BORANE, BORYL AND BORYLENE COMPLEXES OF ELECTRON RICH METAL CENTRES

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

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This thesis is dedicated to my family
Abstract

The synthesis and characterisation of a series of novel borane, boryl and borylene complexes of electron rich group 8 and 9 metal centres are described in this thesis.

Chapter 3 reports on the properties of a highly nucleophile tolerant borylene system, [CpFe(dmpe)(BNMe₂)]⁺, together with its surprising formation via an unprecedented spontaneous halide ejection process. The incorporation of strongly electron releasing ancillary phosphine ligands is reflected by an Fe-B distance (ca. 1.80 Å) which is more akin to alkyl/aryl substituted borylene complexes, and perhaps more strikingly, by the very low exothermicity associated with the binding of pyridine to the two-coordinate boron centre (ΔH = -7.4 kcal mol⁻¹ cf. -40.7 kcal mol⁻¹ for BCl₃). Despite the strong π electron release from the metal fragment implied by this suppressed reactivity and short Fe-B bond, the barrier to rotation about the Fe=B bond in the asymmetric variant [CpFe(dmpe){BN(C₆H₄OMe-4)Me}]⁺ is very small (ca. 2.9 kcal mol⁻¹). This apparent contradiction is rationalised by the orthogonal orientations of the HOMO and HOMO-2 orbitals of the [CpML₂]⁺ fragment, which mean that the M-B π interaction does not fall to zero even in the highest energy conformation.

The reactivities of the aminoboryl complexes, CpFe(CO)₂B(NR₂)Cl (R = Me, Cy), towards electrophiles (H⁺, Me⁺) are discussed in Chapter 4, with a view to probing potential modification of the boryl ligand substituents. The reaction of CpFe(CO)₂B(NCy₂)Cl with [Me₂O][BF₄] leads to the formation of CpFe(CO)₂B(NCy₂)F. Subsequent reactivity with Brookhart’s acid results in the formation of the known difluoroboryl system CpFe(CO)₂BF₂. Reaction of the dimethylaminoboryl complex CpFe(CO)₂B(NMe₂)Cl with [Me₂O][BF₄] generates CpFe(CO)₂BF₂ directly; however, reaction of CpFe(dmpe)B(NMe₂)Cl with [Me₂O][BF₄] is limited to the formation of CpFe(dmpe)B(NMe₂)F, presumably on steric grounds. Additionally, given the enhanced stability of the bis(phosphine) ligated systems, [CpM(PR₃)₂(BNR₂)]⁺ compared to related dicarbonyl ligated complexes, it has also proved possible to synthesise other borylene complexes e.g. [CpFe(dmpe)(BOMes)]⁺ which are otherwise unstable under ambient conditions.

Chapter 5 reports the coordination and B-H bond activation of aminoboranes at ruthenium and iridium metal centres. Reaction of aminoboranes, H₂BNR₂, with 14-electron fragments of the type [Cp*RuL]⁺, leads to κ² coordination. The interaction with 16-electron fragments, [CpRu(PR₃)₂]⁺, has also been probed. In contrast to side on-binding of isoelectronic alkene donors, an alternative κ¹-(σ-BH) mode of aminoborane ligation has been established, albeit with binding energies only ~ 8 kcal mol⁻¹ greater than for those for analogous dinitrogen complexes. Variations in ground-state structure and exchange dynamics as a function of the phosphine ancillary ligand set are consistent with chemically significant back-bonding into an orbital of B-H σ* character. By contrast, simple borane coordination compounds prove difficult to isolate on addition of aminoboranes, H₂BNR₂, to in situ generated sources of [(µ-cymene)Ru(PR₃)Cl]⁺; spontaneous loss of HCl to generate a rare class of primary hydridoboryl complexes is witnessed instead. Attempts to synthesise boryl complexes via simple oxidative addition of monomeric aminoboranes have also proved successful, through the use of electron rich iridium precursors containing the [Ir(PMe₃)₃] fragment. This step results in the synthesis of novel amino(hydrido)boryl complexes, L₄(H)M⁺B(H)NR₂; subsequent conversion (on loss of an ancillary ligand) to a borylene dihydride system proceeds via a novel B-to-M α hydride migration. The latter step is unprecedented for group 13 ligand systems and is remarkable in offering α-substituent migration from a Lewis acidic centre as a route to a two-coordinate ligand system.
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Notes

The following abbreviations were used in the text:

Ar = aryl
ArCl = C₆H₃Cl₂-3,5
Arf = C₆H₃(CF₃)₂-3,5
br = broad
μ = bridged
"Bu = -CH₂CH₂CH₂CH₃
‘Bu = -(CH₃)₃
calc. = calculated
cat = 1,2-O₂C₆H₄
coe = cyclooctene
Cp = cyclopentadienyl, η⁵-C₅H₅
Cp’ = methylcyclopentadienyl, η⁵-C₅H₄Me
Cp* = pentamethylcyclopentadienyl, η⁵-C₅Me₅
Cy = cyclohexyl
δ = NMR chemical shift
d = doublet, days
d d = double doublet
DCM = dichloromethane
dctype = 1,2-bis(dicyclohexylphosphino)ethane
dmap = 4-dimethylaminopyridine
dmpbz = 1,2-bis(dimethylphosphino)benzene
dmpe = 1,2-bis(dimethylphosphino)ethane
EI = electron ionisation
ES = electrospray
Fc = Cp₂Fe
Fp = (η⁵-C₅H₅)Fe(CO)₂
FT = Fourier Transform
fwhm = frequency width at half maximum
h = hours
IMes = 1,3-dimesityl imidazolin-z-ylidene
'Ir = -CH(CH₃)₂
IR = infrared
J = coupling constant
λ = wavelength
m = multiplet
md = medium
Me = -CH₃
Mes = mesityl, 2,4,6-Me₃C₆H₂
min. = minutes
MS = mass spectrometry
N = coupling constant
ν = stretching frequency
NMR = nuclear magnetic resonance
obs. = observed
Ph = -C₆H₅
pin = 1,2-O₂C₂Me₄
ppm = parts per million
PPN = bis(triphenylphosphine)iminium
q = quartet
ref. = reference
RT = room temperature
s = singlet
sept = septet
sh = shoulder
st = strong
T = triplet
THF = tetrahydrofuran
VT-NMR = variable temperature
w = weak
1 Torr = 1 mmHg = 133.3 Pa
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Introduction

1.1 Introduction

Classical two-centre two-electron bonds between transition metals and first row p-block elements have been extensively reported throughout the literature.\textsuperscript{1,2} However, until relatively recently this was not the case for boron, and recent research has therefore sought to probe both fundamental structure/bonding and reactivity issues for systems containing M-B and related bonds.\textsuperscript{3-10} Since transition metals generally react as electrophilic species, the limited success in constructing M-B bonds presumably reflected the historic lack of nucleophilic boron-based reagents. Despite this, in the past decade, rapid advances in the field have been made, and parallels have emerged with classical organometallic ligand systems such as carbenes, vinylidenes and even CO. The heavier group 13 elements have also some precedent as donor atoms with a GaI complex being reported by Aldridge \textit{et al.} in 2008.\textsuperscript{11}

Complexes containing conventional metal-boron bonds can be classified as one of five types according to the coordination number of the boron atom and number of M-B bonds [Figure 1.1].
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These classes comprise borane, boryl, bridging and terminal borylene complexes, and metalla-borylenes. Borane complexes are Lewis acid-base adducts that exploit the Lewis acidic nature of boranes\cite{12,13}; the boron centre in these complexes is four-coordinate.\cite{12,13} Boryl complexes are three-coordinate and are much more widely developed.\cite{7,12-14} Borylene complexes contain the BX fragment and feature two main coordination modes: μ₂-bridging and terminal borylene complexes. Metalla-borylene complexes feature a ‘naked’ boron atom between two metal centres.\cite{12,13,15-17}

This introduction will predominantly focus on group 8 and 9 boryl and borylene complexes which are most relevant to the subsequent experimental work. Sigma complexes of electron rich metal centres will also be reviewed, with particular attention focusing on sigma complexes of boranes.

1.2 Boryl Complexes

In 1960, Nöth and Schmid reported the synthesis of the first boryl complexes. However, these systems were not structurally characterised,\cite{18,19} and their identities were later questioned when crystallographically characterised compounds yielded different spectroscopic data from initial reports.\cite{20} Research in the field recommenced in the early 1990’s, largely due to the implication of rhodium and iridium boryl complexes as intermediates in the catalysis of
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hydroboration reactions and in the functionalisation of hydrocarbons.\textsuperscript{10,21-23} Recently, a number of reviews discussing the synthesis/structure and reactivity of boryl complexes have been published and the reader is referred to these for a comprehensive treatment.\textsuperscript{7,12-14}

Theoretical studies reveal that the M-B bond in systems such as CpFe(CO)$_2$BX$_2$ have a 60 – 70 % contribution from covalent terms.\textsuperscript{24} The major interaction is σ donation from the formally anionic [BX$_2$]$^-$ fragment, with weak π back bonding from the HOMO of the metal fragment to the p-orbital on the boron atom accounting for only around 15 %, even in the most favourable cases [Figure 1.2]. This endorses the convention of assigning the metal-boron interaction as a single bond in boryl complexes.

![Figure 1.2: σ donor and π acceptor properties of the boryl ligand.](image)

Boryl complexes are characterised by $^{11}$B NMR resonances ranging from $\delta$ 24 – 141 ppm; these shifts are at lower field compared to the resonances typically observed for precursor boranes. Halo-boryl complexes can be used as precursors to cationic borylene complexes, via halide abstraction. Since boryl complexes are generally much less Lewis acidic than the corresponding cationic borylene compounds, manipulation of these complexes (e.g. via ligand substitution) typically occurs on the boryl system prior to conversion. This approach has been exploited heavily throughout this thesis and demonstrates the importance of precursor boryl complexes in the formation of novel borylene systems.
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### 1.2.1 Synthesis

#### 1.2.1.1 Salt Elimination

In 1993, Hartwig reported the reactions of an anionic metal fragment, \([\text{CpFe(CO)}_2^-]\), with a haloborane precursor in the synthesis of a diaryl boryl complex. Moreover, using this approach a number of diaryl complexes of the type \((\eta^5\text{-C}_5\text{R}_5)\text{Fe(CO)}_2\text{B(C}_6\text{X}_5)_2\) \((\text{R}_5 = \text{H}_5, \text{Me}_5, \text{X} = \text{F}; \text{R}_5 = \text{H}_5, \text{X} = \text{H})\) have now been synthesised and fully characterised [Scheme 1.1].

![Scheme 1.1: Synthesis of diarylboryl systems.](image)

Related complexes containing a catecholato group and related systems featuring methyl, tert-butyl and chloro substituents have also been synthesised by an analogous method. The ruthenium analogues are also known [Scheme 1.2].
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In 2002, Aldridge et al. developed the first group 8 dihaloboryl complex utilising the reaction between Na[CpFe(CO)$_2$] and BCl$_3$ [Scheme 1.3].$^8$ CpFe(CO)$_2$BCl$_2$ was subsequently structurally authenticated in 2004 by Braunschweig and co-workers, and CpFe(CO)$_2$BX$_2$ (X = F, Br) and Cp*Fe(CO)$_2$BX$_2$ (X = F, Cl, Br) have since been reported.$^{28,29}$ The related ruthenium systems, Cp'Ru(CO)$_2$BCl$_2$ and CpRu(CO)$_2$BF$_2$, have also been characterised.$^{28,30}$ However, the iodide compounds are reported to be too labile to be fully characterised.

**Scheme 1.2:** Synthesis of catecholboryl systems.

**Scheme 1.3:** Synthesis of dihaloboryl complexes.

Amido substituents have been shown to electronically stabilise the electron deficient boron centre in boryl complexes. In 1998, Braunschweig and co-workers synthesised the first amino(halo)boryl complexes via the reaction of Na[(η$^5$-C$_5$R$_5$)Fe(CO)$_2$] (R$_5$ = H$_5$, H$_4$Me, Me$_5$)
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with Me₂NBCl₂ in benzene [Scheme 1.4]. The reaction with Me₂NBBr₂ proved more complex, yielding a 1:1 mixture of \((\eta^5-C_5R_5)Fe(CO)_2B(NMe_2)Br\) and \(\{[\eta^5-C_5R_5]Fe(CO)\}_2(\mu-BNMe_2)\) which could not be separated. This method can be further exploited to synthesise the more bulky iPr and Cy boryl complexes, with greater selectivity being observed for the boryl product over disubstituted bridging borylene complexes presumably on steric grounds. The related ruthenium aminoboryl complexes, CpRu(CO)₂B(NR₂)X (R = Me, X = Cl, Br; R = Cy, X = Cl) can also be synthesised by the same route [Scheme 1.4].

\[ \text{Scheme 1.4: Iron and ruthenium amino(halo)boryl complexes.} \]

In a similar manner, oxygen can also provide \(\pi\) donor stabilisation at the boron centre (albeit to a lesser degree). Recent research has investigated the efficacy of alkoxy and aryloxy substituents as \(\pi\)-donors given the increased electronegativity of oxygen over nitrogen. The mesitoxy systems \((\eta^5-C_5R_5)Fe(CO)_2B(OMes)X\) (\(R_5 = H, X = Cl, Br; R_5 = Me, X = Cl\)) have been prepared using an analogous method to amino substituted systems. This methodology has been expanded to synthesise a variety of asymmetric haloboryl systems with other boron-bound substituents (aryl, ferrocenyl, cymantrenyl, silyl, germyl) by salt elimination between a metal anion and haloborane. Thus, for example \((\eta^5-\)
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C₃R₃Fe(CO)₂B(Mes)Br (R₃ = H₅, H₄Me, Me₃) and Cp*Fe(CO)₂B(Ph)Cl were also synthesised by this salt elimination route [Scheme 1.5].

\[ \text{Scheme 1.5: Synthesis of asymmetric aryl(halo)boryl complexes.} \]

Conversely, the associated fluoro/chloro/iodo systems Cp*Fe(CO)₂B(Mes)X (X = F, Cl, I) were obtained from the addition reaction of the related cationic terminal borylene complex with a source of halide [Scheme 1.6].

\[ \text{Scheme 1.6: Synthesis of mesityl(halo)boryl complexes by halide addition chemistry.} \]

Recent developments in the chemistry of boryl anions has allowed for an alternative approach to boryl complex formation by means of salt elimination. A boryllithium reagent can be utilised as a source of the boryl ligand in transition metal chemistry. A range of boryl complexes have been made by nucleophilic attack of boron at an electrophilic metal centre such as titanium, hafnium or a group 11 metal [Scheme 1.7].
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Scheme 1.7: Synthesis of a titanium boryl complex using a boryl anion.

1.2.1.2 Oxidative Addition

Oxidative addition to a coordinatively unsaturated transition metal complex centre is a fundamental process in organometallic chemistry and finds application in various catalytic cycles; in this process, the metal centre is formally oxidised by two electrons.\textsuperscript{22,23,46,47} The first crystallographically characterised boryl complexes were synthesised by the oxidative addition of the B-H bond in various boranes, \( R_2BH \), to Ir(I) complexes.\textsuperscript{10} Since then, this method has been extended to a range of metal fragments.

In 1997, Roper and co-workers developed a route to a number of compounds featuring a range of boron substituents and ancillary ligands.\textsuperscript{48} The oxidative addition of borane B-H bonds to hydrido-ruthenium complexes was investigated, giving rise to a range of coordinatively unsaturated boryl complexes containing five-coordinate metal centres, with the accompanying elimination of PPh\textsubscript{3} and H\textsubscript{2} [Scheme 1.8].
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Mirroring the approach reported for related ruthenium systems, a number of five-coordinate osmium boryl complexes have also been synthesised.\textsuperscript{49} Reaction of Os(Ph)Cl(CE)(PPh\textsubscript{3})\textsubscript{2} (E = O, S) with R\textsubscript{2}BH yields the corresponding complexes Os(BR\textsubscript{2})Cl(CE)(PPh\textsubscript{3})\textsubscript{2}, with the elimination of benzene [Scheme 1.9].

\begin{equation}
\text{E} = \text{O}, \text{R}_2 = \text{Cat}; \text{E} = \text{O}, \text{R}_2 = 1,2-\text{O}_2\text{C}_{10}\text{H}_6; \text{E} = \text{O}, \text{R}_2 = 3-\text{MeCat}; \text{E} = \text{O}, \text{R}_2 = 1,2-(\text{NH})_2\text{C}_6\text{H}_4; \text{E} = \text{O}, \text{R}_2 = 1-\text{S}-2-\text{NHC}_6\text{H}_4; \text{E} = \text{S}, \text{R}_2 = \text{Cat}; \text{E} = \text{S}, \text{R}_2 = 1-\text{S}-2-\text{NHC}_6\text{H}_4; \text{E} = \text{N} \text{p-tolyl}, \text{R}_2 = \text{Cat}
\end{equation}

\textbf{Scheme 1.8:} Syntheses of ruthenium boryl complexes involving B-H oxidative addition.

Wilkinson’s catalyst is a highly selective catalyst for the hydroboration of alkenes and alkynes. Thus, the reaction of Wilkinson’s catalyst RhCl(PPh\textsubscript{3})\textsubscript{3} with boranes is probably the most widely investigated oxidative addition of a B-H bond to a metal centre.\textsuperscript{50-52} Reaction of RhCl(PPh\textsubscript{3})\textsubscript{3} with HBCat yields (CatB)RhHCl(PPh\textsubscript{3})\textsubscript{2} with elimination of PPh\textsubscript{3}. However, the expelled PPh\textsubscript{3} affords subsequent reactivity, yielding a variety of boron, phosphorus and
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ruthenium-containing side products. This problem can be circumvented by the reaction of the dimeric [Rh(PPh$_3$)$_2$(μ-Cl)$_2$] with HBCat since no PPh$_3$ is released [Scheme 1.10].$^{4,53}$

\[ \text{Scheme 1.10: Oxidative addition of HBCat to dimeric [Rh(PPh$_3$)$_2$(μ-Cl)$_2$].} \]

Similar iridium boryl complexes were obtained by oxidative addition of B-H bonds to low valent iridium complexes with accompanying ligand dissociation. Thus, for example, the addition of HBCat to the 16-electron complex IrCl(PMe$_3$)$_3$, generated in situ from the 18-electron IrCl(PMe$_3$)$_3$(coe), yields mer-CatBIrHCl(PMe$_3$)$_3$ [Scheme 1.11].$^{10}$

\[ \text{Scheme 1.11: Oxidative addition giving the first crystallographically characterised boryl complex.} \]

There is also evidence for oxidative addition to iridium centres without prior ligand dissociation. Thus, for example, the oxidative addition of HBCat to IrX(NO)(PR$_3$)$_2$ [X = halide] yields trans-(CatB)IrHX(NO)(PR$_3$)$_2$.$^{54,55}$

The methods discussed above for the oxidative addition of a B-H bond have successfully been extended to the addition of B-B and B-X bonds to a range of late transition metal fragments.$^{56-58}$ Irradiation of Fe(CO)$_5$ in the presence of B$_2$R$_4$, for example, yields bis(boryl) complexes of the type (CO)$_4$Fe(BR$_2$)$_2$ (R$_2$ = Cat, 1,2-O$_2$-4-4′BuC$_6$H$_3$, 1,2-O$_2$-3,5-}
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'BuC₆H₂' [Scheme 1.12]. Incidentally, the same complexes can be synthesised by a salt elimination route between [Fe(CO)₄]²⁻ and two equivalents of the appropriate chloroborane.

\[
\text{Fe(CO)}_5 \xrightarrow{\text{B}_2\text{R}_4 \text{hv}} \text{OC} \quad \text{Fe} \quad \text{BR}_2 \quad \text{OC} \quad \text{BR}_2
\]

\[ \text{R}_2 = \text{Cat, 1,2-O}_2\text{-4-‘BuC}_6\text{H}_3,1,2\text{-O}_2\text{-3,5-‘Bu}_2\text{C}_6\text{H}_2 \]

**Scheme 1.12:** Formation of an iron bis(boryl) complex.

In similar fashion, cis-Ru(BCat)₂(CO)L(PPh₃)₂ (L = CO, CN-p-tolyl) can be synthesised via the oxidative addition reaction between B₂Cat₂ and Ru(CO)L(PPh₃)₃ [Scheme 1.13].

\[
\text{Ru(PPh}_3)_3\text{(CO)L} \xrightarrow{\text{B}_2\text{Cat}_2 \text{hv}} \text{Ph}_3\text{P} \quad \text{L} \quad \text{BCat} \quad \text{Ph}_3\text{P} \quad \text{BCat} \quad \text{CO}
\]

\[ \text{L} = \text{CO, CN-p-tolyl} \]

**Scheme 1.13:** Synthesis of a ruthenium bis(boryl) complex.

An assortment of bis(boryl) complexes of group 9 metals have been synthesised utilising oxidative addition reactions of diboranes, with accompanying displacement of labile ligands. Thus for example, the reaction of Co(PMe₃)₄ with B₂Cat₂ affords the bis(boryl) complex (CatB)₂Co(PMe₃)₃ via the loss of a phosphine molecule. A range of five-coordinate bis(boryl) systems has also been synthesised by the oxidative addition of diborane precursors to Rh(I) centres. Again, use of the chloride bridged dimer [Rh(PPh₃)₂(µ-Cl)]₂ rather than Wilkinson’s catalyst prevents the need for PPh₃ loss and therefore reduces the extent of competing reactivity.
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Scheme 1.14: Synthetic route to rhodium bis(boryl) complexes.

A further illustrative example of the oxidative addition of a B-B bond to a metal centre is the reaction between B₂Cat₂ with (Et₃P)₃IrCl, leading to the isolation of the five-coordinate system trans-(Et₃P)₃IrCl(BCat)₂. Moreover, Marder and co-workers also report NMR evidence for the formation of the tris(triethylphosphine) complex (Et₃P)₃IrCl(BCat)₂. The high lability of the phosphine ligand trans to the BCat ligand is presumably responsible for the isolation of the bis(triethylphosphine) complex.

Further work by Marder has demonstrated that the oxidative addition of a boron-halide bond can be used to generate the trans-boryl complexes trans-(CatB)PtCl(PPh₃)₂ and trans-(CatB)PtBr(PPh₃)₂ from the reaction of Pt(PPh₃)₂(η²-C₆H₄) with CatBX (X = Cl, Br). In a similar vein, Braunschweig and co-workers have synthesised a series of Pt(II) boryl complexes of the form trans-(Cy₃P)₂Pt(Br)(BF₃) via the oxidative addition of the B-Br bond of various bromoboranes to Pt(PCy₃)₂. Within the scope of these reactions, the synthesis of trans-(Cy₃P)₂Pt(Br)(BBr₂) is notable as a rare example of a dihaloboryl complex. By extension, the same group also reported the reaction of Pt(PCy₃)₂ with two equivalents of BF₃, leading to the formation of trans-(Cy₃P)₂Pt(H)(BF₃) and trans-(Cy₃P)₂Pt(BF₂)(BF₃) of an initial ratio 1:2. Due to the instability of trans-(Cy₃P)₂Pt(BF₂)(BF₃), a more stable derivative was sought by substituting the coordinated [BF₄]⁻ ligand. Therefore, the synthesis
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was carried out in the presence of \([\text{NBu}_4]\text{Cl}\) which yielded the corresponding chloro complex \(\text{trans-}(\text{Cy}_3\text{P})\text{Pt}(\text{BF}_2)(\text{Cl}).\)

1.2.1.3 Sigma Bond Metathesis

A more recently developed synthetic route involving sigma bond metathesis gives access to nickel and cobalt boryl complexes [Scheme 1.15].\(^6\) The systems in question feature metals held in a square planar arrangement by a PNP pincer ligand (PNP = N\([2-\text{P(CHMe}_2]_2-4-\text{MeC}_6\text{H}_3]_2\)). The generation of a strong B-O linkage is thought to make concurrent M-B bond formation thermodynamically viable.

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{O'Bu} \\
\text{P} & \quad \text{P} & \quad \text{B}_{2}\text{R}_4 \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{B}_{2}\text{R}_4 \\
\text{P} & \quad \text{P} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{M} & \quad \text{BR}_2 \\
\text{P} & \quad \text{P} & \quad \text{O}\text{Bu} \\
\end{align*}
\]

Scheme 1.15: A schematic \(\sigma\)-bond metathesis route to boryl complexes.

1.2.2 Reactivity

Since ‘free’ boryls are formally anionic, boryl complexes are ordinarily only weakly Lewis acidic, especially when coupled with \(\pi\) donor substituents such as amino groups. This allows substitution chemistry of ancillary ligands at the metal centre to occur through the addition of Lewis basic ligands.\(^3\) The most commonly used modification at the metal centre is the substitution of carbonyl groups for trialkyl phosphine ligands. Work by Hartwig showed that the reaction of \(\text{CpFe(CO)}_2\text{BCat}\) with \(\text{PMe}_3\) under photolytic conditions leads to the
substitution of both π acidic carbonyl ligands and the formation of a bis(phosphine) substituted complex [Scheme 1.16].

Modification of an existing boryl complex can also be achieved by substitution at the boron atom. This is typically achieved by using a nucleophile which forms a stronger B-X bond than the original precursor. For example, the substitution of boron bound chloro substituents by amino or fluoro groups has been reported, together with an interesting case of simultaneous modification of both the metal and boron centres [Scheme 1.17].
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Scheme 1.17: Modification of existing boryl complexes by boron-centre substitution chemistry.

Due to the enhanced Lewis acidity at the boron centre of imino boryl complexes, addition chemistry can also be demonstrated for such systems, as shown in work by Braunschweig and co-workers [Scheme 1.18].

Scheme 1.18: Reaction of a platinum iminoboryl complex with a Lewis base.

Although the boron atom in boryl complexes is clearly not Lewis basic, the α-substituent often is. This feature has been exploited by Braunschweig and co-workers, who utilised the reaction with a potent Lewis acid to generate a borylene complex [Scheme 1.19].
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![Scheme 1.19: Reaction of a platinum iminoboryl complex with a Lewis acid.](image)

The increased research interest in boryl complexes is, on the whole, predominantly due to their possible application for the functionalisation of both saturated and unsaturated hydrocarbons. The metal catalysed hydroboration of unsaturated organic molecules invokes boryl complexes as key intermediates. The first examples of this chemistry involved the use of Wilkinson’s catalyst, RhCl(PPh₃)₃. The favoured mechanism involves elimination of PPh₃, oxidative addition of a B-H bond, elimination of a second PPh₃ ligand, side on coordination of the alkene, addition of PPh₃ and insertion of the alkene into the rhodium-hydrogen bond, and finally reductive elimination of the alkylborane and regeneration of the reactive metal complex.

Controlled C-H activation processes remain a key target in organometallic chemistry, potentially allowing the conversion of cheap, abundant hydrocarbon feedstocks into synthetically useful functionalised products. The photolytic reaction of various boryl complexes with organic substrates leads to C-H activation and the formation of the corresponding borylated hydrocarbon. C-H activation of pentane by a tungsten boryl complex exemplifies this reactivity, displaying good selectivity for the terminal C-H bond [Scheme 1.20].
Scheme 1.20: Functionalisation of pentane by a tungsten boryl complex.

Additionally, simple metal-boryl complexes containing the \([\text{CpFe(CO)}_2]\) fragment react with benzene under photochemical conditions to generate arylboronate esters in quantitative yields [Scheme 1.21].

Scheme 1.21: Functionalisation of an aryl C-H bond by an iron boryl complex.

In 2000, Hartwig and co-workers reported the formation of alkylboronate esters in high yields with high selectivity for primary C-H bonds via the reaction of an alkane with \(\text{B}_2(\text{pin})_2\), catalysed by 2.5 mol % of \(\text{Cp}^*\text{Rh}(\eta^4-\text{hexamethylbenzene})\) [Scheme 1.22]. \([\text{Cp}^*\text{RhCl}_2]_2\) also catalyses the functionalisation of alkanes with the same selectivity.

Scheme 1.22: Catalytic C-H borylation of an alkane.

Hartwig and Smith reported the development of an iridium catalyst for the borylation of arenes. Initial studies were conducted with both phosphine and bipyridine-ligated...
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iridium\textsuperscript{75} catalysts, but catalysts containing heteroaromatic nitrogen ligands proved to be more reactive [Scheme 1.23].

\[
\begin{align*}
\text{B}_2\text{pin}_2 + \text{H-Ar} & \xrightarrow{1/2\text{[IrCl(COD)]}_2/bpy (3 \text{ mol \%})} \text{80°C} 2 \text{Ar-Bpin + H}_2
\end{align*}
\]

**Scheme 1.23:** Iridium catalyst for the borylation of arenes.

1.3 Borylene Complexes

The chemistry of borylene complexes, although a relatively new field, has evolved from the stage where such systems might have been regarded merely as structural novelties to one in which their reactivity can now be exploited synthetically, in some cases catalytically. For example, recent reports from the group of Braunschweig implicating group 6 metal borylene complexes in the controlled functionalisation of organic substrates and in the catalysis of C-C bond-forming reactions, hint at broader exploitation of the chemistry of this class of compound.\textsuperscript{77}

Borylene systems (BX) have been the focus of a number of theoretical studies concerning their ligating properties and their relationship to the related ligands CO and N\textsubscript{2}.\textsuperscript{78,79} Due to their isolobal relationship, BF, CO and N\textsubscript{2} potentially offer similar \(\sigma\) donor and \(\pi\) acceptor capabilities as ligands [Figure 1.3].
Figure 1.3: Bonding in EX (e.g. BF) and CO, demonstrating potentially similar σ donor and π acceptor interactions.

While the relevant orbital symmetries are identical, theoretical studies have shown that the BF ligand is actually a better σ donor than CO and N\textsubscript{2} due to the higher energy of the HOMO compared to CO and N\textsubscript{2}.\textsuperscript{80,81} The BF ligand is also a similar π acceptor due to the comparable energies of the relative π* orbitals [Figure 1.4].

Figure 1.4: Valence orbital energies of N\textsubscript{2}, CO and BF and % contributions to the HOMO and LUMO for N\textsubscript{2}, CO and BF.
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As a consequence of these properties, complexation of the borylene ligand at transition metal fragments is calculated to result in complexes with high thermodynamic stabilities [Figure 1.5]. This is exemplified by the greater bond dissociation energy of BF compared to CO when complexed to [Fe(CO)₄] and [Cr(CO)₅] [Figure 1.5].

![Figure 1.5: Bond dissociation energies for BF and CO for complexation to Cr(CO)₅ and Fe(CO)₄ fragments.](image)

<table>
<thead>
<tr>
<th>EX</th>
<th>BDE (Dₑ / kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF (Cr)</td>
<td>62.1</td>
</tr>
<tr>
<td>BF (Fe)</td>
<td>73.8</td>
</tr>
<tr>
<td>CO (Cr)</td>
<td>41.8</td>
</tr>
<tr>
<td>CO (Fe)</td>
<td>48.4</td>
</tr>
</tbody>
</table>

However, unlike these well established diatomics, sources of free B(I) ligands, BX, are extremely difficult to synthesise. In 1967, Timms reported that the synthesis of the BF molecule from elemental boron and BF₃ requires temperatures greater than 2000°C and that the BF diatomic itself has a high kinetic lability due to the polarity of the B-F bond. The small HOMO-LUMO gap increases on complexation but the imbalance between the strong σ donation and weak π acceptance leads to a build-up of positive charge at the boron centre, making it an attractive targets for nucleophiles. A number of strategies have therefore been employed to overcome the intrinsic lability of borylene complexes, for example by making use of sterically demanding or strongly π donating substituents at boron, or by the coordination of a Lewis base. While complexes containing the simplest of these ligands, BF, remain a challenging synthetic target (for a terminal mode of coordination at least), related complexes containing the BNR₂ and BAr ligands have been synthesised.
1.3.1 Synthesis of Charge Neutral Terminal Borylene Complexes

1.3.1.1 Salt Elimination

Chronologically, the first terminal borylene complexes were synthesised in 1998 by Cowley and by Braunschweig using double salt elimination chemistry. Cowley demonstrated that the reaction between K$_2$[Fe(CO)$_4$] and Cl$_2$BCp* at -78 °C leads to the elimination of two moles of KCl and yields the terminal borylene complex (OC)$_4$Fe(BCp*) in 30 % yield [Scheme 1.24].$^{84}$ The unsaturation of the terminal borylene moiety is partially relieved by a change in denti city of the Cp* ring from $\eta^1$ to $\eta^5$ on complexation.

![Scheme 1.24: Synthesis of (OC)$_4$Fe(BCp*).](image)

Braunschweig and co-workers reported a similar reaction between the dianionic group 6 metal carbonylates Na$_2$[M(CO)$_5$] (M = Cr, Mo, W) and X$_2$BN(SiMe$_3$)$_2$ (X = Cl, Br) to synthesise the aminoborylene complexes (OC)$_5$M[BN(SiMe$_3$)$_2$] (M = Cr, W, Mo) [Scheme 1.25].$^{85}$ Furthermore, it also proved possible to synthesise the closely related iron compound (OC)$_4$Fe[BN(SiMe$_3$)$_2$] in similar manner.$^{85}$
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A related silylborylene, \((\text{CO})_5\text{Cr}[\text{BSi(SiMe}_3)_3]\), can also be synthesised in 81 % yield from \(\text{Na}_2[\text{Cr(CO)}_5]\) and \(\text{Cl}_2\text{BSi(SiMe}_3)_3\).\(^{86}\) However, due to the lack of \(\pi\) donor stabilisation from the \(\text{Si(SiMe}_3)_3\) substituent, this compound readily decomposes at room temperature, unlike its aminoborylene analogue. Additionally, the germanium analogue \((\text{OC})_5\text{Cr}[\text{BGe(SiMe}_3)_3]\) has been characterised spectroscopically.\(^{86}\)

In related chemistry, metallaaryl complexes \((\text{OC})_n\text{M}[\text{BFe(CO)}_2\text{Cp}^*]\) \((\text{M} = \text{Cr}, n = 5; \text{M} = \text{Fe}, n = 4)\) displaying a ‘naked’ bridging boron atom between two transition metal centres have also been formed by double salt elimination chemistry [Scheme 1.26].\(^{87}\)

Despite the apparent simplicity of the salt elimination route and the extensive range of \(\text{di(halo)boranes}\) and metal carbonylate dianion precursors available, double salt elimination has been restricted to relatively few examples and is not a favoured route for the formation of many novel systems.
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1.3.1.2 Photolytic Borylene Transfer

Braunschweig and co-workers also made a notable progress in the borylene field by demonstrating the transfer of aminoborylene ligands between metal fragments as a viable method for the synthesis of borylene complexes (which in many cases could not otherwise be accessed using salt elimination methodology). The first demonstration of this approach involved transfer of the borylene fragment BN(SiMe₃)₂ from (OC)₅W[BN(SiMe₃)₂] to (OC)₅Cr(NMe₃) at -30 °C giving the known compound (OC)₅CrBN(SiMe₃)₂. Moreover, photolysis of CpV(CO)₄ with (CO)₅W[BN(SiMe₃)₂] also leads to the transfer of the borylene fragment and to the formation of CpV(CO)₃[BN(SiMe₃)₂], the first half sandwich terminal borylene complex [Scheme 1.27]. No suitable salt elimination method has been developed to afford this product.

Scheme 1.27: Formation of the first vanadium borylene complex via photolytic transfer.

Mechanistically, the key step in the transfer of the borylene fragment is dissociation of a ligand (typically CO) from the ‘acceptor’ metal system. The resulting unsaturated fragment then receives the borylene ligand, with transfer effected via a proposed bridged bimetallic intermediate.

These group 6 metal precursors have also been exploited in the synthesis of group 9 borylene complexes by thermal transfer of the BX ligand. Solutions of the molybdenum complex (OC)₅Mo[BN(SiMe₃)₂] and either CpRh(CO)₂ or Cp*Ir(CO)₂ were stirred in C₆D₆ at
room temperature, leading to the formation of the first terminal borylene complexes of rhodium and iridium [Scheme 1.28]. However, of these complexes, only the iridium complex \(\text{Cp}^*\text{Ir(CO)}[\text{BN(SiMe}_3)_2]\) was structurally characterised, presumably due to the increased steric and electronic stabilisation offered through the \(\text{Cp}^*\) ancillary ligand and electron rich iridium centre.

\[\text{Scheme 1.28: Synthesis of group 9 terminal borylene complexes by thermal transfer of BX.}\]

Furthermore, reaction of the borylene, \((\text{OC})_3\text{M}[\text{BN(SiMe}_3)_2] (\text{M} = \text{Cr, W})\) with \({\text{RhCl(CO)}}_2\}_2\) at ambient temperature yields the tertranuclear rhodium bis(borylene) complex, \((\text{OC})_2\text{Rh(μ-Cl)}_2\text{Rh(μ-CO)}[\text{μ-BN(SiMe}_3)_2]_2\text{Rh(μ-Cl)}_2\text{Rh(CO)}_2\) [Scheme 1.29]. The complex features a chain of four rhodium atoms, with the two internal metal centres bridged by a pair of borylene fragments and a carbonyl ligand. In the solid state the tetramers were reported to aggregate into linear neutral chains.

\[\text{Scheme 1.29 Synthesis of (OC)}_2\text{Rh(μ-Cl)}_2\text{Rh(μ-CO)}[\text{μ-BN(SiMe}_3)_2]_2\text{Rh(μ-Cl)}_2\text{Rh(CO)}_2.\]
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1.3.1.3 α-Migration of a Boron-Bound Substituent

α-Migration of a boron-bound substituent has also been exploited synthetically in systems featuring an electron-deficient, coordinatively unsaturated metal centre and a haloboryl ligand. This approach was first investigated by Roper in the formation of an intramolecularly base-stabilised terminal borylene complex. Reaction of Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ with 8-aminoquinoline generates Os[B(NHC$_9$H$_6$N)]Cl$_2$(CO)(PPh$_3$)$_2$ in 85 % yield [Scheme 1.30]. The reaction involves a 1,2-halide shift from boron to osmium, with the driving force being the formation of a strong BN bond and the alleviation of unsaturation at the osmium centre.

Scheme 1.30: Formation of an osmium base-stabilised borylene complex.
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Unfortunately, the resulting complex could not be structurally authenticated, but reaction with a source of iodide led to the mixed chloro/iodo complex Os[B(NHC₉H₆N)]ClI(CO)(PPh₃)₂ which was structurally verified. The high trans influence of the borylene ligand is presumably responsible for the substitution of the trans chloride ligand by iodine.

In related chemistry, the reaction of the same dichloroboryl precursor with 2-aminopyridine has been shown to yield a mixture of an amino(chloro)boryl complex and a base-stabilised borylene complex depending on the regiochemistry of the addition of the nitrogen donors to the boron and osmium centres [Scheme 1.31].

![Scheme 1.31: Tethered osmium boryl and base-stabilised borylene complex.](image)

At present, literature reports are restricted to halide migration driven by the addition of a Lewis base. Base-free 1,2 substituent shifts do, however, find precedent in related silicon chemistry. Thus, silylene complex synthesis has been achieved through a 1,2- hydride shift without the addition of an external base, as in the formation of the platinum silylene complex [(dippe)(H)Pt=SiMes₂]+.  

1.3.1.4 Modification of an Existing Borylene Complex

In principle, modification of an existing metal borylene complex represents an attractive route for the formation of novel borylene complexes. However, in practice this
approach is somewhat limited, presumably reflecting the lability of the metal-boron bond under the conditions required for substitution of either the metal bound ligands or the borylene substituent. That said, Roper and co-workers have demonstrated such chemistry occurring at both the metal and boron centres in Os[B(Cl)(NC₅H₄NMe)]Cl(CO)(PPh₃)₂ [Scheme 1.32]. Reaction with NaBH₄ targets the osmium centre, leading to the formation of the hydride complex Os[B(Cl)(NC₅H₄NMe)]H(CO)(PPh₃)₂, which undergoes subsequent hydrolysis to form [Os[B(OH)(NC₅H₄NMe)]Cl(CO)(PPh₃)₂] [Scheme 1.32].

Scheme 1.32: Modification of an osmium borylene complex.

Os[B(Cl)(NC₅H₄NMe)]Cl(CO)(PPh₃)₂ also reacts readily with ethanol producing the resultant ethoxyborylene complex which was characterised crystallographically [Scheme 1.33].

Scheme 1.33: Ethanolysis of Os[B(Cl)(NC₅H₄NMe)]Cl(CO)(PPh₃)₂.

In 2007, Braunschweig and co-workers reported the conversion of group 6 aminoborylene complexes (OC)₅M[BN(SiMe₃)₂] (M = Cr, Mo, W) to trans-(Cy₃P)(OC)₄M[BN(SiMe₃)₂] (M = Cr, Mo, W) by irradiation in the presence of PCy₃. Such complexes not only provide good evidence for the labilisation of the carbonyl ligand trans to
the borylene, but also reveal significant reductions in the M-B bond lengths and by implication, increased metal-ligand bond orders on substitution.

1.3.1.5 Addition of Primary Boranes RBH₂ to a Metal Fragment

A simple, highly convenient synthesis of a borylene complex has recently been developed by Sabo-Etienne and co-workers. Starting with RuHCl(H₂)(PCy₃)₂, a terminal ruthenium mesitylborylene complex was obtained via κ² coordination of the borane followed by net dehydrogenation [Scheme 1.34]. Interestingly, the process is reversible.

Scheme 1.34: Synthesis of a terminal borylene complex from a primary borane.

1.3.1.6 Oxidative Addition/Elimination

Recently it has emerged that the ligand BO⁻ (which is isoelectronic with BF) is accessible in the coordination sphere of a transition metal at ambient temperatures, representing a significant development in the field. The oxoboryl complex trans-(Cy₃P)₂BrPt(B=O) is reported to be synthesised by means of the reversible liberation of
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trimethylsilyl bromide from the boron-bromine oxidative addition product of dibromo(trimethylsilyloxy)borane and Pt(PCy₃)₂ [Scheme 1.35]. Equilibrium is reached at a ratio of roughly 4:1 in favour of the BO complex, and can be driven to completion by removal of the volatile by-product BrSiMe₃ in vacuo. This synthetic route is similar to that reported in the synthesis of (trimethylsilyl)iminoboryl compounds. The Pt-B distance in trans-(Cy₃P)₂BrPt(B≡O) is slightly longer than that in the corresponding iminoboryl complex trans-(Cy₃P)₂BrPt(B≡NSiMe₃).

\[
\text{Pt} \quad \text{PCy}_3 \quad \text{Br}_2\text{BOSiMe}_3 \quad \begin{array}{c} \text{PCy}_3 \\
\text{Br} \\
\text{PCy}_3 \\
\text{Br}
\end{array} \quad \begin{array}{c} \text{OSiMe}_3 \\
\text{BrSiMe}_3 \\
\text{PCy}_3
\end{array} \quad \begin{array}{c} \text{Pt} \\
\text{B} \\
\text{=O} \\
\text{PCy}_3
\end{array}
\]

**Scheme 1.35:** Synthesis of a platinum complex with a terminal BO⁺ ligand.

1.3.2 Synthesis of Cationic Terminal Borylene Complexes

1.3.2.1 Halide Abstraction

In 2003, the Aldridge group developed the field further by reporting the first cationic terminal borylene complex. In this approach a transition metal haloboryl complex is initially targeted (typically by salt elimination) which subsequently undergoes halide abstraction from boron to form a cationic terminal borylene complex. This is now the most widely exploited route to cationic terminal borylene complexes. In the first such example, reaction of \(\text{Cp}^*\text{Fe(CO)}_2\text{B(Mes)}\text{Br}\) with \(\text{Na}[\text{BAR}^4]\) in dichloromethane yielded the cationic terminal borylene complex \([\text{Cp}^*\text{Fe(CO)}_2(\text{BMes})][\text{BAR}^4]\) with precipitation of NaBr [Scheme 1.36]. The reaction is characterised by complete conversion to the borylene complex by \(^{11}\text{B} \text{NMR}\)
spectroscopy with the appearance of a broad resonance at $\delta_B$ 145. In addition, the carbonyl stretching bands (2055, 2013 cm$^{-1}$) are shifted to higher wavenumber compared to the boryl complex precursor (2006, 1961 cm$^{-1}$).

Scheme 1.36: Synthesis of the first cationic terminal borylene complex.

This methodology has more recently been applied to a series of cationic aminoborylene complexes, [CpFe(CO)$_2$(BNR$_2$)][BAR’$_4$] (R = ‘Pr, Cy, Me) [Scheme 1.37].$^{33,34,41,83}$ The dimethylamino complex is thermally unstable, decomposing at temperatures above –20 °C. However, the bulkier dicyclohexyl- and diisopropyl-aminoborylene complexes can be isolated in good yields and characterised crystallographically. The analogous ruthenium complexes have also been synthesised by a similar halide abstraction route.$^{36}$

Scheme 1.37: Formation of cationic aminoborylene complexes.

Another putative example of heteroatom functionalised borylene complexes are aryloxy substituted systems. The reaction of CpFe(CO)$_2$B(OMes)Cl with Na[BAr’$_4$] however
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yields CpFe(CO)\(_2\)B(OMes)F as a red oil [Scheme 1.38].\(^{33}\) The postulated mechanism involves transient formation of the cationic borylene species \([\text{CpFe(CO)}_2\text{B(OMes)}]^+\) which rapidly abstracts fluoride from the \([\text{BAR}^4_4]^-\) counter anion. Presumably, this is a consequence of insufficient steric and electronic stabilisation at boron from the mesityloxy group.

\[
\begin{array}{c}
\text{Fe} & \text{B} & \text{OMes} \\
\text{C} & \text{O} & \text{Cl}
\end{array}
\xrightarrow{\text{Na}[\text{BAR}^4_4]} \begin{array}{c}
\text{Fe} & \text{B} & \text{OMes} \\
\text{C} & \text{O} & \text{F}
\end{array}
\]

Scheme 1.38: Synthesis of a fluoroboryl complex by fluoride abstraction.

As a progression from the first Cp*\(\text{B}\) complex synthesised by Cowley, the use of the pentamethylcyclopentadienyl substituent has also been examined in the synthesis of a cationic complex featuring a metal-boron single bond [Scheme 1.39].\(^{100}\) As in the case of the earlier compound \((\text{OC})_4\text{Fe(BCp*)}\), the Cp* substituent changes its coordination mode from \(\eta^1\) to \(\eta^5\) on formation of the borylene complex.

\[
\begin{array}{c}
\text{Fe} & \text{B} & \text{Cl} \\
\text{C} & \text{O}
\end{array}
\xrightarrow{\text{AlCl}_3} \begin{array}{c}
\text{Fe}^+ & \text{B} \\
\text{C} & \text{O}
\end{array}
\]

Scheme 1.39: Synthesis of \([\text{CpFe(CO)}_2\text{Fe(BCp*)}][\text{AlCl}_4]\).

The halide abstraction methodology can be extended to boryl complexes synthesised by oxidative addition. The cationic platinum complex \(\text{trans-}[(\text{Cy}_3\text{P})_2\text{Pt(BMes)Br}]^+\) has been synthesised by the reaction of Na[BAR\(^4\)_4] with the oxidative addition product \(\text{trans-}[(\text{Cy}_3\text{P})_2\text{Pt}\{\text{B(Mes)Br}\}]\text{Br}\).\(^{95}\) The complex failed to produce single crystals suitable for X-ray
diffraction. However, the use of K[B(C₆F₅)₄] in CD₂Cl₂ led to the structural authentication of the terminal borylene complex [Scheme 1.40].

![Scheme 1.40: Formation of the cationic complex, trans-[(Cy₃P)₂Pt(BMes)Br][B(C₆F₅)₄].](image)

Moreover, the halide abstraction approach can also be utilised to remove a halide substituent from a bridging haloborylene complex. The extremely air and moisture sensitive cationic metallaborylene [{(OC)₅Mn}₂(μ-B)]⁺ is initially formed from the reaction of (μ-BBr)[Mn(CO)₅]₂ with Na[BAr₄] [Scheme 1.41]. However, due to the sensitive nature of this complex, the metallaborylene abstracts fluoride from the [BAr₄]⁻ counterion to give {(OC)₅Mn}₂(μ-BF) over a period of two hours.

