text{-H}_2(\text{Bpin}))$, we considered an alternative identity for the catalyst.

6.4.3.2 Aluminium hydrides: Nothing but a pre-catalyst?

The rapid reactivity of $\mathbf{3.4^{OTf}}$ towards benzaldehyde to form $\mathbf{6.1^{OTf}}$ (and lack of reactivity of $\mathbf{6.1^{OTf}}$ towards HBpin) indicates that $\mathbf{6.1^{OTf}}$ is likely not to be present in significant quantities under catalytic conditions. In light of this, and that β -diketiminato-ligated complexes of aluminium which *do not* bear hydride functionalities have been reported to catalyse the hydroboration of benzaldehyde (e.g. $[\text{Mes}\mathbf{1}]\text{Al}(\text{SCH}_2\text{Ph})_2$ and $[\text{Ar}\mathbf{1}]\text{AlCl}_2$ ($\text{Ar} = 2\text{-}^i\text{Pr-C}_6\text{H}_4$)), it was considered that a species other than $\mathbf{3.4^{OTf}}$ (even $\mathbf{6.1^{OTf}}$ itself) might be the catalyst for this process.³³ Indeed, pre-mixing $\mathbf{6.1^{OTf}}$ and HBpin (1.1 equiv.) in benzene- d_6 (which do not react), followed by the addition of PhCHO (1.1 equiv.) leads to complete consumption of the aldehyde, with accompanying formation of one equivalent of PhCH₂OBpin. The rate of this reaction (under these stoichiometric conditions) is so fast that it is complete even before a ^1H NMR spectrum could be obtained. Moreover, it can be shown that $\mathbf{6.1^{OTf}}$ (at 1 mol% loading) catalyses the reduction of benzaldehyde (in my hands) with comparable, or even better activity to $\mathbf{3.4^{OTf}}$ (Figure 6.15).ⁱ Therefore, a series of studies were undertaken in order to elucidate how $\mathbf{6.1^{OTf}}$ might catalyse this process.

ⁱ In my hands the activity of $\mathbf{3.4^{OTf}}$ was found to be somewhat lower than that reported by Yang *et al.*²⁶

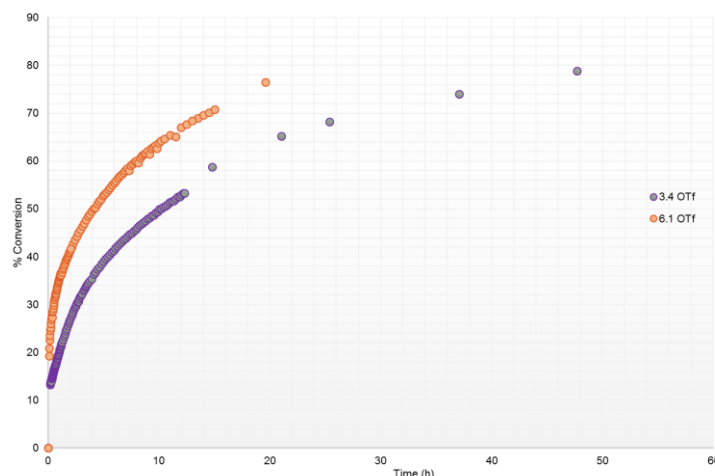
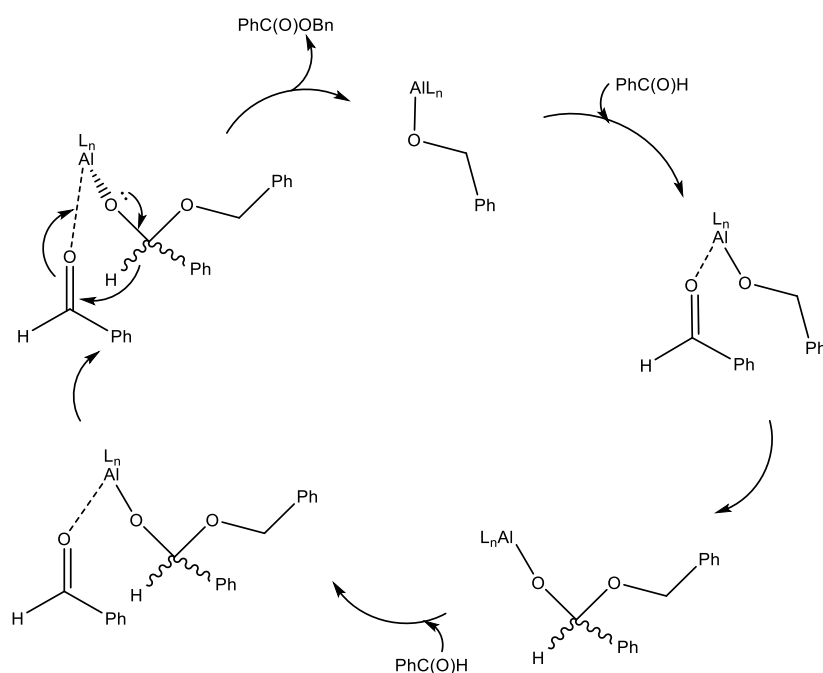


