

Geometry Constrained Main-Group Compounds for The Activation of Small Molecules



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Abstract

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A series of base-supported group 13 complexes bearing *N,N*-bis(3,5-di-*tert*-butyl-2-phenolate)amide pincer ligand, $(\text{ONO})^{3-}$, are reported ($\text{E}(\text{ONO})\cdot\text{L}$ ($\text{E} = \text{B}, \text{Al}, \text{Ga}$; L = Lewis base). $\text{B}(\text{ONO})$ type compounds were formed *in-situ* and are capable of THF activation. Alternatively, a NMe_3 stabilised boron compound was shown to activate the O–H bond of water and ethanol via frustrated Lewis pair (FLP) type reactivity. The aluminium analogue of $\text{E}(\text{ONO})\cdot\text{L}$ displays a bimetallic structure in its molecular structure and was shown to be capable of O–H bond cleavage of ethanol across the Al–N bond. Finally, a neutral gallium hydride species, $\text{Ga}(\text{H})\{\text{ON}(\text{H})\text{O}\}$, was synthesised which is capable of activating aldehydes to form gallium alkoxide compounds. These alkoxide compounds could be employed as an active catalyst for the hydroboration with benzaldehyde.

Group 14 geometrically constrained anionic compounds, $[\text{E}(\text{ONO})]^-$ ($\text{E} = \text{Ge}, \text{Sn}$), can be prepared via a two-step process. In the case of $[\text{Ge}(\text{ONO})]^-$, it undergoes facile addition of water and ethanol to form trigonal bipyramidal germanium(IV) complexes. In the case of $[\text{Sn}(\text{ONO})]^-$, it undergoes a transmetallation reaction with gallium chloride allowing to access a bimetallic $\{\text{Ga}(\text{ONO})\cdot\text{THF}\}_2$ complex. In addition, four novel neutral constrained geometry group 14 species bearing a xanthene based ligand framework, $\text{E}(\text{NON})$, are also reported. The LUMOs of such species are chemically accessible using KO^tBu .

The arsenic analogue, $\text{As}(\text{ONO})$, was prepared and shown that it exhibits no reactivity towards ammonia in contrast to its phosphorus analogue which gives rise to a phosphorus(V) complex, highlighting the increased stability of the +3 oxidation state on descending group

15, and the difficulty associated with accessing arsenic(V) complexes. The HOMO and LUMO of As(ONO) were accessible by KNu (Nu = O^tBu and NPh₂) and ROTf (R = H, Me), respectively. In addition, we report the synthesis of a phosphorus(III) complex bearing the 2,2'-[iminobis(methylene)]-bis[4-methoxy-phenol] ligand, (P(ONO*)), which undergoes hydrolysis reactions. The lone pair on phosphorus was accessible using borane to afford Lewis acid–base adducts.

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List of abbreviations

$\{^1\text{H}\}$	^1H decoupled
$(\text{ONO})^{3-}$	<i>N,N</i> -bis-(3,5-di- <i>tert</i> -butyl-2-phenolate)amide
$(\text{ONO}^*)^{3-}$	2,2'-[iminobis(methylene)]-bis[4-methoxy-phenolate]
18-crown-6	1,4,7,10,13,16-hexaoxacycloocatadecane, $\text{C}_{12}\text{H}_{24}\text{O}_6$
2,2,2-crypt	4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, $\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$
Å	Ångström
AAC	Alkyl-amino carbene
Ad	1,3-bis(adamantly)imadozol-2-ylidene
Anal.	elemental analysis
Ar	aryl
atm	atmosphere
benzene	C_6H_6
br	broad
butyl	C_4H_9
BPh_3	triphenylboron
Bz	benzyl

°C	degrees Celsius
cAAC	cyclic alkyl-amino carbene
Calcd	calculated
CCD	charge-coupled device
CSD	Cambridge Structural Database
Cy	cyclohexyl
d	doublet
d_n	deuterated with n deuterium atoms
DABCO	1,4-diazabicyclo[2.2.2]octane
DCM	dichloromethane, CH ₂ Cl ₂
DFT	density functional theory
dioxane	1,4-dioxane, C ₄ H ₈ O ₂
diethyl ether	Et ₂ O
Dipp	2,6-diisopropylphenyl
DMAP	4-(dimethylamino)pyridine
$\epsilon_a - \epsilon_d$	orbital energy difference between acceptor and donor
EI MS	electron impact mass spectrometry
ESI MS	electrospray ionisation mass spectrometry

Et	ethyl, CH_2CH_3
EtOH	ethanol
eV	electronvolt
FLP	frustrated Lewis pair
g	gram
h	hour
H_2	dihydrogen
H_2O	water
$\text{H}_3\text{B}\cdot\text{NH}_3$	ammonia borane
$\text{H}_3\text{B}\cdot\text{PPh}_3$	triphenylphosphine borane
$\text{H}_3\text{B}\cdot\text{NHMe}_2$	dimethylamine borane
$\text{H}_3\text{B}\cdot\text{SMe}_2$	dimethylsulfide borane
HBpin	pinacolborane
HCat	catecholborane
hexane	C_6H_{14}
HMDS	hexamethyldisilylamide, $\text{N}(\text{SiMe}_3)_2$
HOMO	highest occupied molecular orbital
Hz	Hertz

I	nuclear angular momentum quantum number
^iPr	isopropyl
IPr	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, $:\text{C}(\text{N}(\text{Dipp}))_2(\text{CH})_2$
I^tBu	1,3-bis(<i>tert</i> -butyl)imidazol-2-ylidene, $:\text{C}(\text{N}(\text{}^t\text{Bu}))_2(\text{CH})_2$
J	Joule
J	coupling constant
k	kilo
K	Kelvin
$\text{K}\alpha$	radiation emitted on transition of an electron from an L shell to K shell
KC_8	potassium graphite
KO^tBu	potassium <i>tert</i> -butoxide
L	litre
LiAlH_4	aluminium hydride
LUMO	lowest unoccupied molecular orbital
m	milli or metre or multiplet
M	mega or molar, mol dm^{-3}
m/z	mass to charge ratio
Me	methyl, CH_3

MeOTf	methyl trifluoromethanesulfonate
Mes	2,4,6-trimethylphenyl
min	minute
mol	mole
n	principal quantum number
nacnac	β -diketiminato
nacnac*	deprotonated β -diketiminato
n	nano
NH ₃	ammonia
ⁿ Bu	normal butyl, CH ₂ CH ₂ CH ₂ CH ₃
NHC	N-heterocyclic carbene
NMe ₃	trimethylamine
NMR	nuclear magnetic resonance
(NON) ²⁻	xanthene-4,5-diamide
OTf	triflate, [CF ₃ SO ₃] ⁻
Ph	phenyl, C ₆ H ₅
ppm	parts per million
propyl	C ₃ H ₇

py	pyridine, C ₅ H ₅ N
[PyH][OTf]	pyridinium trifluoromethanesulfonate
q	quartet
PPh ₃	triphenylphosphine
R	hydrocarbonyl ligand
<i>r</i>	radius
rt	room temperature
s	singlet
SIDep	1,3-bis(diethylphenyl)-4,5-di-hydroimidazol-2-ylidene
t	triplet
^t Bu	tertiary butyl, C(CH ₃) ₃
<i>tert</i>	tertiary
THF	tetrahydrofuran, C ₄ H ₈ O
δ	chemical shift
Δ	difference or heating
γ	gyromagnetic or magnetogyric ratio
Σ	sum
μ	micro or bridging ligand

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Chapter 1

Introduction

1.1 The emergence of main-group compound catalysts

Controlled activation of small molecules, such as dihydrogen (H_2) and ammonia (NH_3), is highly desirable, as these substrates can serve as abundant and inexpensive precursors for the synthesis of more complex chemicals.¹ Activation of these small molecule substrates is challenging because of high activation energy barriers.² Precious metals possess valence d-orbitals that are relatively close in energy, allowing them to readily cycle between their n and $n+2$ oxidation states.³ This allows them to access a reversible redox mechanism, commonly known as oxidative addition and reductive elimination. These processes have been well investigated over the past decades and precious metals are commonly used as catalysts in the synthesis of many chemicals on an industrial scale.^{4–7} However, most transition metals, particularly precious metals, are typically expensive, rare and often toxic. Therefore, finding abundant main-group alternatives suitable for catalysis is highly desirable.

However, main-group complexes often have large HOMO–LUMO gaps, and their valence p-orbitals are far apart in energy, therefore unavailable for small molecule activation.² Recent studies have focused on manipulating main-group systems to narrow the HOMO–LUMO gaps and exhibit similar frontier orbitals to that of precious metal complexes. As a result, these systems are capable of reacting with small molecule substrates.^{2,8,9}

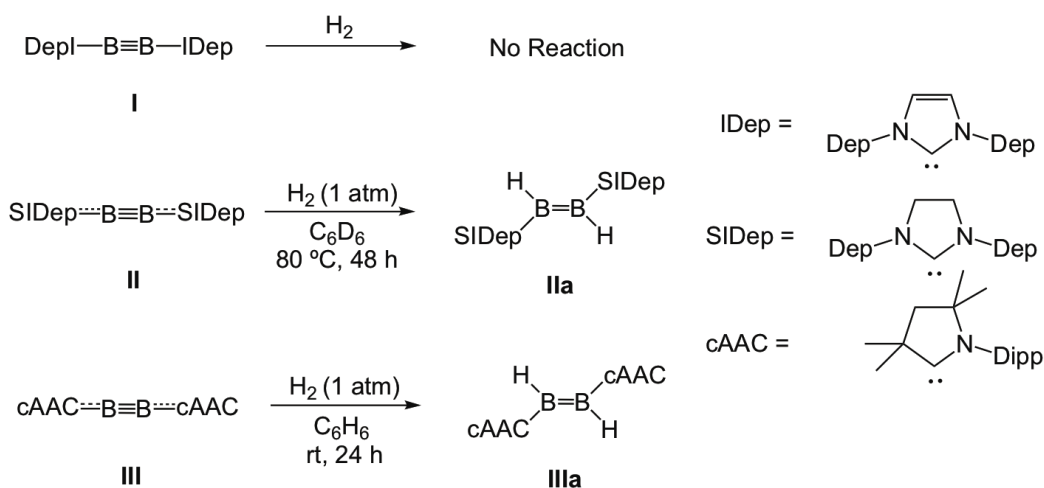
While H–H bond cleavage has been well studied with precious metals, polar X–H bond activation, such as the N–H bond in ammonia, is often difficult for precious metals as they favour formation of Lewis acid–base adducts owing to their Lewis acidity.^{10–12} To date, there are only a limited number of transition metal using pincer ligands have demonstrated the ability to activate X–H bonds.¹³

In this chapter, an overview of main-group compounds that are capable of activating small molecule substrates possessing X–H bonds (X = H, N or O) is provided.

1.2 Small molecule activation by compounds featuring low-valent main-group elements

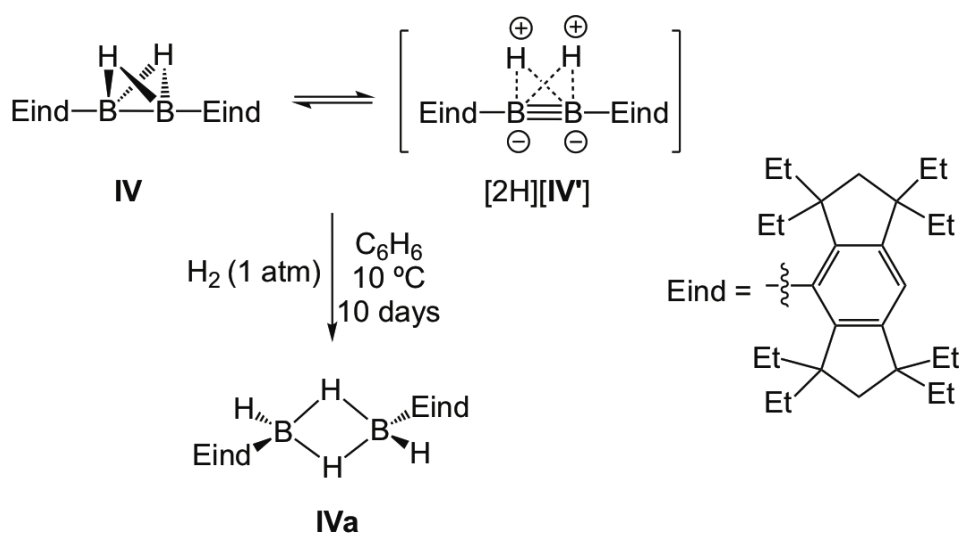
1.2.1 Small molecule activation with low-valent boron compounds

Systems containing group 13 elements have been shown to be reactive towards small molecules, their high electrophilicity and empty p-orbitals act as a site for initial coordination. Braunschweig has investigated the hydrogenation of a series of diborynes (**I**–**III**) stabilised by different N-heterocyclic carbenes (NHCs) and cyclic alkyl-amino carbenes (cAACs). These species have two boron atoms in a formal +1 oxidation state, which in the presence of H₂ are oxidised to the +2 oxidation state. Comparing the reactivity of the diborynes shows that a subtle trend of electronic and steric factors is in play when it comes to H–H bond activation. While the unsaturated NHC stabilised **I** showed no reaction towards H₂, the more π -accepting saturated NHC stabilised **II** reacted slowly with H₂ at elevated temperatures to give **IIa**. In contrast, a strongly π -accepting and less sterically demanding cAAC stabilised diboryne **III** allows for facile H₂ addition at room temperature to give **IIIa** (Scheme 1.1).¹⁴



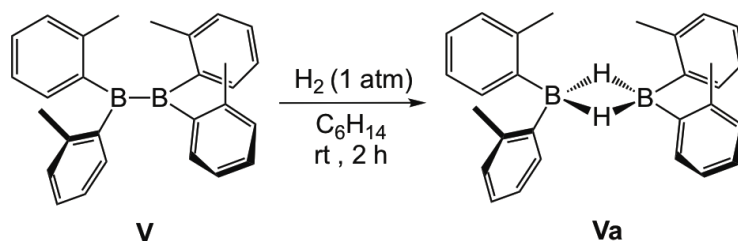
Scheme 1.1: Reactions of **I**–**III** with H₂.¹⁴

Tamao has reported a diborane (**IV**) stabilised by a bulky aryl group (Eind, see Scheme 1.2) which has C_{2v} symmetry through the B–B bond. The C_{2v} symmetry allows **IV** to have one B–B single bond and two B–H–B three-centre, two-electron (3c-2e) bonds which are thought to be related to a protonated diboryne dianion species, $[2H][IV']$. Single crystal X-ray diffraction studies reveal that **IV** shows B–B triple bond character as the corresponding bond length is 1.4879(7) Å which is shorter than the value of a B=B (1.56 Å) bond length. The theoretical studies show that **IV** possesses a π -symmetry HOMO and a π^* -symmetry LUMO at the boron centres. These frontier orbitals interact with the H_2 frontier orbitals to facilitate H_2 splitting. Experimentally, treatment of **IV** with 1 atm of H_2 very slowly converted into the hydrogen bridged diborane species, **IVa**, over the course of ten days (Scheme 1.2).¹⁵



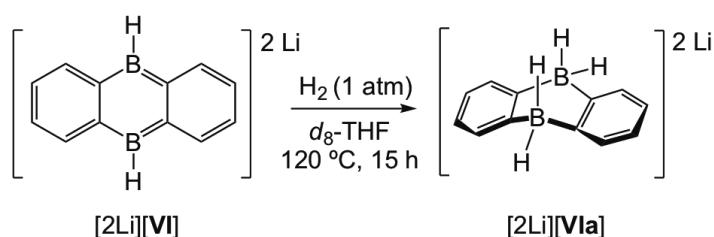
Scheme 1.2: Reaction of **IV** with H_2 .¹⁵

In line with the Tamao's diborane compound, Yamashita reported the synthesis of tetra(*o*-tolyl)diborane (**V**). Treatment of **V** with 1 atm of H_2 resulted in H–H and B–B bond cleavage to afford the di(*o*-tolyl)hydroborane compound (**Va**) (Scheme 1.3). The reactivity of **V** is attributed to the interaction between the frontier orbital of H_2 and two empty p-orbitals located at the two boron atoms which are parallel to each other.¹⁶



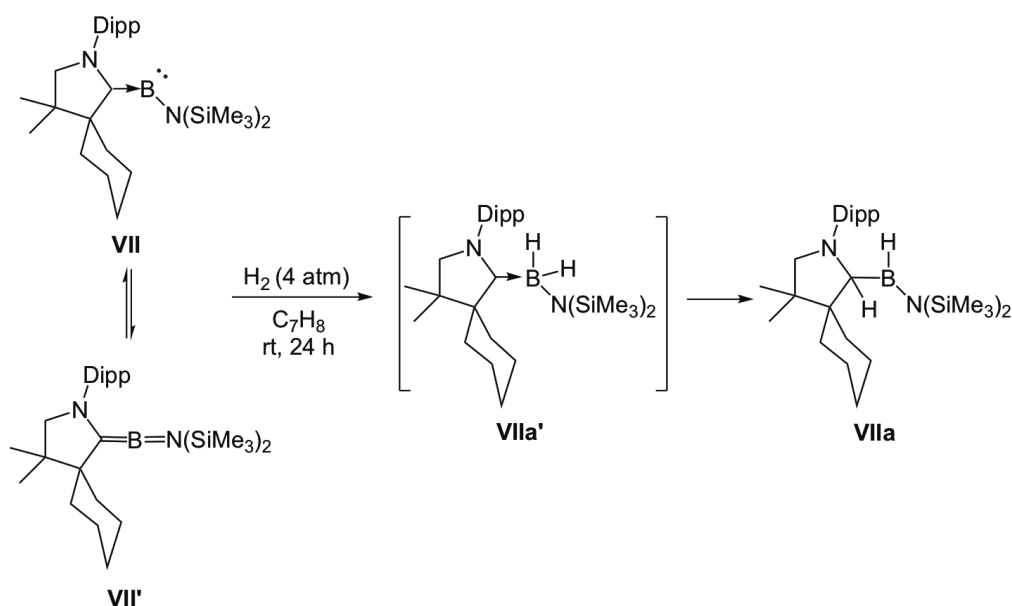
Scheme 1.3: Reaction of **V** with H_2 .¹⁶

In addition, Wagner has reported an ambiphilic aryl borane compound ($[2\text{Li}][\text{VI}]$) which contains two boron atoms separated by a rigid ligand framework. $[2\text{Li}][\text{VI}]$ was shown to convert into $[2\text{Li}][\text{VIa}]$ in the presence of 1 atm of H_2 after two days at 100 °C. DFT calculations at the DFT level of theory show that both H_2 frontier orbitals interact with the highly electrophilic boron p-orbitals at two boron atoms in **VI** to drive H_2 addition. Unfortunately, H_2 could not be liberated from $[2\text{Li}][\text{VIa}]$ under dynamic vacuum at 100 °C, and elevated temperatures revealed thermal decomposition. (Scheme 1.4).¹⁷



Scheme 1.4: Reaction of $[2\text{Li}][\text{VI}]$ with H_2 .¹⁷

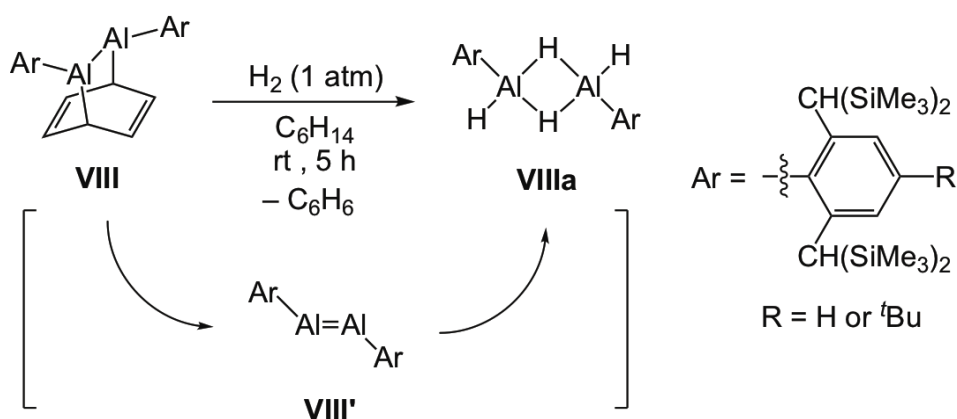
Bertrand and Stephan have jointly reported the isolation of a cAAC-aminoborylene adduct (**VII**) which displays an allenic configuration (**VII'**). The strongly π -donating amino- and silyl- substituents stabilise the electron deficient boron atom, while the strongly π -accepting cAAC ligand withdraws excessive electron density from the boron atom. Treatment of **VII** with 4 atm of H_2 gas formed a four-coordinate di-hydride boron species (**VIIa'**) ($\Delta G = -18 \text{ kcal}\cdot\text{mol}^{-1}$) which subsequently rearranged to a three-coordinate boron hydride species (**VIIa**) through 1,2-hydride migration ($\Delta G = -12 \text{ kcal}\cdot\text{mol}^{-1}$).¹⁸



Scheme 1.5: Reaction of **VII** with H_2 .¹⁸

1.2.2 Small molecule activation with low-valent aluminium compounds

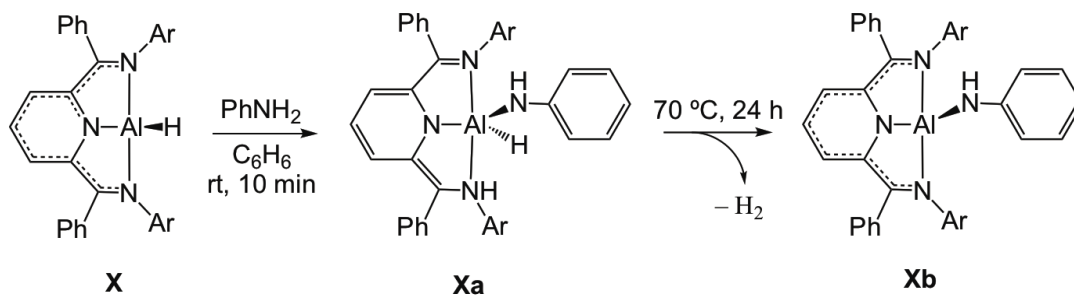
Tokitoh has synthesised a barrelene-type dialumane (**VIII**) which can be thought as a masked form of a 1,2-diaryldialumene (**VIII'**). When **VIII** was reacted with an excess of H_2 gas (1 atm), an equivalent of benzene was released and **VIII'** was formed via a reverse [2+4] cycloaddition. Subsequently, **VIII'** further reacted with two equivalents of H_2 to give the dihydroalumane product, **VIIIa**, which possess two terminal hydrides and two bridging hydrides (Scheme 1.6).¹⁹



Scheme 1.6: Reaction of **VIII** with H_2 .¹⁹

Prior to this work, Roesky reported the synthesis of an aluminium (I) species chelated to a β -diketiminato (nacnac) ligand (**IX**),²⁰ and Nikonov demonstrated that **IX** is capable of splitting a wide range of X–H bonds (X = H, N or O) to give four-coordinate aluminium(III) hydride products, **IXa–IXc** (Scheme 1.7). The HOMO of **IX** is mainly composed of the lone pair orbital of the aluminium atom and the LUMO is the π^* symmetry orbital of the ligand Al–N bond. This symmetry arrangement resembles to the frontier orbitals of the cAACs that are also capable of activating X–H bonds (see Section 1.2.5 for more details).²¹

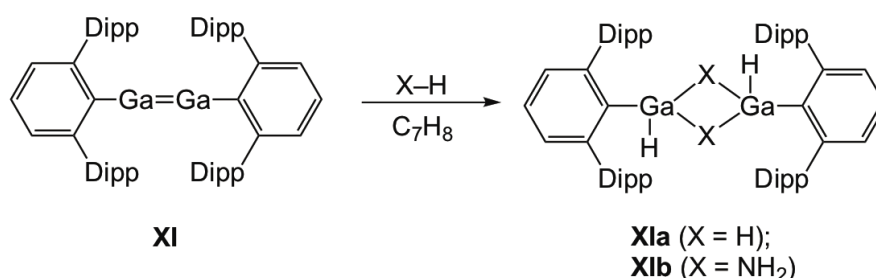
Scheme 1.7: Reactions of **IX** with selected small molecules substrates.²¹



Scheme 1.8: Reaction of **X** with aniline.²²

1.2.3 Small molecule activation with low-valent gallium compounds

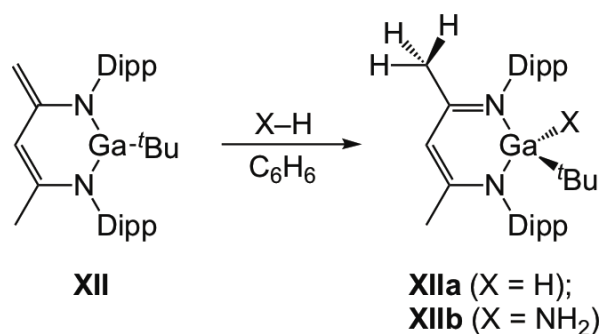
In 2008, Power reported a digallane species, **XI**, featuring gallium in the +1 oxidation state. Treatment of **XI** with 1 atm of H_2 in solution at room temperature resulted in splitting of the Ga–Ga and H–H bonds to afford the dimeric gallium hydride product, **XIa**. The analogous reaction with liquid ammonia at $-78\text{ }^\circ\text{C}$ gave rise to the related dimeric gallium compound, **XIb**, bridged by two NH_2 units (Scheme 1.9).²³ Theoretical calculations using DFT methods reveal that the reaction between the monomeric form of **XI** and H_2 has a high activation barrier ($209\text{ kJ}\cdot\text{mol}^{-1}$) making this pathway kinetically unfavourable. Alternatively, the calculations suggest that the reaction between **XI** and H_2 firstly forms a 1,2-dihydride intermediate ($\text{ArGa(H)}\text{--Ga(H)Ar}$) with a lower activation energy barrier ($98\text{ kJ}\cdot\text{mol}^{-1}$), subsequently the intermediate reacts with another equivalent of H_2 resulting in Ga–Ga bond splitting and formation of two ArGa(H)_2 intermediates, which dimerise to give **XIa**.



Scheme 1.9: Reactions of **XI** with i) H_2 (1 atm, rt); (ii) NH_3 ($-78\text{ }^\circ\text{C}$ to rt).²³

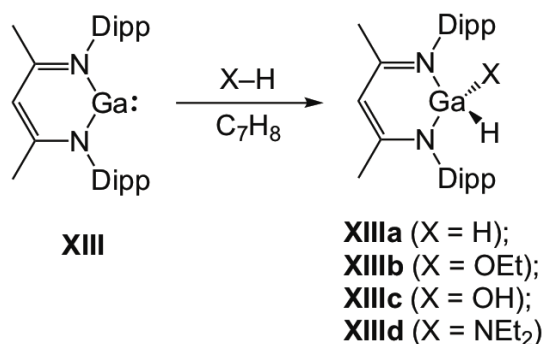
Aldridge reported an N-heterocyclic gallium species bearing a deprotonated β -diketiminato ligand (nacnac*), **XII**. Treatment of **XII** with H_2 (4 atm) or NH_3 (1 atm) afforded the substituted 1,4-addition gallium(III) hydride products, **XIIa** and **XIIb**, respectively (Scheme 1.10).²⁴ In line with the experimental results, theoretical studies show that **XII** exhibits ambiphilic behaviour and its HOMO is mainly distributed over the exocyclic ligand carbon atom whereas the LUMO has empty 4p-orbital character of the gallium atom. In the presence of ammonia, it is proposed that one equivalent of ammonia attacks the Lewis

acidic gallium atom, followed by hydrogen transfer from the NH₃ substituent to the exocyclic ligand carbon atom, to afford **XIIb**.



Scheme 1.10: Reactions of **XII** with i) H₂ (1 atm, 70 °C) and ii) NH₃ (rt, 30 min).²⁴

In related work, Linti's gallium (I) species bearing a nacnac ligand, **XIII**, exhibits a similar electronic structure to its aluminium analogue (**IX**) and is capable of splitting a wide range of X-H bonds (X = H, O or N) to exclusively give the 1,1-addition gallium hydride products (**XIIIa–XIIIId**) (Scheme 1.11).²⁵

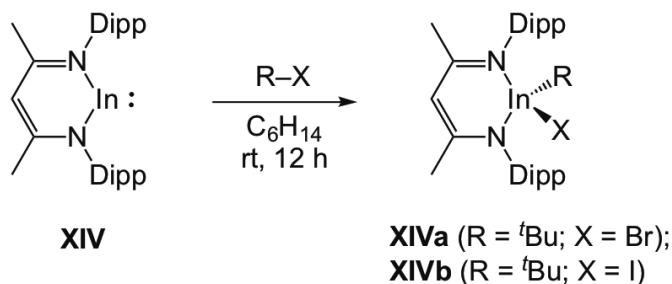


Scheme 1.11: Reactions of **XIII** with: i) H₂ (1 atm, 4 h); ii) HOEt (−78 °C to rt, 10 h), iii) H₂O (−78 °C to rt, 10 h); iv) NH₃ (rt, 10 h).²⁵

1.2.4 Small molecule activation with low-valent indium compounds

Hill reported that the indium(I) analogue (**XIV**) of Linti's gallium(I) species (**XIII**) underwent oxidative addition with alkyl halides to give 1,1-addition products, **XIVa** and **XIVb** (Scheme 1.12), but no reaction was observed towards H₂ or NH₃.²⁶ Bickelhaupt and Fernandez have jointly investigated the different reactivity observed between **XIII** and **XIV**, their theoretical calculations revealed that the activation barriers for oxidative addition

increase on descending group 13 systems due to the inert pair effect. Therefore, the indium lone pairs are less nucleophilic towards the X–H (X = H, N) σ^* -bonding LUMO of H₂ or NH₃, instead, **XIV** prefers a radical reaction pathway consistent with the observed alkyl halide reactivity.²⁷



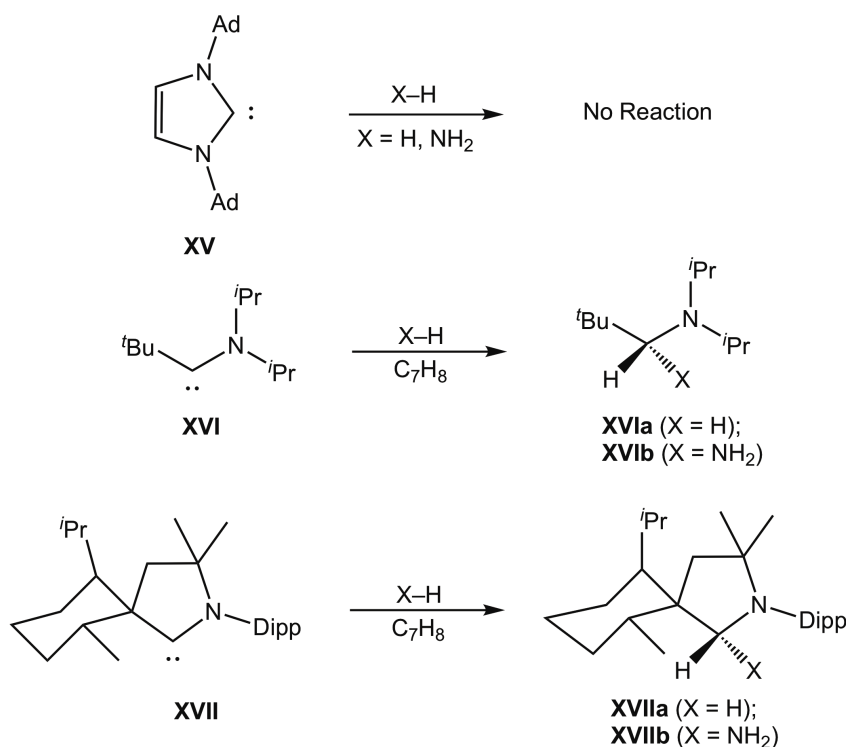
Scheme 1.12: Reactions of **XIV** with alkyl halides.²⁶

1.2.5 Small molecule activation with low-valent carbon compounds

Carbenes contain a neutral divalent carbon atom with six valence electrons, therefore they are electron deficient and highly reactive. In their singlet state, all six valence electrons are paired, and the HOMO has σ -lone pair character while the LUMO is a p_π -symmetry orbital, therefore the HOMO–LUMO gap of singlet carbenes is related to the σ – p_π energy gap.²⁸

In 1991, Arduengo isolated the first singlet carbene, **XV**, stabilised by two σ -withdrawing and π -donating nitrogen substituents.²⁹ The lone pair of **XV** is regarded as highly nucleophilic, noted by the breadth of reported coordination chemistry with NHCs.³⁰ In line with this, **XV** shows no reactivity towards H₂ and NH₃ substrates due to its large HOMO–LUMO gap (6.70 eV) (Scheme 1.13).³¹

In 2005, Bertrand reported the synthesis and characterisation of an acyclic alkyl-amino carbene (aAAC) (**XVI**) and a cyclic alkyl-amino carbene (cAAC) (**XVII**). Treatment of **XVI** and **XVII** with 1 atm of H₂ resulted in oxidative addition to give **XVIa** and **XVIIa** respectively.³² The analogous reactions with ammonia afforded **XVIb** and **XVIIb** in a similar fashion.



Scheme 1.13: Reactions of **XV–XVII** with i) H_2 (1 atm, 35 °C) and ii) NH_3 (–78 °C to rt).³²

Comparing the electronic properties of alkyl-amino carbenes (**XVI** and **XVII**) and Arduengo's N-heterocyclic carbene (**XV**), one of the σ -withdrawing and π -donating amino substituents in **XV** is replaced with a σ -donating quaternary carbon centre, therefore the carbon atoms of **XVI** and **XVII** are considerably more electrophilic and nucleophilic. This narrowing of the HOMO–LUMO gap allows for the observed reactivity of alkyl-amino complexes towards small molecule substrates.^{33,34} In addition, theoretical studies show that AAC compounds possess frontier orbitals mimicking the frontier orbital arrangement of transition metal complexes. In this orbital arrangement, the lone pair orbital of AACs interacts with the $X-H$ ($X = H$ or N) σ^* -antibonding orbital, while the $X-H$ σ -bonding orbital donates electron density to the empty p_π -orbital. This weakens the $X-H$ bond allowing for a formal oxidative addition (Figure 1.1).⁸

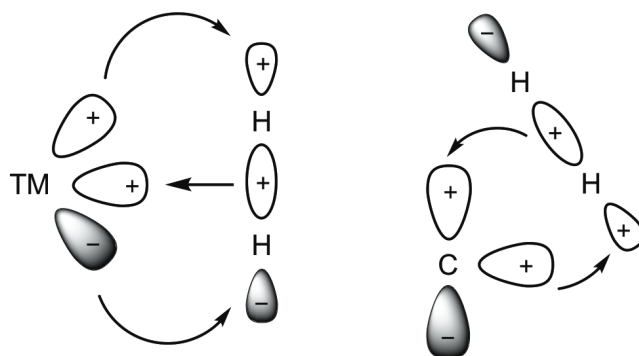
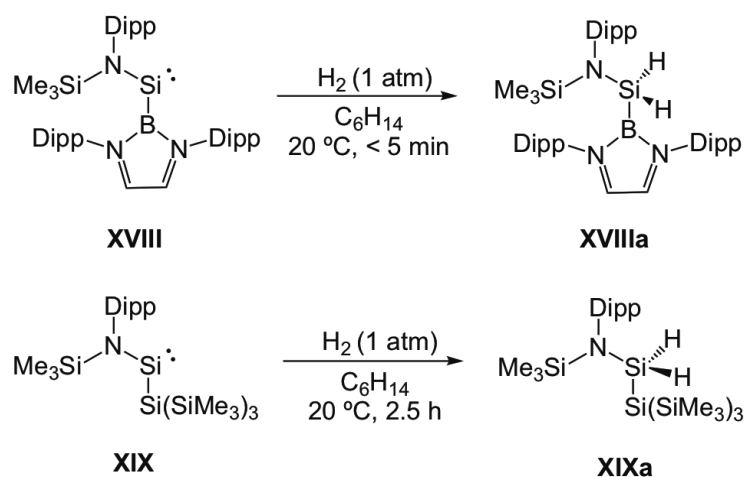


Figure 1.1: Orbital arrangements of: (L) transition metal mediated H-H bond activation; (R) singlet carbene mediated H-H bond activation.⁸

1.2.6 Small molecule activation with low-valent silicon compounds

Heavier group 14 carbene analogues, tetralenes ($:\text{ER}_2$) ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$; $\text{R} = \text{alkyl}$ or aryl), are more readily isolable and their ns^2np^2 valence electron configuration is increasingly more favourable on descending group 14 due to the inert pair effect.^{35,36} These species are very reactive and often require bulky substituents to prevent dimerisation of the tetrel(II) centres. Tetralenes compounds possess a vacant coordination site and an accessible lone pairs of electrons, making them ideal for reactivity towards small molecule substrates.³⁶

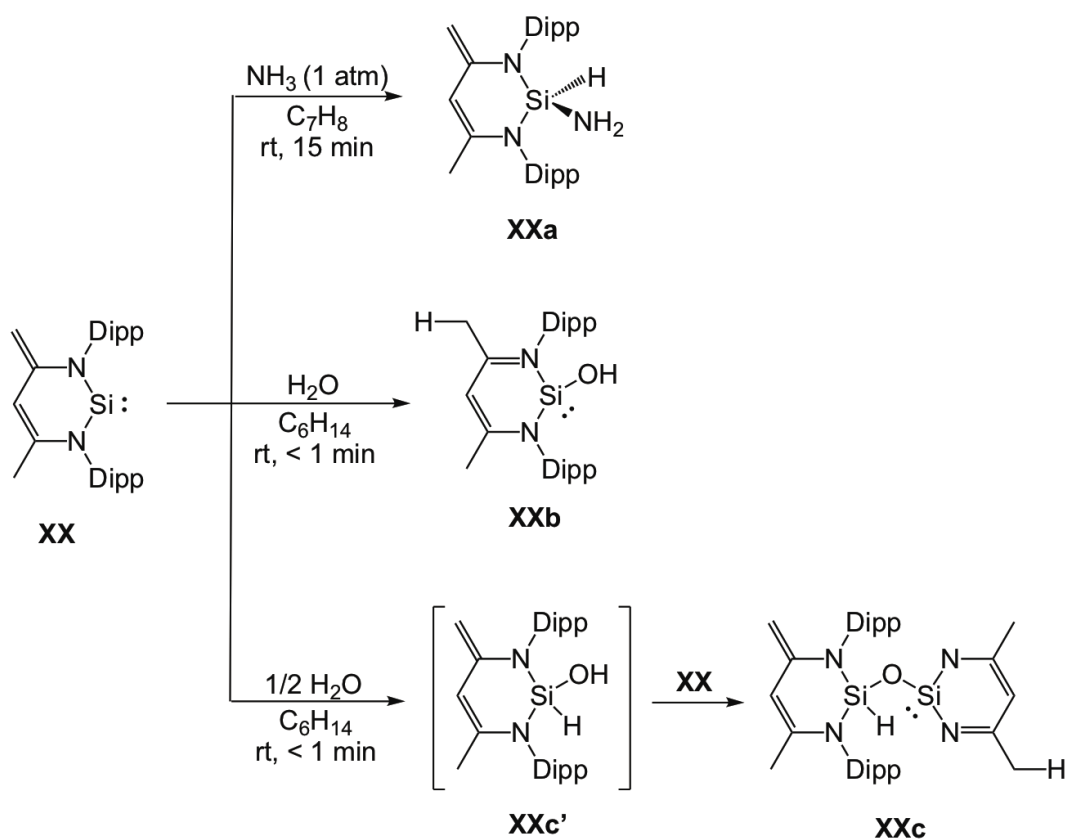


Scheme 1.14: Reactions of XVIII and XIX with H₂.^{37,38}

Aldridge, Jones and Mountford have jointly reported the isolation and characterisation of a two-coordinate acyclic silylene, XVIII, stabilised by a strongly σ -donating and bulky boryl

substituent, $[\text{B}(\text{NDippCH})_2]^-$. **XVIII** was shown to readily undergo single site oxidative addition of H_2 to give a four-coordinate Si(IV) product, **XVIIIa**, at room temperature (Scheme 1.14).³⁷

Similar to the reactivity of **XVIII**, Aldridge, Jones and Mountford also have jointly reported a related two-coordinate silylsilylene, **XIX**. These $\text{RSi}(\text{SiR}_3)$ compounds are known for their rearrangement to become isomeric disilenes, $\text{R}_2\text{Si}=\text{SiR}_2$. Treatment of **XIX** with 1 atm of H_2 at room temperature gave the dihydrosilane product, **XIXa** (Scheme 1.14).³⁸



Scheme 1.15: Reactions of **XX** with NH_3 and H_2O .^{39,40}

In related studies, Power reported the synthesis of an N-heterocyclic silylene bearing the nacnac* ligand, **XX**. It was found that **XX** showed no reactivity towards H_2 .⁴¹ Whereas, Roesky later reported that reaction of **XX** with ammonia resulted in 1,1-addition at the Si(II) centre yielding the substituted Si(IV) hydride product, **XXa**.³⁹ Interestingly, Driess reported that treatment of **XX** with one equivalent of water resulted in the 1,4-addition

product, **XXb**, while treatment of **XX** with half equivalent of water exclusively yielded the oxygen bridged hydroxo-silylene, **XXc**, via the 1,1-addition hydroxo-silylene intermediate, **XXc'** (Scheme 1.15).⁴⁰

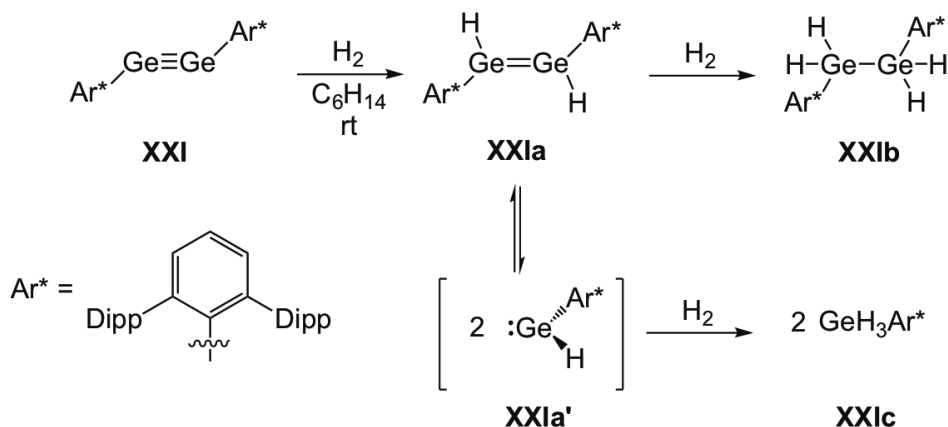
Table 1.1 – Summary of X–Si–X angles and HOMO–LUMO gap of **XVIII–XX**.⁴²

	X–Si–X angle (°)	HOMO–LUMO gap (eV)
XVIII	118.1	2.04
XIX	116.9	1.99
XX	90.5	4.26

To explain why **XX** does not react with H₂, single crystal X-ray diffraction studies and DFT calculations of **XVIII–XX** reveal a correlation between the X–Si–X bond angles (angles between the Si atom and its substituents) and their HOMO–LUMO gap (Table 1.1). The X–Si–X bond angle of **XX** is significantly smaller than **XVIII** and **XIX** making the HOMO–LUMO energy gap of **XX** larger than that in **XVIII** and **XIX**, this is consistent with the diminished reactivity towards H₂. In line with these observations, Kuriakose and Vanka found that, in the case of **XVIII** and **XIX**, their LUMO has the 4p-orbital character on the silicon atom, whereas **XX** does not have the correct frontier orbital arrangement for H₂ activation.⁴²

1.2.7 Activation of H₂ and NH₃ with compounds featuring low-valent germanium atoms

In 2008, Power isolated the digermene compound, **XXI**, stabilised by bulky substituents and showed its capability of activating H₂ at room temperature yielding a mixture of germanium hydride products, **XXIa–XXIc** (Scheme 1.16).⁴³



Scheme 1.16: Reaction of **XXI** with H_2 .⁴³

Based on these germanium hydride products, Power has proposed a reaction mechanism in which **XXI** attacks a molecule of H_2 to give **XXIa**. This species subsequently reacts with another equivalent of H_2 to afford **XXIb**. Meanwhile, **XXIa** is also thought to dissociate into two monomers, **XXIa'**, which can further react with an additional equivalent of H_2 molecule to give the **XXIc** product. In addition, DFT calculations reveal that **XXI** possesses frontier orbitals resembling that of a transition metal, hence facilitating the H_2 addition. The σ -bonding orbital of H_2 donates electron density into the unoccupied non-bonding LUMO of **XXI**, while the π -HOMO orbital of **XXI** simultaneously back-donates electron density to the σ^* LUMO of H_2 (Figure 1.2).²

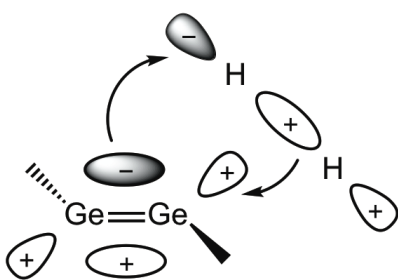
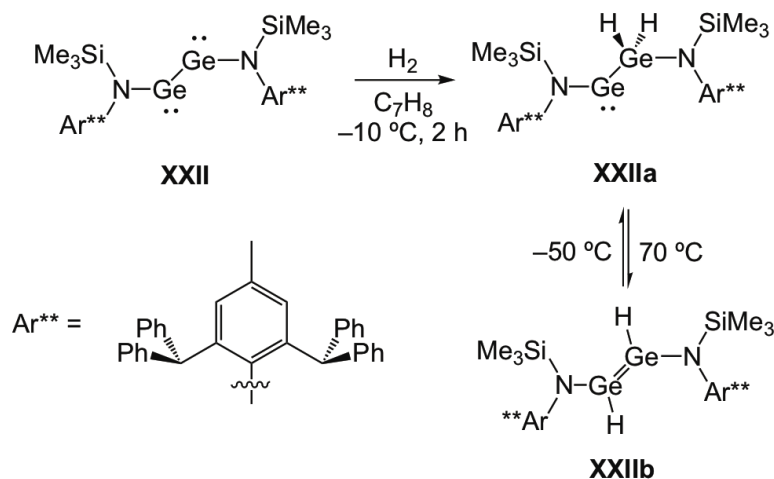


Figure 1.2: Orbital arrangements of **XXI** mediated H–H bond activation.²

Jones has reported the synthesis of the dimeric amido bisgermylene, **XXII**, a germanium analogue of an alkyne. However, single crystal X-ray diffraction studies show that the Ge–Ge bond length is 2.7093(7) Å which is within the value of a typical Ge–Ge single bond

distance, leaving a lone pair of electrons located at each germanium atom. Treatment of **XXII** with 1 atm of H₂ in solution at –10 °C resulted in formation of the stable germanium di-hydride product, **XXIIa** (Scheme: 1.17).⁴⁴

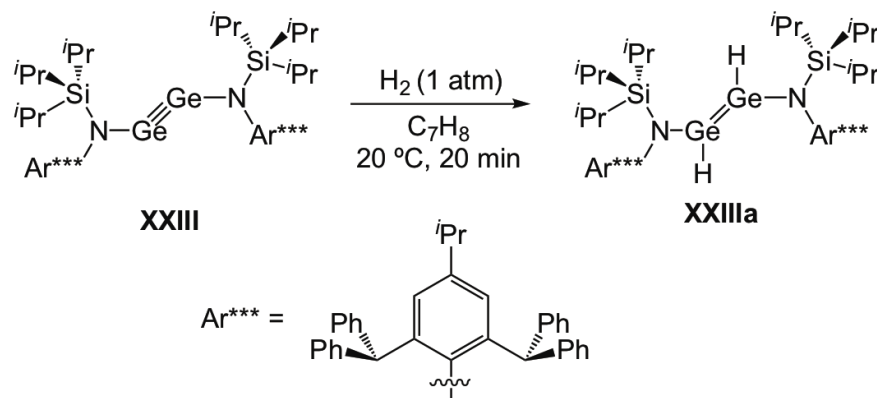


Scheme 1.17: Reaction of **XXII** with H₂.⁴⁴

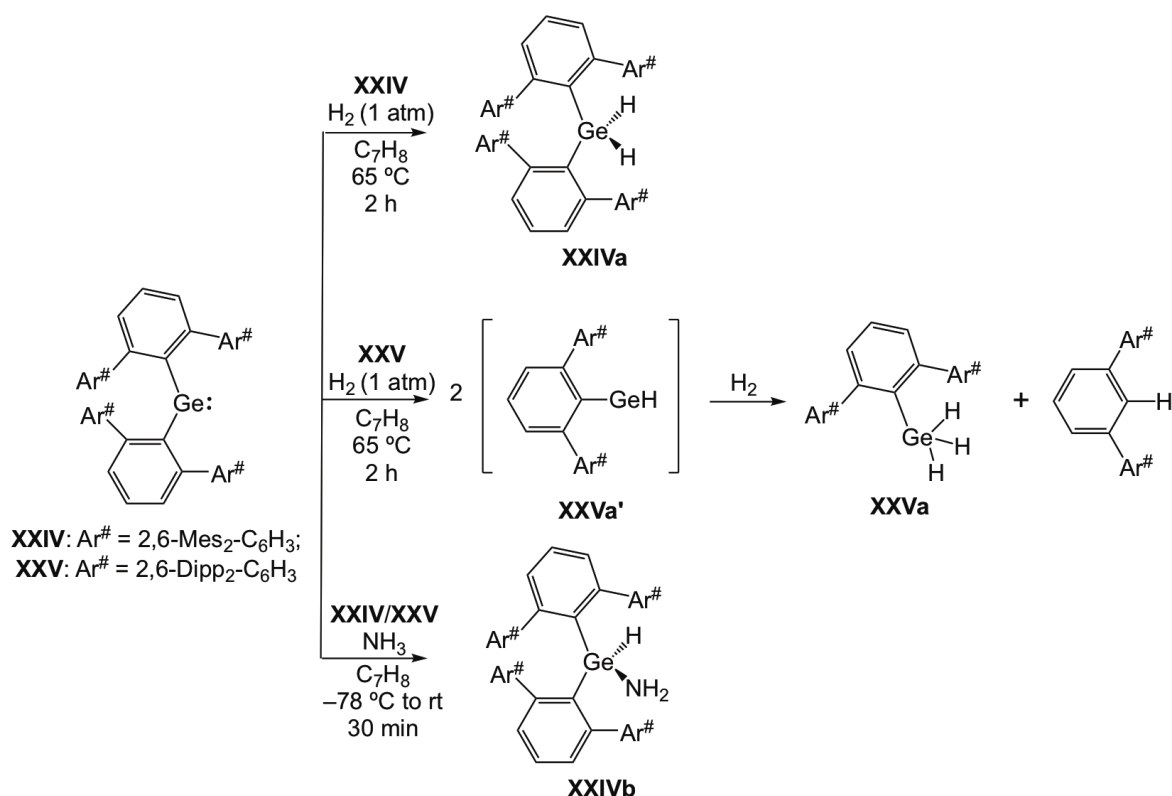
Interestingly, in the absence of any solvents, crystalline **XXII** also reacted with H₂ at 20 °C to afford **XXIIa** in an almost quantitative yield (95%), while repeating the reaction at –10 °C afforded **XXIIa** in 60% yield after one hour. Under such reaction conditions, no second hydrogenation is observed, unlike Power's digermine complex (**XXI**).⁴⁴ In a variable-temperature NMR spectroscopy study, two sets of resonances attributed to the amide ligands were observed at –50 °C, consistent with the formation of **XXIIa**, whereas one set of amide resonances were observed for the amide ligand at 70 °C, consistent with the formation of **XXIIb** (Scheme 1.17). Theoretical calculations using DFT reveal a reaction pathway where first there is H₂ addition to **XXII**, initiated by the attack of the lone pair of electrons of germanium to the σ^* -orbital of H₂, followed up by nucleophilic attack of the negatively polarised hydrogen to the germanium atom.⁴⁴

In the case of Jones' digermine, a Ge–Ge bond length of 2.3568(3) Å was observed, 0.35 Å shorter than the analogous bond of **XXI**. This bond length is more consistent with multiple bonding character between the two germanium centres. Theoretical studies show that the

non-planar Ge–N–Si–Ar*** moiety prevents the delocalisation from the nitrogen lone pair to the germanium atom, hence allowing for the formation of a Ge–Ge multiple bond. Treatment of **XXIII** with 1 atm H₂ gas resulted in the di-hydride Ge=Ge product, **XXIIIa** (Scheme 1.18).⁴⁵



Scheme 1.18: Reaction of **XXIII** with H₂.⁴⁵

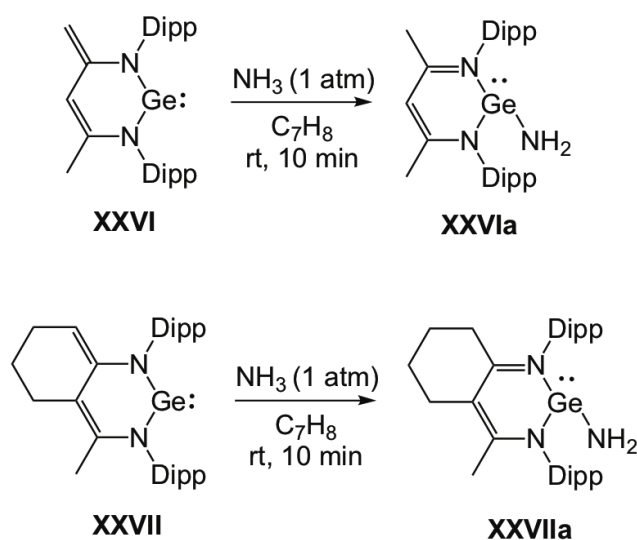


Scheme 1.19: Reactions of **XXIV** and **XXV** with H₂ and NH₃.⁴⁶

Power also reported on the synthesis of a two-coordinate divalent germylene, **XXIV**, which reacted with H₂ (1 atm) to form the di-hydride germanium product, **XXIVa**. However,

moving to a bulkier substituent, **XXV**, the analogous reaction with **XXV** resulted in formation of a germanium species, **XXVa**, as well as elimination of an arene, via the $\text{Ar}^\# \text{Ge}(\text{H})$ intermediate, **XXVa'**. Both **XXIV** and **XXV** react with NH_3 exclusively to form **XXIVb** (Scheme 1.19).⁴⁶

In 2006, Driess isolated an ambiphilic N-heterocyclic germylene, **XXVI**, bearing a nacnac* ligand.⁴⁷ Although no reactivity was shown in the reaction between **XXVI** and H_2 , Roesky reported activation of the N–H bond in ammonia using **XXVI**, which resulted in the formation of the amido germanium(II) species, **XXVIa**, via 1,4-addition, rather than the 1,1-addition observed for its silylene analogue (**XX**) (Scheme 1.20).⁴⁸ Theoretical calculations using DFT reveal that the 1,4-addition is kinetically and thermodynamically more favourable for two reasons. Firstly, the formation of a markedly stronger C–H bond via the 1,4-addition is energetically more favourable than the formation of a Ge–H bond via the 1,1-addition pathway. Secondly, the oxidation from Ge(II) to Ge(IV) is energetically more costly compared to the oxidation of Si(II) to Si(IV) due to the inert pair effect.⁴⁹ Driess later reported a related β -diketiminato based N-heterocyclic germylene, **XXVII**, and found that this species was also capable of splitting N–H bond of ammonia, resulting in the 1,4-addition product, **XXVIIa**, exclusively (Scheme 1.20).⁵⁰

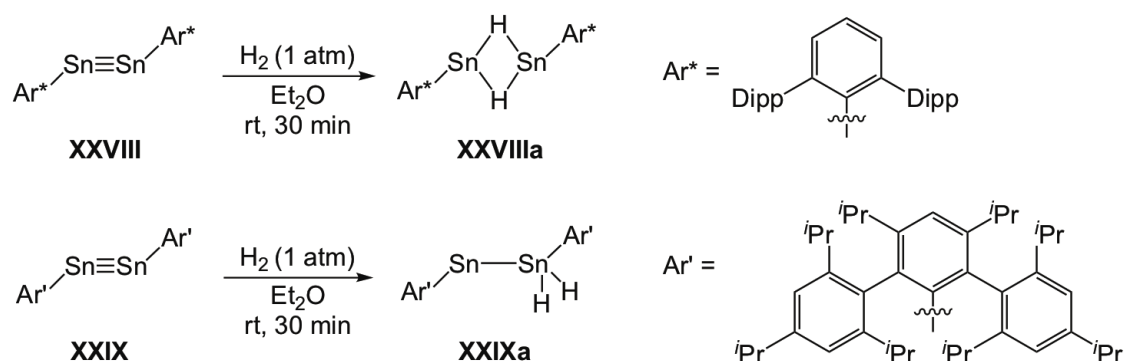


Scheme 1.20: Reactions of **XXVI** and **XXVII** with NH_3 .^{48,50}

1.2.8 Activation of H₂ and NH₃ with compound featuring low-valent tin atoms

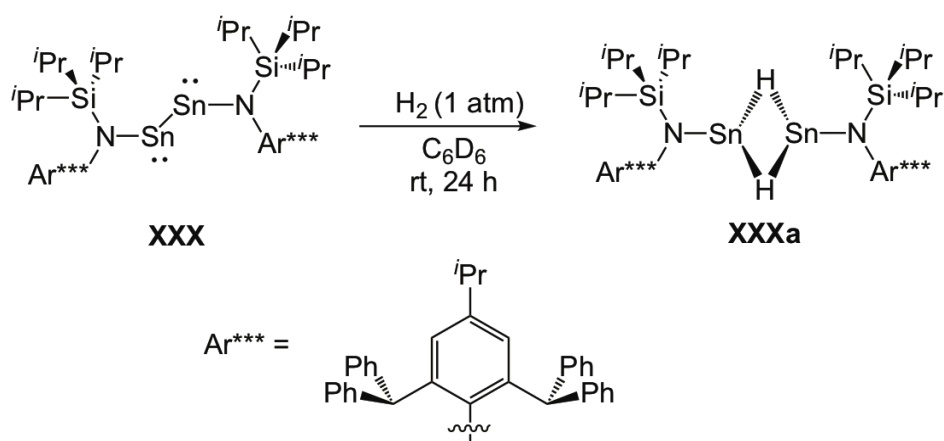
Power has also reported on the synthesis of a distannyne analogue, **XXVIII**, of his digermynes (**XXI**) and found that it activated H₂ to form a hydrogen bridged tin species (**XXVIIIa**) (Scheme 1.21), as opposed to the products formed by the analogous digermynes H₂ activation.⁵¹

The DFT calculations performed by Wang and Schleyer revealed that H₂ activation begins with the formation of a hydride bridging Sn(μ -H)SnH intermediate, then isomerises to a Sn(H)=Sn(H) species which subsequently dissociates into two equivalents of an Sn–H species. This compound can further dimerise to give the Sn(μ -H)₂Sn product, **XXVIIIa**.⁵² In the case of a distannyne stabilised by a bulkier substituent, **XXIX**, treatment of **XXIX** with 1 atm of H₂ gas afforded the dihydride tin product, **XXIXa** (Scheme 1.21). The **XXVIIIa** and **XXIXa** products are both kinetically and thermodynamically more stable than their germanium analogues since the lone pair on tin is more stable due to the inert pair effect, this is consistent with no further observed hydrogenation.⁵¹



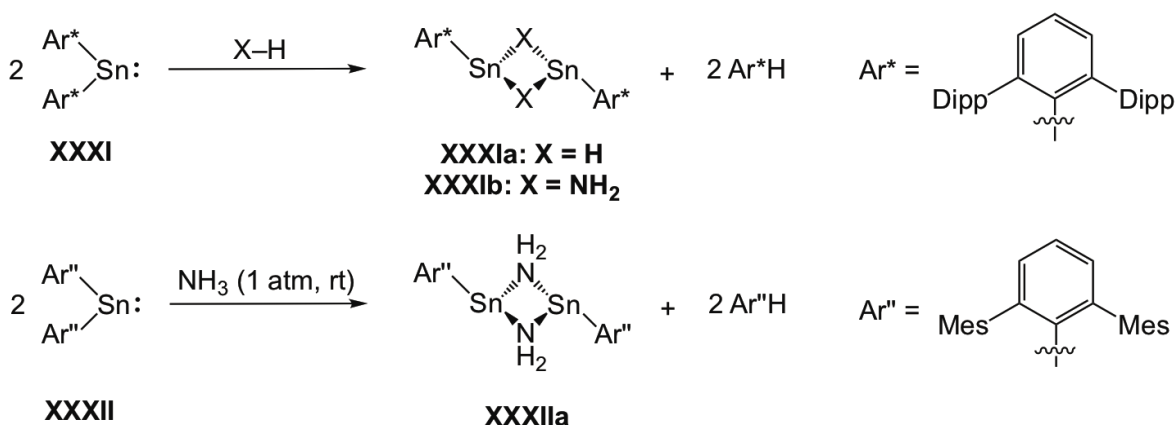
Scheme 1.21: Reactions of **XXVIII** and **XXIX** with H₂ and NH₃.⁵¹

Jones reported an amido-disstannyne species, **XXX**, analogous to his digermynes complex (**XXII**). **XXX** is stabilised by very bulky substituents on the amido units and shown to possess a very long Sn–Sn single bond (3.1434(5) Å). Treatment of **XXX** with 1 atm of H₂ gas under ambient conditions exclusively gave the dihydride bridging product, **XXXa** (Scheme 1.22).⁵³



Scheme 1.22: Reaction of **XXX** with H_2 .⁵³

Power reported the isolation of distannylene complexes (**XXXI** and **XXXII**) with bulkier substituents and investigated their reactivity towards H_2 and NH_3 . In the case of **XXXI**, reaction with 1 atm of H_2 or NH_3 resulted in formation of the hydrogen bridging tin compounds, **XXXIa** and **XXXIb** respectively, and the elimination of two equivalents of arene (Scheme 1.23), akin to their germanium analogues.⁵⁴

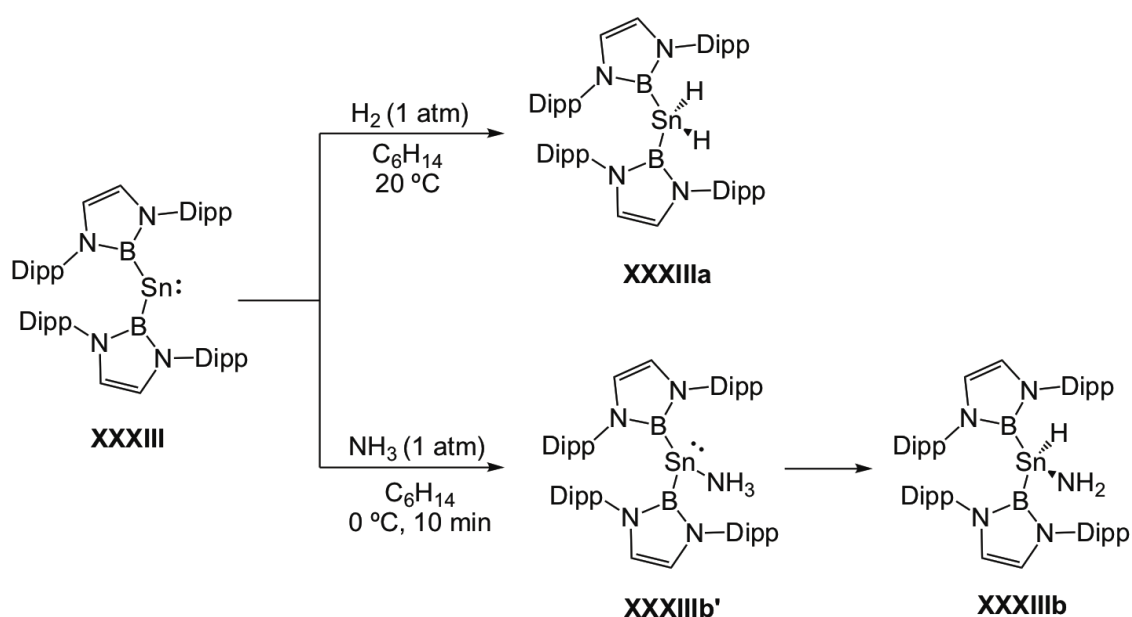


Scheme 1.23: Reactions of **XXXI** and **XXXII** with i) H_2 (1 atm, 70 °C) and ii) NH_3 (1 atm, rt).⁵⁴

Conversely, **XXXII** showed no reactivity towards H_2 but underwent N–H bond splitting with 1 atm of NH_3 to give **XXXIIa**. The reactivity difference of **XXXI** and **XXXII** towards H_2 and NH_3 is aligned with the observed reactivity of silyenes towards H_2 (see Chapter 1.2.6). **XXXI** has a smaller HOMO–LUMO energy gap when compared to **XXXII**,

consistent with a wider C–Sn–C bond angle ($117.6(2)^\circ$ for **XXXI** and $114.7(2)^\circ$ for **XXXII**), and diminished reactivity towards H_2 .⁵⁵

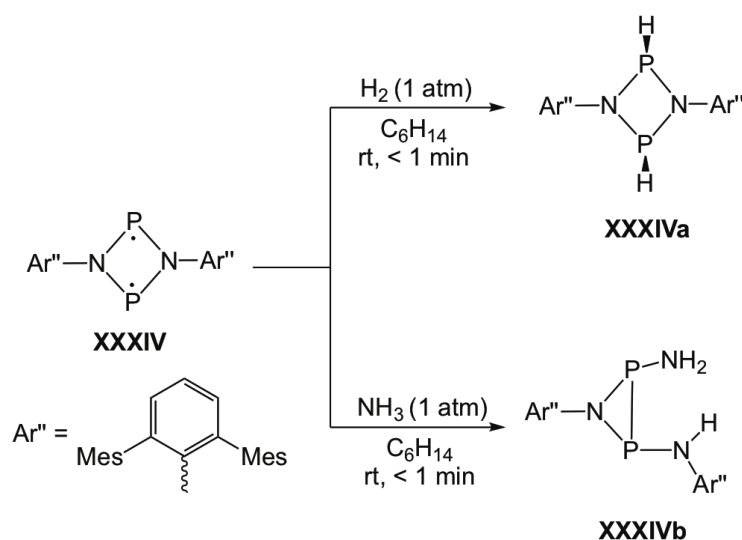
Aldridge, Jones and Mountford described the synthesis of a Sn(II) complex with two bis(boryl) ancillary ligands, **XXXIII**. The strongly σ -donating bis(boryl) ancillary ligand destabilises the HOMO of **XXXIII**, effectively making the HOMO–LUMO energy gap smaller.⁵⁶ As expected, this change in the HOMO–LUMO gap make these compounds more susceptible to reactivity with small molecules. Treatment of **XXXIII** with H_2 (1 atm) resulted in facile oxidative addition to give the Sn(IV) dihydride product (**XXXIIIa**). In the analogous reaction with NH_3 , it is proposed that **XXXIII** undergoes a two-step reaction pathway initiated by ammonia coordinating to the Sn(II) centre to form an amino Lewis acid–base adduct, **XXXIIIb'**, followed by proton transfer to form the four-coordinate Sn(IV) product (**XXXIIIb**) (Scheme 1.24).



Scheme 1.24: Reactions of **XXXI** and **XXXII** with H_2 and NH_3 .⁵⁶

1.2.9 Small molecule activation with low-valent phosphorus compounds

Seminal work in this field was reported by Schulz with the synthesis of a di-phosphorus(II) biradicaloid, **XXXIV** in which two phosphorus centres are in a formal +2 oxidation state. **XXXIV**, therefore, reacted with H₂ at room temperature to give **XXXIVa** in *cis*-configuration exclusively (Scheme 1.25). Interestingly, upon heating the **XXXIVa** at 60 °C, it recovered **XXXIV** and liberated one equivalent of H₂. In addition, the analogous reaction with 1 atm of NH₃ gas afforded the azadiphosphiridine product, **XXXIVb**.⁵⁷



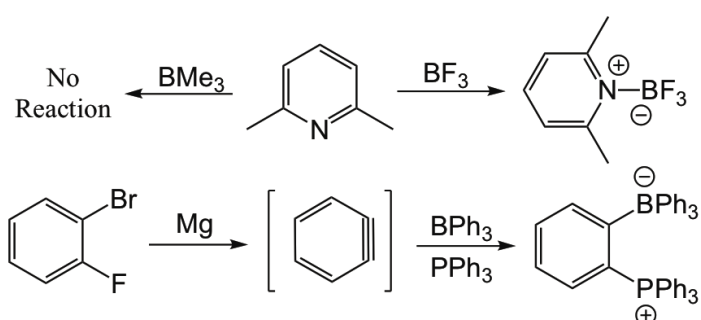
Scheme 1.25: Reactions of **XXXIV** with H₂ and NH₃.⁵⁷

1.3 Small molecule activation with frustrated Lewis pair compounds

1.3.1 Development of frustrated Lewis pairs

The term “Lewis acid” and “Lewis base” are used to describe an electron pair acceptor and an electron pair donor, respectively. Lewis basic compounds have a high energy HOMO which can interact with the LUMO of associated Lewis acidic compounds, resulting in formation of stable Lewis acid–base adducts. For example, ammonia stabilised borane (H₃N·BH₃) is commercially available.