![Scheme 1.41: Synthesis of a metallaborylene complex.](image)

In 2009, the Aldridge group reported the reaction of the unsupported bridging BF complex with the Lewis acidic borane B(C₆F₅)₃, resulting in the formation of two products: a cationic metallaborylene complex [{CpRu(CO)}₂(μ-B)]⁺ and the difluoroboryl complex CpRu(CO)₂BF₂. The same products are synthesised from the analogous reaction with one equivalent of AlCl₃ [Scheme 1.42]. Notably, the reaction with a greater than three-fold excess
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of AlCl₃ affords the metallaborylene quantitatively. Intriguingly, this system reacts in the opposite direction to [{(OC)₅Mn}₂(μ-B)]⁺ which abstracts fluoride from [BAR₄⁺].

Scheme 1.42: Fluoride abstraction from {CpRu(CO)₂}₂(μ-BF).

1.3.2.2 α-Migration of a Boryl Substituent

As with charge neutral borylene complexes, formation of an electron deficient, coordinatively unsaturated metal centre in a boryl system can lead to the synthesis of a base-stabilised borylene complex by base-promoted migration of a boryl substituent. Trans-(Cy₃P)₂Pt{B(Fc)Br}Br reacts with Na[BAR₄⁺] to generate the T-shaped boryl system trans-[(Cy₃P)₂Pt{B(Fc)Br}][BAR₄⁺]. Although the combination of the sterically demanding PCy₃ ligand and the strong trans labilising effect of the boryl ligand inhibits nucleophilic attack at platinum from Lewis bases such as THF, stronger nucleophiles such as 4-picoline react to form trans-[(Cy₃P)₂Pt{BFc(4-pic)}Br][BAR₄⁺] [Scheme 1.43], via a 1,2- halide shift from boron to platinum.

Scheme 1.43: Synthesis of a platinum boryl by α-migration of bromide promoted by the addition of a base.
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1.3.3 Reactivity

Although the reactivity of terminal borylene complexes is a relatively new field, it has developed over recent years to produce numerous versatile and diverse modes of reactivity. Patterns of reactivity have been shown to change depending on the nature of the boron bound substituent and on the net charge. Thus for example, the cationic complex [CpFe(CO)$_2$(BMes)]$^+$ is characterised by significant electrophilicity and therefore reactions proceed by either addition at boron or displacement of the borylene fragment.$^{40}$ Conversely, aminoborylene complexes [CpFe(CO)$_2$(BNR$_2$)]$^+$ exhibit much more varied reactivity including cycloaddition, metathesis and hydride transfer chemistry, which are more characteristic of M=E bonds.$^{34, 83, 104}$

1.3.3.1 Coordination at Boron

The electrophilic nature of cationic borylene complexes means that the main mode of reactivity with hard nucleophiles is by charge driven attack at the boron centre. Aldridge and co-workers have reported numerous examples of addition of halides (e.g. [PPN]Cl, [Ph$_4$P]Br, [tBu$_4$N$I$, [tBu$_4$N][BF$_4$]) to the boron centres in [Cp*$\text{Fe(CO)}_2$(BMes)][BAr$_4^+$], [Cp*$\text{Fe(CO)}_2$(BNMe$_2$)][BAr$_4^+$] and [CpFe(CO)$_2$(BNiPr$_2$)][BAr$_4^+$] to form the corresponding haloboryl complexes [Scheme 1.44].$^{33,39-41}$ These reactions are, of course, effectively the reverse of halide abstraction, the method by which these borylene complexes are initially synthesised.
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Scheme 1.44: Addition of halides to cationic terminal borylene complexes.

Cationic aminoborylene complexes also react with neutral 2-electron donors such as THF and 4-picoline, resulting in base stabilised cationic borylene complexes [Scheme 1.45].

Scheme 1.45: Borylene adduct formation.

Interestingly, \([\text{CpFe(CO)}_2(\text{BNCy}_2)][\text{BAR}_4']\) coordinates THF reversibly while the mesityl substituted analogue decomposes upon addition of THF. Presumably, this reflects the milder electrophilicity of the aminoborylene complex, in comparison to aryl substituted systems. Moreover, softer nucleophiles react with \([\text{CpFe(CO)}_2(\text{BMes})]^+\) at the iron centre rather than at boron; thus addition of \([\text{BPh}_4^-]\) generates \(\text{Cp}^*\text{Fe(CO)}_2\text{Ph}\), presumably due to the predominant localisation of the LUMO at iron [Scheme 1.46].
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Scheme 1.46: Reaction of [CpFe(CO)$_2$(BMes)][BAr$^4$] with [BPh$_4$].

Similar neutral borylene complexes are also vulnerable to nucleophilic attack. The reaction of (OC)$_5$M[BN(SiMe$_3$)$_2$] (M = Cr, W) with electron rich fragments M'(PCy$_3$)$_2$ (M' = Pd, Pt) affords bridging borylene complexes of the type (OC)$_4$M[μ-BN(SiMe$_3$)$_2$](μ-CO)M' (PCy$_3$).$^{105,106}$ The W-Pt system reacts slightly differently, yielding (Cy$_3$P)(OC)$_3$W[μ-BN(SiMe$_3$)$_2$](μ-CO)Pt(PCy$_3$) seemingly due to the displacement of the carbonyl ligand trans to the borylene moiety by liberated PCy$_3$. Similarly, the reaction between CpMn(CO)$_2$(BtBu) with M'(PCy$_3$)$_2$ (M' = Pd, Pt) gives the semi-bridging borylene complexes CpMn(CO)(μ-CO)(μ-BtBu)M'(PCy$_3$) [Scheme 1.47].$^{107}$

Scheme 1.47: Synthesis of the semibridging borylene complex

CpMn(CO)(μ-CO)(μ-BtBu)M'(PCy$_3$) (M' = Pd, Pt).
1.3.3.2 Metathesis

Metathesis chemistry is one of the most important molecular processes developed for the formation of C=C bonds e.g. the Wittig reaction and olefin metathesis.\textsuperscript{1,108,109} Metathesis utilising borylene complexes has been observed for both neutral and cationic systems although interestingly, the mechanisms established for the two classes of compound suggest differing intermediate structures.

The reaction of the neutral borylene complex CpMn(CO)\textsubscript{2}(B\textsuperscript{t}Bu) with benzophenone results in a [2+2] cycloaddition [Scheme 1.48].\textsuperscript{110} Moreover, in solution the complex CpMn(CO)\textsubscript{2}{\kappa^2-B(Bu)OCPh}\textsubscript{2} undergoes cyclo-reversion to produce the manganese carbene CpMn(CO)\textsubscript{2}(CPh\textsubscript{2}) and tri-tert butylboroxime. This metathesis process occurs via a mechanism analogous to classical M=C systems.

![Scheme 1.48: Metathesis of CpMn(CO)\textsubscript{2}(B\textsuperscript{t}Bu) with Ph\textsubscript{2}CO via cycloaddition.](image)

The reactivity of the cationic complexes [CpFe(CO)\textsubscript{2}(BN\textsuperscript{t}Pr\textsubscript{2})]\textsuperscript{+} with Ph\textsubscript{3}PE (E = O, S) leads to the formation of (\textsuperscript{t}Pr\textsubscript{2}NBE)\textsubscript{n} (E = O, n = 3; E = S, n = 2) [Scheme 1.49].\textsuperscript{33,34} Similar reactivity is also observed with Ph\textsubscript{3}AsO. Moreover, [CpFe(CO)\textsubscript{2}{BN\textsuperscript{t}Pr\textsubscript{2}(OPPh\textsubscript{3})}][BA\textsuperscript{t}r\textsubscript{4}] was isolated as an intermediate in the (slower) reaction with Ph\textsubscript{3}PO suggesting an overall metathesis mechanism occurring via simple coordination at the boron centre and an acyclic
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intermediate. This contrasts with the metallacyclic intermediate observed for neutral complex CpMn(CO)$_2$B'Bu with Ph$_2$CO.

Scheme 1.49: The first example of metathesis chemistry involving a cationic borylene complex.

An interesting caveat to this metathesis chemistry is the reaction of the same borylene complex and benzophenone. Initially, the reaction proceeds by similar coordination of the organic substrate at the boron centre. Surprisingly, instead of generating an iron carbene complex, intramolecular Meerwein-Ponndorf hydride transfer occurs to generate an imine donor-stabilised alkoxyborylene system [Scheme 1.50]. Thus it appears that, in conjunction with base-stabilisation, stable cationic alkoxyborylenes can be accessed (Section 1.3.2.1).
Scheme 1.50: Meerwein-Ponndorf-Verley-type hydride transfer within a cationic base-stabilised terminal borylene complex.

The reactions of aminoborylenes \([\text{CpFe(CO)}_2(\text{BNR}_2)][\text{BAR}_4]\) (R = Cy, iPr) with heteroallenes such as isocyanates and carbodiimides have also been investigated and provide yet another unprecedented mode of reactivity.\(^{111,112}\) Insertion of two molecules of dicyclohexylcarbodiimide (CyNCNCy), one into each of the \(\text{Fe}=\text{B}\) and \(\text{B}=\text{N}\) bonds, generates the spirocyclic boronium complex \([\text{CpFe(CO)}_2\text{C(NCy}_2)_2\text{B(NCy}_2)_2\text{CNCy}_2][\text{BAR}_4]\) [Scheme 1.51].
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Scheme 1.51: Insertion into the Fe=B and B=N bonds of a cationic aminoborylene complex by a heteroallene.

On the other hand, isocyanates RNCO (R = Ph, Cy, 2,6-Xyl) react to form the corresponding isonitrile complexes [CpFe(CO)₂(CNR)]⁺ via a net oxygen abstraction process [Scheme 1.52]. In both cases, the overall reactions involve pre-coordination of the heteroallene at the boron centre.

Scheme 1.52: Oxygen abstraction from isocyanates, RNCO.

1.3.3.3 Borylene Transfer Chemistry

A widely studied mode of reactivity for neutral borylene complexes is photochemical and thermal borylene transfer between metal centres, as discussed above (Section
1.3.1.2) In addition, borylene transfer reagents have also been used to functionalise unsaturated organic molecules.

Braunschweig and co-workers have shown that (CO)$_5$M[BN(SiMe$_3$)$_2$] (M = Cr and W) undergo [2+1] cycloaddition reactions with alkynes (Me$_3$SiC≡CSiMe$_3$, PhC≡CPh and EtC≡CEt) under photolytic conditions [Scheme 1.53]. The resulting borirene products are inherently stable under photolytic conditions, being isoelectronic with the cyclopropenium cation and hence aromatic.

**Scheme 1.53:** [2+1] Cycloaddition reactions of group 6 borylene complexes with internal alkynes.

In further work, the reaction of (CO)$_5$M[BN(SiMe$_3$)$_2$] with the bifunctional substrate bis(trimethylsilyl)buta-1,3-diyne gives an unprecedented bis(borirene) [Scheme 1.54].

**Scheme 1.54:** Formation of a bis(borirene).
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Interestingly, borylene transfer to a heavy metal bis(alkynyl) complex, Hg(C≡CR)$_2$, was also attempted under photolytic conditions but resulted instead in the formation of the mercury free diborirene. The reaction proceeds by initial demercuration of Hg(C≡CR)$_2$ to form the diyne RC≡CC≡CR followed by transfer of the borylene fragment. Under thermal conditions, a stoichiometric reaction leads to the formation of 1,4 diphenyl-buta-1,3-diyne and elemental mercury. Repeating the reaction with catalytic amounts of the aminoborylene complex (10 mol %) also results in full conversion to the diyne and mercury [Scheme 1.55]. This chemistry therefore represents the first example of a borylene complex acting as a catalyst.\textsuperscript{77}

\[ \text{Scheme 1.55: Demercuration of bis(alkynyl)mercurials with a borylene catalyst.} \]

Insertion chemistry represents another route for borylene transfer. Aldridge and co-workers have reported the insertion of a borylene fragment into a C-H bond. Reaction of [Cp*Fe(CO)$_2$(BMes)][BAR]$^+$ towards CO, H$_2$C=CH$^+$Bu or the relatively poor electron donors benzophenone and acetone leads to displacement of the borylene fragment and the formation of the cationic complexes [Cp*Fe(CO)$_2$L][BAR]$^+$ (L = CO, H$_2$C=CH$^+$Bu, OCPh$_2$, OCH$_2$) [Scheme 1.56].\textsuperscript{41} Kinetic studies have shown that the ejected borylene fragment BMes inserts into a C-H bond of the dichloromethane solvent.
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Scheme 1.56: Displacement of the borylene fragment by various ligands.

A further mode of reactivity of the aminoborylene complex $[\text{CpFe(CO)}_2\text{B(NCy}_2\text{)}][\text{BARf}_4]$ has been explored by the Aldridge group. The reaction of $[\text{CpFe(CO)}_2\text{B(NCy}_2\text{)}][\text{BARf}_4]$ with 3,5-ditert-butyl-ortho-benzoquinone yields the first example of a net [4+1] cycloaddition reaction involving a borylene complex [Scheme 1.57].

Scheme 1.57:[4+1] cycloaddition of 3,5-ditert-butyl-ortho-benzoquinone.

1.3.4 Electronic Structure and Bonding in Cationic Borylene Complexes

The use of different metals, borylene substituents and even overall charges have resulted in notable structural variations in terminal borylene complexes synthesised to date. Studies on cationic systems have shown that the boron bound substituent has a profound effect.
on the nature of the metal-boron bond and the reactivity of the borylene complex. Table 1.1 lists a series of cationic iron-containing systems featuring aryl, amino, and pentamethylcyclopentadienyl substituents and the systematic variation in the parameters associated with the Fe-B bond.

**Table 1.1**: Fe-B bond lengths (Å), DFT calculated σ:π contribution to covalent bonding, NMR shifts and carbonyl stretching frequencies for cationic terminal borylene complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>d(Fe-B) / Å</th>
<th>σ:π</th>
<th>δ_B (ppm)</th>
<th>υ(CO) / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cp*Fe(CO)₂(BMes)]⁺</td>
<td>1.792(8)</td>
<td>62:38</td>
<td>145</td>
<td>2055, 2013</td>
</tr>
<tr>
<td>[Cp'Fe(CO)₂(BN'Pr₂)]⁺</td>
<td>1.835(3)</td>
<td>70:30</td>
<td>93.8</td>
<td>2065, 2023</td>
</tr>
<tr>
<td>[CpFe(CO)₂(BNCy₂)]⁺</td>
<td>1.859(6)</td>
<td>71:29</td>
<td>93.1</td>
<td>2071, 2028</td>
</tr>
<tr>
<td>[CpFe(CO)₂(BCp*)]⁺</td>
<td>1.977(3)</td>
<td>86:14</td>
<td>-37.9</td>
<td>2020, 1962</td>
</tr>
</tbody>
</table>

On descending the table an increase in the Fe-B bond length is observed, due to an increase in π donation from the borylene substituent, a reduction in electrophilicity at boron and hence a reduction in back-bonding from the metal to the boron centre. This can be described superficially as a change from a Fischer carbene like Fe=B double bond to a simple donor/acceptor bond. DFT studies which have quantified the σ and π contributions to the Fe-B bond, further support this assertion.

The base-stabilised cationic terminal borylene complexes are widely accepted as containing a formal M-B single bond implying limited M→B π-interaction [Table 1.2]. Elongated Fe-B bond lengths and lower carbonyl stretching frequencies support this bonding
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description (e.g. [CpFe(CO)₂{BNCy₂(C₅H₄PPh₃)}]⁺: 2.102(5) Å and 1985, 1927 cm⁻¹; c.f. [CpFe(CO)₂{B(NCy₂)}]⁺: 1.859(6) Å and 2071, 2028 cm⁻¹). These observations imply little residual M to B π back-bonding.⁸³

Table 1.2: Fe-B bond lengths (Å), DFT calculated σ:π contribution to covalent bonding,¹¹B NMR shifts and carbonyl stretching frequencies for base-stabilised cationic terminal borylene complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>d(Fe-B) / Å</th>
<th>σ:π</th>
<th>δB (ppm)</th>
<th>υ(CO) / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CpFe(CO)₂{BNCy₂(4-pic)}]⁺</td>
<td>2.049(4)</td>
<td>87:13</td>
<td>56.9</td>
<td>2019, 1962</td>
</tr>
<tr>
<td>[CpFe(CO)₂{BNPr₂(NPrCMe₂)}]⁺</td>
<td>2.058(9)</td>
<td>88:12</td>
<td>53.7</td>
<td>2007, 1951</td>
</tr>
<tr>
<td>[CpFe(CO)₂{BNPr₂(OPPh₃)}]⁺</td>
<td>2.057(4)</td>
<td>89:11</td>
<td>48.9</td>
<td>2004, 1949</td>
</tr>
<tr>
<td>[CpFe(CO)₂{BNCy₂(C₅H₄PPh₃)}]⁺</td>
<td>2.102(5)</td>
<td>90:10</td>
<td>60.0</td>
<td>1985, 1927</td>
</tr>
</tbody>
</table>

Variation in the metal/ligand framework is another way of influencing electronic structure. Work in the Aldridge group has used ruthenium fragments as (potentially more strongly electron releasing) alternatives to previously reported iron systems. M=B distances in the ruthenium borylene complexes are longer than those for iron, as expected on the basis of the differing covalent radii for the two metals (1.950(8) and 1.960(6) Å for [CpRu(CO)₂(NPrCMe₂)]⁺ and [CpRu(CO)₂(BNCy₂)]⁺, respectively, cf. 1.835(3) and 1.859(6) Å for [CpFe(CO)₂(NPrCMe₂)]⁺ and [CpFe(CO)₂(BNCy₂)]⁺). Both iron and ruthenium systems, however, reveal a M-B shortening of ca. 10 % on going from boryl to borylene system,³⁶ despite CpRu(CO)₂ being a better π donor than CpFe(CO)₂. DFT calculations confirm these
observations, revealing a similar $\sigma:\pi$ contribution to the covalent bond for iron and ruthenium (71:29 and 68:32, respectively, for the BNCy$_2$ compounds).

**Table 1.3** Fe-B bond lengths (Å), DFT calculated $\sigma:\pi$ contribution to covalent bonding, $^{11}$B NMR shifts and carbonyl stretching frequencies for cationic terminal borylene complexes of ruthenium.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$d$(Ru-B) / Å</th>
<th>$\sigma:\pi$</th>
<th>$\delta_B$(ppm)</th>
<th>$\nu$(CO) / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CpRu(CO)$_2${B(NiPr$_2$)}]}$^+$</td>
<td>1.950(8)</td>
<td>$\alpha$</td>
<td>92.0</td>
<td>2020, 1955</td>
</tr>
<tr>
<td>[CpRu(CO)$_2${B(NCy$_2$)}]}$^+$</td>
<td>1.960(6)</td>
<td>68:32</td>
<td>90.0</td>
<td>2022, 1957</td>
</tr>
</tbody>
</table>

"Not available

### 1.4 Sigma Complexes

Transition metal complexes coordinated by an H-X (X = H, C, B or Si) bond to a metal centre have attracted much research interest due to their fundamental role in coordination chemistry. Moreover, the fact that a $\sigma$ complex may precede E-H oxidative addition means that such systems are also of primary relevance in catalysis.$^{116-120}$ Of these complexes, $\sigma$-dihydrogen$^{117,120}$ and $\sigma$-silane$^{121,122}$ complexes have been the most extensively reported.

#### 1.4.1 Dihydrogen, Alkane and Silane Sigma Complexes

In 1984 the seminal complex W(CO)$_3$(PPr$_3$)$_2$(H$_2$) was reported by Kubas and co-workers, featuring a metal-bound dihydrogen ligand. Kubas’ complex represents the first example of stable intermolecular coordination of any sigma bond, with the bonding comprised
of both $\sigma$ and $\pi$ interactions.\textsuperscript{123} It is based on a three-centre two-electron interaction with dominant $\sigma$ donation from the H-H bond into an empty $d_\sigma$ orbital at M and weaker $\pi$ back donation from a filled $d_\pi$ orbital to H-H $\sigma^*$ [Figure 1.6].\textsuperscript{124,125} As a result, the H-H bond is weakened as revealed e.g. by reduced coupling constants in H-D derivatives. The geometric consequences of these orbital overlap requirements support a side-on mode of coordination.
Figure 1.6: Molecular orbital diagram for dihydrogen coordination to a metal.
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There are now numerous examples of dihydrogen complexes, including the neutral system Ru(H)\(_2\)(H\(_2\))(PCy\(_3\))\(_2\)\(^{126}\) and the isoelectronic cationic analogues [Rh(H)\(_2\)(H\(_2\))(PCy\(_3\))]\([\text{BARf}_4]\)\(^{127}\) and [Ir(H)\(_2\)(H\(_2\))(PCy\(_3\))]\([\text{BARf}_4]\).\(^{128}\) Such dihydrogen systems are distinct from classical dihydride complexes, which are formally the product of complete oxidative addition of dihydrogen at the metal centre. This occurs when the dihydrogen bond is sufficiently weakened due to greater backbonding into the antibonding σ* orbital of dihydrogen; clearly the position of a particular complex along the H\(_2\) oxidation profile is a consequence of both the metal and ancillary ligand set [Figure 1.7].\(^{129}\)

\[
\begin{array}{c}
\text{M} \\
\text{H} \\
\text{H}
\end{array}
\]

Dihydride Complex

\[
\begin{array}{c}
\text{M} \\
\text{H}
\end{array}
\]

Dihydrogen Complex

**Figure 1.7:** Metal dihydride and dihydrogen complexes.

Thermodynamic studies have shown that Kubas’ compound actually exists in equilibrium between the dihydrogen and dihydride complexes in a 4:1 ratio.\(^{130}\) However, due to poorer backbonding, more electron deficient cationic complexes such as [(Cy\(_3\)P)\(_2\)Mn(CO)\(_3\)H\(_2\)]\(^+\) and [(Ph\(_3\)P)\(_2\)Re(CO)\(_3\)H\(_2\)]\(^+\) are best described as ‘true’ dihydrogen complexes.\(^{131,132}\)

A very limited range of intermolecular alkane complexes have also been reported together with a much wider range of intramolecular ‘agostic’ systems. In 1998, Ball reported that irradiation of CpRe(CO)\(_3\) in cyclopentane resulted in the short lived alkane complex CpRe(CO)\(_2\)(cyclo-C\(_5\)H\(_{10}\)). Such complexes provide useful insight into the mechanisms of C-H activation.\(^{133}\)
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More recently, Brookhart and co-workers characterised a methane sigma complex in solution. $^{13}$C labelling revealed that the signal of the rhodium-bound methyl group shifted dramatically upfield upon protonation, indicating $\sigma$ bound $^{13}$CH$_4$ [Scheme 1.58].

![Scheme 1.58: Synthesis of a cationic rhodium $\sigma$ alkane complex.]

In the 1980’s, work by Schubert led to the characterisation of many hydrosilane complexes containing Si-H-M linkages. The bonding interactions in these complexes may be described using a Dewar-Chatt-Duncanson model involving synergic interactions, in a similar manner to dihydrogen systems [Figure 1.8].

![Figure 1.8: Synergic bonding interactions for a Si-H bond with a metal centre.]

Hydrosilane sigma complexes are more susceptible towards oxidative addition than their dihydrogen analogues due to the polarity of the heteronuclear Si-H bond. This raises the energy of the HOMO (Si-H $\sigma$ orbital) and lowers the LUMO (Si-H $\sigma^*$ orbital) making back donation from the transition metal $d_\pi$ orbital more energetically feasible. Here too, appropriate choice of the metal and ligand framework can strengthen the Si-H-M interaction.
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In 2009, McGrady et al. set out to investigate the effects of electronegative silicon-bound substituents on the Si-H interaction in compounds of the type Cp’Mn(CO)₂(HSiR₃) (R₃ = Ph₂H, Ph₂F, Cl₃).¹³⁷ These workers deduced that the electronegativity had little impact on the Mn-H interaction, implying that the Mn-H bond is formed at an early stage of the oxidative addition process. However, the extent of the Mn-Si interaction increases as the energy of the σ* LUMO is lowered by the more electronegative ligands. As a result, hydrosilane complexes containing more electronegative ligands are thought to lie further along the reaction pathway with regard to oxidative addition. Molecular orbital calculations and photoelectron spectroscopy studies on CpMn(CO)₂(HSiCl₃) predicted oxidative addition to be 80% complete, with a strong Mn-Si interaction compared to Si-H.¹³⁸

1.4.2 Borane Sigma Complexes

1.4.2.1 Sigma Complexes of Borane-Lewis Base Adducts

The chemistry of the tetrahydroborate ion BH₄⁻ has received significant attention due to its isoelectronic relationship with CH₄. In mononuclear complexes, three different coordination modes involving one (κ¹), two (κ²) or three (κ³) bridging hydrogen atoms have been found [Figure 1.9].¹³⁹ However, the anionic nature of the BH₄⁻ ligand makes electrostatic contributions dominant when considering the bonding. Therefore, these complexes do not represent a truly analogous comparison to other E-H-M systems.
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![Coordination modes of BH₄⁻ to a single metal centre.](image)

**Figure 1.9:** Coordination modes of BH₄⁻ to a single metal centre.

Analogous to the silane complexes discussed above, sigma complexes of neutral boranes have also been an active area of research. Lewis base adducts BH₃·L have been shown to form sigma complexes with electron deficient transition metal centres, in some cases in monodentate fashion. Thus, in 1999, Shimoi and co-workers demonstrated the first example of a borane sigma complex. Photolysis of group 6 hexacarbonyls with BH₃·L (L = PMe₃, PPh₃, NMe₃) leads to the ejection of CO, thereby providing a vacant site for the coordination of the borane [Scheme 1.59].

![Scheme 1.59: The first examples of borane sigma complexes.](image)

**Scheme 1.59:** The first examples of borane sigma complexes.

More recently, irradiation of various carbonyl complexes [CpMn(CO)₃ and M(CO)₆ (M = Cr, Mo, W)] in the presence of 1,3, dimethylimidazol-2-ylideneborane (BH₃·IMe) has been shown to afford the new borane complexes CpMn(CO)₂(κ¹⁻BH₃·IMe) and M(CO)₅(κ¹⁻BH₃·IMe) (M = Cr, Mo, W). The BH₃·NHC moiety was found to be coordinated to the metal centre through a B-H-M three-centre two-electron bond without any significant M-B interaction.
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Experimental and theoretical studies have identified that the bonding in such complexes is primarily through B-H sigma donation. Back donation is negligible due to the relative high energy of the B-H σ* orbital. This is consistent with ‘end on’ κ¹ coordination of the borane. Furthermore, it was found that CpMn(CO)₂(k¹-BH₃·NR₃) (where R = Me experimentally, and R = H for the corresponding theoretical model) acts as a sigma donor only. The adduct was classified as an ‘unstretched sigma complex’ since both the terminal and bridging B-H distances were found to be similar, presumably due to minimal dπ back donation. The complex possesses a large Mn-H-B bond angle (142°) in accordance with an ‘end-on’ binding mode; the molecular orbitals of the model system reveal that the manganese centred HOMO and B-H σ* LUMO do not have a symmetry match and consequently make no contribution to the bonding interaction. As in hydrosilane complexes, substituent effects on complex stability have been studied for borane sigma complexes. Shimoi’s systems M(CO)₅(k¹-BH₂R·L) and CpMn(CO)₂(k¹-BH₂R·L) (where M = Cr, W and L = tertiary amine or phosphine) have been investigated with this in mind. It was discovered that a more electron withdrawing ancillary ligand set at the metal results in a more stable borane adduct as it lowers the energy of the metal LUMO, creating a better energy match with the B-H sigma bonding orbital. Similarly, a more electron releasing substituent at the borane stabilises the M-H-B linkage because the substituent acts to raise the energy of the B-H bonding σ orbital and create a better energy match with the metal LUMO. These considerations have led to the coordination of boranes at cationic transition metal centres [Scheme 1.60]. Interestingly, while the neutral complexes containing [M(CO)₅] fragments decompose by dissociation of the borane, these cationic complexes appear to undergo B-H bond cleavage. This is rationalised by the weakened B-H bond in the cationic systems due to enhanced sigma donation.
Amineborane complexes at electron deficient metal centres are of particular interest due to their nature as potential intermediates in the dehydrocoupling chemistry yielding poly/oligomeric aminoboranes. The Weller group have targeted similar systems containing amineboranes bound at low coordinate metal centres such as the 12-electron \(\text{[Rh(P}^3\text{Pr}_3)\text{]}^+\) fragment generated from \(\text{[Rh(P}^3\text{Pr}_3)\text{]}(\eta^6\text{-C}_6\text{H}_5\text{F})\text{[BAR}^4\text{]}\) by the dissociation of fluorobenzene [Scheme 1.61]. The resulting 16-electron species is square planar and the amineborane is thought to bind exclusively by B-H σ donation.

Conversely, reaction of \(\text{[Rh(P}^3\text{Bu}_3)\text{]}\text{[BAR}^4\text{]}\) with two equivalents of dimethylamineborane gives the square planar system \(\text{[Rh(P}^3\text{Bu}_3)\text{]}(\kappa^2\text{-H}_3\text{B}\cdot\text{NMe}_2\text{H})\text{[BAR}^4\text{]}\) which rapidly reacts further to yield \(\text{[Rh(H)}_2(\text{P}^3\text{Bu}_3)\text{]}(\kappa^2\text{-H}_3\text{B}\cdot\text{NMe}_2\text{H})\text{[BAR}^4\text{]}\) and \(\text{[H}_2\text{BNMe}_2\text{]}_2\) [Scheme 1.62].
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Scheme 1.62: Reaction of two equivalents of dimethylaminoborane with \([\text{Rh}(\text{P}^3\text{Bu}_3)_2]^+\).

1.4.2.2 Sigma Complexes of Three Coordinate Boranes

The first reported example of a sigma complex in which the borane ligand is a neutral three-coordinate species was the bis(borane) adduct \(\text{Cp}_2\text{Ti(HBCat)}_2\) synthesised by Hartwig and co-workers in 1996 [Figure 1.10].\(^{148}\) Subsequently, a related monoborane complex \(\text{Cp}_2\text{Ti(PMe}_3\text{)(HBCat)}\) was isolated by combining \(\text{Cp}_2\text{Ti(PMe}_3\text{)}_2\) and \(\text{Cp}_2\text{Ti(HBCat)}_2\) in equimolar ratios.\(^{149}\)

Figure 1.10: First sigma complex containing a three-coordinate borane.

Unlike borane-Lewis base adducts, the boron p\(_x\) orbital in these complexes is formally vacant and can potentially engage in \(\pi\) back donation with the metal fragment. Hence, the bonding considerations in these complexes are markedly different to those for four-coordinate
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systems.\textsuperscript{150} With the aim of establishing the influence of the boron bound substituents in such systems, the structures of the $\sigma$ borane complexes $\text{Cp}'\text{Mn(CO)}_2(\kappa^1\text{-HBCat})$, $\text{Cp}'\text{Mn(CO)}_2(\kappa^1\text{-HBPin})$ and $\text{Cp}'\text{Mn(CO)}_2(\kappa^1\text{-HBCy}_2)$ were compared [Figure 1.11].

![Figure 1.11: Manganese $\sigma$ borane complexes.](image)

$\text{Cp}'\text{Mn(CO)}_2(\kappa^1\text{-HBCy}_2)$ displays the longest Mn-B bond and the shortest B-H and Mn-H bonds of the three complexes. These observations indicate a weaker Mn-B interaction and a more hydridic character for the borane hydrogen. Kinetic studies also reveal that the HBCy\textsubscript{2} borane complex has a smaller binding energy compared to the other two alkoxyborane complexes. Further examination of the geometries revealed a change in bond angles, with a ‘pivoting’ of the borane about the B-H bond centroid as the sigma donating capacity of the borane increases. The catecholborane complex best represented ‘side-on’ coordination whilst the HBCy\textsubscript{2} borane complex resembled ‘end-on’ binding. The outcome of this study highlights the enlarged effect of B-H $\sigma$ donation and simultaneous decline in Mn d$_\pi$ back-bonding as the electron donating ability of substituents at the boron centre increases.

More recently, compounds in which the borane coordinates through two geminal B-H bonds have also been reported. Thus, Sabo-Etienne and co-workers reported the first example of such a system from the addition of H\textsubscript{2}BMes to Ru(H)\textsubscript{2}(H\textsubscript{2})\textsubscript{2}(PCy\textsubscript{3})\textsubscript{2}.\textsuperscript{151}
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![Figure 1.12](image)

Figure 1.12: The first $\kappa^2$ bound borane complex.

A similar coordination mode has been observed by Stradiotto and co-workers for cationic systems. The reaction of $\text{Cp}^*\text{Ru}(\text{P}^3\text{Pr}_3)\text{Cl}$ with $\text{H}_2\text{BMes}$ followed by halide abstraction leads to the formation of the $\kappa^2$ coordinated cationic product [Scheme 1.63].\textsuperscript{152} Chloride transfer from ruthenium to boron occurs prior to halide abstraction, giving rise to a chloroborate intermediate. Upon coordination, the B-H distances in the $\text{H}_2\text{BMes}$ fragment increase due to $\sigma$ donation from the B-H bonds. $d_\pi$ back donation from ruthenium to the formally vacant p orbital on boron also occurs.

![Scheme 1.63](image)

Scheme 1.63: $\kappa^2$ Aminoborane coordination at a cationic ruthenium centre.

1.4.2.3 Sigma Complexes of Aminoboranes

Aminoboranes are the topic of considerable research interest due to their potential as monomeric building blocks for novel inorganic polymers, and their role as the first formed products in the dehydrogenation of a class of BN-containing hydrogen storage materials.\textsuperscript{145,153-158} In 2010, Manners and co-workers reported the metal catalysed polymerisation of methylamineborane, $\text{H}_3\text{B} \cdot \text{NMeH}_2$, by ruthenium, rhodium and palladium complexes to give high-molecular-weight poly(aminoboranes), $[\text{H}_2\text{BNMMe(H)}]_n$.\textsuperscript{159, 160} These are the BN
analogues of poly(propylene) and the reaction is thought to proceed by initial dehydrogenation of H$_3$B·NMeH$_2$ and subsequent polymerisation of the momomeric H$_2$BNMeH so formed. Therefore, the primary modes of interaction of aminoboranes with catalytically relevant late transition metals are of significant interest.

Alcaraz and Sabo-Etienne have reported the synthesis of the bis(σ-BH) ruthenium aminoborane complexes Ru(H)$_2$(κ$^2$-H$_2$BNMe$_{2-n}$)(PCy$_3$)$_2$ ($n = 0 - 2$) via the reaction of Ru(PCy$_3$)$_2$(H)$_2$(H$_2$)$_2$ with H$_3$B·NH$_n$Me$_{2-n}$ ($n = 1 - 3$) under stoichiometric conditions$^{161}$ This bis(σ-borane) mode of coordination contrasts markedly with the classical ‘side-on’ mode of binding typically observed for isoelectronic alkene donors towards transition metals. Consistent with this assertion, the same authors reported that the ‘end-on’ bis(σ-BH) binding motif is the most stable isomer of the model complex trans-Ru(PMe$_3$)$_2$(H)$_2$(H$_2$BNH$_2$) with alternative modes of interaction utilising the BN π system being $> 14$ kcal mol$^{-1}$ higher in energy.

Aldridge and co-workers have characterised cationic σ complexes of amine- and aminoboranes featuring N-heterocyclic carbene co-ligands$^{162,163}$ Both types of complex feature the borane ligand bound via a κ$^2$ mode of coordination [Scheme 1.64].

**Scheme 1.64:** Dehydrogenation of an amineborane to form an aminoborane complex.
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More recently, the isoelectronic aminoborane complexes $\text{Ru}(H)_2(\kappa^2-H_2\text{BN'Pr}_2)(\text{PCy}_3)_2$ and $[\text{M}(H)_2(\kappa^2-H_2\text{BN'Pr}_2)(\text{PCy}_3)_2][\text{BAr}'_4]$ (M = Rh, Ir) have been prepared by the groups of Weller and Sabo-Etienne by the direct interaction of the aminoborane precursor with ruthenium and cationic rhodium/iridium metal centres [Scheme 1.65].

![Scheme 1.65](image)

**Scheme 1.65**: Syntheses of isoelectronic ruthenium and cationic rhodium and iridium aminoborane complexes.

For these systems, the M–B and M-H distances increase as the B-H bond distances decrease in the order Ru < Ir < Rh. This indicates that there is a stronger interaction with the neutral ruthenium complex than cationic rhodium system. This is a consequence of the compressed orbitals due to the positive charge. The cationic iridium system is intermediate in nature, due to the more radially extended 5d orbitals. These aminoborane systems bind to metal centres in a similar manner to amineboranes. However, donation from the two germinal B-H bonds into a low-lying vacant orbital, in this case the M-H $\sigma^*$ orbital, is reinforced by $\pi$-back-donation from the metal to the $\pi^*$ BN orbital of the aminoborane [Figure 1.13].
In 2010, Esteruelas et al. suggested that highly electrophilic transition metal fragments can promote hydride abstraction from amine- and alkoxy-boranes to form \( \sigma(BH) \) bound borinium complexes of transition metals.\(^{165} \) They report that in the presence of an amineborane, OsH\(_2\)Cl\(_2\)(P\(^3\)Pr\(_3\))\(_2\) generates the putative 14-electron fragment [OsHCl(P\(^3\)Pr\(_3\))]\(_2\) and that the amineborane dehydrogenates to form the corresponding aminoborane. They then propose that hydride transfer occurs from the amino borane to OsHCl(P\(^3\)Pr\(_3\))\(_2\) to afford the anionic metal fragment [OsH\(_2\)Cl(P\(^3\)Pr\(_3\))]\(_2\) which supposedly traps and stabilises the borinium cation [HBNR\(_2\)]\(^+\) [Scheme 1.66].

![Diagram of bonding interactions](image)

**Figure 1.13:** Bonding interactions [M(H)\(_2\)] fragment with aminoboranes.

In a similar fashion, the same group reported that the treatment of OsH\(_2\)Cl\(_2\)(P\(^3\)Pr\(_3\))\(_2\) with pinacol borane yields the \( \sigma \) borinium derivative [Scheme 1.67].

**Scheme 1.66:** Proposed formation of a \( \sigma \) borinium complex.

In a similar fashion, the same group reported that the treatment of OsH\(_2\)Cl\(_2\)(P\(^3\)Pr\(_3\))\(_2\) with pinacol borane yields the \( \sigma \) borinium derivative [Scheme 1.67].
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Scheme 1.67: Suggested hydride transfer to form an alkoxy borinium σ complex.

1.5 **Research Proposal**

The use of strongly σ-basic trialkyl phosphine co-ligands has previously been shown to bring about dramatic changes in the stability of carbene and silylene complexes compared to related carbonyl substituted complexes.\(^{166,167}\) An initial aim of the current research was therefore to target more electron rich metal centres [such as half-sandwich bis(phosphine) systems] in order to isolate borylene complexes which are otherwise unstable under ambient conditions, and investigate modulated patterns of reactivity.

Although the salt elimination/halide abstraction route to cationic aminoborylene complexes has proved to be extremely successful in the synthesis of novel complexes [Section 1.3.2.1], such a two-step process is not viable in catalytic cycles leading, for example, to the functionalisation of organic molecules. Therefore, a further research aim was to probe the possibility of synthesising aminoborylene complexes by the direct interaction of dihydroaminoboranes at transition metal fragments.
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Chapter II

Experimental Techniques

2.1 Manipulation of Air-Sensitive Compounds

The majority of the compounds used during this research were highly sensitive to air and moisture. This made it necessary to employ inert atmosphere and high vacuum techniques instead of traditional bench top methods for the manipulation of these compounds.

2.1.1 Inert Atmosphere Techniques

The two most common types of inert atmosphere techniques involve the use of a Schlenk line or a glove box. Both allow the handling of air and moisture sensitive compounds by using argon or nitrogen gas to achieve an inert atmosphere.\(^1,2\)

Schlenk line techniques proved more convenient and efficient when using solutions of air- and moisture-sensitive compounds, reducing the risk of decomposition by hydrolysis and oxidation.\(^3\) The line used consisted of a dual Pyrex glass manifold with several ports to which apparatus could be attached [Figure 2.1]. One manifold was connected to a source of purified inert gas and the other to a vacuum pump. This allowed both for a positive pressure of argon gas, and for the evacuation of glassware to give pressures of ca. \(10^{-2}\) Torr. A ‘pump and purge’ cycle was usually repeated three times to achieve an essentially oxygen- and moisture-free environment. The inert gas line was vented through a mercury bubbler to avoid excessive
pressures, while solvent vapours and gaseous reaction products were prevented from contaminating the pump through a liquid nitrogen cold trap. All ground glass joints and two-way taps were lubricated with high vacuum grease thereby providing an air-tight seal. Cannulae and syringes were used to transfer liquids and solutions between flasks without exposing them to the external atmosphere.

A glove box was used for the handling of air-sensitive solids. It consisted of a sealed, air-tight stainless steel container designed to allow manipulation of compounds in an inert atmosphere. Neoprene gloves were built into the sides of the glove box allowing tasks to be performed inside the box. The box atmosphere, usually nitrogen, was purified by scrubbing through activated copper metal and molecular sieves to remove oxygen and moisture. Compounds and apparatus were admitted to the box through a side port using the standard ‘pump and purge’ method.
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2.1.2 High Vacuum Techniques

The high vacuum line was used for the removal of trace solvent from compounds where the standard Schlenk line proved insufficient.\(^1\,^2\) The vacuum line consisted of a rotary pump, a mercury diffusion pump, a cold trap, and single manifold with Young’s greaseless taps. The combination of the rotary pump and mercury diffusion pump allowed pressures of ca. \(10^{-4}\) Torr. A Tesla coil, which produced a discharge at pressures between 1 and \(10^{-3}\) Torr, was used to assess the pressure in the line and check for leaks.

2.2 Spectroscopic Techniques

2.2.1 NMR Spectroscopy

NMR spectra were recorded on a Varian ‘Mercury’ 300 MHz or Varity Unity +500 spectrometer. The residual signals of deuterated solvents were used as references for \(^1\)H and \(^{13}\)C NMR measurements. \(^{11}\)B, \(^{19}\)F and \(^{31}\)P NMR spectra were referenced against Et₂O·BF₃, CFCl₃ and 85 % aqueous H₃PO₄ respectively. Sample preparation involved generating an inert atmosphere within a Young’s NMR tube using the ‘pump and purge’ method, followed by solution transfer by cannula.

2.2.2 Infrared Spectroscopy

Infrared spectra were measured as a solution in a compatible solvent, contained within a solution infrared cell. Spectra were recorded on a Nicolet 500 FT-IR spectrometer.
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2.2.3 Mass Spectrometry

Samples for mass spectrometry were submitted to the EPSRC National Mass Spectrometry Service Centre, Swansea University if the compound was charge-neutral (e.g. boryl complexes). Charged compounds (e.g. cationic borylene complexes) were analysed by the use of a Bruker MicroTOF ESI mass spectrometer linked to a glove box via PEEK tubing. The ESI mass spectrometry experiments were performed by Mr. Ian Riddlestone of the Aldridge research group.

2.2.4 X-Ray Crystallography

Determination of crystal structures were carried out by Dr. Dragoslav Vidovic, Mr. Michael Kelly, Mr. Ian Riddlestone and Mr. Nicholas Phillips of the Aldridge research group, University of Oxford. Crystal data was collected on a Bruker-Nonius KappaCCD diffractometer.

2.2.5 Theoretical Calculations

The majority of calculations were carried out by the author, with assistance from Mr. Tobias Kraemer of the McGrady research group and Mr. Joshua Bates of the Aldridge research group, University of Oxford using the Gaussian03/09 packages. Other theoretical calculations (looking at solvent dependent equilibria) were carried out by Mr Dibyendu Mallick and Prof. Eluvathingal D. Jemmis at the Indian Institute of Science, Bangalore. A detailed description of the computational methodologies used can be found in the appendix.
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2.2.6 Photolysis Experiments

Photolysis experiments were carried out using a Spectral Energy mercury arc lamp (1 kW) with samples contained within quartz Schlenk vessels.

2.2.7 Elemental Analyses

Elemental Analyses were performed by Dr. Stephen Boyer of the London Metropolitan University.

2.3 Preparation and Purification of Starting Materials

A list of commercially available chemicals used along with their sources, quoted purity and purification methods is given on the appendix CD.

2.3.1 Synthesis of Starting Materials

Certain precursors were not themselves available from commercial sources and as a result had to be synthesised from readily available reagents listed on the appendix CD.

Preparation of Na[B{C₆H₃(CF₃)₂-3,5}_4], Na[BAr^4]

The method employed for the formation of Na[B{C₆H₃(CF₃)₂-3,5}_4] followed that reported by Reger et al.⁵ A 3-necked round-bottomed flask fitted with a reflux condenser and a dropping funnel was charged with activated magnesium turnings (1.58 g, 66 mmol) and diethyl ether (300 cm³). 1-bromo-3,5-trifluoromethyl benzene (8.0 cm³, 46 mmol) was added dropwise to the solution over 2 h. BF₃·OEt₂ (1.4 cm³, 11 mmol) was then added via syringe, and the solution refluxed for 6 h, the reaction being monitored by in situ ¹¹B NMR spectroscopy. The solution was then filtered into aqueous Na₂CO₃ and stirred vigorously. After separation of the
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Et₂O layer, the remaining aqueous fraction was washed with Et₂O (4 x 30 cm³). The solvent was removed from the combined Et₂O fractions \textit{in vacuo} to yield a pale brown powder. Recrystallisation from a minimal amount (~ 50 cm³) of a 1:1:1 mixture of Et₂O, THF and dichloromethane layered with hexane gave a pale brown solid, which was dried \textit{in vacuo} at 140°C for ~ 60 h, the final product being a white powder in 69 % yield. Spectroscopic data matched those given in the literature.⁵

Preparation of Na[B\{C₆H₃Cl₂-3,5\}_₄], Na[BARF₄]⁴

The method employed for the formation of Na[B\{C₆H₃Cl₂-3,5\}_₄] followed that reported by Anulewicz-Ostrowska \textit{et al.} ⁶ Na[BF₄] (2.74 g, 25 mmol) and magnesium turnings (2.43 g, 100 mmol) were placed in a reaction flask, and Et₂O (10 cm³) was added. 1-bromo-3,5-dichlorobenzene (22.60 g, 100 mmol) dissolved in Et₂O (30 cm³) was added dropwise over 2 h. The reaction was then left to stand for 12 h, checked by ¹¹B NMR spectroscopy for the appearance of the [B\{C₆H₃Cl₂-3,5\}_₄]⁻ resonance (δB -6.7 ppm), and then slowly poured into an aqueous solution of Na₂CO₃ (20 g in 300 cm³). The yellow Et₂O layer was separated and the aqueous layer washed with Et₂O (2 x 50 cm³). The combined ethereal fractions were pumped dry \textit{in vacuo} and the resulting white precipitate washed with water and hexane. The dried product was obtained in 90 % yield. Spectroscopic data matched those given in the literature.⁶

Preparation of [H(OEt₂)]₂[B\{C₆H₃(CF₃)₂-3,5\}_₄], [H(OEt₂)]₂[BARF₄]⁴

The method employed for the formation of [H(OEt₂)]₂[B\{C₆H₃(CF₃)₂-3,5\}_₄] followed that reported by Brookhart \textit{et al.} ⁷ A solution of HCl in Et₂O (3.0 cm³ of a 2 M solution, 6 mmol) was added to a solution of Na[B\{C₆H₃(CF₃)₂-3,5\}_₄] (1.00 g, 1.13 mmol) also in Et₂O (20 cm³) at -30°C, and stirred for 30 min. The reaction mixture was then filtered, the solution concentrated to 5 cm³ and cooled to -78°C. After standing for 1 h, hexane was added slowly to
precipitate the product. The supernatant was filtered and drying the precipitate in vacuo afforded the product in 75 \% yield. Spectroscopic data matched those given in the literature.\textsuperscript{7}

\textit{Preparation of \([\text{Et}_3\text{Si}][\text{B}((\text{C}_6\text{F}_5)_4)]\)}

The method employed for the formation of \([\text{Et}_3\text{Si}][\text{B}((\text{C}_6\text{F}_5)_4)]\) followed that reported by Lambert \textit{et al.}\textsuperscript{8} A solution of \([\text{Ph}_3\text{C}][\text{B}((\text{C}_6\text{F}_5)_4)]\) (0.25 g, 0.27 mmol) in \text{Et}_3\text{SiH} (5 cm\textsuperscript{3}) was sonicated overnight. Filtration and drying in vacuo afforded the product which was used in subsequent reactions without further purification.

