Studies of Pi-bonding in Late Transition Metal Boryl Complexes

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A thesis submitted to the University of Wales in accordance with the
requirements for the degree of Doctor of Philosophy in the Faculty of Science,
School of Chemistry, University of Wales, Cardiff.

September 2004

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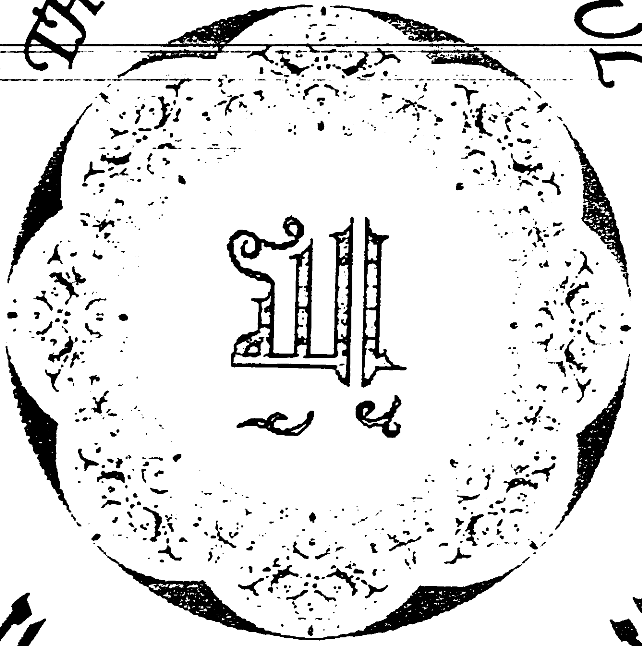
IN THE NAME OF ALLAH
THE MOST GRACIOUS
THE MOST MERCIFUL



بسم الله الرحمن الرحيم

Dedication

This work is dedicated to the memory of my
father, who spent his life in the cause of
education in Saudi Arabia.
And to the memory of my brother Saleh, who
gave me a special care and encouragement
during my childhood.
And to my mother who spent her life looking
after me, supporting me, and praying for me.

Acknowledgements

First of all, I'd like to extend my Praise and thanks to Allah without whose help this thesis would not have been completed.

Also I'd like to extend sincerest thanks and deep appreciation to Dr. Simon Aldridge, my supervisor, for his guidance and support throughout this research.

I would like to acknowledge the contributions made by the following people:

The people who performed the crystallography described in this thesis: Drs. Li-ling Ooi, Simon Coles, Mark E. Light and Prof. Michael B. Hursthouse.

Drs. Anthony Dickinson and David J. Willock for performing the DFT calculation described in this thesis.

Drs. Angelo J. Amoroso and Ian A. Fallis for letting me borrow their chemicals and equipment.

The technical staff: Alan, Rob Jenkins, Ricky, Robin, Gary, and Sham for keeping the department running.

The EPSRC National Crystallography and Mass Spectrometry Service Centres at Southampton and Swansea, respectively.

I wish to thank Saudi government for granting me a scholarship and financial support.

Big thanks to the members of Labs 1.124 and 1.125 past and present for providing an enjoyable research environment.

A big thank must go to my friend Haileh Al-Ubaidey for her unforgotten help with moving home, taking care of my children and cooking for me especially in Ramadhan.

Big thanks are given to my mother for her emotional support and prayers for me during the hard times.

Big thanks must go to my brother Ibrahim Al-Fawaz for his encouragement and support.

A big thank you to my two wonderful daughters, Noha and Najla, and my lovely son, Mohammad, for their patience and immeasurable love that helped me to finish this thesis.

Finally, special thanks and gratitude are given to my husband, Ibrahim Al-hudaithy, for unlimited love and support for every thing in my life.

Abstract

The synthesis, spectroscopic and structural characterisation of the first transition metal complexes containing the bis(pentafluorophenyl)boryl ligand, $(C_5H_5)Fe(CO)_2B(C_6F_5)_2$ and $(C_5Me_5)Fe(CO)_2B(C_6F_5)_2$ are reported. Also reported are the syntheses and spectroscopic characterisation of the related manganese complexes $(CO)_5MnB(C_6F_5)_2$ and $(C_5H_4Me)Mn(CO)_2HB(C_6F_5)_2$, the latter being prone to decomposition via loss of the $HB(C_6F_5)_2$ fragment. The formation of a rare example of an unsupported bridging borylene complex, $[(C_5H_5)Fe(CO)_2]_2BAr$ is also detailed, in this case making use of an alternative fluorinated ligand substituent [Ar = $3,5\text{-}(CF_3)_2C_6H_3$].

Oxidative addition reactions of $ClB(C_6F_5)_2$ and $[HB(C_6F_5)_2]_n$ with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ and $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ have also been attempted, as a second possible route to M-B bonds. The reaction of $ClB(C_6F_5)_2$ with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$, however, ultimately generates $EtB(C_6F_5)_2$ and chloro-platinum(II) species including *trans*-$(Ph_3P)_2Pt(C_6F_5)Cl$ (which has been structurally characterised). On the other hand, the reaction of $[HB(C_6F_5)_2]_n$ with $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ generates products resulting from ligand abstraction (either chloride or phosphine) from rhodium by the highly electrophilic borane.