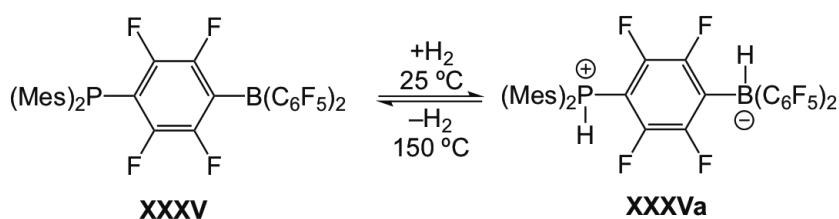
Frustrated Lewis pairs (FLP), a term coined by Stephan, are compounds featuring Lewis acidic and Lewis basic sites that are sterically encumbered preventing formation of an adduct.⁵⁸ The first FLP was reported in 1942 when no reactivity was observed in the reaction between lutidine with trimethylborane, as the Lewis basic nitrogen atom is sterically shielded by the methyl substituents in the *ortho*-position. By contrast, reaction of lutidine with trifluoroborane formed a N–B adduct due to the reduced steric bulk of BF₃ (Scheme 1.26).⁵⁹



Scheme 1.26: Early examples of frustrated Lewis pairs.^{59,60}

Later in 1959, Wittig and Benz reported that reaction of an *in-situ* generated benzyne in the presence of triphenylphosphine (PPh₃) and triphenylboron (BPh₃), which formed a zwitterionic salt across the *in-situ* benzyne triple bond via 1,2-addition (Scheme 1.26).⁶⁰

1.3.2 H₂ activation by intramolecular frustrated Lewis pairs

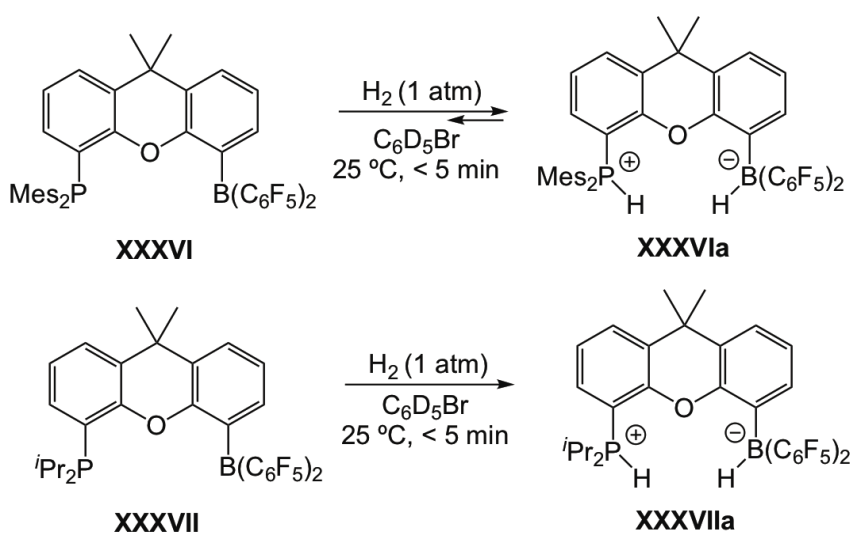


Scheme 1.27: Reaction of **XXXV** with H₂.⁹

In 2006, Stephan reported the first reversible H₂ activation using the FLP, **XXXV**. Exposure of **XXXV** to H₂ (1 atm) at room temperature in solution caused H–H bond cleavage

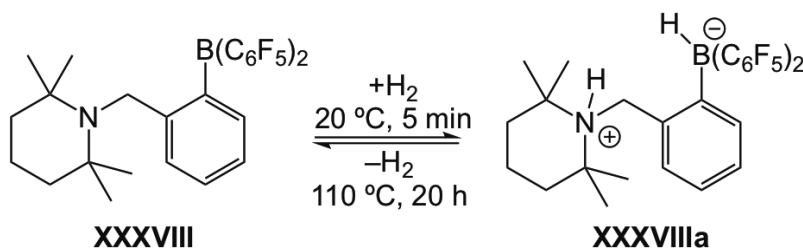
resulting in the zwitterionic phosphonium borate salt, **XXXVa**. Upon heating the solution at 150 °C, H₂ gas was liberated and **XXXVa** converted back to **XXXV** (Scheme 1.27).⁹

To achieve reversible H₂ activation, the energy barrier must be low in both directions and the ΔG° must be small. One approach is to employ geometrically constrained systems that not only pre-organises the FLP encounter cavity by a rigid ligand framework, and lowers the magnitude of entropy ($\Delta S^\ddagger$), but also separates the phosphine and borane in a range of 4.2–4.8 Å which is thought to be the ideal separation distance of a phosphine and borane pair for a H₂ activation.⁶¹ Aldridge has reported the isolation of two FLPs with a dimethyl xanthane backbone (**XXXVI** and **XXXVII**), featuring phosphines and boranes with P···B separations of 4.243(3) Å and 4.487(3) Å, respectively.⁶² Treatment of **XXXVI** and **XXXVII** with 1 atm of H₂ resulted in formation of phosphonium borohydride zwitterionic salts (**XXXVIa** and **XXXVIIa**) (Scheme 1.28). In the case of **XXXVIa**, redissolving crystalline **XXXVIa** in C₆D₅Br resulted in 5% conversion to the **XXXVI** species. The liberation of H₂ could also monitored by ¹H NMR spectroscopy. In the case of **XXXVIIa**, which featured a more basic phosphine, no H₂ liberation was observed in C₆D₅Br even at elevated temperatures.⁶²



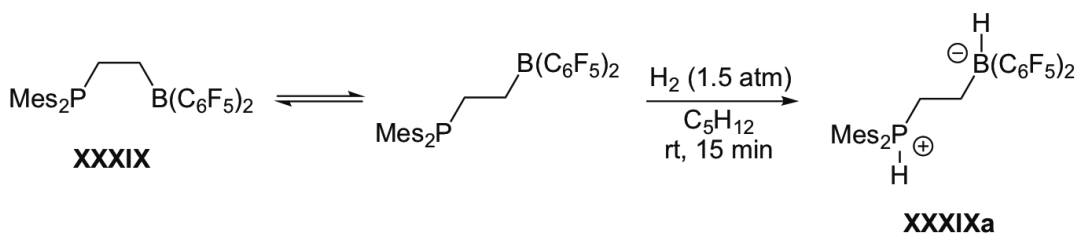
Scheme 1.28: Reactions of **XXXVI** and **XXXVII** with H₂.⁶²

Furthermore, Repo prepared an intramolecular FLP, ansa-aminoborane (**XXXVIII**) featuring amide and borane substituents and showed that **XXXVIII** is capable of reversibly activating H_2 to afford the ammonium hydridoborate zwitterionic salt, **XXXVIIIa**. Upon heating the solution of **XXXVIIIa** to 110 °C, quantitative recovery of **XXXVIII** could be observed (Scheme 1.29).⁶³



Scheme 1.29: Reaction of **XXXVIII** with H_2 .⁶³

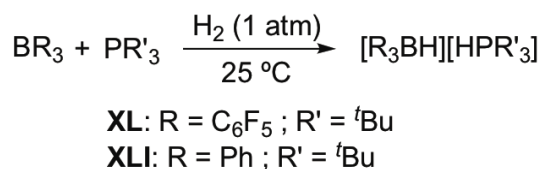
Early work in this area was reported by Erker with the preparation of **XXXIX**, an intramolecular phosphine–borane FLP separated by a C2 linker. DFT studies show that the gas phase structure of **XXXIX** exhibits a *trans*-configuration. The *trans*-configuration is stabilised by the π -stacking between a mesityl substituent of the phosphane and C_6F_5 substituents of the borane. The $P\cdots B$ separation of **XXXIX** is ca. 2.21 Å, consistent with a weak Lewis acid–base interaction. Furthermore, theoretical studies also reveal that the *cis*-isomer of **XXXIX** (**XXXIX'**) is only 7 kcal·mol^{−1} higher in energy, suggesting that both isomers exist in solution.⁶⁴ Experimentally, treatment of **XXXIX** with H_2 (1.5 atm) resulted in H–H bond cleavage at room temperature to afford **XXXIXa** in a quantitative yield (Scheme 1.30). However, no H_2 liberation was observed even at elevated temperature.⁶⁴



Scheme 1.30: Reaction of **XXXIX** with H_2 .⁶⁴

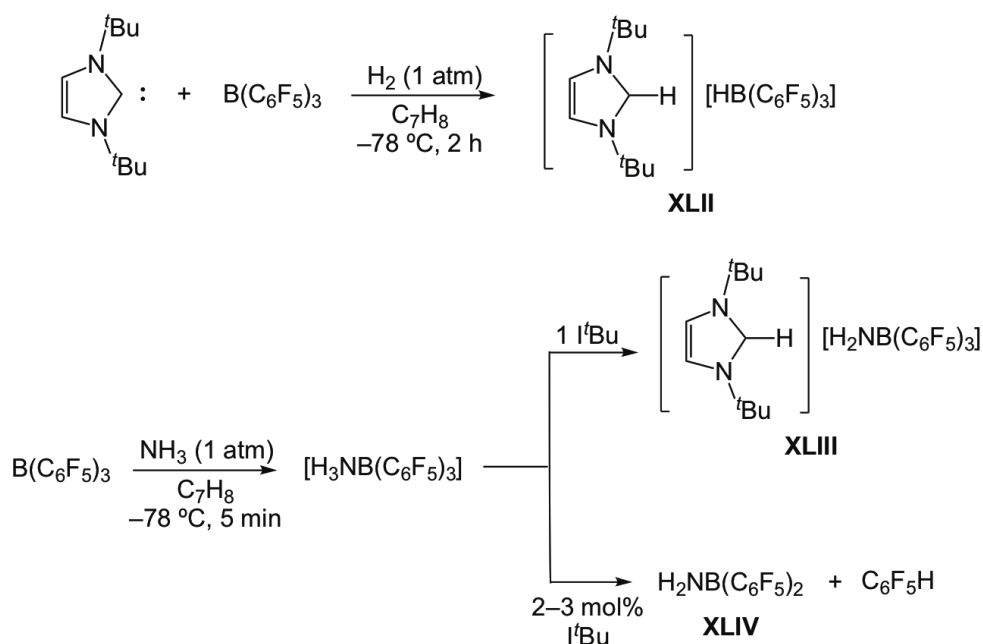
1.3.3 Small molecule activation by intermolecular frustrated Lewis pairs

Numerous examples of intermolecular FLPs where the Lewis acid and base components are too sterically encumbered to form adducts have also been extensively investigated. Stephan has reported intermolecular H₂ activation using a series of Lewis acidic boranes (BR₃ (R = C₆F₅, Ph)) and a Lewis basic phosphines (PR'₃ (R' = *t*Bu or Me). The reaction mixtures were monitored by ¹H NMR spectroscopy and showed no evidence of formation of an adduct between 25 °C to –50 °C. In the presence of H₂ gas (1 atm), the mixture of P'*t*Bu₃ and B(C₆F₅)₃ converted into a phosphonium borate salt, **XL**. The analogous reaction with the mixture of P'*t*Bu₃ and BPh₃ also resulted in the phosphonium borate salt, **XLI**, but required longer reaction times and gave lower yields due to the diminished Lewis acidity at the boron centre (Scheme 1.31). By contrast, reacting PMe₃ and B(C₆F₅)₃ with H₂ gas resulted in the phosphine–borane adduct and no H₂ activation was observed, due to the lack of steric protection around the phosphorus atom.⁶⁵



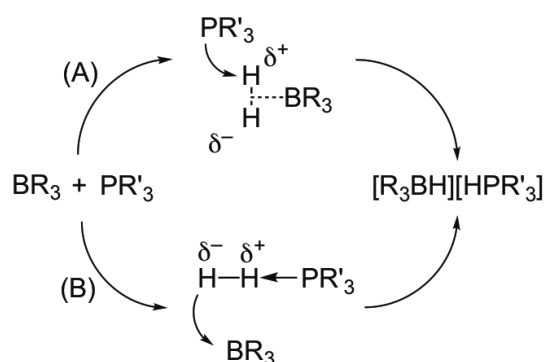
Scheme 1.31: Formation of **XL** and **XLI**.⁶⁵

Stephan has also reported carbenes as competent bases for FLP activation of H–H and N–H bond activation. Mixture of the *tert*-butyl substituted N-heterocyclic carbene (I'*t*Bu) and B(C₆F₅)₃ in the presence of 1 atm H₂ at room temperature resulted in formation of an imidazolium borate salt, **XLII**.^{66–68} Similarly, the mixture of I'*t*Bu and B(C₆F₅)₃ in the presence of 1 atm NH₃ at room temperature resulted in formation of the imidazolium aminoborate salt, **XLIII**, exclusively. Interestingly, B(C₆F₅)₃ reacted with 1 atm of ammonia with a catalytic amount of I'*t*Bu (2–3 mol%) afforded C₆F₅H and an aminoborane, **XLIV** (Scheme 1.32).⁶⁷



Scheme 1.32: Formation of **XLII–XLIV**.⁶⁷

Considering the mechanism of the intramolecular H₂ activation, Stephan has proposed that the reaction was initiated by a side-on interaction of H₂ with a Lewis acidic borane polarising a H–H bond, followed by protonation of the phosphine (Scheme 1.33; A).⁶⁵ On the other hand, theoretical calculations performed by Sweaney suggested a Lewis base cooperative pathway where the lone pair of base interacted with the σ*-orbital of H₂ resulting in H–H bond polarisation, then the negatively charged hydrogen atom attacked the Lewis acidic borane (Scheme 1.33; B).⁶⁹



Scheme 1.33: Possible mechanisms for intermolecular H₂ activation: (A) Stephan's Lewis acid cooperative pathway; (B) Sweaney's Lewis base cooperative pathway.^{65,69}

Since the seminal FLP work reported by Stephan and Erker, DFT studies by Grimme proposed that a strong electric field established in the internal cavity between a Lewis acidic and a Lewis basic sites polarise the H–H bond, hence facilitating the H₂ activation (Figure 1.3; A).⁷⁰ The Papai group discuss this internal cavity as formation of an “encounter complex” which holds a H₂ molecule between the Lewis acidic and basic sites. This orientation facilitates an interaction between an electron lone pair of a Lewis base to the σ^* -orbital of H₂ and donation of electron density from the σ -orbital of H₂ to the empty orbital on the Lewis acid, polarising the H–H bond (Figure 1.3; B).⁶¹ Papai’s calculations also suggest that, in the case of a H₂ activation using a phosphine/borane pair, the ideal separation of the encounter complex is in the range of 4.2–4.8 Å. Also, the rate determining step for such H₂ activation is when the H₂ molecule enters the cavity.⁷¹

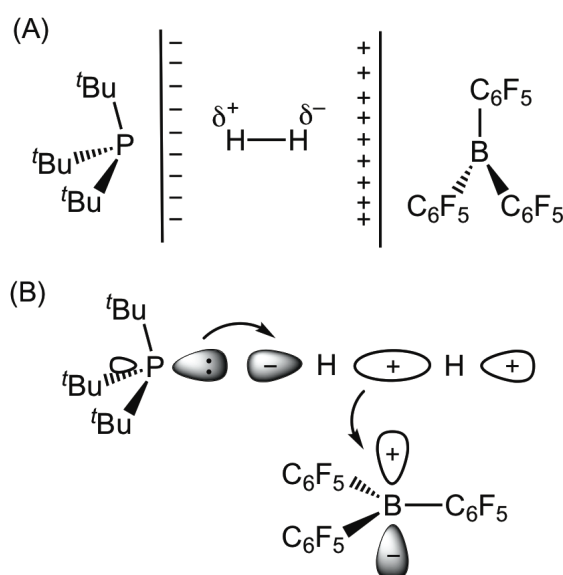
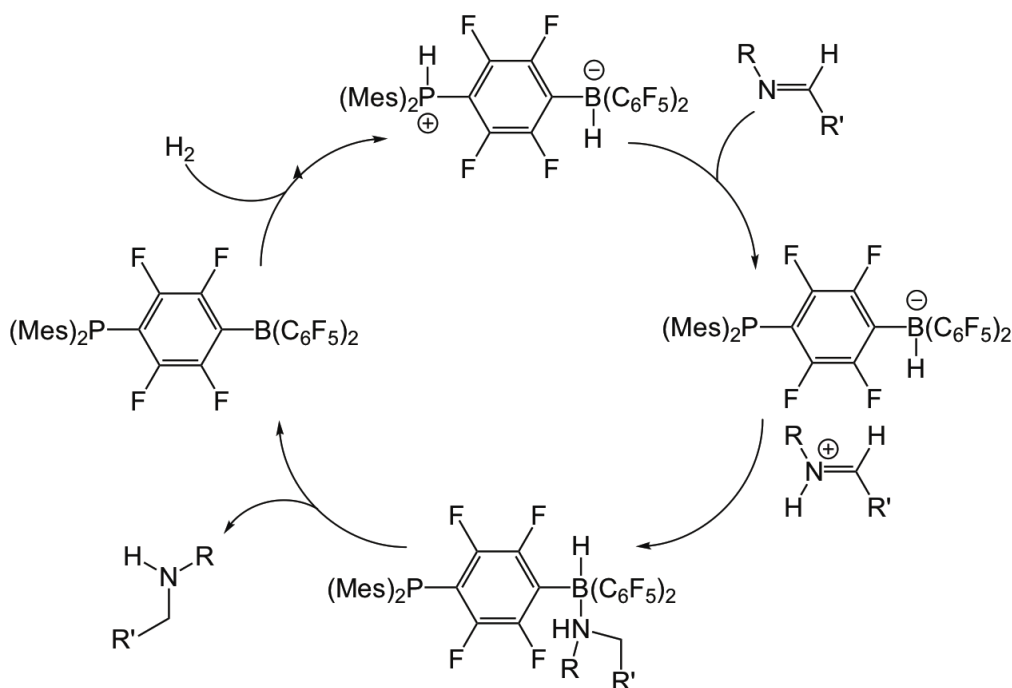


Figure 1.3: H₂ activation by FLP explaining by (A) Grimme’s electric field based model; and (B) Papai’s molecular orbital based model.^{61,70}

1.3.4 Reduction of unsaturated substrates with frustrated Lewis pair H₂ adducts

Stephan’s compound **XXXV** demonstrates reversible H₂ activation and was further employed for the catalytic reduction of imines using the zwitterionic compound, **XXXVa**. Under catalytic conditions, **XXXVa** (5% mol) reacted with a variety of imines under 1 atm

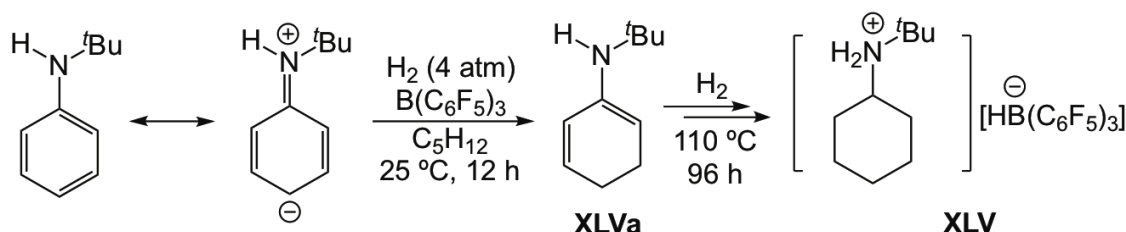
of H₂ resulting in hydrogenation of the substrates to the corresponding amines (Scheme 1.34).⁷² DFT calculations reveal that the catalytic reduction is initiated by proton transfer from phosphorus to the imine nitrogen atom, followed by hydride transfer to the positively charged nitrogen atom of imine. The basicity of imine and resulting amine can potentially poison the borane, therefore the substrate scope is often limited to bulky substituents at the nitrogen atom of imines. Unhindered or electron deficient imines require longer reaction times or higher H₂ pressures. Consistent with the theoretical calculations, it is found that bulky and basic imines undergo full conversion in a mild conditions (80–120 °C, 1–5 atm of H₂).⁷²



Scheme 1.34: Catalytic imine hydrogenation by Stephan's **XXXVa**.⁷²

In addition to imine reductions by **XXXVa**, Stephan has also shown an unprecedented hydrogenation of anilines to the cyclohexylamine borohydride salts. The delocalisation of the lone pair of the aniline nitrogen atom increases the electron density of the *para*-position, allowing for heterolytic H₂ cleavage. NMR spectroscopy studies show no reaction in the mixture of amine ^tBuNHPh and B(C₆F₅)₃ at room temperature. However, in the presence of

H₂ (4 atm), amine ^tBuNHPh reacted with B(C₆F₅)₃ at room temperature to afford **XLVa** which can be isolated in a high yield (83%). Upon heating the solution of **XLVa** at 110 °C for ninety-six hours, it further hydrogenated and yielded the corresponding cyclohexylamine borohydride salt, **XLV** (Scheme 1.35).⁷³

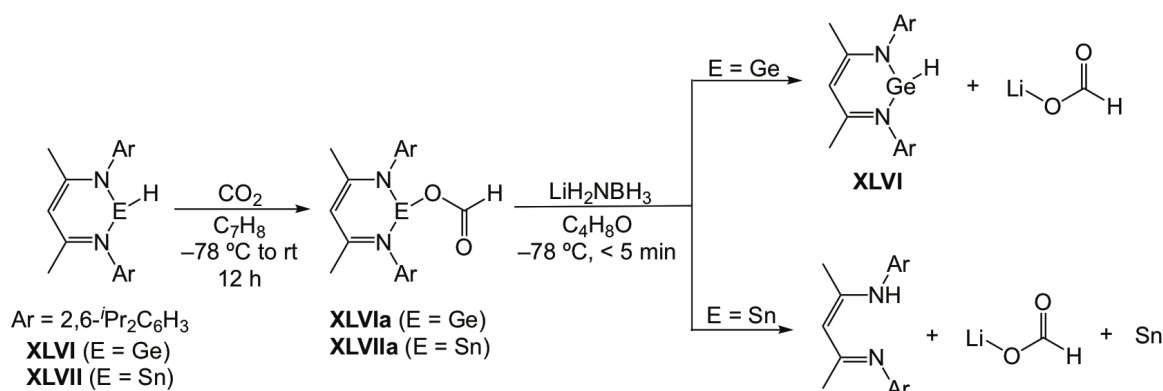


Scheme 1.35: Reduction of aniline using B(C₆F₅)₃ and H₂.⁷³

1.4 Compounds of heavier low-valent p-block elements as homogeneous catalysts

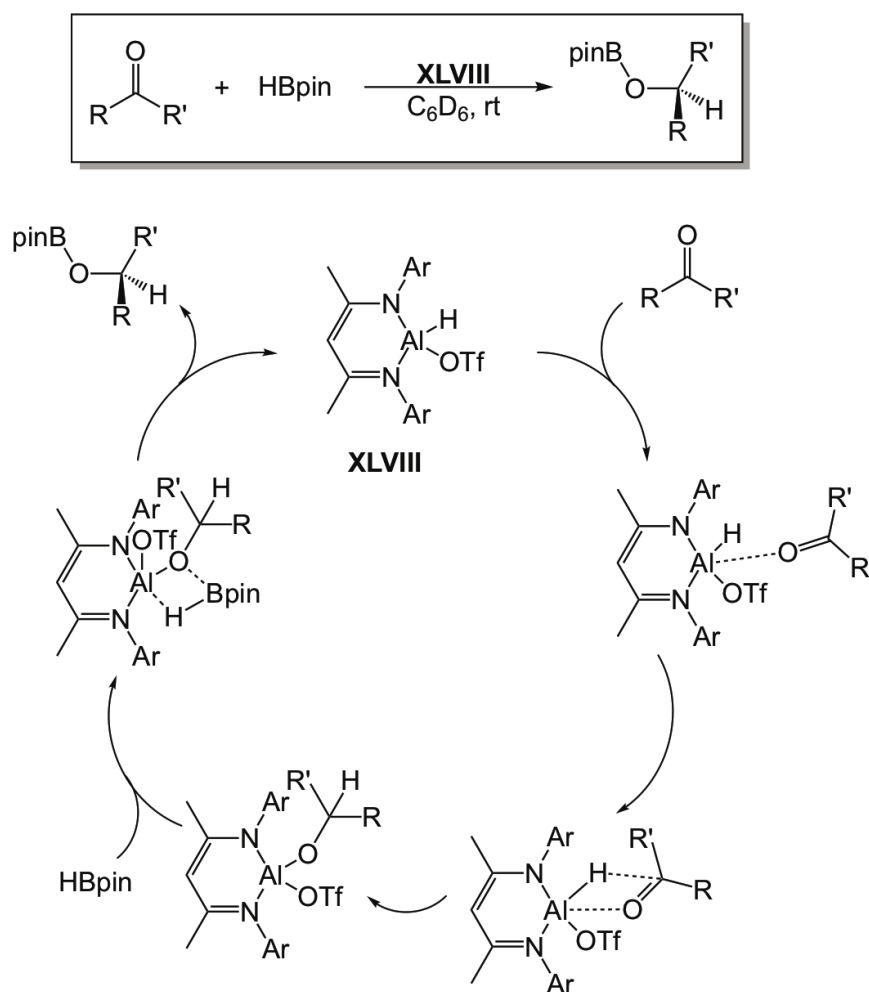
1.4.1 Reduction of carbonyl compounds using p-block main-group hydrides

In 2010, Roesky demonstrated that germanium(II) and tin(II) hydride compounds bearing a nacnac ligand (**XLVI** and **XLVII**, respectively) can reduce carbon dioxide to give the corresponding aldehydes, **XLVIa** and **XLVIIa** (Scheme 1.36).⁷⁴ The subsequent reaction of **XLVIa** with LiH₂N·BH₃, which acts as a source of hydrogen, resulted in clean formation of **XLVI** and lithiated formic acid. In contrast, reaction of **XLVIIa** with LiH₂N·BH₃ results in free protonated nacnac ligand, lithiated formic acid and elemental tin.



Scheme 1.36: Reaction of **XLVI** and **XLVII** with CO₂ and the subsequent reaction with LiH₂N·BH₃.⁷⁴

1.4.2 Hydroboration of carbonyl compounds with group 13 compounds



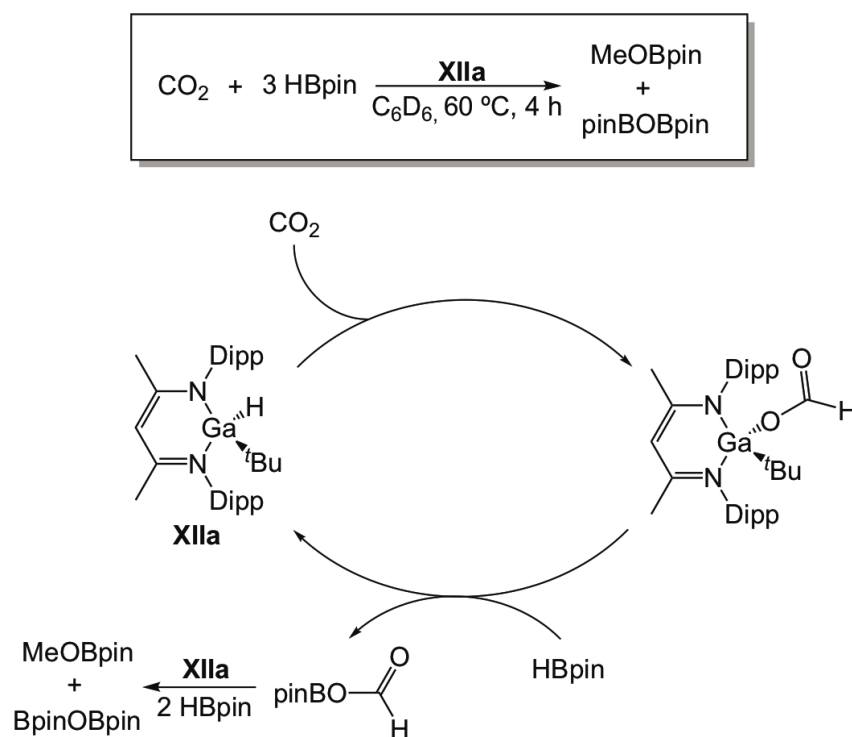
Scheme 1.37: Reduction of carbonyl compounds using **XLVIII**.⁷⁵

Following this work, Roesky has reported on the catalytic reduction of aldehydes and ketones to their alcohol equivalents using an aluminium hydride compound bearing a nacnac ligand, **XLVIII**. An electron withdrawing triflate group was employed to increase the Lewis acidity of the catalyst. Under catalytic conditions (1 mol% of **XLVIII**), benzaldehyde was quantitatively reduced to its alcohol equivalent within one hour. DFT calculations suggest the mechanism proceeds via insertion of the C=O bond to the aluminium hydride to form an aluminium alkoxide, followed by a σ -bond metathesis between the alkoxide and pinacolborane (HBpin), which served as a source of hydrogen, forming the corresponding borate ester and regenerating the aluminium hydride (**XLVIII**).

(Scheme 1.37).⁷⁵ It was found that hydroboration of ketones required longer time and twice the catalytic loading (2 mol%) of **XLVIII** (Table 1.2). This diminished reactivity may be attributed to the diminished Lewis basicity of the oxygen atom in ketones when compared to aldehydes impeding the C=O bond insertion step.⁷⁵

Table 1.2 – Reduction of carbonyl compounds using **XLVIII**. Only selected samples are presented in the table.⁷⁵

Entry	Substrate	Cat/mol %	Time/ h	Yield/ %
1	PhC(O)H	1	1	99
2	(C ₆ H ₅ (<i>p</i> -CH ₃))C(O)H	1	1	99
3	(C ₆ H ₅ (<i>o</i> -F))C(O)H	1	1.5	99
4	PhC(O)Me	2	6	51
5	(C ₆ H ₅ (<i>p</i> -CH ₃))C(O)Me	2	6	58

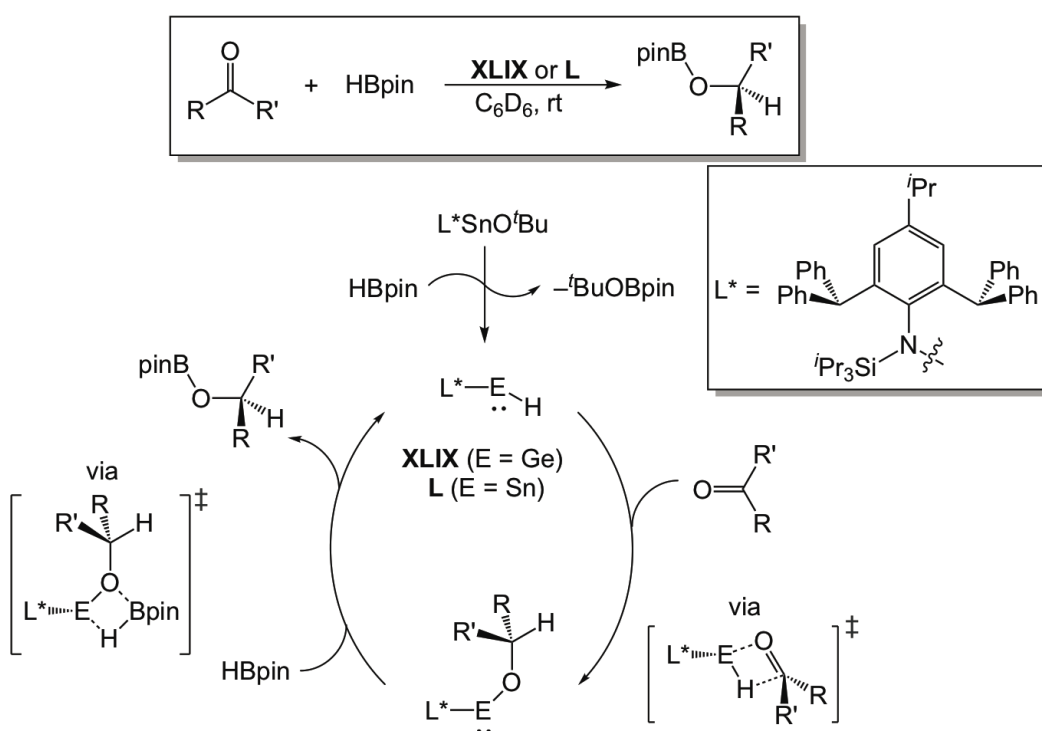


Scheme 1.38: Catalytic reduction of CO₂ with **XIIa** and HBpin.²⁴

Furthermore, Aldridge has reported that the gallium hydride (**XIIa**) as an active catalyst for reduction of carbon dioxide (CO₂) to its methanol equivalent (MeOBPin). Under catalytic conditions (10 mol% of **XIIa**), CO₂ was completely converted to MeOBPin and pinBOBpin in four hours at 60 °C. **XIIa** reacts with CO₂ to form the alkoxide species, which then reacts

with HBpin in solution to generate the corresponding aldehyde regenerating **XIIa**. The aldehyde then reacts with **XIIa** resulting in formation of an alkoxide which subsequently reacts with two equivalents of HBpin to give the MeOBpin and pinBOBpin as well as the recovery of **XIIa** (Scheme 1.38).²⁴ The reaction rates were improved compared to magnesium and calcium hydride compounds prepared by Hill, which gave a complete CO₂ reduction in a solution at 60 °C over four days (Ca) or six days (Mg) using the same catalyst loadings (10 mol%).⁷⁶

1.4.3 Hydroboration of carbonyl compounds with group 14 compounds



Scheme 1.39: Catalytic reduction of carbonyl compounds with **XLIX** and **L**.⁷⁷

Jones found that germanium(II) hydride (**XLIX**) and an *in-situ* generated tin(II) hydride (**L**) compounds are both effective catalysts for hydroboration of carbonyls with HBpin (Scheme 1.39).⁷⁷ Both **XLIX** and **L** are two-coordinate in solution and possess an empty p-orbital at the metal centre enhancing the electrophilicity of the metal. Jones proposed that the metal hydrides first react with the carbonyl to form a metallalkoxide, via a charge transfer from

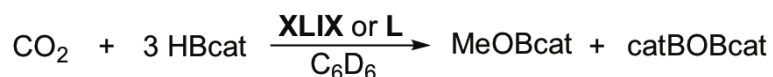
the Ge–H σ -orbital to the C=O π^* -orbital of the carbonyl compounds, followed by a reaction with an equivalent of HBpin to recover the metal hydride compound and yield the corresponding alcohol derivative via a σ -bond metathesis (Scheme 1.39).⁷⁷

Table 1.3 compares the yield and the conversion times of the hydroboration with different carbonyl compounds using **XLIX** or **L**. Reactions of **XLIX** and **L** with aldehydes often gave quantitative yields of the corresponding alcohol. It was found that the reactions with **L** are faster due to the higher polarity of Sn–O bond, which facilitates the hydrogenation process. It is also noteworthy that the hydroboration of an aliphatic-substituted aldehyde is faster than that of an aryl-substituted aldehyde, presumably because of the increased stability of an aryl-substituent metalla-alkoxide transition state.⁷⁷

Table 1.3 – Reduction of carbonyl compounds using **XLIX** and **L**. Only selected samples are presented in the table.⁷⁷

Entry	Substrate	Cat/mol %	Time/ h	Yield/ %
1	PhC(O)H	XLIX / 1	1.5	99
2	PhC(O)H	L / 0.05	2.5	99
3	EtC(O)H	XLIX / 0.05	<0.15	99
4	EtC(O)H	L / 0.05	1	99
5	PhC(O)CF ₃	XLIX / 2.5	<0.15	99
6	PhC(O)CF ₃	L / 0.5	0.25	99
7	<i>i</i> PrC(O) <i>i</i> Pr	XLIX / 1.25	24	80
8	<i>i</i> PrC(O) <i>i</i> Pr	L / 0.5	168	95

More recently, Jones demonstrated reduction of CO₂ to its methanol derivative using **XLIX** or **L** and catecholborane (HBcat), a stronger hydride donor compared to HBpin (Scheme 1.40). Consistent with the previous carbonyl reduction report, compound **L** was found to be a more efficient catalyst than **XLIX**. At 10 mol% catalyst loading of **XLIX**, the reduction of CO₂ was completed after twenty-four hours at 20 °C. At 1 mol% catalyst loading, longer reaction times were required and only moderate conversion observed. Whereas, complex **L** showed complete reduction of CO₂ within five minutes at 20 °C, even with a catalyst loading of 1 mol%.⁷⁸



Scheme 1.40: Catalytic reduction of CO₂ with **XLIX** and **L**.⁷⁸

1.5 Small molecule activation with geometry constrained main-group compounds

1.5.1 Geometry constrained main-group compounds

Three-coordinate complexes of phosphorus(III) generally exhibit pyramidal geometries due to the presence of a stereochemically active lone pair. However, in 1987, Arduengo reported the synthesis of a series of planar geometry constrained main-group compounds bearing a tridentate pincer ligand enforcing a planar ‘T-shaped’ geometry. It was found that the lone pair of electrons on nitrogen is delocalised into the empty p-orbital of the pnictogen centre, resulting in a ten electron count at the pnictogen centre, i.e. a 10-E-3 system (E = N, P, As, Sb, Bi). The planar T-shaped geometry is stabilised by extensive delocalisation along the π plane of the 10-E-3 molecule (Figure 1.4).⁷⁹

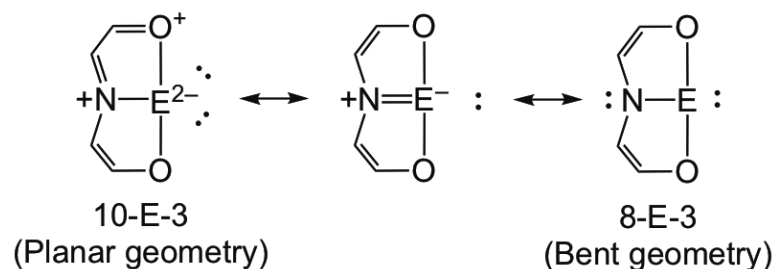


Figure 1.4: Resonance structures of constrained geometry group 15 compounds.⁷⁹

These constrained geometry species have two orthogonal orbitals (one filled: lone pair; one empty: stabilised via π -delocalisation) resembling the orbital arrangement of alkyl amino-carbenes reported by Bertrand. These planar ‘T-shaped’ P(III) complexes were later investigated for the activation of polarised X–H bond (e.g. X = N or O) resulting in five-coordinate trigonal bipyramidal P(V) activation products.⁷⁹ Constrained geometry

complexes also favour small molecule activation by minimising the reorganisation energy during the activation process (Figure 1.5).

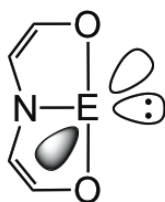
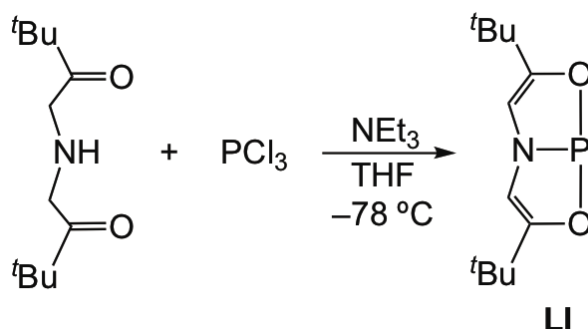


Figure 1.5: Orbital configuration of a 8-E-3 system.⁷⁹

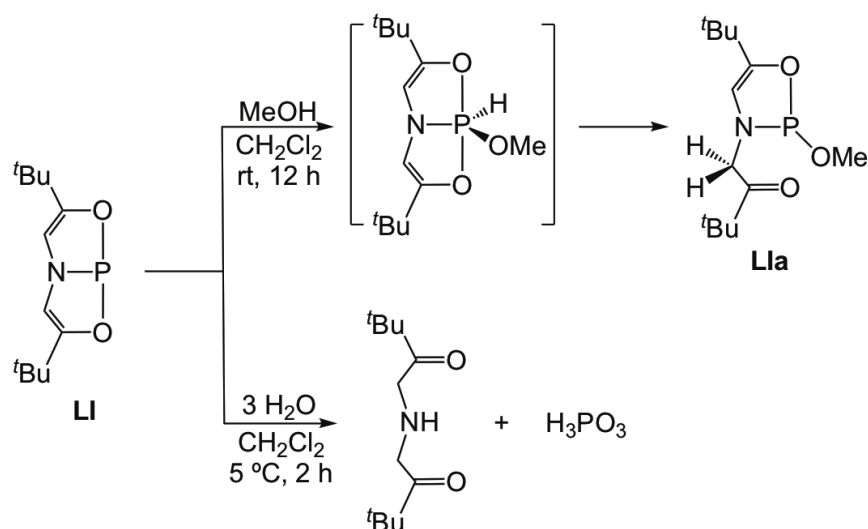
1.5.2 Small molecule activation by a geometry constrained compound supported by a bis(alkoxide) amide ligand

The first phosphorus(III) geometry constrained compound, **LI**, was prepared by reacting diketoamine with phosphorus trichloride in the presence of trimethylamine at $-78\text{ }^{\circ}\text{C}$ (Scheme 1.41).



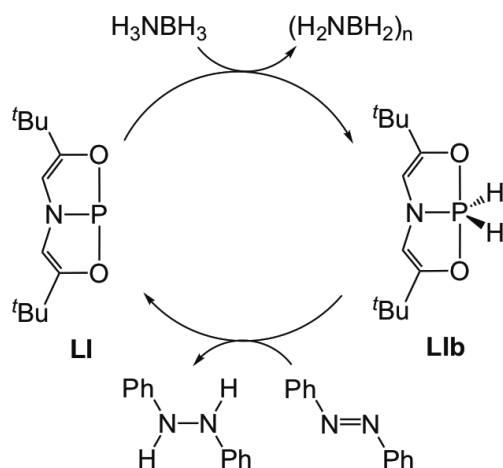
Scheme 1.41: Synthesis of **LI**.⁷⁹

Arduengo demonstrated that **LI** underwent facile addition with methanol to form a P(V) trigonal bipyramidal intermediate, followed by proton transfer to the ligand backbone to afford **LIa**. In related work, **LI** can be rapidly hydrolysed at room temperature to form phosphorous acid and the corresponding protonated ligand (Scheme 1.42).



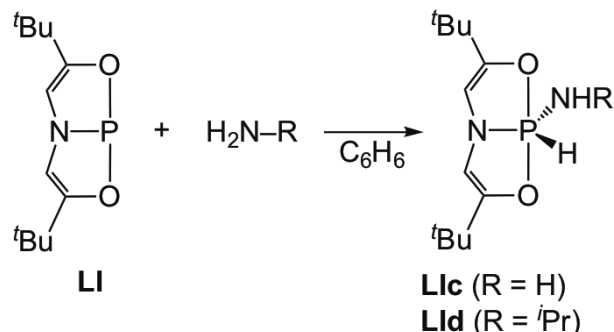
Scheme 1.42: Reaction of **LI** with methanol and water.⁷⁹

In 2012, Radosevich demonstrated **LI** as an efficient catalyst in reduction of azobenzene using ammonia-borane ($\text{H}_3\text{N}\cdot\text{BH}_3$) as a hydrogen surrogate (Scheme 1.43).⁸⁰ In the reaction of **LI** and $\text{H}_3\text{N}\cdot\text{BH}_3$, the P(III) centre of **LI** oxidatively activated the N–H and B–H bonds of $\text{H}_3\text{N}\cdot\text{BH}_3$ to yield a trigonal bipyramidal P(V) compound, **LIb**. Then, **LIb** transferred two protons to azobenzene resulting in formation of 1,2-diphenylhydrazine, and regenerating **LI**. It was shown that, with a 10 mol% catalytic loadings of **LI**, reaction of $\text{H}_3\text{N}\cdot\text{BH}_3$ and azobenzene converted into diphenylhydrazine in 80% yield in twenty-four hours and 94% in forty-eight hours, as determined by the ^1H NMR spectrum of the crude reaction mixtures.⁸⁰



Scheme 1.43: Catalytic hydrogenation of azobenzene by **LI**.⁸⁰

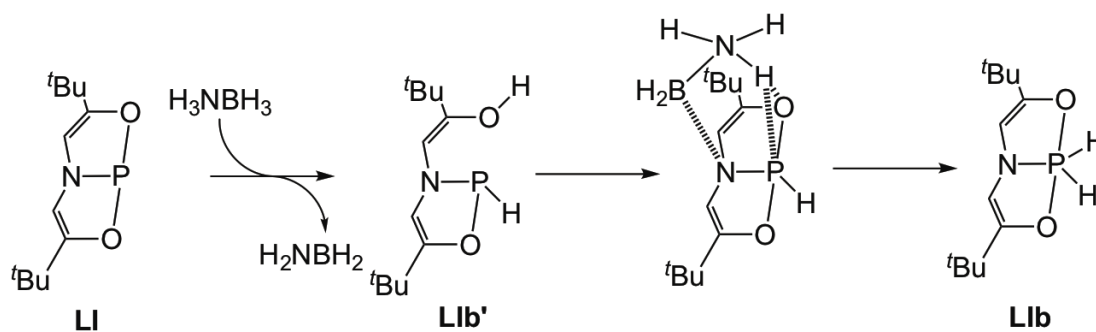
Radosevich also found that **LI** underwent N–H oxidative additions with ammonia and primary amines to afford a range of trigonal bipyramidal P(V) hydrido-amido substituted compounds (**Llc–Lld**) under mild conditions (Scheme 1.44).⁸¹



Scheme 1.44: Reaction of **LI** with: i) NH_3 (-78°C to rt, 30 min); ii) $\text{H}_2\text{N}^i\text{Pr}$ (rt, 30 min).⁸¹

1.5.2.1 Mechanistic studies of N–H bond activation by **LI**

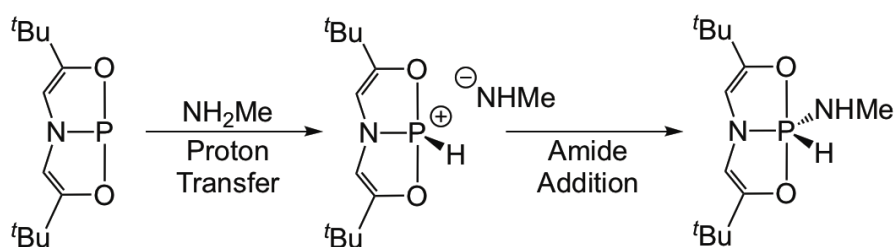
Theoretical calculations performed by Sakaki investigated the mechanism of the ammonia-borane dehydrogenation by **LI** and showed that the concerted mechanism pathway is energetically unfavourable, requiring an activation barrier of $+42.7 \text{ kcal}\cdot\text{mol}^{-1}$. Instead, the reaction proceeds through a step-wise mechanism, with the phosphorus centre and one of its adjacent oxygen atom being protonated by $\text{H}_3\text{N}\cdot\text{BH}_3$ to afford the **Llb'** intermediate which subsequently undergoes an intermolecular hydrogen transfer to yield **Llb** (Scheme 1.45).⁸² Such cooperative pathways have previously been reported for the dehydrogenation of alcohols employing transition metal complexes bearing pincer ligands.^{83,84}



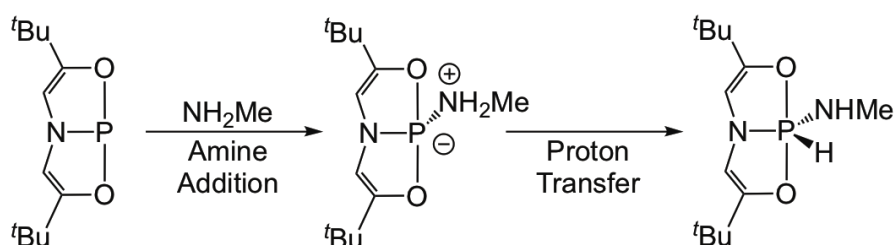
Scheme 1.45: Sakaki's proposed mechanism of the reaction of **LI** with BH_3NH_3 .⁸²

Radosevich has investigated the mechanism of the N–H bond activation with **LI** and methylamine (NH_2Me) and found that the oxidative addition did not proceed via a concerted mechanism, because of the high activation barrier ($+50.1 \text{ kcal}\cdot\text{mol}^{-1}$). Subsequently, Radosevich investigated two stepwise mechanisms: a) a nucleophilic mechanism initiated by deprotonation of the amine, followed by amide addition to the positively charged phosphorus centre; b) an electrophilic mechanism initiated by amine addition to the electrophilic phosphorus centre, followed by P–H bond formation via proton transfer (Scheme 1.46).⁸¹

A) Nucleophilic Mechanism



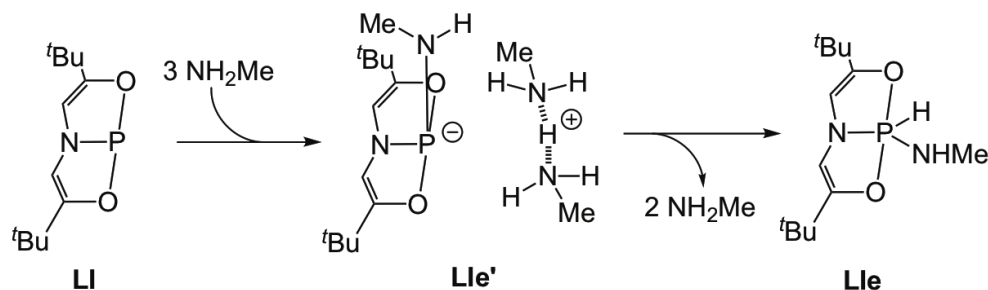
B) Electrophilic Mechanism



Scheme 1.46: Radosevich's hypothesised mechanisms for the reaction of **LI** with H_2NMe .⁸¹

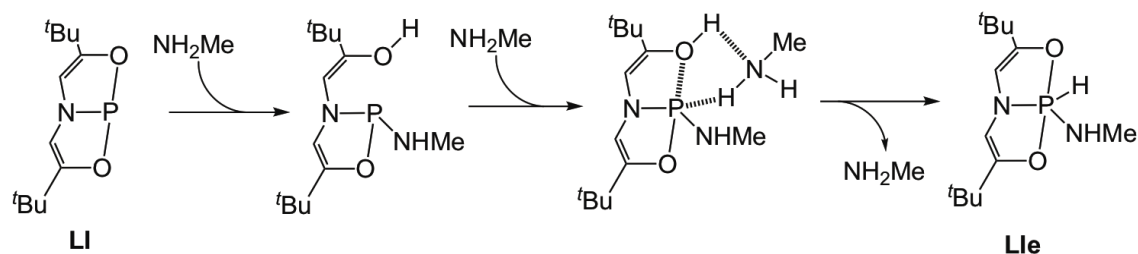
Radosevich's DFT calculations demonstrated that the deprotonation of the less acidic methylamine by **LI** has an energy barrier of $87.7 \text{ kcal}\cdot\text{mol}^{-1}$. The high activation barrier effectively rules out the nucleophilic pathway. In the case of the electrophilic pathway, it was calculated that the phosphorus(III) centre possesses a low lying LUMO (-1.0 eV) and has a relatively favourable electron affinity ($\text{EA} = -2.2 \text{ eV}$), consistent with the phosphorus(III) centre of **LI** being a better electrophile. Radosevich proposed a stepwise electrophilic pathway involving three methylamine molecules. Firstly, a Lewis basic amine

initiated an attack to the electrophilic phosphorus centre forming a phosphoramidate intermediate, **Lle'**, with a relatively low energy barrier (10.1 kcal·mol⁻¹), the second step involves an amine assisted proton transfer to afford the product **Lle** (Scheme 1.47).



Scheme 1.47: Radosevich's proposed mechanism of the reaction of **LI** with NH_2Me .⁸¹

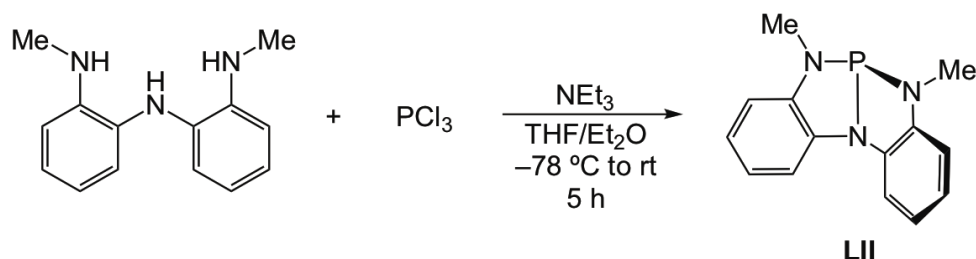
More recently, Pal and Vanka proposed a ligand cooperative mechanism initiated by protonation of the phosphorus centre and a ligand oxygen atom, akin to the first step of the Sukaki's proposed mechanism, followed by proton transfer across the P–O bond mediated by another methylamine molecule (Scheme 1.48).⁸⁵



Scheme 1.48: Pal and Vanka's proposed mechanism of the reaction of **LI** with NH_2Me .⁸⁵

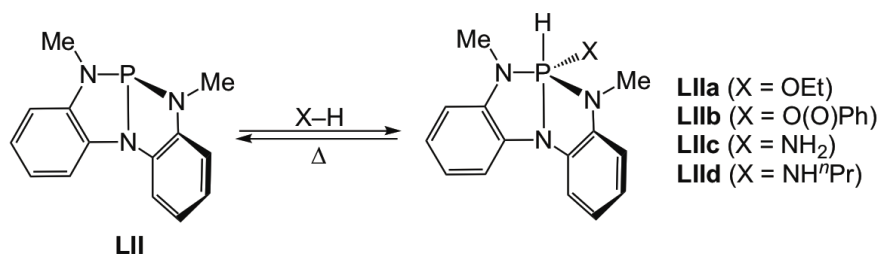
1.5.3 Small molecule activation by a geometry constrained compound supported by triamide ligand

In 2014, Radosevich reported that reaction of a tridentate triamide ligand and phosphorus trichloride in the presence of triethylamine resulted in formation of the phosphorus triamide compound, **LII** (Scheme 1.49).⁸¹



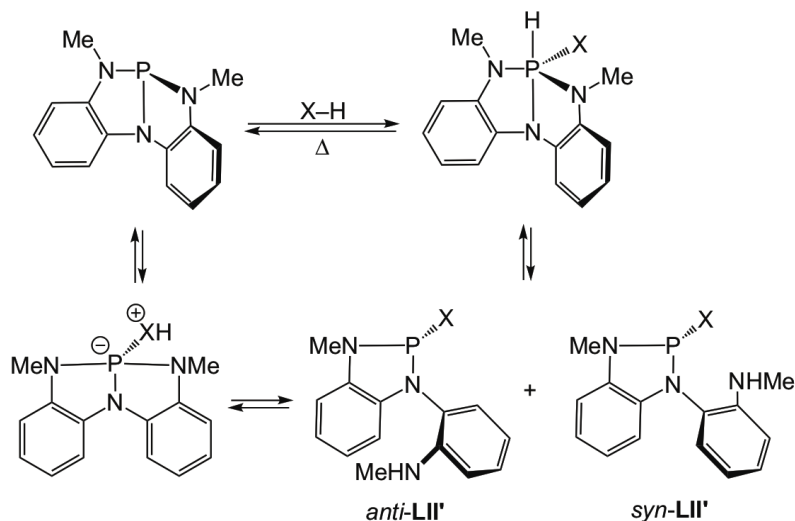
Scheme 1.49: Synthesis of **LII**.⁸¹

In contrast to Arduengo's 'T-shape' compound (**LI**), the structure of **LII** is not planar, but highly distorted ($\text{O-P-O} = 167.4(1)^\circ$ for **LI**; $\text{N-P-N} = 115.2(1)^\circ$ for **LII**). **LII** exhibited poor nucleophilic reactivity, but instead underwent oxidative addition with alcohols, carboxylic acids, ammonia and amines at room temperature to yield trigonal bipyramidal P(V) adducts (**LIIa-LIIId**) (Scheme 1.50). It was also shown that the oxidative addition for some of P(V) activated products was reversible and regenerated **LII** at elevated temperatures.

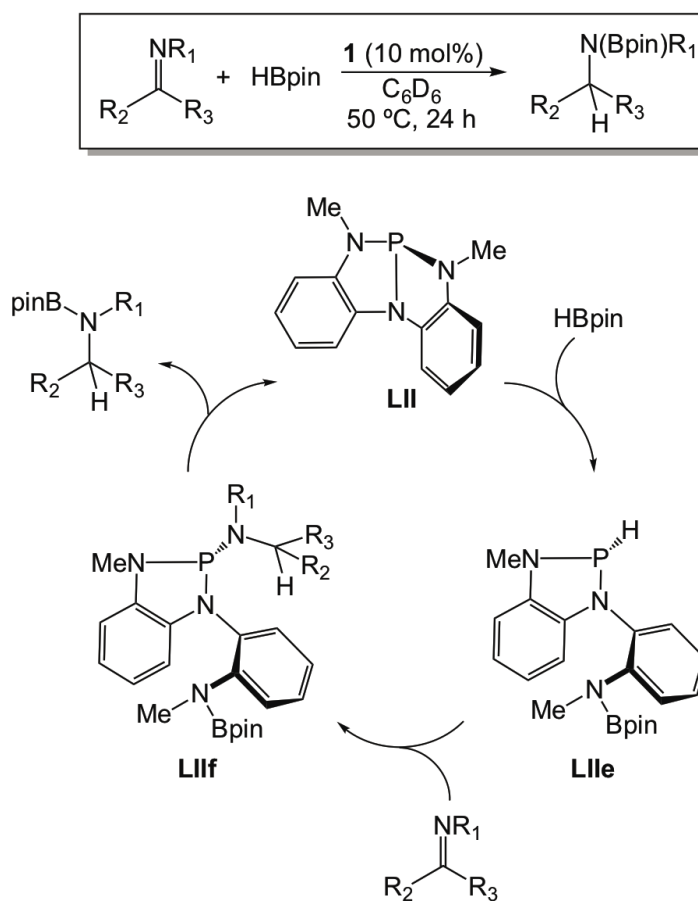


Scheme 1.50: The N-H bond and O-H bond activation by **LII**.⁸¹

Radosevich proposed a stepwise mechanism that is initiated by substrate coordination to the electrophilic phosphorus centre to form a Lewis acid-base adduct, followed by proton transfer to the ligand nitrogen atom adjacent to the phosphorus centre to give *anti*-**LII'** and *syn*-**LII'** diastereomers which subsequently underwent an intramolecular $\sigma^3\text{-P}$ to $\sigma^5\text{-P}$ tautomerism to form a P(V) activation product (Scheme 1.51).⁸¹



Scheme 1.51: Radosevich's proposed mechanism of the X–H bond activation by **LII**.⁸¹



Scheme 1.52: Catalytic reduction of imines by **LII** and the Radosevich's proposed mechanism.⁸⁶

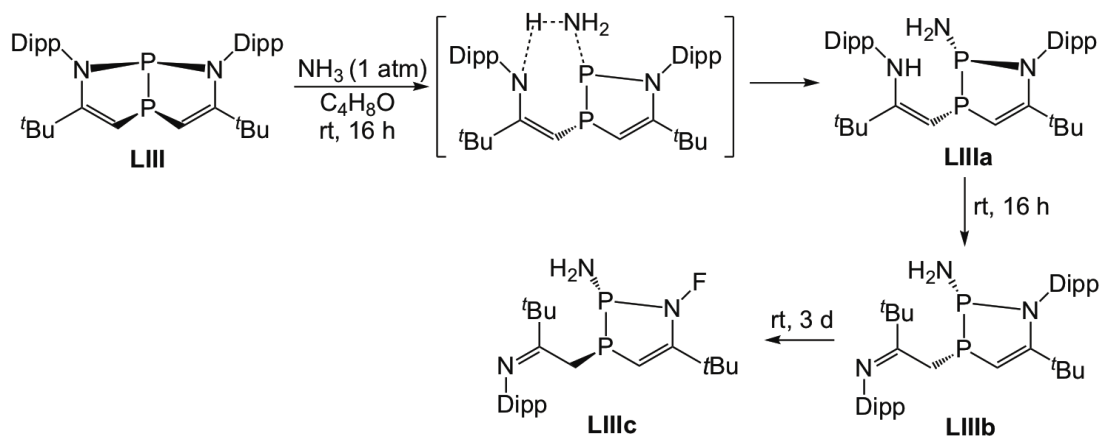
Recently, Radosevich also reported on catalytic reduction of imine by **LII** with HBpin. It was found that imines reacted with HBpin with catalytic loadings of **LII** (10 mol%) to afford the corresponding amine. Scheme 1.52 depicts a phosphorus ligand cooperative

mechanism which is initiated by addition of HBpin to **LII** to form the P–H bond giving the intermediate, **LIIf**, followed by insertion of an imine substrate to the P–H bond to yield **LIIf**. Subsequently, **LIIf** undergoes an intramolecular boryl transfer to form the corresponding amine and **LII** is regenerated (Scheme 1.52).⁸⁶

1.5.4 Small molecule activation by a geometry constrained diazadiphosphapentalene compound

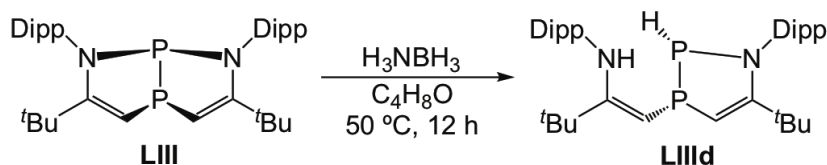
In 2014, Kinjo reported the synthesis of a geometry constrained diazadiphosphapentalene derivative, **LIII**, which exhibited a bent structure around a phosphorus (III) centre. The presence of two phosphorus atoms at the bridgehead in **LIII** resulted in a higher energy barrier to obtain the 10-P-3 planar configuration.

LIII was capable of activating ammonia to afford the 1-aza-2,3-diphospholene derivative, **LIIIc** (Scheme 1.53). However, the ammonia activation is thought to be initiated by formal σ -bond metathesis between the N–H bond of ammonia and the endocyclic P–N bond of **LIII** to afford **LIIIa**. After sixteen hours at room temperature, **LIIIa** underwent proton transfer and tautomerised to its imine derivative **LIIIb**. Finally, after three days at room temperature, **LIIIb** slowly converted to its *trans*-configuration through a pyramidal inversion about the phosphorus between the two carbon atoms to yield **LIIIc** (Scheme 1.53).⁸⁷



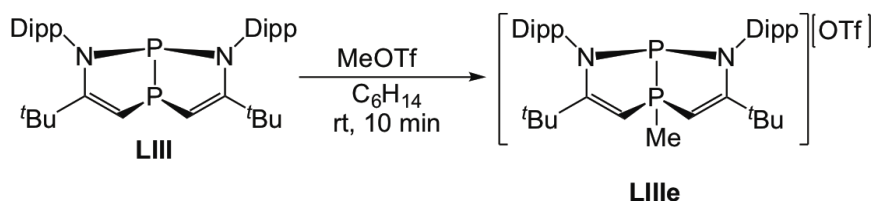
Scheme 1.53: Reaction of **LIII** with ammonia.⁸⁷

In a similar fashion, Kinjo has also reported the reaction of **LIII** with ammonia-borane which afforded **LIIId** (Scheme 1.54).⁸⁸ The observation was consistent with Sakaki's proposed mechanism with the initial step being the bond cleavage between the phosphorus and one of its adjacent atoms (for **LI**, P–O bond; for **LIII**, P–N bond).



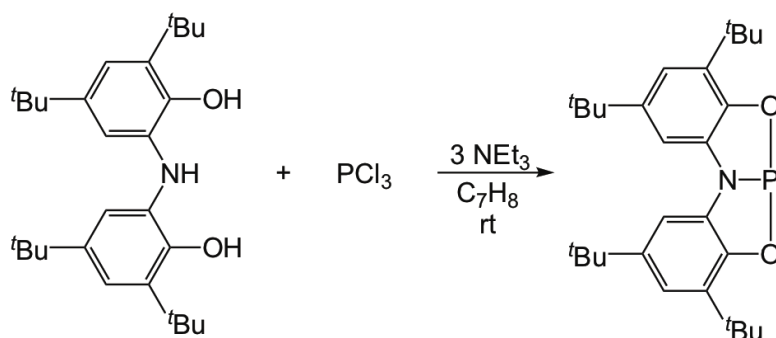
Scheme 1.54: Reaction of **LIII** with ammonia-borane.⁸⁷

The nucleophilicity at the phosphorus centre of **LIII** was demonstrated by reaction of **LIII** with an electrophile, methyl trifluoromethanesulfonate (MeOTf), which resulted in a facile reaction forming a P–CH₃ bond to afford **LIIIe** (Scheme 1.55).⁸⁸



Scheme 1.55: Reaction of **LIII** with MeOTf.⁸⁸

1.5.5 Small molecule activation by a geometry constrained compound supported by a bisphenolate amide ligand



Scheme 1.56: Synthesis of **LIV**.⁸⁹

Aldridge and Goicoechea jointly reported the isolation of a geometrically constrained phosphorus(III) compound, **LIV**, bearing a bis(3,5-di-*tert*-butyl-2-phenolate)amide ligand

(ONO)³⁻. Prepared by reacting the protonated ligand, H₃(ONO), and phosphorus trichloride in the presence of triethylamine at room temperature (Scheme 1.56).⁸⁹

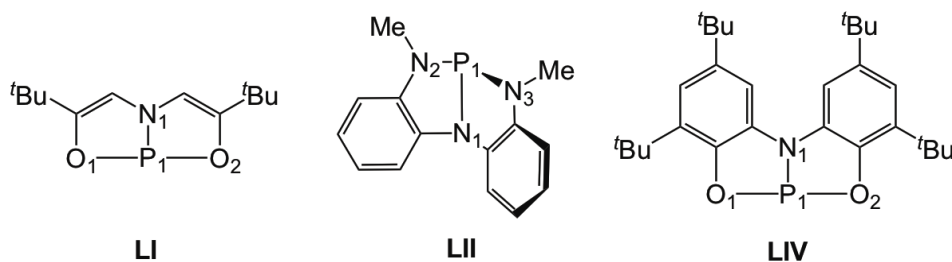


Figure 1.6: Atom labelled for **LI**, **LII** and **LIV** for illustration of the Table 1.4.

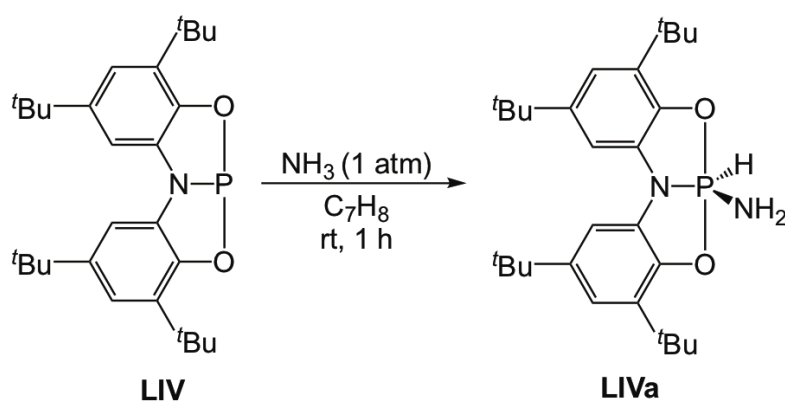
Table 1.4 compares the selected bond angles and bond lengths of **LI**, **LII** and **LIV** for comparison. The solid state structure of **LIV** reveals that **LIV** exhibits a bent structure (i.e. a 8-P-3 bent configuration) around the phosphorus(III) centre, which differs from the relatively planar structure of **LI** (i.e. 10-P-3 planar configuration), consistent with the observation that the X1–P–X2 bond angle of **LIV** is close to that of **LII** but more acute than that of **LI**. The P–N1 bond length of **LIV** is longer than that of **LI**, which reveals a pyramidal geometry around the phosphorus centre, consistent with diminished delocalisation of the nitrogen lone pair to the phosphorus centre. DFT calculations show that the planar isomer of **LIV** is only 4 kJ·mol⁻¹ above its bent isomer, revealing that **LIV** can exhibit both planar and bent geometries in solution.

Table 1.4 – Selected bond angles and bond lengths for **LI**, **LII** and **LIV** (Figure 1.6) (X= O for **LI** and **LIV**; X= N for **LII**).^{79,87,89}

	LI	LII	LIV
P1–N1	1.703(2) Å	1.761(1) Å	1.757(1) Å
P1–X1	1.835(2) Å	1.701(2) Å	1.652(1) Å
P1–X2	1.792(2) Å	1.719(2) Å	1.659(1) Å
X1–P1–X2	167.7(1)°	115.2(1)°	109.6(1)°
N1–P1–X1	83.5(1)°	90.1(1)°	93.2 (1)°
N1–P1–X2	84.2(1)°	90.5(1)°	93.4(1)°
Total angle around P1	335.4°	295.8°	296.2°

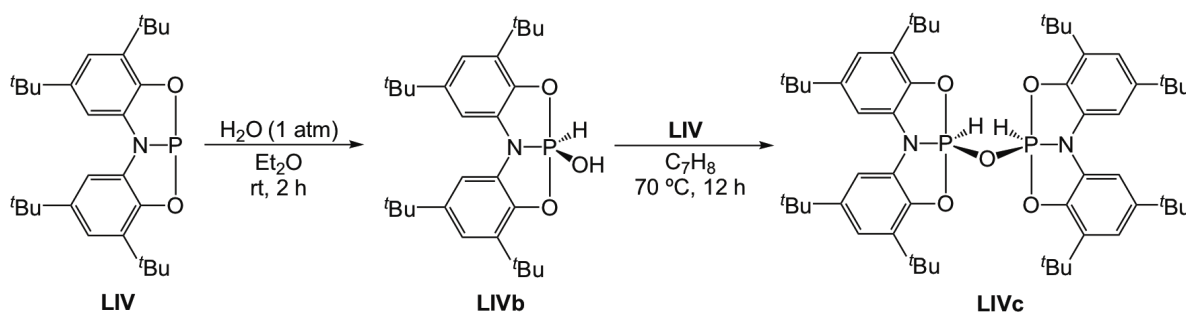
When the electronic properties of **LIV** were investigated via DFT calculation, it was found that the LUMO is the empty and energetically accessible p-orbital located at the phosphorus centre, and its HOMO is largely composed of the lone pair orbital of the nitrogen atom of the ligand backbone.

Similar to the reactivity of **LI–LIII**, the reaction of **LIV** with 1 atm of NH₃ gas resulted in oxidative addition of the N–H bond to afford the trigonal bipyramidal P(V) compound, **LIVa** (Scheme 1.57), with the ONO moiety of the ligand exhibiting a planar conformation, resembling to the solid state structure of **LIc** from the reaction of **LI** and ammonia.



Scheme 1.57: Reaction of **LIV** with NH₃.⁸⁹

The analogous reaction of **LIV** with one equivalent of water resulted in the corresponding trigonal bipyramidal phosphorus(V) compound, **LIVb** (Scheme 1.58). This observation differs from the hydrolysis of **LI** which yielded a free protonated ligand and phosphoric acid. Interestingly, treatment of **LIVb** with the second equivalent of **LIV** at 70 °C exclusively formed **LIVc** which features a bridging oxygen atom (Scheme 1.58). This observation of stepwise water activation is unprecedented in any geometry constrained main group systems, but is comparable to Driess' silylene (**XX**) reaction with water, which have been shown to form **XXb** and **XXc** (see Scheme 1.15 in Chapter 1.2.6). Alternatively, **LIVc** can be synthesised in the analogous reaction with half equivalent of water at elevated temperatures.



Scheme 1.58: Reaction of **LIV** with water.⁸⁹

1.6 Project aims

Based on the findings of our own research regarding the reactivity of the geometrically constrained phosphorus (III) compound, **LIV**, we have decided to develop novel compounds with group 13, 14 and 15 elements exploiting the Lewis acidic character of group 13 elements, and the E(II)/E(IV) (E = Ge, Sn) and E'(III)/E'(V) (E' = P, As) redox pairs, respectively.

Chapter 2 will discuss the synthesis of complexes of boron, aluminium and gallium complexes bearing the *N,N*-(bis(3,5-di-*tert*-butyl-2-phenolate)amide ligand and their reactivity towards the activation of small molecule substrates. Chapter 3 will discuss the synthesis of group 14 complexes that bear the (ONO)³⁻ ligand, and the bidentate pincer ligands, 5-(*N,N'*-bis-cyclohexylamino)-2,7-di-*tert*-butyl-9,9-dimethyl-xanthene (^{Cy}NON²⁻) and 4,5-(*N,N'*-bis-mesitylamino)-2,7-di-*tert*-butyl-9,9-dimethyl-xanthene (^{Mes}NON²⁻). Furthermore, the reactivity of these species toward small molecules will also be discussed. Chapter 4 details the synthesis of an arsenic complex bearing a tridentate (ONO)³⁻ ligand and its reactivity towards charged nucleophiles, electrophiles and oxidants. The second part of the chapter 4 will report the synthesis of a phosphorus (III) complex bearing the 2,2'-[iminobis(methylene)]-bis[4-methoxy-phenol] ligand and its hydrolysed products. Finally, chapter 5 will provide detailed experimental procedures and complete spectroscopic data for all compounds reported in this thesis.

1.7 Reference

- (1) van der Vlugt, J. I. *Chem. Soc. Rev.* **2010**, 39 (6), 2302.
- (2) Power, P. P. *Nature* **2010**, 463 (7278), 171.
- (3) Halpern, J. *Acc. Chem. Res.* **1970**, 3 (11), 386.
- (4) Smeltz, J. L.; Boyle, P. D.; Ison, E. A. *J. Am. Chem. Soc.* **2011**, 133 (34), 13288.
- (5) Johansson, R.; Jarenmark, M.; Wendt, O. F. *Organometallics* **2005**, 24 (19), 4500.
- (6) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, 107 (94), 4440.
- (7) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, 106 (2), 451.
- (8) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science (80-.)*. **2007**, 316, 439.
- (9) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science (80-.)*. **2006**, 314, 1124.
- (10) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, 106 (19), 5472.
- (11) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, 26 (7), 971.
- (12) Banaszak Holl, M. M.; Wolczanski, P. T.; Van Duyne, G. D. *J. Am. Chem. Soc.* **1990**, 112 (22), 7989.
- (13) Zhao, J.; Goldman, A. S.; Hartwig, J. F. *Science (80-.)*. **2005**, 307, 1080.
- (14) Arrowsmith, M.; Böhnke, J.; Braunschweig, H.; Celik, M. A.; Dellermann, T.; Hammond, K. *Chem. - A Eur. J.* **2016**, 22 (48), 17169.
- (15) Shoji, Y.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. *J. Am.*

- Chem. Soc.* **2010**, *132* (24), 8258.
- (16) Tsukahara, N.; Asakawa, H.; Lee, K. H.; Lin, Z.; Yamashita, M. *J. Am. Chem. Soc.* **2017**, *139* (7), 2593.
- (17) von Grotthuss, E.; Diefenbach, M.; Bolte, M.; Lerner, H. W.; Holthausen, M. C.; Wagner, M. *Angew. Chem. Int. Ed.* **2016**, *55* (45), 14067.
- (18) Dahcheh, F.; Martin, D.; Stephan, D. W.; Bertrand, G. *Angew. Chem. Int. Ed.* **2014**, *53* (48), 13159.
- (19) Nagata, K.; Murosaki, T.; Agou, T.; Sasamori, T.; Matsuo, T.; Tokitoh, N. *Angew. Chem. Int. Ed.* **2016**, *55* (41), 12877.
- (20) Cui, C.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem. Int. Ed.* **2000**, *39* (23), 4274.
- (21) Chu, T.; Korobkov, I.; Nikonov, G. I. *J. Am. Chem. Soc.* **2014**, *136* (25), 9195.
- (22) Myers, T. W.; Berben, L. A. *J. Am. Chem. Soc.* **2013**, *135* (27), 9988.
- (23) Zhu, Z.; Wang, X.; Peng, Y.; Lei, H.; Fettingner, J. C.; Rivard, E.; Power, P. P. *Angew. Chemie. Int. Ed.* **2009**, *48* (11), 2031.
- (24) Abdalla, J. A. B.; Riddlestone, I. M.; Tirfoin, R.; Aldridge, S. *Angew. Chem. Int. Ed.* **2015**, *54* (17), 5098.
- (25) Seifert, A.; Scheid, D.; Linti, G.; Zessin, T. *Chem. - A Eur. J.* **2009**, *15* (44), 12114.
- (26) Hill, M. S.; Hitchcock, P. B.; Pongtavornpinyo, R. *Inorg. Chem.* **2007**, *46* (9), 3783.
- (27) García-Rodeja, Y.; Bickelhaupt, F. M.; Fernández, I. *Chem. - A Eur. J.* **2016**, *22* (38), 13669.
- (28) R. Geiter, R. H. *J. Am. Chem. Soc.* **1968**, *90* (20), 5457.
- (29) Kline, M.; Harlow, R. L. *J. Am. Chem. Soc.* **1991**, No. 21, 363.

- (30) Crabtree, R. H. *J. Organomet. Chem.* **2005**, 690, 5451.
- (31) Martin, D.; Lassauque, N.; Donnadiou, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2012**, 51, 6172.
- (32) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, 2 (3), 389.
- (33) Lavallo, V.; Canac, Y.; Dehope, A.; Donnadiou, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2005**, 44 (44), 7236.
- (34) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadiou, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2005**, 44 (35), 5705.
- (35) Driess, M.; Grutzmacher, H. *Angew. Chem. Int. Ed. Engl.* **1996**, 35 (8), 828.
- (36) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, 109, 3479.
- (37) Protchenko, A. V.; Birjkumar, K. H.; Dange, D.; Schwarz, A. D.; Vidovic, D.; Jones, C.; Kaltsoyannis, N.; Mountford, P.; Aldridge, S. *J. Am. Chem. Soc.* **2012**, 134 (15), 6500.
- (38) Protchenko, A. V.; Schwarz, A. D.; Blake, M. P.; Jones, C.; Kaltsoyannis, N.; Mountford, P.; Aldridge, S. *Angew. Chem. Int. Ed.* **2013**, 52 (2), 568.
- (39) Jana, A.; Schulzke, C.; Roesky, H. W. *J. Am. Chem. Soc.* **2009**, No. 131, 4600.
- (40) Yao, S.; Brym, M.; Van Wüllen, C.; Driess, M. *Angew. Chem. Int. Ed.* **2007**, 46 (22), 4159.
- (41) Rekken, B. D.; Brown, T. M.; Fettingner, J. C.; Tuononen, H. M.; Power, P. P. *J. Am. Chem. Soc.* **2012**, 134 (15), 6504.
- (42) Kuriakose, N.; Vanka, K. *Dalton. Trans.* **2014**, 43, 2194.
- (43) Spikes, G. H.; Fettingner, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, 127 (35), 12232.
- (44) Li, J.; Schenk, C.; Goedecke, C.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2011**,

- 133 (46), 18622.
- (45) Hadlington, T. J.; Hermann, M.; Li, J.; Frenking, G.; Jones, C. *Angew. Chem. Int. Ed.* **2013**, 52 (39), 10199.
- (46) Peng, Y.; Guo, J. D.; Ellis, B. D.; Zhu, Z.; Fettingner, J. C.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2009**, 131 (44), 16272.
- (47) Driess, M.; Yao, S.; Brym, M.; Van Wüllen, C. *Angew. Chem. Int. Ed.* **2006**, 45 (26), 4349.
- (48) Jana, A.; Objartel, I.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2009**, 48 (3), 798.
- (49) Alberto, M. E.; Russo, N.; Sicilia, E. *Chem. - A Eur. J.* **2013**, 19 (24), 7835.
- (50) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Organometallics* **2011**, 30 (23), 6490.
- (51) Peng, Y.; Brynda, M.; Ellis, B. D.; Fettingner, J. C.; Rivard, E.; Power, P. P. *Chem. Commun.* **2008**, 45, 6042.
- (52) Zhao, L.; Huang, F.; Lu, G.; Wang, Z. X.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **2012**, 134 (21), 8856.
- (53) Hadlington, T. J.; Jones, C. *Chem. Commun.* **2014**, 50 (18), 2321.
- (54) Peng, Y.; Ellis, B. D.; Wang, X.; Power, P. P. *J. Am. Chem. Soc.* **2008**, 130 (37), 12268.
- (55) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, 16, 1920.
- (56) Protchenko, A. V.; Birjkumar, K. H.; Dange, D.; Schwarz, A. D.; Vidovic, D.; Jones, C.; Kaltsoyannis, N.; Mountford, P.; Aldridge, S. *J. Am. Chem. Soc.* **2012**, 134, 6500.
- (57) Hinz, A.; Schulz, A.; Villinger, A. *Angew. Chem. Int. Ed.* **2016**, 55 (40), 12214.
- (58) Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, 49 (1), 46.

- (59) Brown, H. C.; Schlesinger, H. I.; Cardon, S. Z. *J. Am. Chem. Soc.* **1942**, *64* (2), 325.
- (60) Wittig, G.; Benz, E. *Chem. Ber.* **1959**, *92* (9), 1999.
- (61) Rokob, T. A.; Bakó, I.; Stirling, A.; Hamza, A.; Pápai, I. *J. Am. Chem. Soc.* **2013**, *135* (11), 4425.
- (62) Mo, Z.; Kolychev, E. L.; Rit, A.; Campos, J.; Niu, H.; Aldridge, S. *J. Am. Chem. Soc.* **2015**, *137* (38), 12227.
- (63) Sumerin, V.; Schulz, F.; Nieger, M.; Atsumi, M.; Wang, C.; Leskelä, M.; Pyykkö, P.; Repo, T.; Rieger, B. *J. Organomet. Chem.* **2009**, *694* (17), 2654.
- (64) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. *W. Chem. Commun.* **2007**, 2 (47), 5072.
- (65) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129* (7), 1880.
- (66) Holschumacher, D.; Bannenberg, T.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Angew. Chem. Int. Ed.* **2008**, *47* (39), 7428.
- (67) Chase, P. A.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2008**, *47* (39), 7433.
- (68) Chase, P. A.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. *Dalt. Trans.* **2009**, 35, 7179.
- (69) Moroz, A.; Sweany, R. L.; Whittenburg, S. L. *J. Phys. Chem.* **1990**, *94* (4), 1352.
- (70) Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, *49* (8), 1402.
- (71) Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. *Angew. Chem. Int. Ed.* **2008**, *47* (13), 2435.
- (72) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chemie. Int. Ed.* **2007**, *46* (42), 8050.

- (73) Mahdi, T.; Heiden, Z. M.; Grimme, S.; Stephan, D. W. *J. Am. Chem. Soc.* **2012**, *134* (9), 4088.
- (74) Jana, A.; Tavčar, G.; Roesky, H. W.; John, M. *Dalton Trans.* **2010**, 39 (40), 9487.
- (75) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, *54* (35), 10225.
- (76) 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.
- (77) Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2014**, *136* (8), 3028.
- (78) Hadlington, T. J.; Kefalidis, C. E.; Maron, L.; Jones, C. *ACS Catal.* **2017**, *7* (3), 1853.
- (79) Arduengo, A. J.; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Mizen, M. B. *J. Am. Chem. Soc.* **1987**, *109* (3), 627.
- (80) Dunn, N. L.; Ha, M.; Radosevich, A. T. *J. Am. Chem. Soc.* **2012**, *134* (28), 11330.
- (81) McCarthy, S. M.; Lin, Y. C.; Devarajan, D.; Chang, J. W.; Yennawar, H. P.; Rioux, R. M.; Ess, D. H.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136* (12), 4640.
- (82) Zeng, G.; Maeda, S.; Taketsugu, T.; Sakaki, S. *Angew. Chem. Int. Ed.* **2014**, *53* (18), 4633.
- (83) Zeng, G.; Guo, Y.; Li, S. *Inorg. Chem.* **2009**, *48* (21), 10257.
- (84) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44* (8), 588.
- (85) Pal, A.; Vanka, K. *Inorg. Chem.* **2016**, *55* (2), 558.
- (86) Lin, Y. C.; Hatzakis, E.; McCarthy, S. M.; Reichl, K. D.; Lai, T. Y.; Yennawar, H. P.; Radosevich, A. T. *J. Am. Chem. Soc.* **2017**, *139* (16), 6008.

- (87) Cui, J.; Li, Y.; Ganguly, R.; Inthirarajah, A.; Hirao, H.; Kinjo, R. *J. Am. Chem. Soc.* **2014**, *136* (48), 16764.
- (88) Cui, J.; Li, Y.; Ganguly, R.; Kinjo, R. *Chem. - A Eur. J.* **2016**, *22* (29), 9976.
- (89) Robinson, T. P.; De Rosa, D. M.; Aldridge, S.; Goicoechea, J. M. *Angew. Chem. Int. Ed.* **2015**, *54* (46), 13758.

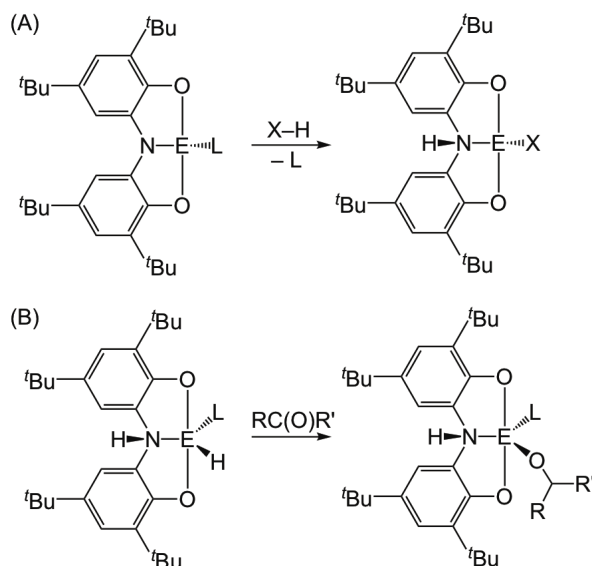
Chapter 2

Complexes of group 13 elements bearing the *N,N*-bis(3,5-di-*tert*-butyl-2-phenolate) amide ligand

2.1 Introduction and objectives

In Chapter 1, a number of main-group complexes capable of activating small molecule substrates that possess X–H bonds (X = N, O, etc.) were highlighted.^{1–5} Of particular relevance to the work described in this thesis are compounds bearing pincer ligands. Mechanistic investigations into Radosevich’s phosphorus(III) complex bearing a bis(alkoxide) amide ligand, **LI**, showed that N–H bond activation is initiated by substrate coordination to the electrophilic phosphorus(III) centre, followed by proton transfer to afford the corresponding trigonal bipyramidal phosphorus(V) complexes (see Section 1.5.2.1 for details). In this work, the phosphorus centre was replaced with strongly electrophilic group 13 elements in an effort to lower the energy of the LUMO in such compounds, and perhaps increase the reactivity with small molecule substrates.

In related work, we prepared a phosphorus(III) compound bearing the *N,N*-bis-(3,5-di-*tert*-butyl-2-phenolate)amide ligand, (ONO)^{3–} (**LIV**), capable of activating the N–H and O–H bonds of ammonia and water, respectively. DFT calculations revealed that the LUMO was localised on the phosphorus centre, consistent with a p-orbital, while the HOMO is largely composed of the lone pair orbital on the nitrogen atom of the ligand. By preparing base-stabilised group 13 element complexes chelated by a constrained geometry ligand, frustrated Lewis pair type activation of small molecules may be possible (Scheme 2.1; A).⁵ Furthermore, related systems such as Roesky’s aluminium hydride (**XLVIII**) and Aldridge’s gallium hydride compounds (**XIIa**) have been shown to undergo catalytic hydroboration and hydrosilylation reactions with carbonyls and carbon dioxide.^{6,7} We hypothesised that E(H){ON(H)O} (E = B, Al, Ga) complexes may exhibit analogous catalytic behaviour (Scheme 2.1; B). In this chapter, the synthesis of a series of group 13 complexes bearing the (ONO)^{3–} ligand and their reactivity towards small molecule substrates is described.



Scheme 2.1: Predicted reactivity of $\text{E(ONO)} \cdot \text{L}$ and $\text{E(H)\{ON(H)O\}} \cdot \text{L}$ complexes ($\text{E} = \text{B, Al, Ga}$).

2.2 Boron compounds bearing the $(\text{ONO})^{3-}$ ligand

Martin *et. al.* have reported on a series of boron containing complexes supported by sterically rigid triamide ligands, **LV**–**LVI**, possessing more distorted geometries around boron than conventional sp^2 -hybridised boron compounds (N2-B-N3 of **LV** = $145.7(3)^\circ$ and sp^2 -hybridised boron angles = 120°) (Figure 2.1). It was found that the B1-N1 bond length ($1.430(5) \text{ \AA}$ for **LV** and $1.436(3) \text{ \AA}$ for **LVI**) was notably shorter than a typical B–N single bond ($1.58 \text{ \AA}$), consistent with donation of the nitrogen lone pair to electrophilic boron atom to stabilise the planar geometry. No reaction of **LV** or **LVI** towards any small molecule substrates has been reported to date.⁸

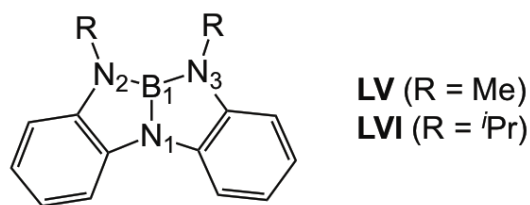


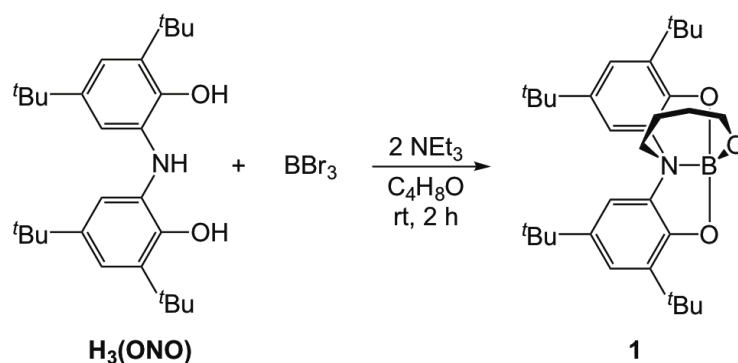
Figure 2.1: Structures of **LV** and **LVI** complexes.