\textit{Preparation of Na[(\(\eta^5\)-C\(_5\)H\(_5\))Fe(CO)\(_2\)]}\textsuperscript{9}

The method employed for the formation of Na[(\(\eta^5\)-C\(_5\)H\(_5\))Fe(CO)\(_2\)] followed that reported by King \textit{et al.}\textsuperscript{9} [(\(\eta^5\)-C\(_5\)H\(_3\))Fe(CO)\(_2\)]\(_2\) (10.38 g, 29 mmol) in THF (120 cm\textsuperscript{3}) was added to sodium amalgam (2 g of sodium in 40 cm\textsuperscript{3} Hg) and allowed to stir for 24 h. Filtration and removal of volatiles in vacuo yielded Na[(\(\eta^5\)-C\(_5\)H\(_3\))Fe(CO)\(_2\)]\(_2\). The yellow solid was washed with hot toluene (3 x 50 cm\textsuperscript{3}), boiling hexane (1 x 50 cm\textsuperscript{3}) and dried in vacuo. The product was used in subsequent reactions without further purification.

\textit{Preparation of Na[(\(\eta^5\)-C\(_5\)H\(_4\)Me)Fe(CO)\(_2\)]}\textsuperscript{9}

The method employed for the formation of Na[(\(\eta^5\)-C\(_5\)H\(_4\)Me)Fe(CO)\(_2\)] also followed that reported by King \textit{et al.}\textsuperscript{9} [(\(\eta^5\)-C\(_5\)H\(_4\)Me)Fe(CO)\(_2\)]\(_2\) was dissolved in THF and reacted with sodium amalgam at room temperature for 48 h. After filtration and removal of the solvent in vacuo, the solid was washed with hot toluene (3 x 50 cm\textsuperscript{3}) and boiling hexane (1 x 50 cm\textsuperscript{3}). The product was used in subsequent reactions without further purification.
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Preparation of \( \text{H}_2\text{BNR}_2 \) [\( R = '\text{Pr}, \text{Cy} \)]

The method employed for the formation of \( \text{H}_2\text{BNR}_2 \) [\( R = '\text{Pr}, \text{Cy} \)] followed that reported by Euzenat et al.\(^{10}\) A solution of BX\(_3\)·THF in THF (5.0 cm\(^3\) of a 1.0 M solution) was mixed with HNR\(_2\) (1 equiv.) and stirred to form the amine-borane adduct H\(_3\)B·NHR\(_2\), as judged by the appearance of a sharp peak in the \( ^{11}\text{B} \) NMR spectrum at \( \delta_{\text{B}} \) -21 ppm. Subsequent thermal dehydrogenation was achieved by refluxing the system for 30 h; the \( ^{11}\text{B} \) NMR spectrum at this stage showed the product as well as significant impurity peaks. Repeated vacuum distillation of the mixture yielded pure \( \text{H}_2\text{BNR}_2 \) [\( R = '\text{Pr}, \text{Cy} \)]. Spectroscopic data matched those given in the literature.\(^{10}\)

Preparation of \( \text{Cl}_2\text{BNCy}_2 \)

An analogous reaction was used to that employed by Gerrard et al. for the preparation of \( \text{Cl}_2\text{BN}'\text{Pr}_2 \).\(^{11}\) A solution of Cy\(_2\)NH (8.0 cm\(^3\), 40 mmol) in CH\(_2\)Cl\(_2\) (20 cm\(^3\)) was added dropwise to a solution of BCl\(_3\) in heptane (52 cm\(^3\) of a 1.0 M solution, 44 mmol) at -80°C. The reaction mixture was stirred for 1 h at -80°C, after which the solvent was removed \textit{in vacuo} and the resulting solid dissolved in a mixture of benzene (40 cm\(^3\)) and Et\(_3\)N (5.0 cm\(^3\), 36 mmol). After stirring for 24 h, volatiles were removed \textit{in vacuo} and the resulting solid extracted into hexanes (3 x 30 cm\(^3\)). The hexane was removed to give the solid product in 57% yield. Spectroscopic data matched those given in the literature.\(^{11}\)

Preparation of \( \text{Cl}_2\text{BNMe}_2 \)

The method employed for the formation of \( \text{Cl}_2\text{BNMe}_2 \) followed that reported by Banister et al.\(^{12}\) A solution of tris(dimethylamino)borane (3.5 cm\(^3\), 20 mmol) in toluene was mixed with 2 equivalents of BCl\(_3\) and stirred for 24 h. The compound was stored as a stock solution in toluene at 10°C. The product was used in subsequent reactions without further purification.
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Preparation of \( \text{Cl}_2\text{BN(Me)Bz} \)

The method employed for the formation of \( \text{Cl}_2\text{BN(Me)Bz} \) followed that reported by Niedenzu et al.\(^\text{13}\) A solution of \( \text{Bz(Me)NH} \) (3.1 cm\(^3\), 24 mmol) in \( \text{CH}_2\text{Cl}_2 \) (30 cm\(^3\)) was added dropwise to a solution of \( \text{BCl}_3 \) in heptane (26.4 cm\(^3\) of a 1.0 M solution, 26 mmol) at \(-80^\circ\text{C}\). The reaction mixture was stirred for 1 h at \(-80^\circ\text{C}\), after which the solvent was removed \textit{in vacuo} and the resulting solid was dissolved in benzene (40 cm\(^3\)) and \( \text{Et}_3\text{N} \) (3.0 cm\(^3\), 24 mmol). After stirring for 24 h, volatiles were removed \textit{in vacuo} and the resulting solid extracted into hexanes (3 x 30 cm\(^3\)). The hexane was removed to give the product as an oil in 75 % yield. Spectroscopic data matched those given in the literature.\(^\text{13}\)

Preparation of \( \text{Cl}_2\text{BN(Me)Ph} \)

The method employed for the formation of \( \text{Cl}_2\text{BN(Me)Ph} \) followed that reported by Blackborow et al.\(^\text{14}\). \( \text{N-methylaniline} \) (3.0 cm\(^3\), 27 mmol) in \( \text{CH}_2\text{Cl}_2 \) (20 cm\(^3\)) was added to \( \text{BCl}_3 \) in heptane (29.7 cm\(^3\) of a 1.0 M solution, 29.7 mmol) at \(-80^\circ\text{C}\) over 15 min and the reaction mixture stirred for 1 h at \(-80^\circ\text{C}\). Removal of the solvent gave a solid that was dissolved in toluene and refluxed at 140\(^\circ\text{C}\) for 18 h. The toluene solvent was then removed \textit{in vacuo} and the product was separated from any remaining amine borane adduct by extraction into hexanes (3 x 20 cm\(^3\)). Removal of hexanes \textit{in vacuo} afforded a pale yellow oil that was stored as a stock solution in \( \text{Et}_2\text{O} \) (0.49 M) at 10\(^\circ\text{C}\). Spectroscopic data matched those given in the literature.\(^\text{14}\)

Preparation of \( \text{Cl}_2\text{BN(4-MeO-C}_6\text{H}_4)\text{Me} \)

The method employed for the formation of \( \text{Cl}_2\text{BN(4-MeO-C}_6\text{H}_4)\text{Me} \) followed that reported by Sugasawa et al.\(^\text{15}\). 4-MeO-\( \text{N-methylaniline} \) (1.12 g, 8.2 mmol) was dissolved in \( \text{CH}_2\text{Cl}_2 \) (20 cm\(^3\)) and added to \( \text{BCl}_3 \) in heptanes (8.2 cm\(^3\) of a 1.0 M solution, 8.2 mmol) at \(-80 \ ^\circ\text{C}\) over 15
min, and the reaction mixture stirred for a further 1 h. After warming to room temperature the solvent was removed in vacuo to give a colourless solid that was extracted into toluene. The toluene solution was then refluxed for 24 h, the solvent removed in vacuo and the product separated from any remaining amine borane adduct by extraction into hexanes (3 x 20 cm$^3$). The hexanes were subsequently removed in vacuo to afford a white solid in 62 % yield. Spectroscopic data matched those given in the literature.$^{15}$

**Preparation of Cl$_2$BOMes**

The method employed for the formation of Cl$_2$BOMes followed that reported by Kays *et al.*$^{16}$ $^t$BuLi in hexanes (5.5 cm$^3$ of a 1.6 M solution, 8.8 mmol) was added dropwise to a solution of 2,4,6-trimethylphenol (1.01 g, 7.3 mmol) in hexane (40 cm$^3$); the resulting mixture was warmed slowly to room temperature and stirred for 16 h. The supernatant was filtered from the solid product which was then washed with hexane (2 x 20 cm$^3$) and dried in vacuo. BCl$_3$ in heptane (7.3 cm$^3$ of a 1.0 M solution, 7.3 mmol) was added to a suspension of the lithium salt in toluene (40 cm$^3$) and the mixture stirred at room temperature for a further 16 h. Filtration of the supernatant provided a stock solution in toluene suitable for further reactions. Spectroscopic data matched those given in the literature.$^{16}$

**Preparation of CpFe(CO)$_2$B(NCy$_2$)Cl**

The method employed for the formation of CpFe(CO)$_2$B(NCy$_2$)Cl followed that reported by Aldridge *et al.*$^{17}$ A mixture of Na[CpFe(CO)$_2$] (1.10 g, 5.5 mmol), Cl$_2$BNCy$_2$ (1.20 g, 4.6 mmol) and Et$_2$O (50 cm$^3$) were stirred for 18 h at room temperature. The reaction mixture was then filtered and the solvent removed in vacuo. The resulting brown solid was extracted into hexane (3 x 20 cm$^3$) and concentrated to 20 cm$^3$. Storing at -30°C overnight yielded a
crystalline yellow solid in 47 % yield. The solid was isolated from the supernatant and dried in vacuo. Spectroscopic data matched those given in the literature.\textsuperscript{17}

**Preparation of\textit{CpFe(CO)}\textsubscript{2}B(NMe\textsubscript{2})Cl**

The method employed for the formation of \textit{CpFe(CO)}\textsubscript{2}B(NMe\textsubscript{2})Cl followed that reported by Braunschweig \textit{et al.}\textsuperscript{18} A solution of Cl\textsubscript{2}BNMe\textsubscript{2} in toluene (14.4 cm\textsuperscript{3}, 4.5 mmol) was added to a slurry of Na[CpFe(CO)\textsubscript{2}] (1.00 g, 5.0 mmol) in toluene and the reaction mixture stirred for 18 h. Filtration and removal of volatiles yielded a red/brown solid, which was extracted into pentane (3 x 20 cm\textsuperscript{3}) and concentrated. Storage at –30 °C overnight afforded a red/brown solid in 50 % yield which was isolated and dried in vacuo. Spectroscopic data matched those given in the literature.\textsuperscript{18}

**Preparation of\textit{CpFe(CO)}\textsubscript{2}B(OMes)Cl**

The method employed for the formation of \textit{CpFe(CO)}\textsubscript{2}B(OMes)Cl followed that reported by Kays \textit{et al.}\textsuperscript{16} A solution of Cl\textsubscript{2}BOMes in toluene (43.0 cm\textsuperscript{3} of a 0.12 M solution, 5.2 mmol) was added to a suspension of Na[(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})Fe(CO)\textsubscript{2}] (1.04 g, 5.2 mmol) in toluene (15 cm\textsuperscript{3}) and the resulting mixture stirred at room temperature for 16 h. Filtration, removal of volatiles \textit{in vacuo} and recrystallisation from hexanes (20 cm\textsuperscript{3}) at -30°C yielded the product as a pale yellow solid in 45 % yield. Spectroscopic data matched those given in the literature.\textsuperscript{17}

**Preparation of\textit{CpFe(CO)}\textsubscript{2}BF\textsubscript{2}**

The method employed for the formation of \textit{CpFe(CO)}\textsubscript{2}BF\textsubscript{2} followed that reported by Braunschweig \textit{et al.}\textsuperscript{19} BF\textsubscript{3}·OEt\textsubscript{2} (0.15 cm\textsuperscript{3}, 1.2 mmol) was added dropwise to a suspension of Na[(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})Fe(CO)\textsubscript{2}] (0.23 g, 1.1 mmol) in toluene (10 cm\textsuperscript{3}) at 0°C. The reaction mixture was allowed to warm to room temperature and was stirred for 15 min, resulting in the
formation of a cloudy red solution. Removal of volatiles in vacuo yielded a red solid. Extraction into hexanes (20 cm$^3$) and cooling to -80$^\circ$C afforded red crystals of the product in 37% yield. Spectroscopic data matched those given in the literature.$^{19}$

**Preparation of CpFe(dmpe)SnMe$_3$**

The method employed for the formation of CpFe(dmpe)SnMe$_3$ followed that reported by Kumar et al.$^{20}$ A solution of SnMe$_3$Cl in toluene (1.03 g, 5.2 mmol) was added to a suspension of Na[($\eta^5$-C$_5$H$_5$)Fe(CO)$_2$] (1.04 g, 5.2 mmol) in toluene (15 cm$^3$) and the resulting mixture stirred at room temperature for 16 h. Filtration, removal of volatiles in vacuo and recrystallisation from hexanes (20 cm$^3$) at -30$^\circ$C yielded CpFe(CO)$_2$SnMe$_3$ as a pale yellow solid in 80% yield. Dmpe (1.7 cm$^3$, 10.4 mmol) was then added to a solution of CpFe(CO)$_2$SnMe$_3$ in toluene and the reaction mixture subjected to UV photolysis for 8 h. Removal of volatiles in vacuo, washing with hexanes and drying in vacuo afforded the product in 60% yield. Spectroscopic data matched those given in the literature.$^{20}$

**Preparation of [CpFe(CO)$_2$(BNR$_2$)]$^+$[BAr$_f$$_4$] ($R =$ Cy, Me)**

The formation of [CpFe(CO)$_2$(BNR$_2$)]$^+$[BAr$_f$$_4$] was accomplished by minor modification of the procedures published by Aldridge et al.$^{21,22}$ A mixture of CpFe(CO)$_2$B(NR$_2$)Cl and Na[BAr$_f$$_4$] (1.1 equiv.) in dichloromethane was sonicated for 20 min. and the reaction judged to be complete by $^{11}$B NMR spectroscopy. Filtration yielded the cationic borylene which was used in subsequent reactions without further purification as a stock solution.

**Preparation of [Ir(coe)$_2$Cl]$_2$**

The method employed for the synthesis of [Ir(coe)$_2$Cl]$_2$ followed that reported by Herde et al.$^{23}$ IrCl$_3$·3(H$_2$O) (2.00 g, 7.5 mmol) was added to a round-bottomed flask equipped with a
reflux condenser. Isopropyl alcohol (22 cm$^3$), H$_2$O (8 cm$^3$), and cyclooctene (4 cm$^3$) were added via syringe, giving a dark purple solution. The mixture was refluxed under argon for 3 h, and the resulting orange solid filtered, washed with ice-cold ethanol (3 x 30 cm$^3$), and dried in vacuo affording the product in 44 % yield (by iridium conversion). Spectroscopic data matched those given in the literature.$^{23}$

Preparation of CpRu(PPh$_3$)$_2$Cl

The method employed for the formation of CpRu(PPh$_3$)$_2$Cl followed that reported by Bruce et al.$^{24}$ PPh$_3$ (21.0 g, 80 mmol) was dissolved in ethanol (800 cm$^3$) by heating. RuCl$_3$·H$_2$O (5.00 g, 20 mmol) was then dissolved in ethanol (100 cm$^3$) by bringing the mixture to the boil and allowing the solution to cool. Freshly cracked CpH (10.0 cm$^3$, 12 mmol) was added to the RuCl$_3$·H$_2$O solution and the mixture transferred to a dropping funnel. The dark brown solution was then added to the PPh$_3$ solution over 10 min whilst maintaining the temperature at the reflux point. The mixture was refluxed for a further 1 h and then filtered in air whilst hot. Storing the solution at -10$^\circ$C overnight yielded orange crystals which were washed with ethanol (4 x 25 cm$^3$) and light petroleum (4 x 25 cm$^3$). Drying in vacuo afforded the product in 90 % yield. Spectroscopic data matched those given in the literature.$^{24}$

Preparation of CpRu(dcype)Cl

The method employed for the formation of CpRu(dcype)Cl followed that reported by Joslin et al.$^{25}$ Dcype (0.685 g, 1.62 mmol) was added to a suspension of CpRu(PPh$_3$)$_2$Cl (1.17 g, 1.6 mmol) in benzene (10 cm$^3$) and the reaction mixture refluxed for 1 h. Removal of the solvent in vacuo yielded a red oil which was extracted into hexanes (3 x 5 cm$^3$). The hexanes solution was placed onto a dry alumina column (ca. 1 cm diameter x 20 cm length) and eluted with hexanes. The elution was continued until all the PPh$_3$ had been removed. Subsequent elution
with THF afforded rapid stripping of the desired complex to give an orange/red solution. Removal of the solvent in vacuo resulted in the formation of an orange solid in 90 % yield. Spectroscopic data matched those given in the literature.\textsuperscript{25}

\textit{Preparation of $[\text{Cp}^{*}\text{RuCl}_2]_n$}

The method employed for the formation of $[\text{Cp}^{*}\text{RuCl}_2]_n$ followed that reported by Tilley \textit{et al.}\textsuperscript{26} \text{Cp}*H (2.6 cm$^3$, 14.7 mmol) was added to a solution of RuCl$_3$·H$_2$O (1.50 g, 7.2 mmol) in ethanol to give a dark brown solution. The reaction mixture was refluxed for 3h. Once cool, the solution was filtered and the precipitated product washed with ethanol (2 x 5 cm$^3$) and diethyl ether (2 x 5 cm$^3$). Drying in vacuo yielded the product in 65 % yield. Spectroscopic data matched those given in the literature.\textsuperscript{26}

\textit{Preparation of $[\text{Cp}^{*}\text{Ru(}\mu_3\text{-Cl})]_4$}

The method employed for the formation of $[\text{Cp}^{*}\text{Ru(}\mu_3\text{-Cl})]_4$ followed that reported by Fagan \textit{et al.}\textsuperscript{27} Lithium triethylborohydride in THF (0.96 cm$^3$ of a 1.0 M, 0.96 mmol) was added to a solution of $[\text{Cp}^{*}\text{RuCl}_2]_n$ (0.30 g, 0.96 mmol) in THF (20 cm$^3$) and the reaction mixture stirred for 45 min. The orange precipitate so formed was isolated by filtration and washed with THF (5 cm$^3$). Drying in vacuo afforded the product in 79 % yield. Spectroscopic data matched those given in the literature.\textsuperscript{27}

\textit{Preparation of $\text{Cp}^{*}\text{Ru(IMes)Cl}$}

The method employed for the formation of $\text{Cp}^{*}\text{Ru(IMes)Cl}$ followed that reported by Baratta \textit{et al.}\textsuperscript{28} IMes (0.46 g, 1.5 mmol) in THF (0.7 cm$^3$) was added to a solution of $[\text{Cp}^{*}\text{RuCl}_2]_n$ (0.30 g, 0.96 mmol) in THF and the reaction mixture stirred at room temperature for 3 h. During this time the reaction mixture turned from brown to deep blue. THF was removed in
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vacuo and the resulting residue extracted into diethyl ether. The diethyl ether was removed in vacuo to afford a blue powder in 70 % yield. Spectroscopic data matched those given in the literature.²⁸

Preparation of Cp*Ru(PCy₃)Cl

The method employed for the formation of Cp*Ru(PCy₃)Cl followed that reported by Arliguie et al.²⁹ [Cp*RuCl₂]ₙ (1.22 g, 3.9 mmol), PCy₃ (1.10 g, 3.9 mmol) and an excess of Zn (2.50 g) were suspended in ethanol (50 cm³) and stirred at room temperature for 2 h. During this time the reaction turned from brown to deep blue. Volatiles were removed in vacuo to yield the crude product which was recrystallised from hexanes to afford a violet product in 53 % yield. Spectroscopic data matched those given in the literature.²⁹

Preparation of [Cp*Ru(PPh₃)Cl]ₙ

The formation of [Cp*Ru(PPh₃)Cl]ₙ was formed by minor modification of the procedure published by Johnson et al.³⁰ A solution of PPh₃ (0.053 g, 0.20 mmol) in pentane (20 cm³) was added to a pentane slurry (20 cm³) of [Cp*Ru(μ₃-Cl)]₄ (0.054 g, 0.050 mmol) and the reaction mixture stirred for 1 h. An orange powder was subsequently isolated and dried in vacuo to give a 75 % isolated yield. Spectroscopic data matched those given in the literature.³⁰

Preparation of [(p-cymene)RuCl₂]₂

The method employed for the formation of [(p-cymene)RuCl₂]₂ followed that reported by Bennett et al.³¹ α-Phellandrene (5.8 cm³, 36 mmol) was added to a solution of RuCl₃·H₂O (0.74 g, 3.6 mmol) in ethanol (40 cm³). The reaction mixture was heated to reflux under argon for 4 h. Once cool, the solution was filtered and the resulting red crystalline material washed
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with methanol (20 cm$^3$). Drying in vacuo afforded the product in 65 % yield. Spectroscopic data matched those given in the literature.$^{31}$

Preparation of (p-cymene)Ru(PPh$_3$)Cl$_2$

The method employed for the formation of (p-cymene)Ru(PPh$_3$)Cl$_2$ followed that reported by Bennett et al.$^{31}$ A suspension of [(p-cymene)RuCl$_2$]$_2$ (0.40 g, 0.64 mmol) and triphenylphosphine (0.40 g 1.5 mmol) in hexanes (30 cm$^3$) was heated under reflux for 4 h. Once cool, the solution was filtered and the resulting orange precipitate washed with hexanes (20 cm$^3$). Drying in vacuo afforded the product in 80 % yield. Spectroscopic data matched those given in the literature.$^{31}$

Preparation of (p-cymene)Ru(PMe$_3$)Cl$_2$

The method employed for the formation of (p-cymene)Ru(PMe$_3$)Cl$_2$ followed that reported by Hodson et al.$^{32}$ A suspension of [(p-cymene)RuCl$_2$]$_2$ (0.20 g, 0.32 mmol) and trimethylphosphine (0.15 cm$^3$, 1.5 mmol) in hexanes (30 cm$^3$) was heated under reflux for 4 h. Once cool, the solution was filtered and the orange precipitate washed with hexane (20 cm$^3$). Drying in vacuo afforded the product in 88 % yield. Spectroscopic data matched those given in the literature.$^{32}$

Preparation of (p-cymene)Ru{P(OPh)$_3$}Cl$_2$

The method employed for the formation of (p-cymene)Ru(P{OMe)$_3$}Cl$_2$ followed that reported by Hodson et al.$^{32}$ A suspension of [(p-cymene)RuCl$_2$]$_2$ (0.10 g, 0.16 mmol) and triphenylphosphite (0.10 cm$^3$, 0.38 mmol) in hexane (30 cm$^3$) was heated under reflux for 4 h. Once cool, the solution was filtered and the orange precipitate washed with hexanes (20 cm$^3$).
Drying in vacuo afforded the product in 99 % yield. Spectroscopic data matched those given in the literature.\(^{32}\)

*Preparation of (p-cymene)Ru(PCy\(_3\))Cl\(_2\)*

The method employed for the formation of (p-cymene)Ru(PCy\(_3\))Cl\(_2\) followed that reported by Demonceau *et al.*\(^{33}\) A solution of tricyclohexylphosphine (0.59 g, 2.1 mmol) in dichloromethane (10 cm\(^3\)) was added at 0\(^\circ\)C to [(p-cymene)RuCl\(_2\)]\(_2\) (0.62 g, 1.0 mmol) and allowed to warm to room temperature with stirring over 1 h. Pentane (15 cm\(^3\)) was then added to the solution and the resulting light brown crystalline solid was filtered off after 3 h, washed with pentane (2 x 5 cm\(^3\)) and dried in vacuo to afford the product in 82 % yield. Spectroscopic data matched those given in the literature.\(^{33}\)

### 2.4 References for Chapter II

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3.1 Introduction

The chemistry of three-coordinate boron halides is dominated by their propensity to act as potent Lewis acids, with the greater acidity of the heavier halo congeners being a matter of discussion in numerous undergraduate textbooks.⁠¹⁴ These and related trigonal planar borane systems have been shown to readily abstract anionic substituents (e.g. hydride, halide, alkyl/aryl anions) to generate four-coordinate borates, and have therefore been widely exploited as Lewis acid catalysts in a range of organic/organometallic systems.⁠¹⁵ Not surprisingly, examples of such electron-deficient systems, \( R_2BX \), acting as sources of halide (\( X^- \)) and the highly unsaturated two-coordinate borinium cation, \([R_2B]^+\) are somewhat rare.⁠⁶⁷ Such behaviour is usually associated with extensively \( \pi \)-stabilised diaminoborinium systems, \([(R_2N)B]^+\), generated from the corresponding neutral precursor \((R_2N)_2BX\) by halide abstraction utilising a more potent Lewis acid (e.g. BBr₃);⁠⁶⁷ examples of the spontaneous ejection of \( X^- \) to generate a borinium cation are, not unexpectedly, very rare indeed (vide infra).
Chapter III (Dimethylamino)borylene and Related Complexes of Electron Rich Metal Fragments

In 2003, the first cationic terminal borylene complex \([L_nM(BX)]^+\) was synthesised via a halide abstraction method similar to that employed for silylenes such as \([\text{Cp}^*\text{Ru}(\text{PMe}_3)_2(\text{SiMe}_2)]\text{B}(\text{C}_6\text{F}_5)_4\).\textsuperscript{11-13} Since then, a range of cationic aminoborylene complexes, \([\text{CpM(CO)}(\text{L})(\text{BNR}_2)][\text{BAR}_4^f]\) (M = Fe, Ru; R = \text{tPr, Cy, Me}; L = CO, PMe\(_3\), dmpe) have been formed by halide abstraction from the corresponding unsymmetrical amino(halo)boryl complex. Moreover, such cationic borylene complexes have been implicated in the functionalisation of organic substrates via a range of mechanisms, including metathesis, cycloaddition, insertion and migration processes.\textsuperscript{11,12,14-20} Despite this, existing examples of cationic borylene complexes suffer from (i) a lack of tolerance to nucleophilic or protic reagents,\textsuperscript{12,17} and (ii) the inconvenience of the two-step (metathesis/halide abstraction) synthetic procedure necessitated from dihaloboranes.\textsuperscript{21-26}

Previous work in the Aldridge group has demonstrated that the reactions of the boryl compounds \(\text{CpM(CO)}_2\text{B(NCy}_2\text{)Cl}\) (M = Fe, Ru) with trimethyl- or triphenylphosphine in toluene under photolytic conditions lead to the formation of the mono-substituted complexes \(\text{CpM(CO)}(\text{PMe}_3)\text{B(NCy}_2\text{)Cl}\) (M = Fe, Ru) and \(\text{CpFe(CO)}(\text{PPh}_3)\text{B(NCy}_2\text{)Cl}\), respectively [Scheme 3.1].\textsuperscript{19} The corresponding cationic terminal borylene complexes \([\text{CpM(CO)}(\text{PR}_3)\text{B(NCy}_2\text{)Cl}]^+\) (M = Fe, Ru; PR\(_3\) = PMe\(_3\), PPh\(_3\)) can then be synthesised using halide abstraction chemistry. In the case of the corresponding chemistry with the bidentate ligand 1,2-bis(dimethylphosphino)ethane (dmpe), a bridged dinuclear boryl complex \([\text{CpFe(CO)}\text{B(NCy}_2\text{)Cl}]_2(\mu\text{-dmpe})\) is generated under similar conditions, from which the dicationic bis(borylene) system \([^\{\text{CpFe(CO)}(\text{BNCy}_2)\}_2(\mu\text{-dmpe})][\text{BAR}_4^f]\) can subsequently be obtained. The reactions of \(\text{CpM(CO)}(\text{PMe}_3)\text{B(NCy}_2\text{)Cl}\) (M = Fe, Ru) with excess PMe\(_3\) under more forcing conditions, however, do not lead to the formation of the bis(phosphine)
complexes \( \text{CpM(PMe}_3\text{)}_2\text{B(NCy}_2\text{)Cl} \); instead extrusion of the borylene fragment is observed and carbonyl-containing cations such as \([\text{CpFe(CO)(PMe}_3\text{)}_2]^+\) are formed [Scheme 3.1].

![Scheme 3.1](image_url)

**Scheme 3.1**: Photolytic carbonyl substitution and borylene extrusion chemistry observed for \( \text{CpFe(CO)}_2\text{B(NCy}_2\text{)Cl} \) in the presence of tertiary phosphine ligands.

### 3.1.1 Aims of Present Research

Given the initial success of carbonyl ligand substitution in boryl complexes in the group and considering the dramatic changes in electronic structure and enhancements in stability brought about in related carbene and silylene systems by replacing ancillary carbonyl ligands with less \( \pi \) acidic phosphines {cf. the relative stabilities of \([\text{CpFe(CO)}_2(\text{CH}_2)]^+\) and \([\text{CpFe(dppe)}(\text{CH}_2)]^+\) and the synthesis of \([\text{Cp}^*(\text{PMe}_3)_2\text{Os=SiR}_2]^+\)}, the current research targeted systems containing more electron rich metal/ligand frameworks.\(^{27,28}\) The use of strongly \( \sigma \)-basic trialkyl phosphine ligands in complexes of the type \([[(\eta^5\text{-C}_5\text{R}_5)\text{M(PR}_3\text{)}_2(\text{BNR}_2)]]^+\) for example, offers a potential way of altering electronic structure (cf. related carbonyl-containing systems) and thereby modulating patterns of chemical reactivity. However, given the problems previously encountered in introducing two such co-ligands by
carbonyl substitution in conjunction with the B(NCy₂)Cl ligand, related chemistry utilising less bulky boryl substituents [e.g. B(NMe₂)Cl] was to be targeted.

3.2 Experimental

Syntheses of CpFe(dmpe)B(NMe₂)Cl, 3.3a, [CpFe(dmpe)(BNMe₂)]Cl, [3.5a]Cl, [CpFe(dmpe)(BNMe₂)][BPh₄], [3.5a][BPh₄], and [CpFe(dmpe)(BNMe₂)][BAR₄ Cl], [3.5a][BAR₄ Cl]

A toluene solution of CpFe(CO)₂B(NMe₂)Cl (3.1) (0.20 g, 0.78 mmol) and dmpe (> 2 equiv.) in a quartz reaction vessel was irradiated for 6 h. Periodic monitoring by ¹¹B and ³¹P NMR spectroscopy revealed sequential formation of an intermediate postulated as CpFe(CO)(κ¹-dmpe)B(NMe₂)Cl (δB 62, δP 53 and -45) followed by CpFe(κ²-dmpe)B(NMe₂)Cl (3.3a; δB 66, δP 75). Attempts to isolate 3.3a by removal of the toluene solvent in vacuo and extraction into pentane resulted instead in the formation of [CpFe(dmpe)(BNMe₂)]Cl ([3.5a]Cl). After washing the residue with pentane and recrystallisation from dichloromethane/hexanes, [3.5a]Cl was obtained as a microcrystalline material. Isolated yield 0.30 mmol, 38 %.

Data for [3.5a]Cl: ¹H NMR (300 MHz, CD₂Cl₂, 20°C): δH 1.55 (m, 2JPH = 11.0 Hz, 5JPH = 1.1 Hz, 6H, PMe), 1.61 (m, 2JPH = 11.3 Hz, 2JPH = 0.7 Hz, 6H, PMe), 1.77 (m, 2JHaHb = 14.4 Hz, 3JHbHb = 7.6 Hz, 2H, PCH₂), 1.97 (m, 3JHaHa' = 9.0 Hz, 3JHbHb' = 7.4 Hz, 2H, PCH₂), 2.69 (s, 6H, NMe₂), 4.61 (t, 4JPH = 1.3 Hz, 5H, Cp). ¹³C NMR (126 MHz, CD₂Cl₂, 20°C): δC 20.3 (m, 1JPC = 25.4 Hz, 4JPC = 4.4 Hz, PMe), 24.7 (m, 1JPC = 38.4 Hz, 4JPC = 0.6 Hz, PMe), 29.7 (m, 1JPC = 36.7 Hz, 2JPC = 10.6 Hz, PCH₂), 33.1 (NMe₂), 78.9 (Cp). ¹¹B NMR (96 MHz, CD₂Cl₂, 20°C): 8B 88 (br, fwhm ca. 340 Hz). ³¹P NMR (121 MHz, CD₂Cl₂, 20°C): 8P 79 (m, 2JPP = 38.3 Hz). MS (positive ion electrospray) m/z: [M]⁺ 326.1049 (100%); exact mass for [M]⁺ 326.1058, calc. 326.1049. Coupling constants were obtained for the second order dmpe
resonances in both $^1$H and $^{13}$C NMR spectra using gNMR. The subsequent syntheses of $[3.5a][\text{BPh}_4]$ and $[3.5a][\text{BAR}^{Cl}_4]$ were carried out in quantitative yield via the reactions of $[3.5a]\text{Cl}$ with the sodium salt of the appropriate anion in fluorobenzene over 20 min at 20ºC. Single crystals of both $[3.5a][\text{BPh}_4]$ and $[3.5a][\text{BAR}^{Cl}_4]$ were obtained from fluorobenzene/hexanes layering at 20ºC.

Data for $[3.5a][\text{BPh}_4]$: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 20ºC): δ$_H$ 1.54 (m, 6H, PMe), 1.62 (m, 6H, PMe), 1.79 (m, 2H, PCH$_2$), 1.99 (m, 2H, PCH$_2$), 2.74 (s, 6H, NMe$_2$), 4.59 (br s, 5H, Cp), 6.92-7.42 (m, 20H, [BPh$_4$]). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 20ºC): δ$_C$ 20.4 (m, PMe), 23.5 (m, PMe), 30.2 (m, PCH$_2$), 35.0 (NMe$_2$), 80.1 (Cp), 122.1 (para-CH of [BPh$_4$]), 126.2 (ortho-CH of [BPh$_4$]), 136.2 (meta-CH of [BPh$_4$]), 165.3 (q, $^1J_{CB} = 47.7$ Hz, ipso-C of [BPh$_4$]). $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$, 20ºC): δ$_B$ 88 (br, fwhm ca. 330 Hz), -6.4 ([BPh$_4$]). $^{31}$P NMR (121 MHz, CD$_2$Cl$_2$, 20ºC): δ$_P$ 79. MS (positive ion electrospray) m/z: [M]$^+$ 326.1 (100%); exact mass for [M]$^+$ 326.1056, calc. 326.1037.

Crystallographic Data: C$_{37}$H$_{47}$B$_2$FeNP$_2$, M$_r$ = 645.20, monoclinic, P 2$_1$/c, $a = 16.3137(2)$, $b = 11.8160(1)$, $c = 19.2319(2)$ Å, $\beta = 109.689(1)^\circ$, V = 3490.5(1) Å$^3$, $Z = 4$, $\rho_c = 1.228$ Mg m$^{-3}$, T = 150 K, $\lambda = 0.71073$ Å. 39887 reflections collected, 7918 independent [R(int) = 0.049] and used in all calculations. $R_1 = 0.0429$, $wR_2 = 0.0968$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1 = 0.0660$, $wR_2 = 0.1068$ for all unique reflections. Max. and min. residual electron densities 0.59 and -0.47 e Å$^{-3}$.

Data for $[3.5a][\text{BAR}^{Cl}_4]$: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 20ºC): δ$_H$ 1.55 (m, 6H, PMe), 1.61 (m, 6H, PMe), 1.77 (m, 2H, PCH$_2$), 1.98 (m, 2H, PCH$_2$), 2.72 (s, 6H, NMe$_2$), 4.58 (s, 5H, Cp), 6.96 (s, 4H, para-CH of [BAR$^{Cl}_4$]), 7.10 (s, 8H, ortho-CH of [BAR$^{Cl}_4$]). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 20ºC): δ$_C$ 20.3 (m, PMe), 23.5 (m, PMe), 30.1 (m, PCH$_2$), 35.0 (NMe$_2$), 80.2 (Cp),
124.1 (para-CH of [BAr\(^{Cl}\)]), 130.0 (meta-C of [BAr\(^{Cl}\)]), 133.2 (ortho-CH of [BAr\(^{Cl}\)]), 165.2 (q, \(^{1}J_{CB} = 48.6\) Hz, ipso-C of [BAr\(^{Cl}\)]). \(^{11}\)B NMR (96 MHz, CD\(_{2}\)Cl\(_{2}\), 20°C): \(\delta_{B}\) 88 (br, fwhm ca. 300 Hz), -6.8 ([BAr\(^{Cl}\)])\(^{-}\).\(^{31}\)P NMR (121 MHz, CD\(_{2}\)Cl\(_{2}\), 20°C): \(\delta_{P}\) 79.

MS (positive ion electrospray) m/z: [M]\(^{+}\) 326.1 (100%), exact mass for [M]\(^{+}\) 326.1058, calc. 326.1037.

Crystallographic Data: C\(_{80}\)H\(_{83}\)B\(_{4}\)Cl\(_{6}\)Fe\(_{2}\)N\(_{2}\)P\(_{4}\), Mr = 1937.63, triclinic, P-1, \(a = 13.6566(1)\), \(b = 14.8733(2)\), \(c = 23.5763(3)\) Å, \(\alpha = 76.576(1)^{\circ}\), \(\beta = 76.915(1)^{\circ}\), \(\gamma = 80.915(1)^{\circ}\), V = 4508.9(1) Å\(^{3}\), \(Z = 4\), \(\rho_{c} = 1.356\) Mg m\(^{-3}\), T = 150 K, \(\lambda = 0.71073\) Å. 61514 reflections collected, 20220 independent [R(int) = 0.042] and used in all calculations. R\(_{1}\) = 0.0551, wR\(_{2}\) = 0.1295 for observed unique reflections [\(F^2 > 2\sigma (F^2)\)] and R\(_{1}\) = 0.0720, wR\(_{2}\) = 0.1459 for all unique reflections. Max. and min. residual electron densities 1.64 and -1.19 e Å\(^{-3}\).

NMR monitored reactions of 3.1 and 3.2 with other phosphines: identification of

[CpFe(dmpbz)(BNMe\(_{2}\))]Cl, [3.5b]Cl, [CpFe(PPhMe\(_{2}\))(CO)]Cl,
[CpFe(PPhMe\(_{2}\))(BNMe\(_{2}\))]Cl, [3.5c]Cl, [CpFe(PMe\(_{3}\))(BNMe\(_{2}\))]Cl, [3.5d]Cl and
[CpRu(dmpe)(BNMe\(_{2}\))]Cl, [3.6a]Cl

Drawing on the methodology used to prepare 3.3a/[3.5a]Cl, typical in situ scoping experiments involved the irradiation of 3.1 or 3.2 (ca. 0.75 mmol) and the respective phosphine (>2 equiv. for the bidentate ligands dmpe and dmpbz, >4 equiv. for the monodentate systems PPhMe, PPhMe\(_{2}\) and PMe\(_{3}\)) in a quartz reaction vessel with periodic monitoring by \(^{11}\)B and \(^{31}\)P NMR spectroscopy. At the stage where these data revealed complete conversion of 3.1 or 3.2 to the corresponding bis(phosphine) system, volatiles were removed in vacuo, the residue washed repeatedly with hexanes (3 x 20 cm\(^{3}\)) and the resulting solid extracted into CD\(_{2}\)Cl\(_{2}\) for analysis by multinuclear NMR spectroscopy and electrospray mass spectrometry. In all four cases spontaneous auto-ionisation of the bis(phosphine) ligated
boryl system in CD$_2$Cl$_2$ to give the corresponding cationic borylene (as the chloride salt) is indicated by these data, with downfield shifted $^{11}$B resonances and $^1$H NMR data indicating equivalent NMe$_2$ methyl groups, being particularly diagnostic.

CpFe(dmpbz)B(NMe$_2$)Cl, 3.3b, and [CpFe(dmpbz)(BNMe$_2$)]Cl, 3.5bCl: initial photolysis for 5 h yielded 3.3b ($\delta_B$ 66, $\delta_P$ 69 ppm).

Data for 3.5bCl: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 20°C): $\delta_H$ 1.64 (m, 6H, PMe), 1.91 (m, 6H, PMe), 2.69 (s, 6H, NMe$_2$), 4.75 (s, 5H, Cp ring), 7.38 (m, 2H, 3-H), 7.54 (m, 2H, 2-H). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 20°C): $\delta_C$ 22.2 (m, PMe), 25.1 (m, PMe), 35.6 (NMe$_2$), 80.6 (Cp), 117.7 (AB multiplet, 2-C), 125.1 (apparent t, 3-C), 150.8 (AB multiplet, 1-C). $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$, 20°C): $\delta_B$ 89 (br, fwhm = 290 Hz). $^{31}$P NMR (121 MHz, CD$_2$Cl$_2$, 20°C): $\delta_P$ 68.0. MS (positive ion electrospray) m/z: [CpFe(dmpbz)Cl]$^+$ 354.0 (100%).

[CpFe(PPh$_2$Me)$_2$(CO)]Cl. Photolysis of 3.1 with PPh$_2$Me (4.0 equiv) in toluene over 60 h leads to the formation of the known salt [CpFe(PPh$_2$Me)$_2$(CO)]Cl as a yellow precipitate. Characterisation was achieved by comparison with previously reported NMR data and by crystallographic analysis of the related [BAR′$_4$] salt formed by the metathesis reaction with Na[BAR′$_4$].

CpFe(PPhMe$_2$)$_2$B(NMe$_2$)Cl, 3.3c, and [CpFe(PPhMe$_2$)$_2$(BNMe$_2$)][BPh$_4$], 3.5cCl: initial photolysis for 60 h yielded 3.3c ($\delta_B$ 66, $\delta_P$ 69 ppm).

Data for 3.5cCl: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 20°C): $\delta_H$ 1.44 (overlapping m, 12H, PMe), 2.90 (s, 6H, NMe$_2$), 4.57 (br s, 5H, Cp), 7.00-7.62 (overlapping m, 10H, Ph of PPhMe$_2$). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 20°C): $\delta_C$ 24.5 (m, PMe), 25.3 (m, PMe), 37.0 (NMe$_2$), 83.4 (Cp), 129.6 (m, ortho-CH of Ph), 130.3 (m, meta-CH of Ph), 130.5 (s, para-CH of Ph), 140.6 (m,
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11B NMR (96 MHz, CD$_2$Cl$_2$, 20°C): δ$_B$ 92 (v br, fwhm ca. 800 Hz). 31P NMR (121 MHz, CD$_2$Cl$_2$, 20°C): δ$_P$ 41.6. MS (positive ion electrospray) m/z: [M]$^+$ 452.1 (100%); exact mass for [M]$^+$ 452.1530, calc. 452.1441.

CpFe(PMe$_3$)$_2$B(NMe$_2$)Cl, 3.3d, and [CpFe(PMe$_3$)$_2$(BNMe$_2$)]Cl, [3.5d]Cl: initial photolysis for 24 h yielded 3.3d (δ$_B$ 67, δ$_P$ 42 ppm).

Data for [5d]Cl: 1H NMR (300 MHz, CD$_2$Cl$_2$, 20°C) δ$_H$ 1.26 (d, $^2J_{PH}$ = 10 Hz, 18H, PMe$_3$), 2.63 (s, 6H, Me), 4.44 (s, 5H, Cp). 13C NMR (126 MHz, CD$_2$Cl$_2$, 20°C) δ$_C$ 26.0 (m, PMe$_3$), 35.7 (m, NMe$_2$), 82.8 (Cp). 11B NMR (96 MHz, CD$_2$Cl$_2$, 20°C) δ$_B$ 91 (br, fwhm ca. 498 Hz).

31P NMR (121 MHz, CD$_2$Cl$_2$, 20°C) δ$_P$ 32.5. MS (positive ion electrospray) m/z: [M]$^+$ 328.1 (weak).

CpRu(dmpe)B(NMe$_2$)Cl, 3.4a, and [CpRu(dmpe)(BNMe$_2$)]Cl, [3.6a]Cl: initial photolysis for 12 h yielded 3.4a (δ$_B$ 60, δ$_P$ 59 ppm).

Data for [3.6a]Cl: 1H NMR (300 MHz, CD$_2$Cl$_2$, 20°C): δ$_H$ 1.43 (m, 6H, PMe), 1.58 (m, 6H, PMe), 1.72 (m, 2H, PCH$_2$), 2.01 (m, 2H, PCH$_2$), 2.64 (s, 6H, NMe$_2$), 4.29 (br s, 5H, Cp). 11B NMR (96 MHz, CD$_2$Cl$_2$, 20°C): δ$_B$ 80 (br, fwhm ca. 470 Hz). 31P NMR (121 MHz, CD$_2$Cl$_2$, 20°C): δ$_P$ 62. MS (positive ion electrospray) m/z: [CpRu(dmpe)]$^+$ 317.0 (100%).

Crystallographic Data: C$_{37}$H$_{47}$B$_2$NP$_2$Ru, M$_r$ = 690.43, monoclinic, P 2$_1$/c, $a$ = 16.5222(2), $b$ = 11.8439(1), $c$ = 19.3552(2) Å, $\beta = 110.547(1)^\circ$, V = 3546.6(1) Å$^3$, Z = 4, $\rho_c$ = 1.293 Mg m$^{-3}$, T = 150 K, $\lambda$ = 0.71073 Å. 56552 reflections collected, 8079 independent [R(int) = 0.000] and used in all calculations. R$_1$ = 0.0445, wR$_2$ = 0.1211 for observed unique reflections [$F^2 > 2\sigma (F^2)]$ and R$_1$ = 0.0587, wR$_2$ = 0.1294 for all unique reflections. Max. and min. residual electron densities 0.74 and -0.71 e Å$^{-3}$. 103
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Reaction of [CpFe(dmpe)(BNMe$_2$)][BPh$_4$], [3.5a][BPh$_4$], with dmap: identification of
[CpFe(dmpe)(BNMe$_2$)·dmap][BPh$_4$], [3.5a·dmap][BPh$_4$], and synthesis of
[CpFe(dmpe)(dmap)][BPh$_4$], [3.7][BPh$_4$]

A sample of [3.5a][BPh$_4$] (0.10 g, 0.15 mmol) in dichloromethane was added to 1.1 equivalents of dmap and stirred for 1 h, at which point $^{11}$B NMR spectroscopy revealed a resonance at $\delta_B$ 68 ppm tentatively assigned to the adduct [3.5a·dmap][BPh$_4$]. After a further 12 h, however, the $^{11}$B NMR spectrum was consistent with the disappearance of the borylene-adduct. After removal of volatiles in vacuo and extraction into fluorobenzene, layering with diethyl ether yielded crystals of [3.7][BPh$_4$] suitable for X-ray diffraction.

Data for [3.7][BPh$_4$] $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 20$^\circ$C): $\delta_H$ 1.21 (m, 6H, PMe), 1.60 (m, 2H, PCH$_2$), 1.64 (m, 2H, PCH$_2$), 1.71 (m, 6H, PMe), 2.84 (s, 6H, NMe$_2$ of dmap), 3.98 (t, $^3J_{PH}$ = 1.8 Hz, 5H, Cp), 6.12 (d, $^3J_{HH}$ = 7.2 Hz, 2H, CH of dmap), 6.77-7.26 (m, 20H, [BPh$_4$]-), 7.79 (d, $^3J_{HH}$ = 7.2 Hz, 2H, CH of dmap). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 20$^\circ$C): $\delta_C$ 16.2 (m, PMe), 19.7 (m, CH$_2$), 31.3 (m, PMe), 39.5 (NMe$_2$ of dmap), 77 (Cp), 108.2 (para-CH of dmap) 122.5 (para-CH of [BPh$_4$]), 126.1 (ortho-CH of [BPh$_4$]), 136.6 (meta-CH of [BPh$_4$]), 152.6 (meta-CH of dmap) 158.3 (ortho-CH of dmap), 164.6 (q, $^1J_{CB}$ = 47.7 Hz, ipso-C of [BPh$_4$]).

$^{11}$B NMR (96 MHz, CD$_2$Cl$_2$, 20$^\circ$C): $\delta_B$ -6.6 ([BPh$_4$]). $^{31}$P NMR (121 MHz, CD$_2$Cl$_2$, 20$^\circ$C): $\delta_P$ 69.1. MS (positive ion electrospray) m/z: [M]$^+$ 393.1 (100%); exact mass for [M]$^+$ 393.1332, calc. 393.1307.