The intermolecular base-stabilised haloboranes $Ph_3P{\cdot}BPhCl_2$, $Ph_3P{\cdot}BCl_3$, 4-Pic·BCl_3, and 4-Pic·$BPhCl_2$ represent useful examples of haloborane complexes containing PPh_3 and 4-picoline donors from which salt elimination chemistry might be used to make M-B bonds. The structures of $Ph_3P{\cdot}BPhCl_2$ and 4-Pic·BCl_3 have been determined by single crystal X-ray diffraction and the structure of THF·BCl_3 has been obtained for comparative purposes. The course of salt elimination chemistry with these boranes is highly dependent on the nature of the coordinated base; a bridging borylene complex $[(C_5H_5)Fe(CO)_2]_2BPh$ has been synthesised and spectroscopically characterized using $Ph_3P{\cdot}BPhCl_2$ as the boron-containing precursor.

Notes

The following abbreviations were used in the text:

Me = $-CH_3$

Et = $-CH_2CH_3$

^{i}Pr = $-CH(CH_3)_2$

^{n}Bu = $-CH_2CH_2CH_2CH_3$

^{t}Bu = $-C(CH_3)_3$

Ph = $-C_6H_5$

Mes = mesityl, 2,4,6- $Me_3C_6H_2$

Cy = cyclohexyl

Cp = cyclopentadienyl, η^5-C_5H_5

Cp* = pentamethylcyclopentadienyl, η^5-C_5Me_5

Cp' = methylcyclopentadienyl, η^5-C_5H_4Me

Fp = $(\eta^5$-$C_5H_5)Fe(CO)_2$

Fp* = $(\eta^5$-$C_5Me_5)Fe(CO)_2$

PPN^+ = $[(Ph_3P)_2N]^+$

pin = $OCMe_2CMe_2O$

cat = 1,2-$O_2C_6H_4$

cat*= 1,2-O_2-4^{t}BuC_6H_3

tart = 1,2-$O_2CH(CO_2Me)CH(CO_2Me)$

tbp' = tris-(3,5-dimethylpyrazol-1-yl)hydroborate

THF = tetrahydrofuran

9-BBN = 9-bora-bicyclo-3,3,1-nonane

cod = cycloocta-1,5-diene

b = broad

st = strong

md = medium

w = weak

h = hours

min = minutes

DFT = density functional theory

1 Torr = 1 mmHg = 133.3 Pa

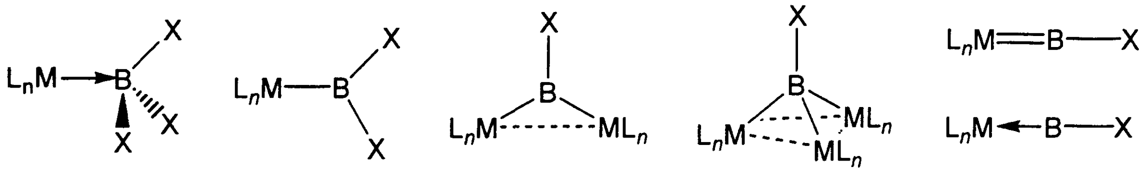
Contents

Chapter one

Introduction

1.1 Introduction

Transition metal boron complexes i.e. those characterized as having a 2 centre - 2 electron bond between the metal and the boron centre have been under investigation since the 1960s.[1-9,14] The first complexes of this type were reported by Nöth and Schmid in 1963, athough there is doubt as to whether these complexes have been correctly formulated.[10] The types of transition metal boron complexes known to date can be classified in terms of four structural types, depending on the coordination number of the boron atom and the number of bonds between the boron and the transition metal; thus these are borane (I), boryl (II), and bridged (III) as well as terminal (IV) borylene complexes (Figure 1.1).



Borane (I) Boryl (II) Bridging borylene (III) Terminal borylene (IV)

Figure 1.1 Structural types of transition metal boron complex.

Borane complexes are Lewis acid base adducts that contain a four-coordinate boron centre. Such complexes were initially reported in the 1960s, however, modern spectroscopic techniques have discredited many of them.[11]

To date there are no crystallographically characterised borane-transition metal complexes featuring an unsupported borane fragment.[12] Boryl complexes feature boron with the coordination number three; this is the most widely known of the four structural types. The borylene fragment, BR, can bridge between two transition metal centres with boron in coordination number three or it can form a two-coordinate centre when terminally bound to a transition metal. Salient features of boryl and borylene systems relevant to the work undertaken in this study are summarised below.