Figure 6.15: A plot of % conversion vs. time for the catalytic reduction of benzaldehyde, catalysed by **3.4^{OTf}** and **6.1^{OTf}**.

6.4.3.3 Aluminium complexes: catalysts for the Tishchenko reaction

During the course of this study, it was demonstrated that Nacnac-ligated aluminium hydrides act as pre-catalysts for the Tishchenko esterification reaction.⁵⁷ This reaction involves disproportionation of an aldehyde by a hydride shift from one molecule to another and typically operates in the presence of a Lewis acid catalyst. The catalytic dimerisation of aldehydes to yield the corresponding esters was first reported in 1887 utilising sodium alkoxide complexes as catalysts.⁵⁸ In 1906, it was demonstrated that aluminum alkoxides are superior to sodium alkoxides as catalysts for this reaction, due to their greater Lewis acidity and reduced basicity, which suppresses undesirable aldol side-reactions and hence promotes the Tishchenko reaction selectively.^{59,60} Since then, a range of aluminium catalysts have been developed to effect this transformation.^{61–68} In many cases, the structures of the catalyst precursors are considerably different compared with traditional aluminum alkoxides. However, it is generally considered that these pre-catalysts are converted into an active species of the form $[M]-OCH_2R$ through a reaction with the aldehydes. These active species function as an alkoxide transfer

agent and a Lewis acid.⁵⁸ It is typically considered that the Tishchenko reaction proceeds *via* the mechanism shown in Scheme 6.9.⁶⁹



Scheme 6.9: The proposed mechanism for the Tishchenko reaction, catalysed by aluminium alkoxides.

In the current study, the aluminium alkoxide complexes **6.1^R** (R = OTf, H, OCH₂Ph, Et), generated by the hydroalumination of benzaldehyde, are shown to catalyse the disproportionation of two further molecules of benzaldehyde at room temperature, selectively yielding benzylbenzoate. The ability of four of the aluminium alkoxide complexes, **6.1^R** (R = OTf, H, OCH₂Ph, Et), to catalyse this process was investigated further. In each case, a benzene-d₆ solution of benzaldehyde was charged with 2 mol% of the respective complex, and the progress of the reaction monitored by ¹H NMR spectroscopy (Figure 6.16). These reactions proceed selectively at room temperature to yield benzylbenzoate, albeit slowly and with relatively unimpressive turnover frequencies (Table 6.3).