Crystallographic Data: C$_{42}$H$_{51}$BFeN$_2$P$_2$, M$_r$ = 712.49, orthorhombic, P b c 2$_1$, a = 9.7910(3), b = 17.9883(7), c = 21.4221(8) Å, V = 3772.9(2) Å$^3$, Z = 4, $\rho_c$ = 1.254 Mg m$^{-3}$, T = 150 K, $\lambda$ = 0.71073 Å. 4470 reflections collected, 4167 independent [R(int) = 0.000] and used in all calculations. $R_1$ = 0.1353, $wR_2$ = 0.3254 for observed unique reflections [F$^2 > 2\sigma$ (F$^2$)] and $R_1$
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= 0.1409, \( wR_2 = 0.3333 \) for all unique reflections. Max. and min. residual electron densities 0.85 and -1.10 \( e \, \AA^{-3} \).

Method used for pyridine binding constant determination

A sample of \([3.5a]Cl\) (0.02 g, 0.055 mmol) was dissolved in a 6 M pyridine/dichloromethane solution leading to the formation of a mixture of the ‘free’ borylene \([3.5a]^+\) and the B-bound adduct \([3.5a\cdot py]Cl\). A van’t Hoff analysis of the equilibrium constant data was obtained from \(^1\text{H} \) NMR measurements by monitoring the intensities of the Cp resonances of \([3.5a]^+\) and \([3.5a\cdot py]^+\) over the temperature range 233-273K.

Syntheses of Me(4-X-C_6H_4)NBCl_2 \([X = CF_3 (3.9), OMe (3.10)]\)

The method employed for the formation of 3.10 followed that of Sugasawa et al.\(^{29}\) For the previously unreported compound 3.9, 4-F_3C-N-methylaniline (1.00 g, 5.7 mmol) was dissolved in CH_2Cl_2 (20 cm\(^3\)) and added to BCl_3 in heptanes (5.7 cm\(^3\) of a 1.0 M solution, 5.7 mmol) at -80°C over 15 min and the reaction mixture stirred for a further 1 h. The solution was at this point green (\( \delta_B 8.1 \) ppm). The reaction mixture was then warmed to room temperature and the solvent removed in vacuo to give a colourless solid which was extracted into toluene. After reflux for 24 h volatiles were removed in vacuo and the product separated from the remaining adduct by extraction into hexane (3 x 20 cm\(^3\)). The hexanes were subsequently removed under in vacuo to afford a pale pink oil in 57 % yield which was used for subsequent chemistry without further purification (\( \delta_B 31.8 \) ppm).

Synthesis of CpFe(CO)_2B\{N(Ph)Me\}Cl, 3.11

To a suspension of Na[CpFe(CO)_2] (1.00 g, 5.00 mmol) in Et_2O (30 cm\(^3\)) was added Me(Ph)NBCl_2 (10.2 cm\(^3\) of a 0.49 M solution in Et_2O, 5.00 mmol) and the reaction mixture
stirred for 18 h. Filtration, removal of solvent and extraction to pentane (3 x 20 cm$^3$) gave a solution of the product which was concentrated (to 15 cm$^3$) and stored at -30$^\circ$C overnight to yield a brown powder. Data for 3.11: $^1$H NMR (300 MHz, C$_6$D$_5$CD$_3$, 20$^\circ$C): $\delta_H$ 3.27 (s, 3H, NMe), 4.11 (s, 5H, Cp), 6.61 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 6.6 Hz, 2H, meta-CH), 6.71 (t, $^3J_{HH}$ = 6.6 Hz, 1H, para-CH), 6.81 (d, $^3J_{HH}$ = 7.0 Hz, 2H, ortho-CH). $^{13}$C NMR (126 MHz, C$_6$D$_5$CD$_3$, 20$^\circ$C): $\delta_C$ 45.3 (NMe), 84.2 (Cp), 125.4 (para-CH), 128.2 (meta-CH), 129.2 (ortho-CH), 151.1 (ipso-C), 215.2 (CO). $^{11}$B NMR (96 MHz, C$_6$D$_5$CD$_3$, 20$^\circ$C): $\delta$ 59.0. IR (cm$^{-1}$) $\nu$(CO) 1960, 2014. MS (EI) m/z: [M]$^+$ 329.2 (100%); MS (CI) m/z: [M-CO]$^-$ 301.0 (100%); exact mass for [M-CO]$^-$ ($^{10}$B, $^{54}$Fe, $^{35}$Cl isotopomer) 298.0218, calc. 298.0211.

**Syntheses of CpFe(CO)$_2$B[N(C$_6$H$_4$-X-4)Me]Cl [X = CF$_3$ (3.12), OMe (3.13)]**

To a suspension of Na[CpFe(CO)$_2$] (X = OMe, 1.10 g, 4.70 mmol; X = CF$_3$, 0.82 g, 3.60 mmol) in Et$_2$O (30 cm$^3$) was added the aminodichloroborane Me(4-X-C$_6$H$_4$)NBCl$_2$ (X = CF$_3$, 0.95 g, 3.30 mmol; X = OMe, 1.09 g, 4.30 mmol). The reaction mixture was stirred for 18 h, filtered, and volatiles removed in vacuo to give a solid which was extracted into hexanes (3 x 20 cm$^3$). For X = OMe, the solid was obtained in 71 % yield and yellow crystals suitable for X-ray diffraction were obtained by storing a concentrated solution at -30$^\circ$C. For X = CF$_3$, the product was obtained after concentration and storage at -30$^\circ$C, as a pale brown solid in 51 % yield.

Data for 3.12: $^1$H NMR (300 MHz, C$_6$D$_5$CD$_3$, 20$^\circ$C): $\delta_H$ 3.15 (s, 3H, NMe), 4.10 (s, 5H, Cp), 6.75 (d, $^3J_{HH}$ = 7.0 Hz, 2H, Ar ortho-CH), 7.33 (d, $^3J_{HH}$ = 7.0 Hz, 2H, Ar meta-CH). $^1$H NMR (300 MHz, C$_6$D$_5$CD$_3$, -60$^\circ$C): (i) E-isomer (minor component, 35 %) $\delta_H$ 2.90 (s, 3H, NMe), 3.95 (s, 5H, Cp), 6.56 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar ortho-CH), 7.32 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar meta-CH); (ii) Z-isomer $\delta_H$ 3.20 (s, 3H, NMe), 3.80 (s, 5H, Cp), 6.45 (d, $^3J_{HH}$ = 8.3 Hz, 2H,
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Ar ortho-CH), 7.10 (d, $^3J_{HH} = 8.3$ Hz, 2H, Ar meta-CH). $^{13}$C NMR (126 MHz, C$_6$D$_5$CD$_3$, 20°C): δ$_C$ 45.0 (NMe), 84.3 (Cp), 124.9 (q, $^1J_{CF} = 246.0$ Hz, CF$_3$), 126.4 (q, $^2J_{CF} = 3.7$ Hz, 3-C), 128.2 (q, $^2J_{CF} = 15.8$ Hz, 4-C), 129.2 (2-CH), 154.5 (1-C), 214.9 (CO). $^{11}$B NMR (96 MHz, C$_6$D$_5$CD$_3$, 20°C): δ 60.0. IR (cm$^{-1}$) ν(CO) 2016, 1962. MS (Cl) m/z: [M-CO]$^-$ 368.9 (3%), [M-2CO]$^-$ 340.9 (5%); exact mass for [M-CO]$^-$ ($^{10}$B, $^{54}$Fe, $^{35}$Cl isotopomer) 366.0090, calc. 366.0085.

Data for 3.13: $^1$H NMR (300 MHz, C$_6$D$_5$CD$_3$, 20°C): δ$_H$ 3.31 (s, 3H, NMe), 3.37 (s, 3H, OMe), 4.14 (s, 5H, Cp), 6.68 (d, $^3J_{HH} = 7.0$ Hz, 2H, 2-CH), 6.83 (d, $^3J_{HH} = 7.0$ Hz, 2H, 3-CH). $^1$H NMR (300 MHz, C$_6$D$_5$CD$_3$, -80°C): (i) E-isomer (minor component, 25 %) δ$_H$ 3.21 (s, 3H, NMe), 3.18 (s, 3H, OMe), 3.99 (s, 5H, Cp), 6.78 (m, 4H, 2- and 3-H). (ii) Z-isomer δ$_H$ 3.18 (s, 3H, OMe), 3.41 (s, 3H, NMe), 3.87 (s, 5H, Cp), 6.63 (m, 4H, 2- and 3-H). $^{13}$C NMR (126 MHz, C$_6$D$_5$CD$_3$, 20°C): δ$_C$ 45.5 (NMe), 54.8 (OMe), 84.2 (Cp), 114.4 (3-C), 129.7 (2-CH), 144.4 (4-C), 158.1 (1-C), 215.3 (CO). $^{11}$B NMR (96 MHz, C$_6$D$_5$CD$_3$, 20°C): δ 58.7. IR (cm$^{-1}$) ν(CO) 2013.0, 1959.6. MS (EI) m/z: [M-CO]$^+$ 331.0 (16%), [M-2CO]$^+$ 303.0 (46%); exact mass for [M-CO]$^+$ ($^{10}$B, $^{54}$Fe, $^{35}$Cl isotopomer) 328.0307, calc. 328.0317. Elemental microanalysis: C 49.58, H 3.97, N 3.79; calc. C 50.13, H 4.21, N 3.90.

Crystallographic Data: C$_{15}$H$_{15}$BClFeNO$_3$, $M_r = 359.40$, monoclinic, P 2$_1$/n, $a = 12.7513(2)$, $b = 18.2904(3)$, $c = 13.3508(2)$ Å, $\beta = 95.100(1)^\circ$, $V = 3804.4(1)$ Å$^3$, $Z = 2$, $\rho_c = 1.545$ Mg m$^{-3}$, $T = 150$ K, $\lambda = 0.71073$ Å. 29043 reflections collected, 13138 independent [R(int) = 0.076] and used in all calculations. $R_1 = 0.0554$, $wR_2 = 0.1429$ for observed unique reflections [$F^2 > 2\sigma (F^2)$] and $R_1 = 0.1011$, $wR_2 = 0.1646$ for all unique reflections. Max. and min. residual electron densities 1.10 and -1.16 e Å$^{-3}$.
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**Synthesis of CpFe(CO)$_2$B{N(CH$_2$Ph)Me}Cl, 3.14**

To a suspension of Na[CpFe(CO)$_2$] (1.1 g, 5.5 mmol) in toluene (30 cm$^3$) was added Me(PhCH$_2$)NBCl$_2$ (20 cm$^3$ of a 0.25 M solution in toluene, 5 mmol) and the reaction mixture stirred for 12h. After filtration and removal of volatiles *in vacuo*, the residual solid was extracted into hexanes (3 x 20 cm$^3$), the solution concentrated (to 15 cm$^3$) and stored at -30°C yielding the product as a beige microcrystalline solid (as a ca. 1:2 mixture of E and Z isomers). Yield 55 %. Data for 3.14: $^1$H NMR (300 MHz, C$_6$D$_5$CD$_3$, 25°C): (i) E-isomer (minor component, 30 %) δ$_H$ 2.90 (s, 3H, NMe), 4.19 (s, 5H, Cp), 4.52 (s, 2H, NCH$_2$), 6.99 – 7.24 (m, 5H, Ph); (i) Z-isomer δ$_H$ 2.75 (s, 3H, NMe), 4.21 (s, 5H, Cp), 4.60 (s, 2H, NCH$_2$), 6.99 – 7.24 (m, 5H, Ph group). $^{13}$C NMR (126 MHz, C$_6$D$_5$CD$_3$, 20°C): δ$_C$ 37.4, 41.0 (NMe), 56.1, 59.8 (NCH$_2$Ph), 83.9, 88.5 (Cp), 127.1, 127.2 (para-CH), 127.3, 127.6 (meta-CH), 128.8, 128.9 (ortho-CH), 139.7, 140.0 (ipso-C), 215.7, 216.0 (CO). $^{11}$B NMR (96 MHz, C$_6$D$_5$CD$_3$, 20°C): δ 57.8. IR (cm$^{-1}$) ν(CO) 1947, 2004. MS (EI) m/z: [M-CO]$^+$ 315.2 (13%), [M-2CO]$^+$ 286.2 (100%); exact mass for [M-CO]$^+$ ($^{10}$B, $^{54}$Fe, $^{35}$Cl isotopomer) 314.0315, calc. 314.0321.

**Synthesis of [CpFe(dmpe){BN(C$_6$H$_4$-OMe-4)Me}]/[BPh$_4$], [3.15a][BPh$_4$]**

A solution of 3.13 (0.20 g, 0.60 mmol) and dmpe (> 2 equiv.) in toluene (20 cm$^3$) was photolysed for 5 h until $^{11}$B and $^{31}$P NMR monitoring revealed complete conversion to the bis(phosphine) substituted boryl complex (δ$_B$ 66 ppm, δ$_P$ 69 ppm). Removal of volatiles *in vacuo* gave a yellow-brown solid that was washed with pentane (5 x 20 cm$^3$). The residual solid was dissolved in dichloromethane (15 cm$^3$), added to Na[BPh$_4$] (0.21 g, 0.60 mmol) and stirred for 10 min. Volatiles were then removed *in vacuo* and the resulting solid recrystallised
from fluorobenzene/diethyl ether yielding yellow crystals of the fluorobenzene hemi-solvate suitable for X-ray diffraction. Yield 30%.

Data for [3.15a][BPh₄]: ¹H NMR (300 MHz, CD₂Cl₂, 20°C): δ_H 1.22 (m, 6H, PMe), 1.32 (m, 6H, PMe), 1.62 (m, 2H, PCH₂), 1.78 (m, 2H, PCH₂), 3.00 (s, 3H, NMe), 3.70 (s, 3H, OMe), 4.55 (s, 5H, Cp), 6.82 (d, ³J_HH = 8.0 Hz, 2H, 2-CH of Ar), 6.97 (d, ³J_HH = 8.0 Hz, 2H, 3-CH of Ar), 6.77-7.26 (m, 20H, [BPh₄]⁻). ¹³C NMR (126 MHz, CD₂Cl₂, 20°C): δ_C 22.5 (m, PCH₂), 24.7 (m, PMe), 31.4 (m, PMe), 36.7 (NMe), 56.0 (OMe), 80.6 (Cp), 115.8 (3-CH), 122.2 (para-CH of [BPh₄]⁻), 126.0 (ortho-CH of [BPh₄]⁻), 126.1 (2-CH), 130.5 (4-C), 136.3 (meta-CH of [BPh₄]⁻), 159.3 (1-C), 164.6 (q, ¹J_CB = 48.1 Hz, ipso-C of [BPh₄]⁻). ¹¹B NMR (96 MHz, CD₂Cl₂, 20°C): δ_B 88.4 (br, fwhm = 200 Hz), -6.5 ([BPh₄]⁻). ³¹P NMR (121 MHz, CD₂Cl₂, 20°C): δ_P 77.3. MS (positive ion electrospray) m/z: [M]⁺ 418.0 (5%).

Crystallographic Data: C₄₆H₅₃.5B₂F₀.5FeNOP₂, M_r = 785.35, monoclinic, P 2₁/n, a = 11.0448(2), b = 19.8456(3), c = 18.7790(3) Å, β = 90.185(1)°, V = 4116.2(1) Å³, Z = 4, ρ_c = 1.267 Mg m⁻³, T = 150 K, λ = 0.71073 Å. 17862 reflections collected, 9341 independent [R(int) = 0.054] and used in all calculations. R₁ = 0.0468, wR₂ = 0.1078 for observed unique reflections [F² > 2σ (F²)] and R₁ = 0.0861, wR₂ = 0.1213 for all unique reflections. Max. and min. residual electron densities 0.75 and -0.72 e Å⁻³.
3.3 Results and Discussion

3.3.1 Synthetic Chemistry

In contrast to previously reported studies of related dicyclohexylaminoboryl systems, use of the less sterically demanding dimethylamino substituent [i.e. employing the starting material CpFe(CO)₂B(NMe₂)Cl], permits substitution of both ancillary carbonyl ligands at the metal centre [Scheme 3.2]. Photolysis of CpFe(CO)₂B(NMe₂)Cl (3.1) with 1,2-bis(dimethylphosphino)ethane (dmpe) in toluene was monitored by ¹¹B and ³¹P NMR spectroscopy. After 3 h, a shift from δ_B 56 ppm to δ_B 62 ppm in the ¹¹B NMR spectrum, and new resonances at δ_P 53 ppm and -45 ppm in the ³¹P NMR spectrum were observed, corresponding to the formation of the mono-substituted phosphine system CpFe(CO)(κ¹-dmpe)B(NMe₂)Cl - featuring a single pendant phosphine donor function. Prolonged photolysis (6 h) led to a further downfield shift to δ_B 66 ppm and to the growth of a single resonance at δ_P 75 ppm. These spectroscopic observations are consistent with the formation of the bis(phosphine) complex CpFe(κ²-dmpe)B(NMe₂)Cl, 3.3a, being in line with similar spectroscopic data reported by Hartwig and co-workers for the formation of CpFe(PMe₃)₂BCat (δ_B 60 ppm) and CpFe(CO)(PMe₃)BCat (δ_B 58) from CpFe(CO)₂BCat (δ_B 52 ppm).³⁰
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Scheme 3.2: Reactions of 3.1 and 3.2 with various phosphines.

This synthetic approach also works for ruthenium, and the corresponding system CpRu(dmpe)B(NMe₂)Cl (3.4a) has also been identified. However, this chemistry is significantly less clean for M = Ru than M = Fe, presumably reflecting the greater strength of the M-CO bond. Moreover, further exploration of this substitution chemistry reveals that there is a necessity for at least one of the amino R substituents to be Me; thus reaction of dmpe with the NPh₂ substituted complex CpFe(CO)₂B(NPh₂)Cl boryl leads to decomposition. However, reaction of the same phosphine with the related N(Me)Ar systems [Ar = Ph, 4-CF₃-C₆H₄, 4-OMe-C₆H₄] can successfully be employed in the synthesis of bis(phosphine) ligated boryl systems (vide infra).

Reactions of the boryl complex 3.1 with other chelating phosphines have also been conducted and monitored by $^{11}$B and $^{31}$P NMR spectroscopy. Thus, irradiation of 3.1 in the presence of the more rigid bidentate ligand 1,2-bis(dimethylphosphino)benzene (dmpbz) gives
rise to the corresponding bis(phosphine) complex 3.3b (δ_B 66 ppm; δ_P 69 ppm) over a similar timeframe to that encountered with dmpe.

The reactivity of 3.1 towards monodentate phosphines has also been examined. Photolysis with PMe_3 also leads to the formation of the bis(phosphine) boryl complex CpFe(PMe_3)_2B(NMe_2)Cl (3.3d) (δ_B 67 ppm, δ_P 43 ppm) after irradiation for 24 h. In addition, photolysis in the presence of PPhMe_2 leads to the formation of the related bis(phosphine) boryl complex CpFe(PPhMe_2)_2B(NMe_2)Cl (3.3c) with a downfield shift in the ^{11}B NMR spectrum (δ_B 66 ppm) and a ^{31}P resonance of δ_P 69 ppm. However, extended irradiation is required to substitute the second carbonyl ligand (approximately 60 h for 3.3c). This is presumably due to the extra steric bulk about the phosphorus centre and the absence of the chelate effect.

By contrast, the reaction of 3.1 with excess PPh_2Me leads to the formation of a mono-substituted phosphine complex CpFe(PPh_2Me)(CO)B(NMe_2)Cl (δ_B 61 ppm, δ_P 67 ppm), which in the presence of excess phosphine under more forcing conditions (UV photolysis for > 6 h) reacts via borylene extrusion to yield the cationic complex [CpFe(PPh_2Me)_2(CO)]^+. Anion metathesis (Cl^-/[BAr_4^+]) was subsequently exploited to obtain the crystalline product [CpFe(PPh_2Me)_2(CO)][BAr_4^-] and thereby verify the identity of cationic component by X-ray crystallography [Figure 3.1]. Presumably the sequentially increased steric demands of the PMe_3, PPhMe_2 and PPh_2Me ligands result in a reduced tendency to form the desired bis(phosphine) ligated boryl complex.
Figure 3.1: Molecular structure of [CpFe(PPh₂Me)₂(CO)][BAr'₄]. Thermal ellipsoids set at the 40 % probability level; hydrogen atoms and counter-ion omitted for clarity.

Table 3.1: Selected bond lengths [Å] and angles [°] for [CpFe(PPh₂Me)₂(CO)][BAr'₄].

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<thead>
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<th>Bond</th>
<th>Distance [Å]</th>
<th>Angle [°]</th>
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<td>Fe(1)-P(2)</td>
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<tr>
<td>Fe(1)-P(16)</td>
<td>2.223(1)</td>
<td></td>
</tr>
<tr>
<td>P(2)-Fe(1)-P(16)</td>
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<td></td>
</tr>
<tr>
<td>Fe(1)-C(30)</td>
<td>1.745(4)</td>
<td></td>
</tr>
</tbody>
</table>
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Varying the steric bulk of the ancillary Cp ligand can also have a profound effect on the extent of substitution of the carbonyl ligands at the metal centre. Thus, Cp'Fe(CO)₂B(NMe₂)Cl [Cp' = η⁵-C₅H₄Me] (3.1'), was reacted with dmpe in toluene under identical photolytic conditions to those employed for 3.1. However, in this case the main organometallic product so isolated, [Cp'Fe(dmpe)(CO)][Cp'Fe(CO)₂] is derived from borylene extrusion, presumably as a result of the extra steric bulk at the Cp ligand. [Cp'Fe(dmpe)(CO)][Cp'Fe(CO)₂] has been characterised by X-ray diffraction and displays independent [Cp'Fe(dmpe)(CO)]⁺ and [Cp'Fe(CO)₂]⁻ fragments [Figure 3.2]. Unfortunately, due to lack of solubility in compatible solvents, it has not been possible to obtain any further data.
Figure 3.2: Molecular structure of [Cp'Fe(dmpe)(CO)][Cp'Fe(CO)₂]. Thermal ellipsoids set at the 40 % probability level; hydrogen atoms omitted for clarity.

Table 3.2: Selected bond lengths [Å] and angles [°] for [Cp'Fe(dmpe)(CO)][Cp'Fe(CO)₂].

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length/Angle</th>
</tr>
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<tr>
<td>Fe(1)-P(6)</td>
<td>2.199(1)</td>
</tr>
<tr>
<td>Fe(1)-C(10)</td>
<td>1.729(3)</td>
</tr>
<tr>
<td>P(2)-Fe(1)-P(6)</td>
<td>86.4(1)</td>
</tr>
</tbody>
</table>
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The proposed mechanism for this unusual transformation is suggested in Scheme 3.3. It is thought that the extra steric bulk of the ancillary Cp' ligand (cf. Cp) leads to extrusion of the borylene fragment to form \([\text{Cp'}\text{Fe}(\text{dmpe})(\text{CO})]^+\text{Cl}^-\) in the initial step, as is observed in the analogous reaction of 3.1 with PPh₂Me \{to give \([\text{CpFe}(\text{PPh₂Me})_2(\text{CO})]\text{Cl}\}\}. This then accounts for the cationic component of the eventual product. Nucleophilic attack of the chloride counter-ion at the boron centre of the starting material, \(\text{Cp'}\text{Fe}(\text{CO})_2\text{B(NMe}_2\text{)}\text{Cl}\), then leads to extrusion of the \([\text{Cp'}\text{Fe}(\text{CO})_2]^-\) fragment and formation of the dichloroborane, \(\text{Cl}_2\text{BNMe}_2\) which dimerises to give the observed co-product \([\text{Cl}_2\text{B(µ-NMe}_2\text{)}]_2\) (δ_B 11 ppm) (Scheme 3.3).

**Scheme 3.3**: Proposed mechanism for the formation of \([\text{Cp'}\text{Fe}(\text{dmpe})(\text{CO})][\text{Cp'}\text{Fe}(\text{CO})_2]\) and \([\text{Cl}_2\text{B(µ-NMe}_2\text{)}]_2\).

Support for this mechanism can be obtained (i) from the independent reaction of 3.1' with a soluble source of chloride (in this case \([\text{PPN}]\text{Cl}\)), which also results in complete conversion of the boryl complex to \([\text{Cl}_2\text{B(µ-NMe}_2\text{)}]_2\); and (ii) from the apparent inertness of \([\text{Cl}_2\text{B(µ-NMe}_2\text{)}]_2\) to reaction with Na[\text{CpFe}(\text{CO})_2] (Scheme 3.4). The dimerisation of the chloroborane under these conditions is clearly crucial to this chemistry. Thus, while the tetra-
coordinate boron centre in \([\text{Cl}_2\text{B}(\mu-\text{NMe}_2)]_2\), is unreactive towards nucleophilic attack, reaction of the corresponding monomer \(\text{Cl}_2\text{BNMe}_2\) with \(\text{Na}[\text{Cp'Fe(CO)}_2]\) under similar conditions proceeds in the opposite sense to generate 3.1.\textsuperscript{31}

\[
\begin{align*}
\text{[PPN]Cl} + \text{Cp'}\text{Fe} - \text{B} - \text{NMe}_2 & \rightarrow \text{[PPN]}^+ \text{Cp'}\text{Fe}^+ - \frac{1}{2} \text{B} - \text{NMe}_2 \text{Cl} \\
\text{Na}^+ \text{Cp'}\text{Fe}^+ - \frac{1}{2} \text{Cl}_{\text{im}} \text{B} - \text{NMe}_2 \text{Cl} & \rightarrow \text{NaCl} + \text{Cp'}\text{Fe} - \text{B} - \text{NMe}_2
\end{align*}
\]

\textbf{Scheme 3.4}: Support for the postulated mechanism for the formation of

\[\text{[Cp'Fe(dmpe)(CO)]}[\text{Cp'Fe(CO)}_2].\]

\subsection{3.3.2 Structure}

In an attempt to isolate the product 3.3a formed from 3.1 and dmpe in toluene [Scheme 3.1], volatiles were removed and the product extracted into pentane. However, \(^{11}\text{B}\) NMR spectroscopy revealed the presence of no boryl containing species in the pentane extract. The product was subsequently extracted into dichloromethane and the resulting solution displayed a resonance at \(\delta_{\text{B}}\) 88 ppm due to the aminoborylene complex \([\text{CpFe(dmpe)}(\text{BNMe}_2)]\text{Cl}\), [3.5a]Cl. Evidently, extraction into dichloromethane leads to spontaneous loss of chloride to give the cationic terminal borylene complex [Scheme 3.5]. Tilley and co-workers have reported a similar phenomenon in the synthesis of the silylene, \([\text{Cp*Os(PMe}_3)_2(\text{SiPr}_2)]\text{[OTf]}\).\textsuperscript{28}
Scheme 3.5: Auto-ionisation of 3.3a,b,c,d and 3.4a to [3.5a,b,c,d]Cl and [3.6a]Cl.

Further evidence for the formation of [3.5a]Cl in solution was provided by (i) in situ positive-ion electrospray mass spectrometry [ESI-MS; Figure 3.3b] which reveals the cation [3.5a]$^+$ with a matching isotopic envelope and accurate mass measurement in agreement with the calculated values; (ii) the presence in the $^1$H NMR spectrum (in CD$_2$Cl$_2$) of a single NMe$_2$ methyl resonance, in contrast to inequivalent alkyl groups found for aminoboryl complexes of the type CpFe(L)$_2$B(NR$_2$)Cl in the same temperature regime;$^{14,31,32}$ and (iii) the essentially identical $^1$H, $^{11}$B, $^{13}$C and $^{31}$P NMR spectra in CD$_2$Cl$_2$ (leaving aside the anion resonances) obtained for the crystallographically characterised [BPh$_4$] and [BAr$_{4}^{CI}$] salts [Figure 3.3a].
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Figure 3.3: Spectroscopic data characterising the auto-ionisation of 3.3a to [3.5a]Cl in dichloromethane: a) $^{11}$B{$^1$H} NMR spectra in toluene (upper) and dichloromethane (middle), plus comparative spectrum of [3.5a][BPh$_4$] in dichloromethane (lower); b) positive ion ESI-MS of a solution in dichloromethane, showing match of the isotopic envelope to

$$[\text{CpFe(dmpe)(BNMe$_2$)}]^+, [3.5a]^+. $$

Once synthesised, each of the bis(phosphine) ligated boryl complexes 3.3b, 3.3c and 3.3d displays similar auto-ionisation behaviour to 3.3a in polar solvents such as dichloromethane and fluorinated aromatics, and a similar null response in toluene (Scheme 3.5). It is therefore apparent that even the reduced electron-donating capabilities of arylidialkylphosphines are sufficient to render the metal center electron rich enough to induce halide ejection. This behaviour is contingent on the incorporation of two phosphine co-ligands, with the corresponding mono(phosphate) mono(carbonyl) complexes showing no tendency towards auto-ionisation.$^{19}$ This phenomenon is also witnessed for the ruthenium analogue 3.4a/[3.6a]Cl.
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Consistent with the spectroscopic data outlined above, DFT studies reveal strong solvent dependency of the relative stabilities of the isomeric species 3.3a and [3.5a]Cl [Figure 3.4]. This is reflected in values of $\Delta G$ for the auto-ionisation of the boryl species which are dependent upon the polarity of the medium. Thus $\Delta G_{3.3a\rightarrow3.5a}$ is calculated to be $+13.2$ kcal mol$^{-1}$ in the gas phase and $+3.2$ kcal mol$^{-1}$ in toluene ($\varepsilon = 2.4$), but $-7.3$ kcal mol$^{-1}$ in dichloromethane ($\varepsilon = 9.1$), consistent with the stabilisation of the solvent separated cation/anion pair, [3.5a]Cl, in the more polar medium. The role of the ancillary ligand set is also crucial, with the corresponding auto-ionisation reaction for dicarbonyl ligated 3.1 being calculated to be strongly disfavoured even in dichloromethane solution ($\Delta G = + 22.5$ kcal mol$^{-1}$) – a finding in line with experimental observations for complex 3.1. Among bis(phosphine) ancillary ligand sets, the finer details of donor properties are predicted to be of relatively minor importance, with exoergic reactions predicted for a range of alkyl and arylphosphines ($-7.2 < \Delta G < -3.1$ kcal mol$^{-1}$).
Figure 3.4: DFT-calculated free energy changes for the auto-ionization reaction

\[
\text{CpFe(L)}_2\text{B(NMe}_2\text{)Cl} \rightarrow \text{[CpFe(L)}_2\text{(B(NMe}_2\text{))]Cl}
\]

as a function of reaction medium and ancillary ligand framework \( L_2 \).

With regard to the metal itself, relatively minor variation in \( \Delta G \) is predicted for the auto-ionisation of \( \text{CpM(dmpe)B(NMe}_2\text{)Cl} \) in dichloromethane (-7.3, -7.4 and -10.8 kcal mol\(^{-1}\) for \( M = \text{Fe}, \text{Ru}, \text{Os} \), respectively), with the similar values for the iron and ruthenium systems also being consistent with experimental observations.

In summary, quantum chemical data are also consistent with the spontaneous ejection of chloride from a range of boryl complexes (3.3) in polar media to generate the corresponding cationic borylene ([3.5]\(^+\)) as the chloride salt. Synthetically, these transformations are without precedent in boron ligand chemistry, and are remarkable in representing spontaneous loss of an anionic ligand from an electrophilic three-coordinate boron centre.\(^4,5,28\)
Although various attempts to crystallise [3.5a]$^+$ as the Cl$^-$ salt have proved unsuccessful, anion exchange was used to isolate single crystals of the borate salts [CpFe(dmpe)(BNMe$_2$)][BPh$_4$], [3.5a][BPh$_4$] [Figure 3.5] and [CpFe(dmpe)(BNMe$_2$)][BAr$^{Cl_4}$], [3.5a][BAr$^{Cl_4}$] [Figure 3.6], from fluorobenzene/hexane layering experiments, thereby providing conclusive evidence for the formation of the bis(phosphine) ligated borylene cation [3.5a]$^+$. The $^{11}$B NMR spectra for these crystalline materials display the expected resonances at $\delta_B$ 88 ppm and $\delta_P$ 79 ppm as seen for the corresponding chloride salt in dichloromethane. $^1$H and $^{13}$C NMR spectra display the expected resonances for the NMe$_2$, Cp, PMe and PCH$_2$ groups. Moreover, ESI-MS measurements of [3.5a][BAr$^{Cl_4}$] reveal an isotopic envelope centred at m/z 326.1 consistent with the expected structure of the cation and accurate mass measurements.
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**Figure 3.5:** Molecular structure of [3.5a][BPh₄]. Thermal ellipsoids set at the 40% probability level; hydrogen atoms omitted for clarity.

**Table 3.3**: Selected bond lengths [Å] and angles [°] for [3.5a][BPh₄].

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<th>Length [Å]</th>
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Figure 3.6: Molecular structure of [3.5a][BAr$_4^-$]C$_6$H$_3$F. Thermal ellipsoids set at the 40% probability level; hydrogen atoms and solvent molecule omitted for clarity.

Table 3.4: Selected bond lengths [Å] and angles [°] for [3.5a][BAr$_4^-$]C$_6$H$_3$F.

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<td>Fe(1)-P(7)</td>
<td>2.161(1)</td>
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<tr>
<td>Fe(1)-B(15)-N(16)</td>
<td>176.0(2)</td>
</tr>
</tbody>
</table>
Chapter III (Dimethylamino)borylene and Related Complexes of Electron Rich Metal Fragments

The geometry of the [3.5a]$^+$ cation is very similar in the [BPh$_4$]$^-$ salt and in the two independent entities present in the [BAR$_4^{Cl_4}$]$^-$ salt, featuring in each case a two-coordinate boron centre with no short intermolecular contacts [Figures 3.4 and 3.5]. Each structure features the near linear Fe-B-N framework ($\angle$Fe-B-N = 175.4(2)$^\circ$ for [3.5a][BPh$_4$], 175.2(3) and 176.0(3)$^\circ$ for [3.5a][BAR$_4^{Cl_4}$]) common to all terminal aminoborylene complexes (cf. 178.8(5)$^\circ$ for [CpFe(CO)$_2$(BNCy$_2$)][BAR$_4$] and 177.7(3)$^\circ$ for [CpFe(CO)(PMe$_3$)(BNCy$_2$)][BAR$_4$]).$^{19,31}$ The unusual feature of the structures of [3.5a]$^+$ is the Fe-B bond length, which is very short indeed [1.811(3) and 1.807(4), 1.801(4) Å, respectively]. These distances and can be compared to that for the related dicarbonyl complex [CpFe(CO)$_2$(BNCy$_2$)]$^+$ [1.859(6) Å] and the intermediate mono-phosphine system [CpFe(CO)(PMe$_3$)(BNCy$_2$)]$^+$ [1.821(4) Å].$^{19,31}$ A similar analysis for the ruthenium cation [3.6a]$^+$ (obtained as the [BPh$_4$]$^-$ salt from a fluorobenzene/hexane layering) [Figure 3.7], reveals a Ru-B separation [1.901(3) Å] which is similarly shorter than the corresponding dicarbonyl and mono-phosphine-ligated species [1.960(6), 1.928(4) Å, respectively]. At a broader level, comparison with other terminal borylene complexes reveals that the M-B distances measured for these two salts of [3.5a]$^+$ are among the shortest yet reported, being comparable to those measured for aryl- and alkyl-borylene systems {c.f. 1.785(8), 1.792(8) Å for [Cp*Fe(CO)$_2$(BMes)]$^+$; 1.780(4) Å for (Cy$_3$P)$_2$Ru(Cl)H(BMes); 1.809(9) Å for CpMn(CO)$_2$(B'Bu)}.$^{11,12,33,34}$ Indeed, the values determined for [3.5a]$^+$ are the shortest yet measured for any aminoborylene system, reflecting a high degree of electronic loading at the metal centre and an enhanced degree of Fe→B $\pi$ back bonding. Consistent with this, the DFT calculated $\sigma:\pi$ ratios for the Fe-B covalent bonding density in the model systems [CpFe(PMe$_3$)$_n$(CO)$_{2-n}$(BNMe$_2$)]$^+$ are 63:37, 67:33 and 71:29 for $n = 2, 1$ and 0, respectively.$^{35,36}$ It is also apparent crystallographically that a small
degree of B-N bond lengthening accompanies the increased electronic loading at the metal centre in [3.5a]/[3.6a]. Thus B-N distances of 1.357(3) and 1.360(4) Å have been determined for these two cations, compared to 1.324(6) and 1.320(7) Å for [CpM(CO)₂(BNCy₂)]⁺ (M = Fe, Ru). Unfortunately, attempts at crystallising [3.5b], [3.5c]⁺ and [3.5d]⁺ using various combinations of solvents and counter anions proved unsuccessful. However, the spectroscopic data reported and comparison with the structurally characterised salts of [3.5a]⁺ provide convincing evidence for the proposed structures.
Figure 3.7: Molecular structure of [3.6a][BPh₄]. Thermal ellipsoids set at the 40% probability level; hydrogen atoms and counter-ion omitted for clarity.

Table 3.5: Selected bond lengths [Å] and angles [°] for [3.6a][BPh₄].

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)-B(15)</td>
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<tr>
<td>Ru(1)-B(15)-N(16)</td>
<td>175.9(3)</td>
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</tr>
</tbody>
</table>
3.3.3 Lewis Acidity

Studies of the fundamental reactivity of \([3.5a]^+\) are consistent with a dramatic reduction in electrophilicity at the boron centre in comparison to other cationic borylene complexes. Thus, for example \([3.5a]^+\) does not coordinate THF at boron (as determined by \textit{in situ} \(^{11}\)B NMR monitoring), in marked contrast to the reactivity witnessed with previously reported dicarbonyl systems. \([\text{Cp}^*\text{Fe(CO)}_2\text{BMes}]^+\) decomposes via Fe-B bond scission on addition of THF,\(^{12}\) while \([\text{CpFe(CO)}_2(\text{BNCy}_2)]^+\) can be shown to bind THF reversibly at boron.\(^{31}\) Additionally, none of Ph\(_2\)CO, Me\(_2\)CO, Ph\(_3\)PO or Et\(_3\)PO coordinate to \([3.5a]^+\), and although pyridine binds, the strength of binding is weak (cf. irreversible binding of picoline to \([\text{CpFe(CO)}_2(\text{BNCy}_2)]^+\)). In the case of \([3.5a]^+\) pyridine (as a 6 M solution in dichloromethane), the presence of an equilibrium between the free borylene the B-bound adduct \([\text{CpFe(dmpe)}(\text{BNMe}_2\cdot\text{py})]^+\) \([3.5a\cdot(\text{py})]^+\) can be established by multinuclear NMR measurements [Scheme 3.6]. The thermodynamics of binding can be investigated over the temperature range 233-273 K using a van’t Hoff analysis of the equilibrium constant data obtained from \(^1\)H NMR measurements [Figure 3.8].
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Scheme 3.6: Reversible binding of pyridine to [3.5a]⁺.

\[
\begin{align*}
\text{Scheme 3.6: Reversible binding of pyridine to } & [3.5a]^{+}. \\
\end{align*}
\]

\[
\begin{align*}
\Delta H &= -7.4 \text{ kcal mol}^{-1} \\
\Delta S &= -31.3 \text{ eu} \\
\end{align*}
\]

Figure 3.8: Van’t Hoff plot describing the temperature dependence of the equilibrium between [3.5a]⁺ and [3.5a(py)]⁺. The values of \( \Delta H \) and \( \Delta S \) quoted in the text are the mean of two independent experiments.

\[
y = 3791.1x - 16.167 \\
R^2 = 0.9902
\]
This analysis yields the thermodynamic parameters $\Delta H = -7.4 \text{ kcal mol}^{-1}$ and $\Delta S = -31.3 \text{ eu}$ for the binding of pyridine to $[3.5a]^+$, a figure which is put into context by the much stronger binding to $\text{BCl}_3$ ($\Delta H = \text{ca. } -40.7 \text{ kcal mol}^{-1}$), despite the boron centre in $[3.5a]^+$ being two coordinate and cationic. Such data presumably reflect strong $\pi$-electron release from the organometallic fragment, with the marked contrast with related CpFe(CO)$_2$-derived systems being in line with the behaviour of related carbene systems.\textsuperscript{27}

Reaction of compound $[3.5a]^+$ with the stronger pyridine donor, dmap, does appear to lead to coordination at the boron centre $[3.5a \cdot \text{(dmap)}]^+$ as observed by a shift in the $^{11}\text{B}$ NMR spectrum to 68.0 ppm (cf. $\delta_B$ 56.9 ppm for $[\text{CpFe(CO)}_2\text{BNCy}_2\cdot \text{(4-pic)}][\text{BAR}_4]$ and $\delta_B$ 68.5 ppm for $[3.5a \cdot \text{(py)}]^+$). Attempts to identify $[3.5a \cdot \text{(dmap)}]^+$ by \textit{in situ} ESI-MS, however, simply reveal the unbound borylene complex $[3.5a]^+$, consistent – even for this more electron-rich pyridine donor – with relatively weak binding at boron. Moreover, upon prolonged reaction time at 20$^\circ$C the borylene fragment is apparently extruded leading to the isolation of $[\text{CpFe(dmpc)}\text{(dmap)}][\text{BPh}_4]$, $[3.7][\text{BPh}_4]$, as the primary organometallic product. The identity of $[3.7][\text{BPh}_4]$ was duly confirmed by single crystal X-ray diffraction [Figure 3.9], multinuclear NMR and mass spectrometry. The quality of the X-ray data in this case is sufficient to provide a solution which provides good evidence for atomic connectivity, but not to permit in depth discussion of metrical parameters.
Figure 3.9: Molecular structure of [3.7][BPh₄]. Thermal ellipsoids set at the 25% probability level, hydrogen atoms and counter-ion omitted for clarity.

Table 3.6: Selected bond lengths [Å] and angles [°] for [3.7][BPh₄].

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length</th>
<th>Angle</th>
</tr>
</thead>
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<td>Fe(1)-P(5)</td>
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</tr>
<tr>
<td>Fe(1)-P(2)</td>
<td>2.217(4)</td>
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<tr>
<td>P(5)-Fe(1)-P(2)</td>
<td></td>
<td>83.3(2)</td>
</tr>
</tbody>
</table>
Chapter III (Dimethylamino)borylene and Related Complexes of Electron Rich Metal Fragments

Incidentally, [3.5a]+ does not react with the strong acid [H(OEt)₂][BAR₄] (Brookhart’s acid) However, it retains the ability to act as a source of the borylene fragment in [4 + 1] cycloaddition chemistry (e.g. in its reactivity towards 3,5-di-tert-butylbenzoquinone) akin to that found for [CpFe(CO)₂(BNC₃₂)][BAR₄].

3.3.4 Rotational Barriers

The barrier to rotation about the Fe-B-N axis in aminoborylene complexes is of considerable interest due to the potential insight it offers into the electronic stabilisation of the boron centre. Previous examples in which restricted rotation about the M-B bond on the NMR timescale has proved to be viable are confined to systems featuring hydride co-ligands (i.e. Ru(PC₃)₂(H)Cl(BMes) and [Ir(IMes)(IMes')(H)(BNC₃₂)]+). In order to probe by ³¹P NMR spectroscopy the potential for restricted rotation about the Fe-B-N axis in an electron-rich half-sandwich coordination environment akin to that found in [3.5a]+, the synthesis of related unsymmetrical borylene complexes is required. This was accomplished according to the chemistry outlined in Scheme 3.7, via the corresponding unsymmetrically substituted boryl systems 3.11-3.13. Thus, reaction of Na[CpFe(CO)₂] with dichloroboranes 3.8, 3.9 and 3.10 led to the formation of the boryl systems 3.11, 3.12 and 3.13, which have been characterised by standard spectroscopic, analytical and (in the case of 3.13) crystallographic techniques [Figure 3.10].
Scheme 3.7: Syntheses of the asymmetric aminoboryl complexes 3.11-3.13 and the related borylene complex [3.15a][BPh₄].

The $^1$H and $^{13}$C NMR spectra of 3.11 and 3.12 display the expected resonances for the Cp ring and the amino-methyl and –aromatic substituents. In each case, a single broad resonance is observed in the $^{11}$B NMR ($\delta_B$ 59.0 for 3.11; $\delta_B$ 60.0 for 3.12). Additionally, mass spectrometry reveals the presence of the [M]$^+$ ion for 3.11 and of the [M-CO]$^-$ and [M-2CO]$^-$ ions for 3.12.

The $^1$H NMR data for complex 3.13 are also in accordance with the proposed structure. A ‘roofed’ second order AB signal in the aromatic region ($\delta_H$ 6.5 – 7.5) is consistent with the C₆H₄OMe-4 unit, and three sharp singlets are observed for the Cp ring, NMe and OMe protons. The $^{13}$C NMR spectrum yields three high field signals for the Cp, OMe and NMe carbons and a single low field peak for the CO ligands. Four separate peaks are observed in the aromatic region ($\delta_C$ 110 – 160), with two peaks significantly downfield due to withdrawing effects of N and O substitutents. The peak at $\delta_B$ 58.7 in the $^{11}$B NMR spectrum is slightly lower than for 3.11, as expected due to reduced involvement of the nitrogen lone pair in the aromatic system and hence increased donation to boron. The species [M-CO]$^+$ and [M-
2CO]⁺ are evident from mass spectrometry data. These spectroscopic inferences were subsequently confirmed crystallographically [Figure 3.10]. 3.13 displays a bent Fe-B-N framework [∠Fe-B-N = 130.6(3)°] and an Fe-B bond [2.035(4) Å] which is similar in length to other iron aminoboryl systems [e.g. 2.027(5) Å for CpFe(CO)₂B(NMe₂)Cl].³⁸
Figure 3.10: Molecular structure of 3.13. Thermal ellipsoids set at the 40 % probability level, hydrogen atoms omitted for clarity.

Table 3.7: Selected bond lengths [Å] and angles [°] for 3.13.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
<th>Angle [°]</th>
</tr>
</thead>
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<td>B(11)-Cl(12)</td>
</tr>
<tr>
<td>B(11)-N(13)</td>
<td>1.399(5)</td>
<td></td>
</tr>
<tr>
<td>Fe(1)-B(11)-N(13)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In addition to the methyl(aryl)aminoboryl complexes 3.11-3.13, the related benzyl complex CpFe(CO)$_2$B{N(CH$_2$Ph)Me}Cl (3.14) has been synthesised by the reaction of Na[FeCp(CO)$_2$] with Me(PhCH$_2$)NBCl$_2$ and has been characterised by standard spectroscopic and analytical techniques. Interestingly, $^1$H and $^{13}$C NMR data at room temperature display two signals in an approximately 2:1 ratio for the Cp, CH$_2$Ph and NCH$_3$ resonances corresponding to the presence of both the $E$ and $Z$ isomers [Scheme 3.8].

Scheme 3.8: $E$ and $Z$ isomers and associated barriers to rotation about the BN bond for unsymmetrical aminoboryl complexes 3.11-3.14 as determined from NMR measurements and DFT calculations.

In general terms, restricted rotation about BN linkages between tri-coordinate boron and nitrogen centres due to the disruption of $\pi$ bonding is a well established phenomenon, but that in metal-substituted systems is less well understood. Thus, the syntheses of the CpFe(CO)$_2$B{N(CH$_2$Ph)Me}Cl together with the three related compounds 3.11-3.13, possessing different para-aryl substituents, allows for the systematic appraisal of electronic influences on BN $\pi$ bonding in aminoboryl complexes. These factors have been probed through variable temperature $^1$H NMR spectroscopy (and complementary DFT studies) since, in the appropriate temperature regime, each compound gives rise to distinct signals due to the
E and Z isomers. Coalescence of the $^1$H NMR signals due to these isomers offers a convenient spectroscopic handle for probing the rotation process.

To determine experimentally the rotational barriers in these systems, the Eyring equation was applied to the rates of exchange at each temperature over a wide range of temperatures. Computational modelling (using gNMR) of the experimental data was carried out, in which the temperature dependence of the chemical shifts and of the relative populations of rotamers were taken into account. From these analyses an exchange rate at each temperature was determined and hence $\Delta G^\ddagger$ obtained from a plot of $\ln(k/T)$ against $-1/T$. This modelling gives a more reliable figure than the simple symmetric two-site exchange approximation for the rotational barrier. Experimental analyses carried out for the methyl(aryl)aminoboryl complexes 3.11-13, together with the related benzyl complex CpFe(CO)$_2$B{N(CH$_2$Ph)Me}Cl (3.14) reveal rotational barriers in the range 10.7-16.1 kcal mol$^{-1}$, values which are in close accordance with the corresponding DFT-calculated barriers [Scheme 3.8 and Figure 3.11].