1.2 Boryl complexes

1.2.1 Introduction

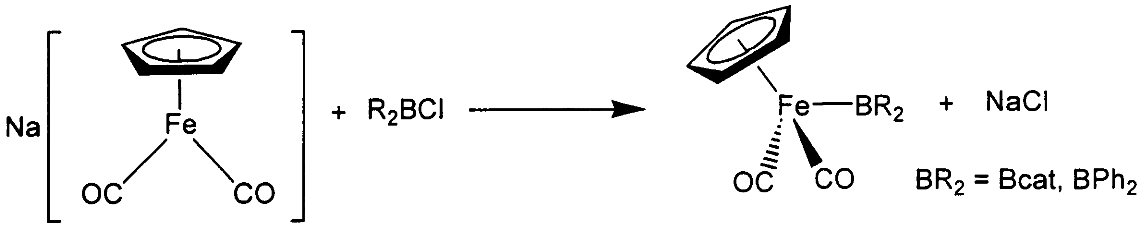
Boryl complexes are the most common type of transition metal boron complexes. The first examples including $[(CH_3)_2N]_2BMn(CO)_5$, and $[(CH_3)_2N]_2BMn(CO)_4P(C_6H_5)_3$ were made in 1963 by Nöth and Schmid.[10] However, there was no conclusive crystallographic evidence that the complexes were correctly formulated and subsequent work has cast doubt on the interpretation of this early spectroscopic and analytical data. For example, the ^{11}B NMR chemical shift of $(C_5H_5)Fe(CO)_2BPh_2$ which was reported by Nöth to be δ_B 37 contrasts with the value obtained by Hartwig for the structurally characterised compound (δ_B 121).[10,13] Moreover, the first crystallographically characterized transition metal boryl complexes were not reported until 1990.[35,36] Subsequently, heightened attention has been given to the boryl transition metal complexes, due to their implication in the hydro- and diboration of carbon-carbon multiple bonds and in the highly selective stoichiometric and catalytic functionalisation of hydrocarbons under either photolytic or thermal conditions.[15-21] Most of the boryl complexes which have been reported so far contain the phenylene-1,2-dioxo or catechol (cat) group or related derivatives, in part reflecting the use of HBcat in early hydroboration studies, and in part the ready availability of starting materials of type XBcat.

1.2.2 Synthesis of transition metal boryl complexes

There are two general synthetic routes which have been proven to be successful for the preparation of transition metal boryl complexes: salt elimination and oxidative addition.

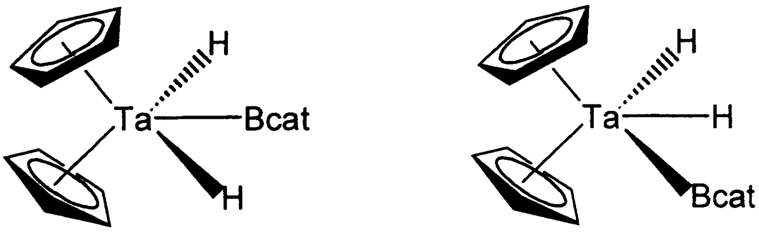
1.2.2.1 Salt elimination

This process involves the reaction between a nucleophilic anionic metal reagent and a haloborane to give a boryl complex and one equivalent of the halide salt. In 1963 Nőth and Schmid were the first to use this reaction;[10] more recently Hartwig et al. have successfully synthesized and structurally characterised a number of boryl complexes using this process. For example, in 1993 Hartwig and Huber reported the syntheses of $(C_5H_5)Fe(CO)_2Bcat$ and $(C_5H_5)Fe(CO)_2BPh_2$ from $Na[(C_5H_5)Fe(CO)_2]$ (Scheme 1.1).[13]



Scheme 1.1 Syntheses of iron boryl complexes by salt elimination.

Moreover, the syntheses of related complexes of manganese and rhenium $(CO)_5MB(cat)$ [M = Mn, Re] as well as half sandwich complexes of ruthenium and tungsten containing various catecholboryl (and related) ligands have been reported.[16,17,22,23118-120] The first isomeric tantalum boryl complexes, endo-and exo-[$Cp_2TaH_2(Bcat)$] (Figure 1.2), were reported by Smith and his group using this synthetic route. The endo-isomer can also be formed by an oxidative addition of HBcat to putative "Cp_2TaH".[24]



a

b

Figure 1.2 Isomeric endo (a) and exo (b) tantalum boryl complexes.

Ligand systems other than Bcat have also been prepared by this route. Braunschweig et al. synthesised the first borazine complexes via salt elimination, from $Na[(C_5H_4Me)Fe(CO)_2]$ and $(ClBNH_3)_3$ (Figure 1.3).[25]