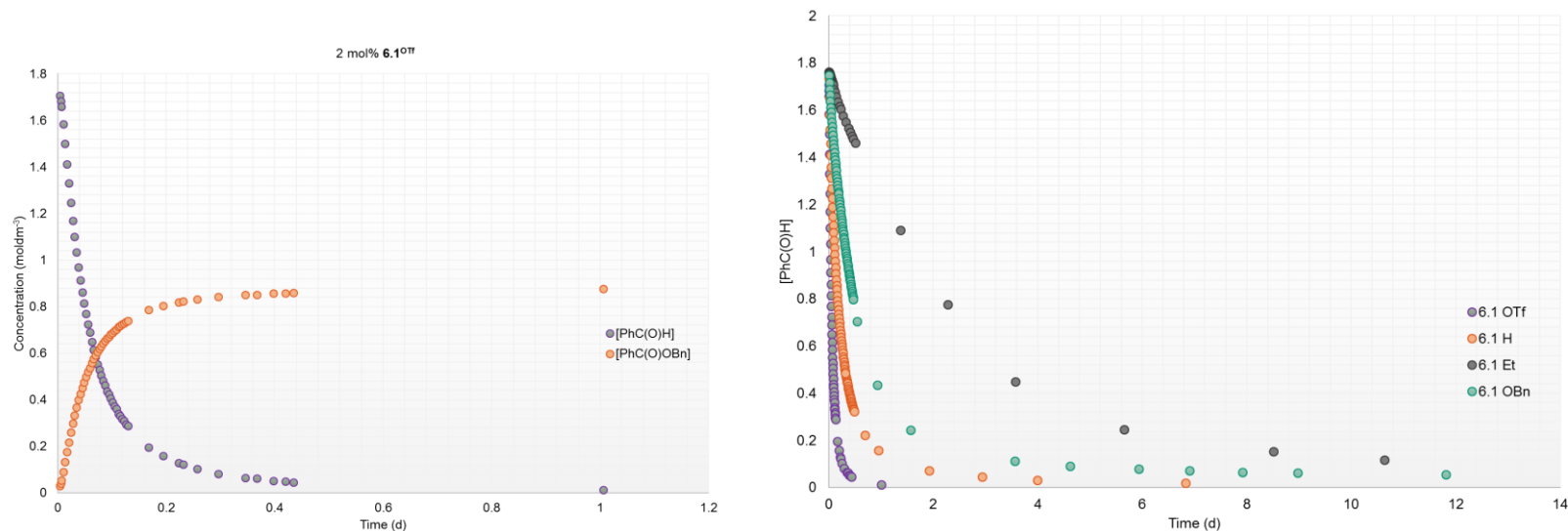


Figure 6.16: Left: A plot of $[\text{PhC(O)H}]$ and $[\text{PhC(O)OCH}_2\text{Ph}]$ *vs.* time for the Tishchenko disproportionation of benzaldehyde to form benzylbenzoate, catalysed by **6.1^{OTf}** ($T = 298\text{ K}$, $2\text{ mol\%}$). Right: A comparative plot of $[\text{PhC(O)H}]$ *vs.* time for this reaction catalysed by **6.1^R** ($2\text{ mol\%}$, $R = \text{OTf, H, OCH}_2\text{Ph, Et}$).

Catalyst	6.1^{OTf}	6.1^H	6.1^{OCH₂Ph}	6.1^{Et}
TOF (h^{-1})	2.08	0.30	0.10	0.06

Table 6.3: Turnover frequencies obtained for the Tishchenko disproportionation of benzaldehyde, catalysed by $[\text{Dipp}\mathbf{1}]\text{Al(R)(OCH}_2\text{Ph)}$ (**6.1^R**; $R = \text{OTf, H, OCH}_2\text{Ph, Et}$).

Chapter VI: Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms

It is typically considered that, in the case of sterically non-hindered aluminium alkoxide complexes, the turnover-limiting step of the catalysis is the hydride shift.⁵⁷ In this case the slow reactivity, and hence low turnover frequencies, may arise due to the sterically encumbered nature and coordinatively-saturated nature of the aluminium centres. Presumably, these features inhibit coordination and activation of the aldehyde equivalents, reducing reactivity.

The requirement for coordination of the aldehyde to the aluminium centre could be demonstrated for the current systems through the addition of one equivalent of a coordinating base, DMAP. The ¹H NMR spectrum of a reaction mixture containing **6.1^{Et}** and DMAP (1 equiv.) suggests that there exists no obvious interaction between the alkoxide and base. By contrast, the addition of one equivalent of DMAP to **6.1^{OTf}** demonstrates the ability of the triflate substituent to dissociate from the aluminium centre, in a similar manner to that observed in the formation of **6.3**. Undertaking of this catalysis in the presence of one equivalent of DMAP, employing **6.1^{OTf}** and **6.1^{Et}** as catalysts, leads to a considerable reduction in catalytic efficiency, consistent with the idea that precoordination of the aldehyde substrate is necessary to facilitate this reactivity.

% aldehyde consumption	6.1^{OTf}	6.1^{OTf}/DMAP	6.1^{Et}	6.1^{Et}/DMAP
24 h	100%	42%	35%	6%
1 week	-	81%	90%	50%

Table 6.4: The presence of a competing Lewis base, DMAP, leads to a significant reduction in the ability of **6.1^{OTf}** and **6.1^{Et}** to catalyse the Tishchenko reaction.

$[[^{\text{Dipp}}\mathbf{1}]\text{Al}(\text{DMAP})(\text{OCH}_2\text{Ph})][\text{OTf}]$ (**6.6**) could be crystallised from a benzene solution at room temperature and characterised by standard spectroscopic/analytical techniques together with single crystal X-ray diffraction (Figure 6.17). The molecular structure of

6.6 is closely related to that of **6.3** and displays the clear displacement of the triflate substituent by DMAP at the aluminium centre. The Al-N_{DMAP} distance, which is longer than the endocyclic Al-N distances supporting the assertion that this is a donor interaction, is marginally shorter than that of **6.3** ($d(\text{Al-N}_{\text{DMAP}})$ 1.9098(13) Å), consistent with the greater Lewis acidity that arises from the replacement of a hydride substituent with an electronegative alkoxide substituent.