Compound 3.11 displays comparable steric bulk to 3.14 but has potential for conjugation of the nitrogen lone pair into the aryl ring system. As a result, the barrier to rotation in 3.11 (12.2 kcal mol$^{-1}$) is significantly lower than that found in 3.14 (16.1 kcal mol$^{-1}$). With this possible conjugation effect in mind, the related derivatives 3.12 and 3.13 had been synthesised bearing electron withdrawing or donating groups in the para position of the aromatic system. The rotational barrier for 3.13 (14.3 kcal mol$^{-1}$) is higher than that for 3.11, while for compound 3.12 a lower barrier to rotation is witnessed (10.7 kcal mol$^{-1}$). These rotational barriers, both experimental and calculated, correlate well with the Hammett parameters of the para-substituent [$\sigma_p = -0.27$ (OMe), 0 (H), 0.54 (CF$_3$)]. Moreover, the
experimental results and theoretical figures derived from DFT show a strong correlation. This gives mutual support for the reliability of the results obtained from either method and supports the initial hypothesis and gives an insight into methods of increasing electron density at the boron centre.

Bond critical point (BCP) calculations were also carried out on the B-N bonds in 3.11-3.14, and in particular the ellipticities of the bonds (ε) determined for the electron density contour around the BCP. Consistent with the data measured/calculated for rotational barriers, the ellipticity of the B-N bond (itself a measure of BN double bond character) is found to increase in the order $3.12 < 3.11 < 3.13 < 3.14$ (0.0858, 0.0949, 0.0970 and 0.1098, respectively).
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Figure 3.11: Barriers to rotation about the BN bond for asymmetric aminoboryl complexes 3.11-3.14 as determined from NMR measurements and DFT calculations.

In accordance with the synthetic strategy outlined in Scheme 3.7, the asymmetric borylene complex [CpFe(dmpe){BN(C₆H₄OMe-4)Me}][BPh₄], [3.15a][BPh₄] was then synthesised in a manner analogous to that used for [3.5a][BPh₄]. The synthesis of [3.15a]⁺ was confirmed by spectroscopic data (¹H, ¹³C, ¹¹B and ³¹P NMR, ESI-MS) and the cation obtained as the crystalline [BPh₄]⁻ salt from a fluorobenzene/ether layering experiment [Figure
3.12. The $^1$H NMR spectrum displays singlets for the Cp, NMe and OMe signals in the ratio 5:3:3. Two multiplets are observed for the magnetically inequivalent pairs of PMe environments and two multiplets of relative intensity two are visible for the CH$_2$ groups from the ethane backbone of dmpe. The aromatic region displays two doublets for the ortho- and meta- protons of the aryl ring, but these overlap with the three signals for the Ph groups of the [BPh$_4$]$^-$ counterion.

The crystal structure [Figure 3.12] reveals an Fe-B bond length [1.800(3) Å] which is statistically identical to that found in [3.5a]$^+$. Moreover, the alignment of the borylene substituents [$\angle$Cp centroid-Fe(1)-N(16)-C(18) = 71.2°] is consistent with previously reported examples (such as [3.5a]$^+$) and reflective of the orientation of the HOMO of the [CpFeL$_2$]$^+$ fragment. Moreover, in the case of [3.15a]$^+$ this alignment is consistent with a static symmetry lower than $C_s$, and with the potential for inequivalent phosphorus environments in the low temperature limit. In the event, even in this electronically loaded system, the $^{31}$P NMR spectrum shows no hint of coalescence at temperatures down to 183 K, implying a barrier to rotation about the Fe-B-N axis of less than 7 kcal mol$^{-1}$. Moreover, DFT calculations on the same molecule imply an even lower rotational barrier of the order of 2.9 kcal mol$^{-1}$. 

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**Figure 3.12**: Molecular structure of \([3.15a][\text{BPh}_4]\) Thermal ellipsoids set at the 40% probability level; hydrogen atoms and counter-ion omitted for clarity.

**Table 3.8**: Selected bond lengths [Å] and angles [°] for \([3.15a][\text{BPh}_4]\).

<table>
<thead>
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<td>Fe(1)-P(2)</td>
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<td>B(15)-N(16)</td>
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<td>Fe(1)-B(15)-N(6)</td>
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A significantly larger barrier has been measured for rotation about the B-N bond in the closely related boryl complex 3.13 ($\Delta G^\ddagger = 14.3$ kcal mol$^{-1}$). This, together with (if anything) a slight strengthening of the BN $\pi$ interaction on halide abstraction/loss, implied by BN bond lengths of 1.399(5)/1.409(5) and 1.378(4) Å for 3.13 (two independent molecules) and [3.15a]$^+$, respectively, implies that the facile rotation around the Fe-B-N axis in [3.15a]$^+$ can best be interpreted in terms of rotation about the Fe-B bond by an essentially fixed BNR$_2$ unit.

In summary, the use of electron-rich bis(phosphine) substituted half-sandwich group 8 metal fragments leads to much less electrophilic borylene systems and exceptionally short M-B bonds. This is most dramatically demonstrated by reactivity (or intrinsic lack of it) towards pyridine. Despite the strong $\pi$ electron release from the metal fragment implied by this reactivity and by the short M-B bonds, the barrier to rotation about the Fe=B bond in [3.15a]$^+$ is very small. This reflects the fact that the [CpML$_2$]$^+$ fragment has HOMO and HOMO-2 orbitals orientated at 90° to one another; hence $\pi$ bonding is possible in either orientation and at intermediate torsion angles through orbital mixing [Scheme 3.9].$^{41}$ Consequently, the barrier to rotation does not reflect the absolute magnitude of the Fe-B $\pi$ bonding but rather the difference in energy between these two conformations.
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\[ \text{Scheme 3.9: (upper) Barrier to rotation about the FeBN axis for the asymmetric aminoborylene complex } [3.15a]^+ \text{ as determined from NMR measurements and DFT calculations; (lower) potential metal-boron } \pi \text{ interactions in } [3.15a]^+ \text{ utilising the metal-based HOMO (a) or HOMO-2 (b).} \]

3.4 Conclusions and Suggestions for Further Research

Spontaneous halide ejection from a three-coordinate boron electrophile has been shown to offer a remarkable new route to cationic transition metal complexes containing chemically robust M=B double bonds. The use of electron-rich bis(phosphine) ligated half-sandwich fragments leads to the *spontaneous* formation in polar solvents of borylene complexes with drastically reduced electrophilicity and exceptionally short M-B bonds. This is reflected by M-B bond distances which are more akin to alkyl/aryl substituted systems, and perhaps most strikingly, by the very low exothermicity associated with the binding of pyridine to a two-coordinate boron centre in a cationic system (\( \Delta H = -7.4 \text{ kcal mol}^{-1} \), cf. -40.7 kcal mol\(^{-1} \) for BCl\(_3\)). Despite the strong \( \pi \) electron release from the metal fragment implied by suppressed reactivity and short M-B bonds, the barrier to rotation about the Fe=B bond in the
asymmetric variant $[\text{CpFe(dmpe)}\{\text{BN(C}_6\text{H}_4\text{OMe-4)Me}\}]^+ [\text{3.15a}]^+$ is found to be very small (ca. 2.9 kcal mol$^{-1}$). This apparent contradiction is rationalised by the orthogonal orientations of the HOMO and HOMO-2 orbitals of the $[\text{CpML}_2]^+$ fragment, which mean that the M-B $\pi$ interaction does not fall to zero even in the highest energy conformation.

Given the enhanced stability of $[\text{CpFe(dmpe)(BNMe}_2)]^+ [\text{3.5a}]^+$ in comparison to $[\text{CpFe(CO)}_2(\text{BNMe}_2)]^+$, brought about by replacing the ancillary carbonyl ligands with less $\pi$ acidic phosphines, subsequent research could target the stabilisation (by formal phosphine substitution) of other dicarbonyl ligated borylene systems which are otherwise unstable under ambient conditions.

3.5 References for Chapter III

Chapter III (Dimethylamino)borylene and Related Complexes of Electron Rich Metal Fragments


Chapter III *Dimethylamino)borylene and Related Complexes of Electron Rich Metal Fragments*


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4.1 Introduction

In recent years, base-stabilised borylene complexes have obtained some precedent in the literature, via a number of synthetic approaches. In 1998, Shimoi demonstrated the reaction between $\mathrm{B_2H_4(PMe_3)_2}$ with $\mathrm{Co_2(CO)_8}$ to give $\{(\mathrm{OC})_3\mathrm{Co}\}_2(\mu-$CO)(μ-BH·PMe) 

\[ \text{Scheme 4.1} \]

**Scheme 4.1**: Synthesis of a dinuclear cobalt complex bridged by nonsubstituted borylene-trimethylphosphine.

Base-stabilised borylene complexes have also been synthesised by the $\alpha$-migration of a boron bound substituent in systems featuring an electron deficient, coordinatively unsaturated
Chapter IV *Synthesis of Novel Boryl and Borylene Complexes via Substituent Modification at Boron*

metal centre and a haloboryl ligand. This approach was first investigated by Roper and co-workers who reported the formation of the intramolecularly base-stabilised terminal borylene complex Os[B(NHC$_6$H$_5$N)]Cl$_2$(CO)(PPh$_3$)$_2$ from the reaction of Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$ with 8-aminoquinolene [Scheme 4.2].

![Scheme 4.2: Formation of a base-stabilised osmium borylene complex.](image)

Interestingly, the reaction of the same boryl complex precursor with 2-aminopyridine yields a mixture of an amino(chloro)boryl complex and a base-stabilised borylene complex, depending on the regiochemistry of the addition of the nitrogen donors to the boron and osmium centres [Scheme 4.3].

![Scheme 4.3: Tethered osmium boryl and base-stabilised borylene complex.](image)

A similar approach has been reported by Braunschweig and co-workers in the synthesis of a series of cationic base-stabilised platinum borylene complexes. The addition of
Chapter IV *Synthesis of Novel Boryl and Borylene Complexes via Substituent Modification at Boron*

Na[Bar\textsuperscript{f}4] and a pyridine Lewis base to boryl complexes of the type *trans*- (Cy\textsubscript{3}P)\textsubscript{2}Pt(Br){B(Br)X} induces a formal 1,2-bromide shift from the boron atom to the platinum centre, resulting in the formation of the base-stabilised borylene complexes of the type *trans* - [(Cy\textsubscript{3}P)\textsubscript{2}Pt(Br){B(L)R}][Bar\textsuperscript{f}4] (R = NMe\textsubscript{2}, pip, Br, L = NC\textsubscript{5}H\textsubscript{4}-4-Me; R = pip, L = NC\textsubscript{5}H\textsubscript{4}-4tBu) [Scheme 4.4].\textsuperscript{4}

![Scheme 4.4: Synthesis of platinum boryl complexes by base promoted α-migration of bromide.](image)

In 2006, the Aldridge group reported the synthesis of [(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})(CO)\textsubscript{2}Fe=B(L)NCy\textsubscript{2}]\textsuperscript{+} (L = THF, 4-pic) from the simple addition of a Lewis base to a cationic borylene complex [Scheme 4.5].\textsuperscript{5}

![Scheme 4.5: Formation of base stabilised borylene complexes by addition of a Lewis base.](image)
4.1.1 Aims of Present Research

Given that the majority of base-stabilised borylene complexes have been synthesised (i) directly from a borylene complex by the addition of a base; or (ii) from a boryl complex via base promoted 1,2 halide migration, initial research in this project began by probing the possibility of synthesising related borylene complexes by electrophilic protonation/alkylation of an aminoboryl complex.

With the exception of very few examples, reactions of boryl complexes with protic reagents HY (Y = OH, OR, NHR, Cl) proceed via cleavage of the metal–boron bond and formation of the borane $X_2BY$. An early example reported by Hartwig is the observation that $\text{Fe(CO)}_4(\text{BCat}^*)_2$ gives EtOBCat and Et$_2$NBCat upon addition of excess EtOH and Et$_2$NH, respectively [Scheme 4.6].

![Scheme 4.6: Reaction of Fe(CO)$_4$(BCat$^*$)$_2$ with protic sources.](image)

A notable exception to this observation are the reactions between Os$(\text{BCl}_2)\text{Cl(CO)(PPh}_3)_2$ and alcohols or secondary amines, which cleanly form Os{$(\text{RO})_2\text{B}_2}\text{Cl(CO)(PPh}_3)_2$ and Os{$(\text{R}_2\text{N})_2\text{B}_2}\text{Cl(CO)(PPh}_3)_2$ respectively, with elimination of
HCl and retention of the M-B bond.\textsuperscript{7} This reflects the greater strength of the Os-B bond in these systems.

A further noteworthy reaction, exemplifying the rare reactivity of a boryl complex with an electrophilic reagent, this time by nucleophilic attack through the metal centre, has been reported by Hartwig. Abstraction of a boryl fragment from the bis(boryl) complexes (OC)\textsubscript{4}Fe(BR\textsubscript{2})\textsubscript{2} (R\textsubscript{2} = Cat, 1,2-\text{o}2-4\text{t}BuC\textsubscript{6}H\textsubscript{5}, 1,2-\text{o}2-3,5\text{t}Bu\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) yield the first examples of anionic boryl complexes. Further reaction of Li[(OC)\textsubscript{4}FeB(1,2-\text{o}2-3,5\text{t}Bu\textsubscript{2}C\textsubscript{6}H\textsubscript{3})] with the electrophilic Me\textsubscript{3}SnCl gives the \textit{cis} stannyl-substituted complex (OC)\textsubscript{4}Fe(SnMe\textsubscript{3})[B(1,2-\text{o}2-3,5\text{t}Bu\textsubscript{2}C\textsubscript{6}H\textsubscript{3})].\textsuperscript{6}

\begin{equation}
\text{Scheme 4.7: Reaction of an anionic boryl complex with Me}_3\text{SnCl.}
\end{equation}

An unprecedented mode of reactivity for a neutral boryl complex with an electrophilic reagent has been reported in work by Roper. The exchange of the ethoxy groups in Os[B(OEt)\textsubscript{2}]Cl(CO)(PPh\textsubscript{3})\textsubscript{3} with 1,2-ethanediol or 1,3-propanediol in the presence of Me\textsubscript{3}SiCl gives the heterocyclic boryl complexes Os(BOC\textsubscript{3}H\textsubscript{4}O)Cl(CO)(PPh\textsubscript{3})\textsubscript{2} and Os(BOC\textsubscript{3}H\textsubscript{4}O)Cl(CO)(PPh\textsubscript{3})\textsubscript{2}, respectively.\textsuperscript{8} Interestingly, the presence of Me\textsubscript{3}SiCl is vital since the OEt groups in Os[B(OEt)\textsubscript{2}]Cl(CO)(PPh\textsubscript{3})\textsubscript{3} do not exchange with the alcohols under neutral conditions. Therefore, the reaction of Me\textsubscript{3}SiCl with the starting material Os[B(OEt)\textsubscript{2}]Cl(CO)(PPh\textsubscript{3})\textsubscript{3} is likely to be key to the reaction mechanism.
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Additionally, since the strength of the Fe-B bond in bis(phosphine) systems is likely to be augmented compared to dicarbonyl systems, research has also sought to examine the reactivity of phosphine substituted systems towards protic or electrophilic alkylating reagents. Furthermore, considering the dramatic changes in structure and significant enhancements in stability brought about in \([\text{CpFe(dmpe})(\text{BNMe}_2)]^+\) cf. \([\text{CpFe(CO)}_2(\text{BNMe}_2)]^+\) upon the exchange of \(\pi\) acidic carbonyl ligands for trialkyl phosphines (Chapter 3), research has attempted to access a series of rare transition metal borylene compounds (\([\text{M}]=\text{BF}, [\text{M}]=\text{BOR}\) which have otherwise lacked sufficient steric/electronic stabilisation to be isolated in ambient conditions.

4.2 Experimental

**Reaction of \(\text{CpFe(CO)}_2\text{B(NCy}_2\text{)Cl} + \text{[H(OEt}_2\text{)]_2}[\text{BAR}_4']\)**

A solution of \(\text{CpFe(CO)}_2\text{B(NCy}_2\text{)Cl} (0.20 \text{ g}, 0.49 \text{ mmol})\) in fluorobenzene (20 cm\(^3\)) was added to a slurry of \([\text{H(OEt}_2\text{)]_2}[\text{BAR}_4']\) (0.50 g, 0.49 mmol) in fluorobenzene (15 cm\(^3\)) and the reaction mixture stirred for 1 h. Monitoring by \(^{11}\text{B NMR}\) spectroscopy revealed a downfield shift to \(\delta_B\) 90 ppm corresponding to \(\text{CpFe(CO)}_2\text{BCl}_2\). Prolonged stirring overnight allowed further conversion to a new complex giving rise to a single \(^{11}\text{B NMR}\) signal at \(\delta_B\) 60 ppm. Solvent was removed *in vacuo* and the resulting precipitate layered with various solvent combinations. Unfortunately, single crystals suitable for X-ray diffraction could not be obtained.

**Synthesis of \(\text{CpFe(CO)}_2\text{B(NCy}_2\text{)F}\), 4.5**

A solution of \(\text{CpFe(CO)}_2\text{B(NCy}_2\text{)Cl} (0.20 \text{ g}, 0.49 \text{ mmol})\) in dichloromethane (20 cm\(^3\)) was added to a solution of \([\text{Me}_3\text{O}][\text{BF}_4] (0.50 \text{ g}, 0.49 \text{ mmol})\) in dichloromethane (5 cm\(^3\)) and the
reaction mixture stirred overnight. Solvent was removed *in vacuo* and the resulting red material extracted with hexane (3 x 20 cm$^3$). Concentrating the solution and storing at -30°C afforded red crystals in 60% yield.

Data for 4.5: $^1$H NMR (300 MHz, C$\text{$_6$D$_6$}$, 25°C): $\delta$H 0.91-1.73 (m, 18H, CH$_2$ of Cy), 2.20 (m, 2H, CH$_2$ of Cy), 2.64 (m, 1H, CH of Cy), 3.61 (m, 1H, CH of Cy), 4.26 (s, 5H, Cp). $^{13}$C NMR (126 MHz, C$\text{$_6$D$_6$}$, 25°C): $\delta$C 25.9, 26.1, 26.7, 27.5, 32.9, 34.9 (CH$_2$ of Cy), 56.3, 59.2 (CH of Cy), 82.9 (Cp) 216.3 (CO). $^{11}$B NMR (96 MHz, C$\text{$_6$D$_6$}$, 25°C): $\delta$B -19.0 (q, $^1$J$_{BF}$ = 116 Hz). $^{19}$F NMR (282 MHz, C$\text{$_6$D$_6$}$, 25°C): $\delta$F -19.0 (q, $^1$J$_{FB}$ = 116 Hz). IR (C$\text{$_6$D$_6$}$ soln.): v(CO) 1997.4, 1935.0. MS (EI) m/z: [M]$^+$ 387.1 (12%), [M-CO]$^+$ 359.1 (30%); exact mass for [M]$^+$ ($^{10}$B, $^{54}$Fe, $^{35}$Cl isotopomers) 384.1548, calc. 384.1546.

Crystallographic Data: C$_{19}$H$_{27}$BFeNO$_2$, M$_r$ = 387.08, monoclinic, P 2$_1$/n, a = 6.5681(2), b = 18.1008(4), c = 15.9732(5) Å, $\beta$ = 91.4065(10)$^\circ$, V = 3157.5(4) Å$^3$, Z = 4, $\rho_c$ = 1.354 Mg/m$^3$, T = 150 K, $\lambda$ = 0.71073 Å, 29524 reflections collected, 4335 independent [R(int) = 0.069] and were used in all calculations. $R_1 = 0.0602$, $wR_2 = 1.524$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1 = 0.0856$, $wR_2 = 0.1650$ for all unique reflections. Max. and min. residual electron densities 1.16 and -1.07 e.Å$^{-3}$.

Reaction of CpFe(CO)$_2$B(NCy)$_2$F (4.5) with [H(OEt)$_2$]$^2$[BAr$_4^f$]: formation of CpFe(CO)$_2$BF$_2$

A solution of CpFe(CO)$_2$B(NCy)$_2$F (0.020 g, 0.050 mmol) in dichloromethane (1 cm$^3$) was added to a slurry of [H(OEt)$_2$]$^2$[BAr$_4^f$] (0.050 g, 0.050 mmol) also in dichloromethane (1 cm$^3$) and the reaction mixture stirred for 1 h. Spectroscopic monitoring revealed the formation of CpFe(CO)$_2$BF$_2$, the data for which matched those given in the literature.
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Reaction of CpFe(CO)$_2$B(NMe$_2$)Cl with [Me$_3$O][BF$_4$]: formation of CpFe(CO)$_2$BF$_2$

A solution of CpFe(CO)$_2$B(NMe$_2$)Cl (0.20 g, 0.75 mmol) in dichloromethane (20 cm$^3$) was added to a solution of [Me$_3$O][BF$_4$] (0.22 g, 1.5 mmol) also in dichloromethane (10 cm$^3$) and the reaction mixture stirred for 1 h. Spectroscopic monitoring revealed the formation of CpFe(CO)$_2$BF$_2$, the data for which matched those given in the literature.$^9$

Synthesis of CpFe(dmpe)B(NMe$_2$)F, 4.8

A solution of CpFe(dmpe)B(NMe$_2$)Cl (0.10 g, 0.20 mmol) in toluene (20 cm$^3$) was added to a suspension of [Me$_3$O][BF$_4$] (0.20 g, 0.20 mmol) also in toluene (10 cm$^3$) and the reaction mixture stirred for 1 h. Solvent was removed in vacuo and the resulting brown material extracted with hexane (3 x 20 cm$^3$). Concentrating the solution and storing at -30°C afforded a brown oil in 20 % yield.

Data for 4.8: $^1$H NMR (300 MHz, C$_6$D$_6$, 25°C): δ$_H$ 1.02 (m, 2H, PCH$_2$), 1.15 (m, 6H, PMe), 1.28 (m, 6H, PMe), 1.33 (m, 2H, PCH$_2$), 2.78 (s, 6H, Me), 4.19 (t, $^3$J$_{PH}$ = 1.8 Hz, 5H, Cp). $^{13}$C NMR (126 MHz, C$_6$D$_6$, 25°C): δ$_C$ 22.0 (m, PMe), 26.7 (m, PMe), 31.9 (m, PCH$_2$), 35.5 (NMe$_2$), 80.0 (Cp). $^{11}$B NMR (96 MHz, C$_6$D$_6$, 25°C): δ$_B$ 56.3 (d, $^1$J$_{BF}$ = 193 Hz). $^{19}$F NMR (282MHz, C$_6$D$_6$, 25°C): δ$_F$ -28.5 (br). $^{31}$P NMR (121MHz, C$_6$D$_6$, 25°C): δ$_P$ 81.1 (d, $^3$J$_{PF}$ = 72Hz). MS (EI) m/z: [CpFe(dmpe)H]$^+$ 272.0 (100%).

Reaction of CpFe(dmpe)B(NMe$_2$)F (4.8) with Na[BAr$_4$]: formation of [CpFe(dmpe)(BNMe$_2$)][BAr$_4$], [3.5a][BAr$_4$]$^-$

A solution of CpFe(dmpe)B(NMe$_2$)F (4.8) (0.020 g, 0.041 mmol) in dichloromethane (0.5 cm$^3$) was added to Na[BAr$_4$] (0.040 g, 0.045 mmol) and the reaction mixture sonicated for 5 min. Spectroscopic monitoring revealed the formation of [CpFe(dmpe)(BNMe$_2$)][BAr$_4$], for which the data matched those given in Chapter 3 ([3.5a][BAr$_4$]$^-$).
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**Synthesis of CpFe(CO)$_2$B(NCy)$_2$H, 4.9**

A solution of [CpFe(CO)$_2$(BNCy)$_2$][BAR$_4$] (0.030 g, 0.024 mmol) in fluorobenzene (0.5 cm$^3$) was added to either Cp$_2$WH$_2$ (0.0085 g, 0.027 mmol) or [PPN][BH$_4$] (0.015 g, 0.027 mmol) and sonicated for 1 h. Solvent was removed *in vacuo* and the resulting yellow/brown precipitate extracted with hexane (3 x 10 cm$^3$). Concentrating the solution and storing at -80°C afforded a pale yellow powder in 30% yield.

Data for 4.9: $^1$H ($^{11}$B) NMR (300 MHz, C$_6$D$_6$, 25°C): $\delta_H$ 0.96-1.88 (m, 20H, CH$_2$ of Cy), 2.85 (m, 1H, CH of Cy), 3.77 (m, 1H, CH of Cy), 4.26 (s, 5H, Cp), 7.60 (br, 1H, BH). $^{13}$C NMR (126 MHz, C$_6$D$_6$, 25°C): $\delta_C$ 26.1, 26.2, 26.6, 27.1, 33.0, 38.0 (CH$_2$ of Cy), 57.4, 63.7 (CH of Cy), 84.5 (Cp) 217.5 (CO). $^{11}$B NMR (96 MHz, C$_6$D$_6$, 25°C): $\delta_B$ 62.0 (d, $^1$J$_{BH}$ = 117 Hz). IR (C$_6$D$_6$ soln.): $\nu$(CO) 1986.3, 1925.3, $\nu$(BH) 2448.0. MS (EI) m/z: [M]$^+$ 369.2 (weak), [M-CO]$^+$ 340.1645, calc. 340.1644.

**Synthesis of CpFe(dmpe)B(OMes)Cl, 4.12**

A toluene solution of CpFe(CO)$_2$B(OMes)Cl (0.20 g, 0.60 mmol) and dmpe (> 2 equiv.) in a quartz reaction vessel was irradiated for 10 h. Periodic monitoring by $^{11}$B and $^{31}$P NMR spectroscopy revealed sequential formation of an intermediate postulated as CpFe(CO)(dmpe)B(OMes)Cl ($\delta_B$ 67.0, $\delta_P$ 49.4 and -48.5) followed by CpFe(dmpe)B(OMes)Cl ($\delta_B$ 67.0, $\delta_P$ 84.0). The solvent was removed *in vacuo* and the resulting product extracted into hexane. Concentrating the solution and storing at -30°C afforded the product (4.12) in 50% yield.

Data for 4.12: $^1$H NMR (300 MHz, C$_6$D$_6$, 25°C): $\delta_H$ 0.94 (m, 6H, PMe), 0.96 (m, 2H, PCH$_2$), 1.42 (m, 6H, PMe), 1.62 (m, 2H, PCH$_2$), 2.18 (s, 3H, para-CH$_3$ of Mes), 2.30 (s, 6H, ortho-CH$_3$ of Mes), 4.27 (t, $^3$J$_{PH}$ = 2.1 Hz, 5H, Cp), 6.82 (s, 2H, aromatic CH). $^{13}$C NMR (126 MHz,
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C₆D₆, 25°C): δC 18.5(ortho-CH₃ of Mes), 19.2 (m, PMe), 20.8 (para-CH₃ of Mes) 21.9 (m, PMe), 24.0 (m, PCH₂), 78.9 (Cp), 129.3 (aromatic CH), 129.6, 131.2 (aromatic quaternary), 153.8 (ipso-C of mesityl ring). ¹¹B NMR (96 MHz, C₆D₆, 25°C): δB 67.0 (br). ³¹P NMR (121MHz, C₆D₆, 25°C): δP 84.0. MS (EI) m/z: [M]⁺ 452.5 (100%); exact mass for [M]⁺ (¹⁰B, ⁵⁴Fe, ³⁵Cl isotopomers) 449.1137, calc. 449.1137.

**Synthesis of [CpFe(dmpe)(BOMes)][BAR₄, [4.13][BAR₄]**

A solution of CpFe(dmpe)B(OMes)Cl (4.12) (0.050 g, 0.11 mmol) in dichloromethane (10 cm³) was added to Na[BAR₄] (0.108 g, 0.12 mmol) or Na[BAR₄Cl] (0.073 g, 0.12 mmol) or [Et₃Si][B(C₆F₅)₄] (0.095 g, 0.12 mmol) and the reaction mixture stirred for 30 min. After which, the solvent was removed in vacuo, washed with hexane and extracted into CD₂Cl₂ (0.5 cm³).

Data for [4.13][BAR₄]: ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δH 0.83 (m, 2H, PCH₂), 1.48 (m, 6H, PMe), 1.53 (m, 6H, PMe), 1.85 (m, 2H, PCH₂), 2.20 (s, 3H, para-CH₃ of Mes), 2.28 (s, 6H, ortho-CH₃ of Mes), 4.60 (s, 5H, Cp), 6.87 (s, 2H, aromatic CH), 7.53 (s, 4H, para-CH of [BAR₄]), 7.69 (s, 8H, ortho-CH of [BAR₄]). ¹³C NMR (126 MHz, CD₂Cl₂, 25°C): δC 18.0 (ortho-CH₃ of Mes), 20.6 (para-CH₃ of Mes), 21.9 (m, PMe), 24.6 (m, PMe), 31.5 (m, PCH₂), 80.5 (Cp), 117.9 (s, para-CH of [BAR₄]), 125.2 (q, ¹JC = 275.0 Hz, CF₃ of [BAR₄]), 126.4 (aromatic CH), 129.2 (q, ²JC = 33.2 Hz, meta-quaternary C of [BAR₄]), 130.4 (aromatic quaternary), 135.2 (s, ortho-CH of [BAR₄]), 136.3 (aromatic quaternary), 146.4 (ipso-C of mesityl ring), 162.2 (q, ¹JC = 50.4 Hz, ipso-quaternary C of [BAR₄]). ¹¹B NMR (96 MHz, CD₂Cl₂, 25°C): δB 59.4 (br), -6.1 ([BAR₄]). ³¹P NMR (121MHz, CD₂Cl₂, 25°C): δP 76.8. ¹⁹F NMR (282 MHz, CD₂Cl₂, 25°C): δF -61.9. MS (positive ion electrospray) m/z: [M]⁺ 417.1 (weak); exact mass for [M]⁺ 417.1362, calc. 417.1369.
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Selected data for [4.13][BAr\textsuperscript{Cl}_4]: \(^{11}\)B NMR (96 MHz, CD\(_2\)Cl\(_2\), 25\(^\circ\)C): \(\delta_B\) 59.5 (br), -6.8 ([BAr\textsuperscript{Cl}_4]). \(^{31}\)P NMR (121MHz, CD\(_2\)Cl\(_2\), 25\(^\circ\)C): \(\delta_p\) 77.0.

Selected data for [4.13][B(C\(_6\)F\(_5\))\(_4\)]: \(^{11}\)B NMR (96 MHz, CD\(_2\)Cl\(_2\), 25\(^\circ\)C): \(\delta_B\) 60.0 (br), -16.2 ([B(C\(_6\)F\(_5\))\(_4\)]). \(^{31}\)P NMR (121MHz, CD\(_2\)Cl\(_2\), 25\(^\circ\)C): \(\delta_p\) 76.9.

4.3 Results and Discussion

4.3.1 Reactions of Aminoboryl and -borylene Systems with Protic Sources

With the initial aim of investigating the reaction of a series of aminoboryl complexes with protic sources, CpFe(CO)\(_2\)B(NCy\(_2\))Cl (4.1) was reacted with Brookhart’s acid, [H(OEt\(_2\))\(_2\)][BAR\textsuperscript{f}_4] [Scheme 4.8]. The reaction leads to a quantitative downfield shift in the \(^{11}\)B NMR spectrum from \(\delta_B\) 56 ppm to \(\delta_B\) 90 ppm after 1 h. Further stirring over a 12 h period results in complete disappearance of the resonance at \(\delta_B\) 90 ppm and the formation of a new sharp peak at \(\delta_B\) 60 ppm.

![Scheme 4.8: Reaction of 4.1 with [H(OEt\(_2\))\(_2\)][BAR\textsuperscript{f}_4].](image)

The resonance at \(\delta_B\) 90 ppm corresponds to the known dichloroboryl compound CpFe(CO)\(_2\)BCl\(_2\) (4.2), the identity of which was additionally confirmed by \(^1\)H NMR spectroscopy.\(^9\) Prolonged reaction times lead to the formation of a second species, postulated to be the cationic base-stabilised borylene complex [CpFe(CO)\(_2\){BCl·(NHCy\(_2\))}]\(^+\), [4.3]\(^+\) (\(\delta_B\)
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60 ppm cf. $\delta_B$ 56.9 ppm for [CpFe(CO)$_2$(BNCY$_2$(4-pic))][BAR$_4$]).$^{10}$ Scheme 4.9 depicts the hypothesised mechanism for this series of transformations.

![Scheme 4.9](image)

**Scheme 4.9:** Postulated mechanism for the formation of [4.3]$^+$ and 4.2.

There are two sites available within the boryl ligand for the protonation of 4.1 i.e. the nitrogen or chlorine atoms. Protonation at nitrogen would result in the formation of the base stabilised borylene complex [4.3]$^+$; protonation at chlorine liberates HCl, forming borylene complex [4.4]$^+$. Presumably, protonation at chloride is likely to be faster, reflecting the more readily available lone pair (the nitrogen lone pair being conjugated with the boron centre and the nitrogen centre consequently being planar). As a result, at short reaction times the concentration of [4.4]$^+$ builds up and the small amount of [4.3]$^+$ which is generated (by alternative N-protonation) is liable to further reaction with an excess of HCl (which is generated in the formation of [4.4]$^+$). Attack on the base stabilised borylene complex [4.3]$^+$ by HCl forms the kinetic product CpFe(CO)$_2$BCl$_2$, 4.2. This is consistent with the appearance of a broad resonance at $\delta_B$ 93 due to [4.4]$^+$ and the preponderance of 4.2 in the reaction mixture.
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after 4 hours. Additionally, *in situ* ESI-MS monitoring reveals the formation of $[\text{H}_2\text{NCy}_2]^+$ at this point.

Spectroscopic monitoring reveals that this reaction is reversible, and over time the thermodynamic product postulated to be $[4.3]^+$ (giving rise to a single $^{11}\text{B}$ signal at $\delta_B$ 60 ppm) is the predominant species in solution [Scheme 4.10].

Consistent with these postulates, the independently performed reaction of borylene complex $[4.4]^+$ with HCl in diethyl ether also results in the initial formation of CpFe(CO)$_2$BCl$_2$, 4.2 which over prolonged reaction times is converted to the thermodynamic product $[4.3]^+$. In effect, both the reaction of $[4.4]^+$ with HCl and the reaction of 4.1 with Brookhart’s acid are accessing the same equilibrium from different starting points [Scheme 4.10].

**Scheme 4.10:** Proposed thermodynamic equilibrium between 4.2 and $[4.3]^+$, accessed from the reactions of 4.1 and $[4.4]^+$ with Brookhart’s acid and HCl/Et$_2$O respectively.
In addition, further weight is given to one of the key individual steps in the proposed mechanism by consideration of the behaviour in the presence of excess HCl. Thus, reaction of [4.3]$^+$ with an excess of an ethereal solution of HCl forms the dichloroboryl complex 4.2 which has been spectroscopically characterised and corresponds well with the reported literature values [Scheme 4.11].

![Scheme 4.11: Independent reaction of [4.3]$^+$ with excess HCl to give 4.2.](image)

In addition, the reaction of boryl complex 4.1 with excess HCl/Et$_2$O also leads to the formation of 4.2 as the main product, presumably due to the greater concentration of the chloride anion in solution and its significantly greater nucleophilicity compared to [BAR$_4^-$].

Various attempts to isolate [4.3]$^+$ have proved difficult, possibly due to the very sensitive nature of the product. Consequently, it has not been possible to gather data on the compound. Therefore, it was decided to try the analogous reactions with a known methylating agent in the hope that they would yield a more stable or crystalline product of the type [CpFe(CO)$_2${B(Cl)NMeR$_2$}]$^+$. 

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4.3.2 Reactions of Aminoboryl and -borylene Systems with [Me$_3$O][BF$_4$]

The reaction of CpFe(CO)$_2$B(NCy)$_2$Cl, 4.1 with [Me$_3$O][BF$_4$] in fluorobenzene leads to the quantitative appearance of a doublet at $\delta_B$ 49.0 ppm ($^1J_{BF} = 116$ Hz), while the $^{19}$F NMR spectrum displays a quartet at $\delta_F$ -19.0 ppm ($^1J_{BF} = 116$ Hz) consistent with the formation of a B-F containing boryl complex [Scheme 4.12]. $^{11}$B NMR shifts are known to be strongly influenced by the $\pi$ donor properties of the boron-bound substituents;$^{11-13}$ the upfield resonance measured for the fluoroboryl complex 4.5 compared to the starting material 4.1 is therefore consistent with the known $\pi$ donor properties of fluoride.

![Scheme 4.12: Synthesis of 4.5 from the reaction of 4.1 with [Me$_3$O][BF$_4$] in fluorobenzene.](image)

$^{1}$H and $^{13}$C NMR spectra for 4.5 display the expected resonances for the Cp and CO groups at similar chemical shifts to 4.1. The resonances observed for the CH$_2$ moieties of the cyclohexyl groups suggests the existence of a weak intramolecular H bond interactions in solution; a multiplet of intensity 18H ($\delta_H$ 0.91-1.73) corresponding to the CH$_2$ protons of the cyclohexyl ring is observed but, in addition, a separate multiplet of intensity 2H with an upfield shift ($\delta_H$ 2.20) is witnessed corresponding to a CH$_2$ group interacting through space with the fluorine atom (verified by $^{19}$F{$^{1}$H} HOESY experiment). As expected, two separate resonances ($\delta_H$ 2.64 and 3.61) are also observed for the inequivalent CH protons of the cyclohexyl rings. EI mass spectrometry shows the [M]$^+$ and [M-CO]$^+$ peaks consistent with the proposed structure and accurate mass measurements are also as expected (meas. 384.1548,
calc. 384.1546 [\textsuperscript{10}B, \textsuperscript{54}Fe isotopomer]). The IR-detected carbonyl stretching frequencies at 1997 cm\(^{-1}\) and 1935 cm\(^{-1}\) are lower than those measured for the related chloroboryl system 4.1 (2000, 1939 cm\(^{-1}\) for CpFe(CO)\(_2\)B(NC\(_2\)\(_2\))Cl).\(^{14}\) This observation is consistent with that witnessed for \((\eta^5-C_5Me_5)Fe(CO)\(_2\)B(Mes)F (1989, 1931 cm\(^{-1}\)) and \((\eta^5-C_5Me_5)Fe(CO)\(_2\)B(Mes)Cl (1996, 1936 cm\(^{-1}\)),\(^{13}\) and reflects the expected decrease in the \(\pi\) acceptor properties of the boryl ligand on substituting Cl with F, and is in turn determined by competing X-B \(\pi\) donation from the halide. Crystals suitable for X-ray diffraction were obtained by storing a hexane extract of 4.5 at -30\(^{\circ}\)C overnight [Figure 4.1].
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![Figure 4.1: Molecular structure of 4.5. Thermal ellipsoids set at the 40% probability level; hydrogen atoms omitted for clarity.](image)

**Table 4.1**: Selected bond lengths [Å] and angles [°] for 4.5.

<table>
<thead>
<tr>
<th>Bond Description</th>
<th>Bond Length [Å]</th>
<th>Bond Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1)-B(11)</td>
<td>2.043(4)</td>
<td></td>
</tr>
<tr>
<td>B(11)-F(12)</td>
<td>1.360(4)</td>
<td></td>
</tr>
<tr>
<td>Fe(1)-B(11)-F(12)</td>
<td>113.6(2)</td>
<td></td>
</tr>
<tr>
<td>F(12)-B(11)-N(13)</td>
<td>115.6(3)</td>
<td></td>
</tr>
<tr>
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<td>B(11)-N(13)-C(20)</td>
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</tbody>
</table>

164
4.5 contains an Fe-B bond which is statistically identical in length to that observed in 4.1 [2.043(4) Å vs 2.053(3) Å]. This contrasts with observations made in previous work by Aldridge et al. where the progression from Cp*Fe(CO)₂B(Mes)Cl to Cp*Fe(CO)₂B(Mes)F results in a significant lengthening of the Fe-B bond [1.985(2) Å vs. 2.017(3) Å]. \(^{13}\) Presumably for aminoboryl systems, in which there is little Fe to B backbonding, the effect of the halide substituent is much less marked. Consistently, the Fe-B bond length measured for Cp*Fe(CO)₂B(Mes)F is significantly shorter than observed for 4.5 due to additional competing π donation from nitrogen which is absent in the case of the Cp*Fe(CO)₂B(Mes)F.

The proposed mechanism for this transformation is depicted in Scheme 4.12. It is believed that the initial step involves the formation of borylene complex [4.4]⁺ (via halide abstraction by [Me₃O]⁺) followed by abstraction of F⁻ from the anion [BF₄]⁻ to synthesise 4.5. This mechanism is supported by the independent reaction of the borylene system [4.4]⁺ (as the [BAR₄]⁻ salt) with one equivalent of [Me₃O][BF₄] which also results in the formation of 4.5. Additionally, monitoring the reaction by \(^{11}\)B NMR spectroscopy shows the presence of BF₃ consistent with abstraction of F⁻ from [BF₄]⁻. By means of literature precedent, cationic borylene complexes of the type [CpFe(CO)₂(BX)]⁺ have previously been shown to abstract F⁻ and Ph⁻ from borate anions of the type [BX₄]⁻. \(^{13}\)

Interestingly, further reaction of 4.5 with Brookhart’s acid results in the formation of the known boryl system CpFe(CO)₂BF₂ (4.6) (δ_B 47.7, t, \(^1J_{BF} = 181\) Hz) with retention of the Fe-B bond. \(^9\) This transformation presumably occurs through protonation at the amine group followed by fluoride abstraction from the [BAR₄]⁻ anion. Such fluoride abstraction reactivity towards the weakly coordinating [BAR₄]⁻ counteranion has precedent in the literature for highly electrophilic species. \(^{15-18}\) By contrast, exposure of 4.5 to a further equivalent of
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[Me_3O][BF_4] affords no further reactivity presumably due to the steric bulk of the cyclohexyl groups at the amine group preventing methylation [Scheme 4.13].

![Scheme 4.13: Reactivity of 4.5 with [H(OEt)_2][BARf_4] and [Me_3O][BF_4].](image)

The important role of sterics in these transformations is further illuminated by the behaviour of CpFe(CO)_2B(NMe_2)Cl. The reaction of this less sterically hindered dimethylamino boryl complex (4.7) with [Me_3O][BF_4] generates a species giving rise to a triplet in the ^{11}B NMR spectrum (δ_B 47.7 ppm, ^1J_{BF} = 181 Hz) and a quartet in the ^{19}F NMR spectrum (δ_F 2.61 ppm, ^1J_{BF} = 181 Hz) corresponding to the formation of CpFe(CO)_2BF_2 (4.6) [Scheme 4.14].\(^9\) In contrast to the reaction with 4.1, the reduced steric bulk at the amine group presumably allows for further methylation (at nitrogen) of the intermediate CpFe(CO)_2B(NMe_2)F leading to the formation of CpFe(CO)_2BF_2 (4.6).

![Scheme 4.14: Synthesis of 4.6 from the reaction of 4.7 with [Me_3O][BF_4] in fluorobenzene.](image)
Chapter IV *Synthesis of Novel Boryl and Borylene Complexes via Substituent Modification at Boron*

As a consequence of the transformation revealed in Scheme 4.14, it was decided to investigate the reactivity of the boryl complex CpFe(dmpe)B(NMe$_2$)Cl (3.3a, Chapter 3) with [Me$_3$O][BF$_4$]. The formation of an analogous difluoroboryl complex CpFe(dmpe)BF$_2$ would potentially offer an ideal precursor for the formation of a BF borylene complex, which is a key goal in borylene chemistry due to its isoelectronic properties with the well established CO and N$_2$ ligands.\textsuperscript{19-21} However, the reaction of 3.3a with [Me$_3$O][BF$_4$] in toluene leads to an upfield shift in the $^{11}$B NMR spectrum and the quantitative appearance of a doublet ($\delta_B$ 56.3 ppm, $^1J_{BF}$ = 193 Hz) corresponding to the formation of CpFe(dmpe)B(NMe$_2$)F (4.8) [Scheme 4.15]. Conceivably, the extra steric bulk from the dmpe ligand (vs. CO) prevents methylation of the amine group, inhibiting the formation of the desired complex CpFe(dmpe)BF$_2$.

![Scheme 4.15](image-url)

Scheme 4.15: Synthesis of 4.8 resulting from the reaction of 3.3a with [Me$_3$O][BF$_4$] in toluene and subsequent reactivity with excess [Me$_3$O][BF$_4$] and Na[Bar$_f$$_4$].

Extraction of 4.8 into hexane allows for the isolation of a brown oil and purification of this boryl complex. The $^{31}$P NMR spectrum displays a doublet ($\delta_P$ 81.1 ppm, $^3J_{PF}$ = 72 Hz)
and the $^{19}$F NMR spectrum exhibits a broad multiplet ($\delta_{F} = -28.5$ ppm). $^1$H and $^{13}$C NMR data present the anticipated resonances for the Cp, NMe$_2$ and dmpe moieties, consistent with the formation of 4.8. Unfortunately mass spectrometry measurements have failed, revealing a peak consistent with the decomposition product [CpFe(dmpe)H]$^+$. Various attempts at isolating 4.8 as crystalline material suitable for X-ray diffraction have proved unsuccessful. However, comparison of NMR data for 4.8 with closely related systems provides strong evidence for the proposed formulation.

Upon removal of volatiles and extraction of 4.8 into dichloromethane, NMR spectroscopy confirmed the retention of the charge neutral boryl formulation. This contrasts starkly the behaviour of the chloro analogue (3.3a) for which extraction into dichloromethane leads to spontaneous loss of chloride to give the cationic terminal borylene complex, as described in Chapter 3. This is presumably a result of the extra strength of the BF bond in comparison to the BCl bond. In accordance with experiment, DFT studies reveal that the identity of the boron-bound halogen is critical in the autoionisation of CpFe(dmpe)B(NMe$_2$)X, with $\Delta G$ values of +32.7, -7.3 and -16.3 kcal mol$^{-1}$ being calculated for CpFe(dmpe)B(NMe$_2$)X, when X = F, Cl and Br, respectively. However, reaction with Na[BAR$_4$] does lead to the formation of the previously synthesised borylene complex [3.5a][BAR$_4$], a transformation which further supports the identity of 4.8 as CpFe(dmpe)B(NMe$_2$)F.

Attempts to synthesise CpFe(dmpe)BF$_2$ or to completely remove the amine group in 4.8 by protonation with Brookhart’s acid proved unsuccessful, with $^{11}$B NMR spectroscopy displaying resonances corresponding to a mixture of decomposition products, even at low
temperatures [Scheme 4.15]. As a consequence, unfortunately this compound does not give a viable route to the related BF borylene system.

Various other synthetic approaches have been conducted in attempts to obtain a BF borylene complex or feasible and practicable precursors to a BF borylene compound (e.g. a BF$_2$ complex). These have included a variety of reactions of the boryl complex 4.7 (in addition to the phosphine substituted boryl and borylene analogues 3.3a and [3.5a]$^+$) with TlF, KF, BF$_3$·OEt$_2$ and [Bu$_4$N][BF$_4$], all of which were monitored by multinuclear NMR spectroscopy as appropriate. Regrettably, these resulted in either no reaction or resonances corresponding to decomposition/undesired product mixtures. In a further attempt, CpFe(CO)$_2$BF$_2$ was photolysed with dmpe in toluene but simply led to decomposition products upon irradiation. Further alternative approaches which were examined include the reaction of CpFe(dmpe)SnMe$_3$ with an excess of BF$_3$·OEt$_2$, targeting for stannyl/boryl ligand exchange. However, the reaction simply led to F/Me exchange leading to the formation of BFMe$_2$ and BF$_2$Me.