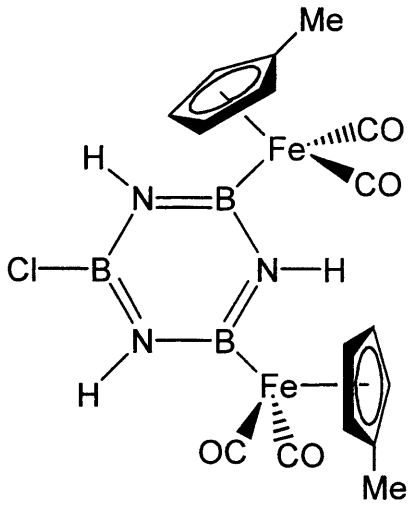
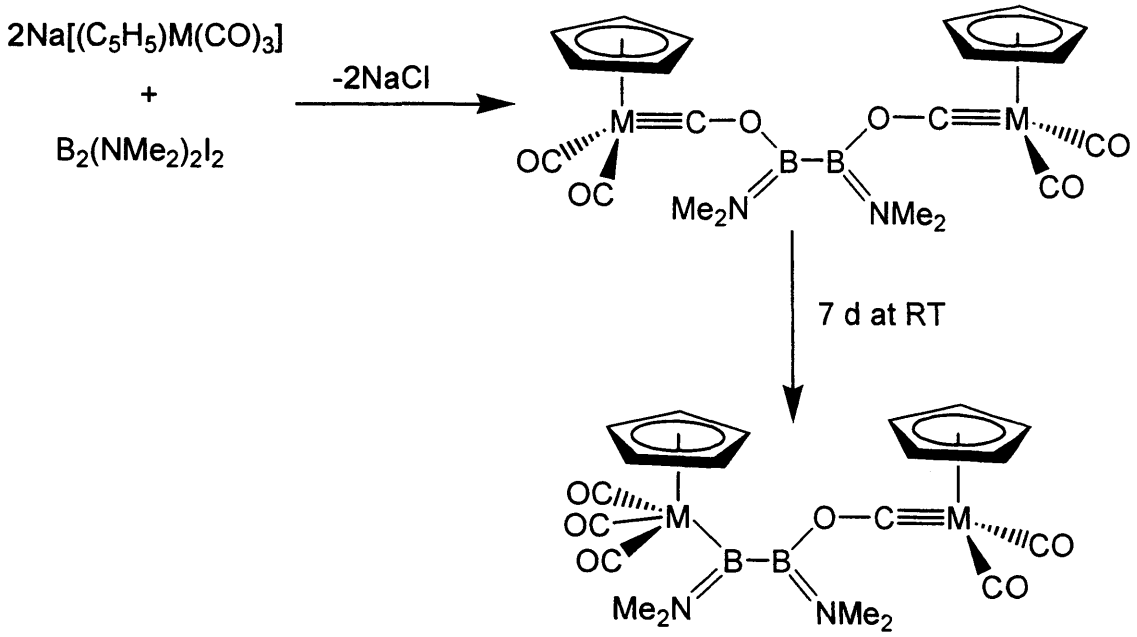


Figure 1.3 The first structurally characterised σ-bound borazine complex of iron.

In addition, Braunschweig has reported the synthesis of metal complexes containing diboran(4)yl ligands, -B(X)-B(X)Y.[26] The reaction of diboranes $B_2(NMe_2)_2Cl_2$ with $Na[(C_5H_5)M(CO)_3]$ to form $(C_5H_5)M(CO)_nB(NMe_2)B(NMe_2)Cl$ (M = Fe, n = 2; M = W, n = 3) proceeds with retention of the boron-boron bond in contrast to the corresponding reactions with manganese anion equivalents (vida infra). Subsequently the corresponding molybdenum complex was synthesised from the more reactive species $B_2(NMe_2)_2Br_2$.[27] The corresponding reactions of the diiododiborane(4) $B_2(NMe_2)_2I_2$ however, yield the dinuclear bis(boryloxycarbyne) complexes $[(C_5H_5)(CO)_2M{=}COB(NMe_2)B(NMe_2)OC{=}M(CO)_2(\eta^5\text{-}C_5H_5)]$ via nucleophilic addition of two CO-oxygen atoms to both boron centres. These complexes undergo a quantitative rearrangement to form the thermodynamically more stable mixed metal boryl/ boryloxycarbyne complexes (Scheme 1.2).[28]



Scheme 1.2 Reaction of $B_2(NMe_2)_2I_2$ with $Na[(C_5H_5)M(CO)_3]$ (M = Mo, W).

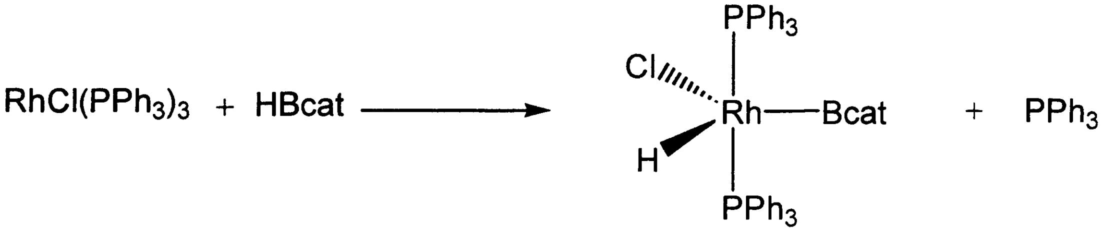
Finally, the salt elimination approach is not limited to monoanionic organometallic precursors, as has been shown by Hartwig through the successful synthesis and characterisation of the bis-boryl complexes $[(CO)_4Fe\{B(1,2\text{-}O_2\text{-}4^tBuC_6H_3)\}_2]$ and $[(CO)_4Fe\{B(1,2\text{-}O_2\text{-}3,5^tBuC_6H_3)\}_2]$ from $[Fe(CO)_4]^{2-}$.[52]

1.2.2.2 Oxidative addition

Oxidative addition of H-B, H-X [X = Cl, Br], B-B, B-Si and even B-Sn bonds to transition metals have been used for the synthesis of mono, bis, and tris-boryl complexes. This reaction involves low valent electron rich metal precursors containing ligands that readily dissociate in solution creating vacant sites in the metal coordination sphere which then allow for the oxidative addition of the boron regent to the metal centre.