We were interested in synthesising related compounds supported by the $(\text{ONO})^{3-}$ ligand, $\text{B}(\text{ONO})\cdot\text{L}$, and explore the reactivity of such compounds towards molecules with polar X–H bonds ($\text{X} = \text{O}, \text{N}$, etc.).

2.2.1 Synthesis and characterisation of $\text{B}\{\text{ON}(\text{OC}_4\text{H}_8)\text{O}\}$ (**1**)

Analogous to the synthesis of $\text{P}(\text{ONO})$ (**LIV**, see Section 1.5.5 for details),⁵ $\text{H}_3(\text{ONO})$ was reacted with BBr_3 in C_6D_6 in the presence of three molar equivalents of NEt_3 . The reaction was monitored by ^1H NMR spectroscopy, which revealed formation of multiple products. The reaction was repeated using polar solvents, such as pyridine and ether, and at low temperatures ($-78\text{ }^\circ\text{C}$), in an effort to control this reactivity, however they also resulted in multiple products, none of which could be isolated.

By contrast, the reaction of $\text{H}_3(\text{ONO})$ and BBr_3 in THF in the presence of two molar equivalents of NEt_3 resulted in the cleavage of a THF molecule to afford **1** in good yield (83%) (Scheme 2.2).



Scheme 2.2: Synthesis of **1**.

The reaction was monitored by ^1H NMR spectroscopy. The aromatic protons and ^tBu protons resonances provided a spectroscopic handle for monitoring the reaction. The reaction had gone to completion cleanly by the time the NMR measurements were acquired. The ^1H NMR spectrum of **1** in C_6D_6 reveals two doublets at 7.31 and 7.20 ppm and two singlets at 1.35 and 1.26 ppm attributed to the aromatic protons and the *tert*-butyl protons,

respectively. It also shows a set of resonances at 3.99, 3.19, 1.35 and 1.17 ppm, corresponding to the methylene protons of the activated THF molecule. The ^{11}B NMR spectrum shows a signal at 14.6 ppm, indicative of a four-coordinate boron environment.

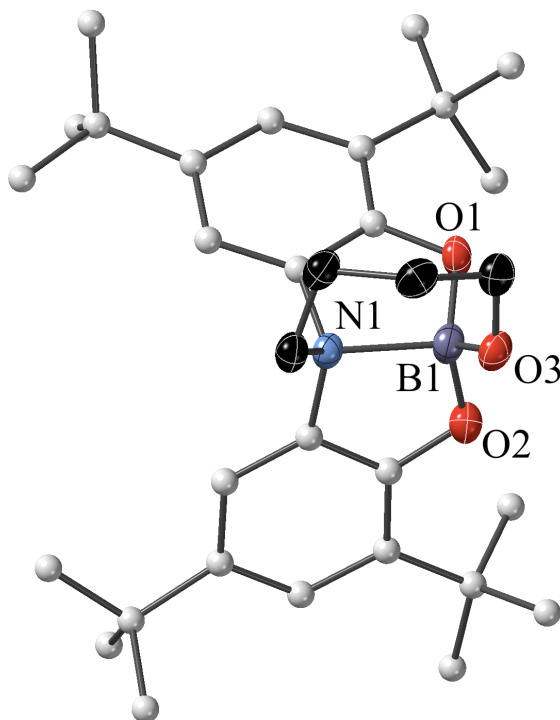


Figure 2.2: Molecular structure of **1**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Crystals of **1** suitable for single crystal X-ray diffraction were grown by slow diffusion of hexane into a concentrated toluene solution of the product at room temperature. The molecular structure of **1** exhibits a tetrahedral boron (B1) centre bridged to nitrogen (N1) by an OC_4H_8 moiety to form a seven-membered heterocyclic ring (Figure 2.2). Table 2.1 shows the selected bond lengths and bond angles for **1**. The boron atom of **1** adopts almost an ideal tetrahedral geometry as the bond angles around boron are very similar. The B1–N1 bond length is 1.763(5) Å which is longer than a typical B–N single bond (1.58 Å) or a dative B–N interaction (1.64 Å).⁸

Table 2.1 – Selected bond lengths and bond angles for **1**.

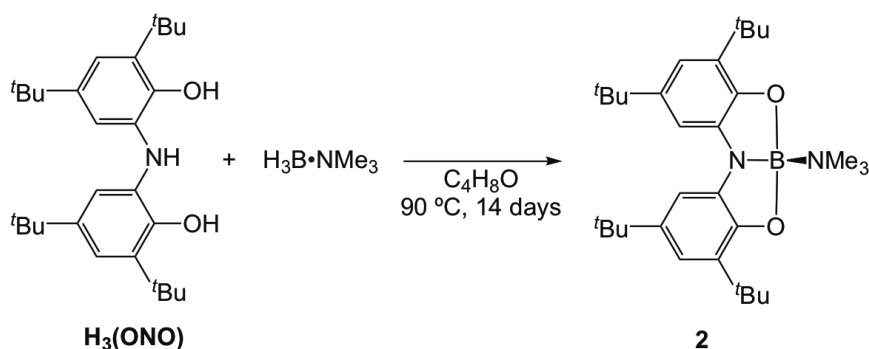
Bond lengths	1	Bond angles	1
B1–N1	1.763(5) Å	O1–B1–O2	113.0(4)°
B1–O1	1.452(5) Å	O1–B1–O3	116.7(4)°
B1–O2	1.450(6) Å	O2–B1–O3	111.5(4)°
B1–O3	1.394(6) Å	N1–B1–O3	112.9(3)°

We propose that **1** was formed by the reaction of a B(ONO) intermediate with THF *in-situ*.

An alternative route towards such compounds was thereby explored.

2.2.2 Reaction of H₃(ONO) with a base-stabilised borane adduct

From the observed reactivity of H₃(ONO) with BBr₃, two-electron donor ligands were investigated to stabilise the highly electrophilic boron centre of the targeted B(ONO) molecule. The reaction between H₃(ONO) and trimethylamine borane (H₃B·NMe₃) at 90 °C for fourteen days evolved H₂ gas and resulted in slow but complete conversion to **2** (Scheme 2.3).

**Scheme 2.3:** Synthesis of **2**.

2 was characterised by ¹H NMR spectroscopy and displays two doublets at 7.60 and 7.15 ppm and two singlets at 1.59 and 1.43 ppm arising from the aromatic protons and the *tert*-butyl protons, respectively. The ¹H NMR spectrum also shows a singlet at 1.87 ppm, which integrates to nine protons, corresponding to the methyl protons of the NMe₃ ligand. The ¹¹B NMR spectrum of **2** reveals a signal at 15.6 ppm, which is comparable to the ¹¹B NMR resonance observed for **1**, again consistent with a four-coordinate boron environment.

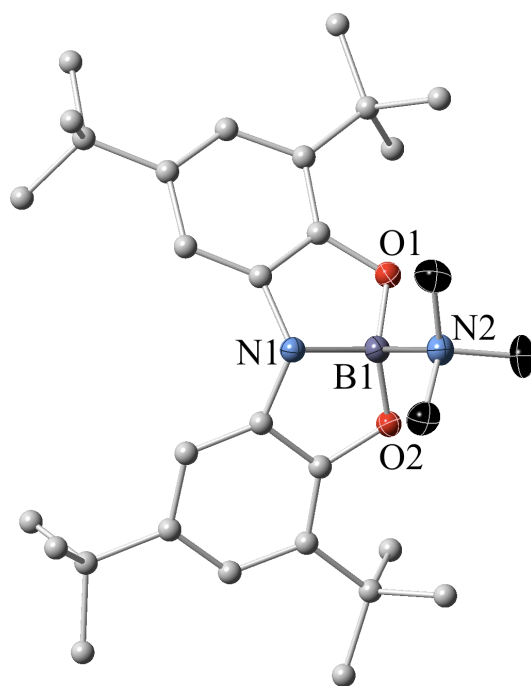


Figure 2.3: Molecular structure of **2**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 2.2 – Selected bond lengths and bond angles for **2**.

Bond lengths	2	Bond angles	2
B1–N1	1.513(2) Å	O1–B1–O2	119.31(11)°
B1–O1	1.466(2) Å	N1–B1–O1	106.21(10)°
B1–O2	1.463(2) Å	N1–B1–O2	106.33(11)°
B1–N2	1.639(2) Å	N1–B1–N2	112.00(10)°

Crystals of **2** suitable for single crystal X-ray diffraction were grown from slow diffusion of hexane into a concentrated toluene solution at room temperature. The molecular structure of **2** exhibits a slightly distorted tetrahedral geometry around the boron atom. Table 2.2 shows selected bond lengths and bond angles for compound **2**. The B1–N1 bond length (1.513(2) Å) is slightly shorter than a typical B–N single bond (1.58 Å), whereas the B1–N2 bond length is almost identical to the B–N bond distance of $\text{H}_3\text{B}\cdot\text{NMe}_3$. All bond angles around the boron centre are similar as **2** exhibits an almost perfect tetrahedral geometry around B1.

The tetrahedral geometry around B1 indicates that the ligand fails to contain the boron atom as the boron atom is too small to fit into the ligand O–N–O binding site without distortion.

Interestingly, during the preparation of **2** on a bulk scale, trace amount of a side product were detected by ^1H NMR spectroscopy. The side product **3** resulted from hydrolysis of the parent compound. The ^1H NMR spectrum of **3** displays more downfield shifted aromatic resonances (7.22 and 6.95 ppm) compared to those of **2**. It also shows a broad signal at 6.09 ppm, corresponding to the N–H protons at the ligand backbone. The ^{11}B NMR resonance of **3** is consistent with that observed for its parent compound, **2**.

The molecular structure of **3** was determined by single crystal X-ray crystallography (Figure 2.4) and shows two pyramidal boron atoms (B1 and B2) bridged by an oxygen atom (O3). Table 2.3 shows the selected bond lengths and bond angles for compound **3**. While the ligand B–O bond lengths of **3** are comparable to those of **2**, the B1–N1 bond length of **3** is longer than that of **2** by 0.175 Å.

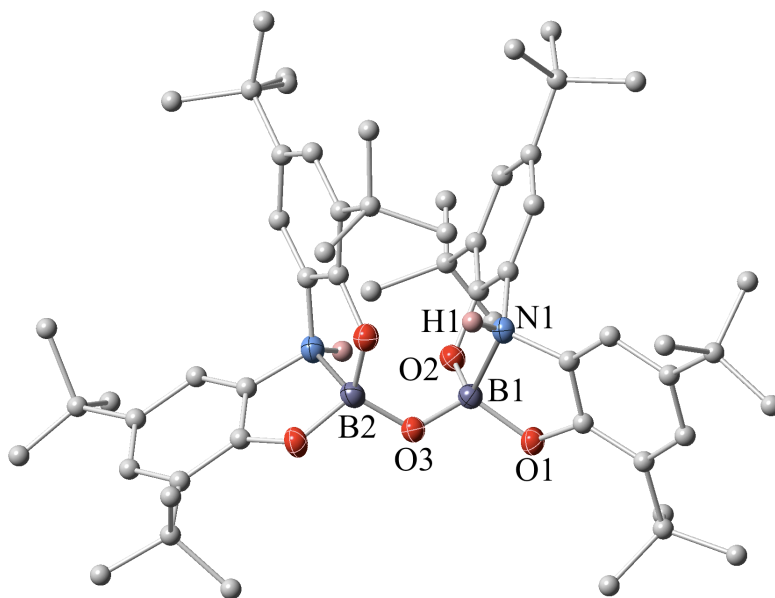
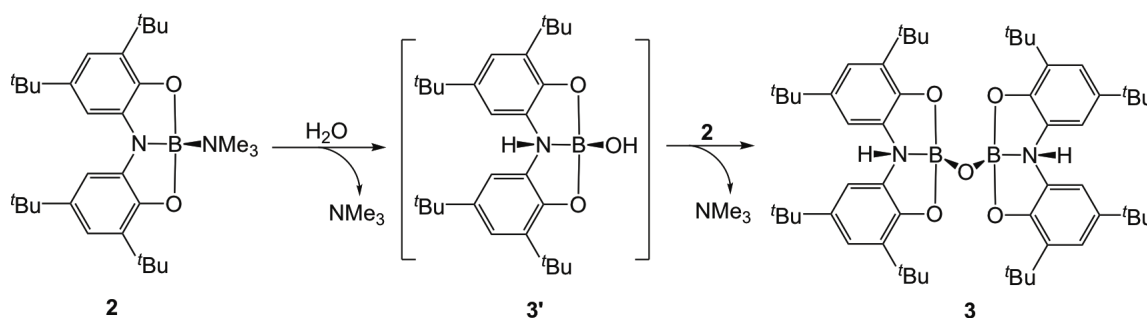


Figure 2.4: Molecular structure of **3**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 2.3 – Selected bond lengths and bond angles for **3**.

Bond lengths	3	Bond angles	3
B1–N1	1.688(3) Å	O1–B1–O2	112.2(2)°
B1–O1	1.464(3) Å	N1–B1–O1	100.9(2)°
B1–O2	1.485(3) Å	N1–B1–O2	101.1(2)°
B1–O3	1.394(3) Å	N1–B1–O3	112.4(2)°

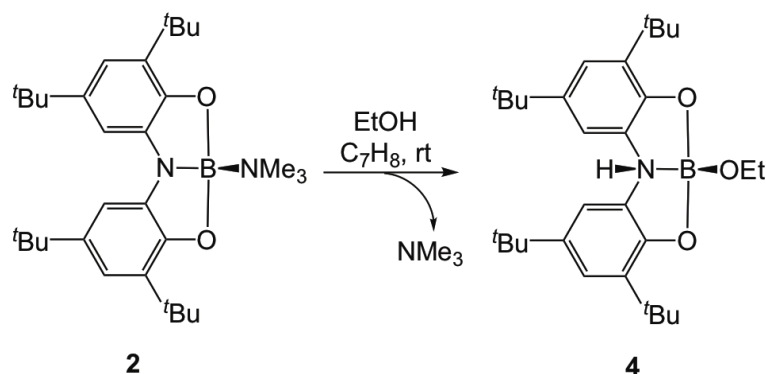
This hydrolysis product **3** is believed to be formed from the reaction of **2** with half molar equivalent of water, which is likely due to minor impurities in the THF solvent (Scheme 2.4). We postulated that **2** liberated NMe₃ and reacted with H₂O resulting in addition of the O–H bond across the B–N bond of **2** to form an intermediate, **3'**. Subsequently, the O–H bond in the intermediate **3'** was activated by another molecule of **2** to afford **3**. Intermediate **3'** was not observed in solution or in the solid-state.

**Scheme 2.4:** Proposed mechanism for the formation of **3**.

2.2.3 Small molecule activation of **2**

2.2.3.1 Reaction of **2** with ethanol

Given that the formation of **3** is consistent with NMe₃ being a labile ligand, this reactivity inspired the subsequent investigation of **2** for small molecule activation. The reaction of **2** with an excess amount of ethanol resulted in O–H bond cleavage to exclusively form **4** (Scheme 2.5), which is the ethanol analogue of the proposed intermediate **3'**.



Scheme 2.5: Synthesis of **4**.

The ^1H NMR and ^{11}B NMR resonances of **4** are consistent with those observed for compound **3**. The resonances attributed to the OCH_2CH_3 moiety can be found at 3.94 ppm and 1.36 ppm as a quartets and triplets, respectively. The ^1H NMR spectrum of **4** displays more downfield shifted aromatic resonances (7.29 and 7.05 ppm) compared to those of the parent compound. It also shows a broad signal at 6.67 ppm, corresponding to the N–H protons of the ligand backbone.

Crystals of **4** suitable for single crystal X-ray diffraction were grown from a concentrated toluene solution at room temperature. Similar to the structure of **3**, the molecular structure of **4** exhibits a slightly distorted tetrahedral geometry around the boron atom (Figure 2.5). Table 2.4 shows selected bond lengths and bond angles for **4**. The B–O and B–N bonds are comparable to those observed for **3**. By contrast, the B1–O3 of **4** (1.428(2) Å) is longer than the B1–O3(μ -O) of **3** (1.394(3) Å) consistent with a stronger electrostatic interaction between the bridging oxygen atom and the boron centre.

Table 2.4 – Selected bond lengths and bond angles for **4**.

Bond lengths	4	Bond angles	4
B1–N1	1.654(2) Å	O1–B1–O2	111.38(13)°
B1–O1	1.469(2) Å	N1–B1–O1	101.73(12)°
B1–O2	1.456(2) Å	N1–B1–O2	103.44(12)°
B1–O3	1.428(2) Å	N1–B1–O3	109.68(13)°

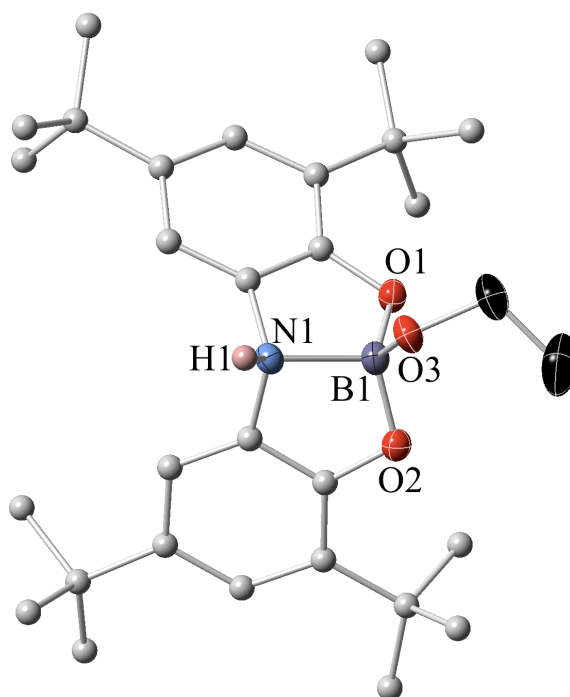


Figure 2.5: Molecular structure of **4**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

2.2.3.2 Reaction of **2** with water and other small molecules

Treatment of **2** with half molar equivalents of water resulted in a mixture of **3** and impurities, from which the starting material, **2**, and the free protonated ligand, $\text{H}_3(\text{ONO})$, could be identified. Unfortunately, compound **3** was not isolable from this mixture. The reaction of **2** with an excess amount of water resulted in formation of the free protonated ligand, $\text{H}_3(\text{ONO})$, $\text{B}(\text{OH})_3$ and NMe_3 .

Upon further investigation, no reaction was observed between **2** and small molecule substrates, such as dihydrogen, ammonia, *tert*-butylamine or carbon monoxide, at room temperature or upon heating to reflux temperatures. These observations are consistent with the oxophilicity of the boron atom, where the energy gain from the formation of B–O bond outweighs the energy spent to dissociate a B–N bond, thus allowing substrate coordination to the boron centre of **2** and NMe_3 liberation. The electrophilicity of the boron atom in **2** is reduced due to the stabilising trimethylamine molecule, thus preventing the association of

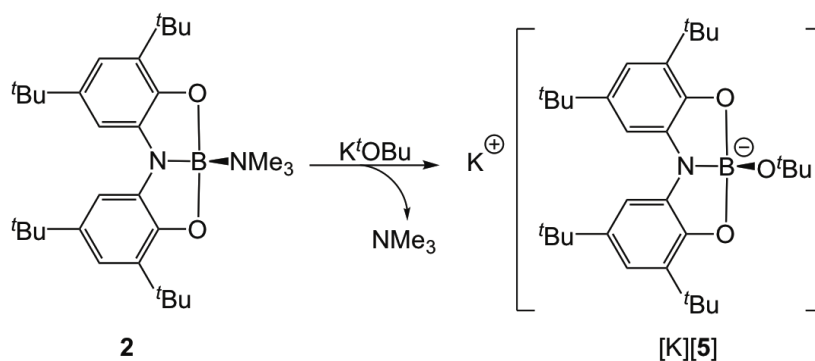
nucleophilic substrates. The reactivity towards ethanol can be rationalised due to the acidity of the O–H bond relative to that of the N–H bond in ammonia and the H–H bond in H₂.

2.2.4 Reactivity of **2** towards electrophiles and nucleophiles

Ethanol activation is mainly attributed to the oxophilicity of boron in **2** and the Lewis basicity of the lone pair located at the ligand nitrogen atom, therefore the reactivity of **2** towards electrophiles and nucleophiles to gain insights into the mechanism of the ethanol activation was investigated.

When one molar equivalent of MeOTf was added to **2** in C₆D₆, the ¹H NMR spectrum revealed the formation of multiple inseparable products.

However, treatment of **2** with one molar equivalent of potassium *tert*-butoxide (KO^tBu), traditionally a strong base but poor nucleophile, resulted in formation of [K][B(O^tBu)(ONO)] ([K][**5**]) (Scheme 2.6).



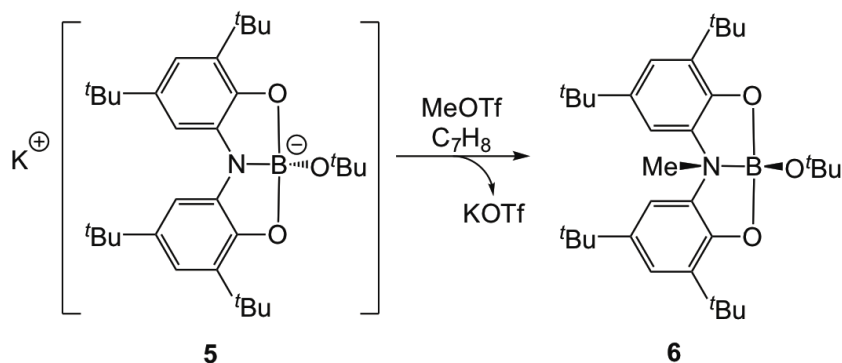
Scheme 2.6: Synthesis of [K][**5**].

The ¹H NMR and ¹¹B NMR resonances of **5** are in agreement with those of its parent compound, **2**. The resonance attributed to the *tert*-butoxide protons is found at 1.94 ppm, integrating to nine protons. As with compound **2**, **5** displays aromatic resonances at 7.98 and 6.68 ppm.

Unfortunately, a single crystal of the product that was suitable for single crystal X-ray diffraction could be isolated.

2.2.5 Reactivity of [K][5] towards MeOTf

Treatment of [K][5] with a molar equivalent of MeOTf in toluene at room temperature resulted in elimination of KOTf and formation of the neutral compound, **6** (Scheme 2.7).



Scheme 2.7: Synthesis of **6**.

This compound was characterised by ^1H NMR spectroscopy in C_6D_6 . The resonance attributed to the $\text{N}-\text{CH}_3$ protons was found at 2.78 ppm, as well as the aromatic and *tert*-butoxide resonances consistent with those observed for species **5**.

Crystals of **6** suitable for single crystal X-ray diffraction were grown from a concentrated hexane solution at room temperature. The molecular structure of **6** reveals that the methyl cation associates to the ligand nitrogen atom. Both the nitrogen (N1) and boron (B1) atoms exhibit distorted tetrahedral geometries (Figure 2.6). Table 2.5 shows selected bond lengths and bond angles for **6**. The ligand B–O bonds are comparable to those of **1–4**. By contrast, the B1–O3 bond length (1.394(2) Å) is significantly shorter than the B1–O3 bond of **4** (1.428(2) Å) suggesting a stronger interaction between the boron and the oxygen atom, further resulting in a lengthening of the B1–N1 bond in relative to that of **4** (1.695(2) Å for **6** and 1.654(2) Å for **4**).

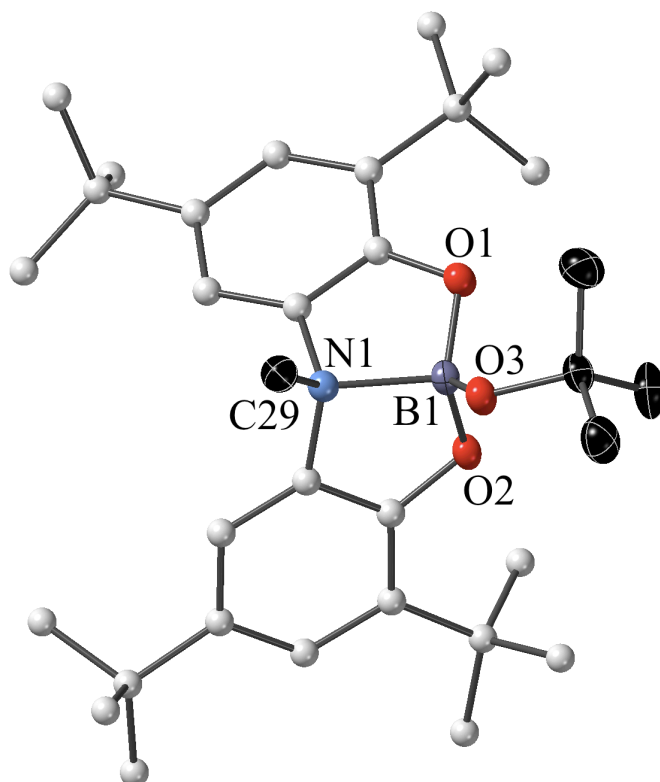
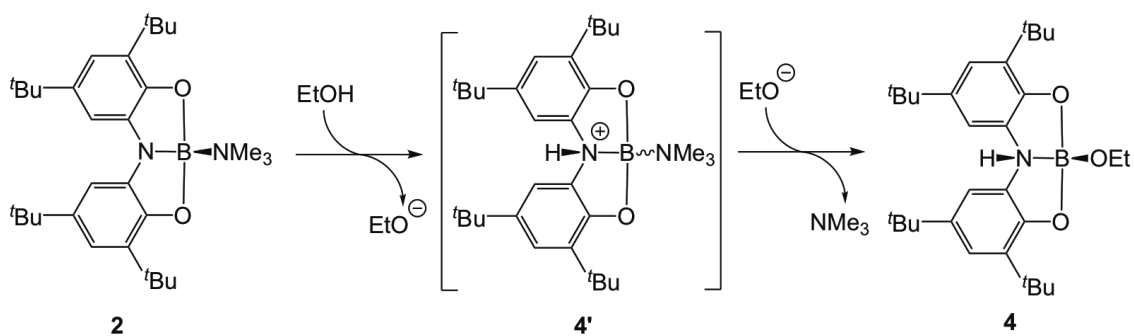


Figure 2.6: Molecular structure of **6**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 2.5 – Selected bond lengths and bond angles for **6**.

Bond lengths	6	Bond angles	6
B1–N1	1.695(2) Å	O1–B1–O2	111.23(14)°
B1–O1	1.469(2) Å	N1–B1–O1	101.98(12)°
B1–O2	1.480(2) Å	N1–B1–O2	99.68(11)°
B1–O3	1.394(2) Å	N1–B1–O3	108.44(13)°

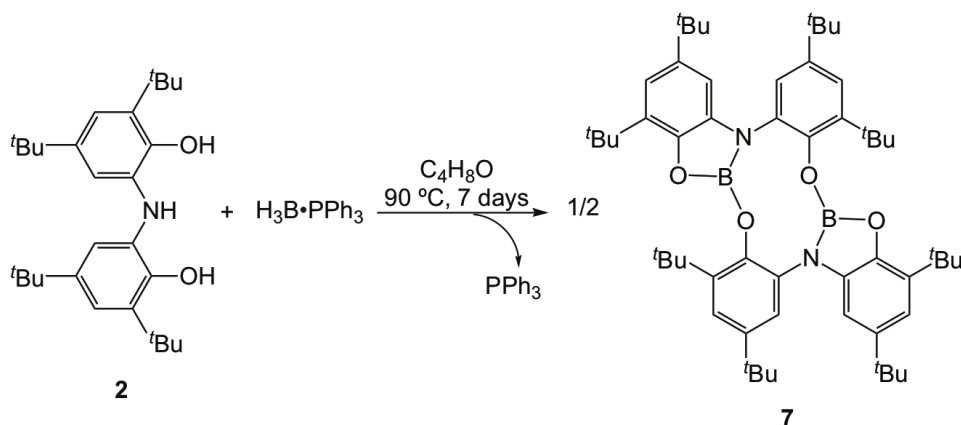
The isolation of **6** and **7** offers useful insights into the mechanism for the O–H bond activation when **2** was allowed to react with ethanol. This reaction is thought to be initiated by protonation of the ligand backbone to form an intermediate **4'**, followed by nucleophilic attack of the negatively charged EtO^- to the boron centre resulting in NMe_3 elimination to afford **4** (Scheme 2.8).



Scheme 2.8: Proposed mechanism for synthesis of **4**.

2.2.6 Reaction of $\text{H}_3(\text{ONO})$ with other base-stabilised borane adducts

During the O–H bond activation, addition of the alkoxide is dependent on elimination of the NMe_3 ligand in **2**, therefore boron centres coordinating different bases were investigated in an effort to increase this dissociation. To begin, triphenylphosphine borane ($\text{H}_3\text{B}\cdot\text{PPh}_3$) was chosen as the B–P bond is weaker than the B–N bond.



Scheme 2.9: Synthesis of **7**.

Unexpectedly, reaction of **3** with $\text{H}_3\text{B}\cdot\text{PPh}_3$ resulted in formation of a neutral $\text{B}_2(\mu^2: \kappa^2\text{-ONO})_2$ (**7**) compound and elimination of PPh_3 (Scheme 2.9). The reaction was monitored by ^1H NMR spectroscopy. The ^1H NMR spectrum of **7** in C_6D_6 displays two doublets at 7.19 and 6.90 ppm and two singlets at 1.38 and 1.15 ppm arising from the aromatic protons and the *tert*-butyl protons, respectively. After work-up, the PPh_3 resonances were not found in the ^1H and ^{31}P NMR spectra, consistent with loss of phosphine. The ^{11}B NMR spectrum

of **7** exhibits a downfield shift at 19.9 ppm, suggesting a three-coordinate boron environment.

Crystals of **7** suitable for single crystal X-ray diffraction were grown from a concentrated hexane solution at room temperature. The molecular structure of **7** shows a dimeric structure with each boron atom adopting a perfectly planar geometry ($\sum_{\text{angles(B1)}} = \sum_{\text{angles(B2)}} = 360^\circ$) (Figure 2.7 and Table 2.6). The solid-state structure reveals that the bond lengths of **7** are consistent with each boron atom drawing additional electron density from the adjacent nitrogen and oxygen atoms. The B1–N1, B1–O1 and B1–O2 bond lengths (1.437(2), 1.364(2), 1.389(2) Å) bonds are shorter than expected for single bonds (1.5–1.7 Å), suggesting partial double bond character. Unfortunately, this structure also indicates that **7** is suspected to have reactivity similar to boronic esters and is therefore not suitable for small molecule activation.

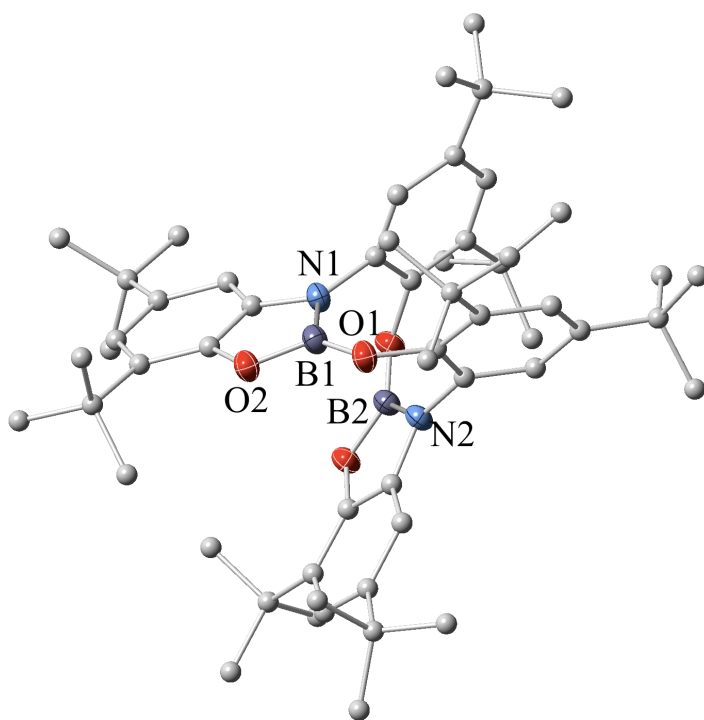


Figure 2.7: Molecular structure of **7**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

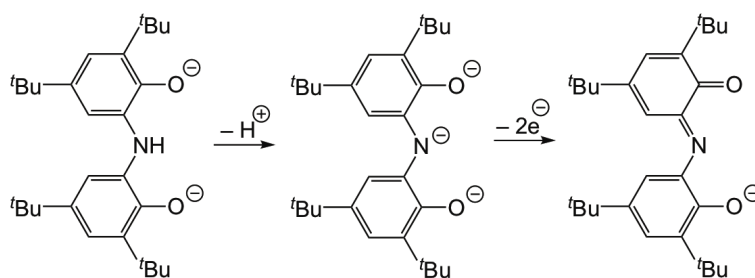
Table 2.6 – Selected bond lengths and bond angles for **7**.

Bond lengths	7	Bond angles	7
B1–N1	1.437(2) Å	O1–B1–O2	118.92(12)°
B1–O1	1.364(2) Å	N1–B1–O1	131.25(12)°
B1–O2	1.389(2) Å	N1–B1–O2	109.82(11)°

Borane adducts, such as $\text{H}_3\text{B}\cdot\text{NH}_3$, $\text{H}_3\text{B}\cdot\text{NHMe}_2$ and $\text{H}_3\text{B}\cdot\text{SMe}_2$, were added to a solution of $\text{H}_3(\text{ONO})$, in an attempt to make the corresponding $\text{B}(\text{ONO})\cdot\text{L}$ compounds. However, in all cases, no reaction was observed at room temperature and subsequent heating resulted in inseparable mixtures of products.

2.3 Aluminium and gallium compounds bearing the $(\text{ONO})^{3-}$ ligand

The $\text{H}_3(\text{ONO})$ ligand can be deprotonated to afford $(\text{ONO})^{3-}$ and oxidised to access monoanionic and dianionic ligands (Scheme 2.10). Heyduk has synthesised aluminium halide compounds (**LVII** and **LVIII**) bearing the dianionic catecholate $\{\text{ON}(\text{H})\text{O}\}^{2-}$ ligand (Figure 2.8).⁹ This section will explore the synthesis of aluminium and gallium complexes bearing the dianionic $\{\text{ON}(\text{H})\text{O}\}^{2-}$ ligand and their reactivity. This work was conducted in collaboration with a Part II student, Mr. Cory Smith.

**Scheme 2.10:** Polydentate forms of the ONO ligand.

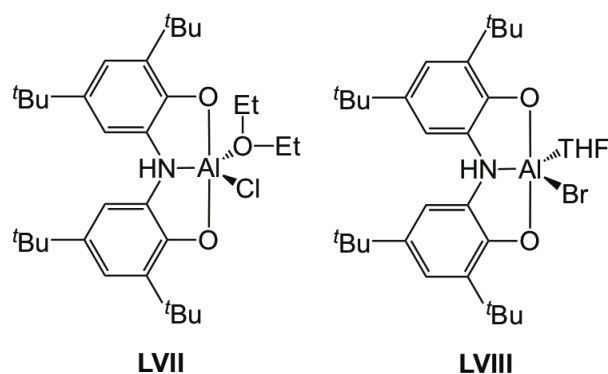
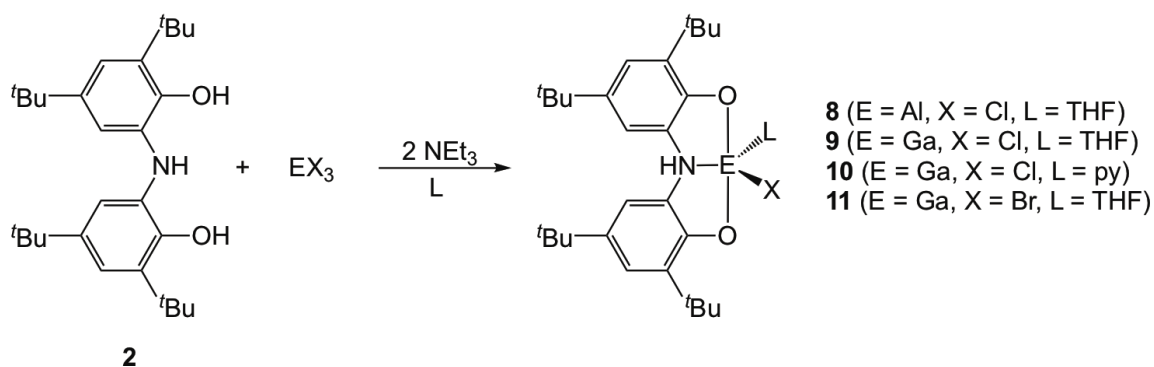


Figure 2.8: Structures of the Heyduk's **LVII** and **LVIII** compounds.

2.3.1 Synthesis of constrained geometry $E(X)\{ON(H)O\} \cdot L$ compounds

Analogous to the preparation of **LVI**, $H_3(ONO)$ and $AlCl_3$ were reacted in C_6D_6 in the presence of three molar equivalents of NEt_3 . The reaction was monitored by 1H NMR spectroscopy which reveals the formation of multiple products. Similar reactivity was observed for the reaction with $GaCl_3$. Therefore, alternative solvents and reaction conditions were explored. Treatment of $H_3(ONO)$ with aluminium and gallium halides resulted in formation of a series of neutral $E\{ON(H)O\}(X) \cdot L$ compounds, **8–11**, listed below (Scheme 2.11).



Scheme 2.11: Synthesis of **8–11**.

2.3.1.1 Synthesis and characterisation of $E(X)\{ON(H)O\} \cdot L$ (**8–11**)

Modified from the preparation of **LVII** and **LVIII**, $H_3(ONO)$ was allowed to react with $AlCl_3$ in the presence of NEt_3 in THF resulting in clean formation of **8** in good yield (84%).

The reaction was monitored by ^1H NMR, revealing two doublets at 7.38 and 7.11 ppm and two singlets at 1.53 and 1.36 ppm assigned to the aromatic protons and the *tert*-butyl protons from the ligand backbone, respectively. It also shows a broad resonance at 4.80 ppm, characteristic of the N–H proton of the ligand backbone.

Reaction of $\text{H}_3(\text{ONO})$ with GaCl_3 was carried out in d_8 -THF in an air-tight Young's tap NMR tube. Again, the ^1H NMR spectrum confirmed the formation of **9**. Compound **9** was also characterised by ^{13}C NMR spectroscopy. However, this product was found to decompose to multiple products upon manipulation. Given the difficulties with isolating compound **9**, GaBr_3 was investigated as a viable starting material, as well as stronger donor solvents such as pyridine. It was found that compounds **10–11** could be prepared in good yields by adapting the synthetic method for preparing **8**. As expected, all the NMR spectra of **9–11** exhibit similar resonances (see Chapter 5 for details).

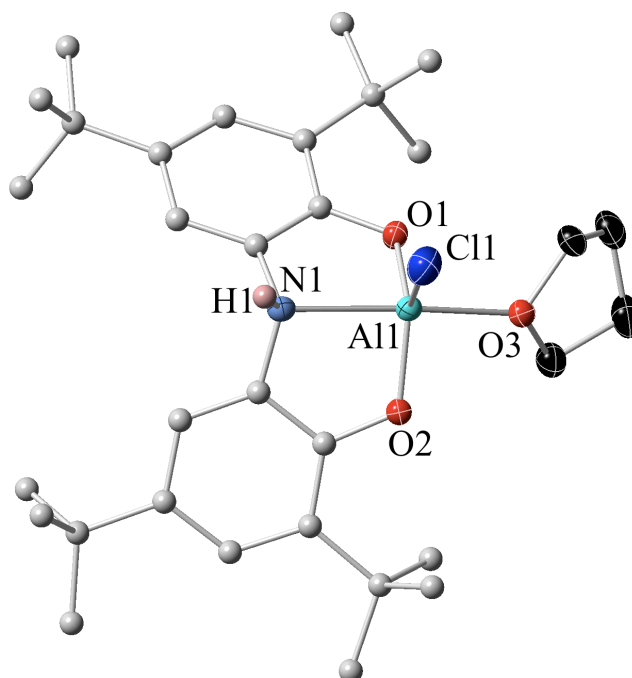


Figure 2.9: Molecular structure of **8**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

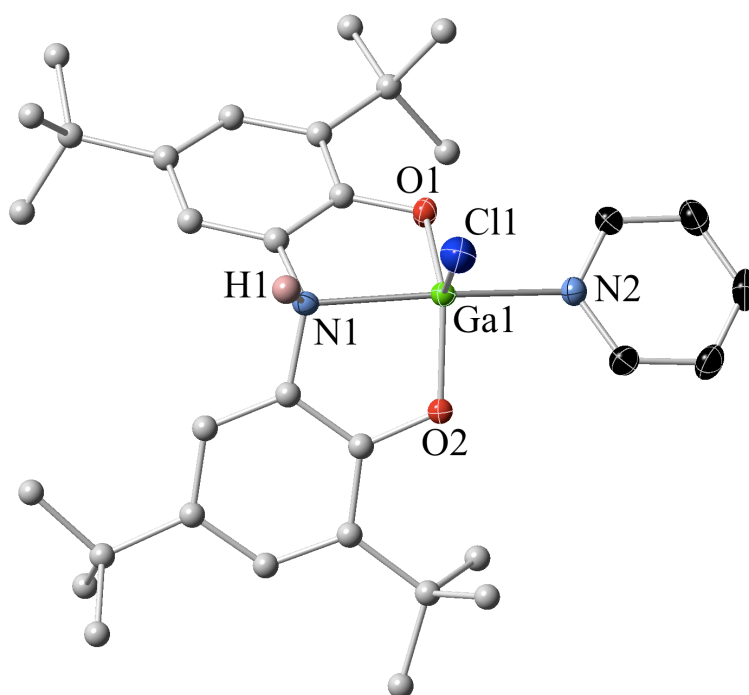


Figure 2.10: Molecular structure of **10**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

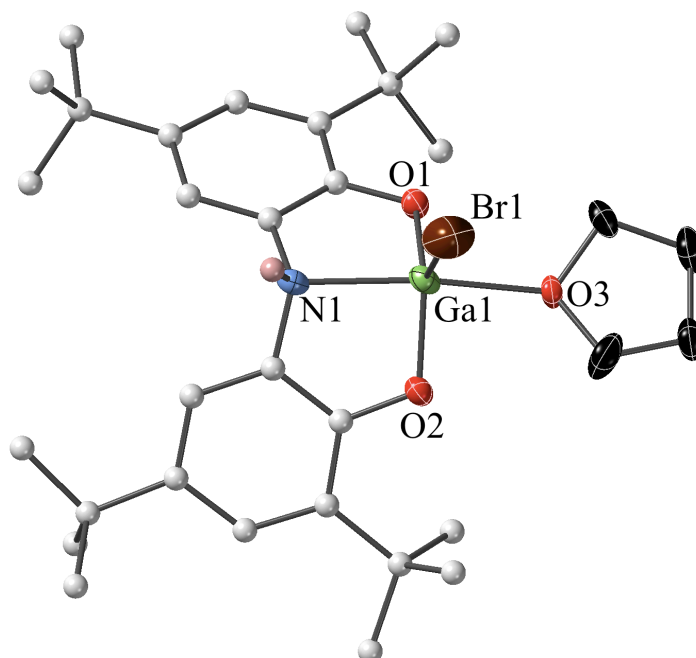


Figure 2.11: Molecular structure of **11**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 2.7 – Selected bond lengths and bond angles for **8**, **10** and **11**.

Bond lengths and bond angles	8 (E = Al; X = O3)	10 (E = Ga; X = N2)	11 (E = Ga; X = O3)
E–N1	2.121(1) Å	2.142(2) Å	2.120(3) Å
E–O1	1.766(1) Å	1.846(1) Å	1.837(2) Å
E–O2	1.765(1) Å	1.846(1) Å	1.833(2) Å
E–X	1.919(1) Å	2.080(2) Å	2.153(7) Å
O1–E–O2	120.80(4)°	122.34(4)°	120.81(10)°
N1–E–O1	84.60(4)°	84.72(4)°	85.87(10)°
N1–E–O2	84.89(4)°	85.10(4)°	86.26(10)°
N1–E–X	170.41(4)°	168.03(4)°	162.1(2)°

Crystals of **8**, **10** and **11** suitable for single crystal X-ray diffraction were grown from concentrated hexane solutions at room temperature. Table 2.7 shows the bond lengths and bond angles of **8**, **10** and **11**.

The molecular structure of **8** shows a distorted trigonal bipyramidal structure around aluminium (Al1) and a distorted tetrahedral environment around nitrogen (N1). The chloride ligand is sitting in the equatorial position, while the THF ligand is *trans* to the nitrogen atom (N1) of the ligand, resulting in a bent coordination of the {ON(H)O}²⁻ ligand (Figure 2.9). Unsurprisingly, the bond lengths and bond angles of **8** are comparable to those of Heyduk's aluminium bromide compound, **LVIII**.

Similar to the molecular structure of **8**, compound **10** adopts a distorted trigonal bipyramidal structure around the gallium centre (Figure 2.10). The Ga1–N2 bond length is shorter than Ga1–N1 bond in **8** by 0.062 Å, in line with stronger donation from pyridine to stabilise the gallium centre. The greater lability of THF relative to pyridine may account for the instability of **9** under reduced pressure.

The molecular structure of **11** also adopts a distorted trigonal bipyramidal geometry around gallium (Ga1) with a bromine atom located in the equatorial position (Figure 2.11). The Ga1–N1, Ga1–O1 and Ga1–O2 bond lengths are all shorter than those found in **10** due to

reduced electronegativity of bromine relative to chlorine and the weaker donor ability of THF relative to pyridine.

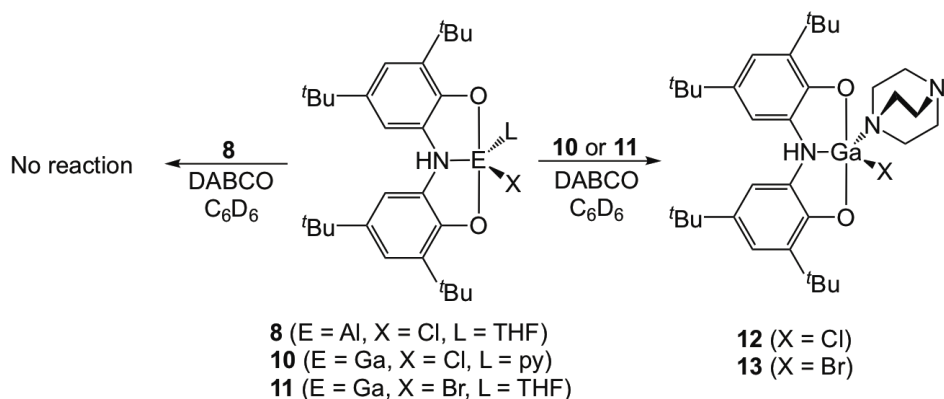
2.3.2 Reactions of **8**, **10** and **11** with bases

2.3.2.1 Reactions of **8**, **10** and **11** with DABCO in C₆D₆

During the preparation of E(ONO)·L (E = Al or Ga; L = ligand), a variety of bases were employed in an effort to abstract the N–H proton and the halide anion.

In both C₆D₆ and *d*₈-THF, compounds **8**, **10** and **11** did not react with bases, such as triethylamine or potassium hydride, even at reflux temperatures.

While no reaction was observed when an excess amount of 1,4-diazabicyclo[2.2.2]-octane (DABCO) was added to **8** at reflux temperatures, addition of one molar equivalent of DABCO to **10** in C₆D₆ resulted in the displacement of pyridine to give **12** cleanly. In addition, the analogous reaction with **11** resulted in formation of **13** which is the bromine analogue of **12** (Scheme 2.13). Single crystals suitable for single crystal X-ray diffraction studies of **12** and **13** could not be obtained.



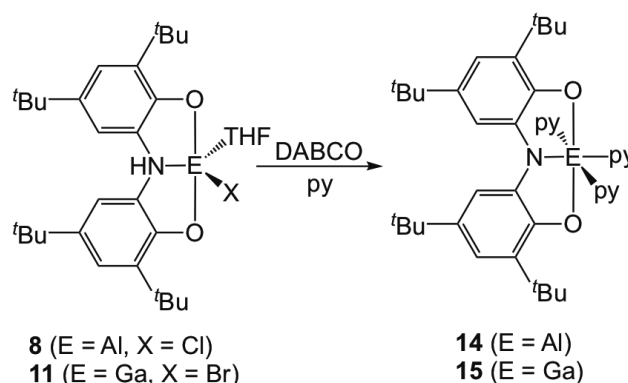
Scheme 2.13: Synthesis of **12** and **13**.

Both **12** and **13** were characterised by ¹H NMR spectroscopy, where the spectrum for **12** displays a set of resonances attributed to the DABCO ligand at 3.30 and 2.46 ppm. In addition, a broad signal at 5.05 ppm was observed, corresponding to the N–H proton of the

ligand backbone, suggesting that DABCO is not basic enough to abstract this proton in species **10** or **11**. The aromatic protons and *tert*-butyl protons resonances of **12** are comparable to those observed for **10**. The ^1H NMR spectrum of compound **13** is similar to that of compound **12**.

2.3.2.2 Reactions of **8** and **11** with DABCO in pyridine

When compounds **8** or **11** were allowed to react with DABCO in pyridine, it led to immediate formation of a dark red solution accompanied by precipitation of red crystals. Single crystal X-ray diffraction studies confirmed the resulting products as $\text{Al}(\text{py})_3(\text{ONO})$ (**14**) and $\text{Ga}(\text{py})_3(\text{ONO})$ (**15**) (Scheme 2.14), correspondingly. Unfortunately, both crystals of **14** and **15** were found to be insoluble in any solvents even at elevated temperatures and further manipulation led to decomposition, therefore suitable NMR spectra for these compounds could not be obtained.



Scheme 2.14: Synthesis of **14** and **15**.

The molecular structure of **14** revealed that the ligand nitrogen atom (N1) has been deprotonated, forcing the ligand to adopt a planar geometry. The $(\text{ONO})^{3-}$ ligand exhibits meridional coordination and three pyridine molecules occupy the remaining sites giving an almost perfect octahedral geometry around the aluminium atom (Figure 2.12 and Table 2.8).

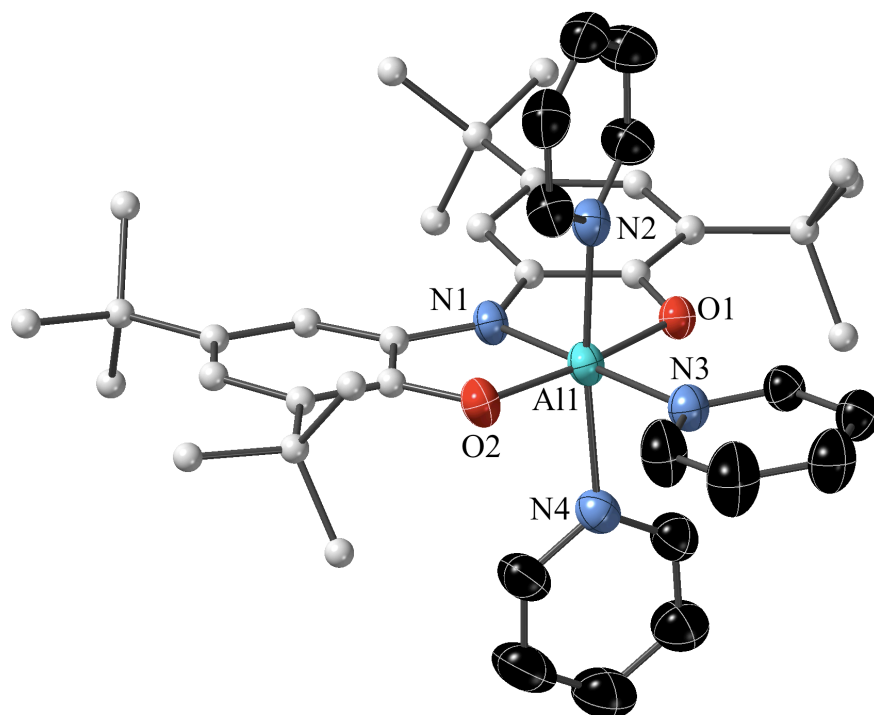


Figure 2.12: Molecular structure of **14**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

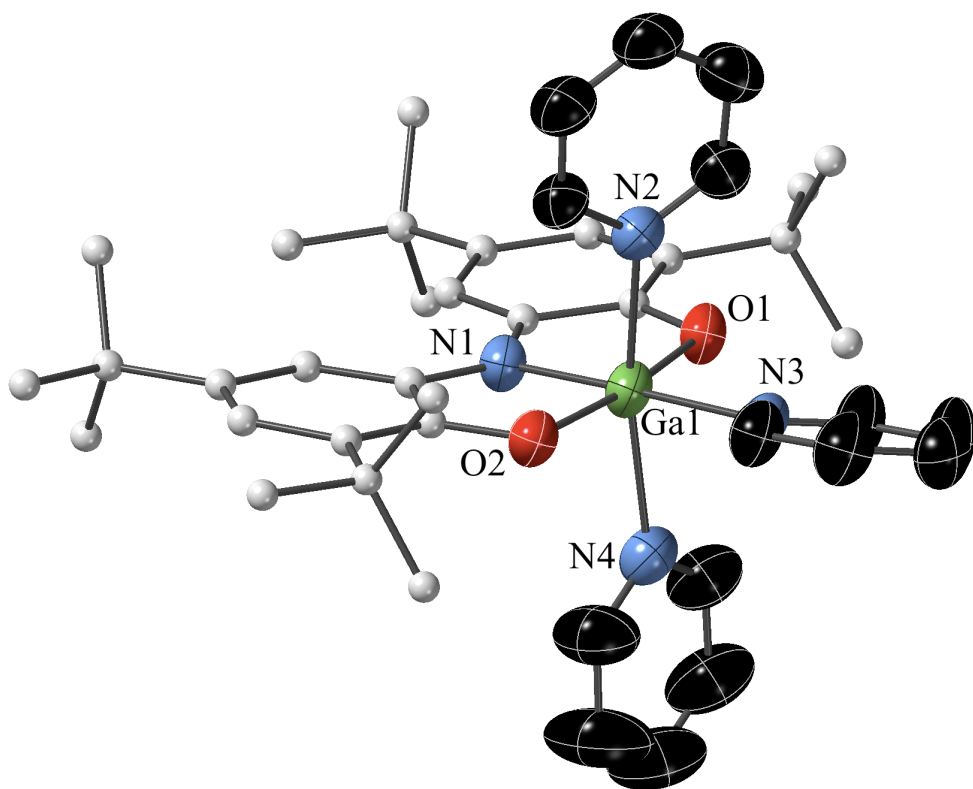


Figure 2.13: Molecular structure of **15**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand, N1, O1 and O2, are pictured as spheres of arbitrary radius.

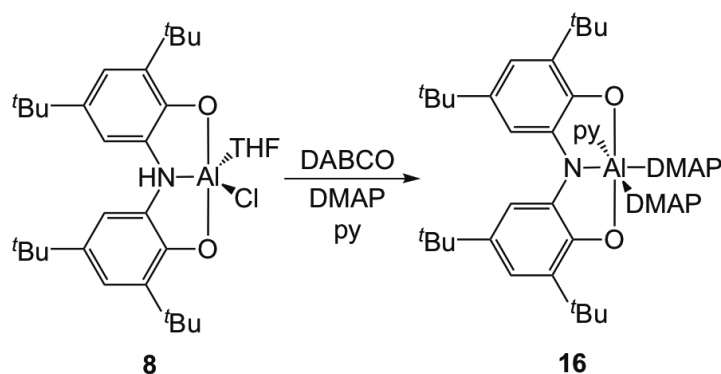
Table 2.8 – Selected bond lengths and bond angles for **14** and **15**.

Bond lengths and bond angles	14	15
Al1–N1	1.873(3) Å	1.909(2) Å
Al1–O1	1.836(3) Å	1.922(2) Å
Al1–O2	1.835(3) Å	1.923(2) Å
Al1–N2	2.169(3) Å	2.205(2) Å
Al1–N3	2.014(2) Å	2.053(2) Å
Al1–N4	2.167(2) Å	2.253(3) Å
O1–Al1–O2	171.4(2)°	170.25(8)°
N1–Al1–O1	85.6(2)°	84.91(9)°
N1–Al1–O2	85.9(2)°	85.36(9)°
N1–Al1–N3	179.89(8)°	178.65(11)°
N1–Al1–N2	94.63(7)°	97.53(10)°
N1–Al1–N4	93.67(7)°	93.71(10)°

Compared to the molecular structure of starting material **8**, the ligand Al1–N1 bond of **14** is significantly shorter by 0.248 Å, consistent with coordination from a formally anionic amide ligand. The Al–N_{py} bond *trans* to the amide (2.014(2) Å) is shorter than the Al–N_{py} bonds orthogonal to the amide (2.169(3) and 2.167(2) Å). Akin to the molecular structure of **14**, the molecular structure of **15** reveals that the (ONO)^{3–} ligand adopts the meridional coordination and three pyridine molecules occupy the remaining sites. The bond metrics exhibited in the structure of **15** are largely identical to those observed for compound **14** (Figure 2.13 and Table 2.8). Recently, the related phosphorus species, [P(py)₃(ONO)]^{2–} (**LIVd**), was reported and found to exhibit a similar octahedral environment around phosphorus.¹⁰

2.3.2.3 Reactions of **8** with DABCO and DMAP in pyridine

Although based-stabilised species E(ONO) (E = Al or Ga) could be prepared, it was found that all coordination sites were occupied, impeding subsequent reactivity. Also, given the low solubility of compounds **14** and **15**, 4-(dimethylamino)pyridine (DMAP) was investigated as a suitable base. However, treatment of DABCO and **8** in the presence of two molar equivalents of DMAP in C₆D₆ resulted in an unidentified white powder.



Scheme 2.15: Synthesis of **16**.

The analogous reaction in THF resulted in a similar insoluble white powder, whereas the reaction in pyridine resulted in red solution accompanied by red crystals, which were found to be compound **16** (Scheme 2.15). As with **14** and **15**, the crystals are insoluble in all solvents employed, therefore no NMR spectra were recorded.

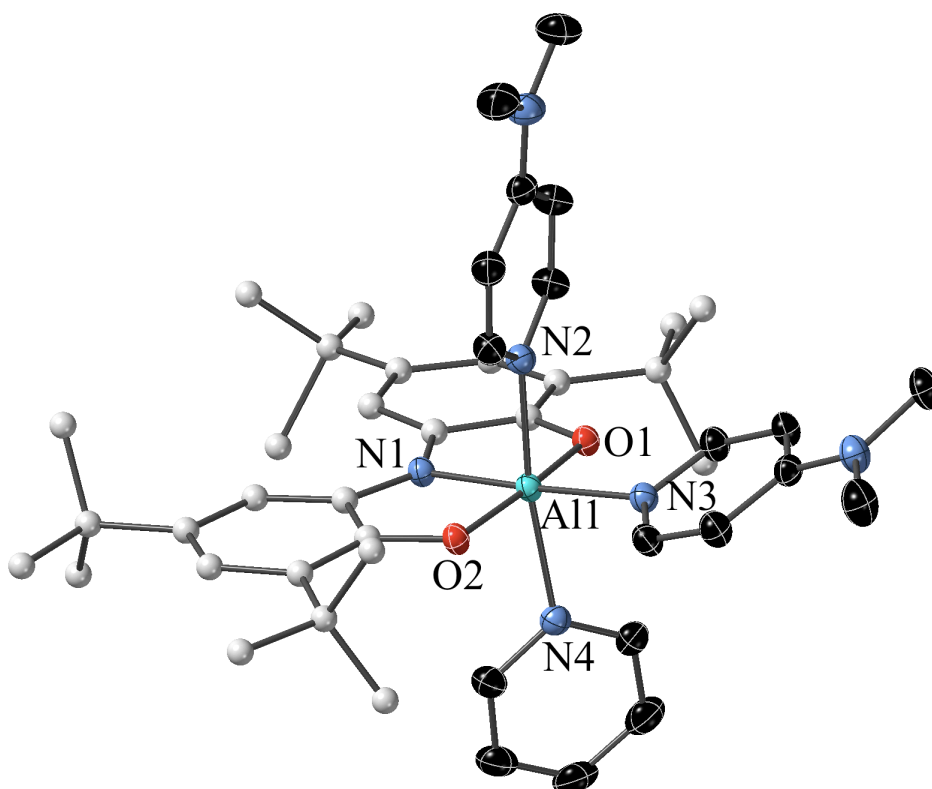


Figure 2.14: Molecular structure of **16**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 2.9 – Selected bond lengths and bond angles for **16**.

Bond lengths	16	Bond angles	16
Al1–N1	1.890(1) Å	O1–Al1–O2	170.04(4)°
Al1–O1	1.838(1) Å	N1–Al1–O1	85.36(4)°
Al1–O2	1.841(1) Å	N1–Al1–O2	85.38(4)°
Al1–N2	2.113(1) Å	N1–Al1–N3	177.33(4)°
Al1–N3	2.014(1) Å	N1–Al1–N2	93.99(4)°
Al1–N4	2.160(1) Å	N1–Al1–N4	94.04(4)°

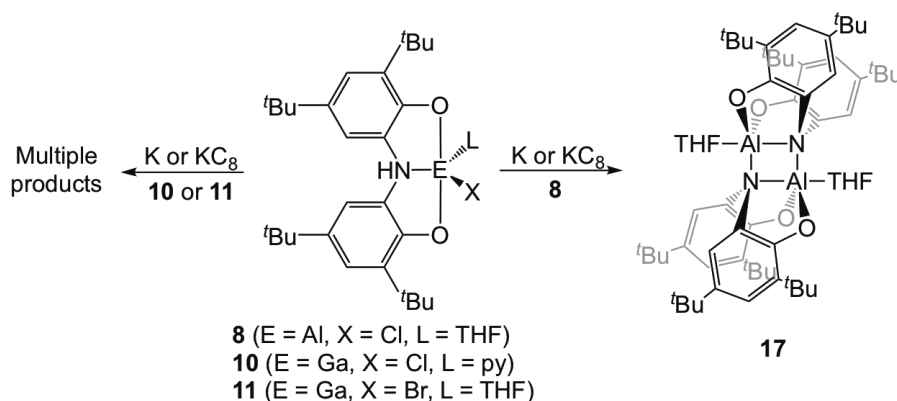
Akin to the molecular structure of **14** and **15**, the molecular structure of **16** revealed meridional coordination of the (ONO)³⁻, and one pyridine and two DMAP molecules occupy the remaining sites to afford a distorted octahedral geometry around aluminium (Figure 2.14). The Ga–O and Ga–N bond lengths and bond angles of **16** are almost identical to those found for **14**.

2.3.3 Reactions of **8**, **10** and **11** with reducing agents

2.3.3.1 Reactions of **8** and **10** with KC₈ or K

In an effort to abstract the proton from the nitrogen atom on the ligand, reactions of reducing agents with compounds **8** and **10** were explored.

To begin, the reaction of **8** with potassium (K) or potassium graphite (KC₈) in toluene at 90 °C overnight resulted in a colourless solution, that afforded transparent crystals upon cooling to room temperature. Single crystal X-ray diffraction studies confirmed the formation of bimetallic compound, **17** (Scheme 2.16). Unfortunately, the isolated yield is relatively low (24%) and the reaction did not scale-up well, as the strongly reducing potassium metal is likely to over-reduce the starting material causing formation of side products. Similar reactions were performed with **10** and **11**, however no reaction was observed at room temperature, and upon heating an inseparable mixture of products was formed.



Scheme 2.16: Reactions of **8–11** with K or KC₈.

Crystalline material of **17** was found to be poorly soluble in common solvents at room temperature, and although this compound could be solubilised at elevated temperatures, it would quickly recrystallise at ambient temperature. Nevertheless, the resonance typically attributed to the N–H proton was absent in the ¹H NMR spectrum of **17**, suggesting successful abstraction of the proton and elimination of the chlorine atom. The aromatic protons of ¹H NMR spectrum of **17** are more downfield shifted than those observed for the parent compound, **8**.

The molecular structure of **17** shows a dimeric species which exhibits a distorted trigonal bipyramidal geometry around each aluminium atom, with a distorted tetrahedral geometry around nitrogen (N1 and N1') of the ligand backbone (Figure 2.15 and Table 2.10). The Al(ONO)·THF moiety dimerises across the Al–N bond forming a four-membered heterocyclic ring. Inside the heterocyclic Al₂N₂ ring, the Al–N1' bond (2.070(2) Å) is longer than the Al–N1 bond (1.923(2) Å), as a result of the dative covalent interaction from the nitrogen lone pair to the Lewis acidic aluminium centre.

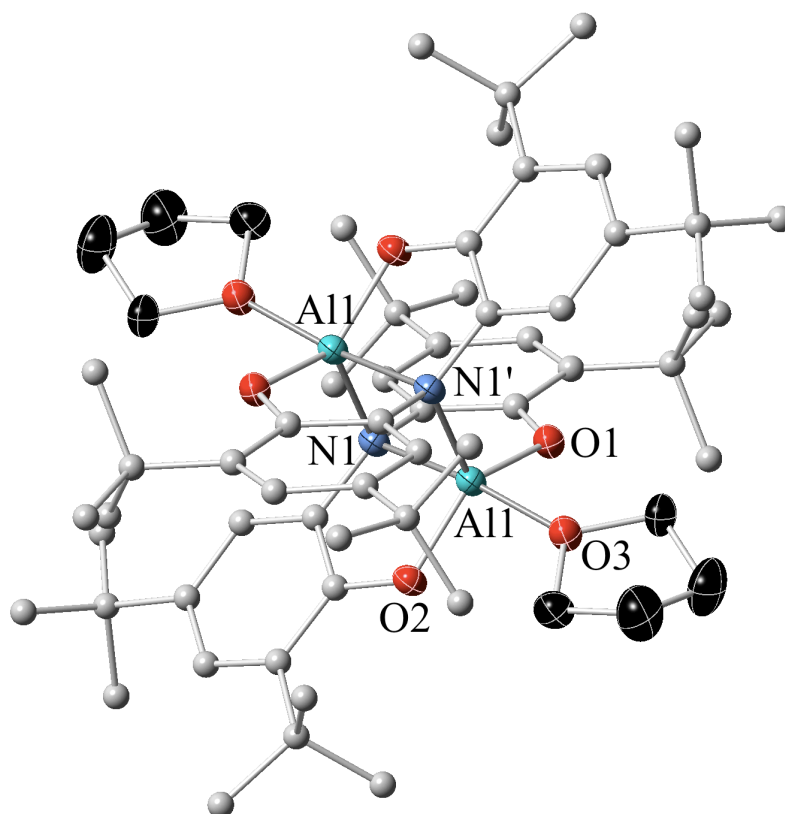


Figure 2.15: Molecular structure of **17**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

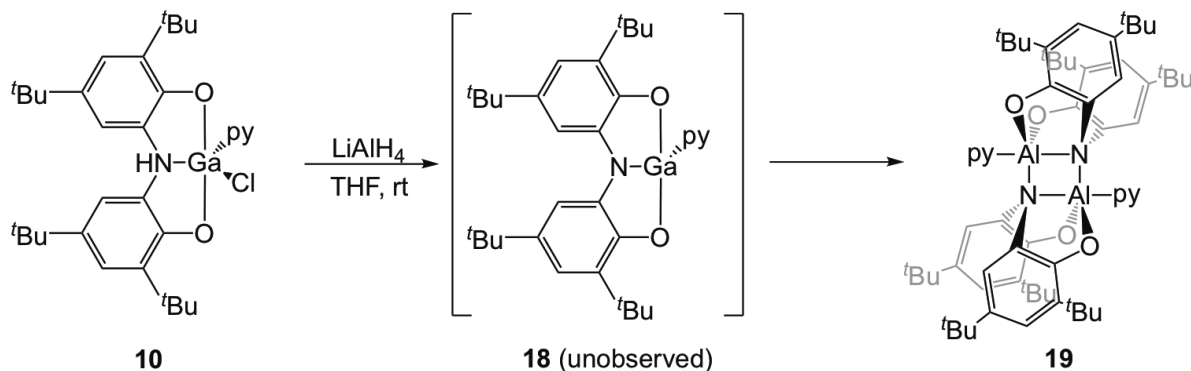
Table 2.10 – Selected bond lengths and bond angles for **17**.

Bond lengths	17	Bond angles	17
Al1–N1	1.923(2) Å	O1–Al1–O2	133.83(5)°
Al1–O1	1.761(1) Å	N1–Al1–O1	86.34(4)°
Al1–O2	1.761(1) Å	N1–Al1–O2	86.14(5)°
Al1–N1'	2.070(2) Å	N1–Al1–N1'	170.45(5)°

2.3.3.2 Reactions of **8** and **10** with LiAlH₄

When compound **8** was allowed to react with lithium aluminium hydride (LiAlH₄) in THF, compound **17** could be isolated in low isolated yield (11%). Unexpectedly, the analogous reaction with **10** immediately turned the reaction mixture from colourless to dark red and evolved gas. Upon inspection by ¹H NMR spectroscopy, the resonance attributed to the N–H proton was absent, which led to us to postulate formation of compound **18**. Upon diffusing hexane into the reaction mixture, colourless crystals suitable for single X-ray

diffraction studies were obtained, accompanied by a grey powder. The colourless crystals were not soluble, impeding characterisation by NMR spectroscopy. However, single crystal X-ray diffraction studies confirmed the structure to be the bimetallic compound **19** (Scheme 2.17) arising from transmetalation from gallium to aluminium. Unfortunately, we were not able to isolate **18** as the transmetalation occurred on manipulation of the mixture.



Scheme 2.17: Synthesis of **19**.

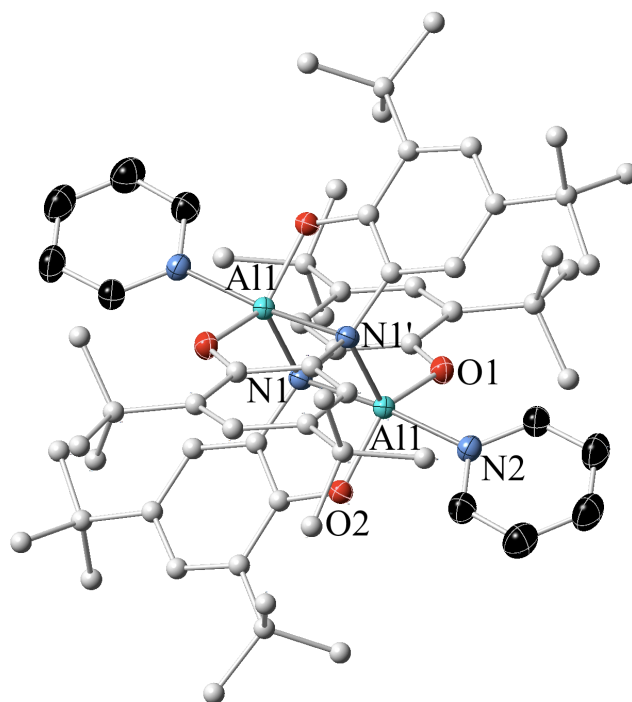


Figure 2.17: Molecular structure of **19**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

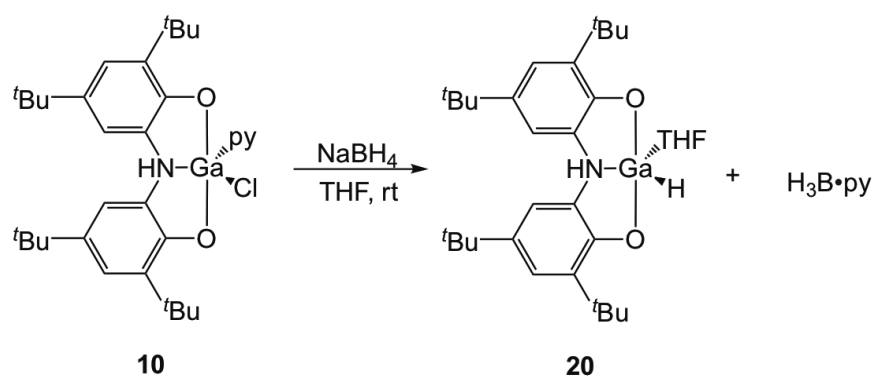
In line with the molecular structure of **19**, compound **17** features a distorted trigonal bipyramidal geometry around each aluminium atom, with a distorted tetrahedral geometry around both nitrogens (N1 and N1') of the ligand backbone (Figure 2.17 and Table 2.11). Both structures dimerise through the aluminium (Al1) and nitrogen (N1) atoms.

Table 2.11 – Selected bond lengths and bond angles for **19**.

Bond lengths	19	Bond angles	19
Al1–N1	1.918(2) Å	O1–Al1–O2	131.90(6)°
Al1–O1	1.762(2) Å	N1–Al1–O1	85.68(5)°
Al1–O2	1.762(2) Å	N1–Al1–O2	85.77(5)°
Al1–N1'	2.087(2) Å	N1–Al1–N1'	169.96(5)°

2.3.3.3 Reactions of **8** and **10** with NaBH₄

In an attempt to independently prepare compound **18**, sodium boron hydride (NaBH₄) was employed as a reducing agent. However, this reaction resulted in the formation of **20** (Scheme 2.18).



Scheme 2.18: Synthesis of **20**.

The ¹H NMR spectrum of **20** shows a resonance at 5.75 ppm as a singlet, corresponding to the Ga–H hydride, whereas the N–H proton of the ligand backbone was found at 4.07 ppm. Also, a set of resonances (three multiplets at 8.14, 6.57 and 6.20 ppm and one equal intensity quartet at 3.49 ppm) attributed to the H₃B·py molecule were also observed. The aromatics resonances and *tert*-butyl protons resonances observed in the ¹H NMR spectrum

of **20** are similar to those found for **10**. Also, the ^{11}B NMR spectrum of **20** reveals a multiplet at -10.7 ppm which collapses to a singlet in the absence of proton coupling, attributed to the BH_3 moiety.

Crystals of **20** suitable for single crystal X-ray diffraction were grown from a concentrated mixture of THF and hexane solution at room temperature. As expected from the molecular structure of starting material **10**, the molecular structure of **20** adopts a distorted trigonal bipyramidal geometry around gallium (Ga1) with a distorted tetrahedral environment around nitrogen (N1) (Figure 2.18). Interestingly, a hydride was located in the coordination sphere of gallium (Ga1). Table 2.12 shows selected bond lengths and bond angles of **20**. Compound **20** has similar Ga–N and Ga–O bond lengths as those of **10**. However, the $(\text{ONO})^{3-}$ ligand moiety adopts a more bent coordination in **20** when compared to compound **10** ($\text{O1-Ga-O2} = 113.37(10)^\circ$ for **20** and $122.34(4)^\circ$ for **10**). This observation is thought to be due to a weaker degree of negative hyperconjugation from the oxygen lone pair into the Ga–H σ^* -orbital in **20** compared to the respective Ga–Cl σ^* -orbital in **10**, forcing the $(\text{ONO})^{3-}$ ligand of **10** to adopt a less planar structure. The single crystal X-ray diffraction results are consistent with DFT calculations, performed by Mr. Cory Smith. The orbital energy difference ($\epsilon_a - \epsilon_d$) between the oxygen lone pair and the Ga–H σ^* -orbital of **20** is 0.02 a.u. larger than that of Ga–Cl σ^* -orbital of **10** ($\epsilon_a - \epsilon_d = 0.52$ a.u. for **20** and 0.50 a.u. for **10**), in line with a better orbital overlap between the oxygen lone pair and the Ga–Cl bond. The molecular structure of **20** was found to co-crystallise with one molecule of pyridine borane ($\text{H}_3\text{B}\cdot\text{py}$). The separation between the N–H proton and the B–H hydride is $2.002(4)$ Å, revealing an intermolecular interaction between these two hydrogen atoms preventing the subsequent deprotonation of the N–H proton and liberation of H_2 .

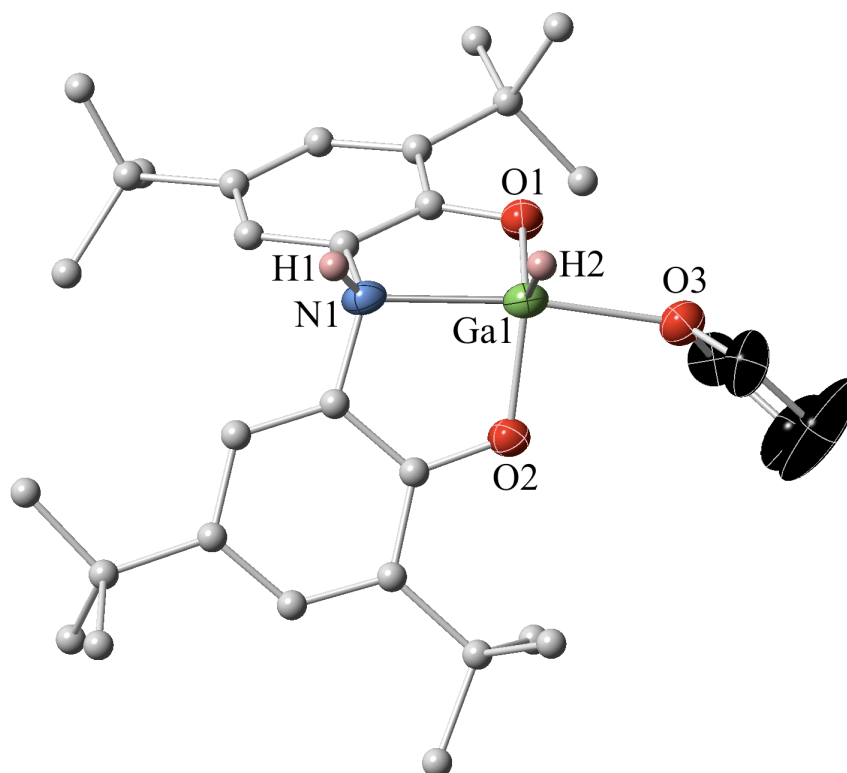


Figure 2.12: Molecular structure of **20**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1 and H2, and H₃B·py are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 2.12 – Selected bond lengths and bond angles for **20**.

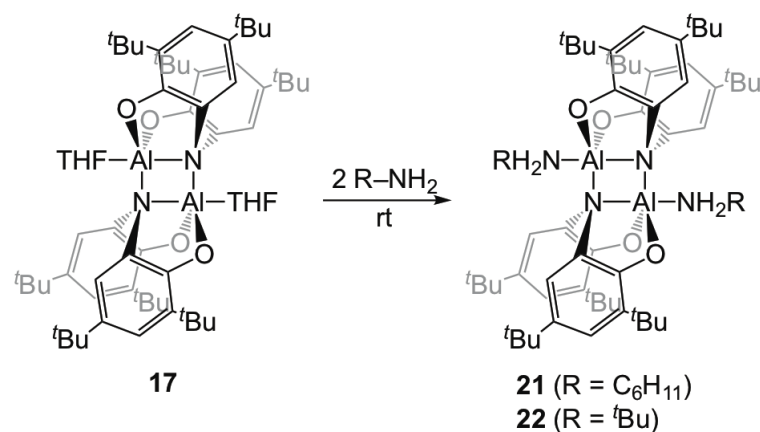
Bond lengths	20	Bond angles	20
Ga1–N1	2.151(2) Å	O1–Ga1–O2	113.37(10)°
Ga1–O1	1.853(2) Å	N1–Ga1–O1	84.59(10)°
Ga1–O2	1.870(2) Å	N1–Ga1–O2	83.27(9)°
Ga1–H2	1.56(4) Å	N1–Ga1–O3	162.21(9)°

2.3.4 Small molecule activation studies with **17**

2.3.4.1 Reactions of **17** with amines

From the molecular structure of **17**, it was noted that the coordination sites at aluminium are occupied, hindering further reactivity with small molecule substrates.