**4.3.3 Formation of a Novel Hydridoboryl Complex**

As a contrast to the aforementioned reactivity with electrophiles, and with a view to further understanding the reactivity of the cationic borylene complexes, [L$_n$M=BX]$^+$, reactions with sources of hydride, such as Cp$_2$WH$_2$ and [PPN][BH$_4$] have also been investigated, resulting in the formation of the novel hydridoboryl complex CpFe(CO)$_2$B(NCy)$_2$H (4.9), which has been characterised spectroscopically. Reaction of [CpFe(CO)$_2$(BNCy)$_2$][BAr$_4^-$] with one equivalent of Cp$_2$WH$_2$ or [PPN][BH$_4$] in fluorobenzene results in an upfield shift in the $^{11}$B NMR spectrum from $\delta_B$ 93 ppm to a sharper peak at $\delta_B$ 62 ppm, characteristic of a boryl system [Scheme 4.16].
Extraction into hexane allows for the purification of this boryl complex; the $^{11}$B NMR resonance of the pure product is a doublet ($^1J_{BH} = 117$ Hz) [Figure 4.2]. $^1$H NMR data shows peaks typical of cyclohexyl and Cp groups but due to coupling to $^{11}$B (I = 3/2) and therefore the broad nature of the hydride resonance, it is not well resolved. However, a $^1$H{$^{11}$B} spectrum displays a sharper peak at $\delta_H$ 7.6 ppm, corresponding to the boron-bound hydride [Figure 4.2]. $^{13}$C NMR data fits the proposed structure (4.9). The IR detected stretching frequencies at 1986 and 1925 cm$^{-1}$ correspond to $\nu$(CO) and are lower than those measured for the related systems CpFe(CO)$_2$B(NCy$_2$)Cl (2000, 1939 cm$^{-1}$) and CpFe(CO)$_2$B(NCy$_2$)F (1997, 1935 cm$^{-1}$). Additionally, the extra stretching frequency at 2448 cm$^{-1}$ is consistent with the $\nu$(BH) stretch. The mass spectrum displays [M]$^+$ and [M-CO]$^+$ consistent with the proposed structure, along with accurate mass measurements for [M-CO]$^+$ (meas. 340.1645, calc. 340.1644 [$^{10}$B isotopomer]).
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**Figure 4.2:** (a) $^1$H NMR spectrum displaying broad hydride resonance and sharp solvent peak (b) $^1$H{${}^{11}$B} NMR spectrum showing sharpening of hydride resonance on $^{11}$B decoupling (c) $^{11}$B NMR spectrum of CpFe(CO)$_2$B(NCy)$_2$H (4.9).

Previous literature reports detail the formation of various base stabilised hydrido boryl complexes including Co(CO)$_4$(BH$_2$(THF)), Cp*M(CO)$_3$BH$_2$PMe$_3$ (M = Mo, W) and Cp*M(CO)$_2$BH$_2$PMe$_3$ (M = Fe, Ru) formed by photolysis or salt elimination reactions.$^{22-24}$ More recently, work carried out as part of this project has led to the formation of iridium and ruthenium primary hydridoboryl complexes, and these results will be discussed further in Chapter 5. That said, 4.9 is among the first examples of non base-stabilised hydridoboryl complexes, in this case, formed uniquely in a direct transformation from a borylene complex.

A fluorobenzene/hexanes layering of the residue from the reaction utilising Cp$_2$WH$_2$ as the hydride source allows for the isolation of the tungsten containing product. The $^1$H NMR spectrum displays a 1:2 ratio of a triplet:doublet resonances in the hydride region [Figure 4.3], with this and the corresponding Cp resonances suggesting the formation of the known cation [(Cp$_2$WH)$_2$(μ-H)]$^+$. In the case of the reaction utilising [PPN][BH$_4$] as the hydride source, *in situ* $^{11}$B NMR spectroscopy shows the presence of B$_2$H$_6$ consistent with abstraction of H$^-$ from [BH$_4$]$^-$. The mechanism observed here is analogous in some respects to that witnessed for the reactions of the boryl (4.1) and borylene [4.4]$^+$ systems with [Me$_3$O][BF$_4$] discussed earlier in which F$^-$ is abstracted from [BF$_4$]$^-$. [Scheme 4.12].
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Figure 4.3: $^1$H NMR spectrum of [(Cp$_2$WH)$_2$(μ-H)]$^+$ in the hydride region displaying a 1:2 intensity ratio of triplet:doublet coupling pattern.

Interestingly, when the borylene complex [CpFe(CO)$_2$(BNCy$_2$)][BARf$_4$] is exposed to $> 1$ equivalent of [PPN][BH$_4$] an additional triplet at $\delta_B$ 37 ppm is also observed in the reaction mixture corresponding to the formation of monomeric H$_2$BNCy$_2$ (4.10), presumably due to the reaction of the excess hydride with the initially formed hydridoboryl complex.$^{25}$ A mechanism is proposed below [Scheme 4.17].

Scheme 4.17: Nucleophilic attack of hydride at the hydridoboryl resulting in the formation of 4.10.

This mechanism was given added weight by the reaction of CpFe(CO)$_2$B(NCy$_2$)Cl with [PPN][BH$_4$] which gives rise to a doublet at $\delta_B$ 37 ppm consistent with the formation of HClBNCy$_2$. $^{26}$ Moreover the displacement of the [CpFe(CO)$_2$]$^-$ anion from boryl complexes by nucleophiles has been demonstrated explicitly in Chapter 3.
4.3.4 Synthesis of an Aryloxyborylene Complex

Recent work by Braunschweig et al. has shown that the BO\(^-\) ligand is accessible at ambient temperatures in the coordination sphere of an appropriate transition metal.\(^{27}\) The species \(\text{trans-}(\text{Cy}_3\text{P})_2\text{BrPt(B≡O)}\) exists in equilibrium with the oxo-boryl complex \(\text{trans-}(\text{Cy}_3\text{P})_2\text{BrPt}\{\text{B(Br)OSiMe}_3\}\) at a ratio of 4:1 in favour of the BO complex. This equilibrium can, however, be driven to the product by removal of volatiles under high vacuum (thus removing the volatile co-product BrSiMe\(_3\)). This example aside, other oxygen bound borylene type complexes have not been extensively reported. Previous work by Aldridge et al. revealed cationic aryloxyborylene systems to be extremely labile and reactive species.\(^{14}\) Thus, the reaction of \(\text{CpFe(CO)}_2\text{B(OMes)Cl} + \text{Na}[\text{BAr}_4^+]\) leads to the isolation of the asymmetric fluoroboryl species \(\text{CpFe(CO)}_2\text{B(OMes)}\text{F}\). This is assumed to occur by the abstraction of a fluoride anion from \([\text{BAr}_4^-]\) by the highly reactive putative terminal borylene complex \([\text{CpFe(CO)}_2(\text{BOMes})]^+\), in a similar fashion to the abstraction of \(\text{F}^-\) from \([\text{BF}_4^-]\) witnessed in the reactions of the boryl \(4.1\) and borylene \(4.4\) systems with \([\text{Me}_3\text{O}][\text{BF}_4^-]\) discussed above. This unusual reactivity contrasts that observed for the mesityl complex \(\text{Cp}^*\text{Fe(CO)}_2\text{B(Mes)Br} + \text{Na}[\text{BAr}_4^+]\) which cleanly generates \([\text{Cp}^*\text{Fe(CO)}_2\text{BMes}][\text{BAr}_4^-]\), presumably due to the difference in steric and electronic properties of the Mes and OMes substituents.\(^{13, 28}\) Given the enhanced stability of \([\text{CpFe(dmpe)(BNMe}_2)]^+\) in comparison to \([\text{CpFe(CO)}_2(\text{BNMe}_2)]^+\), brought about by replacing the ancillary carbonyl ligands with less \(\pi\) acidic phosphines (Chapter 3) it was decided to attempt the substitution of the carbonyl ligands in \(\text{CpFe(CO)}_2\text{B(OMes)Cl} (4.11)\) with dmpe ultimately in the hope of increasing the stability of a derived aryloxyborylene system.
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Photolysis of CpFe(CO)$_2$B(OMes)Cl (4.11) with dmpe in toluene was monitored by $^{11}$B NMR spectroscopy [Scheme 4.18]. After 3 h, a shift from $\delta_B$ 62 ppm to $\delta_B$ 67 ppm was observed, typical of the formation of the mono-substituted product. Prolonged photolysis for 10 h led to no change in the $^{11}$B NMR spectrum. Hence, $^{31}$P NMR spectroscopy proved more useful in monitoring of the reaction. After 3 h two doublets were observed at $\delta_P$ 49.4 and $\delta_P$ -48.5 ($^3J_{PP} = 26.6$ Hz), corresponding to the mono-substituted phosphine complex CpFe(CO)(κ$^1$-dmpe)B(OMes)Cl. Upon prolonged photolysis these resonances diminished and the growth of a new peak at $\delta_P$ 84.0 ppm was observed, typical of bis-substituted boryl compounds. Presumably, the broad nature of the $^{11}$B NMR resonance means that the shift on transformation from mono- to bis-phosphine substituted product is not easily resolved.

![Scheme 4.18: Synthesis of 4.12.](image_url)

Removal of volatiles, extraction into pentane and storing at -30°C overnight allows for the isolation of the product 4.12. Moreover, $^{11}$B and $^{31}$P NMR spectroscopy confirm the retention of the neutral boryl species in the pentane extract. This contrasts the behaviour of the analogous aminoborylene complexes (Chapter 3) which autoionise on removal of solvent and extraction into dichloromethane. The formation of the product 4.12 has been further verified by spectroscopic studies. $^1$H and $^{13}$C NMR spectroscopy confirm the presence of the expected resonances for the Cp, PMe and PCH$_2$ moieties in addition to the ortho- and para- CH$_3$ groups of OMes, along with the aromatic protons and carbons. The mass spectrum displays the
molecular ion peak $[\text{M}]^+$ consistent with the structure proposed along with satisfactory accurate mass measurements (meas. 449.1137, calc. 449.1137 [$^{10}\text{B}, ^{54}\text{Fe}, ^{35}\text{Cl}$ isotopomer]).

Given the successful demonstration of phosphine substitution in 4.11, attempts have been made to substitute the CO ligands for phosphines in other aryl- and alkyloxy boryl systems $\text{CpFe(CO)}_2\text{B(OR)}\text{Cl}$, e.g. where $R = \text{Me, Ph and } ^i\text{Pr}$ [Scheme 4.19]. In all cases, attempted substitution with dmpe does not lead to the desired disubstituted products as inferred by $^{11}\text{B}$ NMR shifts of $\delta_\text{B} < 50$ ppm.

Scheme 4.19: Failed substitution of the ancillary carbonyl ligands with dmpe.

However, when $R = 2,6$-dimethylphenoxy, carbonyl substitution proves possible implying that steric shielding in the 2- and 6- positions of the aromatic ring is crucial for successful substitution at iron.

The reaction of 4.12 with Na[$\text{BAr}^\text{t}_4$] in $\text{CH}_2\text{Cl}_2$ was monitored by $^{11}\text{B}$ NMR spectroscopy. Intriguingly, instead of observing a broad downfield resonance as would typically be expected for the formation of a cationic borylene complex from the corresponding boryl precursor, an upfield shifted broad resonance ($\delta_\text{B}$ 59 ppm) was witnessed [Scheme 4.20].
An initial hypothesis to account for this unexpected $^{11}$B shift involved the coordination of trace water to the two-coordinate boron centre. Therefore, the analogous reaction was attempted with the moisture incompatible halide abstraction agent $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$.

However, monitoring by $^{11}$B and $^{31}$P NMR spectroscopy revealed the identical resonances present as in the reaction with Na[BAR$_f^4$]. Various attempts to crystallise the product using different counter-anions (including [BAR$_f^\text{Cl}_4$]) and solvent combinations have so far proved unsuccessful as unfortunately the product is an oil. It has however proved possible to obtain remarkably clean spectroscopic data from this oil. The $^1$H and $^{13}$C NMR spectra contain resonances for the Cp, OMes, PCH$_2$ and PMe groups in addition to the [BAR$_f^4$] anion with the expected relative integrals for the cationic mesitoxyborylene complex [4.13][BAR$_f^4$]. The $^{31}$P NMR spectrum displays a resonance at $\delta_P$ 76.8 ppm, typical of a bis-substituted cationic terminal borylene complex (cf. $\delta_P$ 79.0 ppm for [CpFe(dmpe)(BNMe$_2$)]$^+$) and the $^{19}$F NMR spectrum exhibits a single peak ($\delta_F$ -7.7) corresponding to [BAR$_f^4$]$^+$. ESI-mass spectrometry also reveals a peak at [M]$^+ = 417.1362$ with a matching isotopic envelope and accurate mass measurement in agreement with the calculated values for the cationic mesitoxyborylene product [4.13]$^+$.  

The one piece of experimental data seemingly at odds with the formulation proposed for cation [4.13]$^+$ is the $^{11}$B NMR resonances at 59.4 ppm. This signal is shifted ca. 8 ppm
upfield with respect to that for the chloroboryl precursor 4.12 (67.0 ppm). By contrast, all reported examples of cationic aminoborylene complexes give rise to downfield shifted $^{11}$B NMR resonances (e.g. $\delta_B$ 66.0 for CpFe(dmpe)B(NMe$_2$)Cl; $\delta_B$ 88.0 for [CpFe(dmpe)(BNMe$_2$)]$^+$). In view of this seemingly anomalous behaviour, DFT calculations were carried out on 4.12, [4.13]$^+$ and a range of reference compounds to calculate the expected $^{11}$B NMR resonances [Table 4.2].

<table>
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<td>BMe$_3$</td>
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<tr>
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</tr>
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<tr>
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</tr>
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**Table 4.2:** DFT calculated $^{11}$B NMR shifts.
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The compounds BF$_3$·OEt, BCl$_3$ and BMe$_3$ were included for the purposes of verifying the predicative accuracy of the method and as can be seen, these values fit within 6 ppm.$^{30,31}$ In addition, the values calculated for the aminoboryl and −borylene systems agree within 4 ppm, and are in accordance with the experimentally observed downfield shift in the $^{11}$B NMR resonance on halide abstraction.$^{13,32}$ Interestingly, this computational approach also correctly predicts the upfield shift observed between 4.12 and [4.13]$^+$, giving a reassuringly close agreement with the experimentally observed shift for the cationic mesitoxyborylene complex. Additionally, the same trend is observed for the closely related methoxyborylene system CpFe(dmpe)B(OMe)Cl and [CpFe(dmpe)(BOMe)]$^+$. The sense of this chemical shift change appears to be anomalous. Some explanation for this unusual observation can be obtained from examining the optimised geometric structures [Figures 4.4 and 4.5].
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**Figure 4.4:** DFT calculated geometry of 4.12.

**Figure 4.5:** DFT calculated geometry of [4.13]$^+$. 
Unique among heteroatom stabilised cationic borylene complexes, [4.13]⁺ contains a heteroatom with two orthogonal lone pairs. One possible resonance form for [4.13]⁺ which has much in common with related aminoborylene complexes is shown below [Scheme 4.21], and involves a bent geometry at oxygen and one O to B π bonding interaction from the heteroatom.

Scheme 4.21: One possible resonance form for [4.13]⁺ compared to a related aminoborylene complex.

Another possibility becomes more relevant as the B-O-C angle approaches 180° and involves a second O to B π interaction [Scheme 4.22]. By analogy with trans-(Cy₃P)₂BrPt(B≡O), such a resonance form has BO triple bond character and consequently less M-B multiple bonding [Scheme 4.22]. Therefore, if this resonance form is contributing to the electronic structure of [4.13]⁺, it might be expected that a somewhat lower $^{11}$B chemical shift analogous to trans-(Cy₃P)₂BrPt(B≡O) might be expected ($\delta_B$ 17.0 ppm). With this in mind, the chemical shift calculated for [CpFe(dmpe)B(OMe)]⁺ in which the B-O-C angle was constrained to be 180° was found to be 43.21 ppm. As such, it seems likely that the unusual chemical shift observed for [4.13]⁺ is due to enhanced π interaction with the heteroatom substituents, with the calculated B-O-C angle (139.2°) falling intermediate between this extreme linear model and the value of 129.5° obtained for chloroboryl precursor 4.12.
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\[ L_nM\overset{\text{2*}}{\text{B=O}}-\overset{\text{+}}{\text{R}} \quad \text{cf.} \quad L_nM\overset{\text{0}}{\text{B=O}}: \]

**Scheme 4.22:** Second possible resonance structure and comparison with \( L_nMB=O \).

### 4.4 Conclusions

In summary, the reactivity of aminoboryl complexes \( \text{CpFe(CO)}_2\text{B(NR}_2\text{)Cl (R = Me, Cy)} \) towards electrophilic sources (\( \text{H}^+, \text{Me}^+ \)) has been investigated. Although the complex could not be isolated, \( {}^1\text{B} \) NMR data suggests the formation of the base stabilised borylene complex \( [\text{CpFe(CO)}_2\{\text{BCl} \cdot (\text{NHCy}_2)\}]^+ [4.3]^+ \) from the reaction of \( \text{CpFe(CO)}_2\text{B(NCy}_2\text{)Cl} \) and \( [\text{H(OEt}_2\text{)}_2][\text{BAR}_4] \). By contrast, the reaction of \( \text{CpFe(CO)}_2\text{B(NCy}_2\text{)Cl} \) with \( [\text{Me}_3\text{O}]\text{[BF}_4] \) leads to the formation of \( \text{CpFeB(NCy}_2\text{)F (4.5)} \) which has been characterised crystallographically. The proposed mechanism involves borylene formation (via halide abstraction with \( [\text{Me}_3\text{O}]^- \)) followed by abstraction of \( \text{F}^- \) from the anion \( \text{[BF}_4]^- \). Subsequent reactivity with Brookhart’s acid results in the formation of the known boryl system \( \text{CpFe(CO)}_2\text{BF}_2 (4.6) \) due to protonation of the amine group followed by fluoride abstraction from \( \text{[BAR}_4^- \). Reaction of the dimethylaminoboryl complex \( \text{CpFe(CO)}_2\text{B(NMe}_2\text{)Cl} \) with \( [\text{Me}_3\text{O}][\text{BF}_4] \) generates \( \text{CpFe(CO)}_2\text{BF}_2 (4.6) \), presumably due to the reduced steric bulk at the amine group allowing for further methylation of the intermediate \( \text{CpFe(CO)}_2\text{B(NMe}_2\text{)F} \). However, reaction of \( \text{CpFe(dmpe)B(NMe}_2\text{)Cl} \) with \( [\text{Me}_3\text{O}][\text{BF}_4] \) is limited to the formation of \( \text{CpFe(dmpe)B(NMe}_2\text{)F (4.8)} \), even when reacted with an excess of the methylating agent, presumably due to the extra steric bulk of the dmpe ancillary ligand. This complex, unlike its chloro analogue \( \text{CpFe(dmpe)B(NMe}_2\text{)Cl (3.3a)} \) does not autoionise upon extraction into dichloromethane.
Chapter IV Synthesis of Novel Boryl and Borylene Complexes via Substituent Modification at Boron

The novel asymmetric hydridoboryl complex CpFe(CO)$_2$B(NCy)$_2$H (4.9) has been reported and spectroscopically characterised from the reaction of [CpFe(CO)$_2$(BNCY$_2$)]$^+$ with sources of hydride such as [PPN][BH$_4$] and Cp$_2$WH$_2$.

It has been possible to synthesise CpFe(dmpe)B(OMes)Cl (4.12), which unlike the dimethyamino precursor CpFe(dmpe)B(NMe$_2$)Cl (3.3a) does not autoionise upon extraction into dichloromethane. Moreover, subsequent reactivity with Na[BAr$_{4}^-$] leads to cationic mesitoxyborylene complex complex [CpFe(dmpe)(BOMes)]$^+$ [4.13]$^+$.

4.5 References for Chapter IV

Chapter IV *Synthesis of Novel Boryl and Borylene Complexes via Substituent Modification at Boron*


Chapter IV Synthesis of Novel Boryl and Borylene Complexes via Substituent Modification at Boron


Chapter V

Coordination and Activation of Aminoboranes at Electron Rich Metal Centres

5.1 Introduction

Aminoboranes, H₂BNRR' are the subject of considerable research focus, not only as the first-formed products in the dehydrogenation of a class of BN-containing hydrogen storage materials but also as the monomeric building blocks from which a number of inorganic polymers can be assembled.¹⁻¹⁰ For example, Manners and co-workers have recently reported the metal catalysed polymerisation of methylamineborane, H₃B·NMeH₂, by ruthenium, rhodium or palladium complexes to give high-molecular-weight poly(aminoboranes), [H₂BNMe(H)]ₙ, i.e. BN analogues of poly(propene).¹¹,¹² Despite their isoelectronic relationship with 1,1-disubstituted alkenes, the coordination chemistry of aminoboranes is, however, restricted to only a few structurally characterised examples. With the exception of the chemistry to be discussed in this chapter, the only reported examples of such complexes feature chelating H₂BNR₂ ligands coordinated to [L₂M(H)₂]⁺⁺ fragments via two B-H-M bridges (M = Ru, n = 0; M = Rh, Ir, n =1; L = N-heterocyclic carbene, tertiary phosphine) formed either by the direct coordination of an aminoborane or by the in situ dehydrogenation of the corresponding amineborane.¹³⁻¹⁸
Thus, for example, Aldridge and co-workers have characterised $\kappa^2\sigma$-complexes of aminoboranes at Group 9 metal centres featuring N-heterocyclic carbene co-ligands from the *in situ* dehydrogenation of amineboranes [Scheme 5.1].\(^{15}\)

**Scheme 5.1**: Synthesis of an aminoborane adduct by dehydrogenation of an amineborane.

Additionally, the related charge neutral ruthenium aminoborane complex Ru(H)\(_2(\kappa^2\cdot\cdot\cdot)\cdot\text{H}_2\text{BN}^{\dagger}\text{Pr}_2)(\text{PCy}_3)_2\) has been prepared by the Weller and Sabo-Etienne groups by direct reaction of the aminoborane itself with a ruthenium bis(dihydrogen) complex [Scheme 5.2].\(^{16}\)

**Scheme 5.2**: Synthesis of a ruthenium aminoborane complex.

Additionally, Stradiotto and co-workers report a similar mode of coordination for mesitylborane, H\(_2\)BMes; the reaction of Cp*Ru(P\(^\dagger\)Pr\(_3\))Cl with (H\(_2\)BMes)\(_n\) followed by halide abstraction yields a similar $\kappa^2$ coordinated product [Scheme 5.3].\(^{19}\)
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Scheme 5.3: $\kappa^2$ aminoborane coordination at a cationic ruthenium centre.

The addition of a primary borane, $\text{H}_2\text{BR}$, to a metal fragment has also been exploited by Sabo-Etienne as a synthetic route to a terminal borylene complex although to date only for a single specific example. Initial coordination of $\text{H}_2\text{BMes}$ to $\text{RuHCl(H}_2\text{(PCy}_3\text{)}_2$ to give a $\kappa^2$ coordinated complex followed by hydrogen elimination yields a mesitylborylene complex [Scheme 5.4].

Scheme 5.4: Synthesis of a terminal borylene complex direct from a primary borane.

Oxidative addition represents an alternative reaction pathway between a borane and an electron rich metal centre. This fundamental step is extensively reported throughout the literature and has been the subject of wide-ranging and systematic study. For example,
early examples of group 9 boryl complexes were obtained by oxidative addition of B-H bonds to low valent iridium complexes with accompanying ligand dissociation.\textsuperscript{24,25} Thus, the reaction of HBCat with the \textit{in situ} generated 16-electron complex IrCl(PMe\textsubscript{3})\textsubscript{3} yields \textit{mer-}(CatB)Ir(H)Cl(PMe\textsubscript{3})\textsubscript{3} [Scheme 5.5].

\textbf{Scheme 5.5}: B-H oxidative addition giving the first crystallographically characterised boryl complex.

\subsection*{5.1.1 Aims of Present Research}

Given the successful synthesis of a mesityl borylene system from a $\sigma$-borane complex, as illustrated by Sabo-Etienne and co-workers,\textsuperscript{20} the current research targeted the synthesis of an aminoborylene complex via a similar approach. Initial studies probed the interaction of aminoborane ligands H\textsubscript{2}BNR\textsubscript{2} (R = \textsuperscript{3}Pr, Cy) with 14-electron metal centres of the type [Cp*Ru(L)]\textsuperscript{+}. Furthermore, with a view to examining the intrinsic two-electron donor capabilities of aminoboranes, synthetic studies continued by exploring the coordination of H\textsubscript{2}BNR\textsubscript{2} at 16-electron fragments of the type [CpRu(PR\textsubscript{3})\textsubscript{2}]\textsuperscript{+}. Additionally, it was decided to study the effects of aryl ligand substitution by considering the reaction of H\textsubscript{2}BNR\textsubscript{2} with [(\textit{p-}cymene)Ru(PR\textsubscript{3})Cl]\textsuperscript{+}.

With the fundamental coordination modes of aminoboranes on a firmer footing, research efforts then focused on the direct conversion of a dihydroborane to a metal borylene complex by exploiting the oxidative addition reactions of H\textsubscript{2}BNR\textsubscript{2} with a more electron rich Ir(I) precursor. Moreover, the primary boryl systems, L\textsubscript{n}M\{B(H)X\}, so formed presumably
offer the possibility for further ligand activation via α-H migration to generate a borylene complex, L₃MBX, in a manner analogous to textbook syntheses of carbene and silylene complexes.²⁶-²⁹ At present, this E to M α-hydride migration step has no precedent for boron, in part because primary boryl complexes are very rare.

5.2 Experimental

**Synthesis of [Cp*Ru(PCy₃)(κ²-H₂BNiPr₂)][BAR₄]**

H₂BNiPr₂ (0.39 cm³ of a 0.28 M solution in C₆H₅F, 0.108 mmol) was added to a solution of Cp*Ru(PCy₃)Cl (0.030 g, 0.054 mmol) in fluorobenzene (ca. 0.7 cm³). The blue reaction mixture was then added to Na[BAR₄] (0.052 g, 0.059 mmol) and an instant colour change to yellow was observed. The solution was filtered, layered with hexanes (30 cm³) and red crystals suitable for X-ray crystallography were obtained in 60 % yield.

Data for [5.2][BAR₄]: ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δH -11.21 (br, 2H, RuBH), 1.11-1.87 (m, 33H, PCy₃), 1.22 (d, 3JHH = 6.6 Hz, 12H, CH₃ of iPr), 1.81 (s, 15H, CH₃ of Cp*), 3.39 (sept, 3JHH = 6.6 Hz, 2H, CH of iPr), 7.47 (s, 4H, ortho-CH of [BAR₄]), 7.64 (s, 8H, para-CH of [BAR₄]). ¹³C NMR (126 MHz, CD₂Cl₂, 25°C): δC 11.9 (CH₃ of Cp*), 24.7, 26.7 (Cy CH₂-3,4), 27.9 (d, 2JPC = 10.1 Hz, Cy CH₂-2), 30.3 (CH₃ of iPr), 37.7 (d, 1JPC = 21.1 Hz, Cy CH), 49.9 (CH of iPr), 95.3 (Cp*), 117.9 (s, para-CH of [BAR₄]), 125.0 (q, 1JCF = 274.0 Hz, CF₃ of [BAR₄]), 129.3 (q, 2JCF = 31.0 Hz, meta-quatarnary C of [BAR₄]), 135.1 (s, ortho-CH of [BAR₄]), 162.1 (q, 1JCB = 50.1 Hz, ipso-quatarnary C of [BAR₄]). ¹¹B NMR (96 MHz, CD₂Cl₂, 25°C): δB 56.2 (br, fwhm = 300 Hz, H₂BNiPr₂), -6.1 ([BAR₄]). ¹⁹F NMR (282 MHz, CD₂Cl₂, 25°C): δF -62.0 (CF₃). ³¹P {¹H} NMR (121 MHz, CD₂Cl₂, 25°C): δP 53.3. MS (positive ion electrospray) m/z: [M]⁺ 630.4 (100%); exact mass for [M]⁺ 630.3980, calc.
630.3922. Elemental microanalysis: calc. (for C₆₆H₇₆B₂F₂₄NPRu) C 53.08, H 5.09, N 0.94; meas. C 52.87, H 4.92, N 0.86.

**Crystallographic Data:** C₆₆H₇₆B₂F₂₄NPRu, Mᵣ = 1492.95, monoclinic, P 2₁/c, a = 19.2398(1), b = 14.1958(1), c = 25.3427(2) Å, β = 99.7258(3)°, V = 3157.5(4) Å³, Z = 4, ρc = 1.453 Mg m⁻³, T = 150 K, λ = 0.71073 Å. 185601 reflections collected, 15523 independent [R(int) = 0.025] and used in all calculations. R₁ = 0.0428, wR₂ = 0.1011 for observed unique reflections [F² > 2σ (F²)] and R₁ = 0.0660, wR₂ = 0.1119 for all unique reflections. Max. and min. residual electron densities 0.93 and -0.82 e Å⁻³.

**Synthesis of [Cp*Ru(PCy₃)(κ²-B₂NPh₂)][BAr₄], [5.3][BAr₄]**

H₂BNCy₂ (0.37 cm³ of a 0.29 M solution in C₆H₅F, 0.108 mmol) was added to a solution of Cp*Ru(PCy₃)Cl (0.03 g, 0.054 mmol) in fluorobenzene (ca. 0.7 cm³). The blue reaction mixture was then added to Na[BAr₄] (0.052 g, 0.059 mmol) and an instant colour change to yellow was observed. The solution was filtered, layered with hexanes (30 cm³) and red crystals suitable for X-ray crystallography were obtained in 65% yield.

Data for [5.3][BAr₄]: ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δH -11.22 (br, 2H, RuBH), 0.97-2.16 (overlapping m, 53H, PCy₃, CH₂ of NCy₂), 1.78 (s, 15H, CH₃ of Cp*), 2.89 (m, 2H, CH of NCy₂), 7.46 (s, 4H, para-CH of [BAr₄]), 7.63 (s, 8H, ortho-CH of [BAr₄]). ¹³C NMR (126 MHz, CD₂Cl₂, 25°C): δC 11.9 (CH₃ of Cp*), 25.6 (NCy₂ CH₂-4), 26.5 (NCy₂ CH₂-3), 26.7 (PCy₃ CH₂-4), 27.9 (d, ₂JPC = 10.3 Hz, PCy₃ CH₂-2), 30.3 (NCy₂ CH₂-2), 36.0 (d, ³JCp = 2.7 Hz, PCy₃ CH₂-3), 37.6 (d, ₁JCP = 20.7 Hz, PCy₃ CH), 58.9 (NCy₂ CH-1), 95.3 (Cp*), 117.9 (s, para-CH of [BAr₄]), 125.0 (q, ₁JCF = 274.0 Hz, CF₃ of [BAr₄]), 129.3 (q, ²JCF = 31.0 Hz, meta-quaternary C of [BAr₄]), 135.1 (s, ortho-CH of [BAr₄]), 162.1 (q, ₁JCB = 50.1 Hz, ipso-quaternary C of [BAr₄]). ¹¹B NMR (96 MHz, CD₂Cl₂, 25°C): δB 56.5 (br, fwhm =
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300 Hz, H₂BNCY₂), -6.1 ([BAR′₄]). ¹⁹F NMR (282 MHz, CD₂Cl₂, 25°C): δF -62.0 (CF₃).
³¹P{¹H} NMR (121 MHz, CD₂Cl₂, 25°C): δp 54.4. MS (positive ion electrospray) m/z: [M]⁺ 710.5 (100%); exact mass for [M]⁺ 710.4505, calc. 710.4550. Elemental microanalysis: calc. (for C₇₂H₈₅B₂F₂₄NPRu) C 55.18, H 5.32, N 0.73; meas. C 54.93, H 5.40, N 0.89.

Crystallographic Data: C₇₂H₈₅B₂F₂₄NPRu, Mᵣ = 1573.08, monoclinic, P ₂₁, a = 12.7773(1), b = 17.3289(1), c = 17.9242(1) Å, β = 98.4578(3)°, V = 3925.55(4) Å³, Z = 2, ρc = 1.331 Mg m⁻³, T = 150 K, λ = 0.71073 Å. 69624 reflections collected, 16317 independent [R(int) = 0.045] and used in all calculations. R₁ = 0.0503, wR₂ = 0.1134 for observed unique reflections [F² > 2σ (F²)] and R₁ = 0.0453, wR₂ = 0.1083 for all unique reflections. Max. and min. residual electron densities 0.95 and -0.49 e Å⁻³.

Synthesis of [Cp*Ru(IMes)(κ²-H₂BNPr₂)][BAR′₄], [5.4][BAR′₄]

H₂BNPr₂ (0.37 cm³ of a 0.28 M solution in C₆H₅F, 0.104 mmol) was added to a solution of Cp*Ru(IMes)Cl (0.030 g, 0.052 mmol) in fluorobenzene (ca. 0.7 cm³). The blue reaction mixture was then added to Na[BAr′₄] (0.051 g, 0.057 mmol) and an instant colour change to yellow was observed. The solution was filtered, layered with hexanes (30 cm³) and red crystals suitable for X-ray crystallography were obtained in 60 % yield.

Data for [5.4][BAR′₄]: ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δH -9.71 (br, 2H, RuBH), 1.10 (d, 3JHH = 6.6 Hz, 12H, CH₃ of iPr), 1.35 (s, 15H, CH₃ of Cp*), 1.98 (br, 12H, ortho-CH₃ of Mes), 2.27 (s, 6H, para-CH₃ of Mes), 3.14 (sept, 3JHH = 6.6 Hz, 2H, CH of iPr), 6.97 (s, 4H, meta-CH of Mes), 7.04 (2?, 2H, NCH of IMes), 7.48 (s, 4H, para-CH of [BAR′₄]), 7.64 (s, 8H, ortho-CH of [BAR′₄]). ¹³C NMR (126 MHz, CD₂Cl₂, 25°C): δC 11.0 (CH₃ of Cp*), 19.6 (para-CH₃ of Mes), 20.2 (ortho-CH₃ of Mes), 21.1 (CH₃ of iPr), 49.4 (CH of iPr), 91.7 (Cp*), 117.9 (para-CH of [BAR′₄]), 124.9 (q, ¹JC = 273.0 Hz, CF₃ of [BAR′₄]), 125.6 (NCH of IMes),

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129.2 (q, $^2J_{CF} = 32.0$ Hz, meta-quaternary C of [BAR$^4$]), 130.0 (ortho-C of Mes), 135.2 (meta-C of Mes), 137.3 (para-C of Mes), 140.1 (ipso-C of Mes), 135.1 (ortho-CH of [BAR$^4$]), 162.2 (q, $^1J_{CB} = 50.1$ Hz, ipso-quaternary C of [BAR$^4$]), 180.2 (RUc of IMes). $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$, 25°C): δ$_B$ 49.9 (br, fwhm = 340 Hz H$_2$BN′Pr$_2$), -6.1 ([BAR$^4$]). $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$, 25°C): δ$_F$ -62.8 (CF$_3$). MS (positive ion electrospray) m/z: [M]$^+$ 654.4 (100%); exact mass for [M]$^+$ 654.3542, calc. 654.3542. Elemental microanalysis: calc. (for C$_{60}$H$_{67}$B$_2$F$_{24}$N$_3$Ru) C 54.61, H 4.45, N 2.77; meas. C 54.76, H 4.27, N 2.65.

**Crystallographic Data:** C$_{60}$H$_{67}$B$_2$F$_{24}$N$_3$Ru, $M_r$ = 1517.42, triclinic, P-1, $a = 12.8454(3)$, $b = 15.9928(4)$, $c = 18.3511(5)$ Å, α = 78.7012(10)°, β = 76.2493(11)°, γ = 77.1539(10)°, V = 3529.3(2) Å$^3$, Z = 2, ρ$_c$ = 1.425 Mg m$^{-3}$, T = 150 K, λ = 0.71073 Å. 20604 reflections collected, 12713 independent [R(int) = 0.038] and used in all calculations. $R_1 = 0.0729$, $wR_2 = 0.1832$ for observed unique reflections [F$^2 > 2\sigma$(F$^2$)] and $R_1 = 0.1003$, $wR_2 = 0.02081$ for all unique reflections. Max. and min. residual electron densities 1.45 and -1.18 e Å$^{-3}$.

**Synthesis of [Cp*Ru(PPh$_3$)(κ$^2$-H$_2$BN′Pr$_2$)][BAR$^4$], [5.5][BAR$^4$]**

H$_2$BN′Pr$_2$ (0.40 cm$^3$ of a 0.28 M solution in C$_6$H$_5$F, 0.112 mmol) was added to a suspension of [Cp*Ru(PPh$_3$)Cl]$_0$ (0.030 g, 0.056 mmol) in fluorobenzene (ca. 0.7 cm$^3$). The orange reaction mixture was then added to Na[BAR$^4$] (0.055 g, 0.062 mmol). The yellow solution was filtered, layered with hexanes (30 cm$^3$) and a brown oil was obtained in 50 % yield.

Data for [5.5][BAR$^4$]: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25°C): δ$_H$ -10.45 (br, 2H, RuBH), 1.47 (d, $^3J_{HH} = 6.6$ Hz, 12H, CH$_3$ of ‘Pr), 1.56 (s, 15H, CH$_3$ of Cp*), 3.04 (sept, $^3J_{HH} = 6.6$ Hz, 2H, CH of ‘Pr), 7.48 (s, 4H, para-CH of [BAR$^4$]), 7.34-7.66 (overlapping m, 15H, PPh$_3$), 7.64 (s, 8H, ortho-CH of [BAR$^4$]). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 25°C): δ$_C$ 10.8 (CH$_3$ of Cp*), 32.0 (CH$_3$ of ‘Pr), 50.6 (CH of ‘Pr), 97.7 (Cp*), 117.9 (s, para-CH of [BAR$^4$]), 125.0 (q, $^1J_{CF} = 274.0$ Hz,
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CF$_3$ of [BAR$_4^-$]), 129.3 (q, $^2$J$_{CF} = 31.0$ Hz, meta-quaternary C of [BAR$_4^-$]), 130.3 (d, $^4$J$_{CP} = 10.5$ Hz, para-CH of Ph), 133.7 (d, $^3$J$_{CP} = 11.7$ Hz, meta-CH of Ph), 134.4 (d, $^2$J$_{CP} = 12.3$ Hz, ortho-CH of Ph), 134.8 (d, $^1$J$_{CP} = 50.0$ Hz, ipso-C of Ph), 135.1 (s, ortho-CH of [BAR$_4^-$]), 162.1 (q, $^1$J$_{CB} = 50.1$ Hz, ipso-quaternary C of [BAR$_4^-$]). $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$, 25°C): \( \delta_B = 57.2 \) (br, fwhm = 380 Hz, H$_2$BNiPr$_2$), -6.1 ([BAR$_4^-$]). $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$, 25°C): \( \delta_F = -62.8 \) (CF$_3$). $^{31}$P{$^1$H} NMR (121 MHz, CD$_2$Cl$_2$, 25°C): \( \delta_P = 50.5 \). MS (positive ion electrospray) m/z: [M]$^+$ 612.2 (weak); exact mass for [M]$^+$ 612.2454, calc. 612.2513.

**Synthesis of [Cp*RuH(C$_6$H$_8$PCy$_2$)][BAR$_4^-$], [5.7][BAR$_4^-$]**

3,3-Dimethyl-1-butane (0.017 cm$^3$, 0.13 mmol) was added to a solution of [5.2][BAR$_4^-$] (0.020 g, 0.013 mmol) in fluorobenzene (ca. 0.7 cm$^3$) and the reaction mixture heated at 60°C for 8 d. In situ monitoring by $^{11}$B NMR spectroscopy revealed the generation of a (volatile) borane species (\( \delta_B = 41.3 \), d, $^1$J$_{BH} = 120$ Hz) over this period. The solution was filtered, layered with hexanes (30 cm$^3$) and yellow crystals suitable for X-ray crystallography were obtained in 45% yield.

Data for [5.7][BAR$_4^-$]: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25°C): \( \delta_H = -10.71 \) (m, 1H, RuH), 1.01-2.03 (m, 27H, C$_6$H$_8$PCy$_2$), 1.89 (s, 15H, CH$_3$ of Cp*), 3.23 (1H, m, CH of C$_6$H$_8$P), 3.70 (1H, m, CH of C$_6$H$_8$P), 3.92 (1H, m, CH of C$_6$H$_8$P), 7.48 (s, 4H, para-CH of [BAR$_4^-$]), 7.64 (s, 8H, ortho-CH of [BAR$_4^-$]). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 25°C): \( \delta_C = 10.9 \) (CH$_3$ of Cp*), 23.0 – 37.3 (overlapping m, two inequivalent Cy), 69.4, 69.9 (Cy CH$_2$-2,3), 78.5 (d, $^1$J$_{PC} = 21.0$ Hz, Cy CH-1), 85.8, 86.2, 97.3, 98.9 (Cy CH-4,5,6 and Cp*), 117.9 (s, para-CH of [BAR$_4^-$]), 125.1 (q, $^1$J$_{CF} = 274.0$ Hz, CF$_3$ of [BAR$_4^-$]), 129.3 (q, $^2$J$_{CF} = 31.0$ Hz, meta-quaternary C of [BAR$_4^-$]), 135.2 (s, ortho-CH of [BAR$_4^-$]), 162.1 (q, $^1$J$_{CB} = 50.1$ Hz, ipso-quaternary C of [BAR$_4^-$]). $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$, 25°C): \( \delta_F = -61.9 \) (CF$_3$). $^{31}$P{$^1$H} NMR (121 MHz, CD$_2$Cl$_2$, 25°C): \( \delta_P = 50.5 \).
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93.3. MS (positive ion electrospray) m/z: [M]+ 515.2 (weak); exact mass for [M]+ 515.2337, calc. 515.2383.

**Crystallographic Data:** \(C_{60}H_{58}BF_{24}PRu, \ M_r = 1377.93, \) monoclinic, \ C2/c, \(a = 18.9717(1), \ b = 17.2717(1), \ c = 36.3666(3) \text{ Å}, \ \beta = 94.5427(3)^\circ, \ V = 11878.9(1) \text{ Å}^3, \ Z = 8, \ \rho_c = 1.541 \text{ Mg m}^{-3}, \ T = 150 K, \ \lambda = 0.71073 \text{ Å}. \) 78601 reflections collected, 13517 independent \([R(int) = 0.000]\) and used in all calculations. \(R_1 = 0.0733, \ wR_2 = 0.1694\) for observed unique reflections \([F^2 > 2\sigma (F^2)]\) and \(R_1 = 0.1168, \ wR_2 = 0.1915\) for all unique reflections. Max. and min. residual electron densities 1.88 and -1.68 e Å\(^{-3}\).

**Synthesis of \([\text{Cp}*\text{Ru(PCI}_3)(t\text{BuNC})_2]^{\text{2-}}\text{[BAr}_4^\text{f}]^{\text{2+}}, \ [5.8]/[\text{BAr}_4^\text{f}]\)**

A solution of \([5.2]/[\text{BAr}_4^\text{f}]\) (0.020 g, 0.013 mmol) in fluorobenzene (ca. 0.7 cm\(^3\)) was added to \(t\text{BuNC}\) (0.017 cm\(^3\), 0.015 mmol) and the reaction mixture sonicated for 5 min. *In situ* monitoring by \(^{11}\text{B} \text{NMR spectroscopy} revealed the generation of \(\text{H}_2\text{BNNiPr}_2\) (\(\delta_B 35.4, \ t, ^1J_{BH} = 126\text{ Hz}\)). The solution was filtered, layered with hexanes (30 cm\(^3\)) and yellow crystals suitable for X-ray crystallography were obtained in 60 % yield.

Data for \([5.8]/[\text{BAr}_4^\text{f}]\): \(^1\text{H} \text{NMR} (300 \text{ MHz, CD}_2\text{Cl}_2, 25^\circ\text{C}): \delta_H 1.10-1.90 \text{ (m, 33H, PCI}_3\), 1.36 (s, 18H, \(t\text{BuNC})), 1.73 (\text{Cp}^*), 7.48 (s, 4H, \text{para-CH of [BAr}_4^\text{f}]\), 7.64 (s, 8H, \text{ortho-CH of [BAr}_4^\text{f}]\)). \(^{13}\text{C} \text{NMR} (126 \text{ MHz, CD}_2\text{Cl}_2, 25^\circ\text{C}): \delta_C 10.8 \text{ (CH}_3\text{ of Cp}^*\), 26.6 \text{ (Cy CH}_2-4\), 27.8 (d, \(^2J_{PC} = 10.4\text{ Hz}, \text{Cy CH}_2-2\)), 30.6 (Cy CH-3), 31.0 (CH\(_3\) of \(t\text{BuNC}\)), 37.4 (d, \(^1J_{PC} = 20.0\text{ Hz, Cy CH-1}\)), 57.9 (\text{Bu quaternary-C of [BAr}_4^\text{f}]\)), 96.3 (\text{Cp}^*), 117.9 (s, \text{para-CH of [BAr}_4^\text{f}]\)), 125.0 (q, \(^1J_{CF} = 274.0\text{ Hz, CF}_3\text{ of [BAr}_4^\text{f}]\)), 129.3 (q, \(^2J_{CF} = 31.0\text{ Hz, meta-quinartary C of [BAr}_4^\text{f}]\)), 135.1 (s, \text{ortho-CH of [BAr}_4^\text{f}]\)), 153.7 (CN of \(t\text{BuNC}\)), 162.1 (q, \(^1J_{CB} = 50.1\text{ Hz, ipso-quinartary C of [BAr}_4^\text{f}]\)\)). \(^{19}\text{F} \text{NMR} (282 \text{ MHz, CD}_2\text{Cl}_2, 25^\circ\text{C}): \delta_F -62.0\text{ (CF}_3\). \(^{31}\text{P}\{^1\text{H}\)
NMR (121 MHz, CD$_2$Cl$_2$, 25°C): $\delta_P$ 57.4. MS (positive ion electrospray) m/z: [M]$^+$ 683.4 (100%); exact mass for [M]$^+$ 683.4011, calc. 683.4012.

**Crystallographic Data:** C$_{70}$H$_{78}$BF$_{24}$N$_2$PRu, $M_r$ = 1546.47, monoclinic, $P 2_1/c$, $a = 13.7489$ (1), $b = 19.5577$ (2), $c = 27.5241$ (2) Å, $\beta = 99.9701(7)^\circ$, $V = 7400.1(1)$ Å$^3$, $Z = 5$, $\rho_c = 1.317$ Mg m$^{-3}$, $T = 293$ K, $\lambda = 1.54180$ Å. 46255 reflections collected, 15368 independent [R(int) = 0.027] and used in all calculations. $R_1 = 0.2099$, $wR_2 = 0.4896$ for observed unique reflections [F$^2 > 2\sigma (F^2)$] and $R_1 = 0.2172$, $wR_2 = 0.5056$ for all unique reflections. Max. and min. residual electron densities 14.47 and -6.26 e Å$^{-3}$.

**Synthesis of [CpRu(PPh$_3$)$_2$(κ$^1$-H$_2$BN$i$Pr$_2$)][BAR$_4$]**

Na[BAR$_4$] (0.040 g, 0.045 mmol) was added to a suspension of CpRu(PPh$_3$)$_2$Cl (0.030 g, 0.041 mmol) in fluorobenzene (ca. 0.7 cm$^3$) under a dinitrogen atmosphere, resulting in the formation of an intensely red solution, which subsequently turned into a paler (amber) solution over a period of ca. 30 s. H$_2$BN$i$Pr$_2$ (0.16 cm$^3$ of a 0.28 M solution in C$_6$H$_5$F, 0.045 mmol) was subsequently added to the solution and the reaction mixture sonicated for 5 min. The bright yellow solution was filtered, layered with hexanes (30 cm$^3$) and yellow crystals suitable for X-ray crystallography obtained in 30% yield. The product is extremely reactive in solution, and hence it has proved impossible to obtain reliable $^{13}$C NMR data due to reaction with the CD$_2$Cl$_2$ solvent.

Data for [5.13][BAR$_4$]: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, -30°C): $\delta_H$ -11.79 (br, 1H, RuBH), 0.95 (d, $^3$J$_{HH}$ = 6.9 Hz, 6H, CH$_3$ of 'Pr), 1.05 (d, $^3$J$_{HH}$ = 6.9 Hz, 6H, CH$_3$ of 'Pr), 3.38 (sept, $^3$J$_{HH}$ = 6.9 Hz, 1H, CH of 'Pr), 3.83 (sept, $^3$J$_{HH}$ = 6.9 Hz, 1H, CH of 'Pr), 4.59 (s, 5H, Cp), 6.78-7.27 (m, 30H, PPh$_3$), 7.52 (s, 4H, para-CH of [BAR$_4$]), 7.70 (s, 8H, ortho-CH of [BAR$_4$]). $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$, 25°C): $\delta_B$ 38.1 (br, fwhm = 420 Hz, H$_2$BN$i$Pr$_2$), -6.1 ([BAR$_4$]). $^{19}$F
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NMR (282 MHz, CD$_2$Cl$_2$, 25°C): $\delta_F$ -61.9 (CF$_3$). $^{31}$P$\{^1$H$\}$ NMR (121 MHz, CD$_2$Cl$_2$, 25°C): $\delta_P$ 32.9. Elemental microanalysis: calc. (for C$_{79}$H$_{63}$B$_2$F$_{24}$NP$_2$Ru) C 56.92, H 3.81, N 0.84; meas. C 56.88, H 3.78, N 0.77.