1.2.2.2.1 Oxidative addition of hydridoboranes

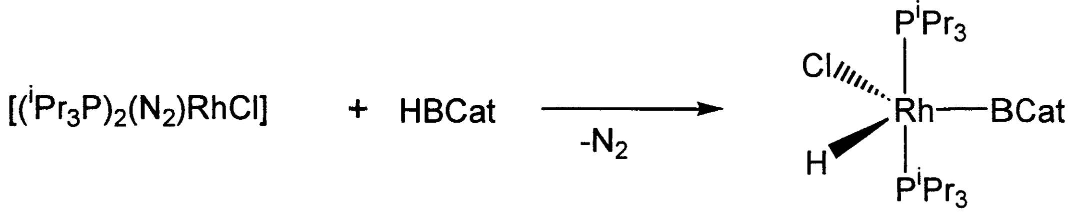
Oxidative addition of B-H bonds has been studied extensively, due its importance in metal catalyzed hydroboration. The oxidative addition of R_2B-H to Wilkinson's catalyst $[RhCl(PPh_3)_3]$ is the most investigated reaction of this kind among studies to date. This work dates from 1975 when Kono et al. reported the oxidative addition of HBcat and 4,4,6-trimethyl-1,3,2-dioxaborinane to Wilkinson's catalyst (Scheme 1.3).[29]



Scheme 1.3 Oxidative addition of HBcat to Wilkinson's catalyst as reported by Kono et al. in 1975.

Ten years later Männig and Schimd showed that this rhodium complex was a highly selective catalyst for the hydroboration of alkenes and 1-hexyne with HBcat.[30] Further studies of the stoichiometric addition of HBcat to Wilkinson's catalyst however, have showed that side products are generated, due in part to the reaction of HBcat with free PPh_3 that has been released from the catalyst.[31] However, reaction with the related Rh(I) dimer $[(Ph_3P)_2RhCl]_2$ produces the $RhHCl(PPh_3)_2(Bcat)$ cleanly; further addition of HBcat to $RhHCl(PPh_3)_2(Bcat)$ then gives the bis-boryl complex $RhCl(PPh_3)_2(Bcat)_2$ with evolution of H_2.[32,33] In a similar fashion, oxidative addition of HBcat to

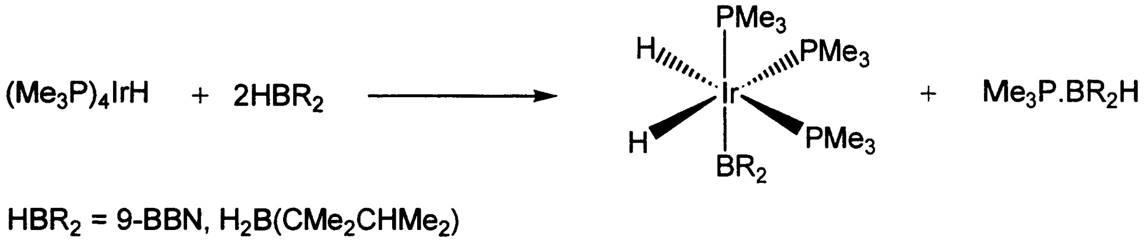
$[RhCl(N_2)(PiPr_3)_2]$ yields the analogous five coordinate Rh(III) boryl complex after loss of the labile ligand N_2 (Scheme 1.4).[31]



Scheme 1.4 Synthesis of a five coordinate Rh(III) complex via oxidative addition of HBcat to $RhCl(N_2)(PiPr_3)_2$.

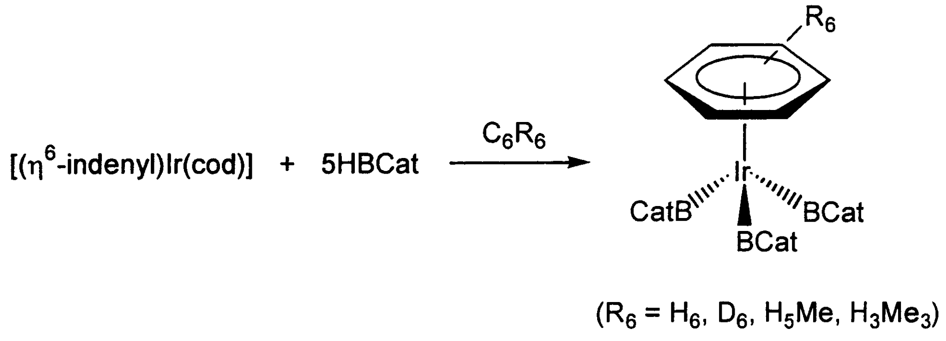
By contrast, reaction of $RhCl(PMe_3)_3$ with HBcat gives the six coordinate complex $RhCl(PMe_3)_3HBcat$ without loss of any labile ligand.[34]

A number of mono, bis, and tris-boryl complexes of iridium have been synthesised by oxidative addition of B-H bonds to low valent iridium complexes. In 1990 Marder et al, reported the two first structurally characterized boryl complexes formed by reacting $IrH(PMe_3)_4$ with two equivalents of $H_2BCMe_2CHMe_2$ or dimeric $[9\text{-}BBNH]_2$ to give *fac*-$(Me_2HCMe_2CBH)IrH_2(PMe_3)_3$ and *fac*-$(H_{14}C_8B)IrH_2$ $(PMe_3)_3$, respectively together with the corresponding phosphine borane adduct (Scheme 1.5).[35]



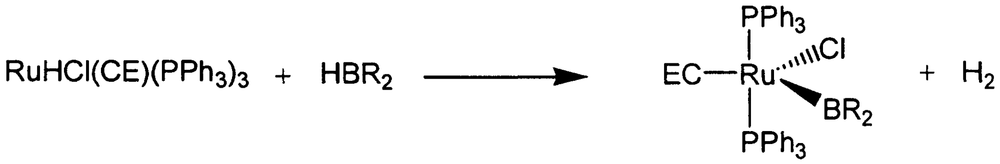
Scheme 1.5 Synthesis of the two first structurally boryl complexes formed by reacting [IrH(PMe_3)$_4$] with $H_2BCMe_2CHMe_2$ or dimeric [9-BBNH]$_2$.