Reaction of **17** with two molar equivalents of cyclohexylamine resulted in a displacement of the THF ligand to afford **21** cleanly. The analogous reaction with *tert*-butylamine yielded **22** in a similar fashion (Scheme 2.19).



Scheme 2.19: Synthesis of **21** and **22**.

Crystals of **21** and **22** suitable for single crystal X-ray diffraction were grown from the C₆D₆ reaction mixture at room temperature. The molecular structures of **21** and **22** are as expected given the molecular structure of **17** (Figures 2.19–2.20 and Table 2.13).

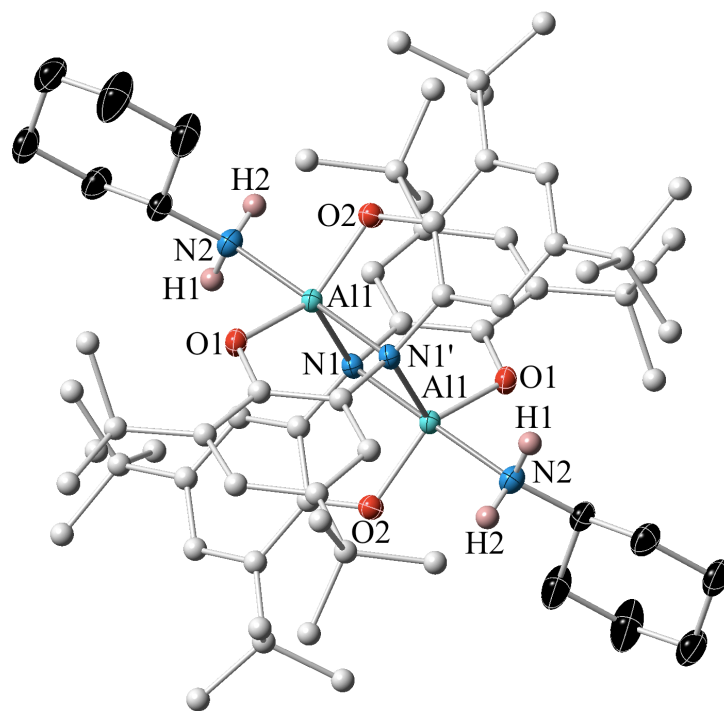


Figure 2.19: Molecular structure of **21**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1 and H2, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

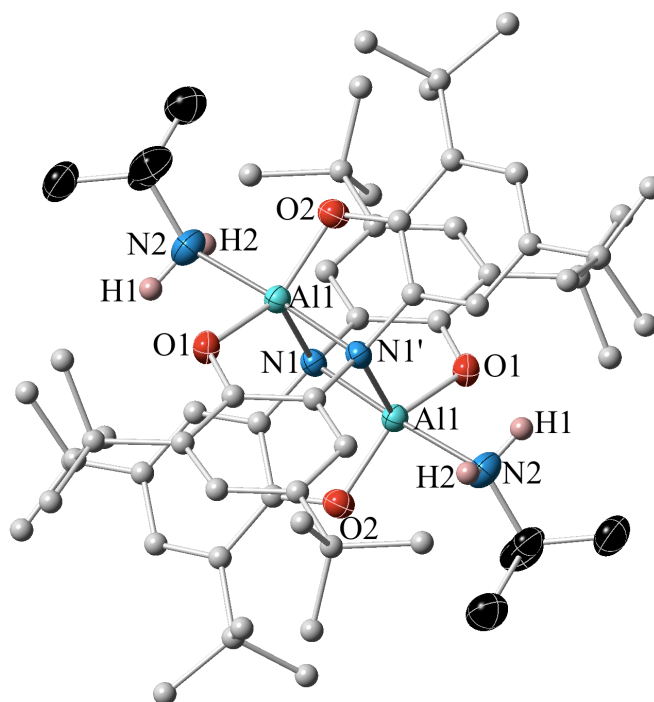


Figure 2.20: Molecular structure of **22**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1 and H2, omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 2.13 – Selected bond length and bond angles for **21** and **22**.

Bond lengths and bond angles	21	22
Al1–N1	1.939(2) Å	1.942(2) Å
Al1–O1	1.778(1) Å	1.767(1) Å
Al1–O2	1.767(2) Å	1.764(1) Å
Al1–N2	2.022(2) Å	2.021(2) Å
Al1–N1'	2.051(2) Å	2.046(2) Å
O1–Al1–O2	131.96(5)°	133.85(5)°
N1–Al1–O1	86.26(4)°	86.17(5)°
N1–Al1–O2	86.71(4)°	86.91(5)°
N1–Al1–N2	175.05(5)°	173.38(6)°
N1–Al1–N1'	88.04(4)°	87.84(5)°

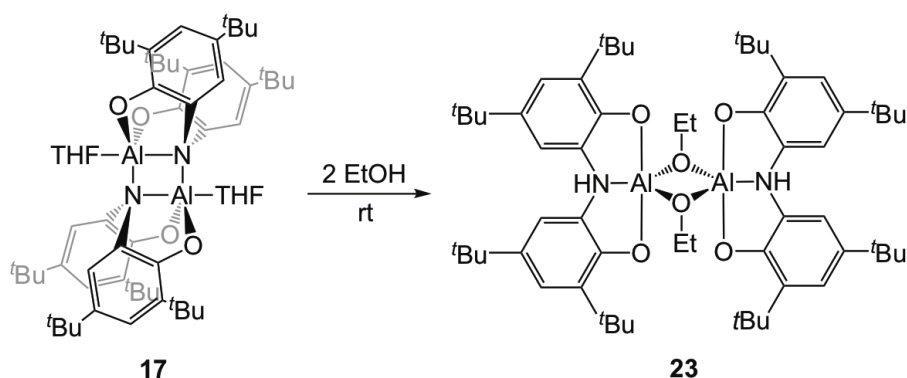
In the ^1H NMR spectrum of **21**, the resonances attributed to the THF relative of **17** were absent and a range of resonances from 3.66 to 1.01 ppm attributed to the cyclohexylamine protons were found. In the case of compound **22**, the ^1H NMR spectrum shows a singlet resonance at 1.35 ppm, corresponding to the N^tBu protons from the amine. The aromatics resonances and *tert*-butyl protons resonances observed for compounds **21** and **22** were

similar to those found in **17**. In both cases, it was not possible to obtain ^{13}C NMR spectra due to poor solubility in any deuterated solvents.

2.3.4.2 Reaction of **17** with ethanol

While the reaction of **17** with primary amines resulted in a displacement of the coordinated THF molecules, reaction of **17** with two molar equivalents of ethanol at room temperature resulted in the formation of **23** via O–H bond activation across the ligand Al–N bond.

The reaction was monitored by ^1H NMR spectroscopy, characteristic resonances at 4.79 ppm for the N–H proton of the ligand backbone and at 4.04 (d, $^3J_{\text{H-H}} = 7\text{Hz}$) and 1.36 ppm (t, $^3J_{\text{H-H}} = 7\text{Hz}$), attributed to the OCH_2CH_3 moiety were found.



Scheme 2.20: Synthesis of **23**.

Crystals of **23** suitable for single crystal X-ray diffraction were obtained from the C_6D_6 reaction mixture at room temperature. The molecular structure of **23** exhibits a distorted trigonal bipyramidal geometry around the aluminium atom, as well as a protonated sp^3 -hybridised nitrogen atom (Figure 2.21). As a result, **23** is observed as a dimer through the aluminium atom (Al1) and the oxygen atoms (O3) from ethanol forming a four-membered Al_2O_2 heterocycle. The molecular structure of **23** exhibits similar Al–O bond lengths as those observed for starting material **17**. However, the ligand Al1–N1 bond length of **23** is longer than that of **17** by 0.201 Å, in addition the $(\text{ONO})^{3-}$ ligand moiety of **23** is more bent than that seen for compound **17** ($\text{O1-Al1-O2} = 120.68(4)^\circ$ for **23** and $133.83(5)^\circ$ for **17**).

These results are consistent with the observation that the nitrogen atom (N1) of the ligand backbone being protonated.

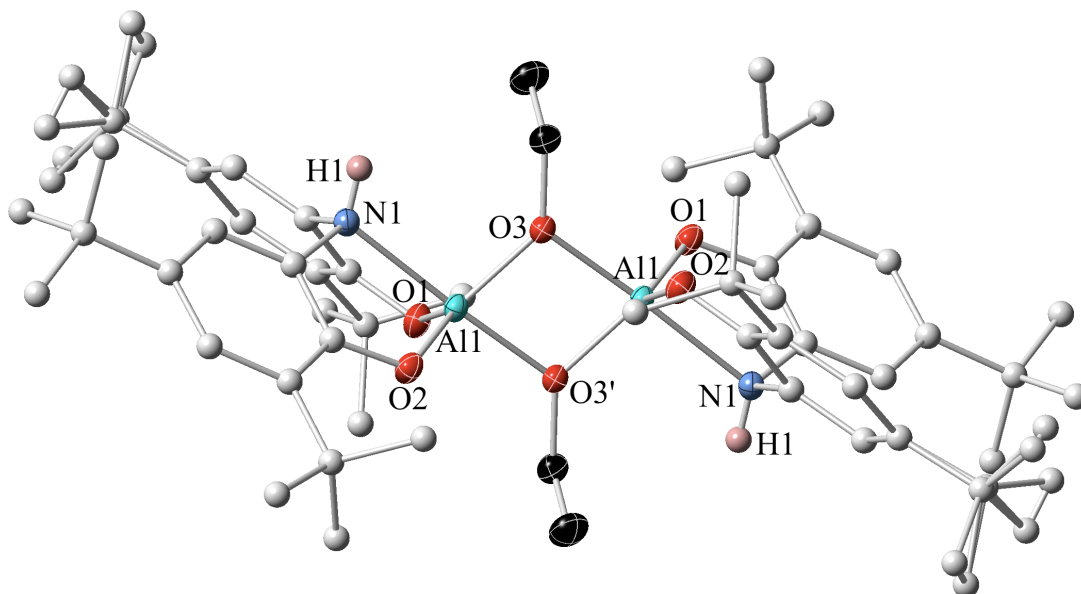
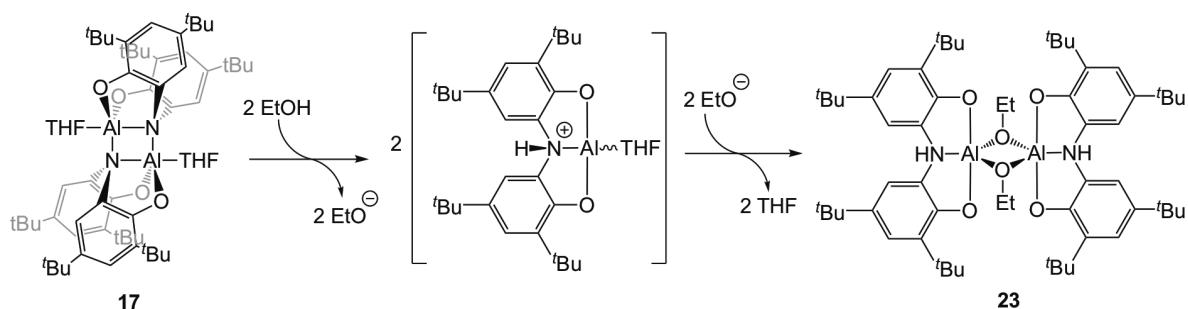


Figure 2.21: Molecular structure of **23**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 2.14 – Selected bond lengths and bond angles for **23**.

Bond lengths	23	Bond angles	23
Al1–N1	2.124(1) Å	O1–Al1–O2	120.68(4)°
Al1–O1	1.757(1) Å	N1–Al1–O1	84.85(4)°
Al1–O2	1.763(1) Å	N1–Al1–O2	85.23(4)°
Al1–O3	1.803(1) Å	N1–Al1–O3	177.31(4)°

The reactivity difference observed for compound **17** between amines and ethanol is attributed to the increased acidity of the O–H proton. It is postulated that protonation of the ligand backbone is the first step of the O–H activation reaction, followed by nucleophilic attack of the boron centre by the alkoxide anion to afford **23** (Scheme 2.21).



Scheme 2.21: Proposed mechanism of synthesis of **23**.

2.3.4.3 Reactions of **17** with other small molecule substrates

When compound **17** was allowed to react with dihydrogen gas (1 atm), decomposition to multiple products was observed, even at $-78\text{ }^{\circ}\text{C}$. Similar decomposition was observed for the analogous reaction with ammonia (1 atm) and water.

2.3.5 Attempts to make an aluminium hydride compound bearing the $\{\text{ON}(\text{H})\text{O}\}^{2-}$ ligand

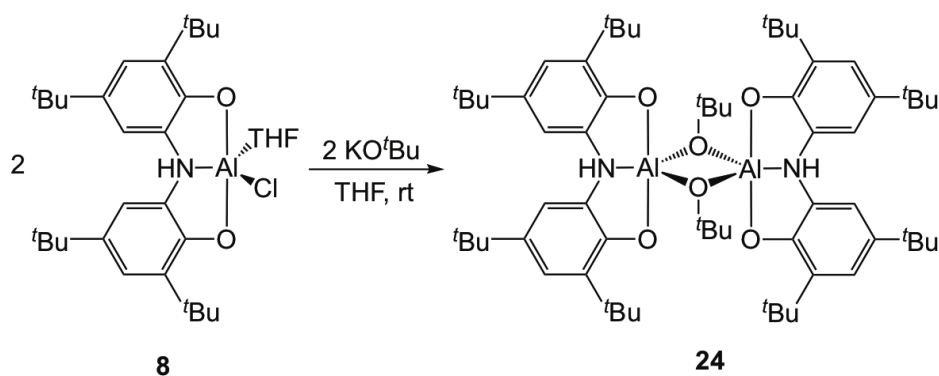
Encouraged by the isolation of a gallium hydride compound **20**, several attempts to access the aluminium analogue were undertaken. Initial efforts were focused on the synthesis alkoxide substituted aluminium compounds and their reactions with hydride sources such as HBpin, HBcat and potassium super-hydride salt.

2.3.5.1 Synthesis of **24**

An aluminium alkoxide, **24**, was prepared by addition of KO^tBu to **8** (Scheme 2.22). This species was characterised by ^1H NMR spectroscopy in C_6D_6 exhibiting a resonance at 1.52 ppm (singlet) attributed to the O^tBu moiety.

Crystals of **24** suitable for single crystal X-ray diffraction were grown from a concentrated hexane solution at room temperature. From these studies, it was found that **24** adopts a distorted trigonal bipyramidal geometry around the aluminium centre with a protonated sp^3 -hybridised nitrogen (N1) atom on the backbone (Figure 2.22). The structure of **24**

dimerises through aluminium (Al1) and oxygen (O3) forming a four-membered Al_2O_2 heterocycle, as observed from the molecular structure of **23**.



Scheme 2.22: Synthesis of **24**.

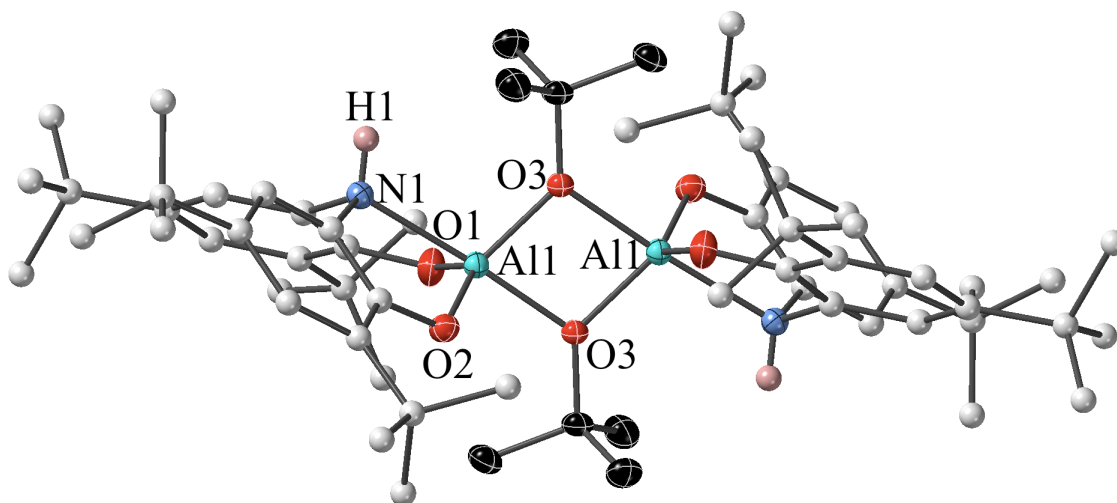


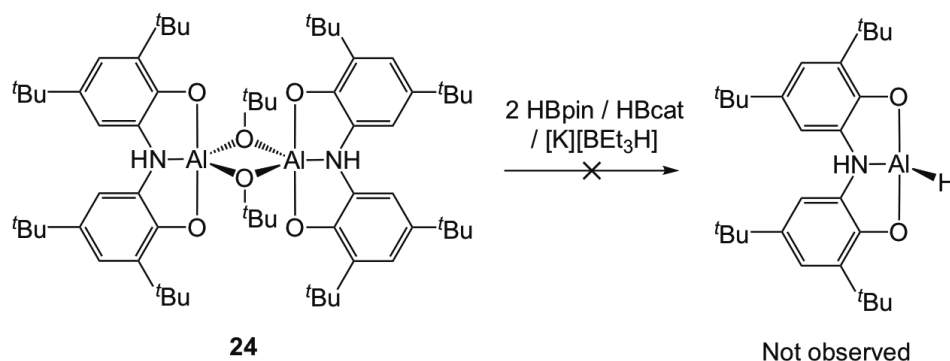
Figure 2.22: Molecular structure of **24**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 2.15 – Selected bond lengths and bond angles for **24**.

Bond lengths	24	Bond angles	24
Al1–N1	2.139(1) Å	O1–Al1–O2	127.52(4)°
Al1–O1	1.781(1) Å	N1–Al1–O1	82.43(4)°
Al1–O2	1.782(1) Å	N1–Al1–O2	83.55(4)°
Al1–O3	1.815(1) Å	N1–Al1–O3	176.61(4)°

2.3.5.2 Reactions of **24** and hydrogen sources

Unfortunately, addition of two molar equivalents of HBpin or, a more potent hydrogen source, HBcat, to **24** did not give any reaction even at elevated temperatures (Scheme 2.23). Also, moving to potassium super-hydride salt resulted in only starting material in the ^1H NMR spectrum. This diminished reactivity is thought to be the result of the strong Al–O bonds formed during dimerisation.

**Scheme 2.23:** Reaction of **24** with potent hydride sources.

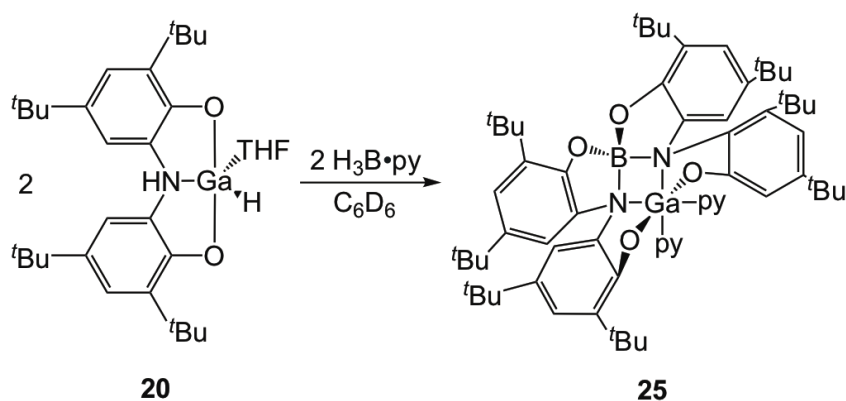
2.3.6 Reactivity of **20** towards small molecule substrates

Compound **20** was found to co-crystallise with one pyridine-borane molecule, deterring further investigations with small molecules as the reducing agent could not be separated.

2.3.6.1 Reactivity upon heating

Dissolving a crystalline sample of **20** in C_6D_6 in an air-tight Young's tap NMR tube and subsequently heating at 70 °C for seven days resulted in a pale yellow solution, accompanied by pale yellow crystals and a grey precipitate. The solution was monitored by

^1H NMR spectroscopy which showed formation of multiple products. Single crystal X-ray diffraction confirmed the structure of the crystalline product to be the dimeric compound **25**. This species forms by reaction of two molecules of **20** resulting in H_2 liberation and, what we believe to be, elemental gallium (Scheme 2.24). Interestingly, this reaction may be considered a partial trans-elementation of gallium to boron from the pyridine-borane which cocrystallises with **20**. Given the poor solubility of **25**, full characterisation by NMR spectroscopy was not possible.



Scheme 2.24: Synthesis of **25**.

The molecular structure of **25** reveals a distorted octahedral geometry around gallium, as well as formation of a four-membered GaBN_2 heterocycle ($\text{N1-B1-N2} = 108.96(12)^\circ$ and $\text{N1-Ga1-N2} = 74.56(8)^\circ$) (Figure 2.23). Selected bond lengths and bond angles for **25** are summarised in Table 2.16. It is also noteworthy that the boron atom adopts the preferred tetrahedral geometry, while the gallium atom is forced into a distorted octahedral environment.

Table 2.16 – Selected bond lengths and bond angles for **25**.

Bond lengths	25	Bond angles	25
Ga1–N1	2.142(2) Å	N1–Ga1–N2	74.56(8)°
Ga1–N2	2.197(2) Å	O1–Ga1–O3	174.49(8)°
B1–N1	1.614(4) Å	N1–B1–N2	108.96(18)°
B1–N2	1.616(3) Å	O2–B1–O4	114.2(2)°

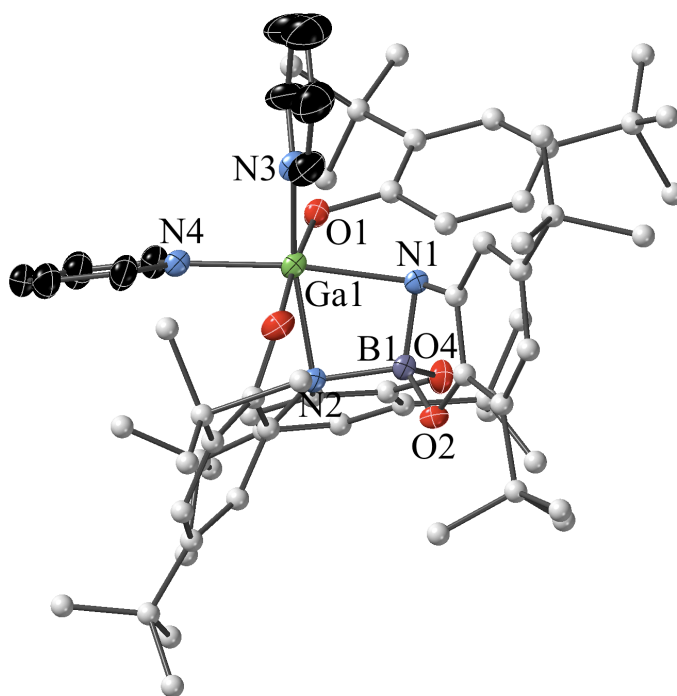
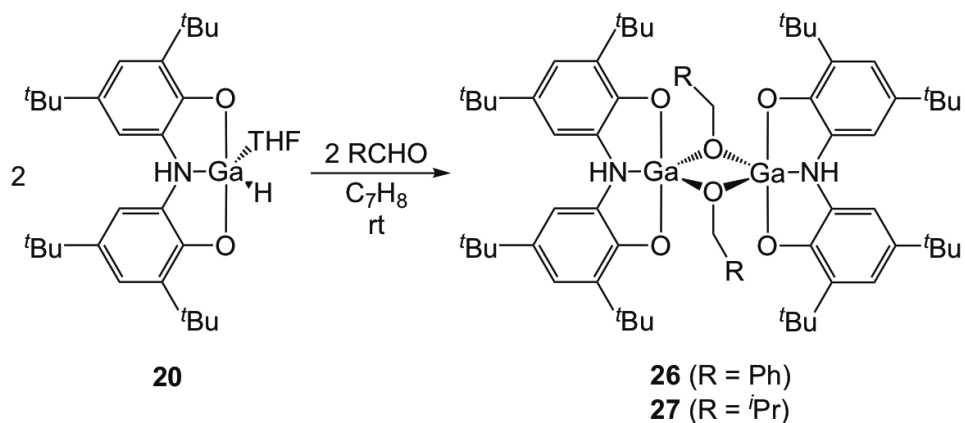


Figure 2.23: Molecular structure of **25**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, N2, O1, O2, O3 and O4, are pictured as spheres of arbitrary radius.

2.3.6.2 Reactivity with aldehydes



Scheme 2.25: Synthesis of **26** and **27**.

As previously reported by Roesky and Aldridge, aluminium-hydride and gallium-hydride compounds react with carbonyls, such as carbon dioxide, aldehydes and ketones.^{6,7} Reaction of **20** with benzaldehyde in C_6D_6 yielded a white precipitate which was subsequently redissolved in d_8 -THF. The 1H NMR spectrum confirmed the formation of a

dimeric gallium alkoxide compound, **26** (Scheme 2.25). Next, *iso*-butyraldehyde was explored and found to yield the related compound **27**.

In the ^1H NMR spectrum of **26**, a resonance attributed to the alkoxide CH_2 protons was observed at 5.29 ppm and a set of resonances attributed to the phenyl protons was found in a range from 7.43 to 6.95 ppm. The set of resonances corresponding to the $\text{H}_3\text{B}\cdot\text{py}$, originally observed for the starting material **20**, had completely disappeared. The aromatic proton resonances of **26** were more upfield shifted than those observed in **20**. Similarly, the ^1H NMR spectrum of **27** displays a set of resonances attributed to the $-\text{CH}_2^i\text{Pr}$ protons which were found at 1.33 and 0.81 ppm. The aromatic proton and *tert*-butyl protons resonance observed in the ^1H NMR spectrum of **27** are similar to those observed for **26**. The analogous reaction in d_8 -THF was monitored by ^1H NMR spectroscopy but showed that no reaction occurred at either room temperature or upon heating. This suggests that the reaction occurs through dissociation of the THF ligand from the Ga centre, followed by coordination of the carbonyl.

Single crystals of **26** and **27** suitable for single crystal X-ray diffraction could be obtained from a concentrated toluene solution at room temperature. The molecular structure of **26** confirms that the gallium atom (Ga1) adopts a distorted trigonal bipyramidal geometry (Figure 2.24). Selected bond lengths and bond angles for compound **26** are given in Table 2.17. The nitrogen atom (N1) and oxygen (O3) from the alkoxide occupy the axial positions giving an almost linear N1–Ga1–O3' bond angle ($179.44(10)^\circ$), in addition the three oxygen atoms (O1, O2 and O3) occupy the equatorial position (the sum of bond angle around the Ga1, O1 and O3 is 360.0°). This solid-state structure is related to that observed for **23** and **24**. The Ga–O3' bond ($1.959(2)$ Å) is longer than the Ga–O3 bond ($1.874(1)$ Å), in line with electrostatic repulsion from the occupied Ga *p*-orbital and the equatorial oxygen O3'. The bond lengths of the Ga–O bonds for O1, O2 and O3 are almost identical to the Ga–O

bonds in the axial positions. The molecule structure of **27** is comparable to that of **26** and their bond metrics within the $\{\text{ON}(\text{H})\text{O}\}^{2-}$ ligand are largely similar (Figure 2.25 and Table 2.17).

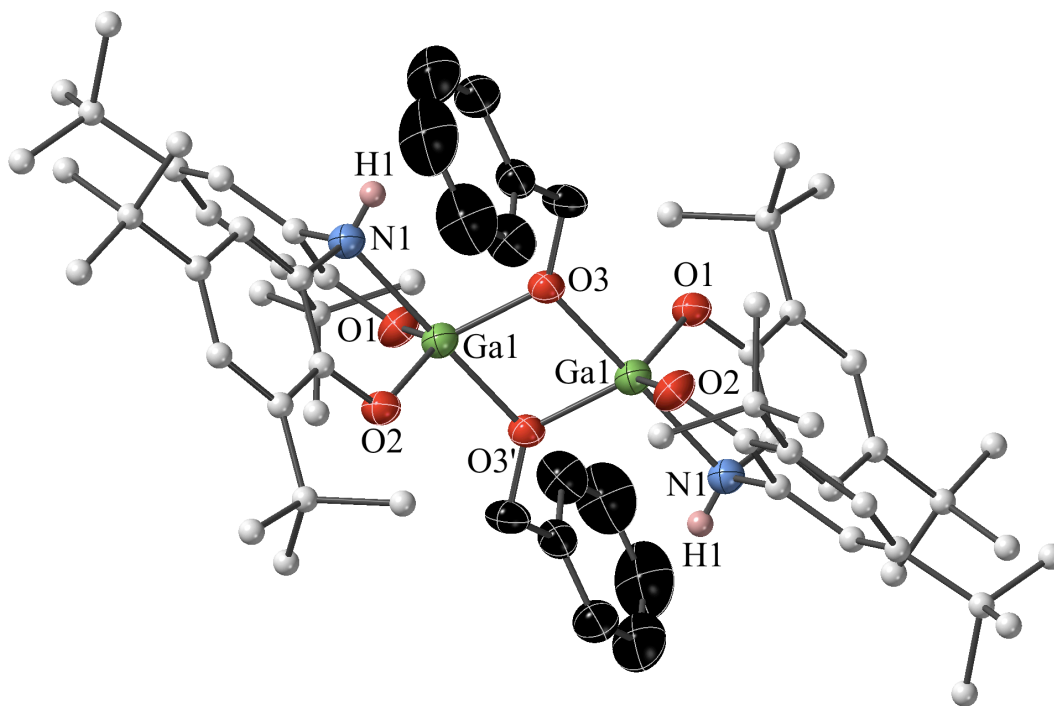


Figure 2.24: Molecular structure of **26**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 2.17 – Selected bond lengths and bond angles for **26** and **27**.

Bond lengths and bond angles	26	27
Ga1–N1	2.132(3) Å	2.152(2) Å
Ga1–O1	1.842(2) Å	1.845(2) Å
Ga1–O2	1.835(2) Å	1.840(2) Å
Ga1–O3	1.874(1) Å	1.885(2) Å
Ga1–O3'	1.959(2) Å	1.963(2) Å
O1–Ga1–O2	121.63(10)°	117.84(9)°
N1–Ga1–O1	85.50(10)°	84.96(8)°
N1–Ga1–O2	84.89(9)°	85.33(8)°
N1–Ga1–O3	101.78(10)°	99.06(8)°
N1–Ga1–O3'	179.44(10)°	174.99(8)°

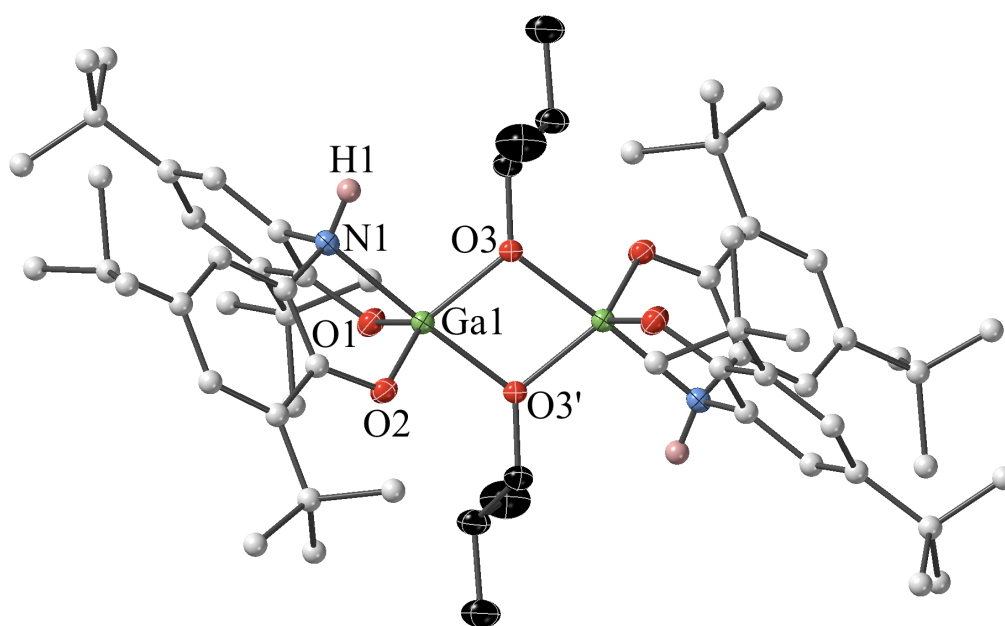


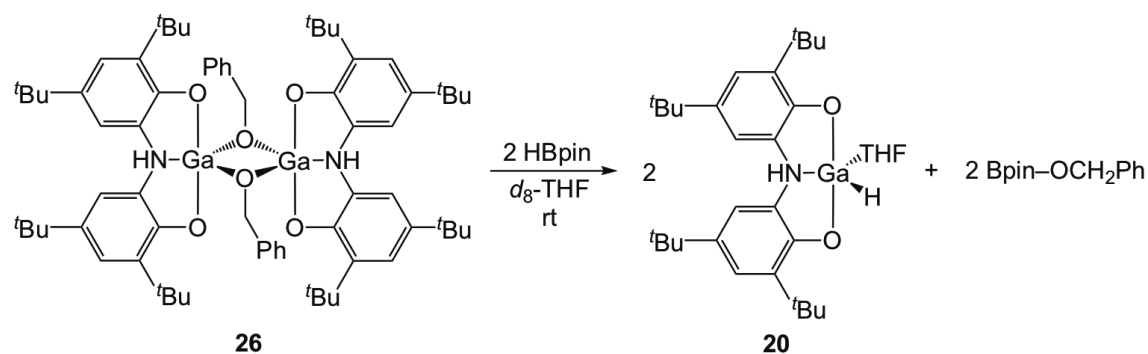
Figure 2.25: Molecular structure of **27**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

2.3.6.3 Reactivity of **20** with other small molecules

Unfortunately, addition of carbon dioxide or phenylacetylene to a solution of **20** gave no reaction, subsequently heating of these samples only gave pale yellow crystals of **25**.

2.3.6.4 Catalytic activity of **26**

Reaction of **26** with two molar equivalents of HBPIn in d_8 -THF solution resulted in formation of boryl-benzyl alcohol and **20**. Further inspection of the ^1H NMR spectrum showed formation of compound **20**, which gives rise to a diagnostic signal at 5.27 ppm (Scheme 2.26). Attempts to isolate **20** from this reaction mixture only resulted in decomposition, as previously observed in the absence of $\text{H}_3\text{B}\cdot\text{py}$.



Scheme 2.26: Reaction of **26** with HBpin.

Inspired by this stoichiometric hydroboration, efforts towards catalytic hydroboration of carbonyls was investigated for compound **26**. We investigated the reaction of **26** (10 mol%) with benzaldehyde and HBpin in C_6D_6 . The 1H NMR spectrum shows 96% conversion to Bpin–OCH₂Ph in less than five minutes at room temperature with a lower catalytic loading of **26** (0.05 mol %), the 1H NMR spectrum shows 92% conversion to the boryl product after twenty minutes and 98% conversion after fifty minutes.

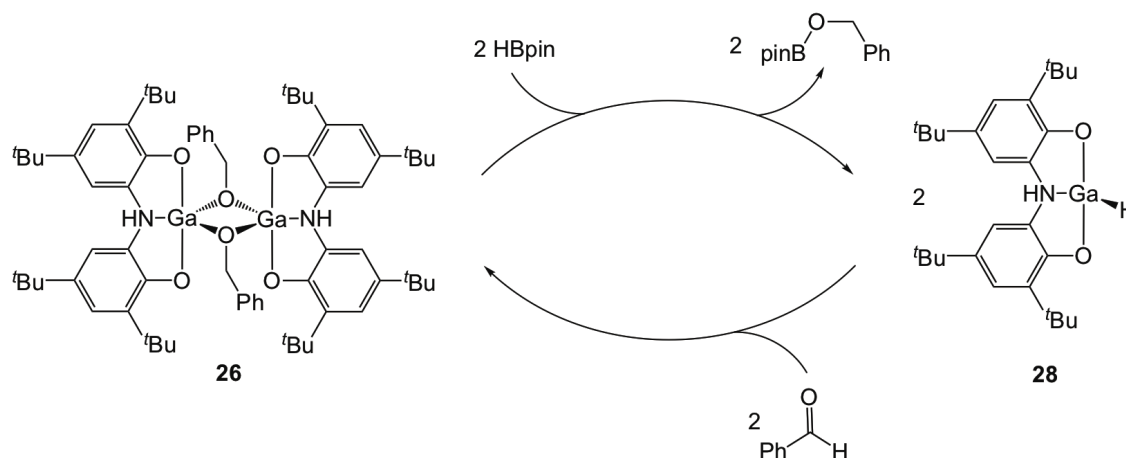
Table 2.18 compares the catalytic activity of **26** with Roesky's aluminium hydride compound (**XLVIII**),⁶ Jones's germanium and tin hydride compounds (**XLIX** for Ge and **L** for Sn)¹¹ as well as Hill's magnesium hydride compound (**LVIII**).¹² It was found that the catalytic activity of **26** is comparable to **LVIII**, which notably gave the greatest conversion in the least amount of time.

Table 2.18 – Comparison of catalytic hydroboration of benzaldehyde.

Catalyst	Mol%	Time / min	Conversion / %
26	10	< 5	96
26	0.05	20	92
26	0.05	50	98
XLVIII	1	60	99
XLIX	1	90	99
L	0.05	150	99
LVIII	0.05	15	95

This hydroboration is thought to proceed via **26** reacting with two HBpin molecules to yield the benzyl boroether and an observed gallium hydride intermediate, **28**, which in the

absence of a coordinated THF molecule further reacts with benzaldehyde to regenerate **26** (Scheme 2.27).



Scheme 2.27: Catalytic cycle for catalytic hydroboration using **26**.

In 2012, Hill reported the reaction of HBpin and benzaldehyde in C_6D_6 at room temperature, which in the absence of catalyst, only gave 2% of the corresponding boroether.¹² However, when the control reaction was further investigated, it was found that HBpin and benzaldehyde gave 23% conversion after ninety minutes and 91% conversion after five hours. This observed reactivity may be the result of borane impurities present in the HBpin, which can act as catalysts.¹³ Nevertheless, the rates reported by **26** or Hill's **LVIII** catalysts are significantly faster.

2.4 Conclusions and future work

In this chapter, we have reported the synthesis of base-supported group 13 complexes, $E(ONO) \cdot L$ ($E = B, Al, Ga$; $L =$ a Lewis base). In the case of the boron complexes, it was found that $B(ONO)$ type species were formed *in-situ* and are capable of THF activation to form **1**. The NMe_3 stabilised boron compound (**2**) was prepared by reacting $H_3(ONO)$ with NMe_3 stabilised borane. However, the molecular structure of **2** showed an almost perfect tetrahedral geometry around boron as the boron atom is too small to be contained by the $(ONO)^{3-}$ ligand binding site making it less reactive towards the small molecule substrates.

Eventually, it was found that **2** is capable of activating O–H bond with water and ethanol to give product **3** and **4**, respectively. The aluminium analogue of E(ONO)·L can be easily accessed via the neutral aluminium chloride compound (**8**) and potassium to give **17**. The molecular structure of **17** revealed a highly stable dimetallic structure. Compound **17** is capable of O–H bond cleavage of ethanol across its Al–N bond to afford **23**. Finally, a gallium hydride species was synthesised, **20**, which is capable of activating aldehydes to form gallium alkoxide compounds, **26** and **27**. Of these compounds, **26** could be employed as an active catalyst for the hydroboration of benzaldehyde.

Further work will involve performing kinetic studies of hydroboration of **26** with a range of aldehydes, in an effort to garner mechanistic insights, as well as expanding the substrate scope to include ketones.

2.5 Reference

- (1) Arduengo, A. J.; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Mizen, M. *B. J. Am. Chem. Soc.* **1987**, *109* (3), 627.
- (2) Dunn, N. L.; Ha, M.; Radosevich, A. T. *J. Am. Chem. Soc.* **2012**, *134* (28), 11330.
- (3) McCarthy, S. M.; Lin, Y. C.; Devarajan, D.; Chang, J. W.; Yennawar, H. P.; Rioux, R. M.; Ess, D. H.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136* (12), 4640.
- (4) Cui, J.; Li, Y.; Ganguly, R.; Inthirarajah, A.; Hirao, H.; Kinjo, R. *J. Am. Chem. Soc.* **2014**, *136* (48), 16764.
- (5) Robinson, T. P.; De Rosa, D. M.; Aldridge, S.; Goicoechea, J. M. *Angew. Chem. Int. Ed.* **2015**, *54* (46), 13758.
- (6) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angew. Chem. Int. Ed.* **2015**, *54* (35), 10225.

- (7) Abdalla, J. A. B.; Riddlestone, I. M.; Tirfoin, R.; Aldridge, S. *Angew. Chem. Int. Ed.* **2015**, *54* (17), 5098.
- (8) Huang, K.; Dutton, J. L.; Martin, C. D. *Chem. - A Eur. J.* **2017**, *23* (44), 10532.
- (9) Szigethy, G.; Heyduk, A. F. *Dalt. Trans.* **2012**, *41*, 8144.
- (10) Robinson, T. P.; De Rosa, D.; Aldridge, S.; Goicoechea, J. M. *Chem. - A Eur. J.* **2017**, *23* (61), 15455.
- (11) Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2014**, *136* (8), 3028.
- (12) Arrowsmith, M.; Hadlington, T. J.; Hill, M. S.; Kociok-Kon, G. *Chem. Commun.* **2012**, *48* (48), 4567.
- (13) Wu, Y.; Shan, C.; Ying, J.; Su, J.; Zhu, J.; Liu, L. L.; Zhao, Y. *Green Chem.* **2017**, *19* (17), 4169.

Chapter 3

Complexes of group 14 elements bearing the *N,N*-bis(3,5-di-*tert*-butyl-2-phenolate) amide ligand and the bidentate xanthene-4,5-diamine ligand

3.1 Complexes of group 14 elements bearing the (ONO)³⁻ ligand

3.1.1 Introduction of geometry constrained group 14 compounds and project aims

While geometrically constrained group 15 compounds have been studied extensively,^{1–5} only few examples of geometrically constrained group 14 compounds have been reported (Figure 3.1). One of the first examples was reported by Arduengo in 1988 with the isolation of a tin(II) stannylene complex supported by a bis(phenolate)amide ligand, **LX**. This compound was prepared using HN{CH₂C(O)*t*Bu}₂) and SnCl₄, which gave rise to an *in-situ* reduction of tin from the +4 to the +2 oxidation state.⁶ To date the germanium(II) analogue of **LX** has not yet been reported, however the analogous reaction with GeCl₄ exclusively yielded the germanium(IV) product, **LXI**.⁷ In a similar fashion, reaction with PhSiCl₃ gave the Si(IV) compound, **LXII**, which was found to dimerise through the nitrogen and silicon atoms.⁸ This dimerisation cannot be prevented by employing bulkier substituents at silicon, and consequently no monomeric forms of **LXII** are known. Recently, Greb reported a series of Si(IV) complexes with a geometrically constrained triamide (NNN)³⁻ ligand which can be isolated in both monomeric and dimeric forms, **LXIII–LXIV**.⁹ Greb also reported the analogous Si(IV) compound bearing the *N,N*-bis(3,5-di-*tert*-butyl-2-(phenolate) amide (ONO)³⁻ ligand, which was found to only exist as a dimer (**LXV**) (Figure 3.2). No small molecule activation has been reported with **LX–LXV**.

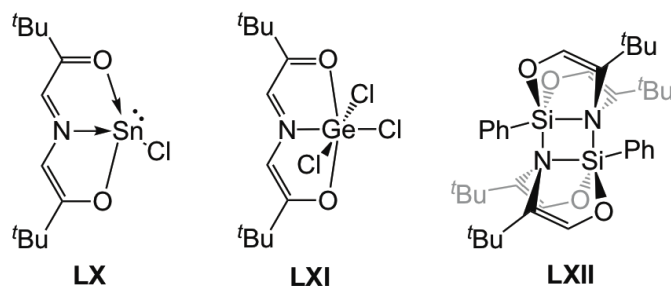


Figure 3.1: Early examples of geometry constrained group 14 compounds.^{6–8}

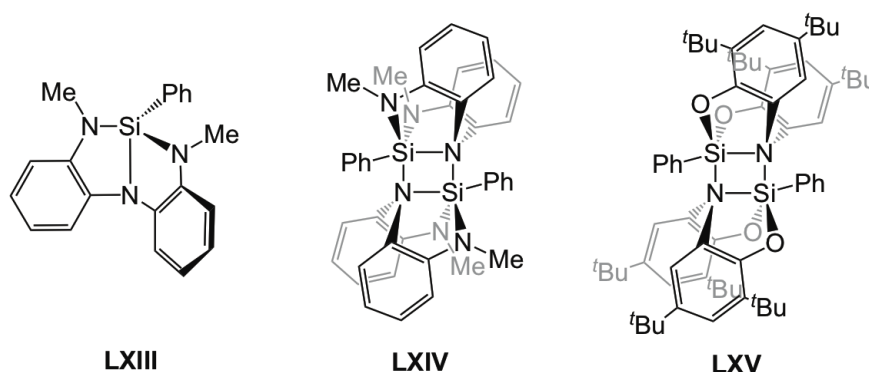
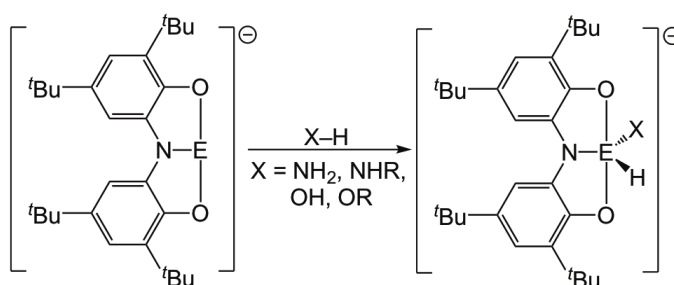


Figure 3.2: Selected geometry constrained group 14 compounds isolated by Greb.⁹

Our own research has recently reported a phosphorus(III) complex bearing the $(\text{ONO})^{3-}$ ligand, **LIV**, which can activate a series of small molecule substrates possessing protic X–H bonds.⁵ In an effort to investigate related isoelectronic compounds, the preparation of anionic group 14 analogues of **LIV**, $[\text{E}(\text{ONO})]^-$ ($\text{E} = \text{Si}, \text{Ge}, \text{Sn}$) was undertaken. Interestingly, the Ge(II)/Ge(IV) and Sn(II)/Sn(IV) redox couples could allow for an alternative oxidative addition pathway towards small molecule activation (Scheme 3.1), akin to the activation chemistry reported for compound **LIV**. Also, the high electron density at the group 14 centre should increase the energy of the HOMO, leading to smaller HOMO–LUMO energy gaps, necessary for the activation of small molecules.

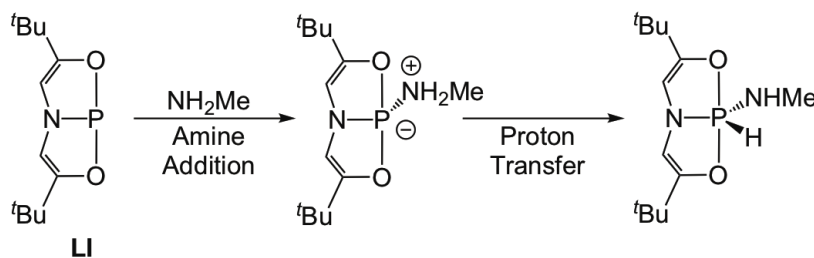


Scheme 3.1: Predicted reactivity of $[\text{E}(\text{ONO})]^-$ species.

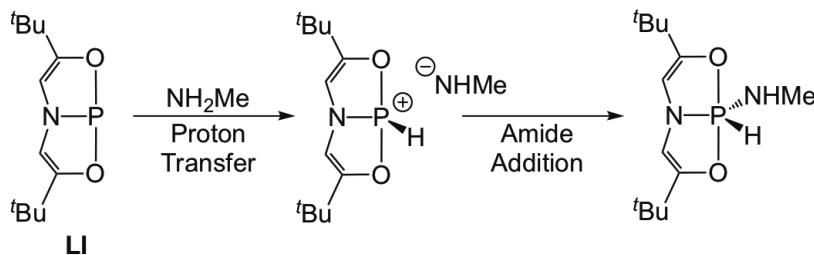
As described in Section 1.5.2, DFT investigations by Radosevich *et al.* for compound **LI** revealed that the activation of the N–H bond in methylamine followed an electrophilic pathway (Scheme 3.2; A).² The reaction was initiated by amine coordination to the electrophilic phosphorus centre, followed by proton transfer to afford a phosphorus(V)

product. By contrast, the negatively charged $[E(ONO)]^-$ species should follow a nucleophilic mechanism (Scheme 3.2; B). This prompted the exploration of these group 14 geometry constrained systems with electrophilic substrates, such as carbonyls, or substrates possessing a hydridic proton, such as phenylsilane.

A) Electrophilic Mechanism

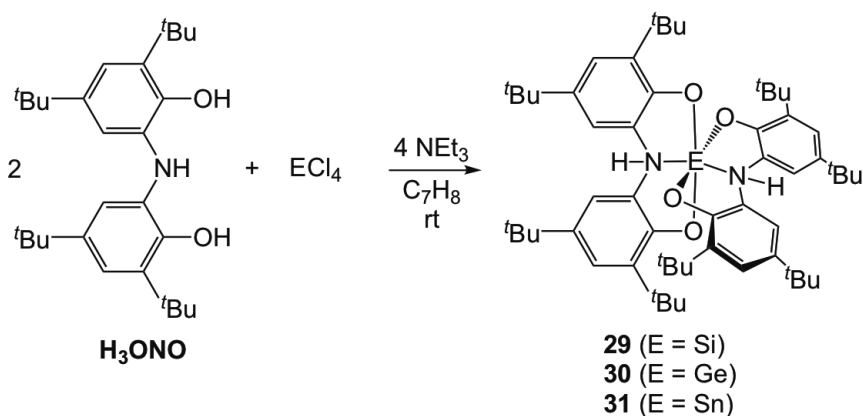


B) Nucleophilic Mechanism



Scheme 3.2: Mechanisms for small molecule activation by **LI**.

3.1.2 Reactions of $H_3(ONO)$ with group 14 tetrachlorides



Scheme 3.3: Synthesis of **29–31**.

Adopting the synthetic method used for the preparation of **LIV**,⁵ the reaction of $H_3(ONO)$ with silicon tetrachloride in the presence of NEt_3 at room temperature resulted in formation

of a neutral compound $\text{Si}\{\text{ON}(\text{H})\text{O}\}_2$ (**29**). However, cleaner reactivity was observed when SiCl_4 was allowed to react with two molar equivalents of $\text{H}_3(\text{ONO})$ in the presence of NEt_3 (Scheme 3.3). The germanium and tin analogues (**30** and **31**, respectively) were also prepared in a similar fashion.

It was found that NEt_3 failed to deprotonate all three protons of $\text{H}_3(\text{ONO})$, therefore stronger bases were explored. Compound **29** could also be formed when employing tetramethylethyldiamine (TMEDA) as the base. Alternatively, to prevent attachment of a second $\{\text{ON}(\text{H})\text{O}\}^{2-}$ ligand to silicon, trichlorophenylsilane (PhSiCl_3) was employed as a source of silicon. Addition of PhSiCl_3 into a solution of $\text{H}_3(\text{ONO})$ in the presence of NEt_3 also resulted in **29** as the exclusive reaction product. About a year after our isolation of **29**, Greb reported the synthesis and characterisation of **29**.⁹

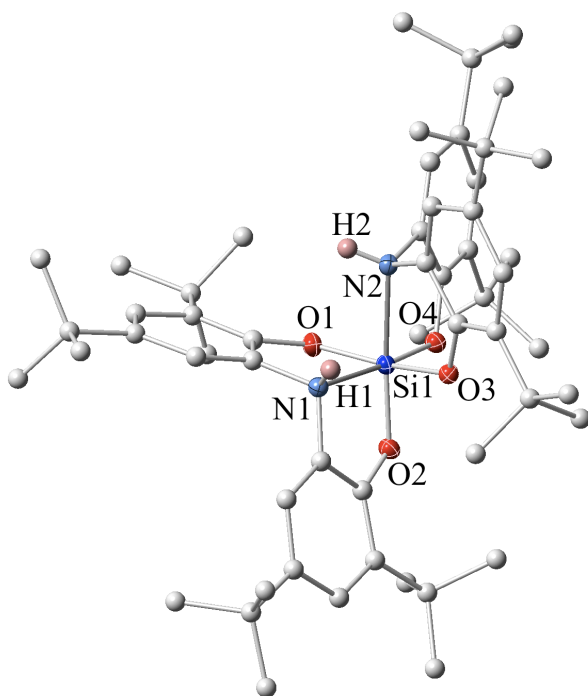


Figure 3.3: Molecular structure of **29**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1 and H2, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

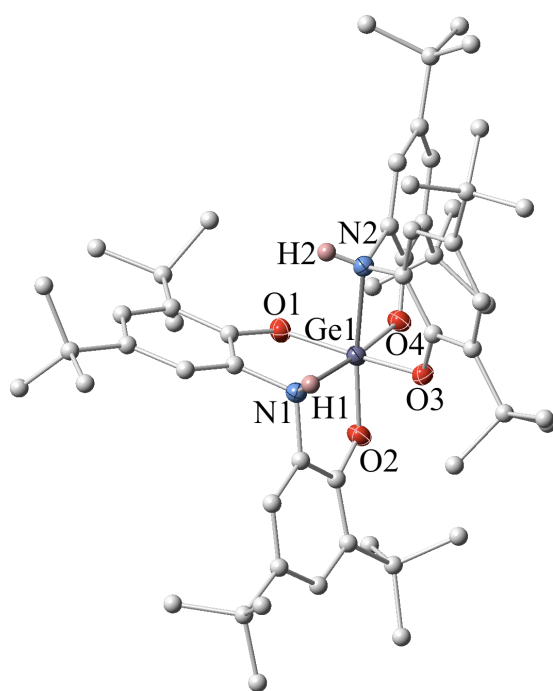


Figure 3.4: Molecular structure of **30**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1 and H2, are omitted for clarity. Atoms of the ligand, N1, O1 and O2, are pictured as spheres of arbitrary radius.

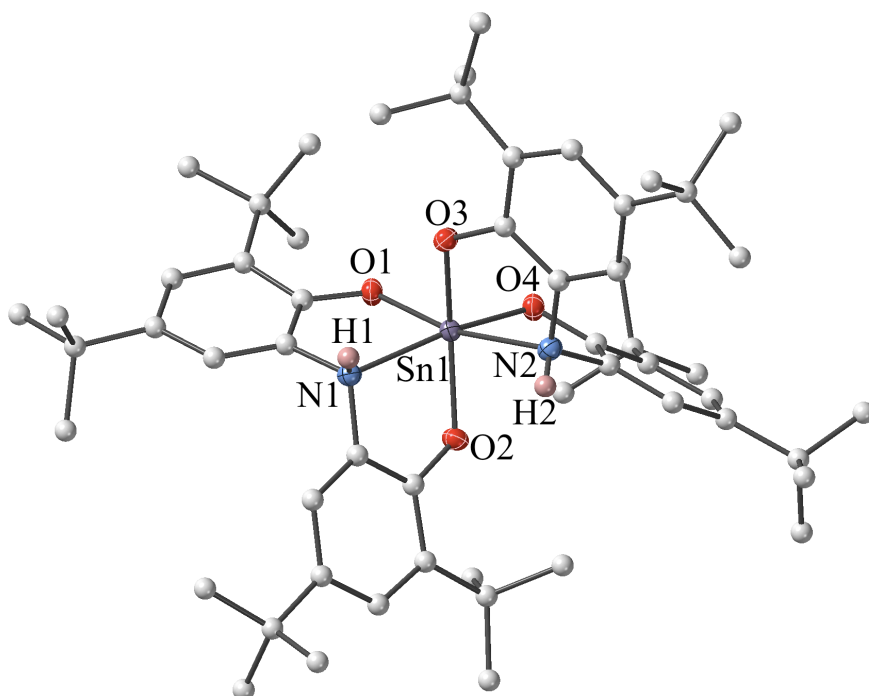


Figure 3.5: Molecular structure of **31**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1 and H2, omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 3.1 – Selected bond lengths and bond angles for **29**, **30** and **31**.

Bond lengths and bond angles	29 (E = Si)	30 (E = Ge)	31 (E = Sn)
E–N1	2.053(1) Å	2.122(2) Å	2.272(2) Å
E–N2	2.057(1) Å	2.125(1) Å	2.282(2) Å
E–O1	1.750(1) Å	1.859(1) Å	1.993(2) Å
E–O2	1.704(1) Å	1.820(1) Å	2.020(2) Å
E–O3	1.749(1) Å	1.859(1) Å	2.011(2) Å
E–O4	1.697(1) Å	1.812(1) Å	2.282(2) Å
O1–E–O2	98.48(4)°	98.74(5)°	103.71(5)°
N1–E–O1	83.37(4)°	82.33(4)°	81.09(4)°
N1–E–O2	87.88(4)°	86.25(5)°	78.40(4)°
N1–E–O3	85.93(4)°	86.87(5)°	88.88(5)°
N1–E–N2	90.99(4)°	93.85(5)°	107.20(5)°
O3–E–O4	99.18(4)°	99.71(5)°	102.38(5)°

Compound **29** was characterised by ^1H NMR spectroscopy in C_6D_6 , this spectrum displays four doublets at 7.35, 7.34, 6.95 and 6.85 ppm and four singlets at 1.74, 1.30, 1.29 and 1.22 ppm attributed to the aromatic protons and the *tert*-butyl protons, respectively. In addition, a broad peak at 5.33 ppm corresponding to the N–H protons was observed. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **29** shows a singlet at –128.6 ppm, consistent with a hexa-coordinate silicon centre. Furthermore, the resonances observed in the ^1H NMR spectra for compounds **30** and **31** are largely similar to those observed for compound **29**.

Crystals of **29–31** suitable for single crystal X-ray diffraction were grown from concentrated toluene solutions at room temperature. The molecular structure of **29** reveals a slightly distorted octahedral geometry around the silicon atom (Si1) (Figure 3.3). The O–Si–O bond angles are wider than that expected for an octahedral structure ($\text{O1–Si1–O2} = 98.48(4)^\circ$ and $\text{O3–Si1–O4} = 99.18(4)^\circ$), in line with the rigidity of the ligand. The Si–N bonds ($\text{Si1–N1} = 2.053(1)$ Å and $\text{Si1–N2} = 2.057(1)$ Å) are longer than the sum of the silicon–nitrogen covalent radii (1.82 Å).¹⁰ The molecular structure of **30** and **31** are comparable to that of **29** (Figures 3.4 and 3.5). Interestingly, the O–E–O bond angles are

increasingly wider on descending the group, owing to the increased covalent radii of tin compared to its lighter congeners (Table 3.1).

3.1.3 Reactions of $\text{H}_3(\text{ONO})$ with group 14 dichlorides

Inspired by the synthetic method used for the preparation of **LIV** and the neutral $\text{Al}(\text{Cl})\{\text{ON}(\text{H})\text{O}\}$ compound, **8**, the reactions of $\text{H}_3(\text{ONO})$ with one molar equivalent of $\text{E}(\text{II})$ dichloride were undertaken.

3.1.3.1 Reaction of $\text{H}_3(\text{ONO})$ with $\text{Si}(\text{II})$ chloride

Reaction of $\text{H}_3(\text{ONO})$ with the NHC stabilised dichlorosilylene adduct ($\text{IPr}\cdot\text{SiCl}_2$) ($\text{IPr} = :\text{C}[\text{N}(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)\text{CH}]_2$) in the presence of NEt_3 at room temperature immediately resulted in a deep purple solution. The reaction was monitored by ^1H NMR spectroscopy revealing the formation of a mixture of products. Colourless crystals were grown from a concentrated hexane solution, which upon single crystal X-ray diffraction studies confirmed the presence of $[\text{HIPr}][\text{Si}(\text{ONO})]$ ($[\text{HIPr}][\textbf{32}]$) (Figure 3.6).

The molecular structure of **32** shows a mono-anionic silicon(IV) species coordinated by the $(\text{ONO})^{3-}$ ligand. The geometry about the silicon centre (Si1) was found to be trigonal bipyramidal. The $(\text{ONO})^{3-}$ ligand moiety adopts a planar geometry ($\text{O1-Si1-O2} = 173.32(18)^\circ$) with the O1 and O2 atoms in the axial position, while N1 , Cl1 and Cl2 occupy the equatorial sites. The Si1-N1 bond of **32** ($1.790(4)$ Å) is shorter than the sum of silicon–nitrogen covalent radii (1.82 Å),¹⁰ consistent with the nitrogen lone pair delocalising onto Si1 . The Si-Cl1 and Si-Cl2 bond lengths are statistically identical. The molecular structure of **32** is also consistent with the oxidation of $\text{Si}(\text{II})$ to $\text{Si}(\text{IV})$. Surprisingly, it was found that IPr abstracted the protons of $\text{H}_3(\text{ONO})$ rather than NEt_3 . As a side note, it is quite uncommon to dissociate a strong Si-C bond from IPrSiCl_2 under such mild conditions.

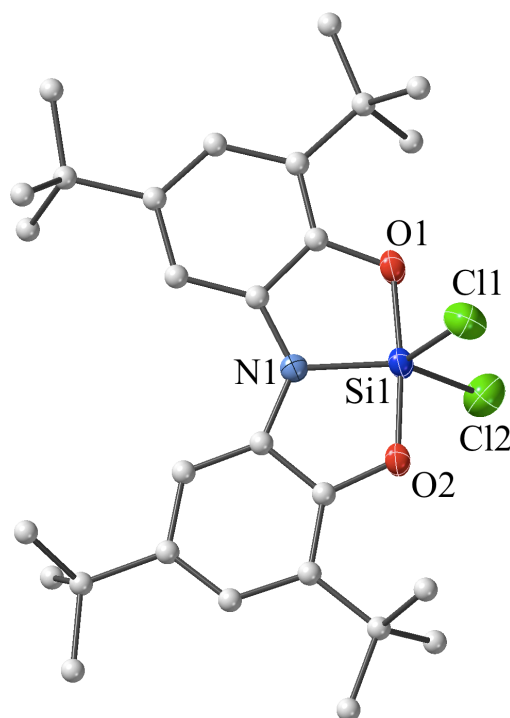


Figure 3.6: Molecular structure of [IPr][**32**]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [IPr]⁺ and all hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

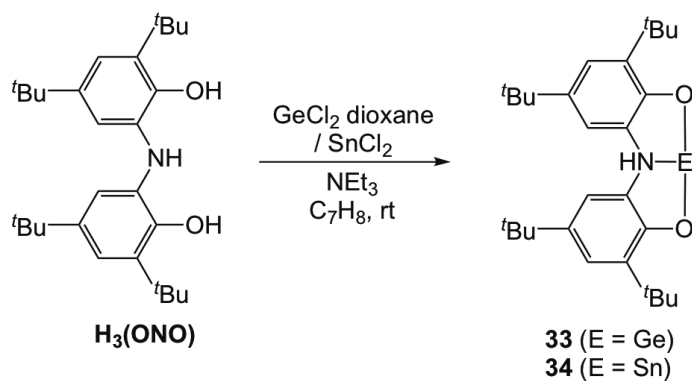
Table 3.2 – Selected bond lengths and bond angles for **32**.

Bond lengths	32	Bond angles	32
Si1–N1	1.790(4) Å	O1–Si1–O2	173.32(18)°
Si1–O1	1.741(4) Å	N1–Si1–O1	86.41(18)°
Si1–O2	1.727(4) Å	N1–Si1–O2	87.10(18)°
Si1–Cl1	2.095(2) Å	N1–Si1–Cl1	127.18(18)°
Si1–Cl2	2.099(2) Å	N1–Si1–Cl2	125.22(18)°

Unfortunately, compound **32** could not be isolated and fully characterised. Nevertheless, the analogous chemistry with Ge(II) and Sn(II) halides was investigated.

3.1.3.2 Reactions of H₃(ONO) with Ge(II) and Sn(II) chlorides

Reaction of H₃(ONO) with germanium dichloride dioxane (GeCl₂·dioxane) in the presence of two molar equivalents of NEt₃ afforded a neutral Ge{ON(H)O} compound, **33** (Scheme 3.4). The tin analogue, **34**, was also prepared by using the same synthetic strategy.



Scheme 3.4: Synthesis of **33–34**.

In the ^1H NMR spectrum of **33**, the presence of a broad resonance at 5.01 ppm corresponding to the N–H protons was observed, indicating the formation of **33**. In addition, two doublets at 7.29 and 7.04 ppm and two singlets at 1.55 and 1.28 ppm attributed to the aromatic protons and the *tert*-butyl protons, respectively, were also observed. The related compound **34** was also characterised by NMR spectroscopy and exhibited a similar ^1H NMR spectrum to **33**. A diagnostic signal in the ^{129}Sn NMR spectrum was seen at 314.7 ppm.

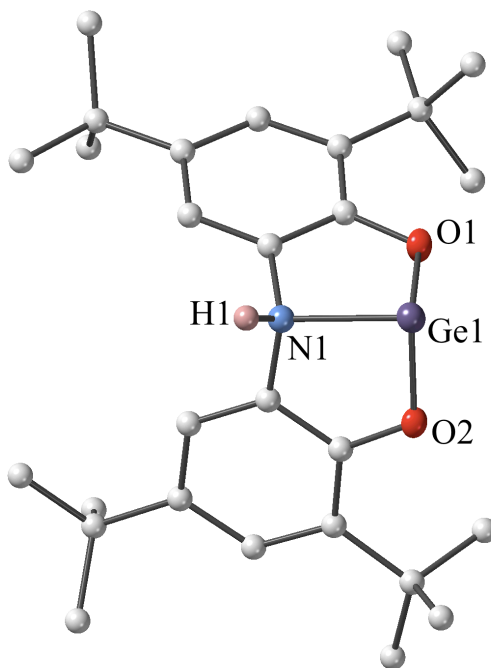


Figure 3.7: Molecular structure of **33**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 3.3 – Selected bond lengths and bond angles for **33**.

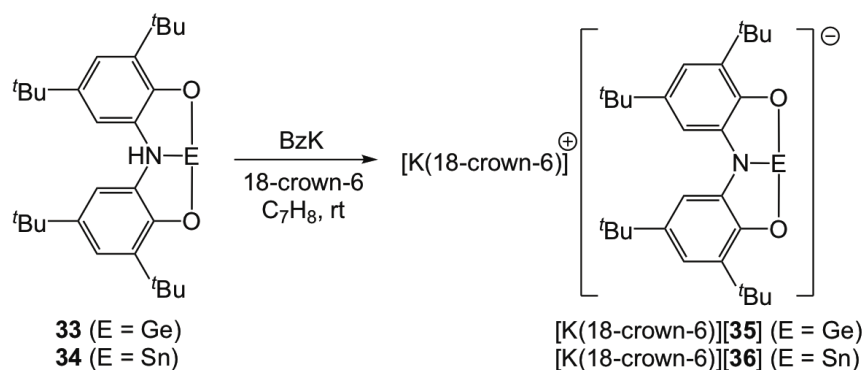
Bond lengths	33	Bond angles	33
Ge1–N1	2.107(1) Å	O1–Ge1–O2	99.21(4)°
Ge1–O1	1.888(1) Å	N1–Ge1–O1	82.78(4)°
Ge1–O2	1.861(1) Å	N1–Ge1–O2	84.37(4)°

The molecular structure of **33** exhibits a bent geometry around germanium (Ge1) with a distorted tetrahedral nitrogen atom (N1) (Figure 3.7 and Table 3.3). In this structure, the Ge1–N1 bond lengths (2.107(1) Å) are longer than the sum of covalent radii of germanium–nitrogen atoms (1.91 Å).¹⁰ The nitrogen (N1) lone pair is bonded to a hydrogen atom which was localised in the Fourier density map.

Despite several attempts, crystals of **34** suitable for single crystal X-ray diffraction studies could not be grown.

3.1.4 Deprotonation of **33** and **34** with benzyl potassium

It was found that NEt₃ was not a competent base for the deprotonation of the amine protons of **33** and **34**. However, addition of benzyl potassium (BzK) to **33** and **34** in the presence of a cation sequestering agent (1,4,7,10,13,16-hexaoxacyclooctadecane; 18-crown-6) resulted in formation of the targeted [K(18-crown-6)][E(ONO)] compounds (E = Ge, Sn), [K(18-crown-6)][**35**] and [K(18-crown-6)][**36**] (Scheme 3.5).

**Scheme 3.5:** Synthesis of [K(18-crown-6)][**35**] and [K(18-crown-6)][**36**].

Both reactions were also repeated using an alternative sequestering agent (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane; 2,2,2-crypt) or no sequestering agent, these reaction mixtures resulted in an inseparable mixture of products.

When **33** was allowed to react with benzyl potassium and 18-crown-6, the ^1H NMR spectrum was consistent with complete deprotonation of the ligand N–H protons. Two doublets at 7.27 and 6.58 ppm and two singlets at 1.39 and 1.29 ppm attributed to the aromatic protons and the *tert*-butyl protons, respectively, were also observed. The resonances observed in ^1H NMR spectrum of **36** are largely similar to those observed for **35**. Furthermore, compound **36** shows a resonance at 32.8 ppm in the ^{129}Sn NMR spectrum.

Crystals of **35** and **36** suitable for single crystal X-ray diffraction were grown from concentrated toluene solutions at room temperature. The molecular structure of **35** closely resembles to that of its phosphorus analogue, **LIV**, exhibiting a 8–Ge–3 bent configuration (Figure 3.8). Table 3.4 shows selected bond lengths and bond angles for **35**. The O1–Ge1–O2 bond angle of **35** is wider than that of starting material **33** (O1–Ge1–O2 for **35** = 106.23(10)° and for **33** = 99.21(4)°), in line with donation of the nitrogen (N1) lone pair delocalises onto the germanium centre (Ge1) to support a more planar geometry. This delocalisation results in multiple bond character between the Ge–N bond, confirmed by the Ge1–N1 bond length of **35** (1.952(2) Å) being shorter than that of **33** (2.107(1) Å). As the structure of **35** is more planar than **33**, this results in a lengthening of the Ge–O bonds (1.960(2) Å and 1.904(2) Å for **35** and 1.888(1) Å and 1.861(1) Å for **33**). It is noteworthy that the elongation of the Ge–O bonds of **35** is not uniform, but rather more pronounced for one of two aryloxy substituents of the ligand. It was found that a potassium atom sequestered by an 18-crown-6 molecule is weakly coordinated to the O2 atom of **35** (K1···O2 = 4.021(3) Å), lessening the electrostatic repulsion from the O2 atom to the germanium centre (Ge1). The sum of the bond angles around the germanium centre (Ge1)

of **35** is 276.89°, confirming the 8-Ge-3 bent configuration. The molecular structure of **35** differs from the planar geometry exhibited by Arduengo's analogous 10-P-3 planar configuration, **LI**. For instance, the molecular structure of **35** is more bent than that of its phosphorus(III) analogue **LIV** ($\sum_{\text{angles(P)}} = 296.12^\circ$), consistent with the negative charge on germanium hindering the delocalisation of the lone pair of the nitrogen atom (N1) onto the germanium centre (Ge1).

The molecular structure of **36** exhibits a bent geometry around the tin atom (Sn1) which closely resembles to its germanium(II) and phosphorus(III) analogues (**35** and **LIV**, respectively) (Figure 3.9). Table 3.4 shows bond lengths and bond angles for **36**. The Sn1–N1 bond distance (2.134 Å) is slightly longer than the sum of tin–nitrogen covalent radii (2.11 Å),¹⁰ suggesting a weak Sn–N bond. It was found that the nitrogen (N1) lone pair weakly coordinates to a potassium atom (K1⋯N1 = 2.931(4) Å) and becomes less available to donate into the empty p-orbital of Sn1.

Although the molecular structure of **35** and **36** exhibit a 8-E-3 bent configuration (E = Ge, Sn), the nitrogen lone pair of the ligand backbone can delocalise into the empty p-orbital of the group 14 elements to stabilise the planar T-shape configuration, thus giving rise to the 10-E-3 planar configuration.

Table 3.4 – Selected bond lengths and bond angles for **35** and **36**.

Bond lengths and bond angles	35 (E = Ge)	36 (E = Sn)
E–N1	1.952(2) Å	2.134(3) Å
E–O1	1.960(2) Å	2.157(3) Å
E–O2	1.904(2) Å	2.135(3) Å
O1–E–O2	106.23(10)°	123.92(13)°
N1–E–O1	84.75(9)°	76.17(13)°
N1–E–O2	85.91(10)°	76.68(13)°

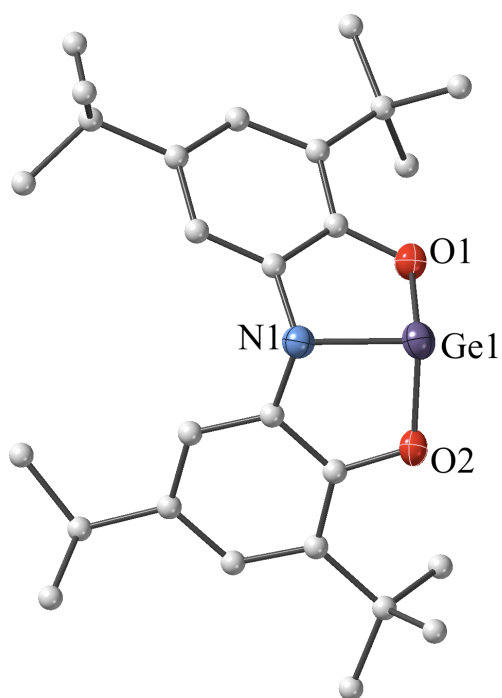


Figure 3.8: Molecular structure of [K(18-crown-6)][35]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [K(18-crown-6)]⁺ and all hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

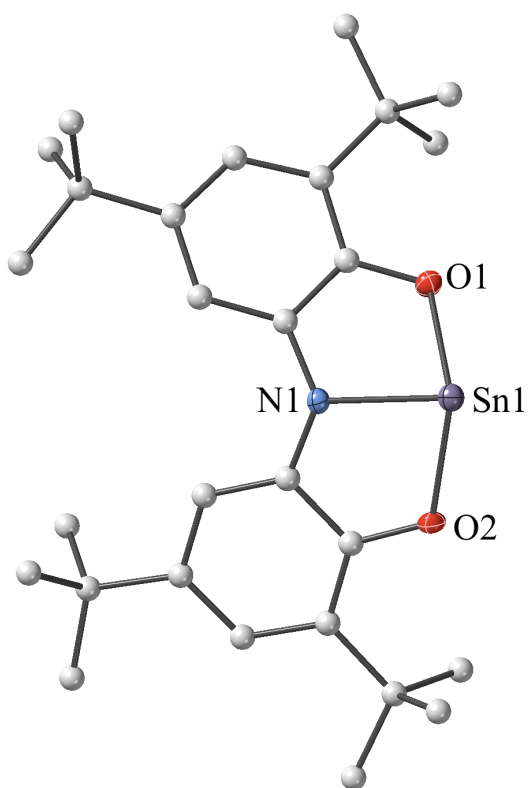


Figure 3.9: Molecular structure of [K(18-crown-6)][36]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [K(18-crown-6)]⁺ and all hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Compounds **35** and **36** are the first examples of monomeric three-coordinate Ge(II) compounds bearing a tridentate pincer ligand. Driess has previously reported on a neutral dimeric germanium(II) compound chelating by a bis(phelionate) amide ligand, **LXVI** (Figure 3.11).⁷ Driess also reported similar four-coordinate dimeric and monomeric tin(II) compound supported by the bis(phenolate) amide ligand, **LXVII** and **LX**.⁷ However, no subsequent small molecule activation was observed.

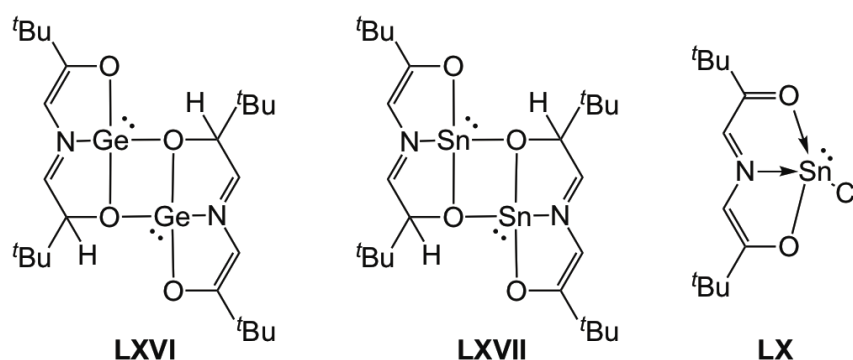


Figure 3.10: Structure of **LX**, **LXVI** and **LXVII**.⁷

3.1.5 Reactivity of **35** and **36** towards small molecule substrates

3.1.5.1 Oxidation of **35**

Compound **35** was isolated as a pale yellow solid and is stable if stored under a nitrogen gas filled glove box. Upon exposure of **35** to air, the solution acquired a more intense yellow colour accompanied by the formation of yellow crystals. Longer reaction times yielded a purple mixture, from which crystals suitable for X-ray diffraction studies could not be obtained.

The molecular structure of the aforementioned yellow crystals reveals a hexa-coordinate germanium(IV) dianion exhibiting a distorted octahedral geometry with two (ONO)³⁻ ligand moieties coordinated to the central germanium atom. The germanium species co-crystallise with two cationic [K(18-crown-6)]⁺ ions to balance the overall charge, i.e. [K(18-crown-6)]₂[**37**] (Figure 3.11). Table 3.5 shows selected bond lengths and bond angles for **37**.

The more planar configuration of (ONO)³⁻ ligand displayed by **37** (O1–Ge1–O2 for **37** = 166.71(5)° and for **35** = 110.04(10)°) is consistent with the observed shortened Ge–N bond distance of **37** (Ge1–N1 for **37** = 1.895(2) Å and for **35** = 1.967(2) Å). The Ge–O bond lengths of **35** are comparable to those seen for **37**.

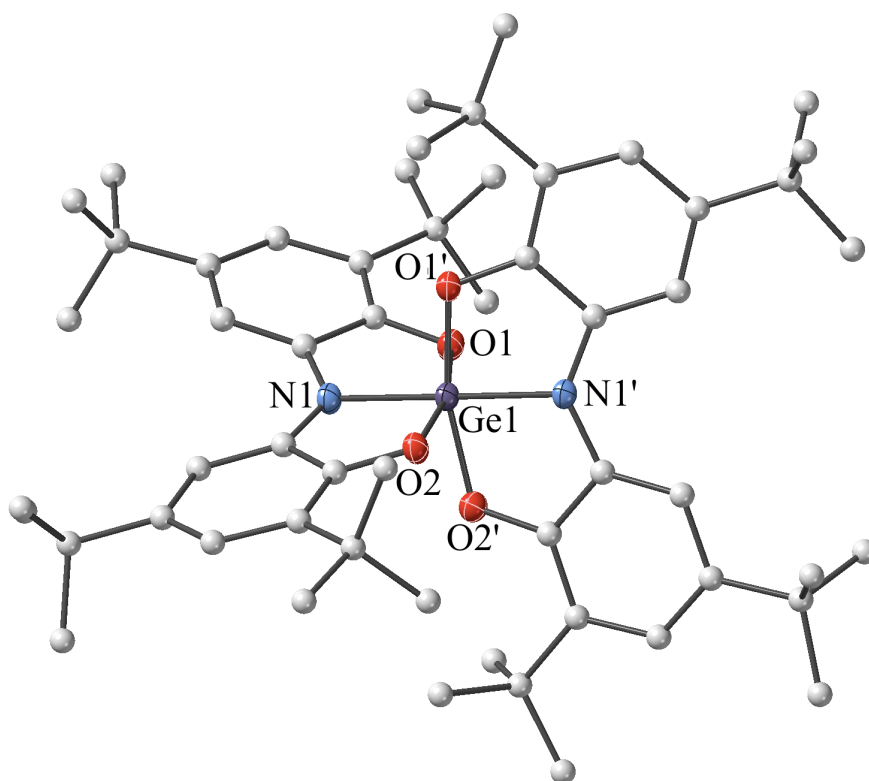


Figure 3.11: Molecular structure of [K(18-crown-6)]₂[**37**]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [K(18-crown-6)]⁺ and all hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 3.5 – Selected bond lengths and bond angles for **37**.