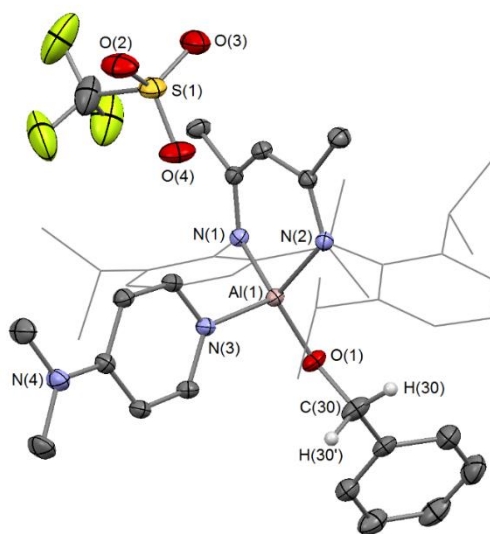


Figure 6.17: Molecular structure of $[[\text{Dipp}]\mathbf{1}]\text{Al}(\text{DMAP})(\text{OCH}_2\text{Ph})[\text{OTf}]$ (**6.6**) as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level. Hydrogen atoms omitted and Dipp groups shown in wireframe for clarity. Key bond lengths (Å) and angles (°): Al(1)-O(1) 1.6934(12), Al(1)-N(1) 1.8729(13), Al(1)-N(2) 1.8741(13), Al(1)-N(3) 1.9007(13), O(1)-C(30) 1.416(2), N(1)-Al(1)-N(2) 99.25(6), O(1)-Al(1)-N(3) 110.06(6), C(30)-O(1)-Al(1) 134.85(11). Distance of Al(1) from least-squares C_3N_2 plane: 0.5 Å.

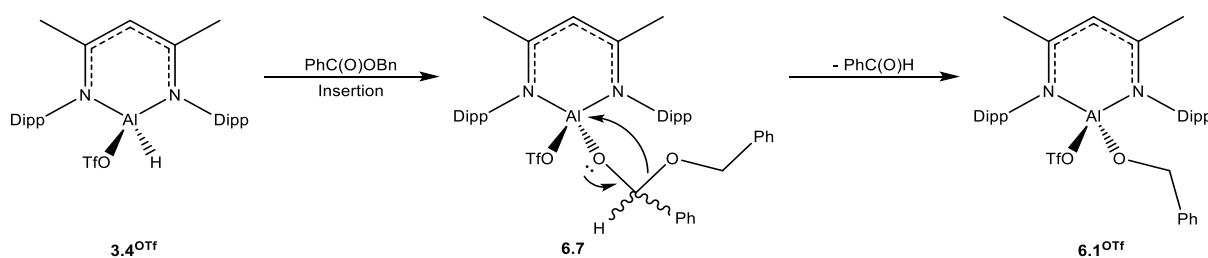
The displacement of the triflate substituent by DMAP is accompanied by an upfield shift of the resonance associated with the γ -H from $\delta_{\text{H}} = 5.00$ ppm (for **6.1^{OTf}**) to $\delta_{\text{H}} = 5.76$ ppm. At room temperature, the resonance associated with the DMAP ligand are very broad. Variable temperature analysis allowed for the calculation of the approximate barriers associated with the fluxional processes exhibited. An approximate barrier of

$\Delta G^\ddagger = 60.7 \text{ kJ mol}^{-1}$ was calculated for rotation around the Al-N_{DMAP} bond (based on the coalescence temperatures for the *o*-CH (T_c 318 K) and *m*-CH (T_c 320 K) resonances of the DMAP ligand). This barrier is marginally higher than that observed for **6.3** ($\Delta G^\ddagger = 40.5 \text{ kJ mol}^{-1}$), consistent with the more sterically encumbered aluminium centre which hinders the rotation. Additionally, the barrier for dissociation (and reassociation) of the DMAP ligand was calculated to be $\Delta G^\ddagger = 72.0 \text{ kJ mol}^{-1}$, based on the coalescence temperature for the Dipp methine resonance (T_c 367 K). In accordance with the greater Lewis acidity of the aluminium centre of **6.6**, resulting in a tighter binding of the DMAP ligand, this barrier is greater than that observed for **6.3** ($\Delta G^\ddagger = 57.7 \text{ kJ mol}^{-1}$).