In the same year the complex *mer*-CatBIrHCl(PMe_3)$_3$ was synthesised from IrHCl(PMe_3)$_3$(coe),[36] and in a similar vane, use of the dimeric precursor [Ir(coe)$_2$(μ-Cl)]$_2$ produced *trans*-(CatB)IrHCl(P*i*Pr$_3$)$_2$. Interestingly, iridium-trisboryl complexes have also been synthesised by oxidative addition of B-H bonds. Depending on the arene solvent used, four complexes of the form Ir(η^6-arene)(Bcat)$_3$ have been synthesised in good yields (Scheme 1.6).[37]



Scheme 1.6 Synthesis of Ir(η^6-arene)(Bcat)$_3$ via oxidative addition of B-H bonds and subsequent ligand redistribution.

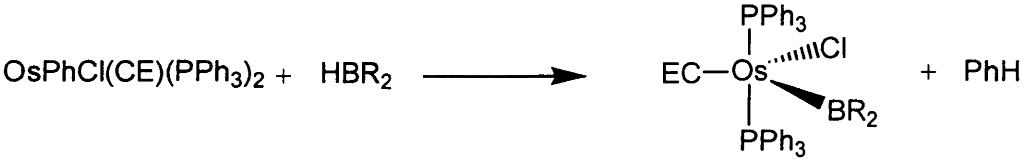
By contrast, reaction of IrH_3(CO)(dppe) with two equivalents of HBcat yields a bisboryl complex.[38] Subsequently, related reactivity of low valent ruthenium and osmium precursors has been investigated, including examples of oxidative addition of HBcat to hydrido-ruthenium and phenyl-osmium species (Schemes 1.7 and 1.8).[3,39,40]



E = O; BR_2 = Bcat, B(2,3-O_2-naphthyl), B[1,2-$(NH)_2C_6H_4$], B[1-S-2-$(NH)C_6H_4$]

E = S; BR_2 = Bcat, B[1-S-2-$(NH)C_6H_4$]

E = N-*P*-tolyl; BR_2 = Bcat



E = O; BR_2 = Bcat, B(1,2-O_2-4-MeC_6H_3), B[1,2-$(NH)_2C_6H_4$], B[1-S-2-$(NH)C_6H_4$]

E = S; BR_2 = Bcat, B[1-S-2-$(NH)C_6H_4$]

Schemes 1.7 and 1.8 Oxidative addition of HBcat to hydrido-ruthenium and phenyl-osmium complexes as reported by Roper and co-workers.

In the case of ruthenium similar compounds can also be made starting from phenyl-ruthenium precursors. However, for the osmium complexes, phenyl precursors were necessary to facilitate the reaction.

Early transition metal boryl complexes have been also been made via oxidative addition. Niobium and tantalum complexes have been prepared from boranes R_2BH and either $(C_5H_5)_2NbH_3$ or $(C_5R_5)_2MH(CH_2{=}CHR')$ (R= H, Me;

M = Nb, Ta; R′ = H, Me).[41,42,43] Both *endo*-(η^5-$(C_5H_5)_2NbH_2(BCat)$ and *endo*-(η^5-$C_5H_5)_2NbH_2(9BBN)$ were obtained from reaction of (η^5-$C_5R_5)_2NbH_3$ with concomitant elimination of H_2. Similarly the endo isomers of $(C_5Me_5)_2NbH_2(BCat)$, $(C_5Me_5)_2NbH_2\{B(1,2\text{-}O_2\text{-}3\text{-}^tBuC_6H_3)\}$, $(C_5H_5)_2TaH_2(BCat)$, $(C_5Me_5)_2TaH_2(BCat)$, and $(C_5Me_5)_2TaH_2(BCat^*)_2$ have been formed by oxidative addition of B-H bonds to the 18-electron alkene complex $(C_5R_5)_2MH(CH_2{=}CHR')$. For the niobium complexes three different possible structures have been identified, depending on the interaction between the boron atom and the two hydride co-ligands. These can be defined by three extremes: (a) d^0 boryl complex, (b) a d^2 dihydroborate complex and (c) a d^2 σ-borane complex (Figure 1.4).[41,42] In practice spectroscopic and structural data imply that type (a) is prevalent for heteroatom stabilised boryl ligands (e.g. R_2 = cat), while (b) is a better structural model for dialkylboryl complexes, presumably as a result of the differing Lewis acidities at boron.