Bond lengths		Bond angles	
	37		37
Ge1–N1	1.895(2) Å	O1–Ge1–O2	166.71(5)°
Ge1–O1	1.921(2) Å	N1–Ge1–O1	83.06(7)°
Ge1–O2	1.931(2) Å	N1–Ge1–O1'	97.57(7)°
-	-	N1–Ge1–O2	83.65(6)°
-	-	N1–Ge1–O2'	95.71(7)°

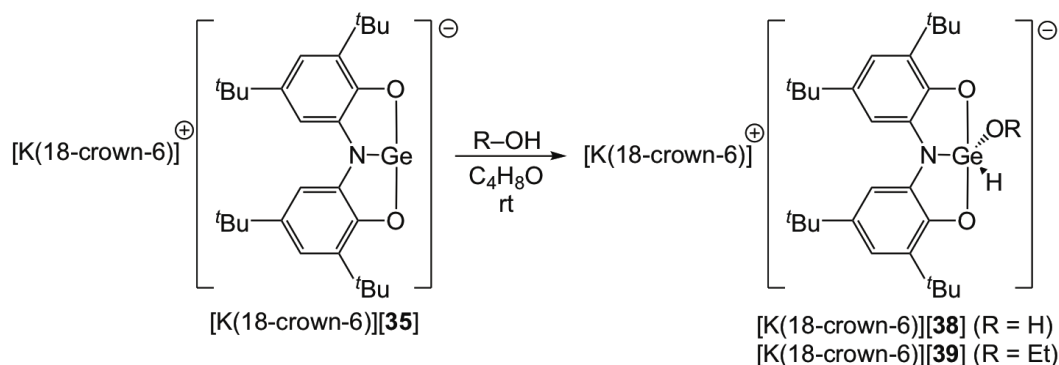
3.1.5.2 Reactivity of [K(18-crown-6)][35] and [K(18-crown-6)][36] towards dihydrogen and ammonia

No reaction was observed when $[K(18\text{-crown-6})][\mathbf{35}]$ was allowed to react with 1 atm of H_2 at room temperature or reflux temperatures. The analogous reaction with 1 atm of ammonia also resulted in no reaction, even upon heating. In both cases, when the reaction solutions were heated at reflux temperatures over three days, they turned an intense yellow colour accompanied by the formation of crystals of $[K(18\text{-crown-6})]_2[\mathbf{37}]$.

In the case of the tin analogue, [K(18-crown-6)][**36**], no reaction was observed on charging a solution of [K(18-crown-6)][**36**] with dihydrogen or ammonia.

3.1.5.3 Reactivity of [K(18-crown-6)][35] towards water and ethanol

Reaction of [K(18-crown-6)][**35**] with one molar equivalent of water or ethanol resulted in the quantitative conversion to new products [K(18-crown-6)][**38**] and [K(18-crown-6)][**39**] (Scheme 3.6).



Scheme 3.6: Reaction of [K(18-crown-6)][**35**] with water and ethanol.

In the ^1H NMR spectrum of **38**, a singlet resonance attributed to the germanium hydride was found at 7.00 ppm. The resonance corresponding to the hydroxide proton environment was not observed, consistent with exchange of the hydroxide proton in solution. A similar observation was reported when a dicationic phosphorus complex activated H_2O .¹¹ The resonances attributed to the aromatic protons and *tert*-butyl protons observed in ^1H NMR

spectrum of **38** are similar to those observed by **35**. The ^1H NMR spectrum of **39** was comparable to that of **38** with an addition of the ethyl proton resonances.

Crystals of **38** and **39** suitable for single crystal X-ray diffraction were grown from a concentrated toluene solution. The molecular structures of **38** and **39** exhibit a distorted trigonal bipyramidal about the germanium(IV) centre with the germanium hydride and hydroxide/ alkoxide substituent occupying the equatorial positions (Figures 3.12 and 3.13). All of the Ge–N and Ge–O bonds of **38** are shorter than those of the starting material **35** due to the increased oxidation state of germanium. The $(\text{ONO})^{3-}$ ligand moiety adopts a planar conformation, as observed for the reported water activation product of the relevant isoelectronic phosphorus compound (**LIVb**) (O1-Ge1-O2 for **38** = $167.56(10)^\circ$ and for **35** = $106.23(10)^\circ$). The axial Ge–O1 and Ge–O2 bonds ($1.896(2)$ Å and $1.901(2)$ Å) are longer than the equatorial Ge–O3 bond ($1.788(3)$ Å). In the case of the structure of **39**, the bond lengths and bond angles of **39** are largely similar to those of **38**.

Table 3.6 – Selected bond lengths and bond angles for **38** and **39**.

Bond lengths and Bond angles	38	39
Ge1–N1	$1.881(2)$ Å	$1.897(2)$ Å
Ge1–O1	$1.896(2)$ Å	$1.924(2)$ Å
Ge1–O2	$1.901(2)$ Å	$1.935(2)$ Å
Ge1–O3	$1.788(3)$ Å	$1.798(3)$ Å
Ge1–H1	$1.53(5)$ Å	$1.69(9)$ Å
O1–Ge1–O2	$167.56(10)^\circ$	$166.47(13)^\circ$
N1–Ge1–O1	$84.26(11)^\circ$	$83.57(13)^\circ$
N1–Ge1–O2	$84.42(11)^\circ$	$82.91(14)^\circ$
N1–Ge1–O3	$123.18(15)^\circ$	$123.54(14)^\circ$
N1–Ge1–H1	$143(3)^\circ$	$131(3)^\circ$

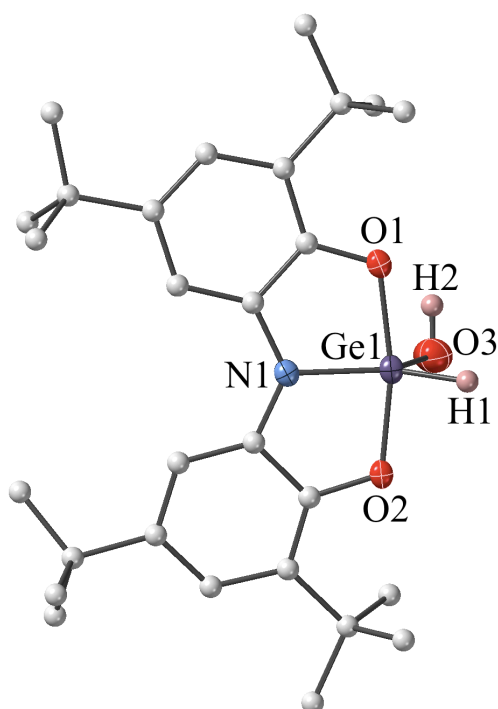


Figure 3.12: Molecular structure of [K(18-crown-6)][38]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [K(18-crown-6)]⁺ and all hydrogen atoms, except H1 and H2, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

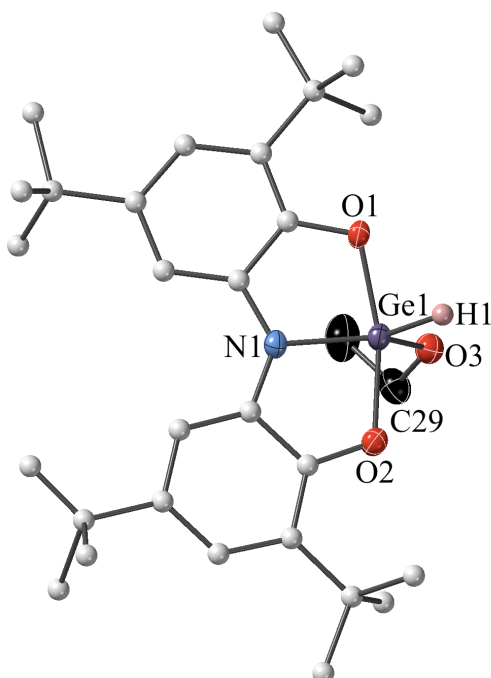
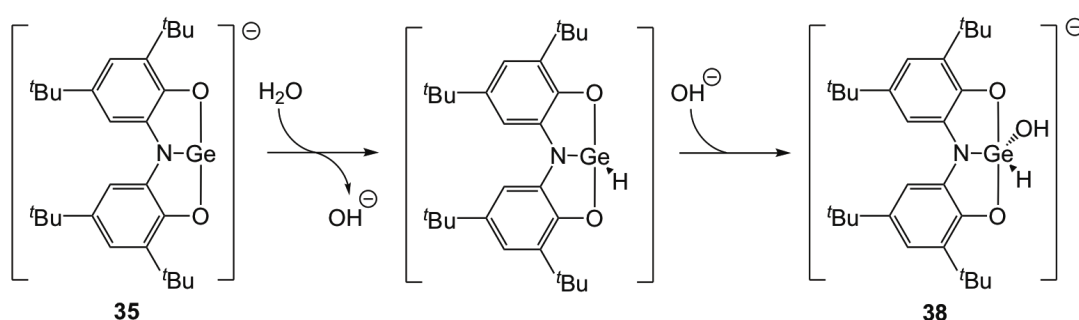


Figure 3.13: Molecular structure of [K(18-crown-6)][39]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [K(18-crown-6)]⁺ and all hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

[K(18-crown-6)][**35**] underwent facile addition with water but no reaction with ammonia, while its phosphorus(III) analogue, **LIV**, underwent addition with both water and ammonia. This observation suggests that the negative charge on the germanium centre of **35** prevents the association of the substrate. Whereas, the water addition was initiated by deprotonation of water (i.e. nucleophilic pathway), followed by addition of the hydroxide substituent to afford [K(18-crown-6)][**38**] (Scheme 3.7). The diminished reactivity with ammonia may be attributed to the lower acidity of NH₃ compared to H₂O.



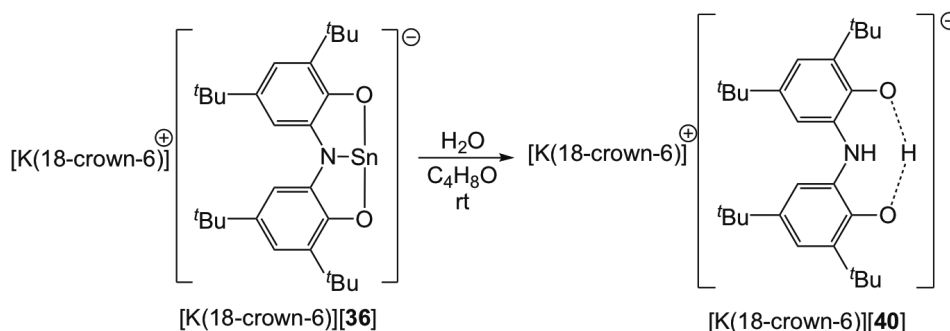
Scheme 3.7: Proposed mechanism of the hydrolysis of **35**.

There are only a few transition-metal complexes examples capable of stoichiometric water activation.¹² Although small molecule substrate activation using main-group complexes has been studied extensively, there are only three examples, including **LIV**, that are capable of performing such activation under mild conditions or non-equimolar loadings of water.^{11,13} In the case of the main-group geometry constrained complexes, Arduengo has reported that reaction of **LI** with water converted into a free ligand and phosphorous acid.¹ Additionally, no water activation has been reported for **LII–LIII**.

3.1.5.4 Reactivity of [K(18-crown-6)][**36**] towards water and ethanol

While [K(18-crown-6)][**35**] has been shown to react with water to give [K(18-crown-6)][**38**], the tin analogue, [K(18-crown-6)][**36**], underwent metal displacement with water to afford [K(18-crown-6)][**40**] (Scheme 3.8). Upon addition of one molar equivalent of water to a solution of [K(18-crown-6)][**36**], the solution turned from yellow to colourless,

accompanied by the precipitation of grey solid, consistent with elemental tin. The reaction mixture was monitored by ^1H NMR spectroscopy which showed that the reaction mixtures contained multiple products. Colourless crystals suitable for single crystal X-ray crystallography were grown from a concentrated toluene solution.



Scheme 3.8: Reaction of $[\text{K}(18\text{-crown-6})][\mathbf{36}]$ with H_2O .

As discussed in Chapter 3.14, the molecular structure of **36** indicates that the tin atom does not fit into the binding site of the ligand and is being pushed away. The molecular structure of **40** provides evidence for the displacement of the tin metal, upon addition of water (Figure 3.14). A proton (H_2) is located between the ligand O_1 and O_2 atoms implying that H_2 is shuttling between the O_1 and O_2 . The pyramidalised nitrogen (N_2) is bonded to a hydrogen atom (H_1) and exhibits an interaction with the sequestered potassium cation (K_1). Table 3.7 shows selected bond lengths and bond angles for **40**. There is no interaction between the N_2 and the H_2 atom as they are 2.437 Å apart.

Table 3.7 – Selected bond lengths and bond angles for **40**.

Bond lengths		Bond angles	
	40		40
H2–O1	1.17(4) Å	O1–H2–O2	174.71(18)°
H2–O2	1.29(4) Å	K1–N1–H1	84.5(18)°
N1–H1	0.90(3) Å	K1–N1–C6	116.86(12)°
N1–K1	2.851(2) Å	K1–N1–C20	116.98(11)°

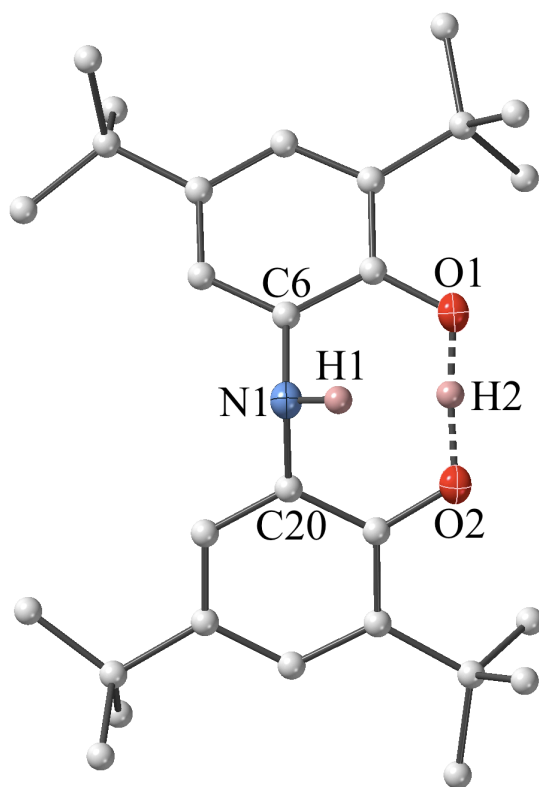


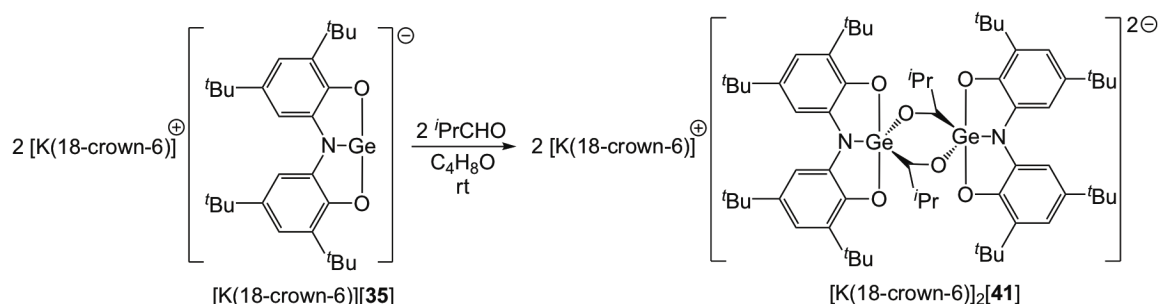
Figure 3.14: Molecular structure of [K(18-crown-6)][**40**]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [K(18-crown-6)]⁺ and all hydrogen atoms, except H1 and H2, are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

No reaction was observed when the tin analogue, [K(18-crown-6)][**36**], was reacted with ethanol even at elevated temperatures. This diminished reactivity is in line with +4 oxidation state being less stable relative to the +2 oxidation state for tin.

3.1.5.5 Reactivity of [K(18-crown-6)][**35**] towards *iso*-butyraldehyde

The activation of water and ethanol by [K(18-crown-6)][**35**] is proposed to take place via a nucleophilic pathway driven by the strongly nucleophilic germanium atom of **35**. The nucleophilicity of **35** was further probed. Reaction of [K(18-crown-6)][**35**] with one molar equivalent of *iso*-butyraldehyde resulted in rapid formation of [K(18-crown-6)]₂[**41**] (Scheme 3.11). **35** acts as a nucleophile and attacks the carbon atom of the of *iso*-

butyraldehyde substrate, which subsequently dimerises through the oxygen and carbon atoms to give the dimeric **41**.



Scheme 3.11: Reaction of [K(18-crown-6)][**35**] with *iso*-butyraldehyde.

In the ^1H NMR spectrum of **41**, two resonances corresponding to the *iso*-propyl substituent protons are found at 3.37, 0.89 and 0.82 ppm. The resonances attributed to the aromatic protons and *tert*-butyl protons are similar to those observed for species **35**.

Crystals of **41** were grown as colourless blocks from a concentrated toluene solution at room temperature. The molecular structure of **41** displays a trigonal bipyramidal geometry around the germanium atom (Ge1) in which the O1 and O2 atoms occupy the axial positions and the N1, O3 and C29 atom occupy the equatorial positions (Figure 3.15). The structure of **41** is a dimer with the C29 and O3 atoms forming a six-membered heterocycle. Two cationic sequestered potassium ions weakly interact with the O3 atom to balance the overall charge. Table 3.8 shows the selected bond lengths and bond angles of **41**. The (ONO) $^{3-}$ ligand moiety adopts a relatively planar configuration (O1–Ge1–O2 = 163.98(6) $^\circ$) with a short Ge1–N1 bond (1.896(2) Å). The axial Ge–O1 and Ge–O2 bonds (1.941(2) Å and 1.946(2) Å) are longer than the equatorial Ge–O3 bond (1.818(2) Å), consistent with bond pair-bond pair repulsion between the axial and equatorial bonds.

Unsurprisingly, the reaction with the tin analogue, [K(18-crown-6)][**36**], did not give any reaction even at elevated temperatures.

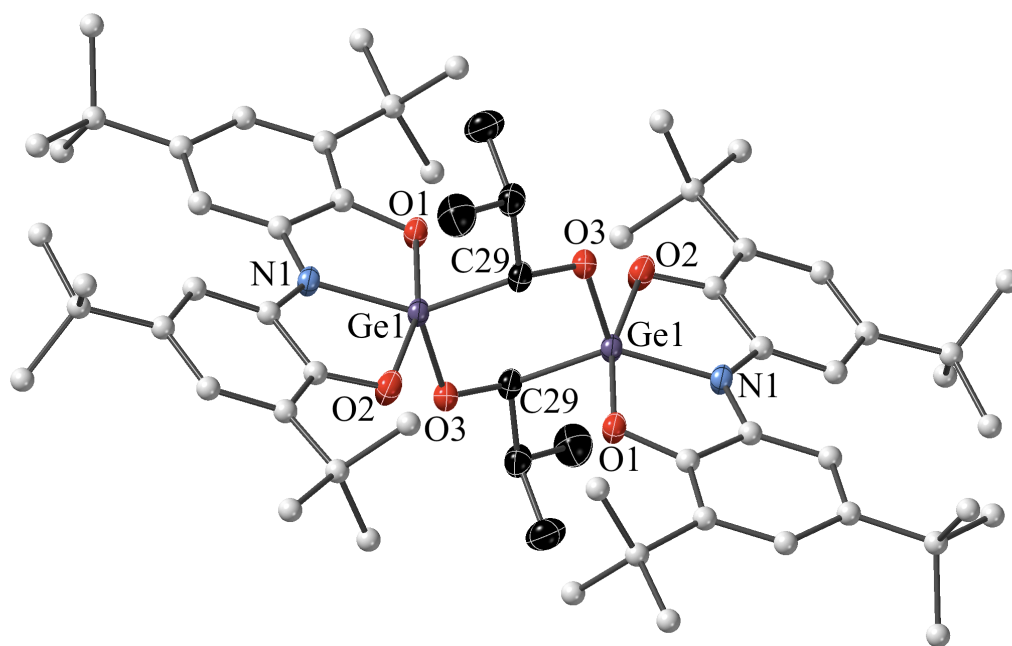


Figure 3.15: Molecular structure of $[K(18\text{-crown-6})]_2[41]$. Anisotropic displacement ellipsoids pictured are set at 50% probability. $[K(18\text{-crown-6})]^+$ and all hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 3.8 – Selected bond lengths and bond angles for **41**.

Bond lengths	41	Bond angles	41
Ge1–N1	1.896(2) Å	O1–Ge1–O2	163.98(6)°
Ge1–O1	1.941(2) Å	N1–Ge1–O1	82.25(6)°
Ge1–O2	1.946(2) Å	N1–Ge1–O2	82.01(6)°
Ge1–O3	1.818(2) Å	N1–Ge1–O3	120.21(6)°
Ge1–C29	1.990(2) Å	N1–Ge1–C29	133.23(7)°

3.1.5.6 Reactivity of $[K(18\text{-crown-6})][35]$ towards charged electrophiles

The aforementioned reactivity of **35** prompted us to explore its reactivity towards charged electrophiles in an attempt to investigate whether the electrophile attacks the negatively charged germanium atom or the nitrogen lone pair located at the ligand backbone of **35**.

With this in mind, the $[K(18\text{-crown-6})][35]$ salt was allowed to react with one molar equivalent of MeOTf was investigated. The reaction was monitored by ^1H NMR spectroscopy and revealed formation of two products in a 2:1 ratio. The reaction was

repeated at low temperature ($-78\text{ }^{\circ}\text{C}$), however the ^1H NMR spectrum still displayed two products with an identical ratio.

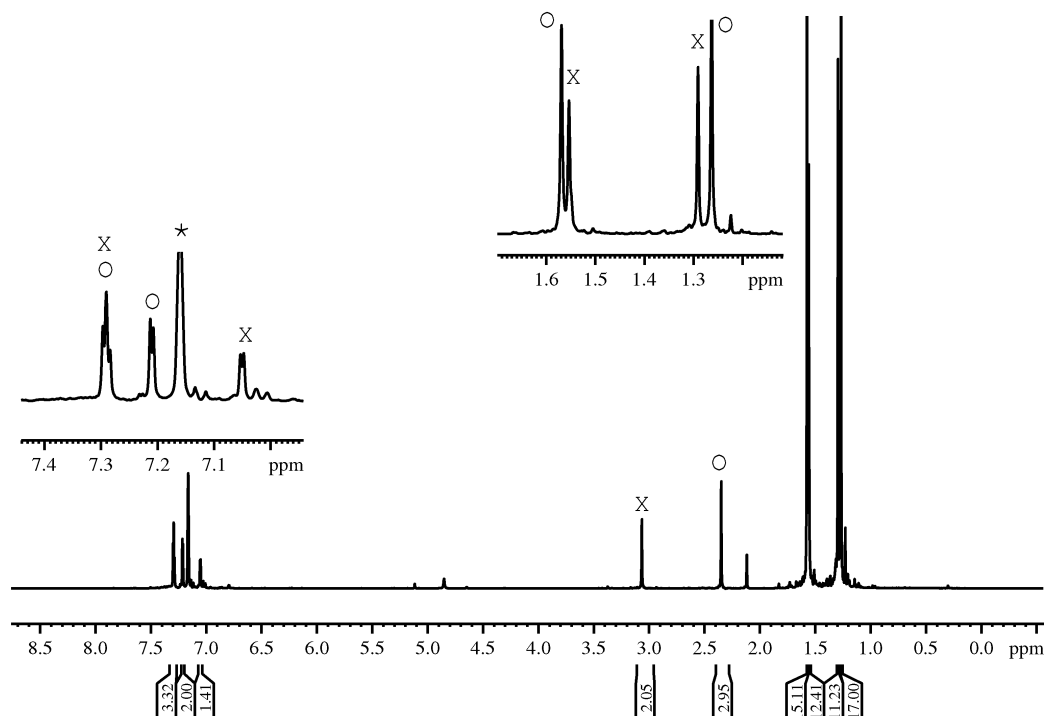
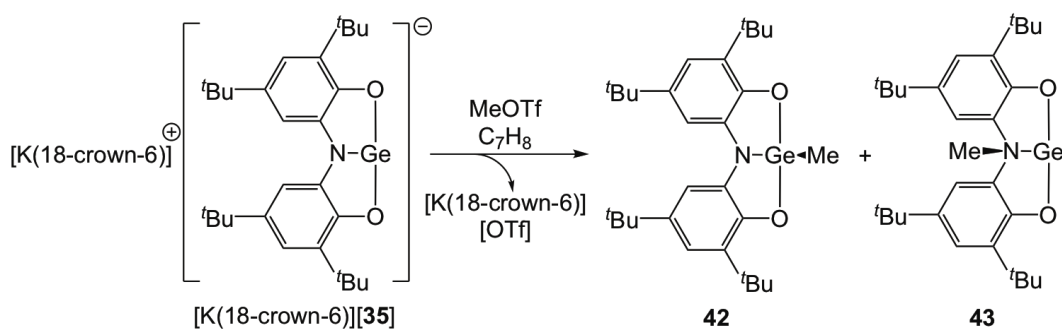


Figure 3.16: The ^1H NMR spectrum of the reaction mixture of $[\text{K}(\text{18-crown-6})][\text{35}]$ and MeOTf (* donates to C_6D_6 solvent, O and X donate to two sets of product).

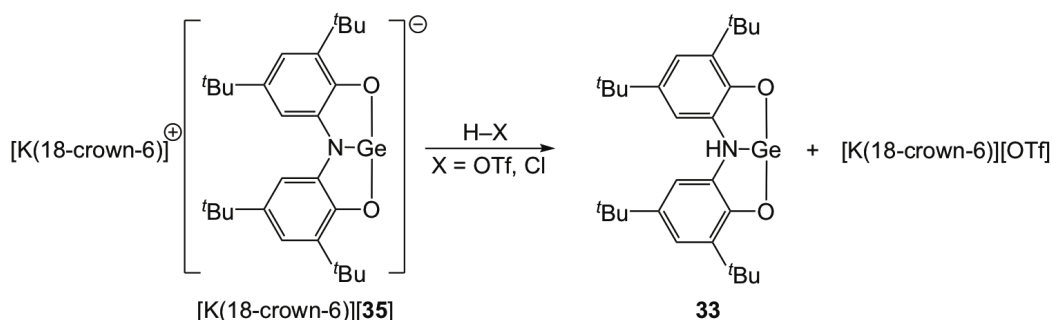
Figure 3.16 shows the ^1H NMR spectrum of the reaction mixture, the major product shows two doublets at 7.29 and 7.21 ppm and two singlets at 1.57 and 1.27 ppm. Later attributed to the aromatic protons and the *tert*-butyl protons, respectively. The methyl protons from the electrophile show at 2.35 ppm as a singlet. In the case of the minor product, two doublets at 7.29 and 7.05 ppm and two singlets at 1.56 and 1.29 ppm attributed to the aromatic protons and the *tert*-butyl protons, respectively, were also found. The spectrum also shows a singlet integrating to three protons at 3.06 ppm corresponding to the methyl protons.



Scheme 3.12: Reaction of $[K(18\text{-crown-}6)][35]$ with MeOTf.

We suspect that both the negatively charged germanium centre and the nitrogen lone pair at the ligand backbone of **35** are prone to attack MeOTf to afford **42** and **43** (Scheme 3.12). This observation is in line with the reactivity observed for germyl anionic compounds (R_3Ge^-) towards charged electrophiles.¹⁴

It is interesting to note that reactions of $[K(18\text{-crown-}6)][35]$ with triflic acid (HOTf) and hydrogen chloride resulted in protonation of the nitrogen atom at the ligand backbone to exclusively yield **33** and elimination of the $[K(18\text{-crown-}6)][OTf]$ salt (Scheme 3.13). The reactivity of $[K(18\text{-crown-}6)][35]$ with HOTf is comparable to the analogous reaction of **LIV** with HOTf which gave rise to a $[(H)P(ONO)][OTf]$ complex (see details in Chapter 4).



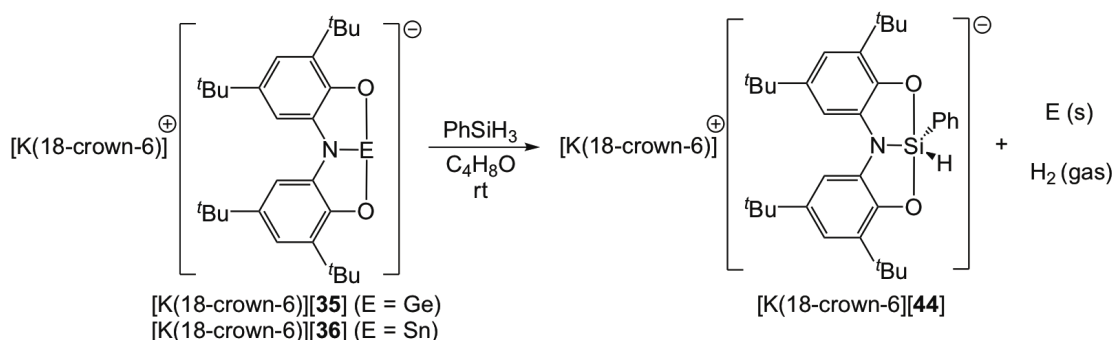
Scheme 3.13: Reactions of $[K(18\text{-crown-}6)][35]$ with HOTf and HCl.

3.1.5.7 Reactivity of $[K(18\text{-crown-}6)][35]$ and $[K(18\text{-crown-}6)][36]$ towards phenylsilane

As $[K(18\text{-crown-}6)][35]$ is capable of activating protic molecules such as water and ethanol, its reactivity towards small molecule substrates possessing a hydridic hydrogen atoms was

probed, such as phenylsilane. It is noteworthy that no reaction is observed in the equivalent reaction between the phosphorus analogue of **35**, **LIV**, and phenylsilane.¹⁵

When a solution of [K(18-crown-6)][**35**] is charged with one molar equivalent of phenylsilane, the reaction solution immediately turned from pale yellow to colourless accompanied by the evolution of gas and the formation of a grey precipitate. This observation is in line with the [K(18-crown-6)][**35**] salt having undergone transmetallation between germanium to silicon to afford [K(18-crown-6)][**44**] in a moderate yield (55%), together with elimination of elemental germanium and dihydrogen gas (Scheme 3.14). The analogous reaction with [K(18-crown-6)][**36**] also rapidly gave [K(18-crown-6)][**44**] with an improved yield (83%). [K(18-crown-6)][**36**] favours the transmetallation as the molecular structure of **36** suggested that the tin atom does not fit into the binding site of the ligand.



Scheme 3.14: Reaction of [K(18-crown-6)][**35**] and [K(18-crown-6)][**36**] with phenylsilane.

The ²⁹Si NMR spectrum of **44** displays a diagnostic singlet at –85.6 ppm. Whereas, in the ¹H NMR spectrum in *d*₈-THF, the resonance attributed to silicon hydride was observed at 6.13 ppm. It also shows a set of resonances in the range of 7.84–6.98 ppm corresponding to the phenyl substituent protons. Its aromatic protons and *tert*-butyl protons resonances were comparable to those observed in **35**.

Crystals of **44** suitable for single crystal X-ray crystallography were grown by slow diffusion of hexane into a concentrated THF solution. However, the crystals were weakly

diffracting, therefore only low angle data was collected. Given the low quality of this data, the atoms in the molecular structure of **44** are pictured as spheres of arbitrary radius (Figure 3.17). The molecular structure of **44** exhibits a trigonal bipyramidal geometry around the silicon(IV) atom (Si1). The (ONO)³⁻ ligand moiety of **44** adopts a planar conformation with O1 and O2 occupying the axial positions, while N1, H1 and O3 are occupying the equatorial sites.

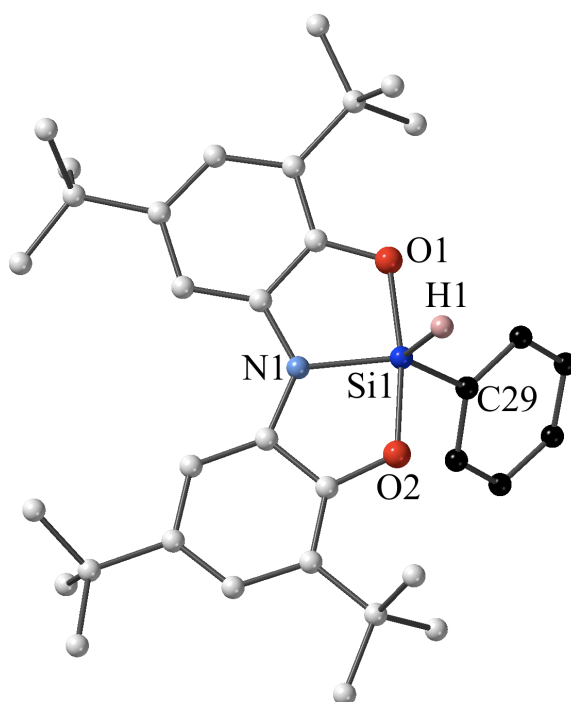


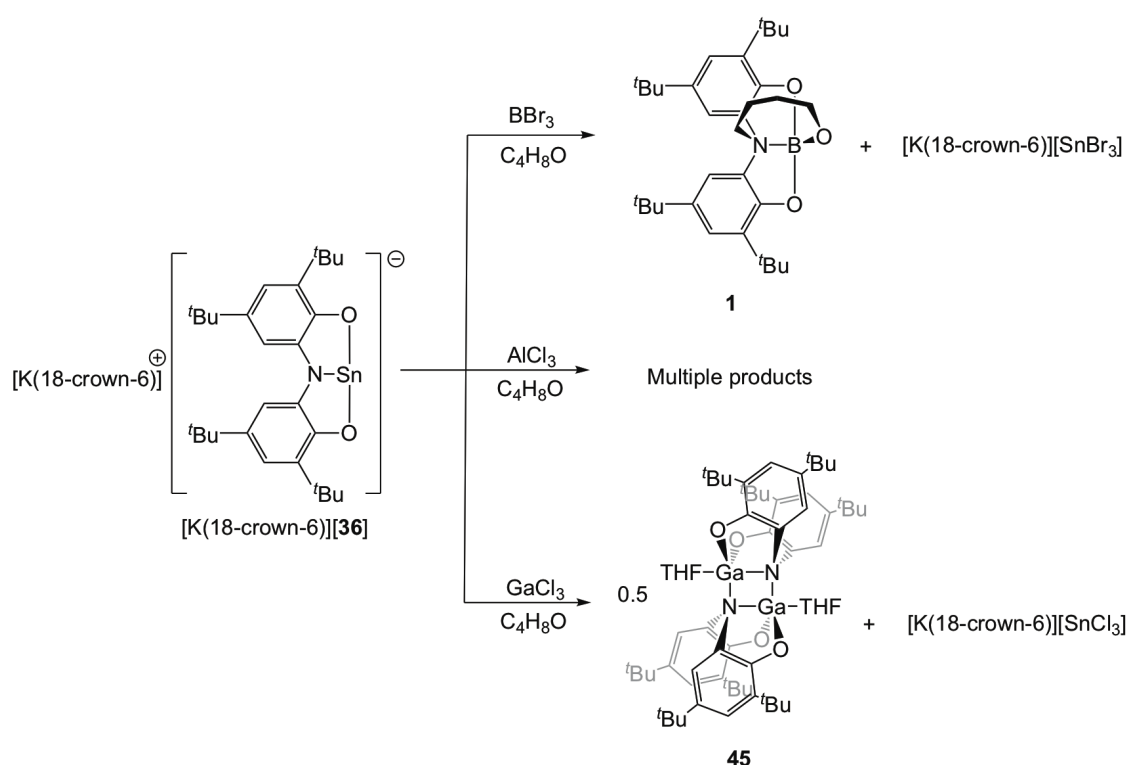
Figure 3.17: Molecular structure of [K(18-crown-6)][**44**]. [K(18-crown-6)]⁺ and all hydrogen atoms are omitted for clarity. All atoms are pictured as spheres of arbitrary radius.

3.1.5.8 Reactivity of [K(18-crown-6)][**36**] with group 13 halides

Encouraged by the transmetallation observed with [K(18-crown-6)][**36**], further investigated reactivity of [K(18-crown-6)][**36**] towards group 13 halides in attempt of accessing group 13 compounds bearing the (ONO)³⁻ ligand was attempted.

Scheme 3.15 depicts the reactivity of [K(18-crown-6)][**36**] towards group 13 halides. Addition of boron tribromide to a THF solution of [K(18-crown-6)][**36**] resulted in conversion to the THF ring-opened boron complex, **1**, which was described in Section 2.2.1,

and elimination of $[\text{K}(18\text{-crown-6})][\text{SnBr}_3]$. Furthermore, reaction of aluminium chloride to $[\text{K}(18\text{-crown-6})][\mathbf{36}]$ in THF was monitored by ^1H NMR spectroscopy and revealed that the reaction mixture contained multiple inseparable products. In the case of gallium, addition of GaCl_3 into a THF solution of $[\text{K}(18\text{-crown-6})][\mathbf{36}]$ resulted in a colourless solution, from which colourless crystals were grown. Single crystal X-ray diffraction studies determined that the colourless crystals are the dimetallic compound $\text{Ga}(\text{ONO})\cdot\text{THF}$ (**45**) and $[\text{K}(18\text{-crown-6})][\text{SnCl}_3]$.



Scheme 3.15: Reactions of $[\text{K}(18\text{-crown-6})][\mathbf{36}]$ with group 13 halides.

The molecular structure of **45** shows a dimeric species with a distorted trigonal bipyramidal geometry around each gallium atom (Figure 3.18). The $\text{Ga}(\text{ONO})\cdot\text{THF}$ moiety dimerise through the formation of $\text{Ga}-\text{N}$ bond affording a four-membered heterocyclic ring. Table 3.9 shows selected bond lengths and bond angles for **45**. Inside the heterocyclic Ga_2N_2 ring, the $\text{Ga}-\text{N}'$ bond ($2.093(2)$ Å) is longer than the $\text{Ga}-\text{N}$ bond ($1.959(2)$ Å) due to dative covalent interaction from nitrogen lone pair to the electrophilic gallium atom. The

molecular structure of **45** resembles that of its aluminium analogue, **17**, which is described in detail in section 2.3.3.1. The transmetallation of [K(18-crown-6)][**36**] with gallium chloride allowed access to dimeric Ga(ONO)·THF complexes (**45**) which are inaccessible by the reactions describe in Chapter 2.

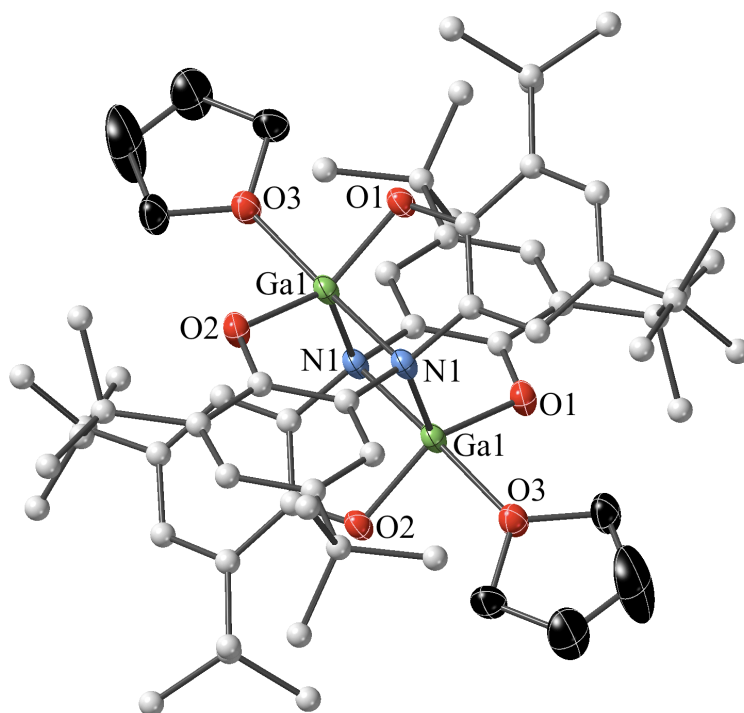


Figure 3.18: Molecular structure of **45**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 3.9 – Selected bond lengths and bond angles for **45**.

Bond lengths	45	Bond angles	45
Ga1–N1	1.959(2) Å	O1–Ga1–O2	130.96(6)°
Ga1–O1	1.842(1) Å	N1–Ga1–O1	113.17(5)°
Ga1–O2	1.839(2) Å	N1–Ga1–O2	115.17(5)°
Ga1–O3	2.037(2) Å	N1–Ga1–O3	99.95(6)°

3.1.6 Conclusions

The isolation of the E(II) and E(IV) complexes bearing a tridentate pincer ligand is reported. Reactions of H₃(ONO) with tetrel(IV) halides allowed us to access hexa-coordinate E{ON(H)O}₂ (E = Si, Ge and Sn) complexes (**29–31**). Anionic species, [E(ONO)][–] (E = Ge,

Sn) can be prepared via a two-step process, first by the synthesis of neutral compounds, E{ON(H)O} (**33** and **34**), followed by deprotonation using benzyl potassium in the presence of 18-crown-6 to afford [K(18-crown-6)][E(ONO)] ([K(18-crown-6)][**35**] and [K(18-crown-6)][**36**]). It was shown that the molecular structure of **35** closely resembles that of its phosphorus(III) analogue, **LIV** and similarly underwent facile addition of water and ethanol to form trigonal bipyramidal germanium(IV) complexes, [K(18-crown-6)][**38**] and [K(18-crown-6)][**40**], respectively. The nucleophilicity of **35** was exploited in the reaction with *iso*-butyraldehyde to give [K(18-crown-6)]₂[**41**]. [K(18-crown-6)][**36**] can easily be protonated to give [K(18-crown-6)][**39**]. It was also shown that [K(18-crown-6)][**36**] undergoes efficient transelementation reactions with phenylsilane which gave a five-coordinate Si(IV) complex ([K(18-crown-6)][**44**]). Transmetallation of [K(18-crown-6)][**36**] with gallium chloride allows us to access the dimetallic Ga(ONO)·THF complex (**45**), which was not accessible using the synthetic protocols described in Chapter 2.

3.2 Complexes of group 14 elements bearing bidentate-xanthene-4,5-diamine ligands

3.2.1 Project aims

In collaboration with a Part II student, Ms. Jessica Whitmore, we have investigated the synthesis and characterisation of novel bidentate complexes of E(II) (E = Ge, Sn) using rigid bidentate pincer ligands, (^{Cy}NON)²⁻ or (^{Mes}NON)²⁻. The xanthene based ligand system was selected because: 1) its ligand framework is relatively geometrically rigid forcing a constrained geometry around the group 14 element; 2) the oxygen atom of the xanthene ligand backbone should promote stabilisation of the planar structure as observed previously for the (ONO)³⁻ ligand.

The resulting geometry constrained E(NON) complexes are isoelectronic with Arduengo's 10-P-3 system (i.e. they both feature a three-coordinate group 14 centre with ten valence

electrons). Also, we want to exploit the Ge(II)/Ge(IV) and Sn(II)/Sn(IV) redox couples which are shown to be accessible allowing us, in principle, to activate small molecules via oxidative addition.

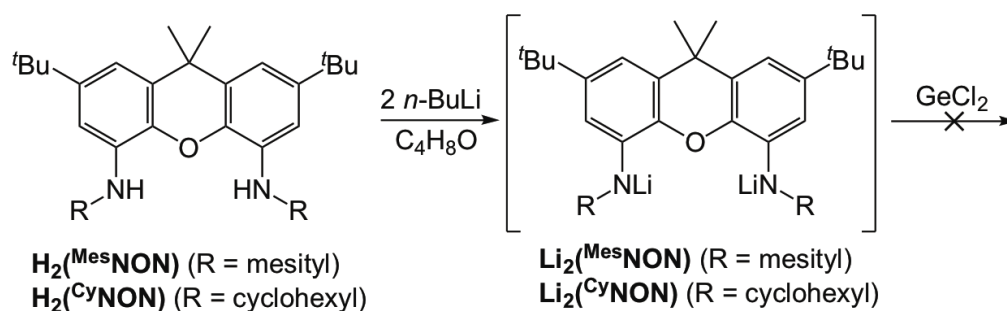
3.2.2 Synthesis of the E(NON) complexes

3.2.2.1 Using triethylamine for ligand deprotonation

Adopting the synthetic method for preparing **LIV**, the preparation of Ge(^{Mes}NON) compound by reacting H₂(^{Mes}NON) with GeCl₂·dioxane in the presence of NEt₃ was attempted. The reaction mixture was monitored by ¹H NMR spectroscopy and showed no change even at elevated temperatures. We postulated that NEt₃ may not be sufficiently basic to deprotonate H₂(^{Mes}NON), therefore stronger bases were investigated. Therefore, this observation led us to consider using a stronger base to deprotonate the amine protons of the xanthene ligand system.

3.2.2.2 Using *n*-BuLi for ligand deprotonation

Addition of *n*-BuLi to a solution of H₂(^{Mes}NON) should afford the corresponding lithiated salt, Li₂(^{Mes}NON), which can be subsequently reacted with germanium(II) or tin(II) chlorides (Scheme 3.16).



Scheme 3.16: Deprotonation of H₂(^{Mes}NON) and H₂(^{Cy}NON) using *n*-BuLi.

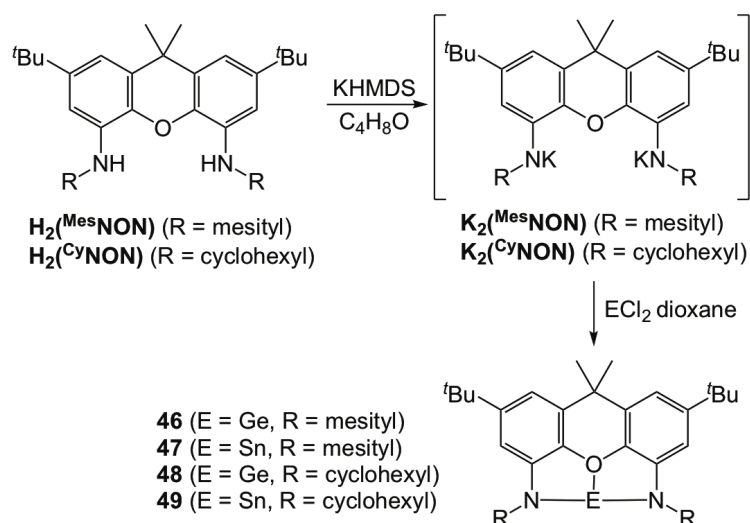
Upon addition of *n*-BuLi to H₂(^{Mes}NON) in a *d*₈-THF solution at −78 °C, the ¹H NMR spectrum of the reaction solution displays eight resonances in a range between 5.61 and

6.64 ppm, implying a loss of symmetry of the ligand. The asymmetric aromatic environment arises from deprotonation of the methyl substituent of the ligand backbone as well as one of the amine protons. The observation implies that *n*-BuLi is too strong of a base and results in excessive deprotonation.

3.2.2.3 Using KHMDS for ligand deprotonation

Potassium bis(trimethylsilyl)amide (KHMDS), was employed, as an alternative base in order to afford $K_2(NON)$, which was subsequently reacted with E(II) chlorides to form the targeted compound E(NON).

Two molar equivalents of KHMDS were added to a THF solution of $H_2(^{Mes}NON)$ at room temperature. The reaction was monitored by 1H NMR spectroscopy and revealed that the resonances attributed to the N–H protons of $H_2(^{Mes}NON)$ were absent, implying successful generation of a potassium salt, $K_2(^{Mes}NON)$. Subsequently, $GeCl_2 \cdot dioxane$ was added to the reaction mixture *in-situ* resulting in conversion to the $Ge(^{Mes}NON)$ complexes, **46** (Scheme 3.16). The reaction was repeated with $SnCl_2 \cdot dioxane$ to afford the tin analogue, $Sn(^{Mes}NON)$ (**47**). Employing the same synthetic method, with the cyclohexyl functionalised ligand, the analogous germanium (**48**) and tin (**49**) compounds were also prepared (Scheme 3.17).



Scheme 3.17: Synthesis of **46–49** using KHMDS with $H_2(^{Mes}NON)$ and $H_2(^{Cy}NON)$.

It is noteworthy that **46–49** are extremely moisture sensitive, therefore all manipulations were carried out inside the glovebox and the Schlenk line manipulation was used only to remove solvents under dynamic vacuum.

3.2.3 Characterisation of **46–49**

3.2.3.1 Characterisation of **46** and **47**

Compound **46** was characterised by ^1H NMR spectroscopy in C_6D_6 revealing two doublets at 6.83 and 6.39 ppm and two singlets at 1.75 and 1.18 ppm attributed to the aromatic protons and the methyl protons from the xanthene ligand, respectively. It also displays a set of resonances at 6.89, 2.24 and 2.16 ppm corresponding to the protons on the mesityl group. The ^1H NMR spectrum of **47** resembles to that of **46**. In addition, the ^{119}Sn NMR spectrum of **47** shows a diagnostic singlet at -189.4 ppm.

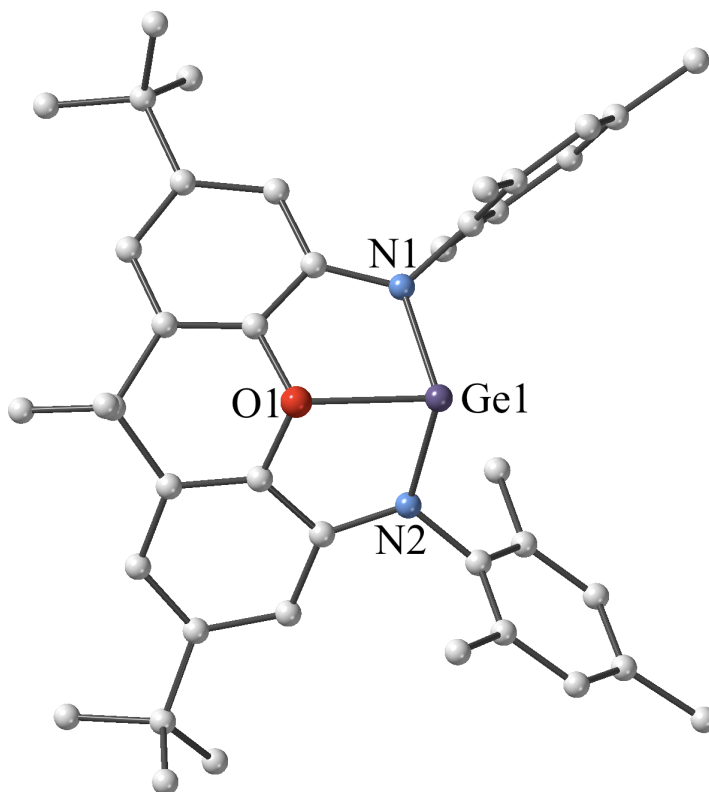


Figure 3.20: Molecular structure of **46**. All hydrogen atoms are omitted for clarity. All atoms are pictured as spheres of arbitrary radii.

Crystals of **46** suitable for single crystal X-ray diffraction were grown from a concentrated hexane solution at room temperature. Unfortunately, due to the high R value of the data set, the data obtained are not suitable for a statistically significant discussion of bond lengths and bond angles. The molecular structure of **46** displays a distorted trigonal pyramidal geometry around the germanium(II) atom (Ge1), with a pyramidalised oxygen atom (O1) (Figure 3.20). The germanium centre (Ge1) is being pushed away from the (NON)²⁻ ligand binding site which may destabilise the Ge1 atom.

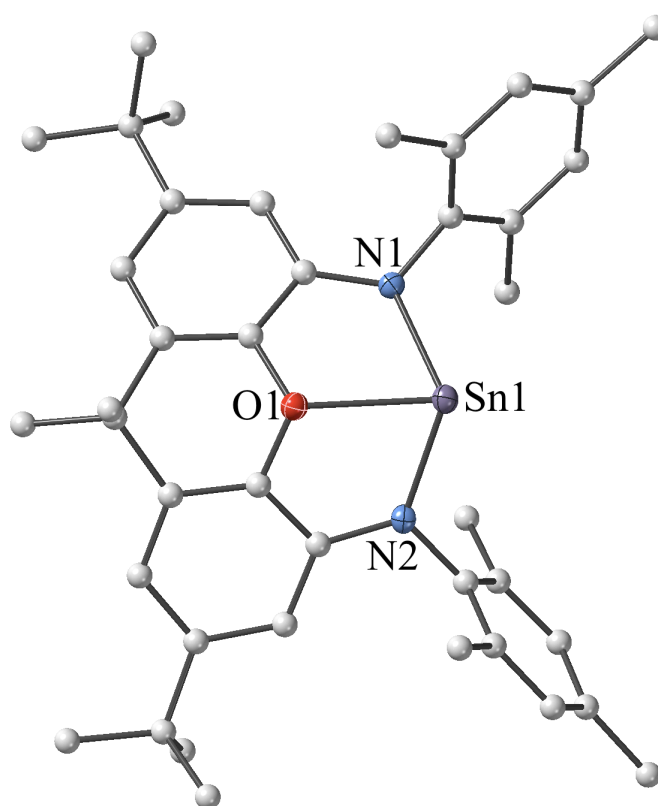


Figure 3.21: Molecular structure of **47**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand, which O1, N1 and N2, are pictured as spheres of arbitrary radius.

Crystals of **47** suitable for single crystal X-ray diffraction were grown from a concentrated hexane solution at room temperature. The molecular structure of **47** displays a distorted pyramidal geometry around the tin(II) centre (Sn1), with a N1–Sn1–N2 bond angle of 116.22(9)° as well as acute N1–Sn1–O angles (70.70(8)° for O1 and 71.07(9)° for O2),

leading to a sum of bond angles of 257.99° (Figure 3.21 and Table 3.10). The structure of **47** is related to the 8-Pn-3 bent configuration of Arduengo's constrained geometry pnictogen systems. The lone pair of electrons on Sn1 is stereochemically active. The oxygen atom (O1) is also pyramidalised with the sum of bond angles of 341.28° around the O1 atom (C5–O1–C6 = 111.3(2)°; C5–O1–Sn1 = 115.14(16)° and C6–O1–Sn1 = 114.84(17)°).

Table 3.10 – Selected bond lengths and bond angles for **47**.

Bond lengths	47	Bond angles	47
Sn1–O1	2.353(2) Å	N1–Sn1–N2	116.22(9)°
Sn1–N1	2.144(2) Å	O1–Sn1–N1	70.70(8)°
Sn1–N2	2.144(3) Å	O1–Sn1–N2	71.07(9)°

The Sn1–N bond lengths of **47** (2.144(2)° Å for N1 and 2.144(3) Å for N2) are consistent with typical Sn–N single bonds (2.15 Å), precluding the delocalisation of the nitrogen lone pair towards the tin atom. The Sn1–O1 bond length (2.353(2) Å) is much longer than the sum of tin-oxygen covalent radii (1.86 Å).¹⁰ Accompanied by the acute N–Sn–O bond angles (70.70(8)° and 71.07(9)°), these observations are consistent with the tin atom weakly coordinating in the binding site of the ligand. Given these results, transmetallation and protonation reactions with **36** were undertaken.

3.2.3.2 Characterisation of **48** and **49**

Compound **48** was characterised by ¹H NMR spectroscopy in C₆D₆ and revealed its NMR spectrum consistent with compounds **46** and **47**. Despite dissolving a compositionally pure sample of **48**, H₂(^{Cy}NON) could be observed as an impurity, highlighting the highly hydroscopic nature of **48**. The elemental analysis of crystalline **48** confirms the compositional purity of this product (elemental analysis calc. (%) for C₃₅H₅₀GeN₂O: C 71.56, H 8.58, N 4.77, found: C 70.57, H 8.34, N 4.72). Crystals of **48** suitable for single crystal X-ray diffraction could not be obtained despite multiple attempts.

The ^1H NMR spectrum of **49** in C_6D_6 displays similar resonances as those observed for **48**, along with a diagnostic ^{119}Sn NMR signal at 112.6 ppm. Interestingly, this resonance is 301.9 ppm more downfield from the resonance displayed in the ^{119}Sn NMR spectrum of **47**. Both **47** and **49** exhibit ^{119}Sn nuclear resonances that are significantly upfield shifted compared to other monomeric tin(II) amide species. Those differences may arise from the additional electron density donation from oxygen atom (O1) to tin atom (Sn1). In addition, the electron donating cyclohexyl substituent enhances electron density delocalisation towards the tin centre, leaving the tin centre of **49** relatively more deshielded.

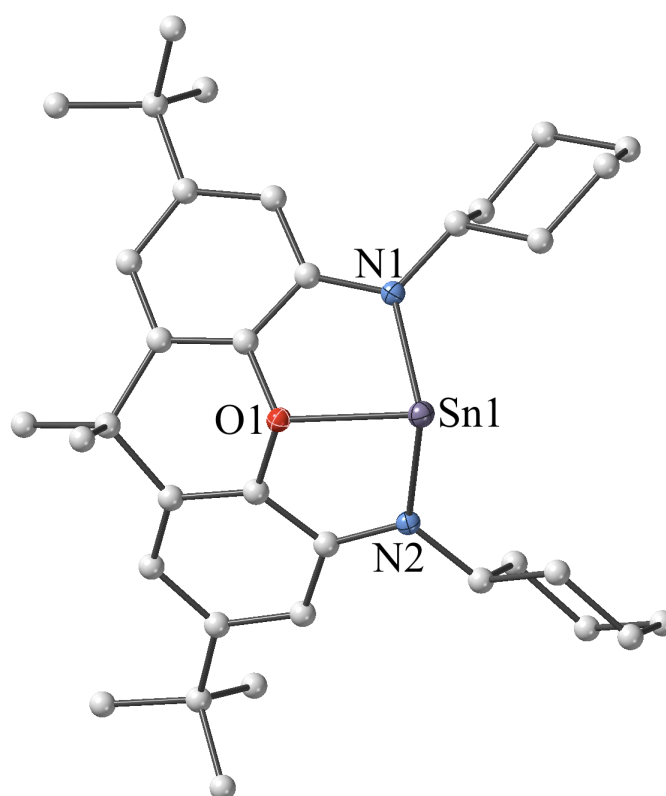


Figure 3.22: Molecular structure of **49**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand, except O1, N1 and N2, are pictured as spheres of arbitrary radius.

Crystals of **49** suitable for single crystal X-ray diffraction were grown from a concentrated hexane solution at room temperature. Similar to the structure of **46** and **47**, the molecular structure of **49** exhibits a distorted pyramidalised geometry around the tin (Sn1) and oxygen

(O1) atoms (Figure 3.22). Table 3.11 shows selected bond lengths and bond angles for **49**. While the Sn1–N1 bond lengths in **49** are comparable to those in **47**, the Sn1–O1 bond is significantly shorter in **49** (2.262(2) Å) than in **47** (2.353(2) Å), this in line with the electron donating cyclohexyl substituent increasing the electron density within the xanthene ligand framework enhancing the delocalisation from the oxygen (O1) lone pair to the empty p-orbital of Sn1.

Table 3.11 – Selected bond lengths and bond angles for **49**.

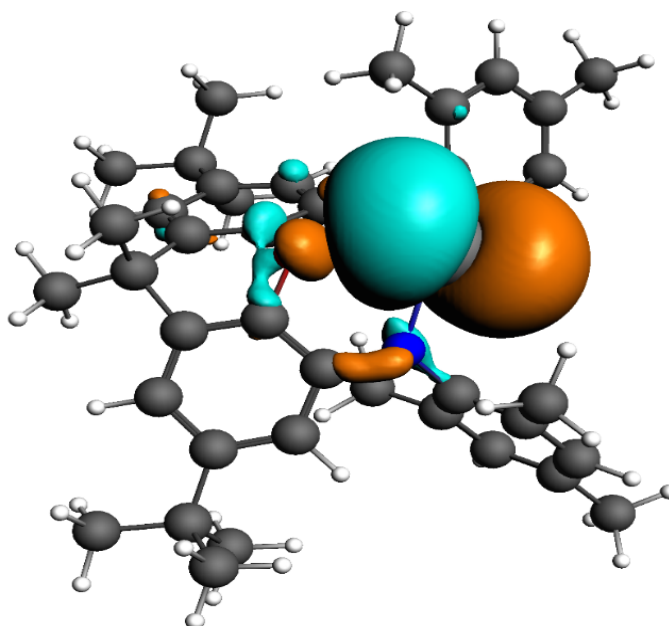
Bond lengths	49	Bond angles	49
Sn1–O1	2.262(2) Å	N1–Sn1–N2	110.43 (9)°
Sn1–N1	2.153(2) Å	O1–Sn1–N1	73.25(8)°
Sn1–N2	2.148(2) Å	O1–Sn1–N2	73.24(7)°

3.2.3.3 Density functional theory studies of **46–49**

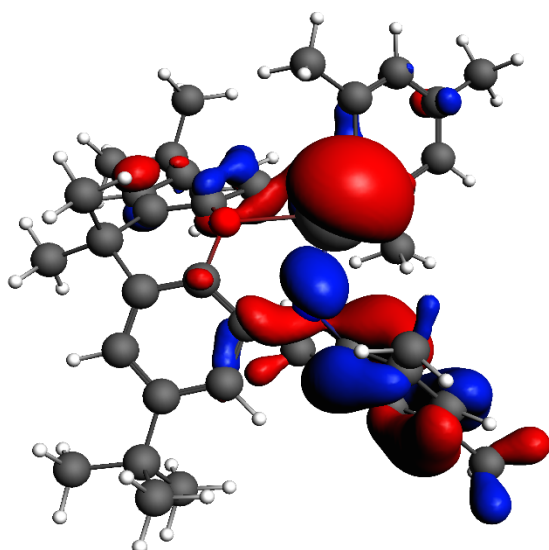
Density Functional Theory (DFT) studies carried out by Dr. Jose Goicoechea for compounds **46–49** and are further discussed below.

The DFT studies conducted on the optimised geometry C_s symmetry, they revealed that the LUMOs of complexes **46–49** are largely located at the tetrel(II) centre and have a substantial p-orbital character. The HOMOs for these complexes are largely distributed on the aryl functionalities of the ligand backbone (Figure 3.23). It is noteworthy that the lone pairs at the tetrel centres of **46–49** are located not in the HOMO, but in the HOMO–2 for **46**, **47** and **48**, and HOMO–3 for **49**. Table 3.12 shows the calculated data for the HOMO–LUMO gap of **46–49** and shows that the computed HOMO–LUMO gaps are comparable to those previously reported group 14 carbene analogues (2.67–2.89 eV), which suggest that compounds **46–49** may be suitable for small molecule activation.¹⁶

i) LUMO of **47**



ii) HOMO-2 of **47**



iii) HOMO-2 of **49**

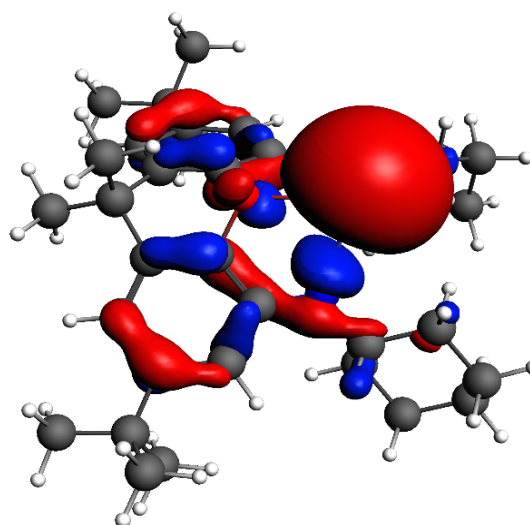


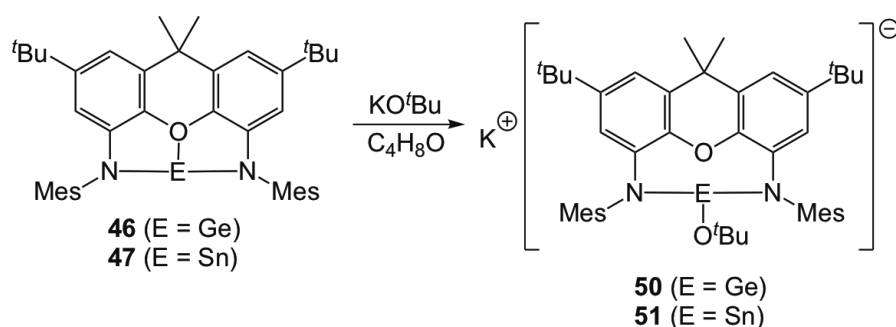
Figure 3.23: Images of the i) LUMO of **47**, ii) HOMO-2 of **47**, and iii) HOMO-2 of **49**.

Table 3.12 – Selected calculated data for the HOMO–LUMO gap and %E atomic orbital character in the LUMOs of **46–49**.

Compounds	HOMO– LUMO gaps	%E character in the LUMO	%E character in the HOMO–2
46	2.442	83.34	15.86
47	1.969	85.95	16.86
48	2.643	80.86	38.73 (HOMO–3)
49	2.220	81.47	48.72

3.2.4 Reactivity of **46** and **47** towards nucleophiles

To probe the accessibility of the LUMOs of **46** and **47**, these compounds were reacted with nucleophiles with an accessible stereochemical lone pair. Reactions of **46** and **47** with triphenylphosphine (PPh₃) revealed no reactivity even at elevated temperatures. By contrast, reacting **46** and **47** with anionic nucleophiles, such as KO^tBu, in the presence of a cation sequestering agent (18-crown-6 and 2,2,2-crypt for **46** and **47**, respectively) resulted in formation of anionic complexes **50** and **51** (Scheme 3.18).



Scheme 3.18: Reaction of **46–47** towards KO^tBu.

3.2.4.1 Characterisation of **50** and **51**

The ¹H NMR spectrum of **50** in d₈-THF displays a singlet at 0.28 ppm, integrating to nine protons, assigned to the *tert*-butoxide proton. It also displays a set of resonances attributed to the mesityl group which can be found at 6.73, 6.71, 2.29, 2.20 and 2.09 ppm, indicating that one of the mesityl CH₃ groups interacts with the *tert*-butoxide substituent through space and restricts the rotation of the mesityl group. The resonances attributed to the aromatic protons of xanthene ligand are upfield shifted when compared to its parent compound.

In the case of **51**, its ¹H NMR spectrum is greatly similar to that observed for compound **50**. In addition, ¹¹⁹Sn NMR spectrum of **51** shows a sharp singlet at –254.3 ppm, this resonance is shifted upfield in comparison to those displayed by **47** (–189.4 ppm). This shift is consistent with the *tert*-butoxide substituent increasing electron density at the tin centre of **51**, which shields the tin nucleus from the external magnetic field.

Both crystals of **50** and **51** suitable for single crystal X-ray diffraction were grown by slow diffusion of hexane into concentrated THF solutions. The molecular structure of **50** reveals that the *tert*-butoxide group is bonded to the germanium atom (Ge1), consistent with the calculation (Figure 3.24). The germanium centre (Ge1) adopts a distorted trigonal pyramidal geometry with the sum of bond angles around Ge1 equaling 290.1° (N1–Ge1–N2 = 108.78(7)°, N1–Ge1–O2 = 90.48(7)° and N1–Ge1–O2 = 90.82(7)°). The interatomic distance of Ge1⋯O1 is 2.49 Å, consistent with dissociation of the Ge–O bond.

As with **50**, the molecular structure of **51** is symmetric through the O1, Sn1 and O2 atoms. The tin atom adopts a distorted trigonal pyramidal structure, with the sum of bond angles around Sn1 of 315.8° (N1–Sn1–N2 = 126.52(12)° and N1/N2–Sn1–O2 = 94.63(8)°) (Figure 3.25). The interatomic distance between Sn1 and O1 atoms is 2.503(3) Å are significantly longer than the Sn1–O1 bond length of **47** (2.253(2) Å), again consistent with bond dissociation between the Sn1 and O1 atoms (Table 3.13).

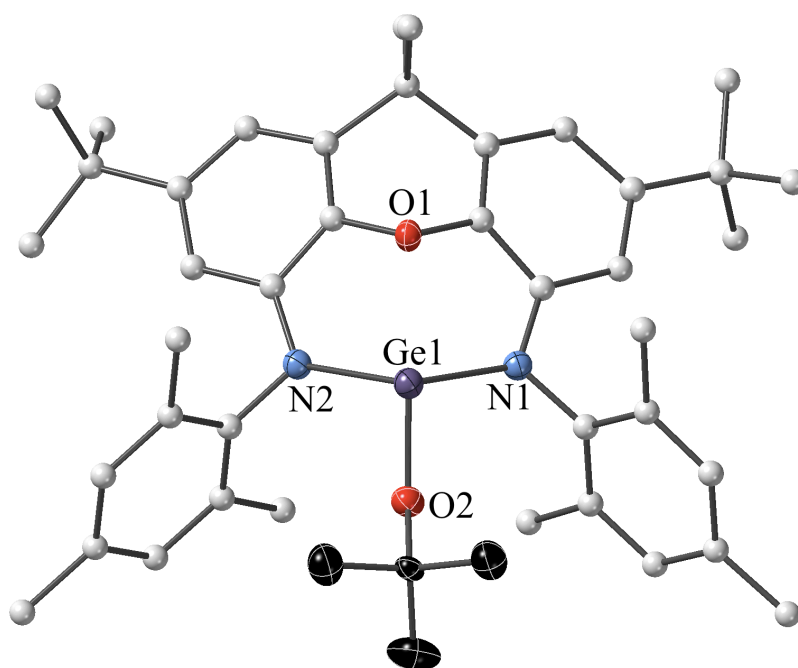


Figure 3.24: Molecular structure of [K(18-crown-6)][**50**]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [K(18-crown-6)]⁺ and all hydrogen atoms are omitted for clarity. Atoms of the ligand are pictured as spheres of arbitrary radius.

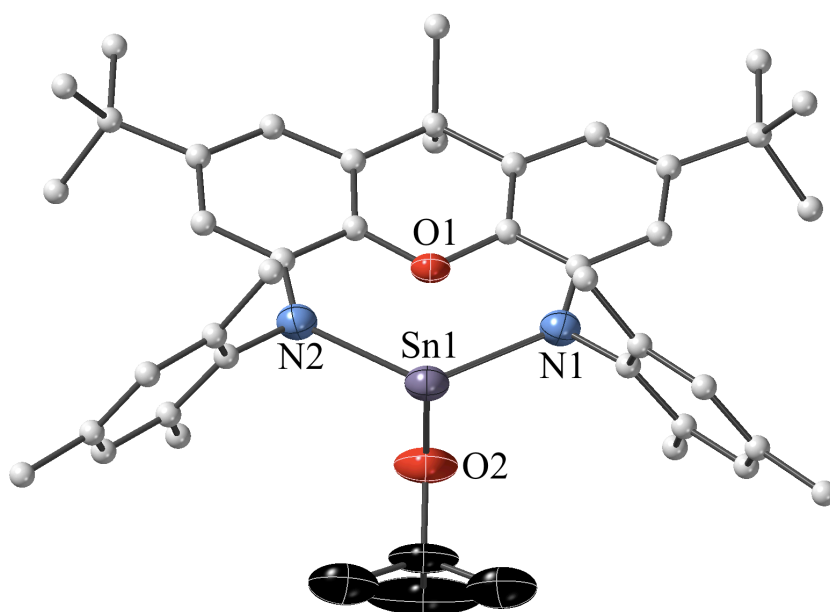


Figure 3.25: Molecular structure of [K(2,2,2-crypt)][**51**]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [K(2,2,2-crypt)]⁺ and all hydrogen atoms are omitted for clarity. Atoms of the ligand, except O1, N1 and N2 are pictured as spheres of arbitrary radius.

Table 3.13 – Selected bond lengths and bond angles for **50** and **51**.

Bond lengths and bond angles	50 (E = Ge)	51 (E = Sn)
E···O1	2.491(3) Å	2.503(3) Å
E–N1	2.098(2) Å	2.297(3) Å
E–N2	2.084(2) Å	2.297(3) Å
E–O2	1.865(2) Å	2.038(4) Å
N1–E–N2	108.78(7)°	126.52(12)°
N1–E–O2	90.48(7)°	94.63(8)°
N2–E–O2	90.82(7)°	94.63(8)°
O1–E–O2	143.84(7)°	84.60(6)°

3.2.5 Reactivity of **46** and **47** towards small molecule substrates

3.2.5.1 Reactivity of **46** and **47** towards water

When one molar equivalent of water was added to either a solution of **46** or **47**, the reaction solution changed colour from yellow to colourless. The reaction mixtures were monitored by ¹H NMR spectroscopy and revealed that both **46** and **47** were hydrolysed rapidly to give

the free protonated ligands, $\text{H}_2(\text{MesNON})$ and $\text{H}_2(\text{CyNON})$, respectively. These results are consistent with the high hydroscopic nature of **46** and **47**, and deterred subsequent studies with small molecules.

3.2.5.2 Reactivity of **46** and **47** towards ammonia

Reactions of **46** and **47** with 1 atm of ammonia also resulted in detection of the free protonated ligands, $\text{H}_2(\text{MesNON})$ and $\text{H}_2(\text{CyNON})$, respectively. Computational studies performed by a postdoctoral fellow Dr. Alexandar Hinz in our own research group reveal that the reaction between NH_3 and **46** is exothermic by 81 kJ mol^{-1} , and the same reaction between NH_3 and **47** is exothermic by 8 kJ mol^{-1} as the increased stabilisation of +2 oxidation state on descending group 14. The analogous reaction of **LIV** with NH_3 to form a phosphorus(V) system is similarly thermodynamically favoured.¹⁵ However, compounds of **46** and **47** are so moisture sensitive that the investigation of small molecule activation by **46** and **47** was hindered by hydrolysis which can be triggered by trace amounts of water.

3.2.5.3 Reactivity of **46** and **47** towards other small molecules

Further investigation of **46** and **47** with CO_2 , H_2 , cyclohexylamine and ammonia–borane either resulted in no reaction or decomposition.

3.2.6 Conclusions

In this section, the synthesis of four novel neutral constrained geometry group 14 systems bearing a xanthene based ligand framework, **46–49** is discussed. Reactions of $\text{H}_2(\text{MesNON})$ and $\text{H}_2(\text{CyNON})$ with two molar equivalents of KHMDS to give $\text{K}_2(\text{MesNON})$ and $\text{K}_2(\text{CyNON})$, respectively, which subsequently reacted with $\text{ECl}_2 \cdot \text{dioxane}$ ($\text{E} = \text{Ge}$ and Sn) *in-situ* to yield **46–49**. The molecular structures of **47** and **49** exhibit a distorted pyramidal geometry about the group 14 centres. In all cases, the group 14 elements are pushed away from the xanthene $(\text{NON})^{2-}$ ligand binding site as evidenced by their long Sn–O and Ge–O

bonds, making them very reactive towards hydrolysis which can be triggered by trace amounts of water. DFT studies showed that the LUMOs of **46–49** mainly consist of the p-orbital on the E(II) centres. The LUMO of **46** and **47** are chemically accessible by KO^tBu, resulting in the formation of negatively charged compounds **50** and **51**. Computational studies also revealed that oxidative addition of ammonia towards **46** and **47** is energetically feasible, however the hydrolysis process out-competed such reactivity. The highly hydroscopic nature of **46–49** hinder further studies with small molecule activation.

3.3 Reference

- (1) Arduengo, A. J.; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Mizen, M. *B. J. Am. Chem. Soc.* **1987**, *109* (3), 627.
- (2) McCarthy, S. M.; Lin, Y. C.; Devarajan, D.; Chang, J. W.; Yennawar, H. P.; Rioux, R. M.; Ess, D. H.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136* (12), 4640.
- (3) Zhao, W.; McCarthy, S. M.; Lai, T. Y.; Yennawar, H. P.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136* (50), 17634.
- (4) Cui, J.; Li, Y.; Ganguly, R.; Inthirarajah, A.; Hirao, H.; Kinjo, R. *J. Am. Chem. Soc.* **2014**, *136* (48), 16764.
- (5) Robinson, T. P.; De Rosa, D. M.; Aldridge, S.; Goicoechea, J. M. *Angew. Chem. Int. Ed.* **2015**, *54* (46), 13758.
- (6) Bettermann, G.; Arduengo, A. J. *J. Am. Chem. Soc.* **1988**, *110* (3), 877.
- (7) Driess, M.; Dona, N.; Merz, K. *Chem. - A Eur. J.* **2004**, *10* (23), 5971.
- (8) Driess, M.; Muresan, N.; Merz, K. *Angew. Chem. Int. Ed.* **2005**, *44* (41), 6738.
- (9) Kramer, N.; Jöst, C.; Mackenroth, A.; Greb, L. *Chem. - A Eur. J.* **2017**, *23* (70), 17764.
- (10) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalt. Trans.* **2008**, No. 21, 2832.

- (11) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidovič, D. *Chem. - A Eur. J.* **2014**, *20* (22), 6628.
- (12) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115* (13), 5875.
- (13) Seifert, A.; Scheid, D.; Linti, G.; Zessin, T. *Chem. - A Eur. J.* **2009**, *15* (44), 12114.
- (14) Yamada, K.; Okano, M. *Angew. Chemie. Int. Ed.* **2008**, *76* (6), 412.
- (15) Robinson, T. P.; Lo, S. K.; De Rosa, D.; Aldridge, S.; Goicoechea, J. M. *Chem. - A Eur. J.* **2016**, *22* (44), 15712.
- (16) Power, P. P. *Nature* **2010**, *463* (7278), 171.

Chapter 4

Complexes of group 15 elements bearing the *N,N*-bis(3,5,di-*tert*-butyl-2-phenolate) amide ligand and the 2,2'-[iminobis(methylene)]-bis[4-methoxyl-phenol] ligand

4.1 Complexes of arsenic bearing the (ONO)³⁻ ligand

4.1.1 Project aims

As discussed in the introduction chapter, Arduengo, Radosevich, Kinjo and our own research group have isolated several related phosphorus(III) geometry constrained complexes, **LI**–**LIV** (Figure 4.1) and demonstrated that such complexes are capable of cleaving the X–H (X = N, O) bonds of substrates such as ammonia, amines, water and alcohols.^{1–6} Theoretical calculations revealed that **LI** and **LII** underwent a stepwise, ligand-cooperative electrophilic pathway resulting in the oxidative addition of substrates over the phosphorus(III) centre to form distorted trigonal bipyramidal phosphorus(V) complexes.^{4,7,8}

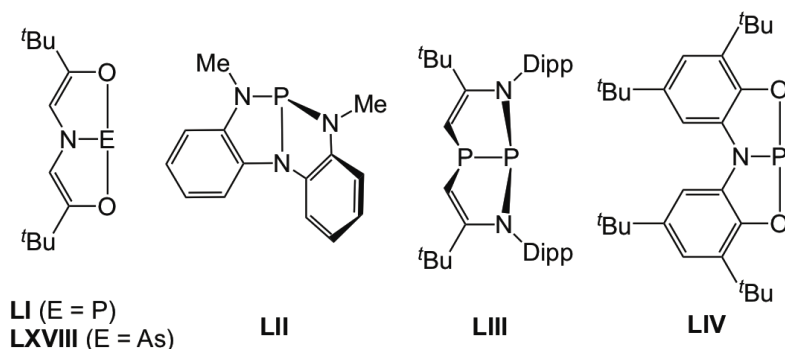


Figure 4.1: Examples of group 15 geometry constrained complexes.