6.4.3.4 Does the Tishchenko reaction play a role in the catalytic cycle?

We sought to understand whether the Tishchenko chemistry, and in particular the hemi-acetal intermediate, [Dipp¹Al(OTf)(OCH(Ph)OCH₂Ph)] (**6.7**) formed *via* alkoxide transfer from **6.1**^{OTf} to a further equivalent of benzaldehyde, might play a role in the catalytic transformation of benzaldehyde into the corresponding pinacolborate ester. The isolation of this intermediate was attempted *via* the addition of one equivalent of benzaldehyde to **6.1**^{OTf}. However, this reaction leads immediately to the selective formation of PhC(O)OCH₂Ph suggesting that **6.7** is unstable in the presence of benzaldehyde. An alternative route proposed for the formation of **6.7** involves the hydroalumination of PhC(O)OCH₂Ph by **3.4**^{OTf}. While **3.4**^{OTf} does indeed react with PhC(O)OCH₂Ph (1.2 equiv.) over the course of 10 days at room temperature, the sole product formed is **6.1**^{OTf}, leaving unreacted ester. It is proposed that **6.1**^{OTf} is formed *via* insertion of the carbonyl functionality of PhC(O)OCH₂Ph into the Al-H bond of **3.4**^{OTf}, therefore forming **6.7**. However, it is apparent that **6.7** can undergo rapid elimination of benzaldehyde to form **6.1**^{OTf} (Scheme 6.10). The liberated benzaldehyde reacts rapidly

with a further equivalent of **3.4^{OTf}**, thereby leaving 50% unreacted ester. Undertaking of this reaction in presence of HBpin yields no PhCH₂OBpin. In light of this, we suggest that it is likely that an intermediate of the form **6.7** is not relevant to the mechanism for the catalytic reduction of aldehydes/ketones.



Scheme 6.10: The reaction of **3.4^{OTf}** is suggested to yield **6.7**, which rapidly undergoes elimination of benzaldehyde.

6.5 Conclusion

The work in this chapter demonstrates that the hydroalumination of benzaldehyde may be effected by a range of Nacnac-ligated aluminium hydrides, albeit at significantly reduced rates compared to that of **3.4^{OTf}**. Whilst it was established in Chapter 4 that a range of Nacnac-ligated gallium hydrides are amenable to CO₂ insertion, their ability to hydrogallate aldehydes is significantly more limited; only one gallium hydride, [Dipp₁]**GaH₂**, was found to be reactive towards benzaldehyde, albeit under particularly forcing conditions. It is proposed that the propensity of these group 13 hydrides to hydrometallate aldehydes depends on (i) the Lewis acidity of the metal centre (for pre-coordination of the aldehyde) and (ii) the polarity of the M-H bond. Although Ga-O/B-H metathesis to regenerate the gallane was found to be rapid, the failure of these hydrides to effect the initial activation of the carbonyl substrate restricts their use in a catalytic manner.

Chapter VI: Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms

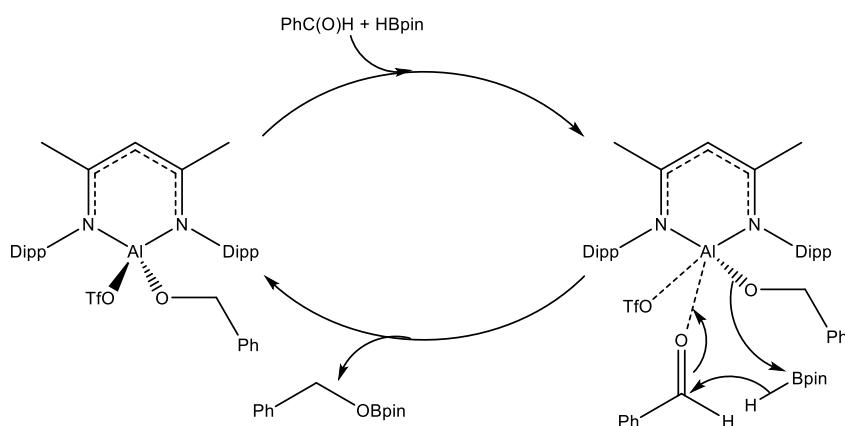
In agreement with the work reported in Chapter 2, no evidence could be found for the key Al-O/B-H metathesis step proposed in the catalytic cycle. Moreover, the reaction of **3.4^{OTf}** (and related hydrides) with PhCH₂OBpin was demonstrated to proceed in a spontaneous manner, showing that the thermodynamic basis of the Al-O/B-H metathesis is unfavourable under the conditions comparable to those used in catalytic runs.