Crystallographic Data: C$_{79}$H$_{63}$B$_2$F$_{24}$NP$_2$Ru, $M_r = 1666.97$, monoclinic, P 2$_1$/n, $a = 20.0982(2)$, $b = 16.8675(2)$, $c = 22.0476(3)$ Å, $\beta = 94.1089(6)^\circ$, $V = 7455.1(1)$ Å$^3$, $Z = 4$, $\rho_c = 1.485$ Mg m$^{-3}$, $T = 150$ K, $\lambda = 0.71073$ Å. 111881 reflections collected, 29276 independent [R(int) = 0.048] and used in all calculations. $R_1 = 0.0552$, $wR_2 = 0.1091$ for observed unique reflections [$F^2 > 2\sigma (F^2)$] and $R_1 = 0.0736$, $wR_2 = 0.1299$ for all unique reflections. Max. and min. residual electron densities 1.62 and -1.53 e Å$^{-3}$.

Synthesis of [CpRu(dcype)(κ$^1$-H$_2$BN$i$Pr$_2$)][BAr$_f^4$], [5.14][BAr$_f^4$]

Na[BAr$_f^4$] (0.047 g, 0.053 mmol) was added to a suspension of CpRu(dcype)Cl (0.03 g, 0.048 mmol) in fluorobenzene (ca. 0.7 cm$^3$) under a dinitrogen atmosphere, resulting in the formation of an intensely red solution, which subsequently turned into a paler (amber) solution over a period of ca. 30 s. H$_2$BN$i$Pr$_2$ (0.19 cm$^3$ of a 0.28 M solution in C$_6$H$_5$F, 0.053 mmol) was subsequently added to the solution and the reaction mixture sonicated for 5 min. The bright yellow solution was filtered, layered with hexanes (30 cm$^3$) and a yellow oil was obtained in 30 % yield. The compound proved difficult to purify and therefore it is not possible to report a complete set of analytical and spectroscopic data.

Data for [5.14][BAr$_f^4$]: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25°C): $\delta_H$ -14.22 (br, 1H, RuBH), 0.71-0.91 (overlapping m, 60H, CH$_2$ and Cy of dcype, CH$_3$ of $^1$Pr), 3.42 (br, 1H, CH of $^1$Pr), 3.78 (br, 1H, CH of $^1$Pr), 4.71 (s, 5H, Cp), 6.1 (br, 1H, BH), 7.45 (s, 4H, para-CH of [BAr$_f^4$]), 7.61 (s, 8H, ortho-CH of [BAr$_f^4$]). $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$, 25°C): $\delta_B$ 37.6 (br, fwhm = 400
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Hz, H$_2$BNIPr$_2$), -6.1 ([BAR$_{4}^{f}$]). $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$; 25°C): $\delta$$_F$ -61.7 (CF$_3$). $^{31}$P$_{^{1}H}$ NMR (121 MHz, CD$_2$Cl$_2$; 25°C): $\delta$$_P$ 81.8.

**Synthesis of [(p-cymene)Ru(PCy$_3$)B(H)$_2$NIPr$_2$][BAR$_{4}^{f}$]. [5.19][BAR$_{4}^{f}$]**

H$_2$BNIPr$_2$ (0.36 cm$^3$ of a 0.28 M solution in C$_6$H$_5$F, 0.102 mmol) was added to a suspension of (p-cymene)Ru(PCy$_3$)Cl$_2$ (0.030 g, 0.051 mmol) in fluorobenzene (ca. 0.7 cm$^3$). The orange reaction mixture was then added to Na[BAR$_{4}^{f}$] (0.050 g, 0.056 mmol); the solution initially turned yellow, darkening over 3-5 min to an orange/brown colour. The reaction mixture was filtered, layered with hexanes (30 cm$^3$) and yellow/orange crystals were obtained in 60 % yield.

Data for [5.19][BAR$_{4}^{f}$]: $^{1}$H NMR (300 MHz, CD$_2$Cl$_2$, 25°C): $\delta$$_H$ -12.53 (br, 1H, RuBH), 1.06 (d, $^3$J$_{HH}$ = 7.2 Hz, 12H, CH$_3$ of $^3$Pr), 1.24 (d, $^3$J$_{HH}$ = 6.97 Hz, 6H, CH$_3$ of p-cymene $^3$Pr), 1.00-1.90 (m, 33H, PCy$_3$), 2.26 (s, 3H, CH$_3$ of p-cymene), 2.50 (sept, $^3$J$_{HH}$ = 7.2 Hz, 1H, CH of $^3$Pr p-cymene), 3.53 (br, 2H, CH of $^3$Pr), 5.30 (AB m, 2H, p-cymene aromatic CH), 5.58 (AB m, 2H, p-cymene aromatic CH), 7.46 (s, 4H, para-CH of [BAR$_{4}^{f}$]), 7.63 (s, 8H, ortho-CH of [BAR$_{4}^{f}$]). $^{13}$C NMR (76 MHz, CD$_2$Cl$_2$, 25°C): $\delta$$_C$ 18.3 (CH$_3$ of p-cymene), 19.1 (Cy CH$_2$-4), 23.0 (CH$_3$ of p-cymene $^3$Pr), 25.4 (Cy CH$_2$-3), 26.7 (d, $^2$J$_{CP}$ = 11.1 Hz, Cy CH$_2$-2), 29.0 (CH$_3$ of $^3$Pr), 31.6 (CH of p-cymene $^3$Pr), 37.0 (d, $^1$J$_{CP}$ = 23.3 Hz, Cy CH-1), 50.9 (CH of $^3$Pr), 84.8, 93.9, 97.1, 108.2 (p-cymene aromatic, 117.9 (s, para-CH of [BAR$_{4}^{f}$]), 125.0 (q, $^1$J$_{CF}$ = 274.0 Hz, CF$_3$ of [BAR$_{4}^{f}$]), 129.3 (q, $^2$J$_{CF}$ = 31.0 Hz, meta- quaternary C of [BAR$_{4}^{f}$]), 135.1 (s, ortho-CH of [BAR$_{4}^{f}$]), 162.1 (q, $^1$J$_{CB}$ = 50.1 Hz, ipso- quaternary C of [BAR$_{4}^{f}$]). $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$, 25°C): $\delta$$_B$ 35.5, d, $^1$J$_{BH}$ = 162 Hz, B(H)NIPr$_2$, -6.1 ([BAR$_{4}^{f}$]). $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$, 25°C): $\delta$$_F$ -61.8 (CF$_3$). $^{31}$P$_{^{1}H}$ NMR (121 MHz, CD$_2$Cl$_2$, 25°C): $\delta$$_P$ 63.4. MS
(positive ion electrospray) m/z: [M]$^+$ 628.4 (weak); exact mass for [M]$^+$ 628.3756, calc. 628.3752.

**Crystallographic Data:** $C_{66}H_{74}B_2NPRuF_{24}$, $M_r = 1491.44$, monoclinic, $P 2_1/c$, $a = 18.7504(1)$, $b = 14.6767(1)$, $c = 26.1631(2) \, \text{Å}$, $\beta = 101.8299(3)^\circ$, $V = 7047.0(1) \, \text{Å}^3$, $Z = 8$, $\rho_c = 1.404 \, \text{Mg m}^{-3}$, $T = 150 \, \text{K}$, $\lambda = 0.71073 \, \text{Å}$. 126395 reflections collected, 15950 independent [R(int) = 0.027] and used in all calculations. $R_1 = 0.0804$, $wR_2 = 0.1668$ for observed unique reflections [$F^2 > 2\sigma (F^2)$] and $R_1 = 0.1027$, $wR_2 = 0.1967$ for all unique reflections. Max. and min. residual electron densities 1.77 and -1.93 e Å$^{-3}$.

**Synthesis of [(p-cymene)Ru(PPh$_3$){B(H)N$i$Pr$_2$}][BAr$_f^4$], [5.20][BAr$_f^4$]**

H$_2$BN$i$Pr$_2$ (0.38 cm$^3$ of a 0.28 M solution in $C_6H_5F$, 0.106 mmol) was added to a suspension of (p-cymene)Ru(PPh$_3$)Cl$_2$ (0.030 g, 0.053 mmol) in fluorobenzene (ca. 0.7 cm$^3$). The orange reaction mixture was then added to Na[BAr$_f^4$] (0.052 g, 0.058 mmol); the solution initially turned yellow, darkening over 3-5 min to an orange/brown colour. The reaction mixture was filtered, layered with hexanes (30 cm$^3$) and yellow/orange crystals were obtained in 55% yield.

Data for [5.20][BAr$_f^4$]: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25°C): $\delta_H$ -11.43 (br, 1H, RuBH), 0.81 (br, 12H, CH$_3$ of $^3$Pr), 1.18 (d, $^3J_{HH} = 6.9$ Hz, 6H, CH$_3$ of p-cymene $^3$Pr), 2.21 (s, 3H, CH$_3$ of p-cymene), 2.59 (sept, $^3J_{HH} = 6.9$ Hz, 1H, CH of p-cymene $^3$Pr), 3.22 (br, 2H, CH of $^3$Pr), 5.18 (AB m, 2H, p-cymene aromatic CH), 5.21 (AB m, 2H, p-cymene aromatic CH), 7.26-7.74 (m, 15H, PPh$_3$), 7.48 (s, 4H, para-CH of [BAr$_f^4$]), 7.65 (s, 8H, ortho-CH of [BAr$_f^4$]). $^{13}$C NMR (121 MHz, CD$_2$Cl$_2$, 25°C): $\delta_C$ 20.1 (CH$_3$ of p-cymene), 24.2 (CH$_3$ of p-cymene $^3$Pr), 32.4 (CH$_3$ of $^3$Pr), 32.9 (CH of p-cymene $^3$Pr), 52.2 (CH of $^3$Pr), 90.2, 96.4, 99.7, 109.5 (p-cymene aromatic), 117.9 (s, para-CH of [BAr$_f^4$]), 125.1 (q, $^1J_{CF} = 274.0$ Hz, CF$_3$ of [BAr$_f^4$]), 129.1
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(d, $^2J_{CP} = 10.0$ Hz, meta-CH of Ph), 129.3 (q, $^2J_{CF} = 31.0$ Hz, meta-quaternary C of [BAR$_4^-$]), 131.7 (para-CH of Ph), 133.2 (d, $^3J_{CP} = 10.0$ Hz, ortho-CH of Ph), 133.8 (d, $^1J_{CP} = 51.0$ Hz, ipso-C of Ph), 135.2 (s, ortho-CH of [BAR$_4^-$]), 162.1 (q, $^1J_{CB} = 50.1$ Hz, ipso-quaternary C of [BAR$_4^-$]). $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$, 25°C): $\delta_{B} = 35.1$ (fwhm $^{11}$B{1H} = 300 Hz, fwhm $^{11}$B = 420 Hz, B(H)N{iPr}$_2$, -6.1 ([BAR$_4^-$]). $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$, 25°C): $\delta_{F} = 61.8$ (CF$_3$).

$^{31}$P{1H} NMR (121 MHz, CD$_2$Cl$_2$, 25°C): $\delta_{P} = 54.9$.

MS (positive ion electrospray) m/z: [M]$^+$ 610.2 (weak); exact mass for [M]$^+$ 610.2355, calc. 610.2357. Elemental Microanalysis: calc. (for C$_{66}$H$_{56}$B$_2$F$_{24}$NPRu) C 53.80, H 3.80, N 0.95; meas. C 53.93, H 3.72, N 0.86.

Crystallographic Data: C$_{66}$H$_{56}$B$_2$F$_{24}$NPRu, $M_r$ = 1472.79, triclinic, P-1, $a = 12.8893(2)$ Å, $b = 13.6791(3)$ Å, $c = 18.9851(4)$ Å, $\alpha = 91.751(9)^0$, $\beta = 90.1685(10)^0$, $\gamma = 90.5343(8)^0$, $V = 3346.5(1)$ Å$^3$, $Z = 2$, $\rho_c = 1.462$ Mg m$^{-3}$, $T = 150$ K, $\lambda = 0.71073$ Å. 46883 reflections collected, 15158 independent [R(int) = 0.040] and used in all calculations. $R_1 = 0.0710$, $wR_2 = 0.1329$ for observed unique reflections [F$^2 > 2\sigma (F^2)$] and $R_1 = 0.1133$, $wR_2 = 0.1779$ for all unique reflections. Max. and min. residual electron densities 1.58 and -1.66 e Å$^{-3}$.

Synthesis of [{(p-cymene)Ru(PMe$_3$)Cl$_2$}[BAR$_4^-$]$_2$, [5.21][BAR$_4^-$]$_2$

H$_2$BN{iPr}$_2$ (0.56 cm$^3$ of a 0.28 M solution in C$_6$H$_5$F, 0.157 mmol) was added to a suspension of (p-cymene)Ru(PMe$_3$)Cl$_2$ (0.030 g, 0.079 mmol) in fluorobenzene (ca. 0.7 mL) and the resulting orange reaction mixture added to Na[BAR$_4^-$] (0.077 g, 0.087 mmol). The orange/brown reaction mixture was filtered, layered with hexanes (30 cm$^3$) and yellow/orange crystals obtained in 70 % yield.

Data for [5.21][BAR$_4^-$]$_2$: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25°C): $\delta_{H} = 1.13$ (d, $^3J_{HH} = 7.2$ Hz, 6H, CH$_3$ of p-cymene {Pr}), 1.47 (d, $^2J_{CP} = 11.1$ Hz, 9H, PMe$_3$), 1.96 (s, 3H, CH$_3$ of p-cymene), 2.73 (sept, $^3J_{HH} = 7.2$ Hz, 1H, CH of p-cymene {Pr}), 5.40 (br AB m, 4H, p-cymene aromatic
CH), 7.48 (s, 4H, para-CH of [BAR₄⁺]), 7.65 (s, 8H, ortho-CH of [BAR₄⁺]). ¹³C NMR (121 MHz, CD₂Cl₂, 25°C): δ_C 16.3 (d, ¹¹J_PC = 33.4 Hz, PMe₃), 18.8 (CH₃ of p-cymene), 21.7 (CH₃ of p-cymene 'Pr), 32.0 (CH of p-cymene 'Pr), 79.3, 85.9, 90.0, 110.0 (p-cymene aromatic), 117.9 (s, para-CH of [BAR₄⁺]), 125.1 (q, ¹¹J_CF = 274.0 Hz, CF₃ of [BAR₄⁺]), 129.3 (q, ²¹J_CF = 31.0 Hz, meta-quaternary C of [BAR₄⁺]), 135.2 (s, ortho-CH of [BAR₄⁺]), 162.1 (q, ¹¹J_CB = 50.1 Hz, ipso-quaternary C of [BAR₄⁺]). ¹⁹F{¹H} NMR (282 MHz, CD₂Cl₂, 25°C): δ_F -61.8 (CF₃). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, 25°C): δ_P 2.7. MS (positive ion electrospray) m/z: [M]²⁺ 347.0 (30%); exact mass for [M]²⁺ 347.0317, calc. 347.0264.

Crystallographic Data: C₉₀H₇₀B₂Cl₂F₃P₂Ru₂, Mᵣ = 2420.06, orthorhombic, Pbca, a = 18.0497(3), b = 19.4109(4), c = 27.3740(5) Å, V = 9590.8(3) Å³, Z = 4, ρ_c = 1.676 Mg m⁻³, T = 150 K, λ = 1.54180 Å. 34544 reflections collected, 9963 independent [R(int) = 0.036] and used in all calculations. R₁ = 0.0716, wR₂ = 0.2117 for observed unique reflections [F² > 2σ (F²)] and R₁ = 0.0822, wR₂ = 0.2249 for all unique reflections. Max. and min. residual electron densities 2.14 and -1.39 e Å⁻³.

**Synthesis of [(p-cymene)Ru(PPh₃)(CN₆H₃Me₂-2,6){B(H)N'Pr₂}]¹⁺[BAR₄⁻], [5.22][BAR₄⁻]**

2,6-dimethylphenyl isocyanide (0.004 g, 0.027 mmol) was added to a solution of [(p-cymene)Ru(PPh₃)B(H)N'Pr₂][BAR₄⁻] (0.020 g, 0.014 mmol) in fluorobenzene (ca. 0.7 cm³) and the reaction mixture sonicated for 1 h, during which time the solution lightened to yellow. The solution was filtered, layered with hexanes (30 cm³) and a yellow oil was obtained in 50% yield.

Data for [5.22][BAR₄⁻]: ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ_H 1.11 (d, ³¹J_HH = 6.9 Hz, 6H, CH₃ of 'Pr), 1.14 (d, ³¹J_HH = 6.9 Hz, 6H, CH₃ of 'Pr), 1.25 (d, ³¹J_HH = 6.9 Hz, 6H, CH₃ of p-cymene 'Pr), 1.86 (s, 6H, ortho-CH₃), 1.97 (s, 3H, CH₃ of p-cymene), 2.50 (sept, ³¹J_HH = 6.9
Hz, 1H, CH of \( p \)-cymene \(^{1} \text{Pr} \), 3.34 (br, 2H, CH of \(^{1} \text{Pr} \)), 5.40 (m, 1H, \( p \)-cymene aromatic CH), 5.52 (m, 1H, \( p \)-cymene aromatic CH), 5.68 (m, 1H, \( p \)-cymene aromatic CH), 5.81 (m, 1H, \( p \)-cymene aromatic CH), 6.85-7.65 (m, 18H, PPh\(_{3}\) and 2,6-Me\(_{2}\)C\(_{6}\)H\(_{3}\)NC aromatic CH), 7.48 (s, 4H, \( para \)-CH of [BAr\(_{4}\)]), 7.65 (s, 8H, \( ortho \)-CH of [BAr\(_{4}\)]. \(^{13}\)C NMR (126 MHz, CD\(_{2}\)Cl\(_{2}\), 25°C): \( \delta \text{C} \) 18.7 (CH\(_{3}\) of \( p \)-cymene), 20.1 (\( ortho \)-CH\(_{3}\)), 21.8 (CH\(_{3}\) of \( p \)-cymene \(^{1} \text{Pr} \)), 29.4 (CH\(_{3}\) of \(^{1} \text{Pr} \)), 32.3 (CH\(_{3}\) of \(^{1} \text{Pr} \)), 32.7 (CH of \( p \)-cymene \(^{1} \text{Pr} \)), 49.6 (2 overlapping signals, CH of \(^{1} \text{Pr} \)), 92.5, 93.6, 95.9, 98.3, 98.6, 100.2 (\( p \)-cymene aromatic), 117.9 (s, \( para \)-CH of [BAr\(_{4}\)]), 125.1 (q, \(^{1} J_{\text{CF}} \) = 274.0 Hz, CF\(_{3}\) of [BAr\(_{4}\)]), 129.3 (q, \(^{2} J_{\text{CF}} \) = 31.0 Hz, \( meta \)-quaternary C of [BAr\(_{4}\)]), 129.0-135.3 (overlapping m, the assignment of the aromatic 2,6-Me\(_{2}\)C\(_{6}\)H\(_{3}\)NC and PPh\(_{3}\) resonances is difficult due to the signals being obscured by CF\(_{3}\), \( meta \)-quaternary C and \( ortho \)-CH groups of [BAr\(_{4}\)]), 135.2 (s, \( ortho \)-CH of [BAr\(_{4}\)]), 162.1 (q, \(^{1} J_{\text{CB}} \) = 50.1 Hz, \( ipso \)-quaternary C of [BAr\(_{4}\)]). \(^{11}\)B NMR (96 MHz, CD\(_{2}\)Cl\(_{2}\), 25°C): \( \delta \text{B} \) 35.0 (fwhm \(^{11}\)B\{\(^{1}\text{H}\}\) = 350 Hz, fwhm \(^{11}\)B = 450 Hz, B(\( H \))N\(^{1} \text{Pr} \)),-6.1 ([BAr\(_{4}\)]). \(^{19}\)F NMR (282 MHz, CD\(_{2}\)Cl\(_{2}\), 25°C): \( \delta \text{F} \) -61.8 (CF\(_{3}\)). \(^{31}\)P\{\(^{1}\text{H}\}\} NMR (121 MHz, CD\(_{2}\)Cl\(_{2}\), 25°C): \( \delta \text{p} \) 56.7. MS (positive ion electrospray) m/z: [M]\(^{+}\) 741.3 (weak); exact mass for [M]\(^{+}\) 741.3116, calc. 741.3095.

**Synthesis of mer-Ir(PMe\(_{3}\))\(_{2}\)Cl(H){B(H)N\(^{1} \text{Pr} \)}**, 5.26

H\(_{2}\)BN\(^{1} \text{Pr} \)(1.22 cm\(^{3}\) of a 0.28 M solution in C\(_{6}\)H\(_{3}\)F, 0.34 mmol) was added to a solution of Ir(coe)(PMe\(_{3}\))\(_{2}\)Cl (0.31 mmol) in toluene (40 cm\(^{3}\)), generated in situ from [Ir(coe)\(_{2}\)(\( \mu \)-Cl)]\(_{2}\) (0.15 g, 0.17 mmol) and PMe\(_{3}\) (0.070 g, 0.92 mmol); the reaction mixture was stirred at 20°C for 10 min. Volatiles were removed in vacuo and the resulting peach coloured powder recrystallised from hexanes at -80°C. The boryl complex 5.26 was isolated as a peach coloured powder in 48% yield.
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Data for 5.26: $^1$H NMR (300 MHz, C$_6$D$_6$, 25°C): $\delta$H -9.04 (dt, $^2$J$_{HP,trans}$ =141.3 Hz, $^2$J$_{HP,cis}$ = 21.0 Hz, 1H, IrH), 0.77 (d, $^3$J$_{HH}$ = 6.9 Hz, 3H, CH$_3$ of $^i$Pr), 0.87 (d, $^3$J$_{HH}$ = 6.9 Hz, 3H, CH$_3$ of $^i$Pr), 1.00 (d, $^2$J$_{HP}$ = 6.9 Hz, 9H, unique PMe$_3$), 1.91 (apparent t, $^2$J$_{PH}$ + $^4$J$_{PH}$ = 3.5 Hz, 18H, PMe$_3$), 2.92 (sept, $^3$J$_{HH}$ = 6.9 Hz, 1H, CH of $^i$Pr), 5.13 (sept, $^3$J$_{HH}$ = 6.9 Hz, 1H, CH of $^i$Pr), 7.18 (br, BH). $^1$H{$^{11}$B} NMR (300 MHz, C$_6$D$_6$, 20°C): $\delta$H 7.18 (d, $^3$J$_{PH}$ = 25.8 Hz). $^{13}$C{$^1$H} NMR (76 MHz, C$_6$D$_6$, 20°C): $\delta$C 14.7 (dt, $^1$J$_{PC}$ = 25.1 Hz, $^3$J$_{PC}$ = 2.9 Hz, unique PMe$_3$), 18.5 (apparent td, $^1$J$_{PC}$ + $^3$J$_{PC,trans}$ = 18.3 Hz, $^3$J$_{PC,cis}$ = 4.6 Hz, PMe$_3$), 20.7, 25.7 (CH$_3$ of $^i$Pr), 43.6, 50.1 (CH of $^i$Pr). $^{11}$B NMR (96 MHz, C$_6$D$_6$, 25°C): $\delta_B$ 46 (br, fwhm $^{11}$B{$^1$H} = 250 Hz, fwhm $^{11}$B = 300 Hz). $^{31}$P{$^1$H} NMR (121 MHz, C$_6$D$_6$, 25°C) $\delta$ -41.1 (d, $^2$J$_{PP}$ = 22.3 Hz, PMe$_3$), -50.0 (t, $^2$J$_{PP}$ = 22.3 Hz, unique PMe$_3$).

Synthesis of mer-Ir(PMe$_3$)$_2$Cl(H){B(H)NCy$_2$}, 5.27

H$_2$BNCy$_2$ (1.18 cm$^3$ of a 0.29 M solution in C$_6$H$_5$F, 0.34 mmol) was added to a solution of Ir(coe)(PMe$_3$)$_3$Cl (0.31 mmol) in toluene (40 cm$^3$), generated in situ from [Ir(coe)$_2$(μ-Cl)]$_2$ (0.15 g, 0.17 mmol) and PMe$_3$ (0.070 g, 0.92 mmol), and the reaction mixture stirred at 20°C for 10 min. Volatiles were removed in vacuo and the resulting peach coloured powder recrystallised from hexanes at -80 °C in 43 % yield. Single crystals were obtained by controlled cooling of a diethyl ether solution.

Data for 5.27: $^1$H NMR (300 MHz, C$_6$D$_6$, 25°C): $\delta$H -8.73 (dt, $^2$J$_{HP,trans}$ =140.7 Hz, $^2$J$_{HP,cis}$ = 21.3 Hz, 1H, IrH), 1.06-1.86 (overlapping m, 20H, CH$_2$ of Cy), 1.31 (d, $^2$J$_{HP}$ = 7.8 Hz, 9H, unique PMe$_3$), 1.49 (apparent t, $^2$J$_{PH}$ + $^4$J$_{PH}$ = 3.6 Hz, 18H, PMe$_3$), 2.84 (m, 1H, CH of Cy), 5.03 (br t, $^3$J$_{HH}$ = 8.4 Hz, 1H, CH of Cy), 7.38 (br, fwhm = ca. 100 Hz, BH). $^{13}$C{$^1$H} NMR (76 MHz, C$_6$D$_6$, 25°C): $\delta_C$ 20.8 (dt, $^1$J$_{PC}$ = 26.4 Hz, $^3$J$_{PC}$ = 2.2 Hz, unique PMe$_3$), 24.5 (apparent td, $^1$J$_{PC}$ + $^3$J$_{PC,trans}$ = 18.4 Hz, $^3$J$_{PC,cis}$ = 3.5 Hz, PMe$_3$), 25.1 (2 overlapping signals),
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25.4, 25.6, 26.7, 31.7 (CH\text{2} of Cy), 56.1, 49.7 (CH of Cy). $^{11}\text{B}$ NMR (96 MHz, C$_6$D$_6$, 25°C): δ$_{\text{B}}$ 43 (br, fwhm $^{11}\text{B}\{^1\text{H}\} = 230$ Hz, fwhm $^{11}\text{B} = 290$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C$_6$D$_6$, 25°C) δ$_{\text{P}}$ 40.1 (d, $^2\text{J}_{\text{PP}} = 21.1$ Hz, PMe$_3$), -43.1 (t, $^2\text{J}_{\text{PP}} = 21.1$ Hz, unique PMe$_3$). Elemental microanalysis: calc. (for C$_{21}$H$_{51}$BClIrNP$_3$) C 38.83, H 7.92, N 2.16; meas. C 38.71, H 7.90, N 2.08.

Crystallographic Data: C$_{21}$H$_{51}$BClIrNP$_3$, M$_r$ = 649.05, monoclinic, P2$_1$/c, $a$ = 16.3710(4) Å, $b$ = 14.3825(2) Å, $c$ = 15.8506(4 Å), β = 109.749°, V = 3512.6(1) Å$^3$, Z = 4, ρ$_c$ = 1.227 Mg m$^{-3}$, T = 150 K, λ = 0.71073 Å. 38213 reflections collected, 9503 independent [R(int) = 0.042] and used in all calculations. $R_1$ = 0.0311, w$R_2$ = 0.0751 for observed unique reflections [F$^2 > 2\sigma$(F$^2$)] and $R_1$ = 0.0504, w$R_2$ = 0.0908 for all unique reflections. Max. and min. residual electron densities 4.62 and -2.84 e Å$^{-3}$.

Synthesis of [fac-Ir(PMe$_3$)$_3$(H)$_2$(BNiPr$_2$)][BAr$_4$], [5.28][BAr$_4$]

A solution of 5.26 (0.100 g, 0.176 mmol) in fluorobenzene (30 cm$^3$) was added to Na[BAr$_4$] (1.1 equiv.) and the reaction mixture stirred at 20°C for 10 min. After filtration, volatiles were removed in vacuo and the residual solid washed with hexane.

Data for [5.28][BAr$_4$]: $^1\text{H}$ NMR (300 MHz, CD$_2$Cl$_2$, 25°C): δ$_{\text{H}}$ -11.98 (AA'X'X' multiplet, 2H, IrH), 1.19 (d, $^3\text{J}_{\text{HH}} = 6.0$ Hz, CH$_3$ of IrPr), 1.51 (d, $^2\text{J}_{	ext{HP}} = 9.3$ Hz, 9H, unique PMe$_3$), 1.58 (d, $^2\text{J}_{\text{HP}} = 8.1$ Hz, 18H, PMe$_3$), 3.27 (sept, $^3\text{J}_{\text{HH}} = 6.0$ Hz, 2H, CH of IrPr), 7.54 (s, 4H, para-CH of [BAr$_4$]), 7.61 (s, 8H, ortho-CH of [BAr$_4$]), $^{13}\text{C}$ NMR (76 MHz, CD$_2$Cl$_2$, 20°C) δ 23.9 (CH$_3$ of IrPr), 24.2 (dt, $^1\text{J}_{\text{PC}} = 27.8$ Hz, $^2\text{J}_{\text{PC}} = 4.5$ Hz, unique PMe$_3$), 24.6 (dd, $^1\text{J}_{\text{PC}} = 34.3$ Hz, $^3\text{J}_{\text{PC}} = 4.5$ Hz, PMe$_3$), 44.7 (CH of IrPr), 117.5 (para-CH of [BAr$_4$]), 123.4 (quart, $^1\text{J}_{\text{CF}} = 276.9$ Hz, CF$_3$ of [BAr$_4$]), 128.9 (quart, $^2\text{J}_{\text{CF}} = 35.1$ Hz, meta-C of [BAr$_4$]), 134.8 (ortho-CH of [BAr$_4$]), 161.2 (quart, $^1\text{J}_{\text{BF}} = 50.3$ Hz, ipso-C of [BAr$_4$]). $^{11}\text{B}$ NMR (96 MHz, CD$_2$Cl$_2$, 203
20°C; δ_B 77 (br, fwhm = 410 Hz, IrBN), -6.1 ([BAR'_4]^+). \(^{19}\)F NMR (282 MHz, CD_2Cl_2, 25°C) - 62.6 (CF_3). \(^{31}\)P \{^1\}H NMR (121 MHz, CD_2Cl_2, 25°C): δ_P -56.4 (d, \(^2\)J_PP = 24.9 Hz, PMe_3), -61.0 (br, unique PMe_3). MS (positive ion electrospray) m/z: [M]^+ 534.2 (10%); exact mass for [M]^+ 534.2329, calc. 534.2328.

**Synthesis of [fac-Ir(PMe_3)_3(H)(BNCy_2)][BAR'_4], [5.29][BAR'_4]**

A solution of \textbf{5.27} (0.10 g, 0.154 mmol) in fluorobenzene (30 cm\(^3\)) was added to Na[BAr'_4] (1.1 equiv.) and the reaction mixture stirred at 20°C for 10 min. After filtration, volatiles were removed \textit{in vacuo} and the residual solid washed with hexane. Recrystallisation from fluorobenzene/hexanes at -30°C gave single crystals suitable for X-ray crystallography in 70-80 % yield.

Data for [5.29][BAR'_4]: \(^1\)H NMR (300 MHz, CD_2Cl_2, 25°C): δ_H -12.06 (AA'MXX' multiplet, 2H, IrH), 0.85-1.60 (overlapping m, 20H, CH\(_2\) of Cy), 1.50 (d, \(^2\)J_HP = 8.7 Hz, 9H, unique PMe_3), 1.57 (d, \(^2\)J_HP = 7.8 Hz, 18H, PMe_3), 2.79 (tt, \(^3\)J_HH = 12.0, 3.3 Hz, 2H, CH of Cy), 7.48 (s, 4H, \textit{para}-CH of [BAr'_4]), 7.65 (s, 8H, \textit{ortho}-CH of [BAr'_4]). \(^{13}\)C NMR (76 MHz, CD_2Cl_2, 25°C) δ 23.2 (dt, \(^1\)J_CP = 32.2 Hz, \(^3\)J_CP = 3.5 Hz, unique PMe_3), 23.5 (dd, \(^1\)J_CP = 36.8 Hz, \(^3\)J_CP = 4.6 Hz, PMe_3), 24.2, 25.3, 34.5 (CH\(_2\) of Cy), 53.0 (CH of Cy), 118.4 (\textit{para}-CH of [BAR'_4]), 123.8 (quart, \(^1\)J_CF = 277.1 Hz, CF\(_3\) of [BAR'_4]), 128.2 (quart, \(^2\)J_CF = 35.1 Hz, \textit{meta}-C of [BAR'_4]), 134.7 (\textit{ortho}-CH of [BAR'_4]), 160.8 (quart, \(^1\)J_BF = 50.3 Hz, \textit{ipso}-C of [BAR'_4]). \(^{11}\)B NMR (96 MHz, CD_2Cl_2, 25°C): δ_B 77 (br, fwhm = 400 Hz, IrBN), -6.1 ([BAR'_4]^+). \(^{19}\)F NMR (282 MHz, CD_2Cl_2, 25°C) -62.6 (CF_3). \(^{31}\)P \{^1\}H NMR (121 MHz, CD_2Cl_2, 25°C): δ_P -56.7 (d, \(^2\)J_PP = 18 Hz, PMe_3), -61.1 (br, unique PMe_3). MS (positive ion electrospray) m/z: [M]^+ 614.3 (100%); exact mass for [M]^+ 614.2915, calc. 614.2956. \textbf{[5.29][BAR'Cl]} was obtained in analogous fashion using Na[BAR'Cl] and typically gave better quality crystals for X-ray
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diffraction. Spectroscopic data for the cationic component [5.29]$^+$ were identical for the two salts.

**Crystallographic Data:** $C_{45}H_{63}B_2Cl_6IrNP_3$, $M_r = 1208.39$, triclinic, P-1, $a = 12.1078(1)$, $b = 15.4482(2)$, $c = 15.9502(2)$ Å, $\alpha = 107.918^{\circ}$, $\beta = 93.832(1)^{\circ}$, $\gamma = 100.156(1)^{\circ}$, $V = 2770.7(1)$ Å$^3$, $Z = 2$, $\rho_c = 1.448$ Mg m$^{-3}$, $T = 150$ K, $\lambda = 0.71073$ Å. 47975 reflections collected, 12563 independent [R(int) = 0.034] and used in all calculations. $R_1 = 0.0349$, $\omega R_2 = 0.0615$ for observed unique reflections [$F^2 > 2\sigma$ ($F^2$)] and $R_1 = 0.0495$, $\omega R_2 = 0.0715$ for all unique reflections. Max. and min. residual electron densities 1.58 and -1.38 e Å$^{-3}$.

**Synthesis of [mer-Ir(PMe$_3$)$_3$Cl(H)(BNiPr)$_3$][BAr$_4$, [5.30][BAr$_4$]**

A solution of 5.26 (0.10 g, 0.176 mmol) in fluorobenzene (30 cm$^3$) was added to [Ph$_3$C][B(C$_6$F$_5$)$_4$, (1.1 equiv.) and the reaction mixture stirred at 20$^\circ$C for 10 min. After filtration, volatiles were removed in vacuo and the residual solid washed with hexane affording a 30-40 % yield.

Data for [5.30][BAr$_4$]: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25$^\circ$C): $\delta$ = -9.40 (dt, $^2J_{HP,trans} = 120.6$ Hz, $^2J_{HP,cis} = 17.6$ Hz, 1H, IrH), 1.30 (d, $^3J_{HH} = 6.3$ Hz, 6H, CH$_3$ of $^1$Pr), 1.56 (d, $^2J_{HP} = 8.4$ Hz, 9H, unique PMe$_3$), 1.77 (apparent t, $^2J_{PH} = 4.2$ Hz, 18H, PMe$_3$), 3.35 (sept, $^3J_{HH} = 6.3$ Hz, 2H, CH of $^1$Pr). $^{13}$C NMR (76 MHz, C$_6$D$_6$, 25$^\circ$C): $\delta_C = 18.8$ (dt, $^1J_{PC} = 32.4$ Hz, $^3J_{PC} = 1.9$ Hz, unique PMe$_3$), 19.5 (apparent td, $^1J_{PC} + ^3J_{PC,trans} = 21.0$ Hz, $^3J_{PC,cis} = 0.9$ Hz, PMe$_3$), 24.9 (CH$_3$ of $^1$Pr), 46.5 (CH of $^1$Pr), 135.7 (m, meta-CF of [B(C$_6$F$_5$)$_4$]), 137.7 (m, para-CF of [B(C$_6$F$_5$)$_4$]), 139.6 (m, ortho-CF of [B(C$_6$F$_5$)$_4$]). $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$, 25$^\circ$C): $\delta_B = -16$ ([B(C$_6$F$_5$)$_4$]), 71 (br, fwhm = 380 Hz, IrBN). $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$, 20$^\circ$C): $\delta_F = -165.4$ (ortho-CF of [B(C$_6$F$_5$)$_4$]), 165.3 (para-CF of [B(C$_6$F$_5$)$_4$]), -130.9 (meta-CF of [B(C$_6$F$_5$)$_4$]). $^{31}$P ($^1$H) NMR (121 MHz, CD$_2$Cl$_2$, 20$^\circ$C): $\delta_P = -43.4$ (d, $^2J_{PP} = 21.2$ Hz, PMe$_3$), -48.7 (t, $^2J_{PP} =$
21.2 Hz, unique PMe₃). The closely related compound [5.30][BAR⁺Cl⁻] can be obtained upon prolonged exposure of [5.28][BAR⁺Cl⁻] to dichloromethane and crystallised from dichloromethane/hexanes. Spectroscopic data for the cationic component [5.30]+ from either source is indistinguishable.

**Crystallographic Data:** C₃₀H₅₄B₂Cl₉IrNP₃, Mᵣ = 1162.70, orthorhombic, P nma, a = 16.4706(1), b = 17.2338(1), c = 17.2338(1) Å, V = 4976.85 Å³, Z = 4, ρc = 1.552 Mg m⁻³, T = 150 K, λ = 0.71073 Å. 54087 reflections collected, 5845 independent [R(int) = 0.034] and used in all calculations. R₁ = 0.0247, wR₂ = 0.0610 for observed unique reflections [F² > 2σ (F²)] and R₁ = 0.0313, wR₂ = 0.0676 for all unique reflections. Max. and min. residual electron densities 1.05 and -1.25 e Å⁻³.

**5.3 Results and Discussion**

**5.3.1 Bis(σ-BH) Coordination**

Initial studies probed the interaction of the aminoborane H₂BNiPr₂ with a series of cationic ruthenium metal centres. Utilising halide abstraction from the 16-electron starting material Cp*Ru(PCy₃)Cl (5.1), a putative 14-electron system can be accessed, promoting the chelating κ² coordination mode of binding [Scheme 5.6].

![Scheme 5.6: Synthesis of κ² aminoborane complexes of ruthenium.](image-url)
Pre-mixing $\text{H}_2\text{BN}^i\text{Pr}_2$ with the 16 electron ruthenium starting material 5.1 leads to no change in the $^{11}\text{B}$ or $^{31}\text{P}$ NMR spectra. However, treatment of the initial intense blue solution with a single equivalent of $\text{Na}[\text{BAR}_4^f]$ results in an immediate colour change to bright yellow. $^{11}\text{B}$ and $^{31}\text{P}$ NMR analysis of the reaction mixture reveals quantitative conversion to a complex giving rise to signals at $\delta_\text{B} \, 56.2$ and $\delta_\text{P} \, 53.3$ ppm. Filtering the sample and layering with hexanes afforded large red crystals suitable for X-ray crystallography in 60 % yield [Figure 5.1]. NMR spectroscopic data obtained on crystalline samples support the formation of [5.2]$^+$ [Scheme 5.6]; the $^1\text{H}$ NMR spectrum features signals associated with the Cp*, PCy$_3$, and [BAR$_4^f$]$_2$ moieties. In addition, a single set of signals corresponding to the CH (sept, $^3J_{\text{HH}} = 6.6$ Hz) and CH$_3$ (d, $^3J_{\text{HH}} = 6.6$ Hz) protons of the $^i\text{Pr}$ groups are observed, indicating the equivalence of the $^i\text{Pr}$ substituents as expected in a symmetrically bound $\kappa^2$ complex. Similar findings have previously been reported by Tang et al. in the synthesis of [M(IMes)$_2$(H)$_2$($\kappa^2$-$\text{H}_2\text{BN}^i\text{Pr}_2$))]$^+$ (M = Rh, Ir). Furthermore, a broad signal in the hydride region ($\delta_\text{H} \, -11.21$ ppm) which resolves to a doublet in the $^1\text{H}$[${}^{11}\text{B}$] spectrum ($^2J_{\text{HP}} = 15.0$ Hz), provides evidence for coordination of the aminoborane to the [Cp*Ru(PCy$_3$)]$^+$ fragment in solution. By means of comparison, the data reported for the high-field region of the $^1\text{H}$ NMR spectrum of the similar $\kappa^2$ complex [Cp*Ru($^i$Pr$_3$)($\kappa^2$-$\text{H}_2\text{BMes}$)]$^+$ is $\delta_\text{H} \, -10.3$ ppm ($^2J_{\text{PH}} = 15.0$ Hz). The $^{13}\text{C}$ NMR spectrum contains signals consistent with the $^1\text{H}$ NMR resonances, and as such is consistent with the structure proposed for [5.2]$^+$. ESI mass spectrometry shows the [M]$^+$ peak, also in accordance with the proposed structure, with accurate mass measurements as expected (meas. 630.3980, calc. 630.3922). Elemental microanalysis of a crystalline sample of [5.2][BAR$_4^f$] is also consistent with the proposed formulation.
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**Figure 5.1:** Molecular structure of [5.2][BAr₄]. Thermal ellipsoids set at the 35 % probability level; hydrogen atoms (except metal-bound hydrogens) and counter-ion omitted, and Cy groups shown in wireframe format for clarity.

**Table 5.1:** Selected bond lengths [Å] and angles [°] for [5.2][BAr₄].

<table>
<thead>
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<th>Bond</th>
<th>Length/Angle</th>
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<tr>
<td>Ru(1)···B(31)</td>
<td>1.965(3)</td>
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<tr>
<td>Ru(1)-P(2)</td>
<td>2.3880(6)</td>
</tr>
<tr>
<td>Ru(1)-B(31)-N(32)</td>
<td>171.6(2)</td>
</tr>
<tr>
<td>B(31)-N(32)</td>
<td>1.362(3)</td>
</tr>
</tbody>
</table>
The structure of the [5.2]$^+$ cation contains an aminoborane ligand featuring a planar C$_2$NBH$_2$ skeleton coordinated to the metal via two B-H-M interactions, and an essentially linear Ru···B-N framework [$\angle$Ru···B-N = 171.6(2)$^\circ$]. This orientation is similar to that observed for other κ$^2$-bound aminoborane ligands [e.g. 179.6(3)$^\circ$ for (IMes)$_2$Rh(H)$_2$(H$_2$BNiPr$_2$)].$^{15}$ The B-N distance [1.362(3) Å] is consistent with considerable π bond character [cf. 1.58 Å for the sum of the respective covalent radii and 1.380(6) Å for the B-N separation in Ph$_2$NBCl$_2$]. The Ru···B separation [1.965(3) Å] is statistically identical to that found for (Cy$_3$P)$_2$Ru(H)$_2$(κ$^2$-H$_2$BNiPr$_2$) [1.980(3) Å],$^{16}$ but significantly shorter than that reported for [CpRu(PMe$_3$)$_2$(κ$^1$-H$_3$B·NMe$_3$)]$^+$ [2.648(3) Å], presumably reflecting the presence of a three (rather than four)-coordinate boron centre and the possibility for Ru to B back-bonding.$^{30}$

A similar mode of coordination is also observed for the product of the analogous reaction with H$_2$BNCy$_2$ [Scheme 5.6]. Similar shifts are observed for [5.3]$^+$ in the $^{11}$B and $^{31}$P NMR spectra (δ$_B$ 56.5 ppm; δ$_P$ 54.4 ppm) and the $^1$H NMR spectrum displays a broad Ru-H-B hydride resonance at an almost identical shift (δ$_H$ = -11.22 ppm cf. -11.21 for [5.2]$^+$). $^1$H and $^{13}$C NMR spectra display the expected resonances for the PCy$_3$, Cp*, [BAR$^{\prime}$]$^4$] and equivalent Cy substituents. Moreover, ESI mass spectrometry, accurate mass measurements and elemental microanalysis are in agreement with the proposed structure, and red crystals suitable for X-ray crystallography were obtained from a fluorobenzene/hexane layering at room temperature. The structure of [5.3][BAR$^{\prime}$]$^4$] in the solid state [Figure 5.2] is very similar to that of [5.2][BAR$^{\prime}$]$^4$], exhibiting a linear Ru···B-N framework [$\angle$Ru···B-N = 169.8(3)$^\circ$] and a statistically identical Ru···B distance [1.986(4) Å]. Moreover, these observations are
consistent with spectroscopic data which features extremely similar $^{11}$B NMR shifts and bridging hydride $^1$H NMR resonances for [5.2]$^+$ and [5.3]$^+$. 
Figure 5.2: Molecular structure of [5.3][BAR₄]. Thermal ellipsoids set at the 35 % probability level; hydrogen atoms (except metal-bound hydrogens) and counter-ion omitted, and Cy groups shown in wireframe format for clarity.

Table 5.2: Selected bond lengths [Å] and angles [°] for [5.3][BAR₄].

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
<th>Angle [°]</th>
</tr>
</thead>
<tbody>
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<td>Ru(1)···B(20)</td>
<td>1.986(4)</td>
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<tr>
<td>Ru(1)-P(2)</td>
<td>2.384(1)</td>
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<tr>
<td>Ru(1)-B(20)-N(5)</td>
<td>169.8(3)</td>
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<tr>
<td>B(20)-N(5)</td>
<td>1.353(6)</td>
<td></td>
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</tbody>
</table>
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It has also proved possible to vary the ancillary two electron donor ligand, L at the ruthenium centre. The corresponding reactions of Cp*Ru(L)Cl (L = IMes, PPh₃) with Na[BAR′₄] and H₂BNiPr₂ yield, in each case, an adduct featuring a closely related κ² mode of coordination [Scheme 5.7].

![Scheme 5.7](image)

**Scheme 5.7:** Structural variation of cationic κ² ruthenium aminoborane complexes.

Both complexes [5.4]⁺ and [5.5]⁺ have been characterised by multinuclear NMR spectroscopy and mass spectrometry. The ¹¹B NMR spectrum of each compound features a broad resonance ([5.4]⁺: δᵦ 49.9 ppm; [5.5]⁺: δᵦ 57.2 ppm) and the corresponding ¹H NMR spectra feature hydride resonances associated with the RuHB hydrogens ([5.4]⁺: δᵦ -9.71 ppm; [5.5]⁺: δᵦ -10.45 ppm). The structure of [5.4][BAR′₄] has also been confirmed by single crystal X-ray diffraction and the molecular structure is shown in Figure 5.3. The structure of the [5.4]⁺ cation is also very similar to that of [5.2]⁺, displaying an almost linear Ru···B-N framework [∠Ru···B-N = 170.6(5)°] and a statistically identical Ru···B separation [1.972(6) Å]. Elemental microanalysis of a crystalline sample of [5.4][BAR′₄] is also consistent with the proposed structure. Unfortunately, crystals of [5.5]⁺ have thus far proved unobtainable; the [BAR′₄]⁻ salt is an oil.
Figure 5.3: Molecular structure of [5.4][BAR$_4^-$]. Thermal ellipsoids set at the 35 % probability level; hydrogen atoms and counter-ion omitted, and mesityl groups shown in wireframe format for clarity.

Table 5.3: Selected bond lengths [Å] and angles [°] for [5.4][BAR$_4^-$].