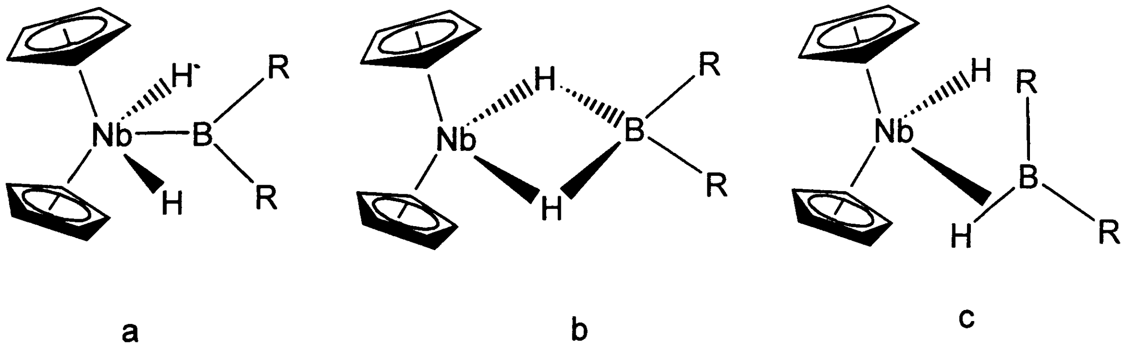
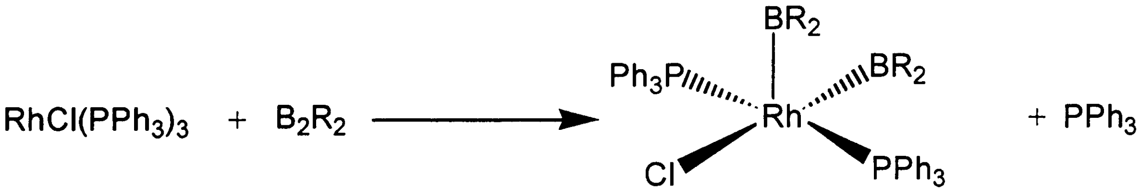


Figure 1.4 The three possible structures for complexes $(C_5H_5)_2NbH_2(BR_2)$.

1.2.2.2.2 Oxidative addition of diboranes (4)

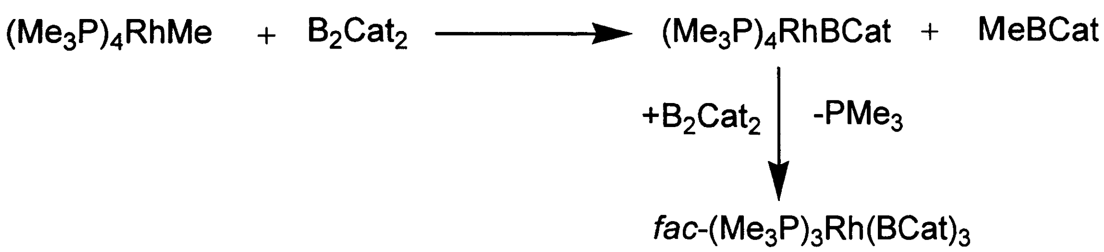
This variant of the oxidative addition methodology proceeds via the addition of a B-B bond to a metal centre that has at least two vacant sites, to form a bis-boryl complex. A wide range of rhodium bis-boryl complexes have been formed by the addition of diboranes(4) following the dissociation of labile phosphine ligands. Wilkinson's catalyst has been reacted with a range of different catechol-based diboranes(4) most of which give identical products with the dimer $[Rh(PPh_3)_3(\mu\text{-}Cl)]_2$ (Scheme 1.9).[44]



BR_2 = BCat, $B(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)$, $B(1,2\text{-}O_2\text{-}3\text{-}MeOC_6H_3)$, $B(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)$, $B(1,2\text{-}O_2\text{-}4\text{-}{}^tBuC_6H_3)$, $B(1,2\text{-}O_2\text{-}3,5\text{-}{}^tBuC_6H_2)$, $B(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)$, $B(1,2\text{-}S_2C_6H_4)$, Btart.

Scheme 1.9 Oxidative addition of diboranes(4) to Wilkinson's catalyst.

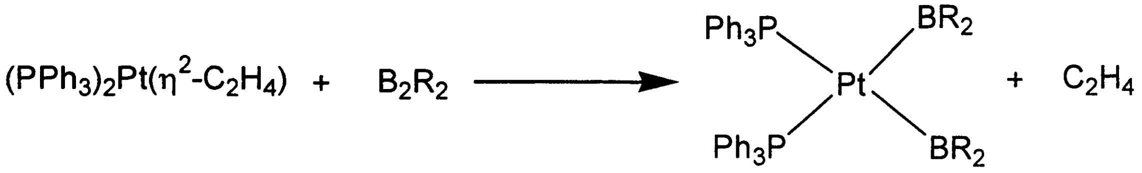
While $RhCl(PPh_3)_3$ reacts with B_2Cat_2 to give a bis-boryl complex, the methyl rhodium complex $RhMe(PMe_3)_4$ demonstrates different chemistry, , reacting with one equivalent of B_2Cat_2 to give the Rh(I) species $Rh(PMe_3)_4(Bcat)$ after loss of MeBcat; further reaction with second equivalent of B_2Cat_2 ultimately forms the novel tris-boryl complex $Rh(PMe_3)_3(Bcat)_3$ (Scheme 1.10).[45]



Scheme 1.10 Oxidative addition of B_2Cat_2 to $RhMe(PMe_3)_4$.