This caused us to re-examine the mechanism previously reported for the reduction of benzaldehyde and question whether **6.1^{OTf}** is chemically competent as an intermediate within this process. Thus, we investigated the potential of mechanisms which avoid the deep thermodynamic well associated with Al-O formation, including those that involve initial activation of the borane by **3.4^{OTf}**. It was demonstrated that the aluminium alkoxide complex **6.1^{OTf}** is in fact capable of catalysing the hydroboration of benzaldehyde, thereby suggesting that aluminium hydride **3.4^{OTf}** merely acts as a precatalyst for this process. Moreover, it was shown that **6.1^{OTf}** can activate aldehydes and operate as a Lewis acid catalyst for the Tishchenko esterification reaction. Whilst it was determined that this Tishchenko chemistry is *not* relevant to the mechanism for the catalytic reduction of aldehydes/ketones, it is suggested that this activation of benzaldehyde by the Lewis acidic aluminium centre of **6.1^{OTf}** is likely to play a key role in this borane-mediated reduction chemistry.

Therefore, while the hydroboration of carbonyl functionalities can be effected by gallium systems based on an inner-sphere mechanism involving insertion and Ga-O/B-H metathesis steps, related aluminium hydride catalysts are irreversibly deactivated by Al-O bond formation. Turnover is proposed instead to proceed *via* an outer-sphere process which avoids net cleavage of the strong Al-O bond. This might involve pre-coordination of the carbonyl substrate at aluminium (which may involve

Chapter VI: Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms

dissociation of the triflate substituent from the aluminium centre), followed by a concerted reaction with HBpin and **6.1^{OTf}** to yield PhCH₂OBpin and regenerate **6.1^{OTf}** (Scheme 6.11). Further studies are however required to elucidate the mechanism by which this proceeds.



Scheme 6.11: One mechanism postulated for the hydroboration of benzaldehyde, catalysed by **6.1^{OTf}**.

6.6 References

- (1) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. *Acc. Chem. Res.* **2015**, *48* (7), 1995–2003.
- (2) Magano, J.; Dunetz, J. R. *Organic Process Research and Development.* **2012**, *16* (6), 1156–1184.
- (3) Cho, B. T. *Chem. Soc. Rev.* **2009**, *38* (2), 443–452.
- (4) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30* (2), 97–102.
- (5) Mäki-Arvela, P.; Hájek, J.; Salmi, T.; Murzin, D. Y. *Applied Catalysis.* **2005**, *292* (1-2), 1–49.
- (6) Koren-Selfridge, L.; Query, I. P.; Hanson, J. A.; Isley, N. A.; Guzei, I. A.; Clark, T. B. *Organometallics* **2010**, *29* (17), 3896–3900.
- (7) Khalimon, A. Y.; Farha, P.; Kuzmina, L. G.; Nikonov, G. I. *Chem. Commun.* **2012**, *48* (3), 455–457.
- (8) Almqvist, F.; Torstensson, L.; Gudmundsson, A.; Frejd, T. *Angew. Chem. Int. Ed. Engl.* **1997**, *36* (4), 376–377.
- (9) Giffels, G.; Dreisbach, C.; Kragl, U.; Weigerding, M.; Waldmann, H.; Wandrey, C. *Angew. Chem. Int. Ed. Engl.* **1995**, *34* (18), 2005–2006.
- (10) Oluyadi, A. A.; Ma, S.; Muhoro, C. N. *Organometallics* **2013**, *32* (1), 70–78.
- (11) Lindsley, C. W.; DiMare, M. *Tetrahedron Lett.* **1994**, *35* (29), 5141–5144.
- (12) Chong, C. C.; Kinjo, R. *ACS Catal.* **2015**, *5* (6), 3238–3259.
- (13) King, A. E.; Stieber, S. C. E.; Henson, N. J.; Kozimor, S. A.; Scott, B. L.; Smythe, N. C.; Sutton, A. D.; Gordon, J. C. *Eur. J. Inorg. Chem.* **2016**, *2016* (11), 1635–1640.
- (14) Arrowsmith, M.; Hadlington, T. J.; Hill, M. S.; Kociok-Köhn, G. *Chem. Commun.* **2012**, *48* (38), 4567–4569.
- (15) Mukherjee, D.; Ellern, A.; Sadow, A. D. *Chem. Sci.* **2014**, *5* (3), 959–964.
- (16) Weetman, C.; Hill, M. S.; Mahon, M. F. *Chem. Commun.* **2015**, *51* (77), 14477–14480.
- (17) Weetman, C.; Anker, M. D.; Arrowsmith, M.; Hill, M. S.; Kociok-Köhn, G.; Liptrot, D. J.; Mahon, M. F. *Chem. Sci.* **2016**, *7* (1), 628–641.
- (18) Fohlmeister, L.; Stasch, A. *Chem. Eur. J.* **2016**, *22* (29), 10235–10246.
- (19) Barman, M. K.; Baishya, A.; Nembenna, S.; Kociok-Koehn, G.; Edwards, A. J.; McIntyre, G. J.; Lemaire,