Heating solid samples of the phosphorus(V) complexes under vacuum shows that the activation processes for **LII** and **LIV** are reversible. Radosevich has demonstrated the use of **LI** as an efficient catalyst in the reduction of azobenzene using H₃N·BH₃ as a hydrogen surrogate.³ For this reason, we targeted the arsenic analogue of **LIV** which should stabilise the As(III) oxidation state. The oxidative activation process for the As(III) analogue is more energetically costly due to the relative stability of the +3 oxidation state, however if possible, the postulated As(V) activation products should allow for the reversibility of this process.

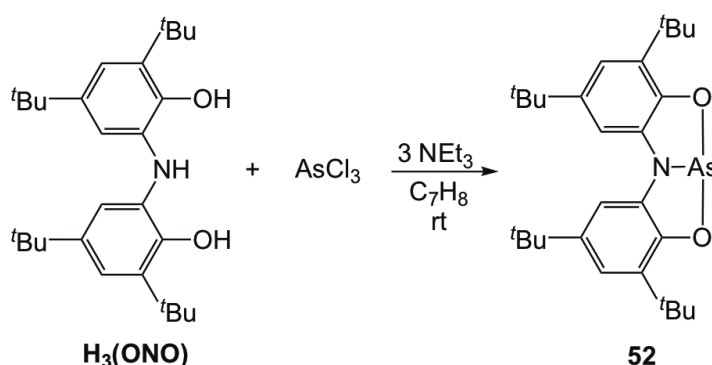
In 1987, Arduengo reported the isolation of the arsenic(III) analogue of **LI**, **LXVIII** (Figure 4.1).¹ **LXVIII** was characterised by single crystal X-ray diffraction and revealed a distorted planar geometry with the sum of bond angles of 320.7° about the arsenic centre (Table 4.1), which gives a more bent structure in comparison to **LI** (the sum of bond angle around phosphorus = 335.4°). While **LI** underwent rapid reaction with water and ethanol (see Scheme 1.42 in Chapter 1), the arsenic analogue **LXVIII** did not react with such molecule.¹

Table 4.1 – Selected bond lengths and bond angles for **LXVIII**.

Bond lengths	LXVIII	Bond angles	LXVIII
As1–N1	1.839(3) Å	O1–As1–O2	160.3(1)°
As1–O1	1.955(3) Å	N1–As1–O1	80.4(1)°
As1–O2	1.998(3) Å	N1–As1–O2	80.0(1)°

4.1.2 Synthesis and characterisation of an arsenic complex bearing the (ONO)^{3–} ligand

An arsenic complex bearing the (ONO)^{3–} ligand can be prepared following a similar synthetic protocol as used for the synthesis of **LVI**. Reaction of the free ligand, H₃(ONO), with arsenic trichloride in the presence of three molar equivalents of NEt₃ yielded **52** quantitatively (Scheme 4.1).



Scheme 4.1: Synthesis of **52**.

Compound **52** was characterised by ¹H NMR spectroscopy displaying two doublets at 8.39 and 7.51 ppm and two singlets at 1.71 and 1.46 ppm attributed to the aromatic protons and the *tert*-butyl protons, respectively.

Crystals of **52** suitable for single crystal X-ray diffraction were grown by cooling a concentrated pentane solution of the product to $-30\text{ }^{\circ}\text{C}$. The molecular structure of **52** exhibits a planar T-shaped geometry about the arsenic(III) centre (As1) with a relatively linear O1–As–O2 bond angle ($164.39(12)^{\circ}$; Figure 4.2). Table 4.2 shows selected bond lengths and bond angles for **52**. The N1–As1–O bond angles approach 90° ($82.9(2)^{\circ}$ for O1 and $82.8(2)^{\circ}$ for O2), giving rise to a sum of bond angles of 329.1° around As1 which is significantly larger than its phosphorus(III) analogue, **LIV** (296.2°). The sum of bond angles around the nitrogen atom (N1) is 359.9° , which is also larger than that of **LIV** (331.6°), consistent with the more planar geometry exhibited by **52**.

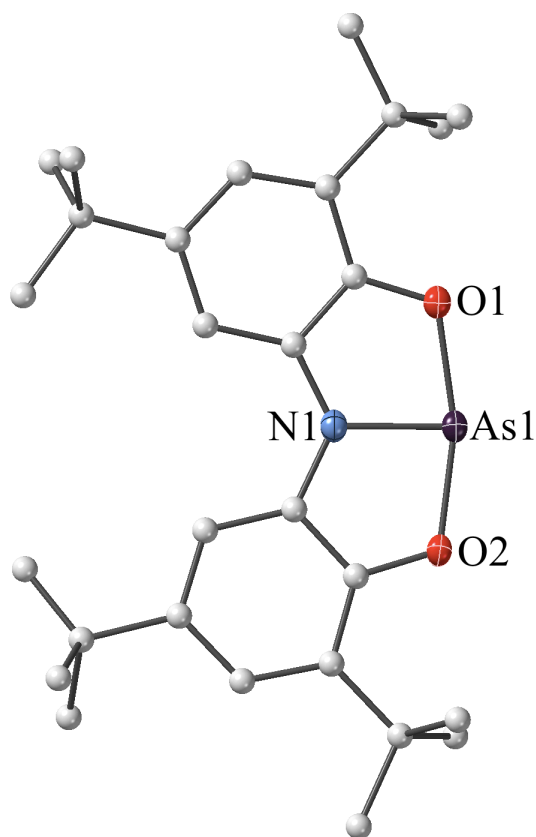


Figure 4.2: Molecular structure of **52**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms are omitted for clarity. Atoms of the ligand are pictured, except N1, O1 and O2, as spheres of arbitrary radius.

Table 4.2 – Selected bond lengths and bond angles for **52**.

Bond lengths	52	Bond angles	52
As1–N1	1.862(3) Å	O1–As1–O2	164.39(1)°
As1–O1	1.933(4) Å	N1–As1–O1	82.9(2)°
As1–O2	1.933(4) Å	N1–As1–O2	82.8(2)°

The As1–O bonds (1.933(4) Å) are slightly longer than the literature reported values for As–O single bonds (1.84–1.85 Å). By contrast, the As1–N1 bond is shorter than the expected values for As–N single bonds (1.90–1.92 Å), implying a significant degree of p_{π} – p_{π} orbital interaction between the nitrogen (N1) lone pair and As1. This partial multiple bond character gives rise to the observed planar geometry. The molecular structure and bond metrics of **52** resemble the planar 10-As-3 compound **LXVIII**.

Theoretical calculations, performed by Dr. Jose Goicoechea, examined the electronic properties of **52** and found that the optimised geometry of **52** is consistent with the molecular structure revealed in the single crystal X-ray diffraction studies. Calculations also revealed that the LUMO of the planar configuration of **52** has significant arsenic p-orbital character perpendicular to the plane of the (ONO)³⁻ ligand framework and p_{π} – p_{π} antibonding character for the As–N and As–O bonds. The HOMO of **52** is largely comprised of the lone pair orbital on the nitrogen atom of the ligand backbone. The frontier orbital arrangement of **52** is comparable to that of **LIV**.

4.1.3 Reactivity of **52** towards nucleophiles

4.1.3.1 Reactivity of **52** towards nucleophiles with a protic X–H bond

While **LIV** was reported to perform facile addition of nucleophilic substrates possessing protic X–H bonds (X = N, O) such as water and ammonia,⁶ no reaction was observed between **52** and ammonia even at reflux temperatures. Hydrolysis of **52** did take place but gave rise to multiple products in the reaction mixtures. In addition, the reaction between **52**

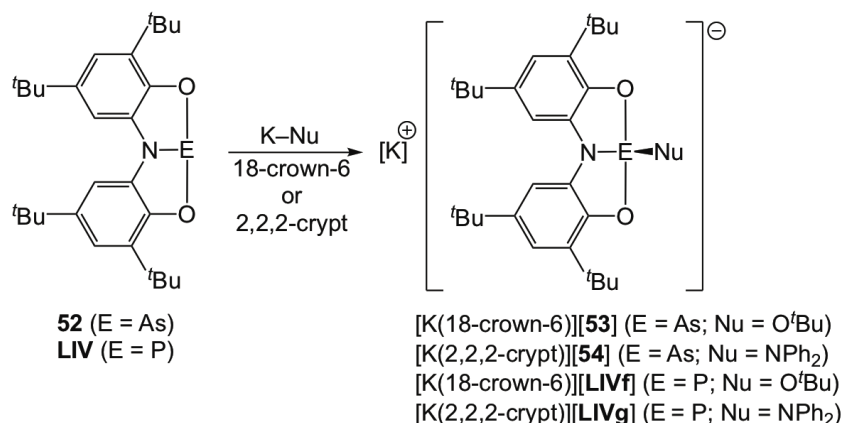
and H₂S, a heavier analogue of H₂O, resulted in formation of the free ligand, H₃(ONO), and a yellow precipitate which is thought to be As₂S₃.

Furthermore, computational studies revealed that the reaction between ammonia and **52** is endothermic by 86 kJ·mol⁻¹, whereas the reaction between ammonia and **LIV** is exothermic by 90 kJ·mol⁻¹. This difference in reactivity is due to the increased stabilisation of the +3 oxidation state on descending group 15.

4.1.3.2 Reactivity of **52** towards neutral and charged nucleophiles

To investigate the accessibility of the LUMO of **52**, we explored its reactivity towards nucleophiles. No reaction was observed when reacting either **51** or **LIV** with neutral nucleophiles, such as pyridine or triphenylphosphine.

Reactions of **52** with charged nucleophiles, such as potassium *tert*-butoxide (KO^tBu) or potassium diphenylamide (KNPh₂), in the presence of a cation sequestering agent (18-crown-6 or 2,2,2-crypt), resulted in formation of the arsenic(III) complexes [K(18-crown-6)][**53**] and [K(2,2,2-crypt)][**54**], respectively (Scheme 4.2). Our group has shown that analogous reactivity of **LIV** towards KO^tBu and KNPh₂ afforded the phosphorus(III) complexes, [K(18-crown-6)][**LIVf**] and [K(2,2,2-crypt)][**LIVg**], respectively.



Scheme 4.2: Reactions of **52** and **LIV** with KNu (Nu = O^tBu and NPh₂).

In the ^1H NMR spectrum of **53**, the resonance attributed to *tert*-butoxide protons was observed at 1.26 ppm. The resonances arising from aromatic protons are shifted upfield with respect to those observed in **52**, due to the increased electron density available on the arsenic centre from the *tert*-butoxide substituent. Similarly, the ^1H NMR spectrum of **54** resembles that of **53**. The amide phenyl protons resonances of **54** were found in the range of 6.76 to 6.41 ppm.

Crystals of **53** and **54** suitable for single crystal X-ray diffraction were grown by slow diffusion of hexane into concentrated THF solutions of the products. The molecular structure of **53** reveals the association of the *tert*-butoxide group with the arsenic centre and the formation of an As–O bond (Figure 4.3). Table 4.3 shows selected bond lengths and bond angles for **53**. The compound exhibits a planar As(ONO) moiety ($\text{O1–As1–O2} = 162.95(4)^\circ$) with the nucleophile orthogonal to the $(\text{ONO})^{3-}$ ligand plane ($\text{N1–As1–O3} = 93.65(4)^\circ$). The coordination of anionic nucleophiles results in significant elongation of the As–O bonds ($\text{As1–O1} = 1.933(4) \text{ \AA}$ and $\text{As1–O2} = 1.933(4) \text{ \AA}$ for **52**; $\text{As1–O1} = 2.028(1) \text{ \AA}$ and $\text{As1–O2} = 1.963(1) \text{ \AA}$ for **53**) while the As–N retains similar values. The elongation of the As–O bonds is not uniform but rather more pronounced for As1–O1 bond than the As1–O2 bond as the O1 atom is weakly coordinated to the cationic potassium atom ($\text{K1}\cdots\text{O1}$ interatomic distance = $2.880(1) \text{ \AA}$) pulling O1 atom away from the arsenic centre.

Similar to the structure **53**, the molecular structure of **54** shows a (diphenyl)amide substituent associated with the arsenic centre (Figure 4.4). Table 4.3 shows selected bond lengths and bond angles for **54** and they are largely similar to those observed for **53**. The amide substituent is orthogonal to the $(\text{ONO})^{3-}$ ligand plane ($\text{N1–As1–N2} = 98.26(8)^\circ$).

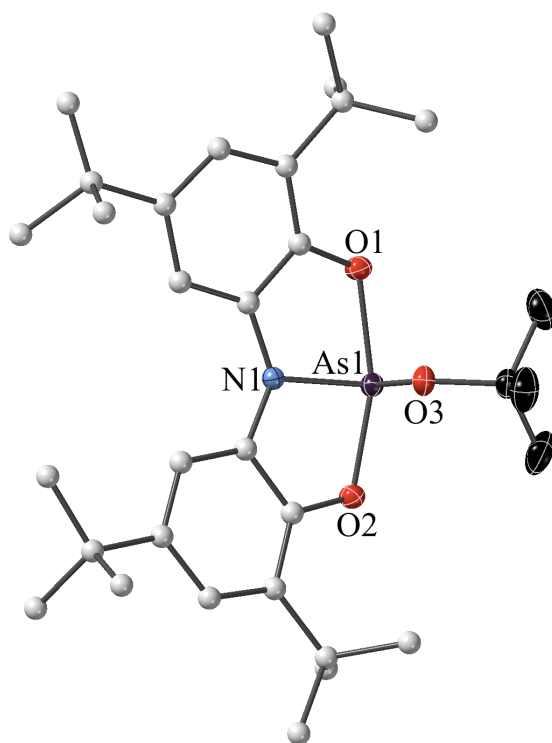


Figure 4.3: Molecular structure of [K(18-crown-6)][53]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [K(18-crown-6)]⁺ and all hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

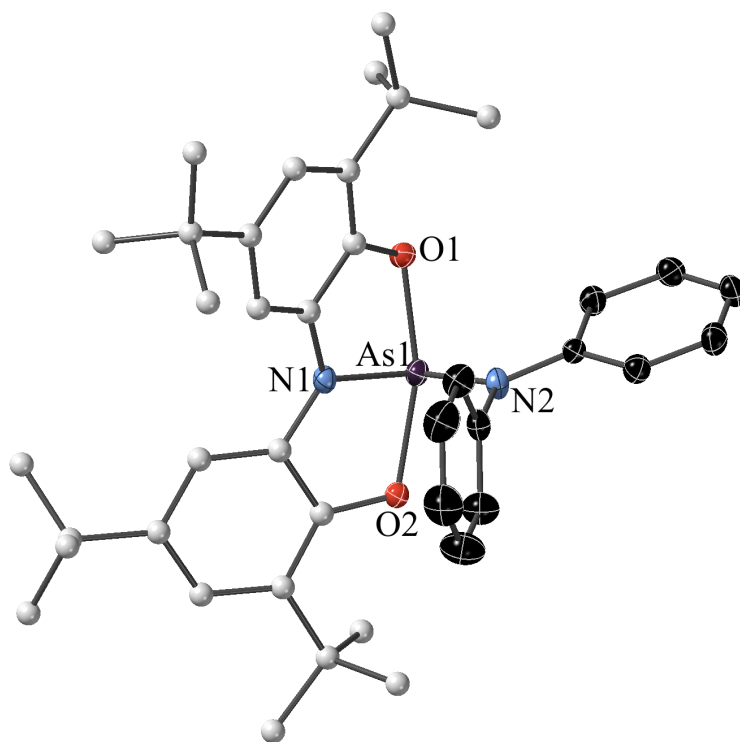
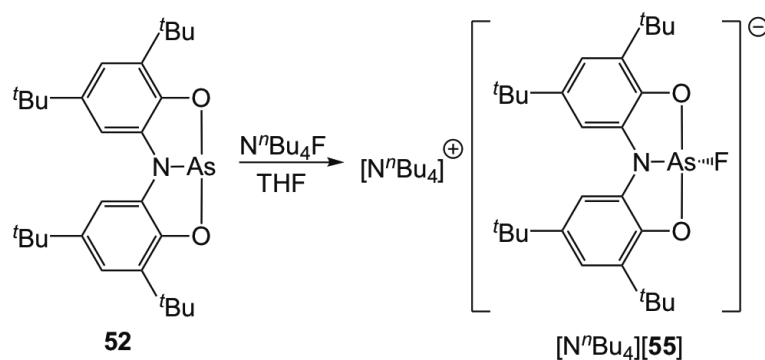


Figure 4.4: Molecular structure of [K(2,2,2-crypt)][54]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [K(2,2,2-crypt)]⁺ and all hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 4.3 – Selected bond lengths and bond angles for **53** and **54**.

Bond lengths and Bond angles	53 (X = O3)	54 (X = N2)
As1–N1	1.898(1) Å	1.874(2) Å
As1–O1	2.028(1) Å	1.995(2) Å
As1–O2	1.963(1) Å	2.051(2) Å
As1–O3	1.820(1) Å	1.924(2) Å
O1–As1–O2	162.95(4)°	161.48(6)°
N1–As1–O1	81.38(4)°	81.37(8)°
N1–As1–O2	82.40(4)°	80.22(8)°
N1–As1–X	93.64(4)°	98.26(8)°

Similarly, addition of tetrabutylammonium fluoride (N^tBu_4F) of a solution of **52** resulted in formation of an arsenic(III) complex, $[N^tBu_4][\mathbf{55}]$ (Scheme 4.3).



Scheme 4.3: Reaction of **52** with N^tBu_4F .

The ^{19}F NMR spectrum of **55** reveals a singlet resonance at -73.1 ppm. The 1H NMR also shows a set of resonances at 2.98, 1.46, 1.40 and 1.34 ppm corresponding to the protons of the $N^tBu_4^+$ cation. It also displays similar aromatic resonances to those observed for **53** and **54**.

Crystals of **55** suitable for single crystal X-ray diffraction were grown by slow diffusion of hexane into a concentrated THF solution. The molecular structure of **55** displays a similar structure to **53** and **54** with a fluorine atom orthogonal to the plane of the $(ONO)^{3-}$ ligand ($N1-As1-F1 = 101.09(10)^\circ$) (Figure 4.5). Table 4.4 shows selected bond lengths and bond

angles for **55**. The elongation of As–O bonds is uniform due to the lack of any ionic interaction with the counteranion (As1–O1 = 1.976(2) Å and 1.987(2) Å).

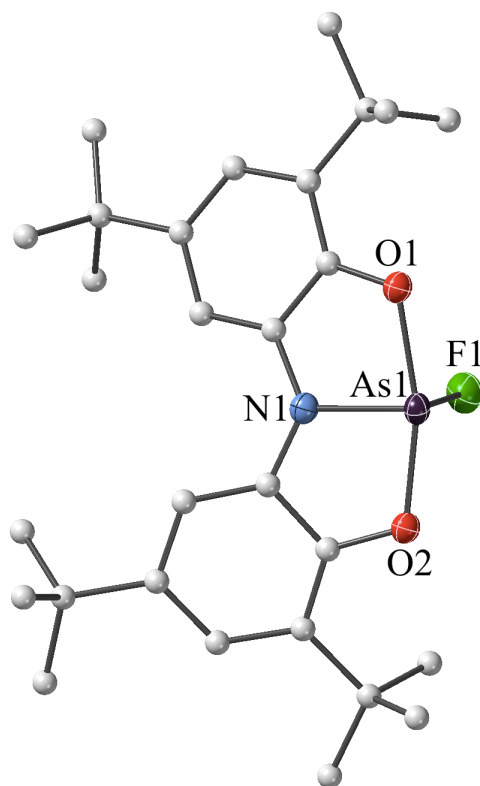


Figure 4.5: Molecular structure of [N^tBu₄][**55**]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [N^tBu₄]⁺ and all hydrogen atoms are omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

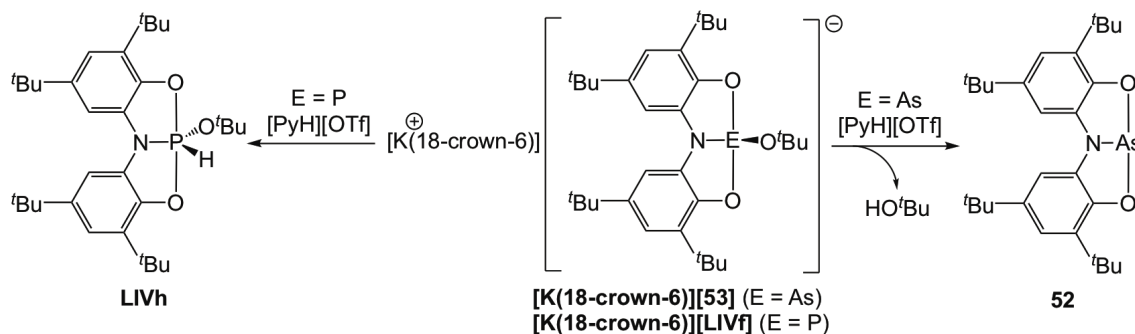
Table 4.4 – Selected bond lengths and bond angles for **55**.

Bond lengths		Bond angles	
	55		55
As1–N1	1.865(2) Å	O1–As1–O2	161.46(7)°
As1–O1	1.976(2) Å	N1–As1–O1	81.68(9)°
As1–O2	1.987(2) Å	N1–As1–O2	81.50(9)°
As1–F1	1.812(2) Å	N1–As1–F1	101.09(10)°

4.1.3.3 Reactivity of **53** and **LIVf** towards [PyH][OTf]

The elongation of Pn–O bonds suggests that [K(18-crown-6)][**53**] and [K(18-crown-6)][**LIVf**] are reactive towards electrophiles. Reaction of [K(18-crown-6)][**LIVf**] with one molar equivalent of pyridinium trifluoromethanesulfonate ([PyH][OTf]) yielded a

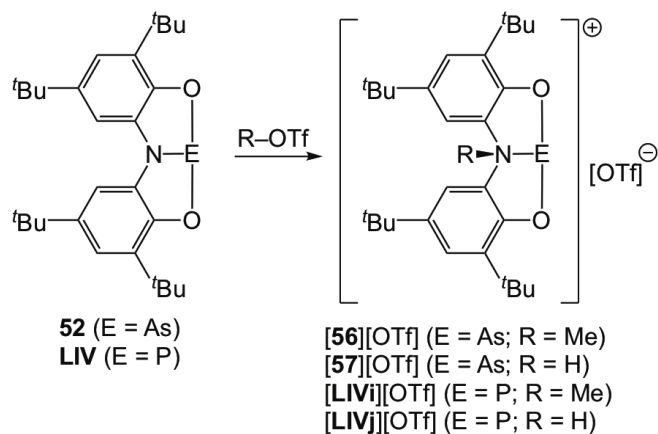
phosphorus(V) complex, **LIVh**, whereas the analogous reaction of [K(18-crown-6)][**53**] with [PyH][OTf] resulted in recovery of **52** and HO^tBu (Scheme 4.4), highlighting the increased stability of +3 oxidation state on descending group 15, and the difficulty associated with accessing arsenic(V) complexes.



Scheme 4.4: Reaction of [K(18-crown-6)][**53**] and [K(18-crown-6)][**LIVf**] with [PyH][OTf].

4.1.4 Reactivity of **LIV** and **52** towards electrophiles

4.1.4.1 Reactivity of **LIV** and **52** towards MeOTf and HOTf



Scheme 4.5: Reactions of **52** and **LIV** with MeOTf and HOTf.

The reactivity of **LIV** and **52** towards electrophiles was investigated in order to understand the accessibility of the HOMO. Reactions of **52** with MeOTf and HOTf resulted in methylation and protonation, respectively, of the nitrogen atom of the ligand backbone affording arsenic(III) compounds [56][OTf] and [57][OTf], respectively (Scheme 4.5). Our

own research showed that the analogous reactions with **LIV** resulted in formation of $[\text{LIVi}][\text{OTf}]$ and $[\text{LIVj}][\text{OTf}]$.

56 was characterised by ^1H NMR spectroscopy revealing a resonance attributed to the N- CH_3 methyl protons at 3.41 ppm. The resonances corresponding to the aromatic protons were upfield shifted with respect to those observed for **52**. The ^{19}F NMR spectrum displays a singlet resonance at -77.9 ppm arising from the OTf^- anion. The ^1H and ^{19}F NMR spectrum of **56** are largely similar to that of **55**. The resonance attributed to the N-H proton was found at 11.64 ppm.

Crystals of **56** suitable for single crystal X-ray crystallography were grown by slow diffusion of hexane in a concentrated dichloromethane solution of the product, whereas those of **57** were grown from a concentrated hexane solution of the product at room temperature. Both the molecular structures of **56** and **57** adopt a distorted tetrahedral geometry around the nitrogen and arsenic atoms (N1 and As1) as pictured in Figures 4.6 and 4.7. In the structure of **56**, the As1-N1 bond is elongated compared to that of **52** (As1-N1 = 2.127(1) Å for **56**; 1.862(2) Å for **52**), whereas the As-O bonds are significantly contracted upon methylation. As the structure of **56** adopts a more bent geometry, the O1 and O2 atoms lose their pseudo-axial arrangement and being drawn closer to As1. The bond metrics of **57** are similar to those observed for **56**. (Table 4.5).

Table 4.5 – Selected bond lengths and bond angles for **56** and **57**.

Bond lengths and bond angles	56	57
As1-N1	2.127(1) Å	2.028(2) Å
As1-O1	1.790(1) Å	1.791(1) Å
As1-O2	1.788(1) Å	1.810(1) Å
O1-As1-O2	100.35(4)°	98.55(5)°
N1-As1-O1	85.00(4)°	87.00(5)°
N1-As1-O2	83.73(4)°	85.69(5)°

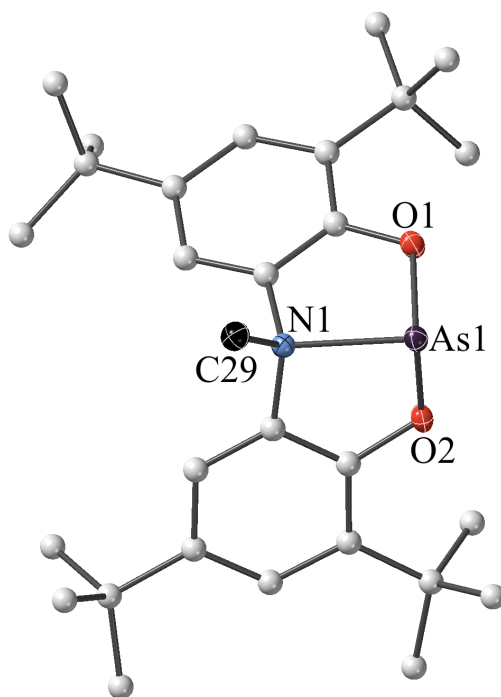


Figure 4.6: Molecular structure of [56][OTf]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [OTf][−] and all hydrogen atoms are omitted for clarity. Atoms of the ligand, except C29, N1, O1 and O2, are pictured as spheres of arbitrary radius.

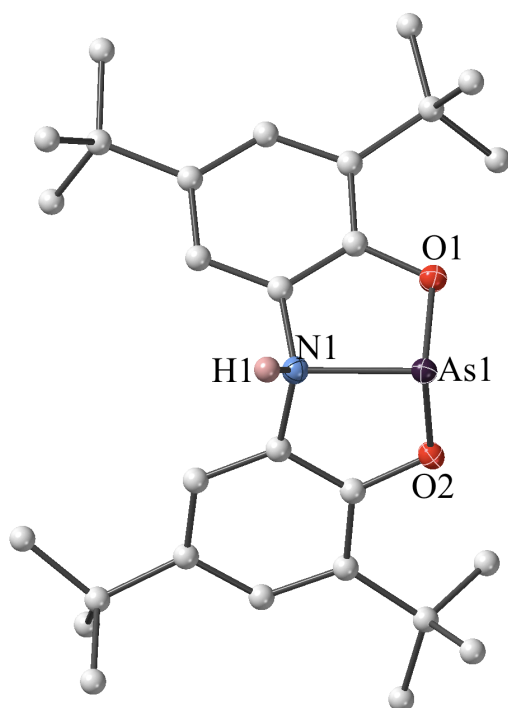
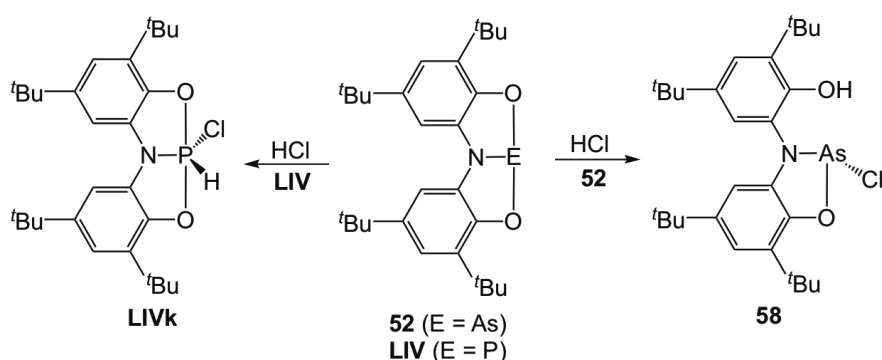


Figure 4.7: Molecular structure of [57][OTf]. Anisotropic displacement ellipsoids pictured are set at 50% probability. [OTf][−] and all hydrogen atoms, except H1, omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

4.1.4.2 Reactivity of **52** towards HCl

While **52** and **LIV** reacted with MeOTf or HOTf to afford pnictogen(III) compounds with methylated and protonated ligand backbones, respectively, the analogous reactions of **52** and **LIV** with an acid that has a more nucleophilic counter-anion, such as HCl, afforded an arsenic(III) species, **58**, and trigonal bipyramid phosphorus(V) complex, **LIVk**, respectively (Scheme 4.6). The observation, once again, highlights that arsenic(V) oxidation state is energetically unfavourable to access.



Scheme 4.6: Reactions of **52** and **LIV** with HCl.

The ^1H NMR spectrum of **58** reveals four doublets at 7.53, 7.41, 7.19 and 6.69 ppm and four singlets at 1.63, 1.57, 1.27, 1.16 ppm attributed to the aromatic protons and the *tert*-butyl protons respectively, indicative of an asymmetric environment of the pincer ligand. Also, the resonance corresponding to the aryloxide proton was observed at 5.48 ppm.

Crystals of **58** suitable for single crystal X-ray diffraction were grown in a concentrated hexane solution. The molecular structure of **58** adopts a distorted trigonal pyramidal geometry around the arsenic atom (As1) giving rise to a sum of bond angles around As1 of 284.8° with a relatively obtuse N1–As1–Cl1 bond angle ($101.58(7)^\circ$) owing to the steric repulsion of the chlorine atom (Cl1) with the free aryloxide substituent of the ligand (Figure 4.8). Table 4.6 shows selected bond lengths and bond angles for **58**. The As1–N1

and As1–O1 bond lengths (1.839(2) Å and 1.783(2) Å, respectively) are shorter than those exhibited by **52** (1.862(3) Å and 1.933(4) Å).

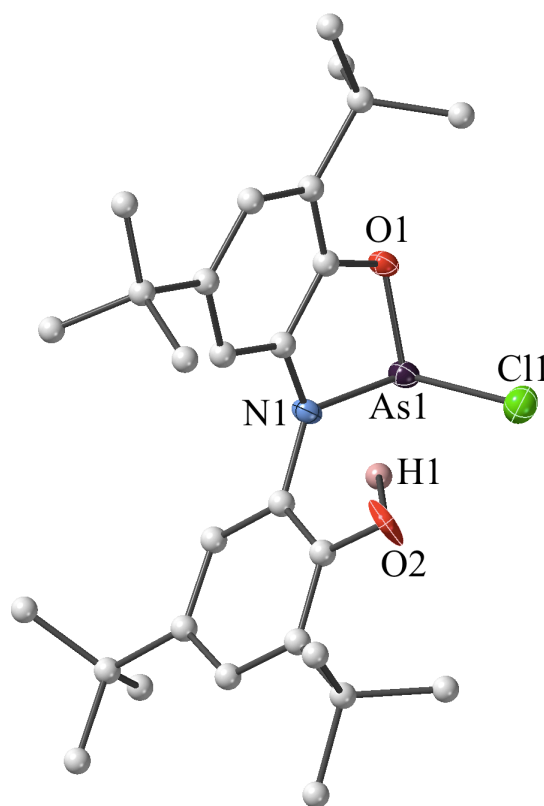


Figure 4.8: Molecular structure of **58**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1, are omitted for clarity. Atoms of the ligand are pictured as spheres of arbitrary radius.

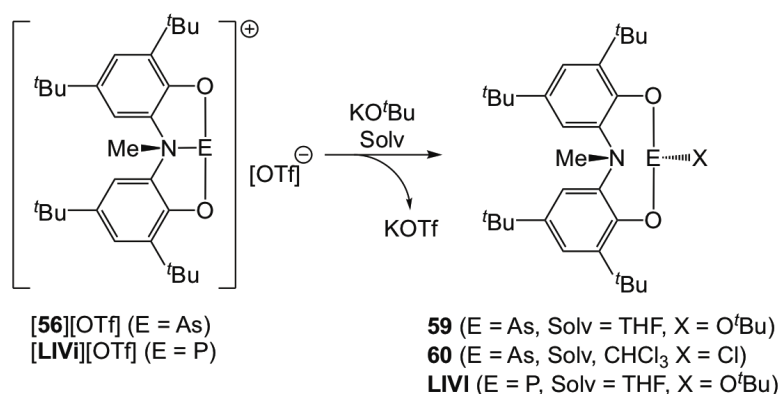
Table 4.6 – Selected bond lengths and bond angles for **58**.

Bond lengths	58	Bond angles	58
As1–N1	1.839(2) Å	O1–As1–Cl1	95.66(5) °
As1–O1	1.783(2) Å	N1–As1–O1	87.51(8) °
As1–Cl1	2.286(1) Å	N1–As1–Cl1	101.58(7) °

4.1.4.3 Reactivity of **56** and **LIVi** towards KO^tBu

Theoretical calculations for **LIVi** and **56** reveal that the pnictogen centre is positively charged, consequently we investigated their reactivity towards charged nucleophiles.

Reaction of **[56][OTf]** with one molar equivalent of KO^tBu in THF at –78 °C yielded **59**. Unfortunately, the sample could not be isolated as a pure compound due to its relative instability and tendency to decompose. Our own research has found that the analogous reaction of **[LIVi][OTf]** with KO^tBu resulted in clean formation of **LIVI** which was successfully characterised by single crystal X-ray diffraction studies and NMR spectroscopy (Scheme 4.7).



Scheme 4.7: Reactions of **[56][OTf]** and **[LIVi][OTf]** with KO^tBu.

Although isolation of **59** has not been possible, spectroscopic data confirm the presence of **59** in the reaction mixture. In the ¹H NMR spectrum of **59**, the resonances attributed to the N–CH₃ methyl proton were observed at 2.62 ppm, respectively. The spectrum also displays two doublets at 7.40 and 7.32 ppm attributed to the aromatic protons. The molecular ion of **59** was also recorded at 586.3241 Da (cal. *m/z* = 586.3140) in the electron impact mass spectrum.

Interestingly, reaction of **[56][OTf]** with KO^tBu in chloroform at room temperature resulted in clean formation of **60** (Scheme 4.7). The formation of **60** indicated that more nucleophilic chloride anion from the chloroform solvent has out-competed the ^tBuO[–] moiety and associated with the arsenic atom of **56**. The ¹H NMR spectrum of **60** displays similar resonances corresponding to aromatic protons and *tert*-butyl protons to those found for **59**. The resonance attributed to N–CH₃ methyl proton was observed at 3.15 ppm.

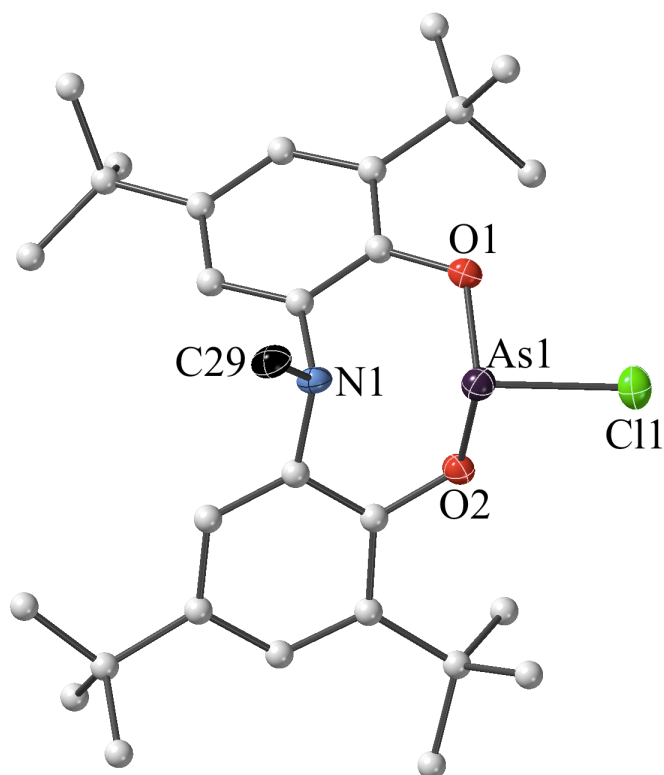


Figure 4.9: Molecular structure of **60**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms omitted for clarity. Atoms of the ligands, except N1, O1 and O2, are pictured as spheres of arbitrary radius

Table 4.7 – Selected bond lengths and bond angles for **60**.

Bond lengths	60	Bond angles	60
As1...N1	2.306(3) Å	O1–As1–O2	100.57(11)°
As1–O1	1.818(2) Å	N1–As1–O1	78.86(9)°
As1–O2	1.807(2) Å	N1–As1–O2	80.57(10)°
As1–Cl1	2.269(1) Å	N1–As1–Cl1	161.05(8)°

Crystals of **60** suitable of single crystal X-ray diffraction studies were grown by slow diffusion of hexane into a concentrated chloroform solution. The molecular structure of **60** reveals that the nucleophilic Cl[−] moiety has associated with the arsenic atom (Figure 4.9). Table 4.7 shows selected bond lengths and bond angles of **60**. Both the nitrogen (N1) and arsenic (As1) centres exhibit a distorted trigonal pyramidal geometry with a sum of the bond angles of 342.8° about N1 and 277.39° about As1. This observation implies increased

planarity owing to the lone pair-lone pair repulsion between N1 and As1, which is evident in the long As $\cdots$ N interatomic distance (2.306(3) Å).

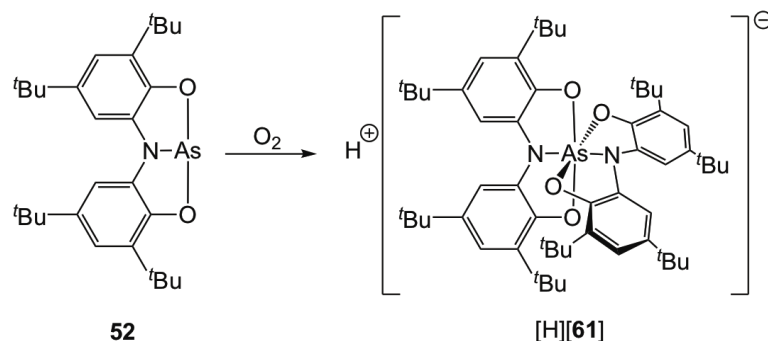
4.1.5 Oxidation of **52**

4.1.5.1 Exposure of **52** to air

We have established that arsenic(V) complexes are thermodynamically inaccessible via reaction with nucleophiles and electrophiles. To access arsenic(V) complexes, we investigated the oxidation of **52**.

Exposure of a solution of **52** to air resulted in a change of colour from orange to dark purple, accompanied by the formation of purple crystals which was shown to be the anionic As(V) octahedral $[(\text{As}(\text{ONO})_2)]^-$ complex, **61** (Scheme 4.8). Single crystal X-ray crystallography confirms the structure of **61**. The ^1H NMR spectrum of **60** showed broad resonances in large part due to the poor solubility of the compound, thus **60** could not be characterised by NMR spectroscopy.

The molecular structure of **61** reveals an arsenic centre coordinated by two $(\text{ONO})^{3-}$ ligands and adopts a slightly distorted octahedral geometry (Figure 4.10 and Table 4.8). The charge balancing proton is disordered in the crystal structure and could not be located in the Fourier difference map.



Scheme 4.8: Exposure **52** to air to afford **[H][61]**.

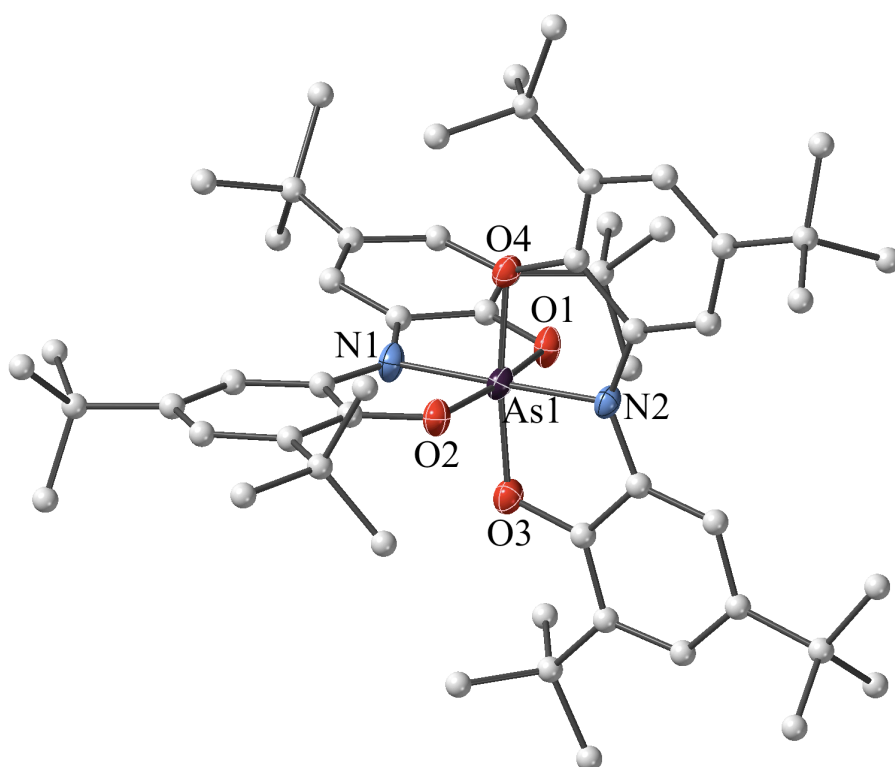


Figure 4.10: Molecular structure of [H][**61**]. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms omitted for clarity. Atoms of the ligand, except N1, N2, O1, O2, O3 and O4, are pictured as spheres of arbitrary radius.

Table 4.8 – Selected bond lengths and bond angles for **61**.

Bond lengths	61	Bond angles	61
As1–N1	1.881(2) Å	O1–As1–O2	171.37(6)°
As1–N2	1.884(2) Å	N1–As1–N2	177.98(8)°
As1–O1	1.846(2) Å	N1–As1–O1	80.57(10)°
As1–O2	1.847(2) Å	N1–As1–O2	85.70(7)°
As1–O3	1.831(2) Å	N1–As1–O3	95.20(8)°
As1–O4	1.841(2) Å	N1–As1–O4	92.58(8)°

4.1.5.2 Reaction of **52** with Selectfluor

In order to investigate oxidation of **52** in a more controlled manner, reaction of **52** with Selectfluor, which acts as a source of strongly oxidising cationic fluorine, was investigated. This resulted in the formation of dark blue solutions accompanied by the precipitation of a dark blue solid. The ^1H NMR spectrum of the solid in d_5 -pyridine reveals broad resonances, therefore the ^1H NMR analysis was not informative. On the other hand, the ^{19}F NMR

spectrum of the reaction mixture displays two sets of doublet at -43.4 and -43.6 ppm as well as two sets of triplet at -63.0 and -62.7 ppm, all with a $^2J_{\text{F-F}}$ coupling constant of 112 Hz, indicative of the formation of two compounds each of which contains three fluorine atoms (Figure 4.11).

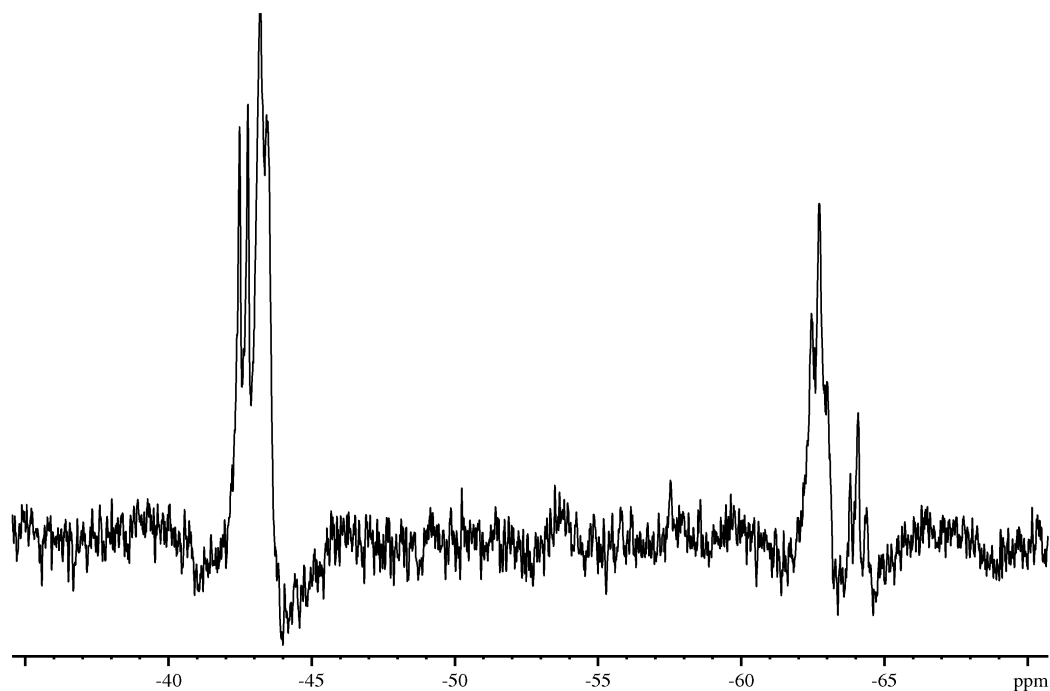
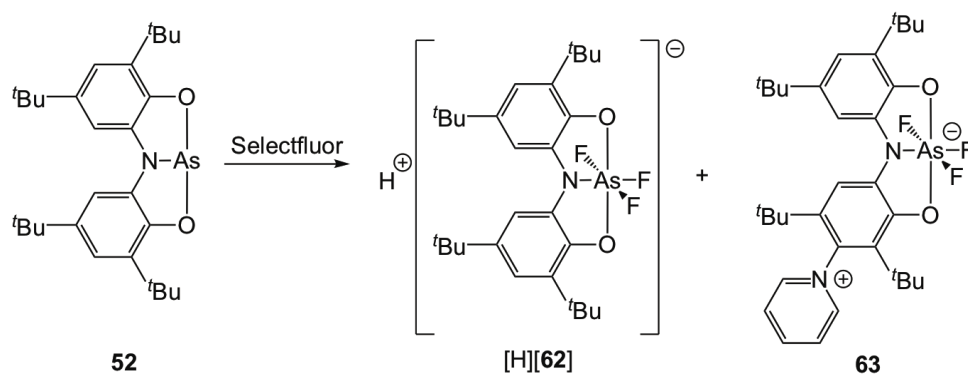


Figure 4.11: ^{19}F NMR spectrum of mixture of **62** and **63**.



Scheme 4.9: Reaction of **52** with Selectfluor.

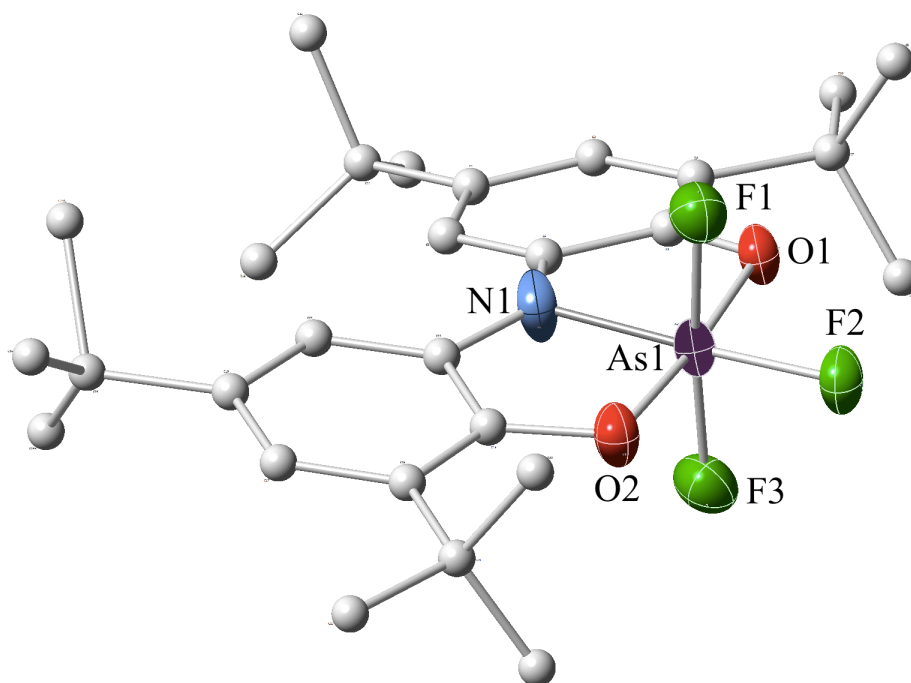


Figure 4.12: Molecular structure of [H][**62**]. Anisotropic displacement ellipsoids pictured are set at 50% probability. Solvent of crystallization and all hydrogen atoms omitted for clarity. Atoms of the ligand are pictured as spheres of arbitrary radius.

Table 4.9 – Selected bond lengths and bond angles for **62**.

Bond lengths	62	Bond angles	62
As1–N1	1.857(2) Å	O1–As1–O2	174.69(7)°
As1–O1	1.815(2) Å	N1–As1–O1	87.04(8)°
As1–O2	1.815(2) Å	N1–As1–O2	87.74(8)°
As1–F1	1.786(2) Å	N1–As1–F1	91.81(9)°
As1–F2	1.713(2) Å	N1–As1–F2	177.75 (9)°
As1–F3	1.762(2) Å	N1–As1–F3	93.46(10)°

Upon slow diffusion of hexane into the deep blue reaction mixtures, yellow and red crystals were obtained. The structures of the yellow (**62**) and red crystals (**63**) were confirmed by single crystal X-ray diffraction. Scheme 4.9 illustrates the reaction of **52** with Selectfluor to afford two arsenic(V) complexes, [H][**62**] and **63**.

The molecular structure of **62** exhibits an anionic hexa-coordinate arsenic(V) complex exhibiting an almost perfect octahedral geometry about the arsenic centre (As1), with two

planar (ONO)³⁻ ligands (O1–As1–O2 for **62** = 174.69(7)°). The (ONO)³⁻ ligand occupies the meridional positions and three fluorine atoms occupy the remaining sites of the octahedron (Figure 4.12). Table 4.9 shows selected bond lengths and bond angles for **62**. The As1–N1 bond length of **62** (1.857(2) Å) is statistically identical to the **52** (1.862(3) Å). Interestingly, the fluorine atom (F2) that is *trans* to ligand nitrogen atom (N1) is significantly shorter than the fluorine atoms (F1 and F3) located at the axial positions.

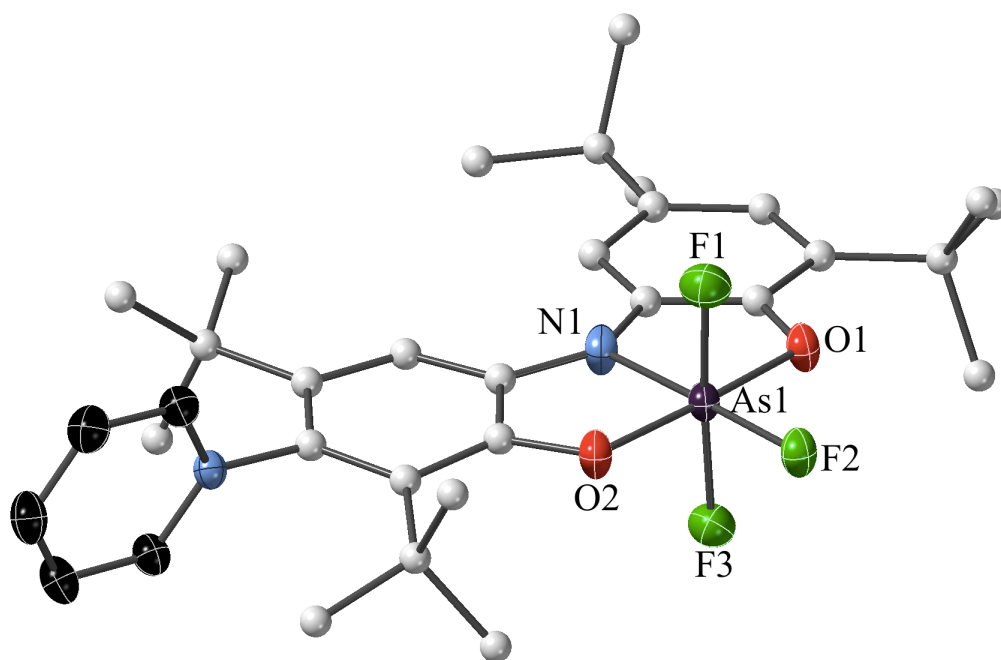


Figure 4.13: Molecular structure of **63**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 4.10 – Selected bond lengths and bond angles for **63**.

Bond lengths		Bond angles	
	63		63
As1–N1	1.853(2) Å	O1–As1–O2	174.97(7)°
As1–O1	1.814(2) Å	N1–As1–O1	87.19(7)°
As1–O2	1.801(2) Å	N1–As1–O2	87.94(7)°
As1–F1	1.747(2) Å	N1–As1–F1	93.78(9)°
As1–F2	1.730(2) Å	N1–As1–F2	178.77(8)°
As1–F3	1.773(2) Å	N1–As1–F3	92.71(8)°

The arrangement of the fluorine atoms revealed by single crystal X-ray diffraction studies is consistent with the observed ^{19}F NMR spectrum. The axial F1 and F3 atoms are chemically equivalent, but not with the equatorial F2 atom. Therefore, the F1 and F3 atoms are coupling to the F2 atom giving rise to a $^2J_{\text{F-F}}$ coupling as a doublet, meanwhile, F2 atom is coupling to the F1 and F3 atoms giving rise to a $^2J_{\text{F-F}}$ coupling as a triplet with the same coupling constant.

The molecular structure of the red crystals (**63**) also reveal an octahedral arsenic(V) complexes. The structure of **63** reveals that C–H bond activation of one of the aromatic protons of the $(\text{ONO})^{3-}$ ligand has taken place and that a pyridinium cation has formed (Figure 4.13 and Table 4.10). The bond matrices of **63** greatly resemble to those found for **62**.

4.1.6 Conclusions

We have reported the characterisation and reactivity of an arsenic(III) complex chelated by the $(\text{ONO})^{3-}$ ligand, **52**. **52** can be prepared by employing the same synthetic protocol used for the synthesis of its lighter phosphorus analogue, **LIV**. **52** exhibits no reactivity towards ammonia in contrast to that which has been previously reported for **LIV**. Computational studies revealed that the reaction between **52** and ammonia is endothermic by $86 \text{ kJ}\cdot\text{mol}^{-1}$ due to the increased stabilisation of the +3 oxidation state on descending group 15. The LUMO of **52** is accessible when reacting the compound with charged nucleophiles (KO^tBu and KNPh_2) affording negatively charged arsenic(III) compounds **53** and **54**, respectively. The reaction of $[\text{K}(18\text{-crown-6})][\textbf{53}]$ with $[\text{PyH}][\text{OTf}]$ yielded **52** and HO^tBu , highlighting the difficulty associated with accessing arsenic(V) complexes. Furthermore, addition of electrophiles (MeOTf and HOTf) resulted in their association with the nitrogenation of the ligand backbone of **52** yielding arsenic(III) complexes, $[\textbf{56}][\text{OTf}]$ and $[\textbf{57}][\text{OTf}]$. Interestingly, reaction of HCl with **51** resulted in cleavage of ligand As–O bond and gave an

arsenic(III) compound, **58**. Oxidation of **51** with air (O₂) or Selectfluor allows us to access to related octahedral arsenic(V) complexes **61–63**.

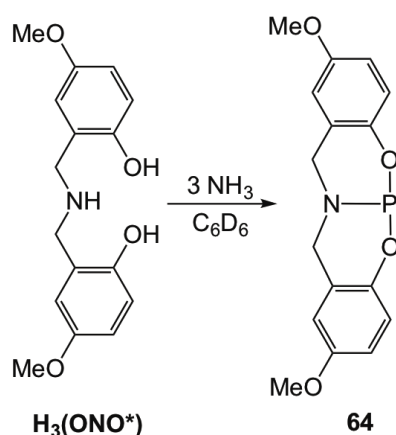
4.2 Complexes of phosphorus element bearing the 2,2'-[iminobis(methylene)]-bis[4-methoxy-phenol] (ONO*)³⁻ ligand

4.2.1 Overviews

We have also investigated a phosphorus(III) complex of the 2,2'-[iminobis(methylene)]-bis[4-methoxy-phenol] (ONO*)³⁻ ligand, which possesses two methylene carbons in the ligand backbone.⁹ Increasing the number of bonds between the donating atoms of a ligand provides more geometric freedom when phosphorus(III) is chelated by the ligand.

4.2.2 Synthesis of a phosphorus(III) complex bearing the (ONO*)³⁻ ligand

The reaction between the free ligand, H₃(ONO*), and PCl₃ in the presence of three molar equivalents of NEt₃ yielded a neutral tri-coordinate phosphorus(III) complex, **64** in a relatively low yield, 33% (Scheme 4.10).



Scheme 4.10: Synthesis of **64**.

The ³¹P NMR spectrum shows a triplet resonance at 114.4 ppm, with ³J_{P-H} coupling constant of 20 Hz arising from the coupling between the phosphorus and protons on the

methylene carbon atoms. The resonance collapses to a singlet in the absence of the proton coupling. In addition, the ^1H NMR spectrum of **64** reveals three sets of resonances at 6.78, 6.43 and 6.24 ppm and two sets of resonances at 4.00 and 3.42 ppm attributed to the aromatic protons and the methylene protons at the ligand backbone, respectively, implying a symmetric chemical equivalent environment about two aryl substituents. The resonance attributed to the O–CH₃ methyl proton was observed at 3.23 ppm.

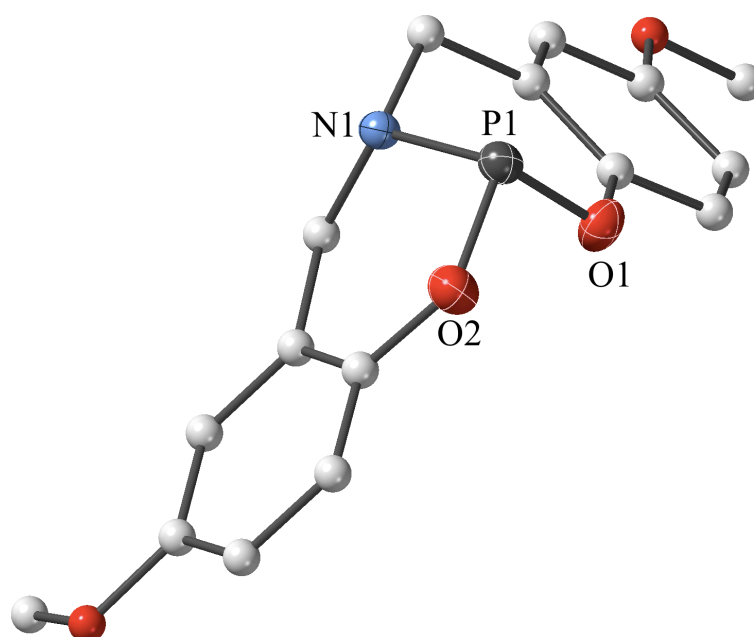


Figure 4.14: Molecular structure of **64**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms omitted for clarity. Atoms of the ligand are pictured as spheres of arbitrary radius.

Table 4.11 – Selected bond lengths and bond angles for **64**.

Bond lengths	64	Bond angles	64
P1–N1	1.699(2) Å	O1–P1–O2	99.36(6) °
P1–O1	1.675(2) Å	N1–P1–O1	99.46(6)°
P1–O2	1.614(2) Å	N1–P1–O2	102.07(6)°

Crystals of **64** suitable for single crystal X-ray diffraction studies were grown from a concentrated toluene solution at room temperature. The molecular structure of **64** exhibits a

distorted pyramidal geometry about the phosphorus centre (P1) (Figure 4.14) as the bond angles around phosphorus are almost identical ($\text{O1-P1-O2} = 99.36(6)^\circ$, $\text{N1-P1-O1} = 99.46(6)^\circ$, $\text{N1-P1-O2} = 102.07(6)^\circ$) giving rise to a sum of bond angles of 300.4° about the phosphorus(III) centre which is greater than that of 8-P-3 bent configuration phosphorus(III) complexes, **LII** and **LIV** (295.8° and 296.2° , respectively) but significantly smaller than that of a 10-P-3 planar configuration phosphorus(III) complex, **LI** (335.4°). Table 4.11 shows the selected bond lengths and bond angles of **64**. The X-ray diffraction analysis highlights that the methylene of the ligand backbone provides enough geometric freedom that phosphorus(III) is not constrained into a T-shaped geometry.

Table 4.12 compares selected bond lengths of **64** against those of **LIV**. The ligand P1–N1 and P1–O2 bond lengths of **64** is significantly smaller than those of **LIV**, while the P1–O1 bond lengths of **64** and **LIV** are statistically identical. As the phosphorus atom of **64** is less constrained by the ligand, it draws the ligand nitrogen and oxygen atoms closer.

Table 4.12 – Selected bond lengths for **64** and **LIV**.

Bond lengths	64	LIV
P1–N1	1.699(2) Å	1.757(1) Å
P1–O1	1.675(2) Å	1.672(1) Å
P1–O2	1.614(2) Å	1.659(2) Å

4.2.3 Reactivity of **64** towards small molecule substrates

4.2.3.1 Reactivity of **64** towards ammonia

Reaction between **64** and liquid ammonia or 1 atm of ammonia resulted no colour change. The reaction was monitored by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum displays negligible conversion to a doublet of multiplets resonances at -71.0 ppm which possesses a $^1J_{\text{P-H}}$ coupling of 800 Hz and collapses to a singlet in the absence of proton coupling (Figure 4.15). The magnitude of the $^1J_{\text{P-H}}$ coupling is comparable to that of the ammonia activation product **LIVa** ($^1J_{\text{P-H}}$ coupling = 819 Hz), which led us to postulate formation of

the phosphorus(V) N–H activation product, **65** (Scheme 4.11). Unfortunately, no further conversion is observed even at reflux temperatures.

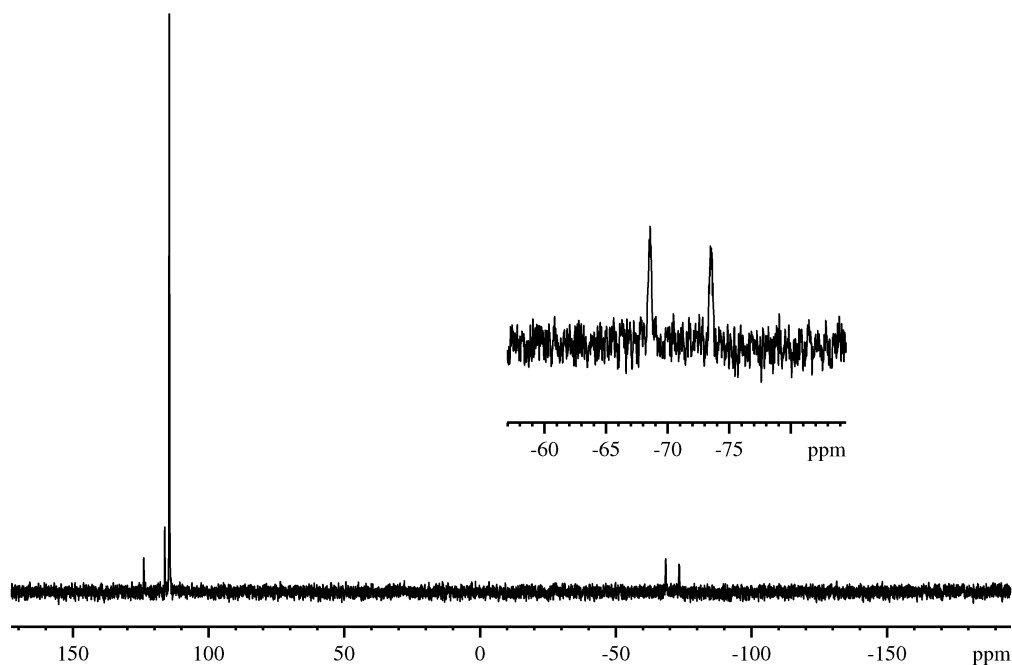
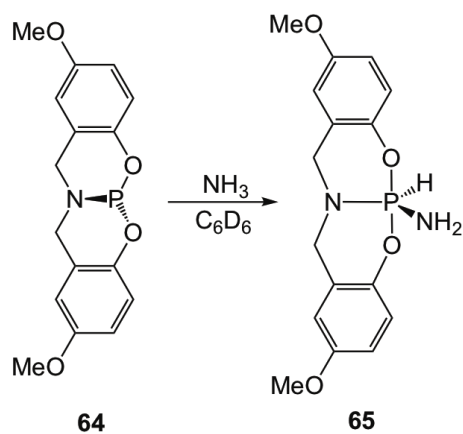


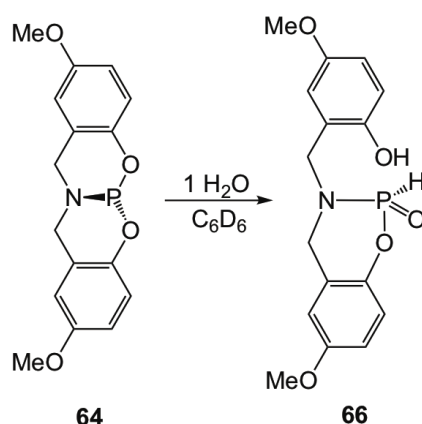
Figure 4.15: ^{31}P NMR spectrum of the reaction mixture when adding 1 atm ammonia to **64**.



Scheme 4.11: Reaction of **64** with 1 atm ammonia resulted in negligible conversion to **65**.

4.2.3.2 Reactivity of **64** towards a stoichiometric quantity of water

These results encouraged us to attempt activation of water. **64** was slowly hydrolysed by a stoichiometric quantity of water to afford a neutral phosphorus(V) compound, **66** (Scheme 4.12). The ^{31}P NMR spectrum of **66** shows a doublet of multiplets resonance at 5.4 ppm ($^1J_{\text{P-H}}$ coupling = 664 Hz) corresponding to the coupling between the phosphorus and an adjacent hydrogen. This resonance collapses to a singlet upon proton decoupling.



Scheme 4.12: Reaction of **64** with one molar equivalent of water.

In the ^1H NMR spectrum of **66**, this hydrogen atom was found at 7.76 ppm as a doublet with a coupling constant of 664 Hz, consistent with the observed ^{31}P NMR spectrum. The resonance attributed to the aryloxyde proton was observed at 12.21 ppm. It also displays six resonances in a region of 7.27–6.64 ppm and four resonances in the region of 5.13–4.30 ppm attributed to the aromatic protons and the methylene protons of the ligand backbone respectively, implying an asymmetric environment about two aryl substituents.

Crystals of **66** suitable of single crystal X-ray diffraction were grown by slow diffusion of hexane into a concentrated pyridine solution of the product. The molecular structure of **66** reveals the cleavage of a ligand P–O bond and displays a tetrahedral structure about the phosphorus atom (Figure 4.16 and Table 4.13) as the bond angles around the phosphorus centre are almost identical. As one of the P–O bonds have been cleaved, the phosphorus(III)

centre is no longer constrained by the ligand, giving rise to a shorter P1–N1 and P1–O1 bonds (P1–N1 = 1.632(2) Å for **66** and 1.699(2) Å for **64**; P1–O1 = 1.601(2) Å for **66** and 1.675(2) Å for **64**). The phosphorus(III) from the precursor has been oxidised to phosphorus(V). The P1–O5 bond length (1.469(2) Å) is shorter than the literature value of P–O double bond (1.52 Å) which is indicative of multiple bond character.

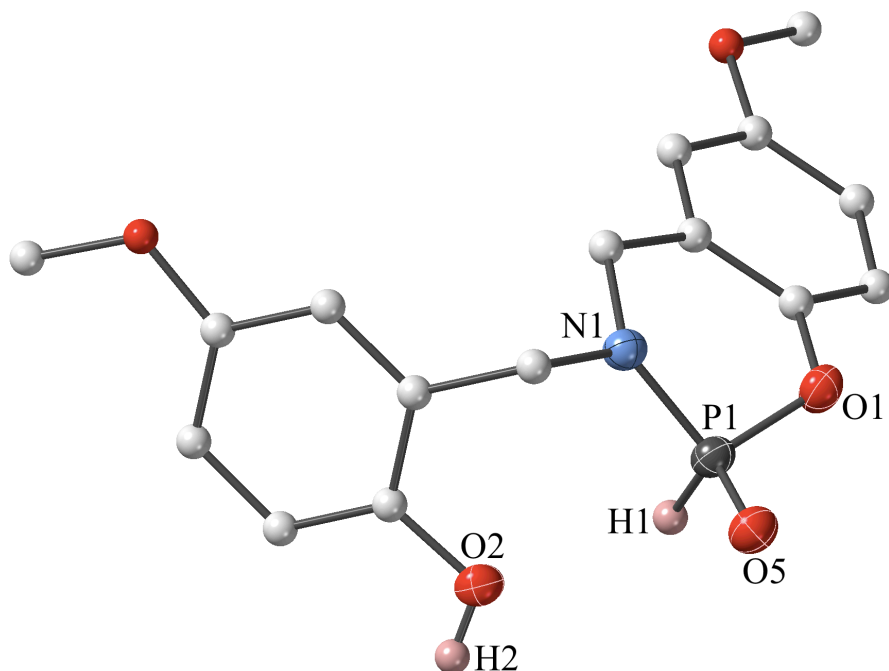


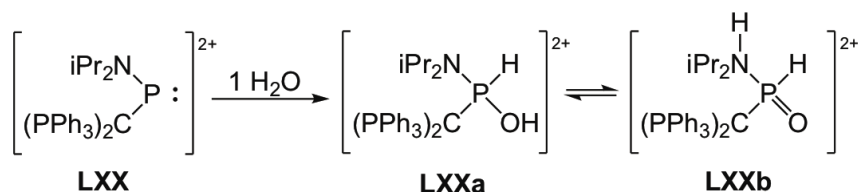
Figure 4.16: Molecular structure of **66**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1 and H2, omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

Table 4.13 – Selected bond lengths and bond angles for **66**.

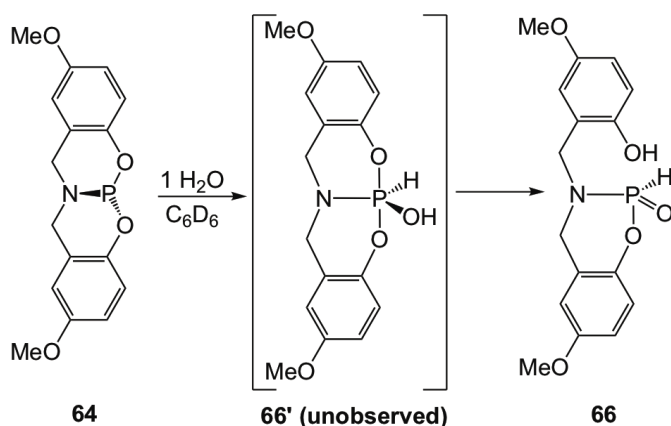
Bond lengths	66	Bond angles	66
P1–N1	1.632(2) Å	O1–P1–O5	110.92(7) °
P1–O1	1.601(2) Å	N1–P1–O1	102.72(6)°
P1–O5	1.469(2) Å	N1–P1–O5	110.92(7)°
P1–H1	1.30(2) Å	N1–P1–H1	111.3(9)°

The hydrolysis of **64** is consistent with the observation of the hydrolysis of an unsaturated phosphorus dication, **LXX**, reported by Vidovic.¹⁰ Vidovic showed that the **LXX** underwent oxidative addition upon hydrolysis to form **LXXa** and his ¹H NMR analysis

showed that a fluxional process occurs between **LXXa** and **LXXb** (Scheme 4.13). It led us to postulate that the mechanism of hydrolysis of **64** involves the deprotonation of water followed by attack of the hydroxide group at the phosphorus centre to yield a phosphorus(V) trigonal bipyramidal intermediate, **66'**. Then, the hydroxide O–H proton migrates to an oxygen atom resulting in the cleavage of the P–O ligand bond to form the more thermodynamically stable product, **66** (Scheme 4.14). The proposed mechanism also explains the reactivity difference of **64** towards water and ammonia. As protons of ammonia are much less Lewis acidic than those of water, **64** is much less reactive towards ammonia.



Scheme 4.13: Hydrolysis of **LXX**, reported by Vidovic.¹⁰



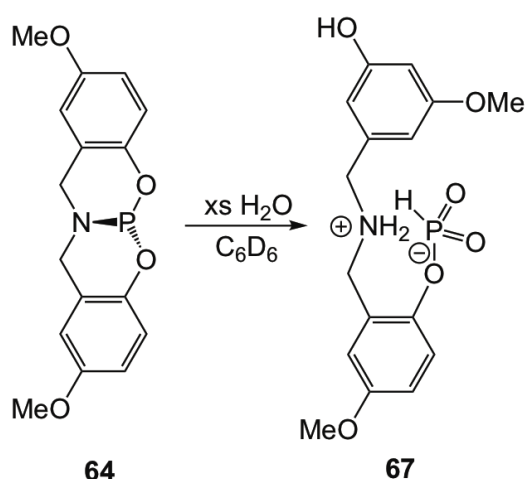
Scheme 4.14: Proposed mechanism for the reaction of **64** with one molar equivalent water.

4.2.3.3 Reactivity of **64** towards excess amounts of water

In the presence of excess amounts of water, a further phosphorus(V) hydrolysis product, **67**, was obtained (Scheme 4.15). The ³¹P NMR spectrum of **67** shows a resonance at 2.9 ppm as a doublet (¹J_{P–H} coupling = 626 Hz) arising from the coupling of the phosphorus(V) atom with an adjacent hydrogen. The ³¹P resonance collapses to a singlet in the absence of the

proton coupling. Similarly, in the ^1H NMR spectrum of **66**, a resonance attributed to the phosphorus bonded hydrogen was observed as a doublet at 7.75 ppm with a $^1J_{\text{P-H}}$ coupling constant of 626 Hz. The aryloxyde proton resonance was found at 13.40 ppm. There were six resonances in the range of 7.72–6.91 ppm attributed to the aromatic protons, implying an asymmetric environment about two aryl substituents.

Crystals of **67** suitable for single crystal X-ray crystallography were grown by slow diffusion of hexane into a concentrated pyridine solution. The molecular structure of **67** shows an almost ideal tetrahedral geometry around the phosphorus(V) atom giving rise to the sum of bond angle of 442.57° , which is similar to the sum of bond angles of a perfect tetrahedron (438°) (Figure 4.17 and Table 4.14). The P1–O5 and P1–O6 bond lengths (1.500(2) Å and 1.471 Å) are close to reported values for P–O double bonds (1.52 Å).



Scheme 4.15: Reaction of **64** with excess amounts of water.

Table 4.14 – Selected bond lengths and bond angles for **67**.

Bond lengths		Bond angles	
	67		67
P1–O1	1.626(2) Å	O1–P1–O5	108.56(8) °
P1–O5	1.500(2) Å	O5–P1–O6	118.51(9)°
P1–O6	1.471(2) Å	O6–P1–H1	111.4(10)°
P1–H1	1.34(2) Å	O1–P1–H1	104.1(10)°

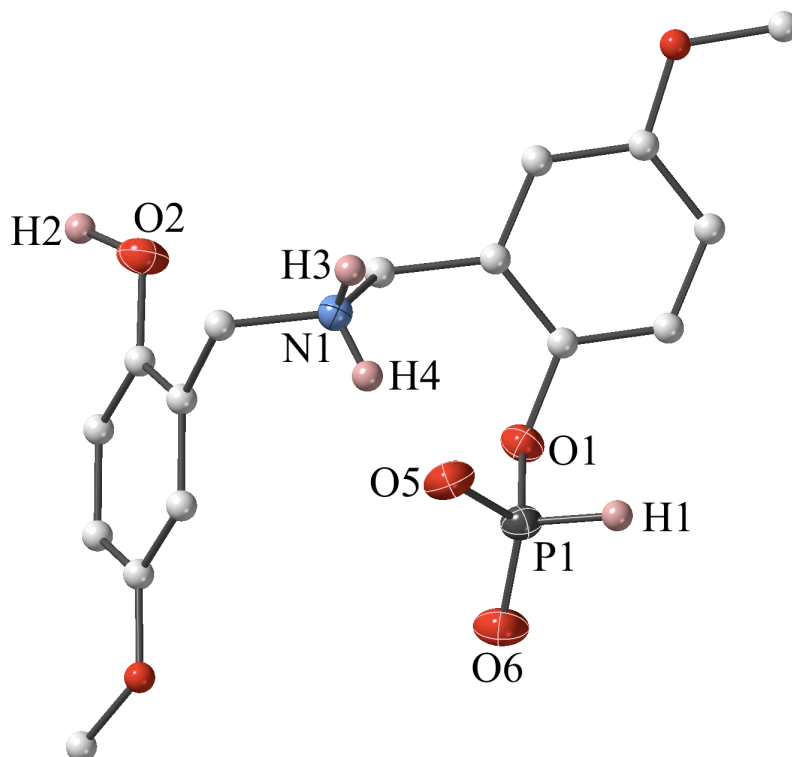
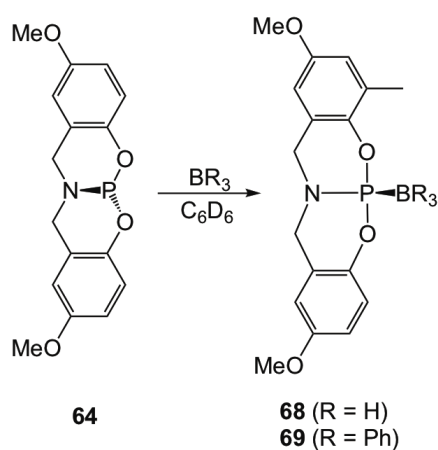


Figure 4.17: Molecular structure of **67**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1–H4, omitted for clarity. Atoms of the ligand, except N1, O1 and O2 are pictured as spheres of arbitrary radius.