<table>
<thead>
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<th>Bond/Angle</th>
<th>Length/Angle</th>
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<tbody>
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<td>Ru(1)⋯B(31)</td>
<td>1.972(6)</td>
</tr>
<tr>
<td>Ru(1)-C(2)</td>
<td>2.113(5)</td>
</tr>
<tr>
<td>Ru(1)-B(31)-N(32)</td>
<td>170.6(5)</td>
</tr>
<tr>
<td>B(31)-N(32)</td>
<td>1.372(7)</td>
</tr>
</tbody>
</table>
Despite their isoelectronic relationship with 1,1-disubstituted alkenes, the coordination chemistry of aminoboranes has only very recently begun to be examined and compounds \([5.2]^+\) - \([5.5]^+\) can be viewed as members of a limited class of isolable cationic complexes featuring \(\kappa^2\) B-H ligation. Such a coordination geometry contrasts with the classical ‘side-on’ binding mode observed for alkene donors within the same framework.\(^{14,15}\) This can be rationalised by the more hydridic nature of the B-H bonds (cf. C-H), and the significantly lower energy of the B=N \(\pi\) system (cf. C=C).\(^{31}\) Consistently, Alcaraz and Sabo-Etienne report an energetic preference of 14.3 kcal mol\(^{-1}\) for the ‘end-on’ \(\text{bis}(\sigma\text{-BH})\) coordination geometry of \(\text{H}_2\text{BNH}_2\) at \([L_2\text{Ru(H)}_2]\).\(^{13}\)

Unlike the analogous mesityl complex \(\text{Ru}((\text{HCl})\text{(PCy}_3)_2(\kappa^2\text{-H}_2\text{BMes})\) reported by Sabo-Etienne, \([5.2][\text{BAR}^4]\) is robust under reduced pressure.\(^{20}\) Additionally, \([5.2]^+\) appears to be thermally stable up to temperatures ~70°C. Therefore, in an attempt to dehydrogenate \([5.2]^+\), the reaction with 3,3-dimethyl-1-butene was examined. Heating a sample of \([5.2][\text{BAR}^4]\) at 60°C for 7 days does not, however, lead to dehydrogenation as anticipated, but to a hydroboration reaction and the isolation of \([5.7]^+\) which features an activated cyclohexyl ring containing an allyl moiety [Scheme 5.8].
Scheme 5.8: Synthesis of [5.7]$^+$ via hydroboration.

*In situ* monitoring of the reaction mixture revealed the generation of a species at $\delta_B$ 41.3 ppm, (d, $^1J_{BH} = 120$ Hz) postulated as 5.6, and the $^{31}$P NMR spectrum revealed slow conversion to a single species at $\delta_P$ 93 ppm. Layering the fluorobenzene reaction solution with hexanes afforded yellow crystals of [5.7][Bar$^{4}$] suitable for X-ray diffraction [Figure 5.4]. The coordination about the ruthenium metal centre involves the Cp* ligand, the phosphine donor and three carbon atoms of a dehydrogenated cyclohexyl group, indicative of an allyl interaction [Ru(1)-C(13) = 2.270(5) Å, Ru(1)-C(12) = 2.096(5) Å, Ru(1)-C(11) = 2.261(5) Å]. The C(11)-C(12) and C(12)-C(13) distances [1.407(9) Å and 1.414(8) Å, respectively] are significantly shorter than the values expected for a single C-C bond in a cyclohexyl group.

NMR spectroscopic data further supports the formation of [5.7][Bar$^{4}$]: $^1$H NMR data features a single hydride resonance ($\delta_H$ -10.71 ppm) and the expected resonance for Cp*. Furthermore, three distinct multiplets between 3 and 4 ppm correspond to the allyl hydrogens. The $^{13}$C
NMR data is also consistent with the assignment of \( [5.7]^+ \). ESI mass spectrometry reveals the \([M]^+\) peak and accurate mass measurements are as expected (meas. 515.2337, calc. 515.2383). Moreover, this data corresponds with an earlier report of the cation as the \([\text{BF}_4]^-\) salt.\(^{32}\) The postulated mechanism for the transformation shown in Scheme 5.8 involves initial hydroboration by the aminoborane fragment to generate \( 5.6 \) and the transient ruthenium fragment \([\text{Cp*Ru(PCy}_3])^+\), which through oxidative addition, \( \beta \) hydride elimination, elimination of dihydrogen and a second CH oxidative addition step leads to the formation of the 18-electron allyl cation \( [5.7]^+ \) [Scheme 5.8].
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**Figure 5.4**: Molecular structure of $[5.7][\text{BAR}_4^t]$. Thermal ellipsoids set at the 35 % probability level; hydrogen atoms (except metal-bound hydrogen) and counter-ion omitted, and Cy groups shown in wireframe format for clarity.

**Table 5.4**: Selected bond lengths [Å] and angles [°] for $[5.7][\text{BAR}_4^t]$.

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<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
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<td>79.8(1)</td>
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<tr>
<td>P(2)-Ru(1)-C(12)</td>
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<td>99.6(2)</td>
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</tbody>
</table>
5.3.2 Mono(σ-BH) Coordination

As previously discussed, in structurally characterised systems reported to date the coordination of aminoboranes occurs exclusively via end-on binding. However, the utilisation of cationic 14-electron metal systems presumably distorts the structural landscape in favour of the four-electron-donating bis(σ-BH) coordination mode over the corresponding (two-electron-donating) side-on π-bound motif. With this in mind, research set out to investigate the intrinsic two-electron donor capabilities of aminoborane ligands.

In an attempt to displace one Ru-H-B bond from the metal coordination sphere and thereby effect a change from bis to mono(σ-BH) binding, [5.2]+ was reacted with a series of neutral two electron donor ligands. These studies revealed that, while [5.2]+ does not react with THF, the reactions with tBuNC, Ph₂CO, PMe₃, PPh₃ and PCy₃ lead in each case to borane extrusion, as indicated by in situ $^{11}$B NMR monitoring. The reaction between [5.2]+ and [PPh₄]Cl results in regeneration of the intensely blue coloured starting material Cp*Ru(PCy₃)Cl (5.1) (δ$_p$ 39 ppm) and H₂BNPr₂. In the case of the reaction with tBuNC, this borane extrusion mode of reactivity was also confirmed by the isolation and structural characterisation of [5.8][BAR₄′] from the reaction mixture [Scheme 5.9].

![Scheme 5.9: Displacement of H₂BNPr₂ from [5.2]+](image)

Single crystals of [5.8][BAR₄′] suitable for X-ray crystallography were obtained from a fluorobenzene/hexane layering [Figure 5.5]. Although specific bond lengths cannot be
discussed due to the poor quality of the data, multinuclear NMR spectroscopy and mass spectrometry (including accurate mass measurements) further supports the proposed formation of [5.8]$^+$. 

**Figure 5.5:** Molecular structure of [5.8][BAR$_4^-$]. Thermal ellipsoids set at the 35 % probability level; hydrogen atoms and counter-ion omitted, and Cy groups shown in wireframe format for clarity.

Because this approach proved unsuccessful in the synthesis of a mono($\sigma$-BH) complex, an alternative strategy was sought via coordination of monomeric H$_2$BNR$_2$ at *in situ* generated cationic 16-electron fragments of the type [CpRu(PR$_3$)$_2$]$^+$. While such metal systems are known to be capable of the ‘side-on’ binding of alkenes, an alternative mono($\sigma$-BH) mode of aminoborane ligation was established for the aminoboranes, H$_2$BNR$_2$ (*vide infra*).
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The reaction of CpRu(PPh$_3$)$_2$Cl (5.9) with Na[BAr$_f^t$]$_4$ under an atmosphere of nitrogen leads to the synthesis of \( [\{CpRu(PPh_3)_2\}_{2}(\mu-N_2)][BAr_f^t]_2 \) (5.11)[BAr$_f^t$]$_2$. Subsequent reaction with H$_2$BNiPr$_2$ generates [CpRu(PPh$_3$)$_2$(κ$_1$-H$_2$BNiPr$_2$)][BAr$_f^t$] (5.13)[BAr$_f^t$]) in near quantitative yield (as judged by multinuclear NMR spectroscopy) [Scheme 5.10]. Cleaner synthesis is achieved through the dinitrogen intermediate [5.11]$^{2+}$; the same reaction under an argon atmosphere yields a mixture of ruthenium and phosphorus containing products.

![Scheme 5.10: Synthesis of κ$_1$ aminoborane complexes [5.13]$^+$ and [5.14]$^+$.](image)

[5.13][BAr$_f^t$]$_4$] has been characterised by $^1$H, $^{11}$B, $^{19}$F and $^{31}$P NMR spectroscopy, elemental microanalysis, and single-crystal X-ray diffraction. The $^{11}$B NMR spectrum features a broad resonance ($\delta_B$ 35 ppm) which is not shifted significantly from the free aminoborane ($\delta_B$ 35.4 ppm). However, the $^1$H NMR spectrum is more informative, featuring distinct resonances associated with the RuHB and BH hydrogens ($\delta_H$ 11.79 and 6.54 ppm), signalling...
the presence of a single Ru-H-B bridging interaction. Moreover, two independent sets of signals for the CH and CH$_3$ protons of the $^i$Pr groups indicate inequivalence of these substituents, as expected for a $\kappa^1$ complex. The $^{31}$P NMR spectrum displays a single resonance ($\delta_P$ 32.9 ppm) at room temperature due to rapid rotation of the aminoborane ligand about the Ru-(BH centroid) axis (vide infra). Yellow crystals suitable for X-ray crystallography were obtained from a fluorobenzene/hexane layering at room temperature [Figure 5.6]. Furthermore, elemental microanalysis is consistent with the proposed formulation.

The structure of the cationic component of [5.13][BAR$^4$] features a three-legged piano stool geometry at ruthenium and a mono($\sigma$-BH) bound aminoborane ligand, characterised by a bent Ru···B-N framework [$\angle$Ru(1)···B(45)-N(46) = 131.5(3)$^\circ$] which contrasts the essentially linear fragment found for $\kappa^2$ H$_2$BN$i$Pr$_2$ complexes (e.g. 171.6(2)$^\circ$ for [5.2]$^+\)$. The presence of a single Ru-H-B bridging interaction is further revealed by disparate Ru-H and B-H contacts in the solid state [$d$[Ru(1)-H(44)] = 1.966, $d$[Ru(1)···H(29)] = 2.896 Å; $d$[B(45)-H(44)] = 1.201, $d$[B(45)-H(29)] = 1.090 Å]. Moreover, the presence of only one bridging hydrogen atom is consistent with a Ru···B distance [2.352(4) Å] which is significantly longer than found in $\kappa^2$ complexes (e.g. 1.965(3) Å for [5.2]$^+\)$. The Ru···B distance is, however, shorter than that in [CpRu(PMe$_3$)$_2$($\kappa^1$-H$_3$B·NMe$_3$)]$^+$ [2.648(3) Å], presumably reflecting the presence of a three coordinate boron centre and the possibility for back-bonding from ruthenium.$^{30}$
Figure 5.6: Molecular structure of [5.13][BAR₄]. Thermal ellipsoids set at the 35% probability level; hydrogen atoms (except boron-bound hydrogens) and counter-ion omitted, and Ph groups shown in wireframe format for clarity.

Table 5.5: Selected bond lengths [Å] and angles [°] for [5.13]+.

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<thead>
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<th>Bond Lengths [Å]</th>
<th>Angles [°]</th>
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<td>Ru(1)-P(21)</td>
<td>2.334(1)</td>
</tr>
<tr>
<td>B(45)-H(29)</td>
<td>1.090</td>
</tr>
<tr>
<td>B(45)-H(44)</td>
<td>1.201</td>
</tr>
<tr>
<td>Ru(1)-B(45)-N(46)</td>
<td>131.5(3)</td>
</tr>
</tbody>
</table>
The synthesis of the related system \([\text{CpRu(dcype)}(\kappa^1-\text{H}_2\text{BN}^\prime\text{Pr}_2)][\text{BAR}^4]\) ([5.14][BAR^4]) has also proved to be possible via the reaction of \(\text{CpRu(dcype)}\text{Cl}\) (5.10) with \(\text{Na[BAR}^4]\) and \(\text{H}_2\text{BN}^\prime\text{Pr}_2\) under a nitrogen atmosphere. [5.14][BAR^4] has been characterised spectroscopically by \(^1\text{H}, ^{11}\text{B}, ^{19}\text{F}, \text{and} ^{31}\text{P NMR spectroscopy. Again, the} ^{11}\text{B NMR spectrum features a broad resonance (δ}_B 35 \text{ ppm) and the} ^{31}\text{P NMR spectrum displays a single resonance at δ}_P 81.8. The} ^1\text{H NMR spectrum is extremely similar to \([5.13][\text{BAR}^4]\) and features distinct resonances associated with the RuHB and BH hydrogens (δ}_H -14.22 \text{ and 6.10 ppm) and distinct sets of signals for the} ^3\text{Pr groups. Interestingly, the bridging hydride is more hydridic than that associated with [5.13]}^+ (\text{vide infra}). Unfortunately, due to the product being an oil, single crystals suitable for X-ray crystallography have proved unobtainable at this time.

Work in the group by Dr. Drasko Vidovic resulted in the synthesis of the analogous dicyclohexylaminoborane complexes \([\text{CpRu(PPh}_3)_2(\kappa^1-\text{H}_2\text{BNCy}_2)][\text{BAR}^4]\) ([5.15][BAR^4]) and \(\text{CpRu(dcype)}(\kappa^1-\text{H}_2\text{BNCy}_2)][\text{BAR}^4]\) ([5.16][BAR^4]) [Scheme 5.11]. Both complexes have been characterised by multinuclear NMR spectroscopy, X-ray diffraction and elemental microanalysis. These data are, as expected, similar to those measured for [5.13][BAR^4] and [5.14][BAR^4].

\[\begin{align*}
\text{Cp} & \quad \text{Na[BAR}^4], \text{N}_2 \text{ atmosphere} \\
\text{Ru} & \quad \text{H}_2\text{BNCy}_2 \\
\text{Cl} & \quad \text{fluorobenzene} \\
\text{R}_3\text{P} & \quad [\text{BAR}^4]^+ \\
\text{R}_3\text{P} & \quad (\text{R}_3\text{P})_2 (\text{R}_3\text{P})_2
\end{align*}\]

\[\begin{align*}
\text{5.9} & \quad (\text{R}_3\text{P})_2 = (\text{Ph}_3\text{P})_2 \\
\text{5.10} & \quad (\text{R}_3\text{P})_2 = \text{dcype} \\
\text{5.15} & \quad (\text{R}_3\text{P})_2 = (\text{Ph}_3\text{P})_2 \\
\text{5.16} & \quad (\text{R}_3\text{P})_2 = \text{dcype}
\end{align*}\]

\textbf{Scheme 5.11}: Synthesis of κ^1 aminoborane complexes [5.15]^+ and [5.16]^+. 
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The $^{11}$B NMR spectrum of each compound exhibits a broad signal at $\delta_B$ 35 ppm and the $^{31}$P NMR spectrum of both compounds displays a single resonance at room temperature. The separate signals associated with RuHB and BH hydrogens are at a similar chemical shift for those found in $[5.13]^+$ and $[5.14]^+$ ($\delta_H$ -11.97 and 6.39 for $[5.15]^+$; $\delta_H$ -14.56 and 5.80 ppm for $[5.16]^+$). Additionally, unequivocal characterisation of both complexes was obtained by X-ray crystallography. The structures are very similar to that reported for $[5.13][\text{BAr}_4^+]$ displaying a bent Ru-B-N fragment ($\angle\text{Ru} \cdots \text{B-N} = 130.2(3)^\circ$ for $[5.15]^+$, 133.1(4)$^\circ$ for $[5.16]^+$) consistent with $\kappa^1$ binding. Here too, differing Ru-H and B-H distances in the solid state confirm the presence of a single Ru-H-B bridging interaction (e.g. for $[5.16]^+$: $d[\text{Ru-H}] = 1.669(1)$, $d[\text{Ru} \cdots \text{H}] = 2.887$ Å; $d[\text{B-H}] = 1.244(6)$, $d[\text{B-H}] = 1.150(5)$ Å). The structures exhibit Ru···B distances of 2.430(4) Å and 2.332(6) Å for $[5.15]^+$ and $[5.16]^+$, respectively; the Ru···B distances measured for $[5.15]^+$ and $[5.13]^+$ are statistically identical.

Further observations are consistent with the possibility for back-bonding from the highest occupied molecular orbital (HOMO) of the $[\text{CpRu(PR}_3)_2]^+$ fragment into a B-H $\sigma^*$ orbital of the coordinated borane in $[5.13]^+$, $[5.14]^+$, $[5.15]^+$ and $[5.16]^+$. The alignment of the coordinated B-H bond with respect to the $[\text{CpRu(PR}_3)_2]^+$ fragment (evident, for example, by a (Cp centroid)-Ru-(BH centroid)-B torsion angle of 113.5$^\circ$ for $[5.13]^+$) maximises the potential for overlap between the respective orbitals [Figure 5.7a,b]. Additionally, the shorter Ru···B distances and longer B-H bonds in $[5.16]^+$ [2.332(6) and 1.244(6) Å, respectively] compared to $[5.15]^+$ [2.430(4) and 1.207(4) Å, respectively] are consistent with greater backbonding from the HOMO of the metal fragment to the B-H $\sigma^*$ orbital of the coordinated borane from the more electron rich $[\text{CpRu(dctype})]^+$ fragment (cf. $[\text{CpRu(PPh}_3)_2]^+$). Moreover, the chemical shifts of the RuHB bridging hydrogen are markedly more hydridic in the case of $[5.14]^+$ and
[5.16]^+ (δ_H 14.22 and 14.56) compared to [5.13]^+ and [5.15]^+ (δ_H 11.79 and 11.97). By contrast, the BN distances for [5.13]^+, [5.15]^− and [5.16]^+ are statistically identical [1.384(6), 1.376(4) and 1.382(7) Å, respectively], suggesting little population of the BN π* orbital which lies effectively orthogonal to the metal-based HOMO [Figure 5.7c]. This behaviour apparently contrasts that witnessed for (Cy3P)2Ru(H)(κ2-H2BNPr2), for example, for which back-bonding into the BN π* orbital is proposed.16,33

Since both complexes utilising the dicyclohexylaminoborane H2BNCy2 have been fully characterised by X-ray crystallography (in contrast to the iPr derivatives [5.13]^+ and [5.14]^+), it was decided to conduct variable temperature NMR spectroscopy and related DFT studies on complexes [5.15]^+ and [5.16]^+. For [5.16]^+, at very low temperatures the 31P NMR spectrum exhibits two resonances (at δP 79 and 83 ppm) due to slow rotation about the Ru-BH centroid [Figure 5.8a]. Coalescence occurs at -50 °C with a barrier to rotation of ΔG‡ = 9.9 kcal mol⁻¹ being calculated. This barrier is marginally greater than that reported by Schlecht and Hartwig for the comparable fluxional process in CpMn(CO)2(HBCat).34 By contrast, the analogous process for [5.15]^+ cannot be frozen out even at -90°C, presumably due to weaker binding of the borane, thereby implying a barrier less than ca. 7 kcal mol⁻¹. A second fluxional
process can be identified for both complexes which involves the exchange of the bound and unbound BH hydrogens, resulting in the coalescence of the RuHB and BH resonances. For \([5.15]^+\), coalescence occurs at 7°C with an associated barrier of \(\Delta G^{\ddagger} = 12.8 \text{ kcal mol}^{-1}\). A larger barrier is obtained for \([5.16]^+\) (\(T_c = 28 \, ^\circ\text{C}, \Delta G^{\ddagger} = 14.3 \text{ kcal mol}^{-1}\)) again due to tighter binding of the borane, as implied crystallographically.

![Diagram of fluxional processes involving the B-H bonds in \(\kappa^1\) aminoborane systems.](image)

**Figure 5.8:** Fluxional processes involving the B-H bonds in \(\kappa^1\) aminoborane systems.

The probable mechanism for the ‘wagging’ exchange process shown in Figure 5.8b has also been investigated for \([5.16]^+\) by Density Functional Theory. A transition state can be identified at a free energy of +17.5 kcal mol\(^{-1}\) with respect to \([5.16]^+\) [Figure 5.9]. The transition state geometry is consistent with a concerted non-dissociative exchange process, featuring a more symmetrically bound aminoborane ligand (\(d[\text{Ru-H}] = 2.261, 2.334 \, \text{Å}; d[\text{B-H}] = 1.200, 1.202 \, \text{Å}\)) and a significantly lengthened Ru···B distance (2.570 Å).
Figure 5.9: Transition state $[5.16_{TS}]^+$ at a free energy of $+17.5$ kcal mol$^{-1}$ with respect to $[5.16]^+$. $[5.16'_{TS}]^+$ is destabilised by $9.6$ kcal mol$^{-1}$ with respect to the global minima. However, $[5.16'_{DFT}]^+$ can be transformed into the ‘mirror image’ of $[5.16_{DFT}]^+$ by a simple rotation around the centre of the Ru-H bond.
In order to quantify the strength of the metal-ligand interaction in mono(σ-BH) complexes, further quantum chemical studies have been carried out and the results are consistent with the structural data in the solid state. Thus, for example, \([5.16]^+\) features a more strongly bound aminoborane fragment than \([5.15]^+\) (\(\Delta G = -26.0 \text{ kcal mol}^{-1}\) for \([5.16]^+\); \(-15.2 \text{ kcal mol}^{-1}\) for \([5.15]^+\)). These free energies can be put into context by comparison with the values for the binding of CO, ethylene and \(\text{N}_2\) to the same cationic Ru fragment \([\text{CpRu(dctype)}]^+\) (-46.5, -19.2 and -17.2 kcal mol\(^{-1}\), respectively). Experimentally, such data are consistent with the displacement of \(\text{N}_2\) by \(\text{H}_2\text{BNCy}_2\) in the synthesis of these aminoborane adducts and with the replacement of \(\text{H}_2\text{BNCy}_2\) with CO to generate \([\text{CpRu(dctype)CO}]^+\) and free aminoborane. Interestingly, \(\text{H}_2\text{BNCy}_2\) appears to bind more strongly than the related alkene complex.

### 5.3.3 Primary Hydridoboryl Complexes

Following the successful coordination of aminoboranes at cationic ruthenium fragments bearing cyclopentadienyl ligands, related chemistry with isoelectronic ruthenium arene systems was targeted via the reactions of \(\text{H}_2\text{BN}^\text{tPr}_2\) with \((p\text{-cymene})\text{Ru(PR}_3\text{)}\text{Cl}_2\) (\(\text{PR}_3 = \text{PCy}_3, \text{PPh}_3\)) in the presence of \(\text{Na}[\text{BAR}_4]\). These metal precursors feature two chloride ligands and therefore were perceived to offer the possibility for synthesising both \(\kappa^1\) and \(\kappa^2\) complexes through stepwise halide abstraction processes. In practice, however, simple coordination chemistry proves inaccessible and instead, loss of HCl to generate 16-electron primary hydridoboryl complexes is observed [Scheme 5.12].
Scheme 5.12: Synthesis of ruthenium primary hydridoboryl complexes.

The $^1$B\{H\} NMR spectra of [5.19]$^+$ (δ$_B$ 35.5 ppm) and [5.20]$^+$ (δ$_B$ 35.1 ppm) are not appreciably different from the free aminoborane (35.4 ppm). However, the $^1$H coupled spectrum is more informative: a doublet is seen for [5.19]$^+$ ($^1$J$_{BH}$ = 162 Hz) and significant broadening of the resonance is also seen for [5.20]$^+$, implying the existence of a single boron-bound hydrogen. Additionally, $^1$H and $^{13}$C NMR data confirm the presence of the $p$-cymene, phosphine and N'iPr$_2$ fragments. A broad upfield resonance is observed for both [5.19]$^+$ (δ$_H$ -12.53 ppm) and [5.20]$^+$ (δ$_H$ -11.43 ppm) corresponding to the BH hydrogen, with the strongly upfield shifted nature of this resonance being indicative of an agostic interaction with the ruthenium metal centre. These shifts are similar to that observed for the agostic interaction of a BH bond with the iridium centre in [Ir(IMes)(IMes')(H)BNCy$_2$][BAR$_4$'] (δ$_H$ -10.85 ppm).

[5.19]$^+$ displays a single resonance integrating to 12 hydrogens corresponding to the methyl groups of the N'iPr$_2$ substituent (δ$_H$ 1.06 ppm, d, $^3$J$_{HH}$ = 7.2 Hz) revealing equivalence of the two iPr substituents on the NMR timescale. Interestingly, for [5.20]$^+$ the corresponding resonance is markedly broadened and for both cations de-coalescence occurs upon cooling (at 257 K for [5.19]$^+$ and 265 K for [5.20]$^+$); a barrier of rotation about the BN bond of 13.9 kcal mol$^{-1}$ for both compounds has thereby been estimated using the Eyring equation. This value is comparable to those obtained for analogous rotation processes in similar aminoboryl
complexes, as discussed in Chapter 3. As expected, a single $^{31}\text{P}$ environment is observed for $[5.19]^+$ ($\delta_p$ 63.4 ppm) and $[5.20]^+$ ($\delta_p$ 54.9 ppm). In addition, single crystals of $[5.19][\text{BAr}^f_4]$ and $[5.20][\text{BAr}^f_4]$ have been obtained from fluorobenzene/hexane layerings at room temperature [Figures 5.10 and 5.11]. The solid-state structures of $[5.19]^+$ and $[5.20]^+$ display bent Ru-B-N frameworks consistent with the proposed boryl formulation [$\angle\text{Ru-B-N} = 129.8(5)^\circ$ and $128.6(4)^\circ$, respectively], and the orientation of the N$i\text{Pr}_2$ groups are as expected for a boryl complex. The two crystal structures feature statistically identical Ru-B distances [2.281(7) Å for $[5.19]^+$; 2.259(6) Å for $[5.20]^+$] which are within the range expected for direct Ru-B single bonds.$^{22}$ Furthermore, elemental microanalysis and ESI-MS are consistent with the proposed formulation of $[5.19][\text{BAr}^f_4]$ and $[5.20][\text{BAr}^f_4]$. Thus, $[5.19]^+$ and $[5.20]^+$ represent rare structurally characterised primary boryl systems.
Figure 5.10: Molecular structure of [5.19][BAr₄]. Thermal ellipsoids set at the 35% probability level; hydrogen atoms (except boron-bound hydrogens) and counter-ion omitted, and Cy groups shown in wireframe format for clarity.

Table 5.6: Selected bond lengths [Å] and angles [°] for [5.19][BAr₄].

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**Figure 5.11:** Molecular structure of [5.20][BAR₄]. Thermal ellipsoids set at the 35 % probability level; hydrogen atoms (except boron-bound hydrogens) and counter-ion omitted, and Ph groups shown in wireframe format for clarity.

**Table 5.7:** Selected bond lengths [Å] and angles [°] for [5.20][BAR₄].

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</tbody>
</table>
A possible pathway for the formation of these products involves initial complexation to give a mono(σ-BH) complex [Scheme 5.13]. Such a species would be isoelectronic with κ¹\text{CpRu(PR₃)₂⁺} containing systems (e.g. [5.13]⁺) and evidence for the formation of a well-defined intermediate is provided by \textit{in situ} monitoring of the reaction mixture by ³¹P NMR spectroscopy in the case of [5.20]⁺. A species giving rise to a single resonance at δₚ 28.6 ppm is observed after short reaction times which is then converted into [5.20]⁺ (δₚ 54.9 ppm). From such an intermediate, oxidative addition of the B-H bond at the ruthenium centre followed by reductive elimination of HCl would yield [5.20]⁺. It is postulated that the eliminated HCl then reacts with excess borane. This postulate is given credence by \textit{in situ} monitoring of the reaction mixture by ¹¹B NMR spectroscopy which reveals a doublet at δₐ 33 ppm corresponding to \textit{i}Pr₂NBHCl. Attempts to repeat the reaction with < 1 eq of H₂NB\textit{i}Pr₂ proved unsuccessful, yielding mixtures of phosphorus and boron containing products, presumably due to subsequent reactivity of the liberated HCl with [5.19]⁺ and [5.20]⁺.
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Scheme 5.13: Postulated mechanism for the formation of [5.19]$^+$ and [5.20]$^+$.

The analogous reaction of H$_2$BN'Pr$_2$ with (p-cymene)Ru(PMe$_3$)Cl$_2$ and Na[BAr$_f^4$] was performed in the hope that a less sterically hindered metal centre might promote full hydride migration to generate a borylene complex [vide infra; Scheme 5.14]. However, the reaction simply leads to the formation of the dimer [(p-cymene)Ru(PMe$_3$)Cl]$_2$$^{2+}$, [5.21]$^{2+}$. The reduced steric hinderance at the metal centre presumably favours dimer formation over borane coordination, whereas this is not feasible in the case of the bulkier PCy$_3$ and PPh$_3$ complexes [Scheme 5.12].
Scheme 5.14: Formation of dimer \[ (p\text{-cymene})\text{Ru(PMe}_3\text{)Cl}_2 \] ^{2+} [5.21]^{2+}.

[5.21]^{2+} has been characterised by multinuclear NMR spectroscopy (\textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F and \textsuperscript{31}P) and mass spectrometry. Single crystals suitable for X-ray crystallography were obtained from a fluorobenzene/hexane layering at room temperature. The reaction of \((p\text{-cymene})\text{Ru(PMe}_3\text{)Cl}_2\) with Na[BA\textsuperscript{f}_4] in the absence of H\textsubscript{2}BN\textsuperscript{i}Pr\textsubscript{2} also leads to the formation of [5.21]^{2+}, as expected.

Figure 5.12: Molecular structure of [5.21][BA\textsuperscript{f}_4]\textsubscript{2}. Thermal ellipsoids set at the 35 % probability level; hydrogen atoms and counter-ion omitted for clarity.
An α agostic interaction is proposed for [5.19]⁺ and [5.20]⁺ on the basis of the high field shifted B-H ¹H NMR signal. Further evidence for the existence of such an agostic Ru H-B interaction in [5.20]⁺ is provided from the reaction of [5.20]⁺ with 2,6-dimethylphenyl isocyanide which generates [(p-cymene)Ru(PPh₃)(CNC₆H₃-Me₂-2,6){B(H)N′Pr₂}]⁺, [5.22]⁺, which has been characterised by multinuclear NMR spectroscopy [Scheme 5.15].

Monitoring the reaction by ³¹P and ¹¹B NMR spectroscopy reveals small shifts to δ₈ 35.0 ppm and δ₈ 56.7 ppm in the ¹¹B and ³¹P NMR spectra. However, more interestingly, the hydride resonance at δ₇ -11.43 ppm disappears due to the inability of the boron-bound hydrogen to interact with the 18-electron ruthenium metal centre, and there are now no signals below δ₇ 0 ppm. Although the resulting (presumably broadened) BH signal could not be definitively located due to overlapping resonances, further spectroscopic data supporting the synthesis of [5.22]⁺ is provided by four distinct proton resonances associated with the para-cymene ligand. This differs from the two sets of slightly ‘roofed’ doublets observed in [5.20]⁺ since the arene protons are rendered inequivalent upon coordination of 2,6-dimethylphenyl isocyanide at the metal centre. Interestingly, the iPr groups appear inequivalent at 298 K with the methyl groups generating two sets of doublets (δ₇ 1.11 ppm and 1.14 ppm, ³J₇₇ = 6.9 Hz).
13C NMR data further confirms the synthesis of [5.22]⁺, and ESI-MS data reveals the presence of [M]⁺ with appropriate accurate mass measurements.

Given the mechanistic proposal for the synthesis of the hydridoboryl complexes [5.19]⁺ and [5.20]⁺, it was predicted that the interaction of H₂BNPr₂ at a more electron poor metal centre may arrest the reaction path at mono(σ-BH) coordination. As a result, H₂BNPr₂ was exposed to (p-cymene)Ru{P(OPh)₃}Cl₂ in the presence of Na[BArf₄]. Unfortunately, single crystals suitable for X-ray crystallography were unobtainable and NMR/ESI-MS data were not definitive.

5.3.4 Boron-to-Metal α-Hydride Migration in Aminoborane Activation

The novel hydridoboryl complexes [5.19]⁺ and [5.20]⁺ are both thought to contain B-H agostic interactions with the electron deficient ruthenium centre, as determined by the high field resonances in the ¹H NMR spectra (δH -12.53 ppm and -11.43 ppm, respectively). However, the hydride atoms are presumably still located primarily on the boron centre as indicated by the bent Ru-B-N frameworks [∠Ru-B-N = 129.8(5)° and 128.6(4)°, respectively], by the broadened doublet ¹¹B NMR resonances (δB 35.5 and 35.1 ppm, respectively) and by the presence of appropriate electron density in the crystallographic difference Fourier map. It was therefore decided to investigate whether alternative systems could be accessed in which complete hydride transfer to the metal could be effected. Such a process is without literature precedent but in theory could be achieved by the formation of a vacant coordination site at an appropriate metal centre.

Initial synthetic steps sought to exploit the reactions of aminoboranes H₂BNR₂ (R = 'Pr, Cy) with an electron rich Ir(I) precursor Ir(PMe₃)₃Cl(coe) (5.24), which has precedent for
B-H bond activation. Ir(Cl)(PMe₃)(coe) (5.24) was synthesised by the in situ reaction of [Ir(coe)₂Cl]₂ (5.23) with PMe₃, as utilised by Knorr and Merola as long ago as 1990.²⁴ Addition of H₂BNR₂ (R = ³Pr, Cy) to the iridium/PMe₃ system leads to oxidative addition of the B-H bond to the iridium centre, presumably by reaction with the 16-electron Ir(PMe₃)Cl (5.25) which is reported to exist in equilibrium with the 18-electron complex Ir(PMe₃)Cl(coe) (5.24) in solution. The hydridoiridium(hydridoboryl) complexes Ir(PMe₃)(H)Cl{B(H)NR₂} (5.26 R = ³Pr; 5.27 R = Cy) are thus generated in reasonable isolated yields (40-50 %) [Scheme 5.16]. 5.26 and 5.27 have been characterised by multinuclear NMR spectroscopy in addition to microanalysis and single-crystal X-ray diffraction for 5.27. Whilst B-H oxidative addition is well documented in the literature, such chemistry represents the first explicit demonstration of such a process for an aminodihydroborane and 5.27 represents a rare structurally characterised primary boryl system.

![Scheme 5.16: Synthesis of novel primary boryl complexes.](image-url)
Boryl complexes 5.26 and 5.27 display characteristic broad \(^{11}\)B NMR signals (\(\delta_B = 46\) and 43 ppm respectively) diagnostic of Ir-B bonded systems. In addition, the \(^{31}\)P\{\(^{1}\)H\} NMR spectra of both systems feature a triplet (integral one) for the phosphine \(\text{trans}\) to the hydride and a doublet for the mutually \(\text{trans}\) phosphines (integral two) \((J_{\text{HP,trans}} = 22.3\ \text{Hz})\), confirming the presence of a planar [Ir(PMe\(_3\))\(_3\)H] unit. The \(^{1}\)H NMR spectrum of each compound has several diagnostic features. Firstly, the hydride signal appears as a doublet of triplets (integral one) at -9.04 ppm for 5.26 \((J_{\text{HP,trans}} = 141.3\ \text{Hz}, J_{\text{HPC,is}} = 21.0\ \text{Hz})\) and -8.73 ppm for 5.27 \((J_{\text{HP,trans}} = 140.7\ \text{Hz}, J_{\text{HPC,is}} = 21.3\ \text{Hz})\). Furthermore, the broad BH signals \((\delta_H = 7.18\ \text{ppm for 5.26 and } 7.38\ \text{ppm for 5.27})\) are observed which sharpen on \(^{11}\)B decoupling. The \(^{1}\)H and \(^{13}\)C NMR spectra also reveal inequivalence of the R groups due to restricted rotation about the BN bond. Attempts to probe the barrier to rotation about the B-N bond using variable temperature NMR up to \(80^\circ\)C suggest that the boryl complexes decompose at a temperature lower than the coalescence point. Single crystals of 5.27 suitable for X-ray crystallography were, however, obtained from a saturated Et\(_2\)O solution at -30°C and confirm the meridional arrangement of the PMe\(_3\) ligands [Figure 5.13]. The Ir-B distance of [2.074(4) Å] is consistent with the value for the related compound \(\text{mer}\)-Ir(PMe\(_3\))\(_3\)(H)Cl(Bcat) [2.023(1) Å], but the Ir-Cl distance in 5.27 [2.590(1) Å] is significantly longer than that found in the Bcat analogue [2.546(2) Å]. Elemental microanalysis of 5.27 is also consistent with the proposed formulation.
Figure 5.12: Molecular structure of 5.27. Thermal ellipsoids set at the 35 % probability level; hydrogen atoms (except metal- and boron-bound hydrogens) omitted, and Cy groups shown in wireframe format for clarity.

Table 5.8: Selected bond lengths [Å] and angles [°] for 5.27.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Length/°</th>
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<tr>
<td>Ir(1)-B(15)</td>
<td>2.074(4)</td>
</tr>
<tr>
<td>B(15)-N(16)</td>
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<td>Ir(1)-P(7)</td>
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<td>Ir(1)-P(11)</td>
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<td>Ir(1)-Cl(2)</td>
<td>2.590(1)</td>
</tr>
<tr>
<td>Ir(1)-B(15)-N(16)</td>
<td>132.0(3)</td>
</tr>
<tr>
<td>P(3)-Ir(1)-P(11)</td>
<td>95.4(1)</td>
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<tr>
<td>P(3)-Ir(1)-P(7)</td>
<td>96.8(1)</td>
</tr>
<tr>
<td>P(7)-Ir(1)-P(11)</td>
<td>167.0(1)</td>
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</tbody>
</table>
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Subsequent reactivity of 5.26 and 5.27 with Na[BAR$_4^-$] leads to the formation of the borylene dihydride complexes ([fac-Ir(PMe$_3$)$_2$(H)$_2$(BN$_3$Pr$_2$)][BAR$_4^-$] [5.28][BAR$_4^-$] and [fac-Ir(PMe$_3$)$_2$(H)$_2$(BNCy$_2$)][BAR$_4^-$] [5.29][BAR$_4^-$], respectively [Scheme 5.17].

**Scheme 5.17**: Synthesis of novel borylene complexes using a halide abstraction agent.

Spectroscopically, the formation of [5.28]$^+$ and [5.29]$^+$ is signalled by a downfield shift in the $^{11}$B NMR spectra (δ$_B$ 77 ppm for both cations), as expected for the formation of a two-coordinate borylene ligand. This shift appears to rule out any appreciable interaction between the boron centre and the hydride co-ligands. Both [5.28]$^+$ and [5.29]$^+$ give rise to two $^{31}$P resonances (with relative intensities 2:1), the latter signal being broadened by the presence of a trans borylene ligand. The $^2J_{PP}$ coupling constant ($J = 24.9$ Hz for [5.28]$^+$; $J = 18.0$ Hz for [5.29]$^+$) is typical for mutually cis orientated PMe$_3$ groups at iridium. Furthermore, the $^1$H hydride region in each case displays a second order signal (integral two) at δ$_H$ -11.98 ppm for [5.28]$^+$ and δ$_H$ -12.06 ppm for [5.29]$^+$, consistent with the AA'MXX' spin system arising from the planar [cis-Ir(PMe$_3$)$_2$(H)$_2$] unit and additional coupling to the third unique PMe$_3$ ligand. Moreover, the $^1$H and $^{13}$C NMR spectra indicate that the amino substituents are no longer inequivalent, consistent with rapid rotation around a linear Ir-B-N axis. In addition, ESI mass spectrometry reveals [M]$^+$ peaks at $m/z = 543.2$ for [5.28]$^+$ and $m/z = 614.3$ for [5.29]$^+$, with
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accompanying isotopic envelopes and accurate mass measurements in agreement with calculated values.

Although it was not possible to crystallise the [BAr$_f$]$_4^-$ salts, crystals of [5.29][BAr$_{Cl}$]$_4^-$ were obtained from a fluorobenzene/hexane layering at -30°C. The structure is consistent with a fac arrangement of the three PMe$_3$ ligands [the three P-Ir-P angles spanning 94.4(5)-101.4(1)°] and the presence of a linear two-coordinate borylene ligand [∠Ir-B-N = 175.9(4)°] within a pseudo-octahedral metal geometry. Diffraction data revealed an Ir-B distance of 1.939(5) Å which is approximately 6.5 % shorter than the corresponding distance in the boryl precursor 5.27 [2.074(4) Å] and consistent with the formal increase in Ir-B bond order from one to two [cf. 1.892(3) for Cp*Ir(CO){BN(SiMe$_3$)$_2$}]. The Ir-B-N angle [175.9(4)°] can also be compared to that of the boryl precursor 5.27 [132.0(3)°], and the widening of the angle is as expected for the reduction in co-ordination number at the boron centre.
Figure 5.13: Molecular structure of [5.29][BAr$_4^{Cl}$]. Thermal ellipsoids set at the 35% probability level; hydrogen atoms (except metal-bound hydrogens) and counter-ion omitted, and Cy groups shown in wireframe format for clarity.

Table 5.9: Selected bond lengths [Å] and angles [°] for [5.29][BAr$_4^{Cl}$].

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<th></th>
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<td></td>
<td>[Å]</td>
<td></td>
<td>[°]</td>
</tr>
<tr>
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<td>Ir(1)-P(6)</td>
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<td>2.326(1)</td>
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<td>175.9(4)</td>
<td>P(2)-Ir(1)-P(10)</td>
<td>101.4(1)</td>
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<td>P(2)-Ir(1)-P(6)</td>
<td>94.4(5)</td>
<td>P(6)-Ir(1)-P(10)</td>
<td>98.6(1)</td>
</tr>
</tbody>
</table>
To complete the conversion from 5.26/5.27 to a borylene dihydride complex, a boron-to-metal hydride migration process is required. As mentioned above, while such a transformation is without previous precedent in the literature, a generic requirement for α-substituent migration however is the availability of a free coordination site cis to the migrating group. The postulated mechanism for the formation of [5.28]$^+$ and [5.29]$^+$ therefore involves migration of one of the mutually trans phosphine groups into the site vacated by chloride abstraction, giving a facial arrangement of the phosphine ligands [Scheme 5.18]. The boron-bound hydrogen atom then undergoes α-migration to the newly vacated cis site. [5.28]$^+$ and [5.29]$^+$ are thus the first examples of borylene complexes synthesised by α-hydride migration and this is the first reported formation of a borylene complex formed by α-migration of any boron-bound substituent without the addition of a base. Base-promoted halide migration has been reported by Braunschweig for a platinum borylene complex, and unassisted α-hydride migration by Tilley in the formation of the platinum silylene complex [Pt(dippe)SiMes$_2$(H)]$^+$.26,36
Given the proposed mechanism above [Scheme 5.18], it should also be possible to generate a borylene complex without a skeletal rearrangement of the phosphine ligands by employing an external hydride sink. Consistently, the use of [Ph$_3$C][B(C$_6$F$_5$)$_4$] as a hydride abstraction agent in fluorobenzene proved successful in the reaction with 5.26 to form [mer-Ir(PMe$_3$)$_3$(H)Cl(BN'Pr$_2$)]$^+$ [5.30]$^+$ [Scheme 5.19].

[5.30]^+ displays an $^{11}$B NMR signal at $\delta_B$ 71 ppm, characteristic of a borylene complex. The $^{31}$P{\textsuperscript{1}H} NMR spectrum shows a doublet and a triplet reminiscent of the boryl precursor 5.26 and quite different to the cations [5.28]^+ and [5.29]^+, indicative of retention of of the mer-[Ir(PMe\textsubscript{3})\textsubscript{3}] moiety. Similarly, the hydride signal in the $^1$H NMR spectrum reveals a doublet of triplets for the iridium-bound hydride, as expected for a planar IrP\textsubscript{3}H subunit. Crystallographic analysis of [5.30][BAR\textsubscript{Cl}\textsubscript{4}] (obtained from the reaction of 5.26 with Na[BAR\textsubscript{Cl}\textsubscript{4}] in CH\textsubscript{2}Cl\textsubscript{2}) confirms the proposed structure, revealing a meridional arrangement of phosphine ligands and a linear Ir-B-N framework [177.2(3)\textdegree]. The Ir-B distance of 1.890(5) Å is somewhat shorter than that found for [5.28]^+ [1.939(5) Å], presumably due to the weaker trans influence of the Cl\textsuperscript{-} ligand (cf. the trans PMe\textsubscript{3} ligand in [5.28]^+). This synthetic route is the first reported example of the use of external hydride abstraction in the synthesis of a borylene complex.
Figure 5.14: Molecular structure of $[5.30][\text{BAr}^{CI}_4]$. Thermal ellipsoids set at the 35 % probability level; hydrogen atoms (except metal-bound hydrogen) and counter-ion omitted for clarity.

Table 5.10: Selected bond lengths [Å] and angles [°] for $[5.30][\text{BAr}^{CI}_4]$.

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</tr>
</tbody>
</table>
5.4 Conclusions and Suggestions for Further Research

The studies described in this chapter have sought to probe the fundamental capabilities of aminoboranes to interact with a variety of metal centres. Complexes [5.2]⁺, [5.3]⁺, [5.4]⁺ and [5.5]⁺ have been characterised featuring a κ² mode of coordination at a 14-electron ruthenium centre. Unfortunately, attempted synthesis of an aminoborylene complex from [5.2]⁺ proved unsuccessful: reaction with 3,3-dimethyl-1-butene leads to hydroboration of the alkene, resulting in the synthesis of the mixed allyl/phosphine donor system [5.7]⁺. Subsequent reactivity of [5.2]⁺ with a series of neutral two-electron donors leads to elimination of the aminoboran ligand.

The first complexes containing an aminoboran ligand coordinated to a 16-electron metal centre have been reported ([5.13]⁺ and [5.14]⁺), thereby defining the intrinsic two-electron donor capabilities of this typical ligand family. Geometric parameters for the monodentate BH-bond ground state structures ([5.15]⁺ and [5.16]⁺) and details of dynamic fluxional processes have been probed as functions of the ancillary phosphine co-ligands.

Simple borane coordination compounds prove inaccessible upon addition of aminoboranes to [(p-cymene)Ru(PR₃)Cl]⁺ (PR₃ = PCy₃, PPh₃); loss of HCl to generate a rare class of primary hydridoboryl complexes is witnessed instead (e.g. [5.19]⁺ and [5.20]⁺).

A series of attempts to synthesise boryl complexes using oxidative addition of monomeric aminoboranes has proved successful through the use of electron rich iridium precursors, resulting in the synthesis of the novel amino(hydrido)boryl complexes 5.26 and 5.27. These represent the first report of B-H oxidative addition involving an aminoborane and further examples of rare primary hydridoboryl complexes. Previously, unknown α-hydride migration from the boron centre to iridium has been utilised in the synthesis of the novel
borylene complexes \([5.28]^+\) and \([5.29]^+\). Moreover, the unprecedented methodology of direct hydride abstraction has been used in the synthesis of the novel compound \([5.30]^+\).

While the fundamental B-H activation steps in the conversion of borane to boryl to borylene are of great interest, the overall route to borylene synthesis suffers from the necessity of a two-stage process. A possible way of incorporating both fundamental steps implicit in borylene synthesis into a one-pot process might be to oxidatively add an aminoborane to a metal alkyl complex, affording alkane elimination through a series of hydride migration processes.

Since both \(\kappa^1\) and \(\kappa^2\) complexes of aminoborane ligands are now reported, an interesting possibility for future research could be to target a \(\kappa^3\) mode of coordination. Given the labile nature of the coordinated acetonitrile ligands in \([\text{Cp}^*\text{Ru}((\text{CH}_3\text{CN})_3)]^+\), such a complex could offer a route to amine borane coordination by displacement of the weakly bound substituents.

As previously discussed (\textit{vide supra}), \(\text{H}_2\text{BNR}_2\) binds to metal centres in an ‘end on’ fashion. This contrasts the coordination of isoelectronic alkenes which are known to bind ‘side-on’ through the \(\text{C}=\text{C}\ \pi\) system. Therefore, it would be of fundamental interest to investigate the coordination mode of \(\text{R}_2\text{BNR}_2\) (\(\text{R} = \text{alkyl}\)) where there is no longer a possibility to bind through the germinal B-H bonds.

### 5.5 References for Chapter V

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6. A. Staubitz, A. P. M. Robertson and I. Manners, Chemical Reviews, 2010, 110, 4079-4124.


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(Dimethylamino)borylene and Related Complexes of Electron Rich Metal Fragments: Generation of Nucleophile Resistant Cations by Spontaneous Halide Ejection.

Borane to Boryl Hydride to Borylene Dihydride: Explicit Demonstration of Boron-to-Metal α-Hydride Migration in Aminoborane Activation.

Probing the Intrinisic Structure and Dynamics of Aminoborane Coordination at Late Transition Metal Centers: Mono(σ-BH) Binding in [CpRu(PR$_3$)$_2$(H$_2$BNCy$_2$)]$^+$. 

Extending the Chain: Synthetic, Structural and Reaction Chemistry of a BN Allenylidene Analogue.

Modelling Fundamental Arene–Borane Contacts: Spontaneous Formation of a Dibromoborenium Cation Driven by Interaction Between a Borane Lewis Acid and an Arene π System.