Chapter VI: Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms

- M.; Pudalov, N. J.; Knapp, S. M. M.; Chianese, A. R. *Dalton Trans.* **2017**, 46 (13), 4152–4156.
- (20) Chong, C. C.; Hirao, H.; Kinjo, R. *Angew. Chem. Int. Ed.* **2015**, 54 (1), 190–194.
- (21) Blake, A. J.; Cunningham, A.; Ford, A.; Teat, S. J.; Woodward, S. *Chem. Eur. J.* **2000**, 6 (19), 3586–3594.
- (22) Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. J. *Am. Chem. Soc.* **2014**, 136 (8), 3028–3031.
- (23) Mukherjee, D.; Shirase, S.; Spaniol, T. P.; Mashima, K.; Okuda, J. *Chem. Commun.* **2016**, 52 (89), 13155–13158.
- (24) Bisai, M. K.; Pahar, S.; Das, T.; Vanka, K.; Sen, S. S. *Dalton Trans.* **2017**, 46 (8), 2420–2424.
- (25) Li, W.; Ma, X.; Walawalkar, M. G.; Yang, Z.; Roesky, H. W. *Coord. Chem. Rev.* **2017**, 350, 14–29.
- (26) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, 54 (35), 10225–10229.
- (27) Jakhar, V. K.; Barman, M. K.; Nembenna, S. *Org. Lett.* **2016**, 18 (18), 4710–4713.
- (28) Keyes, L. K.; Todd, A. D. K.; Giffin, N. A.; Veinot, A. J.; Hendsbee, A. D.; Robertson, K. N.; Geier, S. J.; Masuda, J. D. *RSC Adv.* **2017**, 7 (59), 37315–37323.
- (29) Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S. Z. *Anorg. Allg. Chem.* **2016**, 642 (22), 1245–1250.
- (30) Pollard, V. A.; Orr, S. A.; McLellan, R.; Kennedy, A. R.; Hevia, E.; Mulvey, R. E. *Chem. Commun.* **2018**, 54 (10), 1233–1236.
- (31) Bismuto, A.; Cowley, M. J.; Thomas, S. P. *ACS Catal.* **2018**, 8 (3), 2001–2005.
- (32) Prashanth, B.; Bhandari, M.; Ravi, S.; Shamasundar, K. R.; Singh, S. *Chem. Eur. J.* **2018**, 24 (19), 4794–4799.
- (33) Liu, Y.; Liu, X.; Liu, Y.; Li, W.; Ding, Y.; Zhong, M.; Ma, X.; Yang, Z. *Inorg. Chim. Acta* **2018**, 471, 244–248.
- (34) Abdalla, J. A. B.; Riddlestone, I. M.; Tirfoin, R.; Aldridge, S. *Angew. Chem. Int. Ed.* **2015**, 54 (17), 5098–5102.
- (35) Downs, A. J.; Himmel, H. J. in *The Group 13 Metals Aluminium, Gallium, Indium and Thallium; Chemical Patterns and Peculiarities* (Eds.: S. Aldridge, A. J. Downs) Wiley, Chichester, UK.
- (36) Cui, C.; Roesky, H. W.; Hao, H.; Schmidt, H. G.; Noltemeyer, M. *Angew. Chem. Int. Ed.* **2000**, 39 (10), 1815–1817.
- (37) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, (21), 2832–2838.
- (38) Singh, S.; Ahn, H.-J.; Stasch, A.; Jancik, V.; Roesky, H. W.; Pal, A.; Biadene, M.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H. G. *Inorg. Chem.* **2006**, 45 (4), 1853–1860.
- (39) Turner, J.; Abdalla, J. A. B.; Bates, J. I.; Tirfoin, R.; Kelly, M. J.; Phillips, N.; Aldridge, S. *Chem. Sci.* **2013**, 4 (11), 4245–4250.
- (40) Singh, S.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Inorg. Chem.* **2006**, 45 (3), 949–951.
- (41) Köster, R.; Tsay, Y. H.; Krüger, C.; Serwatowski, J. *Chem. Ber.* **1986**, 119 (4), 1174–1188.
- (42) Piers, W. E.; Marwitz, A. J. V.; Mercier, L. G. *Inorg. Chem.* **2011**, 50 (24), 12252–12262.
- (43) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, 77 (2), 263–293.
- (44) Hubbard, J. L.; Kramer, G. W. *J. Organomet. Chem.* **1978**, 156 (1), 81–94.
- (45) Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A. *Organometallics* **2007**, 26 (16), 4076–4079.
- (46) Spielmann, J.; Harder, S. *Chem. Eur. J.* **2007**, 13 (32), 8928–8938.
- (47) Babón, J. C.; Esteruelas, M. A.; Fernández, I.; López, A. M.; Oñate, E. *Inorg. Chem.* **2018**, 57, 4482–4491.
- (48) Montiel-Palma, V.; Lumbierres, M.; Donnadiou, B.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **2002**, 124 (20), 5624–5625.
- (49) Choi, J. H.; Schloerer, N. E.; Berger, J.; Precht, M. H. G. *Dalton Trans.* **2014**, 43 (1), 290–299.
- (50) Gunanathan, C.; Hölscher, M.; Pan, F.; Leitner, W. *J. Am. Chem. Soc.* **2012**, 134 (35), 14349–14352.
- (51) Xi, Y.; Hartwig, J. F. *J. Am. Chem. Soc.* **2017**, 139 (36), 12758–12772.
- (52) Press, L. P.; Kosanovich, A. J.; McCulloch, B. J.; Ozerov, O. V. *J. Am. Chem. Soc.* **2016**, 138 (30), 9487–9497.
- (53) Hebden, T. J.; Denney, M. C.; Pons, V.; Piccoli, P. M. B.; Koetzle, T. F.; Schultz, A. J.; Kaminsky, W.; Goldberg, K. I.; Heinekey, D. M. *J. Am. Chem. Soc.* **2008**, 130 (32), 10812–10820.
- (54) Hatanaka, T.; Ohki, Y.; Tatsumi, K. *Chem. Asian J.* **2010**, 5 (7), 1657–1666.
- (55) Chakraborty, S.; Zhang, J.; Patel, Y. J.; Krause, J. A.; Guan, H. *Inorg. Chem.* **2013**, 52 (1), 37–47.
- (56) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2012**, 51 (7), 1671–1674.
- (57) Tormakangas, O. P.; Koskinen, A. M. P. *Recent Res. Dev. Org. Chem.* **2001**, 5 (1), 225–255.
- (58) Seki, T.; Nakajo, T.; Onaka, M. *Chem. Lett.* **2006**, 35 (8), 824–829.
- (59) Tischtenko, W. *J. Russ. Phys. Chem.* **1906**, 38 (355), 482.