4.2.3.4 Reactivity of **64** towards boranes

To order to investigate the accessibility of the lone pair on phosphorus in **64**, we have investigated the reactivity of **64** towards Lewis acids. Reactions between **64** and $\text{H}_3\text{B}\cdot\text{py}$ and BPh_3 yielded Lewis acid–base adducts **68** and **69**, respectively (Scheme 4.16).



Scheme 4.16: Reactions of **64** with boranes ($\text{H}_3\text{B}\cdot\text{py}$ and BPh_3).

The ^{31}P NMR spectrum of **68** displays a multiplet at 111.3 ppm and the ^{11}B NMR spectrum shows a doublet at -40.4 ppm with a $^1J_{\text{B-P}}$ coupling of 88 Hz. The ^1H NMR spectrum in C_6D_6 displays a set of borane proton resonances in the range from 1.40 to 2.24 ppm. The resonances attributed to the ligand protons are similar to those found in the parent compound.

Both crystals of **68** and **69** suitable for single crystal X-ray crystallography were grown by slow diffusion of hexane into concentrated toluene solutions. The molecular structures of **68** and **69** show almost ideal tetrahedral geometries around the phosphorus(III) atom giving rise to a sum of bond angles of 445.58° and 432.74° (for **68** and **69**, respectively) (Figures 4.18 and 4.19). Tables 4.15 show selected bond lengths and bond angles for **68** and **69**. All P1–N1 and P1–O bonds of **68** and **69** are shorter than those of starting material **64**, implying that the Lewis acidic borane draws electron density from the ligand framework shortening P–N and P–O interaction. The B1–P1 bond length of **69** is longer than that of **68** (1.871(2) Å), arising from the steric repulsion from the phenyl substituents.

Table 4.15 – Selected bond lengths and bond angles for **68** and **69**.

Bond lengths and Bond angles	68	69
P1–N1	1.664(2) Å	1.661(2) Å
P1–O1	1.601(2) Å	1.605(1) Å
P1–O2	1.601(2) Å	1.605(1) Å
P1–B1	1.871(2) Å	1.971(2) Å
O1–P1–O2	$108.48(6)^\circ$	$107.17(5)^\circ$
N1–P1–O1	$104.22(6)^\circ$	$104.43(5)^\circ$
N1–P1–O2	$114.22(6)^\circ$	$103.00(5)^\circ$
N1–P1–B1	$118.66(8)^\circ$	$118.14(5)^\circ$

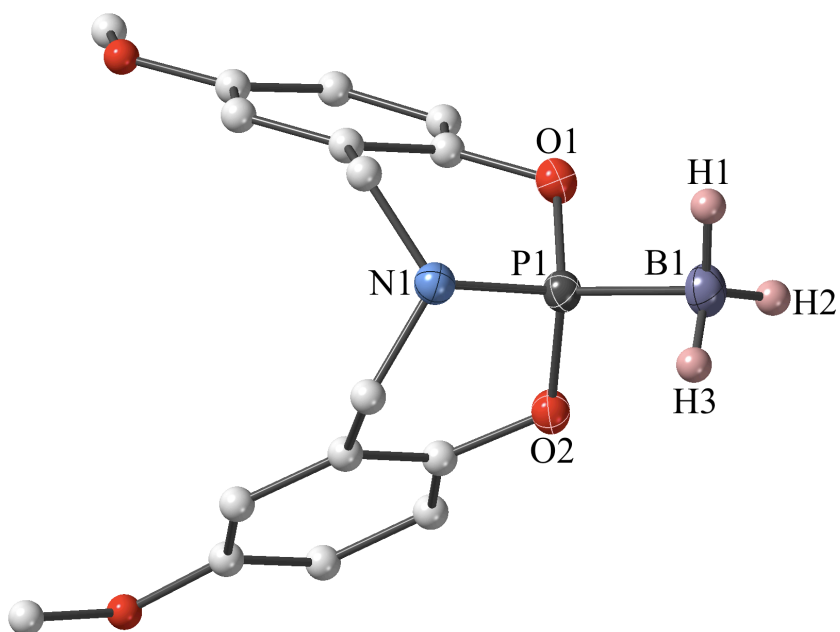


Figure 4.18: Molecular structure of **68**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms, except H1–H3, omitted for clarity. Atoms of the ligand, N1, O1 and O2, are pictured as spheres of arbitrary radius.

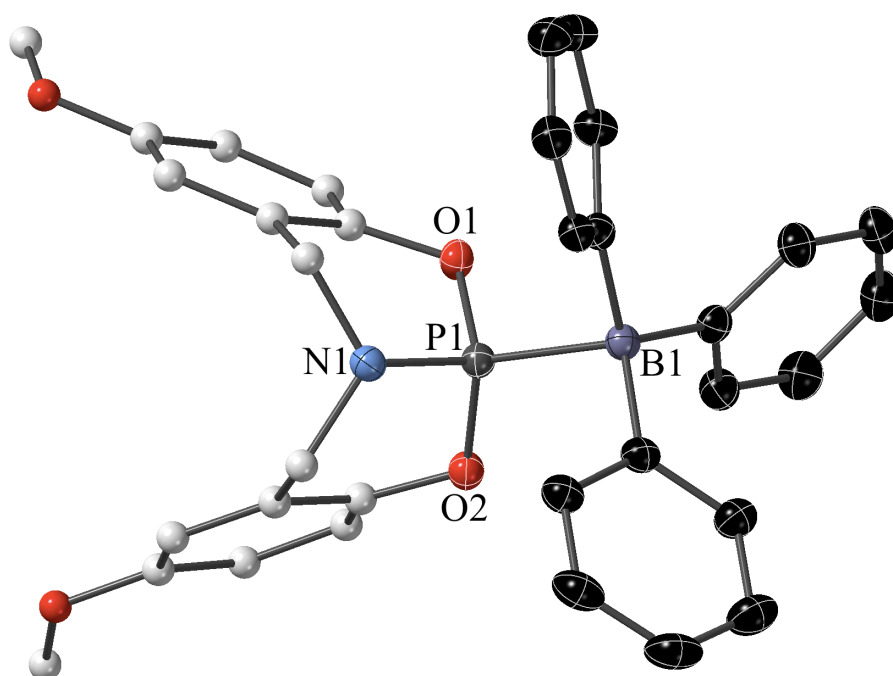


Figure 4.19: Molecular structure of **69**. Anisotropic displacement ellipsoids pictured are set at 50% probability. All hydrogen atoms omitted for clarity. Atoms of the ligand, except N1, O1 and O2, are pictured as spheres of arbitrary radius.

4.2.4 Conclusions

We have investigated a phosphorus(III) complex bearing the (ONO*)³⁻ ligand (**64**) which possesses two methylene carbons in the ligand backbone and provides a less rigid coordination environment for P(III). The molecular structure of **64** exhibits an ideal pyramidal geometry about the phosphorus(III). Reaction of **64** with ammonia resulted in negligible conversion to a P(V) compound, **65**. In addition, hydrolysis of **64** resulted in formation of P(V) compounds **66** and **67**. We hypothesise that the formation of **66** come from a P(V)(H)(OH) intermediate (**66'**) via a stepwise nucleophilic pathway. The lone pair on phosphorus in **64** can also react with borane to afford Lewis acid–base adducts, **68** and **69**.

4.3 Reference

- (1) Arduengo, A. J.; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Mizen, M. B. *J. Am. Chem. Soc.* **1987**, *109* (3), 627.
- (2) Zhao, W.; McCarthy, S. M.; Lai, T. Y.; Yennawar, H. P.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136* (50), 17634.
- (3) Dunn, N. L.; Ha, M.; Radosevich, A. T. *J. Am. Chem. Soc.* **2012**, *134* (28), 11330.
- (4) McCarthy, S. M.; Lin, Y. C.; Devarajan, D.; Chang, J. W.; Yennawar, H. P.; Rioux, R. M.; Ess, D. H.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136* (12), 4640.
- (5) Cui, J.; Li, Y.; Ganguly, R.; Inthirarajah, A.; Hirao, H.; Kinjo, R. *J. Am. Chem. Soc.* **2014**, *136* (48), 16764.
- (6) Robinson, T. P.; De Rosa, D. M.; Aldridge, S.; Goicoechea, J. M. *Angew. Chem. Int. Ed.* **2015**, *54* (46), 13758.

- (7) Pal, A.; Vanka, K. *Inorg. Chem.* **2016**, 55 (2), 558.
- (8) Zeng, G.; Maeda, S.; Taketsugu, T.; Sakaki, S. *Angew. Chem. Int. Ed.* **2014**, 53 (18), 4633.
- (9) Searcey, M.; Grewal, S. S.; Madeo, F.; Tsoungas, P. G. *Tetrahedron Lett.* **2003**, 44 (35), 6745.
- (10) Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidovič, D. *Chem. - A Eur. J.* **2014**, 20 (22), 6628.

Chapter 5

Conclusions and future work

5.1 Conclusions and future work

In this work, a number of phosphorus(III) complexes bearing geometry constrained ligands were prepared, and their ability to activate small molecules possessing polar X–H bonds (X = N, O, etc.) was investigated.^{1–6} We explored the electronic and steric properties of these geometry constrained systems in an effort to enhance their reactivity.

The synthesis of base-supported group 13 complexes bearing the *N,N*-bis(3,5-di-*tert*-butyl-2-(phenolate) amide (ONO)^{3–} ligand, E(ONO)·L (E = B, Al, Ga; L = Lewis base) was also studied. We reasoned that by replacing the phosphorus centre with group 13 elements this would lower the energy of the LUMO, making these systems more electrophilic. In the case of the boron complexes, it was found that B(ONO) type species were formed *in-situ* and are capable of THF activation. A base-stabilised boron compound could be prepared by reacting H₃(ONO) with NMe₃·BH₃ and was found to further activate the O–H bonds in water and ethanol. The aluminium analogue of E(ONO)·L revealed a highly stable bimetallic structure, which was capable of O–H bond cleavage. Finally, a gallium hydride species, Ga(H)(THF){(ON(H)O)} was synthesised which is capable of activating aldehydes to form gallium alkoxide compounds, which could be employed as an active catalyst for the hydroboration of benzaldehyde. Future work in this field will involve exploring the mechanism of this catalytic cycle with a range of aldehydes and ketones.

We postulated that an alternative route to decreasing the HOMO–LUMO gap of these geometry constrained complexes would be to prepare anionic group 14 analogues, as these systems are more electron rich at the group 14 centre. Anionic group 14 systems, [E(ONO)][–] (E = Ge, Sn) can be prepared via a two-step process, first by the synthesis of neutral compounds, E{ON(H)O}, followed by deprotonation using benzyl potassium in the presence of 18-crown-6. It was shown that the molecular structure of [Ge(ONO)][–] closely resembles that of its phosphorus(III) analogue,⁶ **LIV**, and that it similarly underwent facile

addition of water and ethanol to form the corresponding trigonal bipyramidal germanium(IV) complexes, whereas $[\text{Sn}(\text{ONO})]^-$ underwent efficient transelementation reactions with phenylsilane resulting in a five-coordinate Si(IV) complex.

The synthesis of four novel neutral constrained geometry group 14 systems bearing a xanthene based ligand framework, $(^{\text{Mes}}\text{NON})^{2-}$ and $(^{\text{Cy}}\text{NON})^{2-}$, was also discussed. First, Reactions of $\text{H}_2(^{\text{Mes}}\text{NON})$ and $\text{H}_2(^{\text{Cy}}\text{NON})$ with two molar equivalents of KHMDS formed $\text{K}_2(^{\text{Mes}}\text{NON})$ and $\text{K}_2(^{\text{Cy}}\text{NON})$, respectively. Which were subsequently reacted with $\text{ECl}_2 \cdot \text{dioxane}$ ($\text{E} = \text{Ge}$ and Sn) to afford $\text{E}(^{\text{Mes}}\text{NON})$ and $\text{E}(^{\text{Cy}}\text{NON})$, correspondingly. The molecular structures of these compounds exhibits a distorted pyramidal geometry about the group 14 centres and the group 14 elements are pushed away from the xanthene ligand binding site, evidenced by their long Sn–O and Ge–O bonds. These systems were found to be very reactive towards hydrolysis, and their highly hydroscopic nature hindered further studies toward small molecule activation.

Finally, we reported the characterisation and reactivity of an arsenic(III) complex chelated by the $(\text{ONO})^{3-}$ ligand, $\text{As}(\text{ONO})$. $\text{As}(\text{ONO})$ exhibits no reactivity towards ammonia. Computational studies revealed that the reaction between $\text{As}(\text{ONO})$ and ammonia is endothermic by $86 \text{ kJ} \cdot \text{mol}^{-1}$ due to the increased stabilisation of the +3 oxidation state on descending group 15. The LUMO of $\text{As}(\text{ONO})$ is accessible when reacting the compound with charged nucleophiles, such as KO^tBu and KNPh_2 , whereas the addition of electrophiles (MeOTf and HOTf) revealed reactivity at the nitrogen on the ligand backbone. In addition, addition of HCl towards $\text{As}(\text{ONO})$ resulted in cleavage of As–O bond and gave an arsenic(III) compound.

A phosphorus(III) complex bearing the 2,2'-[iminobis(methylene)]- bis[4-methoxy-phenol] $(\text{ONO}^*)^{3-}$ ligand, $\text{P}(\text{ONO}^*)$, was prepared. This complex possesses two methylene carbons

on the ligand backbone, which provides a less rigid coordination environment for P(III). It was found that the molecular structure of P(ONO*) exhibits an ideal pyramidal geometry about the phosphorus(III). Reaction of P(ONO*) with 1 atm. of ammonia resulted in negligible conversion to the P(V) compound, however P(ONO*) would undergo hydrolysis. P(ONO*) was shown to exhibit similar reactivity to classical phosphines, as its lone pair on was found to coordinate boranes to afford the Lewis acid–base adducts.

5.2 References

- (1) Arduengo, A. J.; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Mizen, M. *B. J. Am. Chem. Soc.* **1987**, *109* (3), 627.
- (2) Dunn, N. L.; Ha, M.; Radosevich, A. T. *J. Am. Chem. Soc.* **2012**, *134* (28), 11330.
- (3) Zhao, W.; McCarthy, S. M.; Lai, T. Y.; Yennawar, H. P.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136* (50), 17634.
- (4) McCarthy, S. M.; Lin, Y. C.; Devarajan, D.; Chang, J. W.; Yennawar, H. P.; Rioux, R. M.; Ess, D. H.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136* (12), 4640.
- (5) Cui, J.; Li, Y.; Ganguly, R.; Inthirarajah, A.; Hirao, H.; Kinjo, R. *J. Am. Chem. Soc.* **2014**, *136* (48), 16764.
- (6) Robinson, T. P.; De Rosa, D. M.; Aldridge, S.; Goicoechea, J. M. *Angew. Chem. Int. Ed.* **2015**, *54* (46), 13758.

Chapter 6

Experimental

6.1 General synthetic methods

All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk or glovebox techniques (MBraun UNILab glovebox maintained at <0.1 ppm O₂ and <0.1 ppm H₂O) unless otherwise noted.

Tetrahydrofuran (THF; Fisher, HPLC grade) and 1,4-dioxane (Alfa Aesar, 99+%, stab. 5-10 ppm BHT) were distilled from a potassium/benzophenone mixture. Pyridine (Alfa Aesar, 99+%) was distilled from CaH₂. Acetonitrile (MeCN; Sigma Aldrich, CHROMASOLV[®] gradient grade for HPLC, ≥99.9%), dichloromethane (CH₂Cl₂; Sigma Aldrich, HPLC grade), chloroform (CHCl₃; Sigma Aldrich, HPLC grade), hexane (Sigma Aldrich, HPLC grade), pentane (Sigma Aldrich, HPLC grade) and toluene (Sigma Aldrich, HPLC grade) were purified using an MBraun SPS-800 solvent system. n-Heptane (Fluka Analytical) was degassed via freeze-pump-thaw method and then used. C₆D₆ (Sigma Aldrich, 99.6%), *d*₈-THF (Eurisotop, >99.5%), *d*₅-pyridine (Eurisotop, >99.5%), CD₂Cl₂ (Eurisotop, >99.5%) and CDCl₃ (Aldrich, 99.8%) were dried over CaH₂, vacuum distilled and degassed before use. All dry solvents were stored under argon in gas-tight ampoules over activated 3 Å molecular sieves. Deionised water was obtained from a Millipore Milli-Q machine and then sparged with N₂ gas overnight before used. Ethanol (Sigma Aldrich, >99.8%) was sparged with N₂ gas for four hours before used and dried over activated 3 Å molecular sieves.

The suppliers and purification procedures for commercially available chemicals are detailed in Table 6.1.

Table 6.1 – Suppliers and purification procedures for commercially purchased chemicals.

Reagents	Suppliers	Purity	Purification
1,4-Diazabicyclo-[2.2.2]octane	Alfa Aesar	98%	Used as received
1,4,7,10,13,16-Hexa-	Alfa Aesar	99%	Purified by sublimation

oxacyclooctadecane			
2-Hydroxy-5-methoxybenzaldehyde	Aldrich	98%	Used as received
3,5-di- <i>tert</i> -butylcatechol	Acros Organics	99%	Used as received
4,4,5,5-Tetramethyl-1,3,2-dioxaborolane	Sigma-Aldrich	97%	Used as received
4,5-Dibromo-2,7-di- <i>tert</i> -butyl-9,9-dimethylxanthene	Chem Cruz	Unspecified	Used as received
4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane	VWR	99%	Used as received
Aluminum chloride	Alfa Aesar	99.985%	Used as received
Ammonia gas	BOC	Anhydrous	Used as received
Ammonium formate	Sigma-Aldrich	97%	Used as received
Ammonium hydroxide	Alfa Aesar	28% aqueous	Used as received
Arsenic(III) chloride	Sigma-Aldrich	99.99%	Used as received
Benzaldehyde	Sigma-Aldrich	99.5%	Used as received
Bis(dibenzylideneacetone)palladium(0)	Acros Organics	Unspecified	Used as received
Borane ammonia	Sigma-Aldrich	97%	Used as received
Borane trimethylamine complex	Sigma-Aldrich	97%	Used as received
Borane triphenylphosphine complex	Sigma-Aldrich	97%	Used as received
Boron tribromide	Aldrich	99+%	Used as received
Carbon dioxide gas	BOC	CP grade	Used as received
Carbon monoxide gas	BOC	99.9%	Used as received
Catecholborane	Sigma-Aldrich	98%	Used as received
Cyclohexylamine	Aldrich	99%	Used as received
Gallium tribromide	Sigma-Aldrich	99.999%	Used as received
Gallium trichloride	Sigma-Aldrich	99.99%	Used as received
Germanium(II) chloride dioxane complex (1:1)	Aldrich	Unspecified	Used as received

Germanium(IV) chloride	Strem	99.99%	Used as received
Graphite powder, crystalline, -325 mesh	Alfa Aesar	99%	Used as received
Hydrochloride	Alfa Aesar	2 M in diethyl ether	Used as received
Hydroxylamine hydrochloride	Alfa Aesar	99%	Used as received
<i>Iso</i> -butyraldehyde	Sigma-Aldrich	99.5%	Used as received
Lithium aluminium hydride	Sigma-Aldrich	95%	Used as received
Methyl trifluoromethanesulfonate	Apollo	98%	Used as received
<i>n</i> -Butyllithium solution	Acros Organics	2.5 M in hexanes	Used as received
Palladium on carbon	Aldrich	10 wt. % loading, matrix activated carbon support	Used as received
Phenylacetylene	Sigma-Aldrich	98%	Used as received
Phenylsilane	Aldrich	97%	Used as received
Phosphorus trichloride	Sigma-Aldrich	99%	Distilled prior to use
Potassium bis-(trimethylsilyl) amide	Sigma-Aldrich	95%	Used as received
Potassium chunks	Strem	99.95%	Used as received
Potassium hydride	Sigma-Aldrich	30% wt dispersion in mineral oil	Washed with hexane, then dried in vacuo before use
Potassium <i>tert</i> -butoxide	Aldrich	≥98%	Used as received
Pyridinium trifluoromethanesulfonate	Alfa Aesar	98%	Used as received
Selectfluor® fluorinating reagent	Aldrich	>95% in F+ active	Used as received
Silicon tetrachloride	Aldrich	99%	Used as received
Sodium borohydride	Sigma-Aldrich	98%	Used as received
Sodium <i>tert</i> -butoxide	Acros Organics	98%	Used as received

Sodium triethylborohydride solution	Aldrich	1.0 M in THF	Used as received
<i>tert</i> -Butylamine	Aldrich	98%	Used as received
Tetrabutylammonium fluoride solution	Aldrich	1 M in THF	Used as received
Tin(II) chloride	Acros Organics	98%	Used as received
Tin(IV) chloride	Aldrich	99%	Used as received
Triethylamine	Alfa Aesar	99%	Distilled from CaH ₂ prior to use
Trifluoroacetic acid	Alfa Aesar	99%	Used as received
Trimethylsilyl cyanide	Aldrich	98%	Used as received

N,N-bis(3,5-di-*tert*-butyl-2-phenol)ammonium trifluoroacetate ([H₄(ONO)][TFA]), *N,N*-bis(3,5-di-*tert*-butyl-2-phenolate)amine (H₃(ONO)) were prepared according to literature procedure.¹⁻²

The synthesis of 4,5-(*N,N'*-bis-mesitylamino)-2,7-di-*tert*-butyl-9,9-dimethyl-xanthene and 4,5-(*N,N'*-bis-cyclohexylamino)-2,7-di-*tert*-butyl-9,9-dimethyl-xanthene were adapted from a literature preparation.³

5-methoxy-2-hydroxybenzaldehyde oxime and 2,2'-[iminobis(methylene)]-bis[4-methoxyphenol] (H₃(ONO)*) were adapted from a literature preparation.⁴⁻⁵

1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene dichlorosilylene (IPrSiCl₂),⁶ benzyl potassium (BzK)⁷ and potassium diphenylamide (KNPh₂)⁸ were prepared via previously reported syntheses.

Tin dichloride dioxane (SnCl₂·dioxane) was synthesized by extracting anhydrous tin dichloride (SnCl₂) with a Soxhlat extraction and allowed to crystallise from hot dioxane, then dried thoroughly under vacuum.

KC₈ was prepared by stirring potassium with eight equivalents of graphite at temperatures greater than 200 °C under argon by using a heat gun to yield a uniform bronze solid.

6.1 Syntheses of compounds

6.1.1 Chapter 2 – Complexes of group 13 elements bearing the *N,N'*-bis(3,5-di-*tert*-butyl-2-phenolate) amide ligand

6.1.1.1 B{ON(OC₄H₈)O} (1)

H₃(ONO) (118 mg, 0.277 mmol) and BBr₃ (26.3 μL, 0.277 mmol) were dissolved in THF (2 mL). NEt₃ (77.4 μL, 0.554 mmol) was added to the stirred solution yielding a colourless solution and white precipitate. The mixture was stirred at room temperature for two hours. All volatiles were removed under a dynamic vacuum and the product was extracted in hexane (3×5 mL). Removal of volatiles *in vacuo* yielded **1** as a pale white solid. Crystals were obtained by slow diffusion of hexane into a concentrated toluene solution of the product. Yield: 116 mg (83%). EI MS: *m/z* calcd. for C₃₂H₄₈BNO₃: 505.3727; found: 505.3741. ¹H NMR (400.20 MHz, C₆D₆, 298 K): δ (ppm) 7.31 (d, ⁴*J*_{H-H} = 2 Hz, 2H; Ar), 7.20 (d, ⁴*J*_{H-H} = 2 Hz, 2H; Ar), 3.99 (m, 2H; BO(CH₂)₄), 3.19 (m, 2H; BO(CH₂)₄), 1.53 (s, 18H; ^tBu), 1.35 (m, 2H; BO(CH₂)₄), 1.26 (s, 18H; ^tBu), 1.17 (m, 2H; BO(CH₂)₄). ¹³C{¹H} NMR (100.63 MHz, C₆D₆, 298 K): δ (ppm) 153.5 (Ar), 141.5 (Ar), 136.2 (Ar), 135.5 (Ar), 123.4 (Ar), 113.9 (Ar), 63.6 (BO(CH₂)₄), 59.3 (BO(CH₂)₄), 35.1 (C(CH₃)₃), 34.7 (C(CH₃)₃), 32.7 (BO(CH₂)₄), 31.8 (C(CH₃)₃), 29.3 (C(CH₃)₃), 24.8 (BO(CH₂)₄). ¹¹B NMR (128.39 MHz, C₆D₆, 298K): δ (ppm) 14.6.

6.1.1.2 B(NMe₃)(ONO) (2) and [B{ON(H)O}]₂μ-O (3)

H₃(ONO) (428 mg, 1.01 mmol) and H₃B·NMe₃ (73.4 mg, 1.01 mmol) were dissolved in THF (5 mL) in an ampoule. The solution mixture was stirred in an oil bath at 90 °C for fourteen days. The solution was then allowed to cool down to room temperature. All volatiles were removed under a dynamic vacuum and the product was extracted in toluene (2×10 mL). Removal of volatiles *in vacuo* yielded **2** as a white solid. Crystals were obtained

by slow diffusion of hexane into a concentrated toluene solution of the product. Yield: 372 mg (75%). ^1H NMR (499.93 MHz, C_6D_6 , 298 K): δ (ppm) 7.60 (d, $^4J_{\text{H-H}} = 2\text{ Hz}$, 2H; Ar), 7.15 (d, $^4J_{\text{H-H}} = 2\text{ Hz}$, 2H; Ar), 1.87 (s, 9H, NCH_3), 1.59 (s, 18H; ^tBu), 1.43 (s, 18H; ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.71 MHz, C_6D_6 , 298 K): δ (ppm) 151.2 (Ar), 143.1 (Ar), 142.0 (Ar), 131.9 (Ar), 116.0 (Ar), 111.7 (Ar), 45.1 (NCH_3), 34.8 ($\text{C}(\text{CH}_3)_3$), 34.7 ($\text{C}(\text{CH}_3)_3$), 32.2 ($\text{C}(\text{CH}_3)_3$), 30.0 ($\text{C}(\text{CH}_3)_3$). ^{11}B NMR (160.40 MHz, C_6D_6 , 298 K): δ (ppm) 15.6 (br).

When synthesising **2** in bulk, trace amounts of hydrolysis product **3** were found and can be extracted into hexane. Removal of volatiles *in vacuo* yielded **3** as a white solid. Crystals were obtained from a concentrated hexane solution of the product at $-30\text{ }^\circ\text{C}$. ^1H NMR (400.20 MHz, C_6D_6 , 298 K): δ (ppm) 7.22 (s, 4H; Ar), 6.95 (s, 4H; Ar), 6.09 (br, 2H; NH), 1.36 (s, 36H; ^tBu), 1.29 (s, 36H; ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, C_6D_6 , 298 K): δ (ppm) 154.0 (Ar), 140.7 (Ar), 135.4 (Ar), 131.0 (Ar), 123.6 (Ar), 116.4 (Ar), 34.9 ($\text{C}(\text{CH}_3)_3$), 34.5 ($\text{C}(\text{CH}_3)_3$), 31.8 ($\text{C}(\text{CH}_3)_3$), 29.3 ($\text{C}(\text{CH}_3)_3$). ^{11}B NMR (128.40 MHz, C_6D_6 , 298 K): δ (ppm) 12.0 (br).

6.1.1.3 **B(OEt){ON(H)O} (4)**

2 (103 mg, 0.209 mmol) was dissolved in toluene and ethanol (61 μL , 1.05 mmol, 5 eq.) was syringed into the toluene solution (1 mL). Colourless crystals were grown overnight in the reaction mixture at room temperature. The solution was filtered and the crystals were dried under a dynamic vacuum. Yield: 82 mg (82%). ^1H NMR (499.93 MHz, C_6D_6 , 298 K): δ (ppm) 7.29 (s, 2H; Ar), 7.05 (s, 2H; Ar), 6.67 (s, 1H; NH), 3.94 (q, $^3J_{\text{H-H}} = 7\text{ Hz}$, 2H; OCH_2CH_3), 1.47 (s, 18H; ^tBu), 1.36 (t, $^3J_{\text{H-H}} = 7\text{ Hz}$, 3H; OCH_2CH_3), 1.26 (s, 18H; ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.71 MHz, C_6D_6 , 298 K): δ (ppm) 153.7 (Ar), 141.1 (Ar), 135.9 (Ar), 130.6 (Ar), 123.7 (Ar), 116.2 (Ar), 58.6 (OEt), 35.0 ($\text{C}(\text{CH}_3)_3$), 34.6 ($\text{C}(\text{CH}_3)_3$), 31.8 ($\text{C}(\text{CH}_3)_3$), 29.4 ($\text{C}(\text{CH}_3)_3$), 18.4 (OEt). ^{11}B NMR (128.39 MHz, C_6D_6 , 298 K): δ (ppm) 13.4 (br).

6.1.1.4 [K][B(O^tBu)(ONO)] ([K][5])

2 (359 mg, 0.729 mmol) and KO^tBu (81.8 mg, 0.729 mmol) were dissolved in THF (2 mL) and the solution mixture was stirred at room temperature for two hours. Removal of volatiles *in vacuo* yielded [K][**5**] as a white solid. Yield: 349 mg (88%). ¹H NMR (400.17 MHz, *d*₈-THF, 298 K): δ (ppm) 6.98 (d, ⁴*J*_{H-H} = 2 Hz, 2H; Ar), 6.68 (d, ⁴*J*_{H-H} = 2 Hz, 2H; Ar), 1.44 (s, 9H; O^tBu), 1.38 (s, 18H; ^tBu), 1.27 (s, 18H; ^tBu). ¹³C{¹H} NMR (125.71 MHz, *d*₈-THF, 298 K): δ (ppm) 153.6 (Ar), 144.2 (Ar), 137.8 (Ar), 130.4 (Ar), 115.2 (Ar), 111.7 (Ar), 34.7 (C(CH₃)₃), 34.7 (C(CH₃)₃), 32.5 (O^tBu), 32.4 (C(CH₃)₃), 30.0 (C(CH₃)₃). ¹¹B NMR (128.39 MHz, C₆D₆, 298 K): δ (ppm) 13.8 (br).

6.1.1.5 B(O^tBu){(ON(Me)O)} (**6**)

5 (340 mg, 0.623 mmol) was dissolved in toluene (2 mL) and MeOTf (68.2 μL, 0.623 mmol) was added to the solution yielding a colourless solution and white precipitate. The solution mixture was stirred overnight at room temperature. The solution was filtered and dried *in vacuo* yielded **6** as white solid. Crystals were obtained from a concentrated hexane solution. Yield: 252 mg (78%). ¹H NMR (400.17 MHz, C₆D₆, 298 K): δ (ppm) 7.28 (d, ⁴*J*_{H-H} = 2 Hz, 2H; Ar), 7.22 (d, ⁴*J*_{H-H} = 2 Hz, 2H; Ar), 2.78 (s, 3H; N-CH₃), 1.67 (s, 9H; O^tBu), 1.53 (s, 18H; ^tBu), 1.25 (s, 18H; ^tBu). ¹³C{¹H} NMR (125.71 MHz, C₆D₆, 298 K): δ (ppm) 153.0 (Ar), 141.1 (Ar), 137.0 (Ar), 136.0 (Ar), 123.5 (Ar), 113.6 (Ar), 71.2 (NCH₃), 44.8 (O^tBu), 35.1 (C(CH₃)₃), 34.6 (C(CH₃)₃), 29.5 (C(CH₃)₃), 29.4 (C(CH₃)₃). ¹¹B NMR (128.39 MHz, C₆D₆, 298 K): δ (ppm) 12.8 (br).

6.1.1.6 B₂(μ²: κ²-ONO)₂ (**7**)

H₃(ONO) (432 mg, 1.02 mmol) and H₃B·PPh₃ (280 mg, 1.02 mmol) were dissolved in THF (5 mL) in an ampoule. The solution mixture was stirred in an oil bath at 90 °C for seven

days. The solution was allowed to cool down to room temperature. All volatiles were removed under a dynamic vacuum and washed with hexane (5 mL). Removal of volatiles *in vacuo* yielded **7** as a white solid. Crystals were obtained by slow diffusion of hexane into a concentrated toluene solution of the product. Yield: 642 mg (73%). Elemental analysis calcd. (%) for $C_{56}H_{80}B_2N_2O_4$: C 77.59, H 9.30, N 3.23; found: C 76.55, H 9.55, N 2.71. 1H NMR (499.93 MHz, C_6D_6 , 298 K): δ (ppm) 7.19 (d, $^4J_{H-H} = 2$ Hz, 2H; Ar), 6.90 (d, $^4J_{H-H} = 2$ Hz, 2H; Ar), 1.38 (s, 18H; t Bu), 1.15 (s, 18H; t Bu). $^{13}C\{^1H\}$ NMR (125.71 MHz, C_6D_6 , 298 K): δ (ppm) 147.7 (Ar), 145.0 (Ar), 136.2 (Ar), 133.1 (Ar), 120.0 (Ar), 115.1 (Ar), 34.9 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 29.8 ($C(CH_3)_3$). ^{11}B NMR (160.40 MHz, C_6D_6 , 298 K): δ (ppm) 19.9 (br).

6.1.1.7 $Al(Cl)(THF)\{(ON(H)O)\}$ (**8**)

$H_3(ONO)$ (1.48 g, 3.48 mmol) and $AlCl_3$ (464 mg, 3.48 mmol) were dissolved in THF (15 mL). NEt_3 (1.21 mL, 8.70 mmol) was added to the stirred solution yielding a pale green solution and white precipitate. The mixture was stirred at room temperature for two hours. All volatiles were removed under a dynamic vacuum and the product was extracted in hexane (3×10 mL). The hexane solution was concentrated to c.a. 5 mL affording colourless crystals at room temperature. The solution was filtered and the crystals were dried *in vacuo* yielded **8** as a white solid. Yield: 1.62 mg (83%). Elemental analysis calcd. (%) for $C_{32}H_{48}AlClINO_3$: C 68.98, H 8.68, N 2.51; found: C 68.91, H 8.97, N 2.85. 1H NMR (400.17 MHz, C_6D_6 , 298 K): δ (ppm) 7.38 (d, $^4J_{H-H} = 2$ Hz, 2H; Ar), 7.11 (d, $^4J_{H-H} = 2$ Hz, 2H; Ar), 4.80 (br, 1H; NH), 4.28 (m, 4H; THF), 1.53 (s, 18H; t Bu), 1.36 (s, 18H; t Bu), 1.29 (m, 4H; THF). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6 , 298 K): δ (ppm) 154.5 (Ar), 139.5 (Ar), 137.1 (Ar), 132.3 (Ar), 122.9 (Ar), 120.3 (Ar), 72.3 (THF), 35.3 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 29.7 ($C(CH_3)_3$), 25.2 (THF).

6.1.1.8 Ga(Cl)(THF){(ON(H)O)} (9)

In an air-tight Young's tap NMR tube, H₃(ONO) (34 mg, 0.080 mmol) and GaCl₃ (14 mg, 0.080 mmol) were added and dissolved in *d*₈-THF (0.5 mL). NEt₃ (22 μL, 0.16 mmol) was added yielding a colourless solution and white precipitate. No yield can be reported, as decomposition occurred upon manipulation. ¹H NMR (400.20 MHz, *d*₈-THF, 298 K): δ (ppm) 7.50 (s, 2H; Ar), 7.14 (s, 2H; Ar), 6.95 (br, 1H; *NH*), 2.82 (m, 4H; THF), 1.42 (s, 18H; ^{*t*}Bu), 1.30 (s, 18H; ^{*t*}Bu), 1.15 (m, 4H; THF). ¹³C{¹H} NMR (100.63 MHz, *d*₈-THF, 298 K): δ (ppm) 154.7 (Ar), 138.7 (Ar), 137.1 (Ar), 131.7 (Ar), 122.7 (Ar), 120.4 (Ar), 47.1 (THF), 35.7 (C(CH₃)₃), 34.6 (C(CH₃)₃), 31.9 (C(CH₃)₃), 29.7 (C(CH₃)₃), 25.2 (THF).

6.1.1.9 Ga(Cl)(py){(ON(H)O)} (10)

H₃(ONO) (1.00 g, 2.35 mmol) and GaCl₃ (414 mg, 2.35 mmol) were dissolved in pyridine (15 mL). NEt₃ (0.655 mL, 4.70 mmol) was added to the stirred solution yielding a pale yellow-orange solution and white precipitate. The mixture was stirred at room temperature for two hours. All volatiles were removed under a dynamic vacuum and the product was extracted in hot hexane (3×10 mL). The hexane solution was concentrated to c.a. 5 mL affording colourless crystals at room temperature. The solution was filtered and the crystals were dried *in vacuo* yielded **10** as a white solid. Yield: 1.06 g (74%). Elemental analysis calcd. (%) for C₃₃H₄₆GaClN₂O₂: C 65.20, H 7.63, N 4.61; found: C 65.12, H 7.73, N 4.78. ¹H NMR (400.20 MHz, C₆D₆, 298 K): δ (ppm) 9.18 (m, 2H; py), 7.41 (d, ⁴*J*_{H-H} = 2 Hz, 2H; Ar), 7.22 (d, ⁴*J*_{H-H} = 2 Hz, 2H; Ar), 6.75 (m, 2H; py), 6.52 (m, 2H; py), 4.61 (br, 1H; *NH*), 1.53 (s, 18H; ^{*t*}Bu), 1.38 (s, 18H; ^{*t*}Bu). ¹³C{¹H} NMR (100.63 MHz, C₆D₆, 298 K): δ (ppm) 154.8 (Ar), 147.7 (py), 140.0 (py), 138.7 (Ar), 137.3 (Ar), 130.9 (Ar), 124.9 (Ar), 122.9 (Ar), 120.8 (Ar), 35.6 (C(CH₃)₃), 34.5 (C(CH₃)₃), 32.0 (C(CH₃)₃), 29.9 (C(CH₃)₃).

6.1.1.10 Ga(Br)(THF){(ON(H)O)} (11)

H₃(ONO) (260 mg, 0.611 mmol) and GaBr₃ (189 mg, 0.611 mmol) and potassium hydride (61 mg, 1.53 mmol) were dissolved in THF (20 mL). The mixture was stirred at room temperature for three hours resulting in a pale orange solution and white precipitate. All volatiles were removed under a dynamic vacuum and the product was extracted in hexane (3×10 mL). The solution was filtered and the solids were dried *in vacuo* yielded **11** as a pale orange solid. Crystals were obtained from a concentrated hexane solution at 50 °C. Yield: 292 mg (74%). Elemental analysis calcd. (%) for C₃₂Br₆AlBrNO₃: C 59.55, H 7.65, N 2.17; found: C 59.00, H 7.73, N 1.98. ¹H NMR (400.20 MHz, C₆D₆, 298 K): δ (ppm) 7.39 (s, 2H; Ar), 7.13 (s, 2H; Ar), 4.57 (br, 1H; NH), 3.96 (m, 4H; THF), 1.55 (s, 18H; ^tBu), 1.38 (m, 4H; THF), 1.35 (s, 18H; ^tBu). ¹³C{¹H} NMR (100.63 MHz, C₆D₆, 298 K): δ (ppm) 154.4 (Ar), 139.0 (Ar), 137.4 (Ar), 130.5 (Ar), 123.2 (Ar), 120.5 (Ar), 69.9 (THF), 35.6 (C(CH₃)₃), 34.5 (C(CH₃)₃), 31.9 (C(CH₃)₃), 29.7 (C(CH₃)₃), 25.5 (THF).

6.1.1.11 Ga(Cl)(DABCO)₂{(ON(H)O)} (12)

10 (105 mg, 0.17 mmol) and DABCO (19 mg, 0.17 mmol) were dissolved in toluene (5 mL). The mixture was stirred at room temperature for an hour. All volatiles were removed under a dynamic vacuum yielded **12** as a white solid. Yield: 68 mg (62%). Elemental analysis calcd. (%) for C₃₄H₅₃GaClN₃O₂: C 63.71, H 8.33, N 6.56; found: C 62.65, H 8.40, N 6.64. ¹H NMR (400.20 MHz, C₆D₆, 298 K): δ (ppm) 7.41 (d, ⁴J_{H-H} = 2 Hz, 2H; Ar), 7.24 (d, ⁴J_{H-H} = 2 Hz, 2H; Ar), 5.05 (br, 1H; NH), 3.30 (t, ⁴J_{H-H} = 7 Hz, 6H; DABCO), 2.46 (t, ⁴J_{H-H} = 7 Hz, 6H; DABCO), 1.56 (s, 18H; ^tBu), 1.37 (s, 18H; ^tBu). ¹³C{¹H} NMR (100.63 MHz, C₆D₆, 298 K): δ (ppm) 154.5 (Ar), 138.7 (Ar), 137.1 (Ar), 130.9 (Ar), 122.8 (Ar), 120.8 (Ar), 46.2 (DABCO), 46.0 (DABCO), 35.5 (C(CH₃)₃), 34.4 (C(CH₃)₃), 32.0 (C(CH₃)₃), 30.0 (C(CH₃)₃).

6.1.1.12 Ga(Br)(DABCO)₂{(ON(H)O)} (13)

11 (68 mg, 0.11 mmol) and DABCO (12 mg, 0.11 mmol) were dissolved in toluene (5 mL). The mixture was stirred at room temperature for an hour. All volatiles were removed under a dynamic vacuum yielded **13** as a pale pink solid. Yield: 54 mg (74%). Elemental analysis calcd. (%) for C₃₄H₅₃BrClN₃O₂: C 59.58, H 7.79, N 6.13; found: C 59.54, H 7.82, N 5.68. ¹H NMR (400.20 MHz, C₆D₆, 298 K): δ (ppm) 7.41 (s, 2H; Ar), 7.18 (s, 2H; Ar), 4.59 (br, 1H; NH), 3.30 (br, 6H; DABCO), 2.45 (br, 6H; DABCO), 1.55 (s, 18H; ^tBu), 1.35 (s, 18H; ^tBu). ¹³C{¹H} NMR (100.63 MHz, C₆D₆, 298 K): δ (ppm) 154.3 (Ar), 138.8 (Ar), 137.1 (Ar), 130.7 (Ar), 123.0 (Ar), 120.8 (Ar), 46.2 (DABCO), 45.9 (DABCO), 35.5 (C(CH₃)₃), 34.4 (C(CH₃)₃), 31.9 (C(CH₃)₃), 30.0 (C(CH₃)₃).

6.1.1.13 Al(py)₃(ONO) (14)

8 (85 mg, 0.152 mmol) and DABCO (17 mg, 0.152 mmol) were dissolved in pyridine (2 mL) resulting in a red solution and red crystals. As decomposition occurred upon removing solvent under a dynamic vacuum, and the crystals were not soluble in any deuterated solvents, no mass spectrometry, yield, elemental analysis or NMR data are available.

6.1.1.14 Ga(py)₃(ONO) (15)

11 (43 mg, 0.067 mmol) and DABCO (7.5 mg, 0.067 mmol) were dissolved in pyridine (0.5 mL) resulting in a red solution and red crystals. As decomposition occurred upon removing solvent under a dynamic vacuum, and the crystals were not soluble in any deuterated solvents, no mass spectrometry, yield, elemental analysis or NMR data are available.

6.1.1.15 Al(DMAP)₂(py)(ONO) (16)

8 (32 mg, 0.057 mmol), DABCO (6.4 mg, 0.057 mmol) and DMAP (21 mg, 0.17 mmol) were dissolved in pyridine (1 mL) resulting in a red solution and red crystals. As decomposition occurred upon removing solvent under a dynamic vacuum, and the crystals

were not soluble in any deuterated solvents, no mass spectrometry, yield, elemental analysis or NMR data are available.

6.1.1.16 $\{\text{Al}(\text{THF})(\text{ONO})\}_2$ (**17**)

Method A: **8** (283 mg, 0.507 mmol) and KC_8 (68.4 mg, 0.507 mmol) were dissolved in toluene (5 mL). The mixture was stirred at 90 °C overnight resulting in a colourless solution and black solid. The hot solution was filtered and concentrated to ca. 1 mL. Colourless crystals were grown at room temperature. The solution was filtered and all volatiles were removed under a dynamic vacuum yielded **17** as a white solid. Yield: 63 mg (24%); Method B: **8** (124 mg, 0.222 mmol) and potassium (8.7 mg, 0.222 mmol) were dissolved in toluene (3 mL). The mixture was stirred at 90 °C overnight resulting in a colourless solution and black solid. The hot solution was filtered and concentrated to ca. 0.5 mL. Colourless crystals were grown at room temperature. The solution was filtered and all volatiles were removed under a dynamic vacuum yielded **17** as a white solid. Yield: 17 mg (15%); Method C: **8** (112 mg, 0.201 mmol) and LiAlH_4 (7.6 mg, 0.201 mmol) were dissolved in THF (3 mL). The mixture was stirred at 90 °C overnight resulting in a colourless solution. The hot solution was filtered and concentrated to ca. 0.5 mL. Colourless crystals were grown at room temperature. The solution was filtered and all volatiles were removed under a dynamic vacuum yielded **17** as a white solid. Yield: 12 mg (11%). ^1H NMR (499.93 MHz, C_6D_6 , 298 K): δ (ppm) 7.68 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 4H; Ar), 7.22 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 4H; Ar), 4.45 (m, 8H; THF), 1.59 (m, 8H; THF), 1.42 (s, 36H; ^tBu), 1.40 (s, 36H; ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.71 MHz, C_6D_6 , 298 K): δ (ppm) 154.2 (Ar), 138.7 (Ar), 138.3 (Ar), 135.9 (Ar), 129.4 (Ar), 119.0 (Ar), 74.3 (THF), 35.0 ($\text{C}(\text{CH}_3)_3$), 34.5 ($\text{C}(\text{CH}_3)_3$), 32.2 ($\text{C}(\text{CH}_3)_3$), 29.7 ($\text{C}(\text{CH}_3)_3$), 25.3 (THF).

6.1.1.17 $\{\text{Al}(\text{py})(\text{ONO})\}_2$ (**19**)

10 (157 mg, 0.258 mmol) and LiAlH_4 (9.8 mg, 0.258 mmol) were dissolved in THF (2 mL), resulting in a red solution. The mixture was stirred for thirty minutes at room temperature. The solution was filtered and concentrated to ca. 0.5 mL. Colourless crystals were grown from slow diffusion of hexane into the solution, alongside a grey precipitate. As the crystals were not soluble in any deuterated solvents and cannot be separated from the grey precipitate, no mass spectroscopy, yield, elemental analysis, or NMR data are available.

6.1.1.18 $\text{Ga}(\text{H})(\text{THF})\{\text{ON}(\text{H})\text{O}\}$ (**20**)

10 (814 mg, 1.34 mmol) and an excess of sodium borohydride (253 mg, 6.69 mmol, 5 eq.) were dissolved in THF (20 mL) giving a colourless solution. The solution was stirred at room temperature for three hours resulting in a colourless solution and white precipitate of NaCl. All volatiles were removed *in vacuo* and the product was extracted into toluene (3x10 mL). Crystals were obtained in a concentrated THF/hexane mixed solution. The solution was filtered and the crystals were dried *in vacuo* yielded **20** as a white solid. Yield: 587 mg (64%). Elemental analysis calcd. (%) for $\text{C}_{32}\text{H}_{50}\text{GaNO}_3$: C 67.34, H 8.86, N 4.47; found: C 66.56, H 8.89, N 4.55. ^1H NMR (400.17 MHz, C_6D_6 , 298 K): δ (ppm) 8.14 (m, 2.6H; py), 7.35 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 2H; Ar), 7.25 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 2H; Ar), 6.57 (m, 1.3H; py), 6.20 (m, 2.6H; py), 5.75 (br, 1H; GaH), 4.07 (br, 1H; NH), 3.91 (m, 4H; THF), 3.49 (m, $^1J_{\text{B-H}} = 99\text{ Hz}$; 3H, BH_3); 1.58 (s, 18H; ^tBu), 1.46 (m, 4H; THF), 1.36 (s, 18H; ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, C_6D_6 , 298 K): δ (ppm) 156.1 (Ar), 147.3 (py), 137.9 (py), 137.8 (Ar), 137.4 (Ar), 132.1 (Ar), 124.7 (py), 122.6 (Ar), 120.4 (Ar), 68.7 (THF), 35.6 ($\text{C}(\text{CH}_3)_3$), 34.4 ($\text{C}(\text{CH}_3)_3$), 32.0 ($\text{C}(\text{CH}_3)_3$), 29.8 ($\text{C}(\text{CH}_3)_3$), 25.5 (THF). ^{11}B NMR (128.39 MHz, C_6D_6 , 298 K): δ (ppm) -10.8 (m, $^1J_{\text{B-H}} = 99\text{ Hz}$; 3H, BH_3). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.39 MHz, C_6D_6 , 298 K): δ (ppm) -10.8 (s).

6.1.1.19 $\{\text{Al}(\text{NH}_2\text{Cy})(\text{ONO})\}_2$ (**21**)

In an air-tight Young's tap NMR tube, cyclohexylamine (1.3 μL , 0.012 mmol) was syringed into a C_6D_6 solution of **17** (6 mg, 0.006 mmol). Colourless crystals were grown from the reaction solution at room temperature overnight. The solution was filtered and the crystals were dried under a dynamic vacuum yielded **21** as a white solid. ^1H NMR (400.17 MHz, C_6D_6 , 298 K): δ (ppm) 7.58 (d, $^4J_{\text{H-H}} = 2\text{ Hz}$, 4H; Ar), 7.20 (d, $^4J_{\text{H-H}} = 2\text{ Hz}$, 4H; Ar), 3.33 (d, $^3J_{\text{H-H}} = 6\text{ Hz}$, 4H, CyNH_2), 2.20–0.89 (20H, cyclohexyl protons), 1.46 (s, 36H; $t\text{Bu}$), 1.36 (s, 36H; $t\text{Bu}$). ^{13}C NMR spectrum was not obtained due to the poor solubility of crystalline **21**.

6.1.1.20 $\{\text{Al}(\text{NH}_2^t\text{Bu})(\text{ONO})\}_2$ (**22**)

In an air-tight Young's tap NMR tube, *tert*-butylamine (1.2 μL , 0.012 mmol) was syringed into a C_6D_6 solution of **17** (6 mg, 0.006 mmol). Colourless crystals were grown in the reaction solution at room temperature overnight. The solution was filtered and the crystals were dried under a dynamic vacuum. ^1H NMR (400.17 MHz, C_6D_6 , 298 K): δ (ppm) 7.57 (d, $^4J_{\text{H-H}} = 2\text{ Hz}$, 4H; Ar), 7.21 (d, $^4J_{\text{H-H}} = 2\text{ Hz}$, 4H; Ar), 1.44 (s, 36H; $t\text{Bu}$), 1.37 (s, 36H; $t\text{Bu}$), 1.35 (s, 18H; N^tBu). ^{13}C NMR spectrum was not obtained due to the poor solubility of crystalline **22**.

6.1.1.21 $[\text{Al}(\text{OEt})\{\text{ON}(\text{H})\text{O}\}]_2$ (**23**)

In an air-tight Young's tap NMR tube, ethanol (1.7 μL , 0.028 mmol) was syringed into a C_6D_6 solution of **17** (15 mg, 0.014 mmol). Colourless crystals were grown in the reaction solution at room temperature overnight. The solution was filtered and the crystals were dried under a dynamic vacuum. ^1H NMR (400.20 MHz, C_6D_6 , 298 K): δ (ppm) 7.45 (d, $^4J_{\text{H-H}} = 2\text{ Hz}$, 4H; Ar), 7.40 (d, $^4J_{\text{H-H}} = 2\text{ Hz}$, 4H; Ar), 4.79 (s, 2H; NH), 4.04 (d, $^3J_{\text{H-H}} = 7\text{ Hz}$, 4H; OCH_2CH_3), 1.56 (s, 36H; $t\text{Bu}$), 1.36 (s, 36H; $t\text{Bu}$), 1.28 (t, $^3J_{\text{H-H}} = 7\text{ Hz}$, 6H; OCH_2CH_3). ^{13}C NMR spectrum was not obtained due to the poor solubility of crystalline **23**.

6.1.1.22 $[\text{Al}(\text{O}^t\text{Bu})\{\text{ON}(\text{H})\text{O}\}]_2$ (**24**)

8 (153 mg, 0.274 mmol) and KO^tBu (30.8 mg, 0.274 mmol) were dissolved in THF (5 mL). The reaction mixture was sonicated for two hours resulting a purple solution and white precipitate. All volatiles were removed under a dynamic vacuum and the product was extracted in hexane. The hexane solution was concentrated to ca. 1 mL. Purple crystals were obtained at room temperature overnight. The solution was filtered and the crystals were dried under a dynamic vacuum yielded **24** as a pale purple solid. Yield: 114 mg (79%). ^1H NMR (400.20 MHz, C_6D_6 , 298 K): δ (ppm) 7.76 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 4H; Ar), 7.47 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 4H; Ar), 5.07 (br, 2H; N-H), 1.61 (s, 36H; ^tBu), 1.52 (s, 18H; O^tBu), 1.38 (s, 36H; ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, C_6D_6 , 298 K): δ (ppm) 154.7 (Ar), 139.2 (Ar), 138.0 (Ar), 131.5 (Ar), 123.6 (Ar), 119.5 (Ar), 74.5 ($\text{OC}(\text{CH}_3)_3$), 35.4 ($\text{C}(\text{CH}_3)_3$), 34.5 ($\text{C}(\text{CH}_3)_3$), 32.0 ($\text{C}(\text{CH}_3)_3$), 31.9 ($\text{OC}(\text{CH}_3)_3$), 30.5 ($\text{C}(\text{CH}_3)_3$).

6.1.1.23 $\text{Ga}(\text{py})_2\text{B}(\mu^2: \kappa^2\text{-ONO})_2$ (**25**)

20 (75 mg, 0.11 mmol) was dissolved in toluene (2 mL) and left to reflux at 70 °C for seven days, resulting in formation of a yellow solution accompanied by yellow crystals and a grey precipitate. As the crystals were not soluble in any deuterated solvents and cannot be separated from the grey precipitate, no mass spectroscopy, yield, elemental analysis, or NMR data are available.

6.1.1.24 $[\text{Ga}(\text{OCH}_2\text{Ph})\{\text{ON}(\text{H})\text{O}\}]_2$ (**26**)

PhCHO (17 μL , 0.16 mmol) was added into a toluene solution of **20** (107 mg, 0.16 mmol) resulting in a pale yellow solution. Colourless crystals of **26** were obtained from the toluene reaction solution at room temperature. The solution was filtered and the white solid was dried under dynamic vacuum. Yield: 80 mg (82%). Elemental analysis calcd. (%) for $\text{C}_{70}\text{H}_{96}\text{Ga}_2\text{N}_2\text{O}_6$: C 70.01, H 8.06, N 2.33; found: C 68.90, H 7.96, N 1.88. ^1H NMR (400.20

MHz, d_8 -THF, 298 K): δ (ppm) 7.43 (m, 4H; Ph), 7.17 (s, 4H; Ar), 7.09 (s, 4H; Ar), 7.06–6.95 (m, 6H; Ph), 5.67 (br, 2H; NH), 5.29 (s, 4H; OCH₂), 1.37 (s, 36H; ^{*t*}Bu), 1.26 (s, 36H, ^{*t*}Bu). ¹³C{¹H} NMR (100.63 MHz, d_8 -THF, 298 K): δ (ppm) 154.7 (Ar), 141.2 (Ph), 138.4 (Ar), 137.4 (Ar), 131.3 (Ar), 128.6 (Ph), 127.8 (Ph), 127.1 (Ph), 122.7 (Ar), 120.0 (Ar), 67.2 (OCH₂), 35.7 (C(CH₃)₃), 34.6 (C(CH₃)₃), 31.9 (C(CH₃)₃), 29.7 (C(CH₃)₃).

6.1.1.25 [Ga(OCH₂^{*i*}Pr)(ON(H)O)]₂ (27)

^{*i*}PrCHO (14 μ L, 0.15 mmol) was added into a toluene solution of **20** (99 mg, 0.15 mmol) resulting in a pale yellow solution. Colourless crystals of **27** were obtained from the toluene reaction solution at room temperature overnight. The solution was filtered and the white solid was dried under dynamic vacuum. Yield: 55 mg (68%). Elemental analysis calcd. (%) for C₆₄H₁₀₀Ga₂N₂O₆: C 67.85, H 8.90, N 2.47; found: C 68.38, H 8.88, N 3.69. ¹H NMR (400.20 MHz, d_8 -THF, 298 K): δ (ppm) 7.52 (s, 4H; Ar), 7.15 (s, 4H; Ar), 6.77 (br, 2H; NH), 3.87 (br, 4H; OCH₂), 1.41 (s, 36H; ^{*t*}Bu), 1.33 (s, 2H, ^{*i*}Pr-*H*), 1.30 (s, 36H, ^{*t*}Bu), 0.81 (br, 12H, ^{*i*}Pr-CH₃). ¹³C{¹H} NMR (100.63 MHz, d_8 -THF, 298 K): δ (ppm) 154.8 (Ar), 139.7 (Ar), 137.6 (Ar), 131.6 (Ar), 122.8 (Ar), 120.0 (Ar), 67.2 (OCH₂), 35.8 (C(CH₃)₃), 34.7 (C(CH₃)₃), 31.9 (C(CH₃)₃), 31.0 (^{*i*}Pr), 29.7 (C(CH₃)₃), 19.2 (^{*i*}Pr).

6.1.1.26 Catalytic hydroboration of HBPIn and PhCHO using **26** (10 mol%)

In an air tight Young's tap NMR tube, **26** (5 mg, 0.0042 mmol) was dissolved in C₆D₆ (0.5 mL). HBPIn (12 μ L, 0.083 mmol) and PhCHO (8.5 μ L, 0.083 mmol) were added subsequently. Reaction was assessed by ¹H NMR integration of the crude reaction mixture. 96% of **26** were converted to product, Bpin–OCH₂Ph, in less than five minutes.

6.1.1.27 Catalytic hydroboration of HBPIn and PhCHO using **26** (0.025 mol%)

In an air-tight Young's tap NMR tube, **26** (2 mg, 0.0017 mmol) was dissolved in C₆D₆ (0.5 mL). HBPIn (970 μ L, 6.7 mmol) and PhCHO (680 μ L, 6.7 mmol) were added subsequently.

Reaction was assessed by ^1H NMR integration of the crude reaction mixture. 92% of **26** was converted to product, Bpin–OCH₂Ph, in twenty minutes, then 98% of **26** was converted to the product in fifty minutes.

6.1.2 Chapter 3.1 – Complexes of group 14 elements bearing the *N,N'*-(bis(3,5-di-*tert*-2-phenolate) amide ligand

6.1.2.1 Si{ON(H)O}₂ (**29**)

H₃(ONO) (200 mg, 0.470 mmol) and SiCl₄ (27.0 μL , 0.235 mmol) were dissolved in toluene (3 mL). NEt₃ (131 μL , 0.940 mmol) was added to the stirred solution yielding a yellow solution and white precipitate. The mixture was stirred at room temperature for four hours. The yellow solution was filtered and all volatiles were removed under dynamic vacuum. Crystals were obtained from a concentrated toluene solution at room temperature and isolated as a white solid. Yield: 109 mg (53%). Elemental analysis calcd. (%) for SiC₅₆H₈₂N₂O₄: C 76.84, H 9.44, N 3.20; found: C 79.18, H 9.20, N 2.96. CI MS *m/z* calc. for SiC₅₆H₈₃N₂O₄ (MH⁺): 875.6044, found 875.6134. ^1H NMR (400.17 MHz, C₆D₆, 298 K): δ (ppm) 7.35 (d, $^4J_{\text{H-H}} = 2$ Hz, 2H; Ar), 7.34 (d, $^4J_{\text{H-H}} = 2$ Hz, 2H; Ar), 6.95 (d, $^4J_{\text{H-H}} = 2$ Hz, 2H; Ar), 6.86 (d, $^4J_{\text{H-H}} = 2$ Hz, 2H; Ar), 5.34 (br, 2H; NH), 1.74 (s, 18H; ^{*t*}Bu), 1.30 (s, 18H; ^{*t*}Bu), 1.29 (s, 18H; ^{*t*}Bu), 1.22 (s, 18H; ^{*t*}Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, C₆D₆, 298 K): δ (ppm) 151.4 (Ar), 150.5 (Ar), 140.7 (Ar), 140.4 (Ar), 138.2 (Ar), 138.1 (Ar), 132.6 (Ar), 129.6 (Ar), 124.1 (Ar), 123.0 (Ar), 117.5 (Ar), 117.4 (Ar), 35.5 (C(CH₃)₃), 35.3 (C(CH₃)₃), 34.6 (C(CH₃)₃), 34.6 (C(CH₃)₃), 31.9 (C(CH₃)₃), 31.8 (C(CH₃)₃), 29.6 (C(CH₃)₃), 29.2 (C(CH₃)₃). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.32 MHz, C₆D₆, 298 K): δ (ppm) –128.6 (s).

6.1.2.2 Ge{ON(H)O}₂ (**30**)

H₃(ONO) (200 mg, 0.470 mmol) and GeCl₄ (50.4 mg, 0.235 mmol) were dissolved in toluene (3 mL). NEt₃ (131 μL , 0.940 mmol) was added to the stirred solution yielding a purple solution and white precipitate. The mixture was stirred at room temperature for four

hours. The purple solution was filtered and all volatiles were removed under dynamic vacuum. Crystals were obtained by a concentrated toluene solution at room temperature and isolated as a white solid. Yield: 39 mg (18%). Elemental analysis calcd. (%) for $\text{GeC}_{56}\text{H}_{82}\text{N}_2\text{O}_4$: C 73.12, H 8.99, N 3.05; found: C 73.10, H 9.06, N 3.18. EI MS m/z calc. for $\text{GeC}_{56}\text{H}_{82}\text{N}_2\text{O}_4$ (M^+): 920.5486, found 920.5534. ^1H NMR (400.17 MHz, C_6D_6 , 298 K): δ (ppm) 7.37 (d, $^4J_{\text{H-H}} = 2$ Hz, 2H; Ar), 7.34 (d, $^4J_{\text{H-H}} = 2$ Hz, 2H; Ar), 7.01 (d, $^4J_{\text{H-H}} = 2$ Hz, 2H; Ar), 6.97 (d, $^4J_{\text{H-H}} = 2$ Hz, 2H; Ar), 5.23 (br, 2H; NH), 1.74 (s, 18H; $t\text{Bu}$), 1.31 (s, 18H; $t\text{Bu}$), 1.29 (s, 18H; $t\text{Bu}$), 1.22 (s, 18H; $t\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, C_6D_6 , 298 K): δ (ppm) 152.0 (Ar), 151.0 (Ar), 140.0 (Ar), 139.9 (Ar), 138.7 (Ar), 138.3 (Ar), 130.8 (Ar), 128.3 (Ar), 124.2 (Ar), 123.2 (Ar), 118.1 (Ar), 118.0 (Ar), 35.8 ($\text{C}(\text{CH}_3)_3$), 35.5 ($\text{C}(\text{CH}_3)_3$), 34.6 ($\text{C}(\text{CH}_3)_3$), 34.5 ($\text{C}(\text{CH}_3)_3$), 31.8 ($\text{C}(\text{CH}_3)_3$), 31.8 ($\text{C}(\text{CH}_3)_3$), 29.7 ($\text{C}(\text{CH}_3)_3$), 29.2 ($\text{C}(\text{CH}_3)_3$).

6.1.2.3 $\text{Sn}\{\text{ON}(\text{H})\text{O}\}_2$ (**31**)

$\text{H}_3(\text{ONO})$ (200 mg, 0.470 mmol) and $\text{SnCl}_4 \cdot 2\text{THF}$ (95.1 mg, 0.235 mmol) were dissolved in toluene (3 mL). NEt_3 (131 μL , 0.940 mmol) was added to the stirred solution yielding a purple solution and white precipitate. The mixture was stirred at room temperature overnight. The purple solution was filtered and all volatiles were removed under dynamic vacuum. Crystals were obtained by a concentrated hexane solution to room temperature and isolated as a white solid. Yield: 7 mg (3%). ^1H NMR (500.30 MHz, C_6D_6 , 298 K): δ (ppm) 7.37 (br, 4H; Ar), 7.13 (d, $^4J_{\text{H-H}} = 2$ Hz, 4H; Ar), 5.22 (br, 2H; NH), 1.51 (br, 36H; $t\text{Bu}$), 1.29 (s, 36H; $t\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.80 MHz, C_6D_6 , 298 K): δ (ppm) 152.8 (br, Ar), 139.5 (br, Ar), 139.3 (Ar), 128.3 (Ar), 123.6 (Ar), 119.5 (Ar), 35.8 ($\text{C}(\text{CH}_3)_3$), 34.5 ($\text{C}(\text{CH}_3)_3$), 31.8 ($\text{C}(\text{CH}_3)_3$), 29.7 ($\text{C}(\text{CH}_3)_3$). ^{119}Sn NMR spectrum was not obtained due to as **31** cannot be obtained in a bigger scale.

6.1.2.4 [HfPr][Si(Cl)₂(ONO)] ([HfPr][32])

H₃(ONO) (65.6 mg, 0.154 mmol) and SiCl₂·IPr (75.1 mg, 0.154 mmol) were dissolved in toluene (3 mL). NEt₃ (43 μL, 0.308 mmol) was added to the toluene solution yielding a purple solution immediately and white precipitate. The mixture was stirred at room temperature for an hour. All volatiles were removed under a dynamic vacuum and the product was extracted with hexane. Crystals were grown in a concentrated hexane solution at room temperature. The ¹H NMR spectrum of the crystals shows multiple products. The structure of **32** was characterised by single crystal X-ray crystallography.

6.1.2.5 Ge{(ON(H)O)} (**33**)

H₃(ONO) (325 mg, 0.764 mmol) and GeCl₂·dioxane (177 mg, 0.764 mmol) were dissolved in toluene (5 mL). NEt₃ (213 μL, 1.53 mmol) was added to the stirred solution yielding a pale yellow solution and white precipitate. The mixture was stirred at room temperature overnight. All volatiles were removed under a dynamic vacuum and the product was washed with hexane (3×10 mL). The remaining white solid was dried *in vacuo* yielded **33** as a white solid. Crystals were obtained by a concentrated toluene solution at room temperature. Yield: 337 mg (89%). Elemental analysis calcd. (%) for C₂₈H₄₁GeNO₂: C 67.77, H 8.33, N 2.82; found: C 67.50, H 8.35, N 3.07. EI MS: *m/z* calc. for C₂₈H₄₁GeNO₂ (M⁺): 497.2349, found 497.2397. ¹H NMR (400.17 MHz, C₆D₆, 298 K): δ (ppm) 7.29 (d, ⁴J_{H-H} = 2Hz, 2H; Ar), 7.04 (d, ⁴J_{H-H} = 2Hz, 2H; Ar), 5.01 (br, 1H; NH), 1.55 (s, 18H; ^tBu), 1.28 (s, 18H; ^tBu). ¹³C{¹H} NMR (100.62 MHz, C₆D₆, 298 K): δ (ppm) 155.6 (Ar), 140.0 (Ar), 138.5 (Ar), 132.0 (Ar), 123.4 (Ar), 118.2 (Ar), 35.6 (C(CH₃)₃), 34.4 (C(CH₃)₃), 31.8 (C(CH₃)₃), 29.6 (C(CH₃)₃).

6.1.2.6 Sn{(ON(H)O)} (34)

H₃(ONO) (210 mg, 0.494 mmol) and SnCl₂ (93.6 mg, 0.494 mmol) were dissolved in toluene (5 mL). NEt₃ (138 µL, 0.987 mmol) was added to the stirred solution yielding a pale yellow solution and white precipitate. The mixture was stirred at room temperature overnight. All volatiles were removed under a dynamic vacuum and the product was washed with hexane (3×10 mL). The remaining solid was dried *in vacuo* yielded **34** as a white solid. Yield: 230 mg (86%). Elemental analysis calcd. (%) for C₂₈H₄₁SnNO₂: C 62.01, H 7.62, N 2.58; found: C 65.09, H 8.09, N 2.92. EI MS: *m/z* calc. for C₂₈H₄₁SnNO₂ (M⁺): 543.2169, found 543.2159. ¹H NMR (400.17 MHz, C₆D₆, 298 K): δ (ppm) 7.30 (d, ⁴J_{H-H} = 2 Hz, 2H; Ar), 7.16 (d, ⁴J_{H-H} = 2 Hz, 2H; Ar), 4.68 (br, 1H; NH), 1.61 (s, 18H; ^tBu), 1.32 (s, 18H; ^tBu). ¹³C{¹H} NMR (100.62 MHz, C₆D₆, 298 K): δ (ppm) 157.4 (Ar), 139.2 (Ar), 138.4 (Ar), 133.5 (Ar), 122.9 (Ar), 120.1 (Ar), 35.7 (C(CH₃)₃), 34.4 (C(CH₃)₃), 31.9 (C(CH₃)₃), 29.8 (C(CH₃)₃).

6.1.2.7 [K(18-crown-6)][Ge(ONO)] ([K(18-crown-6)][35])

33 (1.03 g, 2.08 mmol), benzyl potassium (241 mg, 2.08 mmol), 18-crown-6 (548 mg, 2.08 mmol) were dissolved in toluene (15 mL). The solution was stirred at room temperature for two hours resulting in a pale yellow solution and pale yellow precipitate. The pale yellow solid was isolated by filtration and dried *in vacuo*. Crystals were obtained by slow diffusion of hexane into a concentrated THF solution at room temperature and isolated as a pale yellow solid. Yield: 1.19 g (72%). ¹H NMR (400.17 MHz, *d*₈-THF, 298 K): δ (ppm) 7.27 (d, ⁴J_{H-H} = 2 Hz, 2H; Ar), 6.58 (d, ⁴J_{H-H} = 2 Hz, 2H; Ar), 3.39 (s, 24H; 18-crown-6), 1.39 (s, 18H; ^tBu), 1.29 (s, 18H; ^tBu). ¹³C{¹H} NMR (100.62 MHz, *d*₈-THF, 298 K): δ (ppm) 154.4 (Ar), 146.4 (Ar), 135.7 (Ar), 132.0 (Ar), 115.5 (Ar), 113.9 (Ar), 70.8 (18-crown-6), 35.3 (C(CH₃)₃), 34.5 (C(CH₃)₃), 32.6 (C(CH₃)₃), 30.2 (C(CH₃)₃).

6.1.2.8 [K(18-crown-6)][Sn(ONO)] ([K(18-crown-6)][36])

34 (850 mg, 1.57 mmol), benzyl potassium (182 mg, 1.57 mmol), 18-crown-6 (414 mg, 1.57 mmol) were dissolved in toluene (10 mL). The solution was stirred at room temperature for two hours resulting in yellow solution and yellow precipitate. The yellow solid was isolated by filtration and dried *in vacuo*. Crystals were obtained by a concentrated toluene solution at room temperature and isolated as a yellow solid. Yield: 860 mg (65%). ^1H NMR (400.20 MHz, d_8 -THF, 298 K): δ (ppm) 7.56 (br, 2H; Ar), 6.60 (br, 2H; Ar), 3.32 (s, 24H; 18-crown-6), 1.66 (s, 18H; t Bu), 1.32 (s, 18H; t Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, d_8 -THF, 298 K): δ (ppm) 155.9 (Ar), 144.4 (Ar), 133.7 (Ar), 132.5 (Ar), 112.4 (Ar), 111.8 (Ar), 70.8 (18-crown-6), 35.6 ($\text{C}(\text{CH}_3)_3$), 34.6 ($\text{C}(\text{CH}_3)_3$), 32.7 ($\text{C}(\text{CH}_3)_3$), 30.3 ($\text{C}(\text{CH}_3)_3$).

6.1.2.9 [K(18-crown-6)]₂[Ge(ONO)₂] ([K(18-crown-6)]₂[37])

Upon exposure [K(18-crown-6)][**35**] (65 mg, 0.081 mmol) to air, the solution turned into a more intense yellow solution accompanied by the formation of yellow crystals within an hour. Then, the reaction mixture turned to a purple solution and the crystals were decomposed to a non-crystalline solid. The structure of yellow crystal was determined as [K(18-crown-6)]₂[**37**] by single crystal X-ray diffraction.

6.1.2.10 [K(18-crown-6)][Ge(H)(OH)(ONO)] ([K(18-crown-6)][38])

Water (1.5 μL , 0.085 mmol) was added into a THF solution of [K(18-crown-6)][**35**] (68 mg, 0.085 mmol) resulting in a colourless solution. The mixture was stirred at room temperature for an hour. Colourless crystals obtained by slow diffusion of hexane into the THF solution. The solution was filtered and the crystals were dried under a dynamic vacuum yielding [K(18-crown-6)][**38**] as a white solid. Yield: 54 mg (78%). ^1H NMR (400.20 MHz, d_8 -THF, 298 K): δ (ppm) 7.47 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 2H; Ar), 7.00 (s, 1H, GeH), 6.54 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 2H; Ar), 3.38 (s, 24H; 18-crown-6), 1.43 (s, 18H; t Bu), 1.33 (s, 18H; t Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR

(100.63 MHz, d_8 -THF, 298 K): δ (ppm) 150.3 (Ar), 135.5 (Ar), 135.2 (Ar), 129.9 (Ar), 110.8 (Ar), 106.2 (Ar), 70.7 (18-crown-6), 35.3 ($C(CH_3)_3$), 34.9 ($C(CH_3)_3$), 32.6 ($C(CH_3)_3$), 30.2 ($C(CH_3)_3$).

6.1.2.11 [K(18-crown-6)][Ge(H)(OEt)(ONO)] ([K(18-crown-6)][39])

Ethanol (3.3 μ L, 0.056 mmol) was added into a THF solution of [K(18-crown-6)][35] (45 mg, 0.056 mmol) resulting in a colourless solution. The mixture was stirred at room temperature for an hour. Colourless crystals obtained by slow diffusion of hexane into the THF solution. The solution was filtered and the crystals were dried under a dynamic vacuum yielded [K(18-crown-6)][40] as a white solid. Yield: 34 mg (71%). 1H NMR (499.93 MHz, d_8 -THF, 298 K): δ (ppm) 7.47 (d, $^4J_{H-H} = 2$ Hz, 2H; Ar), 7.00 (s, 1H, GeH), 6.54 (d, $^4J_{H-H} = 2$ Hz, 2H; Ar), 3.38 (s, 24H; 18-crown-6), 2.32 (q, 2H; CH_2CH_3), 1.43 (s, 18H; t -Bu), 1.33 (s, 18H; t -Bu), 1.00 (t, 3H; CH_2CH_3).

6.1.2.12 [K(18-crown-6)][H{ON(H)O}] ([K(18-crown-6)][40])

Water (1.86 μ L, 0.10 mmol) was added into a THF solution of [K(18-crown-6)][36] (87 mg, 0.10 mmol) resulting in a colourless solution. The mixture was stirred at room temperature for an hour. Colourless crystals obtained by slow diffusion of hexane into the THF solution. The solution was filtered by cannula and the crystals were dried under a dynamic vacuum yielded 40 as a white solid.

6.1.2.13 [K(18-crown-6)]₂[{Ge(OCH₂^{*i*}Pr)(ONO)}₂] ([K(18-crown-6)]₂[41])

Iso-butyraldehyde (9.1 μ L, 0.056 mmol) was added into a THF solution of [K(18-crown-6)][35] (80 mg, 0.10 mmol) resulting in a colourless solution. The mixture was stirred at room temperature for an hour. Colourless crystals obtained by slow diffusion of hexane into the THF solution. The solution was filtered and the crystals were dried under a dynamic vacuum yielded [K(18-crown-6)]₂[41] as a white solid. Yield: 80 mg (92%). 1H NMR

(400.20 MHz, d_8 -THF, 298 K): δ (ppm) 7.52 (s, 4H; Ar), 6.57 (s, 4H; Ar), 3.89 (m, 2H; GeCH), 3.37 (s, 48H; 18-crown-6), 1.99 (br, 2H; i Pr), 1.43 (s, 18H; t Bu), 1.33 (s, 18H; t Bu), 0.89 (d, $^3J_{\text{H-H}} = 7\text{Hz}$, 6H; i Pr), 0.82 (d, $^3J_{\text{H-H}} = 7\text{Hz}$, 6H; i Pr). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.71 MHz, d_8 -THF, 298 K): δ (ppm) 149.6 (Ar), 149.0 (Ar), 111.1 (Ar), 111.0 (Ar), 106.7 (Ar), 106.5 (Ar), 77.4 (GeCH), 70.8 (18-crown-6), 35.3 ($\text{C}(\text{CH}_3)_3$), 35.2 ($\text{C}(\text{CH}_3)_3$), 34.9 (i Pr), 30.4 ($\text{C}(\text{CH}_3)_3$), 30.3 ($\text{C}(\text{CH}_3)_3$), 20.9 (i Pr), 19.4 (i Pr).

6.1.2.14 Ge{ON(Me)O} and Ge(Me)(ONO) (42 and 43)

MeOTf (17.3 μL , 0.056 mmol) was added into a toluene solution of [K(18-crown-6)][**35**] (122 mg, 0.153 mmol) resulting in a colourless solution. All volatiles were removed under a dynamic vacuum. The reaction was monitored by ^1H NMR spectroscopy in C_6D_6 and revealed formation of two products in about 2:1 ratio. The major product: ^1H NMR (400.20 MHz, C_6D_6 , 298 K): δ (ppm) 7.29 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 2H; Ar), 7.21 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 2H; Ar), 2.35 (s, 3H; NCH_3 or GeCH_3), 1.57 (s, 18H; t Bu), 1.21 (s, 18H; t Bu). The minor product: ^1H NMR (400.20 MHz, C_6D_6 , 298 K): δ (ppm) 7.29 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 2H; Ar), 7.05 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 2H; Ar), 3.06 (s, 3H; NCH_3 or GeCH_3), 1.56 (s, 18H; t Bu), 1.29 (s, 18H; t Bu).

6.1.2.15 [K(18-crown-6)][Si(H)(Ph)(ONO)] ([K(18-crown-6)][44])

Method A: Phenylsilane (17.2 μL , 0.139 mmol) was added into a THF solution of [K(18-crown-6)][**35**] (111 mg, 0.139 mmol) resulting in a colourless solution accompanied with grey solids and gas evolved. The mixture was stirred at room temperature for an hour. Colourless solution was filtered and concentrated to c.a. 0.5 mL. Colourless crystals were obtained by slow diffusion of hexane into the THF solution. The solution was filtered and the remaining crystals were dried under a dynamic vacuum yielded [K(18-crown-6)][**44**] as a white solid. Yield: 64 mg (55%); Method B: Phenylsilane (19.0 μL , 0.154 mmol) was added into a THF solution of [K(18-crown-6)][**36**] (130 mg, 0.154 mmol) resulting in a colourless solution accompanied with grey solids and gas evolved. The mixture was stirred

at room temperature for an hour. Colourless solution was filtered and concentrated to c.a. 0.5 mL. Colourless crystals were obtained by slow diffusion of hexane into the THF solution. The solution was filtered and the remaining crystals were dried under a dynamic vacuum yielding [K(18-crown-6)][**44**] as a white solid. Yield: 106 mg (83%). ^1H NMR (499.92 MHz, d_8 -THF, 298 K): δ (ppm) 7.81 (m, 1H; Ph), 7.28 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 2H; Ar), 7.04–6.96 (m, 3H; Ph), 6.55 (d, $^4J_{\text{H-H}} = 2\text{Hz}$, 2H; Ar), 3.25 (s, 24H; 18-crown-6), 1.48 (s, 18H; $t\text{Bu}$), 1.34 (s, 18H; $t\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.71 MHz, d_8 -THF, 298 K): δ (ppm) 150.7 (Ar), 149.6 (Ph), 137.2 (Ph), 136.3 (Ar), 136.2 (Ar), 129.0 (Ar), 126.6 (Ph), 126.4 (Ph), 111.0 (Ar), 105.7 (Ar), 70.7 (18-crown-6), 35.0 ($\text{C}(\text{CH}_3)_3$), 34.9 ($\text{C}(\text{CH}_3)_3$), 32.6 ($\text{C}(\text{CH}_3)_3$), 30.4 ($\text{C}(\text{CH}_3)_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.32 MHz, C_6D_6 , 298 K): δ (ppm) –85.6 (s).