Chapter VI: Catalytic reduction of aldehydes by aluminium and gallium hydride catalysts: inner sphere vs outer sphere mechanisms

- (60) Tischenko, W. *Chem. Zvesti* **1906**, 77 (1), 1554.
- (61) Maruoka, K. *Catal. Today* **2001**, 66 (1), 33–45.
- (62) Ooi, T.; Ohmatsu, K.; Sasaki, K.; Miura, T.; Maruoka, K. *Tetrahedron Lett.* **2003**, 44 (15), 3191–3193.
- (63) Ooi, T.; Miura, T.; Takaya, K.; Maruoka, K. *Tetrahedron Lett.* **1999**, 40 (43), 7695–7698.
- (64) Hon, Y. S.; Chang, C. P.; Wong, Y. C. *Tetrahedron Lett.* **2004**, 45 (16), 3313–3315.
- (65) Mascarenhas, C. M.; Duffey, M. O.; Liu, S. Y.; Morken, J. P. *Org. Lett.* **1999**, 1 (9), 1427–1429.
- (66) Simpura, I.; Nevalainen, V. *Tetrahedron* **2003**, 59 (38), 7535–7546.
- (67) Han, H. F.; Zhang, S. F.; Guo, Z. Q.; Tong, H. B.; Wei, X. H. *J. Clust. Sci.* **2015**, 26 (6), 1971–1982.
- (68) Guo, Z.; Wang, S.; Wei, X. *J. Organomet. Chem.* **2016**, 818, 115–122.
- (69) Ogata, Y.; Kawasaki, A.; Kishi, I. *Tetrahedron* **1967**, 23 (2), 825–830.