6.1.2.16 {Ga(THF)(ONO)}₂ (**45**)

In a sealable Young's tap NMR tube, [K(18-crown-6)][**36**] (28 mg, 0.033 mmol) and GaCl_3 (5.8 mg, 0.033 mmol) were dissolved in d_8 -THF resulting in a colourless solution. Colourless crystals were grown from the reaction solution at room temperature. Single X-ray crystallography diffraction determined that the structure of those colourless crystals are **45** and [K(18-crown-6)][SnCl_3]. As the crystals were not soluble in any deuterated solvents and cannot be separated from grey precipitates, no mass spectroscopy, yield, elemental analysis, or NMR data are available.

6.1.3 Chapter 3.2 – Complexes of group 14 elements bearing the bidentate-xanthene-4,5-diamine ligand

6.1.3.1 $\text{Ge}^{(\text{Mes})\text{NON}}$ (**46**)

KHMDS (302 mg, 1.51 mmol) was added to the THF (5 mL) solution of $\text{H}_2^{(\text{Mes})\text{NON}}$ (446 mg, 0.757 mmol) and the reaction solution was stirred for thirty minutes. $\text{GeCl}_2 \cdot \text{dioxane}$ (175 mg, 0.757 mmol) was subsequently added resulting in formation of a bright red solution and white precipitate. All volatiles were removed under a dynamic vacuum and the

product was extracted in hexane (3×5 mL). The hexane solution was concentrated to c.a. 2 mL affording red crystals at room temperature. The solution was filtered and the crystals were dried *in vacuo* yielded **47** as a red solid. Yield: 255 mg (51%). Elemental analysis calc. (%) for C₅₇H₈₃GeKN₂O₈: C 66.08%, H 8.08%, N 2.70%, found: C 66.24%, H 8.52%, N 2.27%. ¹H NMR (400.17 MHz, C₆D₆, 298 K): δ (ppm) 6.89 (s, 4H; mesityl Ar), 6.83 (d, ⁴J_{H-H} = 1 Hz, 2H; xanthene Ar), 6.39 (d, ⁴J_{H-H} = 1 Hz, 2H; xanthene Ar), 2.24 (s, 12H; mesityl CH₃), 2.16 (s, 6H; mesityl CH₃), 1.75 (s, 6H, xanthene CH₃), 1.18 (s, 18H; ^tBu). ¹³C{¹H} NMR (100.62 MHz, C₆D₆, 298 K): δ (ppm) 149.7 (xanthene Ar), 146.7 (mesityl Ar), 139.0 (mesityl Ar), 137.6 (mesityl Ar), 137.1 (xanthene Ar), 136.9 (xanthene Ar), 135.3 (xanthene Ar), 130.0 (mesityl Ar), 108.2 (xanthene Ar), 108.2 (xanthene Ar), 39.1 (xanthene-CH₃), 35.0 (s; C(CH₃)₃), 31.8 (s; C(CH₃)₃), 26.4 (s; xanthene-CH₃), 21.0 (s; mesityl CH₃), 19.5 (s; mesityl CH₃).

6.1.3.2 Sn(^{Mes}NON) (**47**)

KHMDS (339 mg, 1.70 mmol) was added to the THF (5 mL) solution of H₂(^{Mes}NON) (500 mg, 0.849 mmol) and the reaction solution was stirred for thirty minutes. SnCl₂·dioxane (236 mg, 0.849 mmol) was subsequently added resulting in formation of a bright red solution and white precipitate. All volatiles were removed under a dynamic vacuum and the product was extracted in hexane (3×5 mL). The hexane solution was concentrated to c.a. 2 mL affording red crystals at room temperature. The solution was filtered and the crystals were dried *in vacuo* yielded **46** as a red solid. Yield: 383 mg (64%). ¹H NMR (400.17 MHz, *d*₈-THF, 298 K): δ (ppm) 6.90 (s, 4H; mesityl Ar), 6.54 (d, ⁴J_{H-H} = 1 Hz, 2H; xanthene Ar), 5.87 (d, ⁴J_{H-H} = 1 Hz, 2H; xanthene Ar), 2.25 (s, 6H; mesityl CH₃), 2.16 (s, 12H; mesityl CH₃), 1.71 (s, 6H, xanthene CH₃), 1.14 (s, 18H; ^tBu). ¹³C{¹H} NMR (100.62 MHz, *d*₈-THF, 298 K): δ (ppm) 148.1 (xanthene Ar), 144.2 (mesityl Ar), 142.4 (mesityl Ar), 140.8 (mesityl Ar), 136.8 (xanthene Ar), 134.9 (xanthene Ar), 133.6 (xanthene Ar), 129.6 (mesityl Ar),

107.7 (xanthene Ar), 105.6 (xanthene Ar), 37.8 (xanthene-CH₃), 35.1 (s; C(CH₃)₃), 32.0 (s; C(CH₃)₃), 27.5 (s; xanthene-CH₃), 20.9 (s; mesityl CH₃), 19.4 (s; mesityl CH₃). ¹¹⁹Sn{¹H} NMR (186.43 MHz, *d*₈-THF, 298 K): δ (ppm) –189.4.

6.1.3.3 Ge(^{Cy}NON) (48)

KHMDS (298 mg, 1.49 mmol) was added to the THF (5 mL) solution of H₂(^{Cy}NON) (386 mg, 0.747 mmol) and the reaction solution was stirred for thirty minutes. GeCl₂·dioxane (173 mg, 0.747 mmol) was subsequently added resulting in formation of a yellow solution and white precipitate. All volatiles were removed under a dynamic vacuum and the product was extracted in hexane (3×5 mL). The hexane solution was concentrated to c.a. 2 mL affording yellow crystals at room temperature. The solution was filtered and the crystals were dried *in vacuo* yielded **48** as a yellow solid. Yield: 79 mg (18%). Elemental analysis calc. (%) for C₃₅H₅₀GeN₂O: C 71.56, H 8.58, N 4.77, found: C 70.57, H 8.34, N 4.72. ¹H NMR (400.17 MHz, C₆D₆, 298 K): δ (ppm) 6.65 (d, ⁴J_{H-H} = 1 Hz, 2H; Ar), 6.63 (d, ⁴J_{H-H} = 1 Hz, 2H; Ar), 3.70 (m, 2H; NCH₂), 1.81–1.05 (m, 20H, Cy), 1.67 (s, 6H; xanthene CH₃), 1.34 (s, 18H; ^tBu). ¹³C{¹H} NMR (100.62 MHz, C₆D₆, 298 K): δ (ppm) 149.8 (Ar), 148.1 (Ar), 139.8 (Ar), 137.3 (Ar), 106.1 (Ar), 105.9 (Ar), 56.3 (Cy), 39.1 (xanthene CH₃), 35.3 (Cy), 33.5 (Cy), 32.0 (C(CH₃)₃), 32.0 (C(CH₃)₃), 31.7 (xanthene CH₃), 26.7 (Cy), 26.6 (Cy), 24.7 (Cy).

6.1.3.4 Sn(^{Cy}NON) (49)

KHMDS (187 mg, 0.937 mmol) was added to the THF (5 mL) solution of H₂(^{Cy}NON) (242 mg, 0.469 mmol) and the reaction solution was stirred for thirty minutes. SnCl₂·dioxane (130 mg, 0.469 mmol) was subsequently added resulting in formation of a red solution and white precipitate. All volatiles were removed under a dynamic vacuum and the product was extracted in hexane (3×5 mL). The hexane solution was concentrated to c.a. 2 mL affording red crystals at room temperature. The solution was filtered and the crystals were dried *in*

vacuo yielded **48** as a red solid. Yield: 83 mg (28%). ^1H NMR (400.17 MHz, C_6D_6 , 298 K): δ (ppm) 6.66 (br, 4H; Ar), 3.91 (m, 2H; NCH_2), 2.50–1.02 (m, 20H, Cy), 1.71 (s, xanthene CH_3), 1.40 (s, 18H; $t\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 298 K): δ (ppm) 149.1 (Ar), 147.9 (Ar), 141.3 (Ar), 136.9 (Ar), 106.3 (Ar), 105.2 (Ar), 57.7 (Cy), 37.6 ($\text{C}(\text{CH}_3)_3$), 37.5 (Cy), 35.3 (Cy), 32.1 ($\text{C}(\text{CH}_3)_3$), 31.9 (xanthene CH_3), 31.6 (xanthene CH_3), 26.9 (Cy). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (186.43 MHz, C_6D_6 , 298 K): δ (ppm) 112.5.

6.1.3.5 $[\text{K}(\text{18-crown-6})][\text{Ge}(\text{O}^t\text{Bu})(^{\text{Mes}}\text{NON})]$ ($[\text{K}(\text{18-crown-6})][\text{50}]$)

46 (94.6 mg, 0.143 mmol), KO^tBu (16 mg, 0.143 mmol) and 18-crown-6 (38 mg, 0.143 mmol) was dissolved in THF (3 mL) in an ampoule. The reaction was stirred at room temperature for thirty minutes. Yellow crystals were grown by slow diffusion of hexane into a concentrated THF solution at room temperature. The solution was filtered and the crystals were dried *in vacuo* yielded $[\text{K}(\text{18-crown-6})][\text{51}]$ as a yellow solid. Yield: 75 mg (50%). ^1H NMR (400.17 MHz, d_8 -THF, 298 K): δ (ppm) 6.73 (s, 2H; mesityl Ar), 6.71 (s, 2H; mesityl Ar), 6.11 (d, $^4J_{\text{H-H}} = 1$ Hz, 2H; xanthene Ar), 5.57 (d, $^4J_{\text{H-H}} = 1$ Hz, 2H; xanthene Ar), 3.57 (s, 24H, 18-crown-6), 2.29 (s, 6H; mesityl CH_3), 2.20 (s, 6H; mesityl CH_3), 2.09 (s, 6H; mesityl CH_3), 1.67 (s, 3H, xanthene CH_3), 1.58 (s, 3H, xanthene CH_3), 1.06 (s, 18H; $t\text{Bu}$), 0.28 (s, 9H; O^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, d_8 -THF, 298 K): δ (ppm) 147.4 (xanthene Ar), 145.7 (mesityl Ar), 145.2 (mesityl Ar), 143.8 (mesityl Ar), 141.0 (mesityl Ar), 137.3 (xanthene Ar), 135.7 (xanthene Ar), 130.5 (xanthene Ar), 128.1 (mesityl Ar), 128.1 (mesityl Ar), 107.0 (xanthene Ar), 101.0 (xanthene Ar), 71.0 (18-crown-6), 38.4 ($\text{OC}(\text{CH}_3)_3$), 34.9 ($\text{C}(\text{CH}_3)_3$), 32.5 ($\text{OC}(\text{CH}_3)_3$), 32.4 ($\text{C}(\text{CH}_3)_3$), 26.2 (xanthene-C), 23.3 (xanthene-C), 21.2 (mesityl CH_3), 20.2 (mesityl CH_3), 20.1 (mesityl CH_3).

6.1.3.6 $[\text{K}(\text{2,2,2-crypt})][\text{Sn}(\text{O}^t\text{Bu})(^{\text{Mes}}\text{NON})]$ ($[\text{K}(\text{2,2,2-crypt})][\text{51}]$)

47 (165 mg, 0.234 mmol), KO^tBu (26 mg, 0.234 mmol) and 2,2,2-crypt (88 mg, 0.234

mmol) was dissolved in THF (3 mL) in an ampoule. The reaction solution was stirred at room temperature for thirty minutes. Yellow crystals were grown by slow diffusion of hexane into a concentrated THF solution at room temperature. The solution was filtered and the crystals were dried *in vacuo* yielded [(K(2,2,2-crypt))[**50**] as a yellow solid. Yield: 204 mg (73%). ESI MS: *m/z* calc. for C₄₅H₅₉N₂O₂Sn (M⁺) 779.36, found 779.24. ¹H NMR (400.17 MHz, *d*₈-THF, 298 K): δ (ppm) 6.74 (s, 4H; mesityl Ar), 6.11 (d, ⁴*J*_{H-H} = 1 Hz, 2H; xanthene Ar), 5.63 (d, ⁴*J*_{H-H} = 1 Hz, 2H; xanthene Ar), 3.53 (s, 12H; 2,2,2-crypt), 3.50–3.47 (m, 12H; 2,2,2-crypt), 2.51–2.49 (m, 12H, 2,2,2-crypt), 2.29 (s, 6H; mesityl CH₃), 2.20 (s, 6H; mesityl CH₃), 2.13 (s, 6H; mesityl CH₃), 1.70 (s, 3H, xanthene CH₃), 1.51 (s, 3H, xanthene CH₃), 1.08 (s, 18H; ^tBu), 0.32 (s, 9H; O^tBu). ¹³C{¹H} NMR (100.62 MHz, *d*₈-THF, 298 K): δ (ppm) 147.3 (xanthene Ar), 145.6 (mesityl Ar), 143.7 (mesityl Ar), 143.5 (mesityl Ar), 140.7 (mesityl Ar), 136.2 (xanthene Ar), 133.2 (xanthene Ar), 130.2 (xanthene Ar), 128.5 (mesityl Ar), 128.0 (mesityl Ar), 106.1 (xanthene Ar), 100.4 (xanthene Ar), 71.1 (2,2,2-crypt), 68.3 (2,2,2-crypt), 54.5 (2,2,2-crypt), 37.2 (OC(CH₃)₃), 34.9 (OC(CH₃)₃), 33.9 (C(CH₃)₃), 32.3 (C(CH₃)₃), 32.0 (mesityl CH₃), 24.1 (mesityl CH₃), 21.2 (mesityl CH₃), 20.2 (xanthene-CH₃), 20.1 (xanthene-CH₃). ¹¹⁹Sn{¹H} NMR (149.24 MHz, *d*₈-THF, 298 K): δ (ppm) –254.3.

6.1.4 Chapter 4.1 – Complexes of arsenic element bearing the *N,N*-bis(3,5,di-*tert*-2-phenolate) amide ligand

6.1.4.1 As(ONO) (**52**)

H₃(ONO) (1.00 g, 2.35 mmol) was dissolved in toluene (10 mL). AsCl₃ (198 μL, 2.35 mmol) was added to the stirred solution followed by NEt₃ (1.00 mL, 7.17 mmol), yielding a dark orange solution and white precipitate. The mixture was stirred at room temperature for three hours. All volatiles were removed under a dynamic vacuum and the product was extracted in pentane (3×10 mL). Removal of volatiles *in vacuo* yielded **52** as a dark orange

solid. Crystals suitable for single crystal X-ray diffraction analysis were grown from a concentrated pentane solution at $-30\text{ }^{\circ}\text{C}$. Yield: 880 mg (75%). Elemental analysis calcd. for $\text{C}_{28}\text{H}_{40}\text{AsNO}_2$: C 67.59, H 8.10, N 2.82; found: C 67.15, H 8.09, N 2.93. EI MS: m/z calcd. for $\text{C}_{28}\text{H}_{40}\text{AsNO}_2$: 497.2275; found: 497.2272. m/z calcd. for $\text{C}_{27}\text{H}_{37}\text{AsNO}_2$: 482.2040 Da; found: 482.1890. ^1H NMR (499.93 MHz, C_6D_6 , 298 K): δ (ppm) 8.39 (s, 2H; Ar), 7.50 (s, 2H; Ar), 1.71 (s, 18H; $t\text{Bu}$), 1.45 (s, 18H; $t\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.72 MHz, C_6D_6 , 298 K): δ (ppm) 154.0 (Ar), 142.3 (Ar), 137.2 (Ar), 135.9 (Ar), 119.9 (Ar), 111.3 (Ar), 35.7 ($\text{C}(\text{CH}_3)_3$), 35.1 ($\text{C}(\text{CH}_3)_3$), 32.0 ($\text{C}(\text{CH}_3)_3$), 30.0 ($\text{C}(\text{CH}_3)_3$).

6.1.4.2 **[K(18-crown-6)][As(O t Bu)(ONO)] ([K(18-crown-6)][53])**

52 (234 mg, 0.470 mmol), KO t Bu (54 mg, 0.470 mmol) and 18-crown-6 (124 mg, 0.470 mmol) were dissolved in THF (10 mL) at room temperature. The mixture was stirred at room temperature for thirty minutes after which the solvent was removed under vacuum. The product was crystallised as white solid from hexane. The solution was filtered and the white solid dried *in vacuo*. Crystals of the product were grown by slow diffusion of hexane into a concentrated THF solution at room temperature and were isolated by filtration. Yield: 355 mg (86 %). Elemental analysis calcd. for $\text{C}_{44}\text{H}_{73}\text{AsKNO}_9$: C 60.46, H 8.42, N 1.60; found: C 60.52, H 8.54, N 1.44. ESI MS (–ve mode, DMF): m/z calcd. for $\text{C}_{32}\text{H}_{49}\text{AsNO}_3$ [M] $^-$: 570.29; found 569.64; m/z calcd. for $\text{C}_{28}\text{H}_{40}\text{AsNO}_3$ 513.22; found: 513.61; ^1H NMR (400.17 MHz, d_8 -THF, 298 K): δ (ppm) 7.53 (d, $^4J_{\text{H-H}} = 2\text{ Hz}$, 2H; Ar), 6.56 (d, $^4J_{\text{H-H}} = 2\text{ Hz}$, 2H; Ar), 3.38 (s, 24H; 18-crown-6), 1.44 (s, 18H; $t\text{Bu}$), 1.33 (s, 18H; $t\text{Bu}$), 1.26 (s, 18H; O t Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, d_8 -THF, 298 K): δ (ppm) 152.7 (Ar), 135.9 (Ar), 133.6 (Ar), 130.4 (Ar), 111.6 (Ar), 107.4 (Ar), 71.2 ($\text{OC}(\text{CH}_3)_3$), 70.8 (18-crown-6), 35.3 ($\text{C}(\text{CH}_3)_3$), 34.9 ($\text{C}(\text{CH}_3)_3$), 32.8 ($\text{C}(\text{CH}_3)_3$), 32.5 ($\text{OC}(\text{CH}_3)_3$), 30.4 (s, $\text{C}(\text{CH}_3)_3$)

6.1.4.3 [K(2,2,2-crypt)][As(NPh₂)(ONO)] ([K(2,2,2-crypt)][54])

52 (160 mg, 0.332 mmol), KNPh₂·THF_{0.15} (70.1 mg, 0.332 mmol) and 2,2,2-crypt (121 mg, 0.332 mmol) were dissolved in THF (5 mL) resulting in a yellow solution. The mixture was stirred at room temperature for fifty minutes after which the solution was concentrated to 0.5 mL *in vacuo*. Crystals of the product were obtained by slow diffusion of hexane into the THF solution and were isolated by filtration. Yield: 245 mg (71%). Elemental analysis calcd. for C₅₈H₈₆AsKN₄O₈: C 64.42, H 8.02, N 5.18; found C 63.48, H 7.84, N 5.23. ESI MS (–ve mode, DMF): *m/z* calcd. for C₂₈H₄₂AsN₂O₂ [(H₂N)As(ONO)][–] 513.24; found: 513.97. ¹H NMR (400.17 MHz, *d*₈-THF, 298 K): δ (ppm) 7.17 (d, ⁴*J*_{H–H} = 2 Hz, 2H; Ar), 6.76–6.70 (m, 8H; NPh₂), 6.50 (d, ⁴*J*_{H–H} = 2 Hz, 2H; Ar), 6.46–6.41 (m, 2H; NPh₂), 3.46 (s, 12H; 2,2,2-crypt), 3.43–3.41 (m, 12H; 2,2,2-crypt), 2.46–2.43 (m, 12H; 2,2,2-crypt), 1.36 (s, 18H; ^tBu), 1.27 (s, 18H; ^tBu). ¹³C{¹H} NMR (100.62 MHz, *d*₈-THF, 298 K): δ (ppm) 152.2 (Ar), 150.5 (NPh₂), 135.8 (Ar), 134.1 (Ar), 130.6 (Ar), 127.9 (NPh₂), 124.5 (br; NPh₂), 119.4 (br; NPh₂), 111.8 (Ar), 107.5 (Ar), 71.0 (2,2,2-crypt), 68.2 (2,2,2-crypt), 54.5 (2,2,2-crypt), 35.2 (C(CH₃)₃), 34.8 (C(CH₃)₃), 32.6 (C(CH₃)₃), 30.3 (C(CH₃)₃).

6.1.4.4 [NⁿBu₄][As(F)(ONO)] ([NⁿBu₄][55])

52 (200 mg, 0.402 mmol) and tetrabutylammonium fluoride (402 μL, 1.0 M in THF, 0.402 mmol) was dissolved in THF yielding a colourless solution. The mixture was stirred at room temperature for one hour. Crystals suitable for single crystal X-ray diffraction analysis were grown from slow diffusion of hexane into a concentrated THF solution. The solution was filtered and the crystals were dried *in vacuo* yielded [NⁿBu₄][55] as a white solid. were isolated by filtration. Yield: 226 mg (74%). Elemental analysis calcd. for C₄₄H₇₆AsFN₂O₂: C 69.63, H 10.09, N 3.69; found: C 70.13, H 10.04, N 3.69. ¹H NMR (400.17 MHz, *d*₈-THF, 298 K): δ (ppm) 7.62 (d, ⁴*J*_{H–H} = 2 Hz, 2H; Ar), 6.69 (d, ⁴*J*_{H–H} = 2 Hz, 2H; Ar), 2.98 (m, 8H; NCH₂CH₂CH₂CH₃), 1.46 (s, 18H; ^tBu), 1.40 (m, 8H;

NCH₂CH₂CH₂CH₃), 1.34 (s, 18H; ^tBu), 1.14 (m, 8H; NCH₂CH₂CH₂CH₃), 0.85 (m, 12H; NCH₂CH₂CH₂CH₃). ¹³C{¹H} NMR (100.62 MHz, *d*₈-THF, 298 K): δ (ppm) 151.5 (Ar), 135.3 (Ar), 134.7 (Ar), 131.4 (Ar), 112.9 (Ar), 107.7 (Ar), 58.7 (NCH₂CH₂CH₂CH₃), 35.3 (C(CH₃)₃), 34.9 (C(CH₃)₃), 32.6 (C(CH₃)₃), 30.1 (C(CH₃)₃), 24.3 (NCH₂CH₂CH₂CH₃), 20.2 (NCH₂CH₂CH₂CH₃), 13.8 (NCH₂CH₂CH₂CH₃).

6.1.4.5 [As{(ON(Me)O)}][OTf] ([56][OTf])

52 (705 mg, 1.417 mmol) was dissolved in toluene (15 mL) and MeOTf (160 μL, 1.417 mmol) was added to the solution, which was stirred at 80 °C for three days, resulting in a precipitation of a white/pink solid. The solid was isolated by filtration and dried *in vacuo* yielded **[56][OTf]** as a white/pink solid. Yield: 733 mg (78%). Anal. Calcd. for C₃₀H₄₃AsF₃NO₅S: C 54.46, H 6.55, N 2.12; found C 54.40, H 6.48, N 2.28. EI MS: *m/z* calcd. for C₂₉H₄₃AsNO₂·CF₃O₃S: 661.2030; found: 661.2022. *m/z* calcd. for C₂₉H₄₃AsNO₂: 512.2528; found: 512.2510. ¹H NMR (400.17 MHz, CDCl₃, 298 K): δ (ppm) 7.31 (d, ⁴*J*_{H-H} = 2 Hz, 2H; Ar), 7.28 (d, ⁴*J*_{H-H} = 2 Hz, 2H; Ar), 3.41 (s, 3H; NCH₃), 1.40 (s, 18H; ^tBu), 1.31 (s, 18H; ^tBu). ¹³C{¹H} NMR (100.62 MHz, CDCl₃, 298 K): δ (ppm) 149.4 (Ar), 145.6 (Ar), 139.7 (Ar), 135.0 (Ar), 124.5 (Ar), 114.8 (Ar), 46.2 (CH₃), 35.5 (C(CH₃)₃), 34.9 (C(CH₃)₃), 31.6 (C(CH₃)₃), 29.4 (C(CH₃)₃). ¹⁹F NMR (376.50 MHz, CDCl₃, 298 K): δ (ppm) -77.9.

6.1.4.6 [As{(ON(H)O)}][OTf] ([57][OTf])

52 (108 mg, 0.217 mmol) was dissolved in hexane (5 mL) and HOTf (19.2 μL, 0.217 mmol) was added, resulting in a pale pink solution and white precipitate. The mixture was stirred at room temperature for fifteen minutes. The solid was isolated by filtration and dried *in vacuo* yielded **[57][OTf]** as a white solid. Yield: 64 mg (46%). Elemental analysis calcd. for C₂₈H₄₁AsF₃NO₅S: C 53.78, H 6.38, N 2.16; found: C 54.33, H 6.80, N 2.21. CI MS (NH₃ carrier gas): *m/z* calcd for C₂₈H₄₀AsNO₂: 498.2353; found: 498.2426. *m/z* calcd for

$C_{27}H_{37}AsNO_2$: 482.2040; found: 482.1884. 1H NMR (400.17 MHz, C_6D_6 , 298 K): δ (ppm) 11.64 (br, 1H; *NH*), 7.84 (d, $^4J_{H-H} = 1.9$ Hz, 2H; Ar), 7.25 (d, $^4J_{H-H} = 1.9$ Hz, 2H; Ar), 1.36 (s, 18H; *t*Bu), 1.23 (s, 18H; *t*Bu). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6 , 298 K): δ (ppm) 151.8 (Ar), 145.5 (Ar), 137.9 (Ar), 131.3 (Ar), 124.5 (Ar), 117.7 (Ar), 35.2 ($C(CH_3)$), 34.9 ($C(CH_3)$), 31.9 ($C(CH_3)$), 29.3 ($C(CH_3)$). $^{19}F\{^1H\}$ NMR (376.54 MHz, C_6D_6 , 298 K): δ (ppm) -78.0 .

6.1.4.7 As(Cl)(HONO) (58)

52 (210 mg, 0.422 mmol) was dissolved in THF (5 mL). HCl (211 μ L, 2M in Et_2O , 0.422 mmol) was added turning the solution pale yellow. The mixture was stirred at room temperature for fifteen minutes and then concentrated *in vacuo* to 0.5 mL promoting the growth of colourless block crystals of the product. The colourless crystals were isolated by filtration and dried *in vacuo* yielded **[57][OTf]** as a white solid. Yield: 155 mg (69%). Elemental analysis for $C_{28}H_{41}AsClNO_2$. C 62.98, H 7.74, N 2.62; found C 62.64, H 7.74, N 2.96. 1H NMR (400.17 MHz, C_6D_6 , 298 K): δ (ppm) 7.53 (d, $^4J_{H-H} = 2$ Hz, 1H; Ar), 7.41 (d, $^4J_{H-H} = 2$ Hz, 1H; Ar), 7.19 (d, $^4J_{H-H} = 2$ Hz, 1H; Ar), 6.69 (d, $^4J_{H-H} = 2$ Hz, 1H; Ar), 5.48 (s, 1H; ArOH), 1.63 (s, 9H; *t*Bu), 1.57 (s, 9H; *t*Bu), 1.27 (s, 9H; *t*Bu), 1.16 (s, 9H; *t*Bu). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6 , 298 K): δ (ppm) 149.7 (Ar), 147.9 (Ar), 146.1 (Ar), 143.5 (Ar), 137.4 (Ar), 137.2 (Ar), 136.7 (Ar), 124.6 (Ar), 124.0 (Ar), 123.6 (Ar), 116.5 (Ar), 108.5 (Ar), 35.6 ($C(CH_3)_3$), 35.1 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 30.0 ($C(CH_3)_3$), 29.8 ($C(CH_3)_3$).

6.1.4.8 As(O^{*t*}Bu){(ON(Me)O)} (59)

[56][OTf] (150 mg, 0.227 mmol) was dissolved in THF (5 mL) and cooled to -78 °C. A solution of KO^{*t*}Bu (25.5 mg, 0.227 mmol) in THF (5 mL) was then added dropwise. The reaction mixture was stirred at -78 °C for thirty minutes, then continued stirring at room temperature for another thirty minutes. All volatiles were removed under a dynamic vacuum

and the product was extracted with hexane (5 mL). The solution was concentrated under a dynamic vacuum yielding **59** as a white solid. Isolation of **59** from other impurities has not been possible, although characterisation data confirms the presence of the expected product. EI MS: m/z calcd. for $C_{33}H_{53}AsNO_3$: 586.3241; found: 586.3140; m/z calcd. for $C_{29}H_{44}AsNO_3$ [(HO)As{ON(Me)O}]: 529.2537; found: 529.2534. m/z calcd. for $C_{29}H_{43}AsNO_2$ [As{ON(Me)O}]: 512.2510; found: 512.2500. 1H NMR (400.17 MHz, C_6D_6 , 298 K): δ (ppm) 7.40 (d, $^4J_{H-H} = 2$ Hz, 2H; Ar), 7.32 (d, $^4J_{H-H} = 2$ Hz, 2H; Ar), 2.62 (s, 3H; NCH₃), 1.59 (s, 18H; ^{*t*}Bu), 1.54 (s, 9H; ^{*t*}Bu), 1.28 (s, 18H; ^{*t*}Bu). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6 , 298 K): δ (ppm) 151.4 (Ar), 142.9 (Ar), 139.0 (Ar), 137.9 (Ar), 121.9 (Ar), 118.0 (Ar), 73.6 (OC(CH₃)₃), 43.0 (NCH₃), 35.7 (C(CH₃)₃), 34.6 (C(CH₃)₃), 33.1 (OC(CH₃)₃), 31.7 (C(CH₃)₃), 30.1 (C(CH₃)₃).

6.1.4.9 As(Cl){(ON(Me)O)} (**60**)

[**56**][OTf] (115 mg, 0.174 mmol) and KO^{*t*}Bu (19.5 mg, 0.174 mmol) were dissolved in chloroform (5 mL) and the reaction mixture was stirred at room temperature for two hours. All volatiles were removed *in vacuo* and the product was extracted with hexane (5 mL) and filtered via cannula. The solution was concentrated under a dynamic vacuum yielding **60** as a white solid. Crystals of **60** were grown from a concentrated hexane solution at room temperature. Yield: 66 mg (69%). 1H NMR (400.17 MHz, CDCl₃, 298 K): δ (ppm) 7.30 (d, $^4J_{H-H} = 2$ Hz, 2H; Ar), 7.22 (d, $^4J_{H-H} = 2$ Hz, 2H; Ar), 3.15 (s, 3H; NCH₃), 1.43 (s, 18H; ^{*t*}Bu), 1.30 (s, 18H; ^{*t*}Bu). $^{13}C\{^1H\}$ NMR (100.62 MHz, CDCl₃, 298 K): δ (ppm) 149.8 (Ar), 144.1 (Ar), 139.0 (Ar), 136.0 (Ar), 123.1 (Ar), 116.4 (Ar), 45.1 (NCH₃), 35.5 (C(CH₃)₃), 34.8 (C(CH₃)₃), 31.7 (C(CH₃)₃), 29.7 (C(CH₃)₃).

6.1.4.10 [H][As(ONO)₂] ([H][**61**])

52 (85 mg, 0.171 mmol) was dissolved in THF (2 mL) and then exposed to air for twenty-four hours resulting in a purple solution accompanied with purple crystals that were suitable

for single crystal X-ray crystallography. Unfortunately, analytical results such as ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, MS cannot be obtained.

6.1.4.11 $[\text{H}][\text{As}(\text{F})_3(\text{ONO})]$ ($[\text{H}][\mathbf{62}]$) and $\text{As}(\text{F})_3(\text{ONO-py})$ ($\mathbf{63}$)

$\mathbf{52}$ (79 mg, 0.159 mmol) and Selectfluor (56 mg, 0.159 mmol) was dissolved in acetonitrile yielding a blue solution and dark blue precipitate. The mixture was stirred at room temperature for one hour. The solution was removed by filtration and the solid was dried under a dynamic vacuum. The dark blue solid was redissolved in c.a. 0.5 mL of pyridine. Upon slow diffusion of hexane into the pyridine solution, yellow crystals and red crystals were grown at room temperature. The structure of the yellow ($\mathbf{62}$) and red crystals ($\mathbf{63}$) were confirmed by single crystal X-ray crystallography. ESI MS (–ve mode, DMF): Calcd. for $\text{C}_{28}\text{H}_{40}\text{AsF}_3\text{NO}_2$ (M^- : 555.27; Observed: 553.92); ^{19}F NMR (376.54 MHz, d_5 -pyridine, 298 K): for $[\text{H}][\mathbf{62}]$, δ (ppm) –43.4 (d, $^2J_{\text{F-F}} = 112$ Hz; F in axial position), –63.0 (t, $^2J_{\text{F-F}} = 112$ Hz; F in equatorial position); for $\mathbf{63}$, δ (ppm) –43.6 (d, $^2J_{\text{F-F}} = 112$ Hz; F in axial position), –62.7 (t, $^2J_{\text{F-F}} = 112$ Hz; F in equatorial position).

6.1.5 Chapter 4.2 – Complexes of phosphorus element bearing the 2,2'-[iminobis(methylene)]-bis[4-methoxy-phenol] ligand

6.1.5.1 $\text{P}(\text{ONO}^*)$ ($\mathbf{64}$)

H_3ONO^* (496 mg, 1.71 mmol) was dissolved in THF (10 mL). PCl_3 (149 μL , 1.71 mmol) was added to the stirred solution followed by NEt_3 (741 μL , 5.31 mmol), giving a colourless solution and white precipitate. The mixture was stirred at room temperature for two hours. All volatiles were removed under a dynamic vacuum. The product and impurities were extracted in toluene. All volatiles were removed under a dynamic vacuum again and impurities were crashed out by addition of hexane. The filtrate was concentrated to 1 mL. Residue oil crystallised as colourless crystals overnight at room temperature. Yield: 180 mg (33%). Elemental analysis calcd. for $\text{C}_{16}\text{H}_{16}\text{NO}_4\text{P}$: C 60.57, H 5.08, N 4.41; found C 60.66,

H 5.15, N 4.11. EI MS: m/z calcd. for $C_{16}H_{16}NO_4P$: 317.0817; found: 317.0816. 1H NMR (400.16 MHz, C_6D_6 , 298 K): δ (ppm) 6.78 (d, $^3J_{H-H} = 9$ Hz, 2H; Ar), 6.43 (dd, $^3J_{H-H} = 9$ Hz, $^4J_{H-H} = 3$ Hz, 2H; Ar), 6.24 (d, $^4J_{H-H} = 3$ Hz, 2H; Ar), 4.00 (dd, $^3J_{P-H} = 16$ Hz, $^4J_{H-H} = 5$ Hz, 2H; NCH), 3.42 (dd, $^3J_{P-H} = 19$ Hz, $^4J_{H-H} = 4$ Hz, 2H; NCH), 3.23 (s, 6H, OCH_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6 , 298 K): δ (ppm) 155.4 (Ar), 144.0 (Ar), 125.6 (d, $^2J_{P-C} = 13$ Hz; Ar), 119.9 (Ar), 113.9 (Ar), 113.0 (Ar), 55.1 (OCH_3), 48.2 (d, $^2J_{P-C} = 4$ Hz, NCH_2). ^{31}P NMR (161.99 MHz, C_6D_6 , 298 K): δ (ppm) 114.4 (t, $^3J_{P-H} = 20$ Hz). $^{31}P\{^1H\}$ NMR (161.99 MHz, C_6D_6 , 298 K): δ (ppm) 114.4 (s).

6.1.5.2 P(H)(O)(HONO*) (66)

Addition of one molar equivalent of water (2.6 μ L, 0.142 mmol) into the THF solution of **64** (45 mg, 0.142 mmol). The solution was stirred at 90 °C for nine days resulting in a colourless solution and white precipitate. The solution was filtered and dried under a dynamic vacuum resulting a white solid. Crystals of **66** were grown by slow diffusion with hexane into the concentrated pyridine solution. The crystals were isolated by filtration as a white solid. Yield: 13 mg (27%). 1H NMR (400.17 MHz, d_5 -pyridine, 298 K): δ (ppm) 12.21 (br, 1H; OH), 7.76 (d, 1H, $^1J_{H-P} = 664$ Hz; PH), 7.27 (d, $^4J_{H-H} = 3$ Hz, 1H; Ar), 7.20 (m, 1H; Ar), 7.18 (m, 1H; Ar), 6.95 (m, 1H; Ar), 6.92 (m, 1H; Ar), 6.64 (d, $^4J_{H-H} = 3$ Hz, 1H; Ar-CH), 5.13 (m, 1H; NCH_2), 4.45 (m, 1H; NCH_2), 4.33 (br, 1H; NCH_2), 4.30 (m, 1H; NCH_2), 3.69 (s, 3H; OCH_3), 3.62 (s, 3H; OCH_3). ^{31}P NMR (162.0 MHz, d_5 -pyridine, 298 K): δ (ppm) 5.4 (dm, $^1J_{P-H} = 664$ Hz); $^{31}P\{^1H\}$ NMR (162.0 MHz, d_5 -pyridine, 298 K): δ (ppm) 5.4 (s).

6.1.5.3 PH(O)₂{O(H)NO*} (67)

Addition of ten molar equivalent of water (37 μ L, 2.05 mmol) into the THF solution of **64** (65 mg, 0.205 mmol). The solution was stirred at 90 °C for nine days resulting a colourless solution and white precipitate. The solution was filtered dried under a dynamic vacuum

resulting a white solid. Crystals suitable of **67** were grown in slow diffusion with hexane into the concentrated pyridine solution. The crystals were isolated by filtration as a white solid. Yield: 13 mg (32%). ^1H NMR (400.17 MHz, d_5 -pyridine, 298 K): δ (ppm) 13.4 (s, 1H; OH), 7.72 (s, 1H; Ar), 7.71 (s, 1H; Ar), 7.20 (s, 1H; Ar), 7.18 (s, 1H; Ar), 6.93 (d, $^4J_{\text{H-H}} = 3$ Hz, 1H; Ar), 6.91 (d, $^4J_{\text{H-H}} = 3$ Hz, 1H; Ar), 4.74 (s, 4H; N-CH₂), 3.73 (s, 6H, OCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, d_5 -pyridine, 298 K): δ (ppm) 153.7 (Ar), 151.7 (Ar), 120.8 (Ar), 118.1 (Ar), 117.7 (Ar), 117.5 (Ar), 68.3 (NCH₂), 56.2 (OCH₃), 46.8 (OCH₃), 46.2 (NCH₂). ^{31}P NMR (162.0 MHz, d_5 -pyridine, 298 K): δ (ppm) 2.9 (d, $^1J_{\text{P-H}} = 626$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, d_5 -pyridine, 298 K): δ (ppm) 2.9 (s).

6.1.5.4 P(BH₃)(ONO*) (**68**)

Addition of borane–pyridine (12 μL , 0.12 mmol) into the THF solution of **64** (38 mg, 0.12 mmol). The solution was stirred at 70 °C for twenty hours. The solution was allowed to cool down to room temperature. The THF solution was concentrated to c.a. 0.5 mL. Crystals that were suitable for single crystal X-ray crystallography were grown by slow diffusion of hexane into the concentrated THF solution. The solution was filtered and the solid was dried *in vacuo* yielded **68** as a white solid. Yield: 19 mg (46%). ^1H NMR (400.17 MHz, C₆D₆, 298 K): δ (ppm) 6.65 (d, $^3J_{\text{H-H}} = 9$ Hz, 2H; Ar), 6.26 (dd, $^3J_{\text{H-H}} = 9$ Hz, $^4J_{\text{H-H}} = 3$ Hz, 2H; Ar), 6.14 (d, $^4J_{\text{H-H}} = 3$ Hz, 2H; Ar), 4.08 (dd, $^3J_{\text{P-H}} = 15$ Hz, $^4J_{\text{H-H}} = 7$ Hz, 2H; NCH), 3.13 (s, 6H, OCH₃), 3.12 (m, 2H; NCH), 2.24–1.40 (m, 3H; BH₃). ^{31}P NMR (162.00 MHz, C₆D₆, 298 K): δ (ppm) 111.3 (br, m). $^{31}\text{P}\{^1\text{H}\}$ NMR (162.00 MHz, C₆D₆, 298 K): δ (ppm) 111.3 (br, m). ^{11}B NMR (128.39 MHz, C₆D₆, 298K): δ (ppm) –40.4 (m). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.39 MHz, C₆D₆, 298K): δ (ppm) –40.4 (d, $^1J_{\text{P-B}} = 88$ Hz).

6.1.5.5 P(BPh₃)(ONO*) (**69**)

57 (40 mg, 0.126 mmol) and triphenylphosphine (31 mg, 0.126 mmol) were dissolved in toluene (2 mL). The solution was stirred at room temperature for two hours. The toluene

solution was concentrated to c.a. 0.5 mL. Crystals that were suitable for single crystal X-ray crystallography were grown by slow diffusion of hexane into the concentrated toluene solution. The solution was filtered and the solid was dried *in vacuo* yielded **69** as a white solid. Yield: 52 mg (72%). ^1H NMR (400.17 MHz, C_6D_6 , 298 K): δ (ppm) 7.94 (dm, $^3J_{\text{H-H}} = 8$ Hz, 6H; BPh), 7.35–7.24 (m, 9H; BPh), 6.56 (d, $^3J_{\text{H-H}} = 9$ Hz, 2H; Ar), 6.21 (dd, $^3J_{\text{H-H}} = 9$ Hz, $^4J_{\text{H-H}} = 3$ Hz, 2H; Ar), 6.07 (d, $^4J_{\text{H-H}} = 3$ Hz, 2H; Ar), 3.90 (dd, $^3J_{\text{P-H}} = 16$ Hz, $^4J_{\text{H-H}} = 4$ Hz, 2H; NCH), 3.08 (s, 6H; OCH_3), 3.03 (dd, $^3J_{\text{P-H}} = 18$ Hz, $^4J_{\text{H-H}} = 3$ Hz, 2H; NCH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 298 K): δ (ppm) 155.9 (s, Ar), 144.1 (Ar), 144.0 (Ar), 137.5 (BPh), 128.2 (BPh), 127.9 (BPh), 127.6 (BPh), 119.6 (d, $^3J_{\text{P-C}} = 2$ Hz; Ar), 113.6 (Ar), 112.7 (Ar), 55.0 (OCH_3), 50.6 (NCH_2). ^{31}P NMR (161.99 MHz, C_6D_6 , 298 K): δ (ppm) 96.4 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.99 MHz, C_6D_6 , 298 K): δ (ppm) 96.4 (m). ^{11}B NMR (128.39 MHz, C_6D_6 , 298K): δ (ppm) 17.7 (br). $^{11}\text{B}\{^1\text{H}\}$ NMR (128.39 MHz, C_6D_6 , 298K): δ (ppm) 17.7 (br).

6.3 Characterisation techniques

6.3.1 Single crystal X-ray diffraction

Single crystal X-ray diffraction data were collected using either an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector or an Enraf-Nonius kappa-CCD diffractometer equipped with a 95 mm CCD area detector. Crystals were selected under Paratone-N[®] oil, mounted on micromount loops, and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Data were collected at 150 K using mirror monochromated Cu $\text{K}\alpha$ radiation ($\lambda = 1.54178$ Å; Oxford Diffraction Supernova) or graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å; Enraf-Nonius kappa-CCD). Data collected on the Oxford Diffraction Supernova diffractometer were processed using the CrysAlisPro package, including unit cell parameter refinement and interframe scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).⁹

Equivalent reflections were merged, and diffraction patterns processed with the CrysAlisPro suite. For data collected on the Enraf-Nonius kappa-CCD, diffractometer equivalent reflections were merged and the diffraction patterns processed with the DENZO and SCALEPACK programs.¹⁰ Structures were subsequently solved using direct methods or using the charge flipping algorithm as implemented in the program SUPERFLIP¹¹ and refined on F^2 using the SHELXL-2013 package.^{12–14}

6.3.2 NMR spectroscopy

NMR samples were prepared inside a glovebox under nitrogen in NMR tubes equipped with a gas-tight valve. ^1H , ^{11}B , $^{13}\text{C}\{^1\text{H}\}$, ^{19}F , $^{29}\text{Si}\{^1\text{H}\}$, ^{31}P , $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra were acquired on a Bruker AVII or AVIII 500 MHz NMR spectrometer at 298 K unless otherwise stated. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are reported relative to tetramethylsilane (TMS) and were referenced to the most downfield residual solvent resonance (C_6D_6 : δ_{H} 7.16 ppm, δ_{C} 128.1 ppm; CD_2Cl_2 : δ_{H} 5.32 ppm, δ_{C} 53.8 ppm; d_8 -THF: δ_{H} 3.58 ppm, δ_{C} 67.6 ppm; d_5 -pyridine: δ_{H} 8.74 δ_{C} 150.35). ^{11}B , ^{19}F , $^{29}\text{Si}\{^1\text{H}\}$, ^{31}P , $^{119}\text{Sn}\{^1\text{H}\}$, NMR spectra were externally referenced to $\text{Et}_2\text{O}\cdot\text{BF}_3$, CFCl_3 , SiMe_4 , an 85% solution of H_3PO_4 in H_2O and SnMe_4 respectively.

6.3.3 Mass spectrometry

Negative ion mode electrospray mass spectra (ESI MS) were recorded on a Waters MassLynx LCT Time of Flight mass spectrometer with a Z-spray source. The samples (10–20 μM) were made up inside a glovebox under nitrogen and rapidly transferred to the spectrometer via a 1 mL air-tight SGE syringe and syringe pump at a rate of 10 $\mu\text{L}\cdot\text{min}^{-1}$.

Positive ion mode electrospray mass spectra were recorded on a Bruker MicroTOF mass spectrometer. The samples (10–20 μM) were prepared inside a glovebox under argon and

the sample injected through a standard PEEK tubing feedthrough directly to the mass analyser at $10 \mu\text{L} \cdot \text{min}^{-1}$.¹⁵

Electron ionisation mass spectrometry (EI MS) were carried out by Colin Sparrow of the University of Oxford. Samples were submitted as solids and spectra were obtained using a Waters GCT Time of Flight mass spectrometer with a temperature-programmed solids probe inlet.

6.3.4 Elemental analyses

Elemental analyses were performed by Elemental Microanalysis Ltd, Devon. 8–10 mg samples were sent in sealed, evacuated Pyrex ampoules. All values are an average of at least two data collections and are given as percentages.

6.4 References

- (1) Chaudhuri, P.; Hess, M.; Weyhermuller, T.; Wieghardt, K. *Angew. Chemie. Int. Ed.* **1999**, 38 (8), 1095.
- (2) Zarkesh, R. A.; Ziller, J. W.; Heyduk, A. F. *Angew. Chemie. Int. Ed.* **2008**, 47 (25), 4715.
- (3) Porter, R. M.; Danopoulos, A. A. *Polyhedron* **2006**, 25 (4), 859.
- (4) Whiting, E.; Lanning, M. E.; Scheenstra, J. A.; Fletcher, S. *J. Org. Chem.* **2015**, 80 (2), 1229.
- (5) Searcey, M.; Grewal, S. S.; Madeo, F.; Tsoungas, P. G. *Tetrahedron Lett.* **2003**, 44 (35), 6745.
- (6) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chemie. Int. Ed.* **2009**, 48 (31), 5683.
- (7) Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Henderson, L. C.; Herber, C.; Liddle, S. T.; Loroño-González, D.; Parkin, A.; Parsons, S. *Chem. - A Eur. J.* **2003**,

- 9 (19), 4820.
- (8) Yin, H.; Lewis, A. J.; Williams, U. J.; Carroll, P. J.; Schelter, E. J. *Chem. Sci.* **2013**, 4 (2), 798.
- (9) CrysAlisPro, Agilent Technologies, Versions 1.171.35.8 and 1.171.37.35.
- (10) Otwinowski, Z.; Minor, W. *Macromol. Crystallogr. Part A* **1997**, 276, 307–326.
- (11) Palatinus, L.; Chapius, G. *J. Appl. Crystallogr.* **2007**, 40, 786–790.
- (12) Sheldrick, G. M. *Acta Crystallogr. A* **1990**, 46 (6), 467–473.
- (13) Sheldrick, G. M. *Acta Crystallogr. A* **2008**, 64 (1), 112–122.
- (14) Sheldrick, G. M. *SHELXL-2013, Programs for Crystal Structure Analysis* **2013**.
- (15) Lubben, A. T.; McIndoe, J. S.; Weller, A. S. *Organometallics* **2008**, 27 (13), 3303–3306.

Appendix A

Single crystal X-ray diffraction data

	1	2	3	4
Formula	C ₃₂ H ₄₈ BNO ₃	C ₃₁ H ₄₉ BN ₂ O ₂	C ₅₆ H ₈₂ B ₂ N ₂ O ₅	C ₃₀ H ₄₆ BNO ₃
Fw [g mol ⁻¹]	505.54	492.54	884.88	479.50
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.0527(11)	14.5737(5)	10.1623(4)	10.4317(7)
<i>b</i> (Å)	11.2697(13)	19.0944(5)	15.1653(8)	10.5626(7)
<i>c</i> (Å)	15.378(2)	12.3383(4)	17.8497(9)	13.4329(12)
α (°)	84.060(10)	90	88.964(4)	95.548(6)
β (°)	74.468(11)	112.520(4)	89.282(3)	97.309(6)
γ (°)	85.640(10)	90	78.573(4)	91.608(5)
<i>V</i> (Å ³)	1501.6(3)	3171.64(19)	2695.8(2)	1459.99(19)
<i>Z</i>	4	2	6	2
Radiation, λ (Å)	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178
ρ_{calc} (g cm ⁻³)	1.122	1.031	1.090	1.091
μ (mm ⁻¹)	0.539	0.481	0.522	0.528
Reflections collected	12895	17587	26501	13857
Independent reflections	5625	6549	11128	6003
Parameters	380	325	742	394
R(int)	0.1177	0.0350	0.0530	0.0396
R1/wR2, ^a I $\geq$ 2 σ I (%)	9.63/26.87	4.51/11.53	5.07/14.16	5.08/13.09
R1/wR2, ^a all data (%)	14.03/28.35	6.19/12.65	8.44/15.46	7.10/15.01
GOF	1.081	1.022	1.072	1.016

^a R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.1451 and 0.6209 for **1**, 0.0664 and 0.4098 for **2**, 0.0298 and 1.3467 for **3** and 0.0706 and 0.1831 for **4**.

	6	[7]·THF	8	10
Formula	C ₈₄ H ₁₃₆ GeKN ₅ O ₉ Si ₂	C ₆₀ H ₈₈ B ₂ N ₂ O ₅	C ₃₂ H ₄₉ AlClINO ₃	C ₃₃ H ₄₆ ClGa ₂ N ₂ O ₂
Fw [g mol ⁻¹]	521.56	938.94	558.15	607.89
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> (Å)	10.0580(5)	10.95940(10)	11.09220(10)	10.3777(3)
<i>b</i> (Å)	19.6035(11)	26.0177(2)	11.62470(10)	11.3696(3)
<i>c</i> (Å)	16.9262(8)	20.0544(2)	25.5405(3)	27.6167(8)
α (°)	90	90	90	90
β (°)	101.660(5)	100.0660(10)	96.1070(10)	100.707(3)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	4443.00(7)	5630.26(9)	3274.59(6)	3201.77(16)
<i>Z</i>	4	4	4	4
Radiation, λ (Å)	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178
ρ_{calc} (g cm ⁻³)	1.060	1.108	1.132	1.261
μ (mm ⁻¹)	0.505	0.526	1.521	2.171
Reflections collected	18986	57491	37302	22572
Independent reflections	6787	11703	6807	6641
Parameters	389	697	363	356
R(int)	0.0551	0.0232	0.0243	0.0245
R1/wR2, ^a I $\geq$ 2 σ I (%)	4.62/10.08	5.26/21.80	3.31/8.51	2.49/6.42
R1/wR2, ^a all data (%)	8.27/11.93	5.95/23.77	3.75/8.90	2.94/6.68
GOF	1.013	1.078	1.012	1.017

^a R1 = $[\sum |F_o| - |F_c|]/\sum |F_o|$; wR2 = $\{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0465 and 0.2806 for **6**, 0.2000 and 0 for [7]·THF, 0.0437 and 1.2569 for **8** and 0.0356 and 0.9623 for **10**.

	11	[14] · ⁵ / ₂ py	[15] · ⁵ / ₂ py	[16] ·3py
Formula	C ₃₂ H ₄₉ BrGaNO ₃	C _{55.5} H _{67.5} AlN _{6.5} O ₂	C _{55.5} H _{67.5} GaN _{6.5} O ₂	C _{59.5} H _{76.5} AlN _{8.5} O ₂
Fw [g mol ⁻¹]	645.35	884.64	927.38	970.78
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>P2₁/n</i>	<i>Pbca</i>	<i>Pbca</i>	<i>I2/a</i>
<i>a</i> (Å)	10.2875(4)	22.9826(2)	23.1420(3)	20.1178(3)
<i>b</i> (Å)	11.3761(4)	28.6582(4)	28.9402(4)	21.8977(3)
<i>c</i> (Å)	27.8336(9)	31.5913(3)	31.8997(3)	27.5483(4)
α (°)	90	90	90	90
β (°)	98.959(4)	90	90	110.890(2)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	3217.7(2)	20807.3(4)	21364.3(5)	11338.2(3)
<i>Z</i>	4	16	16	4
Radiation, λ (Å)	Cu K α , 1.54178	Cu K α , 1.54184	Cu K α , 1.54178	Cu K α , 1.54184
ρ_{calc} (g cm ⁻³)	1.332	1.130	1.153	1.137
μ (mm ⁻¹)	2.857	0.691	1.045	0.684
Reflections collected	17644	65969	244032	33537
Independent reflections	6659	18332	22342	11715
Parameters	404	1199	1076	702
R(int)	0.0274	0.0341	0.0911	0.0199
R1/wR2, ^a I $\geq$ 2 σ I (%)	4.79/10.34	6.05/17.20	6.27/15.44	3.81/10.21
R1/wR2, ^a all data (%)	5.95/11.07	7.94/18.64	8.47/17.45	4.69/10.75
GOF	0.988	1.086	1.074	1.055

^a R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0223 and 11.1024 for **11**, 0.1021 and 9.0569 for **[14]**·⁵/₂py, 0.0738 and 20.6375 for **[15]**·⁵/₂py and 0.0577 and 4.9191 for **[16]**·3py.

	[17]·5C₆H₆	19	[20]·³/2H₃B·py	21
Formula	C ₉₄ H ₁₂₆ Al ₂ N ₂ O ₆	C ₆₆ H ₉₀ Al ₂ N ₄ O ₄	C _{39.5} H ₆₂ B _{1.5} GaN _{2.5} O ₃	C ₆₈ H ₁₀₆ Al ₂ N ₄ O ₄
Fw [g mol ⁻¹]	1433.92	1057.37	705.85	1097.52
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>C2/c</i>	<i>P2₁/c</i>
<i>a</i> (Å)	10.4261(2)	14.0505(3)	36.8096(17)	13.3093(3)
<i>b</i> (Å)	25.8004(4)	14.3772(3)	12.9162(5)	12.6008(3)
<i>c</i> (Å)	16.2842(3)	16.9337(4)	17.8272(7)	20.7135(5)
α (°)	90	90	90	90
β (°)	104.667(2)	114.153(3)	108.325(4)	107.170(2)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	4237.67(14)	3121.26(14)	8045.9(6)	3319.00(14)
<i>Z</i>	2	2	8	2
Radiation, λ (Å)	Cu Kα, 1.54178	Cu Kα, 1.54178	Cu Kα, 1.54178	Cu Kα, 1.54178
ρ _{calc} (g cm ⁻³)	1.124	1.125	1.165	1.098
μ (mm ⁻¹)	0.715	0.791	1.212	0.755
Reflections collected	25335	20189	23137	18533
Independent reflections	8771	6471	8256	6857
Parameters	525	355	507	372
R(int)	0.0226	0.0336	0.0689	0.0226
R1/wR2, ^a I ≥ 2σI (%)	4.81/12.68	4.13/10.88	4.76/11.47	4.02/10.66
R1/wR2, ^a all data (%)	5.46/13.35	5.63/12.30	9.22/13.23	4.81/11.56
GOF	1.045	1.025	1.034	1.053

^a R1 = $[\sum ||F_o| - |F_c||]/\sum |F_o|$; wR2 = $\{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0666 and 1.7773 for **[17]·5C₆H₆**, 0.0671 and 0.6956 for **19**, 0.0537 and 0.7818 for **[20]·³/2H₃B·py** and 0.0556 and 1.4572 for **21**.

	22	[23] ·4C ₆ H ₆	[24] ·2C ₇ H ₈	[25] · ³ / ₂ C ₆ H ₆
Formula	C ₇₆ H ₁₁₄ Al ₂ N ₄ O ₄	C ₈₄ H ₁₁₆ Al ₂ N ₂ O ₆	C ₇₈ H ₁₁₆ Al ₂ N ₂ O ₆	C ₇₅ H ₉₉ BGa ₄ N ₄ O ₄
Fw [g mol ⁻¹]	1201.67	1303.74	1231.68	1201.11
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	18.9030(4)	9.9244(4)	9.9944(3)	14.3940(6)
<i>b</i> (Å)	19.3902(5)	14.0953(7)	14.2040(4)	16.8552(4)
<i>c</i> (Å)	20.1013(4)	14.8821(11)	14.3560(3)	28.5653(8)
α (°)	90	72.851(5)	104.187(2)	90
β (°)	90	89.369(4)	96.980(2)	93.450(3)
γ (°)	90	85.883(4)	95.687(3)	90
<i>V</i> (Å ³)	7367.8(3)	1984.0(2)	1943.52(9)	6917.8(4)
<i>Z</i>	2	1	1	4
Radiation, λ (Å)	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54184	Cu K α , 1.54178
ρ_{calc} (g cm ⁻³)	1.083	1.091	1.052	1.153
μ (mm ⁻¹)	0.720	0.718	0.705	0.922
Reflections collected	72283	20397	19159	42156
Independent reflections	7700	8206	8010	14344
Parameters	495	554	457	960
R(int)	0.0613	0.0190	0.0191	0.0560
R1/wR2, ^a I $\geq$ 2 σ I (%)	4.32/10.97	3.78/9.76	4.42/12.05	5.66/12.01
R1/wR2, ^a all data (%)	5.92/12.24	4.27/10.43	4.88/12.60	9.84/14.10
GOF	1.019	1.056	1.038	1.056

^a R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0587 and 2.2817 for **22**, 0.0512 and 0.5784 for **[23]**·4C₆H₆, 0.0700 and 0.6644 for **[24]**·2C₇H₈ and 0.0292 and 4.0332 for **[25]**·³/₂C₆H₆.

	[26]·3C ₇ H ₈	[27]·3C ₇ H ₈	[29]· ³ /2C ₆ H ₆	[30]· ⁵ /2C ₆ H ₆
Formula	C ₉₁ H ₁₂₀ Ga ₂ N ₂ O ₆	C ₈₅ H ₁₂₄ Ga ₂ N ₂ O ₆	C ₇₁ H ₉₇ N ₂ O ₄ Si	C ₇₁ H ₉₇ GeN ₂ O ₄
Fw [g mol ⁻¹]	1477.32	1409.29	1070.59	1115.09
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.1748(4)	10.9400(4)	15.1802(4)	15.3024(3)
<i>b</i> (Å)	13.5915(7)	10.9575(4)	15.5030(5)	15.6107(3)
<i>c</i> (Å)	16.6911(11)	19.5421(8)	16.3205(6)	16.3827(3)
α (°)	73.425(5)	83.885(4)	105.505(3)	104.913(2)
β (°)	87.080(4)	85.067(3)	113.916(3)	113.935(2)
γ (°)	71.718(4)	61.298(4)	97.707(2)	97.973(2)
<i>V</i> (Å ³)	2098.8(2)	2041.45(15)	3252.6(2)	3322.97(12)
<i>Z</i>	1	1	2	2
Radiation, λ (Å)	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178
ρ_{calc} (g cm ⁻³)	1.169	1.146	1.093	1.114
μ (mm ⁻¹)	1.182	1.189	0.675	0.975
Reflections collected	18902	19231	35093	73288
Independent reflections	7381	8342	13435	13811
Parameters	570	535	739	710
R(int)	0.0650	0.0304	0.0211	0.0493
R1/wR2, ^a I $\geq$ 2 σ I (%)	5.18/11.50	5.59/14.80	3.69/9.35	4.05/10.91
R1/wR2, ^a all data (%)	7.31/12.47	6.18/15.23	4.31/9.84	4.43/11.40
GOF	0.854	1.084	1.022	1.031

^a R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0378 and 2.9326 for [26]·3C₇H₈, 0.0699 and 3.1549 for [27]·3C₇H₈, 0.0488 and 0.8022 for [29]·³/2C₆H₆ and 0.0668 and 1.4009 for [30]·⁵/2C₆H₆.

	[31] $\cdot$ C ₇ H ₈	[HfPr][32]	[33] $\cdot$ THF	[K(18-crown-6)][35]
Formula	C ₆₃ H ₉₀ N ₂ O ₄ Sn	C ₇₇ H ₉₄ Br ₂ N ₄ O ₄ Si	C ₃₂ H ₄₉ GeNO ₃	C ₄₀ H ₆₄ GeKNO ₈
Fw [g mol ⁻¹]	1058.05	1327.47	568.31	798.67
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P2₁/n</i>	<i>Pca2₁</i>	<i>P2₁/n</i>	<i>P2₁/c</i>
<i>a</i> (Å)	14.36400(10)	20.0265(6)	10.72530(10)	9.9362(2)
<i>b</i> (Å)	25.17060(10)	12.5656(5)	20.46630(10)	22.9796(7)
<i>c</i> (Å)	17.54390(10)	21.1521(9)	14.30120(10)	18.7421(4)
α (°)	90	90	90	90
β (°)	104.1200(10)	90	97.8110(10)	91.306(2)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	6151.36(7)	5322.8(3)	3110.09(4)	4278.27(18)
<i>Z</i>	4	4	4	2
Radiation, λ (Å)	Cu K α , 1.54178	Cu K α , 1.54184	Cu K α , 1.54178	Cu K α , 1.54178
ρ_{calc} (g cm ⁻³)	1.142	1.137	1.214	1.648
μ (mm ⁻¹)	3.634	1.621	1.567	3.511
Reflections collected	124645	19451	35690	26101
Independent reflections	12821	12695	6470	8850
Parameters	697	9028	396	514
R(int)	0.0353	0.0533	0.0176	0.0649
R1/wR2, ^a I $\geq$ 2 σ I (%)	2.72/7.37	5.45/13.28	2.50/6.76	4.99/11.97
R1/wR2, ^a all data (%)	2.80/7.45	7.61/15.47	2.62/6.86	7.84/13.81
GOF	1.039	1.044	1.019	1.013

^a R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0403 and 3.9533 for [**31**] $\cdot$ C₇H₈, 0.0699 and 2.4582 for [HfPr][**32**], 0.0386 and 1.0963 for [**33**] $\cdot$ THF and 0.0668 and 0.3362 for [K(18-crown-6)][**35**].

	[K(18-crown-6)][36]	[K(18-crown-6)] ₂ [37]·2THF	[K(18-crown-6)][38]	[K(18-crown-6)][39]·C ₆ H ₆
Formula	C ₄₀ H ₆₄ KNO ₈ Sn	C ₁₀₄ H ₁₇₆ GeK ₂ N ₂ O ₂₂	C ₄₀ H ₆₆ GeKNO ₉	C ₄₈ H ₇₆ GeKN ₄ O ₉
Fw [g mol ⁻¹]	844.71	1957.25	816.62	922.78
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁	<i>Cc</i>
<i>a</i> (Å)	10.3569(2)	21.5035(5)	9.4519(3)	13.9660(2)
<i>b</i> (Å)	15.7716(2)	24.2952(6)	9.9776(3)	14.5790(2)
<i>c</i> (Å)	13.9097(3)	21.9065(5)	23.5234(8)	25.5574(4)
α (°)	90	90	90	90
β (°)	111.234(2)	100.699(2)	95.861(3)	95.630(2)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	2117.82(7)	11245.7(5)	2206.83(12)	5178.65(13)
<i>Z</i>	2	4	2	4
Radiation, λ (Å)	Cu Kα, 1.54184	Cu Kα, 1.54178	Cu Kα, 1.54178	Cu Kα, 1.54178
ρ _{calc} (g cm ⁻³)	1.325	1.156	1.229	1.184
μ (mm ⁻¹)	6.067	1.547	2.188	1.921
Reflections collected	11668	34674	21831	14971
Independent reflections	6993	11640	7667	7277
Parameters	472	720	487	594
R(int)	0.0225	0.0437	0.0396	0.0425
R1/wR2, ^a I ≥ 2σI (%)	3.16/8.48	4.69/11.74	3.43/8.69	4.31/11.30
R1/wR2, ^a all data (%)	3.32/9.34	6.43/13.03	3.73/8.99	4.53/11.59
GOF	1.105	1.034	1.023	1.043

^a R1 = $[\sum |F_o| - |F_c|]/\sum |F_o|$; wR2 = $\{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0633 and 1.1757 for [K(18-crown-6)][**36**], 0.0677 and 6.2014 for [K(18-crown-6)]₂[**37**]·2THF, 0.0477 and 0.5156 for [K(18-crown-6)][**38**] and 0.0801 and 0 for [K(18-crown-6)][**39**]·C₆H₆.

	[40]·THF	[K(18-crown-6)] ₂ [41]·3C ₇ H ₈	[K(18-crown-6)] ₂ [44]·C ₆ H ₆	[45]·2THF
Formula	C ₄₄ H ₇₄ KNO ₉	C ₁₀₉ H ₁₆₈ Ge ₂ K ₂ N ₂ O ₁₈	C ₄₆ H ₇₀ KNO ₈ Si	C ₇₂ H ₁₁₂ Ga ₂ N ₂ O ₈
Fw [g mol ⁻¹]	800.14	2017.82	832.23	1273.07
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.9887(5)	11.8151(5)	13.1085(7)	10.5944(4)
<i>b</i> (Å)	12.9868(7)	14.5441(4)	22.9913(9)	13.7419(5)
<i>c</i> (Å)	17.9251(8)	18.4582(7)	17.0105(9)	14.0171(6)
α (°)	105.341(4)	67.500(3)	90	115.139(4)
β (°)	91.993(4)	76.710(3)	108.784(6)	104.508(3)
γ (°)	104.014(4)	73.382(3)	90	95.313(3)
<i>V</i> (Å ³)	2380.1(2)	2781.91(19)	4853.6(4)	1741.78(13)
<i>Z</i>	2	1	2	1
Radiation, λ (Å)	Cu K α , 1.54184	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54184
ρ_{calc} (g cm ⁻³)	1.116	1.204	1.278	1.214
μ (mm ⁻¹)	1.371	1.830	3.083	1.361
Reflections collected	24625	29177	30661	16828
Independent reflections	9826	11504	10049	7194
Parameters	519	638	611	468
R(int)	0.0518	0.0348	0.0739	0.0181
R1/wR2, ^a I $\geq$ 2 σ I (%)	5.28/12.87	4.15/10.27	11.47/31.18	3.51/9.15
R1/wR2, ^a all data (%)	8.41/14.95	5.02/11.04	15.76/36.19	3.78/9.42
GOF	1.013	1.035	1.264	1.033

^a R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0663 and 0.5231 for [**40**]·THF, 0.0510 and 1.4890 for [K(18-crown-6)]₂[**41**]·3C₇H₈, 0.2000 and 0 for [K(18-crown-6)]₂[**44**]·C₆H₆ and 0.0477 and 1.1050 for [**45**]·2THF.

	46	47	49	[K(2,2,2-crypt)][50]·THF·C ₆ H ₁₄
Formula	C ₄₁ H ₅₀ GeN ₂ O	C ₄₁ H ₅₀ N ₂ O ₁ Sn	C ₃₅ H ₅₀ N ₂ OSn	C ₆₇ H ₁₀₅ GeKN ₂ O ₉
Fw [g mol ⁻¹]	659.49	705.52	633.46	1194.21
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Fdd</i> 2	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	27.8248(6)	41.3413(8)	6.0518(2)	9.81350(10)
<i>b</i> (Å)	9.3175(2)	38.1107(7)	14.0572(5)	16.2378(3)
<i>c</i> (Å)	28.1379(5)	9.2395(2)	18.9260(5)	21.9684(4)
α (°)	90	90	97.819(3)	86.731(2)
β (°)	90.584(2)	90	91.291(2)	81.4600(10)
γ (°)	90	90	92.243(3)	72.9510(10)
<i>V</i> (Å ³)	7294.6(3)	14557.3(5)	1593.24(9)	3309.37(9)
<i>Z</i>	4	16	2	2
Radiation, λ (Å)	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178
ρ_{calc} (g cm ⁻³)	1.339	1.288	1.320	1.198
μ (mm ⁻¹)	1.549	5.822	6.581	1.617
Reflections collected	95826	44587	14795	50445
Independent reflections	15210	6657	6601	13706
Parameters	827	434	352	738
R(int)	0.0971	0.0320	0.0323	0.0394
R1/wR2, ^a I $\geq$ 2 σ I (%)	14.26/41.10	2.48/6.47	4.07/10.53	4.80/13.31
R1/wR2, ^a all data (%)	15.41/41.65	2.60/6.55	4.18/10.66	5.89/14.13
GOF	1.106	1.050	1.046	1.056

^a R1 = $[\sum||F_o| - |F_c||]/\sum|F_o|$; wR2 = $\{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.1261 and 175.0681 for **46**, 0.0476 and 8.1657 for **47**, 0.0775 and 0.9927 for **49** and 0.0806 and 1.8318 for [K(2,2,2-crypt)][**50**]·THF·C₆H₁₄.

	[K(18-crown-6)][51] $\cdot$ C ₆ H ₁₄	52	[K(18-crown-6)][53] $\cdot$ THF	[K(2,2,2-crypt)][54]
Formula	C ₆₇ H ₁₀₃ KN ₄ O ₈ Sn	C ₂₈ H ₄₀ AsNO ₂	C ₄₈ H ₈₁ AsKNO ₁₀	C ₅₈ H ₈₆ AsKN ₄ O ₈
Fw [g mol ⁻¹]	1250.32	497.53	946.15	1081.32
Crystal system	Hexagonal	Tetragonal	Monoclinic	Orthorhombic
Space group	<i>P63/m</i>	<i>I</i> -4	<i>P2</i> ₁ / <i>n</i>	<i>Pna</i> 2 ₁
<i>a</i> (Å)	22.012(3)	13.7548(19)	14.62750(10)	30.0623(2)
<i>b</i> (Å)	22.012(3)	13.7548(19)	21.81250(10)	10.61730(10)
<i>c</i> (Å)	24.554(5)	28.807(6)	17.23910(10)	18.49220(10)
α (°)	90	90	90	90
β (°)	90	90	113.4330(10)	90
γ (°)	120	90	90	90
<i>V</i> (Å ³)	10303(4)	5450.1(19)	5046.71(6)	5902.35(8)
<i>Z</i>	6	8	4	4
Radiation, λ (Å)	Mo K α , 0.71073	Mo K α , 0.71073	Cu K α , 1.54178	Cu K α , 1.54178
ρ_{calc} (g cm ⁻³)	1.209	1.213	1.245	1.217
μ (mm ⁻¹)	0.485	1.270	2.082	1.836
Reflections collected	78054	6126	55837	71276
Independent reflections	7995	6111	10494	11961
Parameters	503	318	642	661
R(int)	0.0797	0.0242	0.0272	0.0322
R1/wR2, ^a $I \geq 2\sigma I$ (%)	5.22/14.53	4.54/9.28	2.79/7.33	3.02/7.88
R1/wR2, ^a all data (%)	7.92/16.33	3.90/8.95	2.96/7.47	3.04/7.92
GOF	1.062	1.028	1.030	1.045

^a R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0928 and 6.3506 for [K(18-crown-6)][**51**] $\cdot$ C₆H₁₄, 0.0517 and 5.7175 for **52**, 0.0384 and 2.2715 for [K(18-crown-6)][**53**] $\cdot$ THF and 0.0610 and 0.7064 for [K(2,2,2-crypt)][**54**].

	[N ⁿ Bu ₄][55]	[56][OTf]	[57][OTf]· ¹ / ₂ C ₆ H ₁₄	58
Formula	C ₄₄ H ₇₆ AsFN ₂ O ₂	C ₃₀ H ₄₃ AsF ₃ NO ₅ S	C ₃₂ H ₄₈ AsF ₃ NO ₅ S	C ₂₈ H ₄₁ AsClNO ₂
Fw [g mol ⁻¹]	759.00	661.63	690.69	533.99
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Iba</i> 2
<i>a</i> (Å)	24.3007(6)	10.7560(2)	13.9248(4)	19.8430(3)
<i>b</i> (Å)	9.3966(2)	12.9728(3)	15.1784(4)	28.1484(4)
<i>c</i> (Å)	19.7048(5)	18.9206(4)	19.1969(4)	10.29740(10)
α (°)	90	72.072(2)	110.964(2)	90
β (°)	100.047(2)	83.509(2)	98.355(2)	90
γ (°)	90	87.014(2)	105.897(2)	90
<i>V</i> (Å ³)	4430.47(19)	4017.25(15)	3507.63(17)	5751.60(13)
<i>Z</i>	1	2	4	8
Radiation, λ (Å)	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178
ρ_{calc} (g cm ⁻³)	1.135	1.321	1.308	1.233
μ (mm ⁻¹)	1.346	2.425	2.321	2.623
Reflections collected	25497	30746	38893	28596
Independent reflections	9193	6896	14480	5313
Parameters	543	370	839	309
R(int)	0.0396	0.0149	0.0231	0.0303
R1/wR2, ^a I $\geq$ 2 σ I (%)	5.02/12.91	2.31/6.03	2.71/6.77	2.26/5.80
R1/wR2, ^a all data (%)	5.51/13.47	2.37/6.08	3.20/7.10	2.36/5.89
GOF	1.057	1.016	1.026	1.040

^a R1 = $[\sum ||F_o| - |F_c||]/\sum |F_o|$; wR2 = $\{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0706 and 2.4932 for [NⁿBu₄][**55**], 0.0328 and 0.7698 for [**56**][OTf], 0.0356 and 1.0102 for [**57**][OTf]·¹/₂C₆H₁₄ and 0.0349 and 2.1351 for **58**.

	60	[H][61]	[H][62] ^{·5/2} py	[63] ^{·2} py
Formula	C ₂₉ H ₄₃ AsClNO ₂	C ₅₆ H ₈₁ AsN ₂ O ₄	C _{40.5} H _{53.5} AsF ₃ N _{3.5} O ₂	C ₄₃ H ₅₄ AsF ₃ N ₄ O ₂
Fw [g mol ⁻¹]	548.03	921.17	753.31	790.85
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
<i>a</i> (Å)	11.0386(4)	11.2486(3)	16.7560(4)	17.52860(10)
<i>b</i> (Å)	13.2657(5)	12.2285(4)	18.5501(3)	16.9139(2)
<i>c</i> (Å)	21.1976(9)	20.6884(6)	26.1766(6)	27.7535(2)
α (°)	82.033(3)	91.115(2)	90	90
β (°)	81.030(3)	104.183(2)	107.338(2)	90
γ (°)	76.975(3)	103.727(2)	90	90
<i>V</i> (Å ³)	2969.9(2)	2671.10(14)	7766.7(3)	8228.28(12)
<i>Z</i>	2	1	13	2
Radiation, λ (Å)	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178
ρ_{calc} (g cm ⁻³)	1.532	1.145	1.255	1.403
μ (mm ⁻¹)	3.190	1.193	1.598	1.616
Reflections collected	28797	27652	47297	98090
Independent reflections	12229	11054	16093	8607
Parameters	639	609	893	498
R(int)	0.0514	0.0228	0.0447	0.0385
R1/wR2, ^a I $\geq$ 2 σ I (%)	6.18/15.99	5.29/13.96	4.93/12.94	4.85/13.53
R1/wR2, ^a all data (%)	7.35/17.21	5.62/14.33	5.79/14.06	5.24/14.10
GOF	1.030	1.043	1.038	1.030

^a R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.1055 and 1.8320 for **60**, 0.0759 and 3.1725 for [H][**61**], 0.0856 and 2.9030 for [H][**62**]^{·5/2}py and 0.0871 and 9.1329 for [py-H][**63**]^{·2}py.

	64	66	67	68
Formula	C ₁₆ H ₁₆ NO ₄ P	C ₁₆ H ₁₈ NO ₅ P	C ₁₆ H ₂₀ NO ₆ P	C ₁₆ H ₁₉ BNO ₄ P
Fw [g mol ⁻¹]	317.27	335.29	353.31	331.10
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	5.05220(10)	10.9987(3)	6.45680(10)	10.5094(6)
<i>b</i> (Å)	16.4626(2)	4.79530(10)	14.5723(4)	12.1360(7)
<i>c</i> (Å)	17.2549(2)	29.3677(7)	17.8078(4)	13.9610(9)
α (°)	90	90	90	109.711(6)
β (°)	90	97.717(2)	96.068(2)	101.072(5)
γ (°)	90	90	90	96.746(5)
<i>V</i> (Å ³)	1435.13(4)	1534.89(6)	1666.16(6)	1612.76(18)
<i>Z</i>	4	1	4	4
Radiation, λ (Å)	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178	Cu K α , 1.54178
ρ_{calc} (g cm ⁻³)	1.468	1.451	1.408	1.364
μ (mm ⁻¹)	1.872	1.830	1.759	1.677
Reflections collected	14921	13566	12987	12435
Independent reflections	2998	3155	3322	6337
Parameters	199	216	233	439
R(int)	0.0188	0.0335	0.0243	0.0180
R1/wR2, ^a I $\geq$ 2 σ I (%)	2.30/6.23	3.57/9.19	4.34/11.50	3.45/9.19
R1/wR2, ^a all data (%)	2.34/6.26	4.09/9.55	4.49/11.62	3.93/9.69
GOF	1.069	1.036	1.086	1.027

^a R1 = $[\sum ||F_o| - |F_c||]/\sum |F_o|$; wR2 = $\{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0418 and 0.1590 for **64**, 0.0480 and 0.5778 for **66**, 0.0510 and 1.5060 for **67** and 0.0528 and 0.5276 for **68**.

	69
Formula	C ₃₄ H ₃₁ BNO ₄ P
Fw [g mol ⁻¹]	559.38
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	13.1101(2)
<i>b</i> (Å)	12.7176(2)
<i>c</i> (Å)	18.1335(3)
α (°)	90
β (°)	107.233(2)
γ (°)	90
<i>V</i> (Å ³)	887.65(8)
<i>Z</i>	4
Radiation, λ (Å)	Cu K α , 1.54178
ρ_{calc} (g cm ⁻³)	1.287
μ (mm ⁻¹)	1.162
Reflections collected	15853
Independent reflections	5961
Parameters	370
R(int)	0.0245
R1/wR2, ^a $I \geq 2\sigma I$ (%)	3.39/8.41
R1/wR2, ^a all data (%)	4.19/8.93
GOF	1.019

^a R1 = $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; wR2 = $\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$; w = $[\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where P = $[(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0460 and 0.6499 for **69**.