Similarly, the iridium and rhodium complexes $(Et_3P)_2MCl(BCat)_2$ and *cis,mer*-$(Me_3P)_3MCl(BCat)_2$ (M = Ir, Rh) can also be synthesised via oxidative addition of B-B bonds.[44,46]

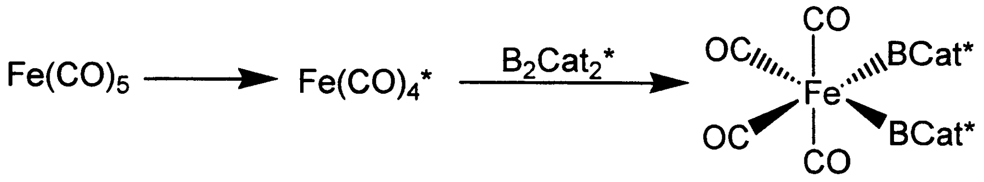
As with rhodium and iridium, many platinum bis-boryl complexes have been synthesised via the oxidative addition of diboranes(4). For example, Iverson and Smith reported the synthesis of $(PPh_3)_2Pt(B_2Cat_2)$ via the displacement of the ethylene group in $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ and subsequent addition of B_2Cat_2.[47] In fact, a variety of platinum bis-boryls have been obtained using the $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ precursor with different diboranes(4) (Scheme 1.11).



R_2 = Cat, B(1,2-O_2-4-^{t}BuC_6H_3),[48] B(1,2-$S_2C_6H_4$), B(1,2-$O_2C_6Cl_4$), B(1,2-$O_2C_6Br_4$),[49] tart, S-O2CH2CHPh, R,R-O2CHPhCHPh,[44] Pin,[50] B(1,2-O_2-3-MeC_6H_3), B(1,2-O_2-4-MeC_6H_3), B(1,2-O_2-3-MeOC_6H_3), B(1,2-S_2-4-MeC_6H_3), B(1,2-O_2-3,5-^{t}Bu$_2C_6H_2$).[3]

Scheme 1.11 Synthesis of different platinum bis-boryl complexes via the oxidative addition of diboranes(4)to $(PPh_3)_2Pt(\eta^2-C_2H_4)$.

Interestingly, oxidative addition of diboranes(4) can also be carried out with a highly reactive organometallic intermediate generated via photochemical ligand loss. For example, Hartwig and co-workers have synthesised the complex $(C_5H_5)_2W(BCat^*)_2$ (Cat* = 1,2-O_2-4-^{t}BuC_6H_3) via the reaction of $B_2Cat_2^*$ with the intermediate $[(C_5H_5)_2W]$, itself obtained by irradiation of $(C_5H_5)WH_2$.[24,51] Similarly, the complexes $(CO)_4Fe(BR_2)_2$ (R_2 = cat, 1,2-O_2-^{t}BuC_6H_3, 1,2-O_2-3,5-^{t}BuC_6H_2) were synthesised by reaction of B_2R_2 with the 16 electron $[Fe(CO)_4]$ intermediate which was obtained upon irradiation of $Fe(CO)_5$ (Scheme 1.12).[52]



Scheme 1.12 Oxidative addition of B_2cat_2 to the 16 electron $[Fe(CO)_4]$ intermediate.

1.2.2.2.3 Oxidative addition of haloboranes

Nőth and Schmid first reported the reaction of haloboranes with a metal hydride to form a metal-boryl complex and one equivalent of HX (Scheme 1.13).[53-55]

$$[ML_nH] + XBR_2 \longrightarrow [ML_nBR_2] + HX$$

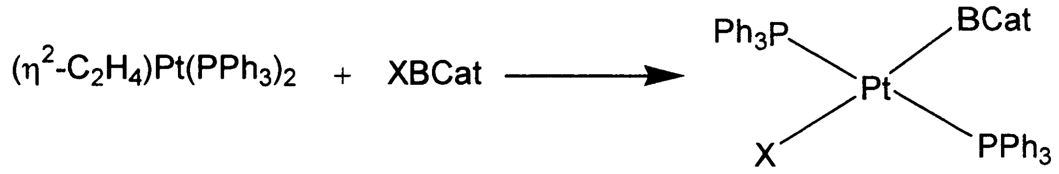
Scheme 1.13 Reaction of haloboranes with a metal hydride.

A 19-electron cobalt complex $Co(dppe)_2(BPh_2)_2$ and the mono-boryl platinum complex $PtCl(PEt_3)_2(BPh_2)$ were also reported to be formed from the reaction of Ph_2BCl with $CoH(dppe)_2$ and $PtHCl(PEt_3)_2$, respectively. Moreover, cobalt complexes of the formula $Co(dppe)(BR_2)_2$ (R = fluorenyl, C_8H_{12}, ClPh, Br_2, I_2) and $Co\{1,2\text{-}(PMe_2)_2C_6H_4\}_2(BR_2)_2$ (R = Ph, $R_2 = C_8H_{12}$) were also reported to have been synthesised using this route (Scheme 1.14).[54,55]

$$[CoH(dppe)_2] + Ph_2BCl \longrightarrow (dppe)_2Co(BPh_2)_2 + HCl$$

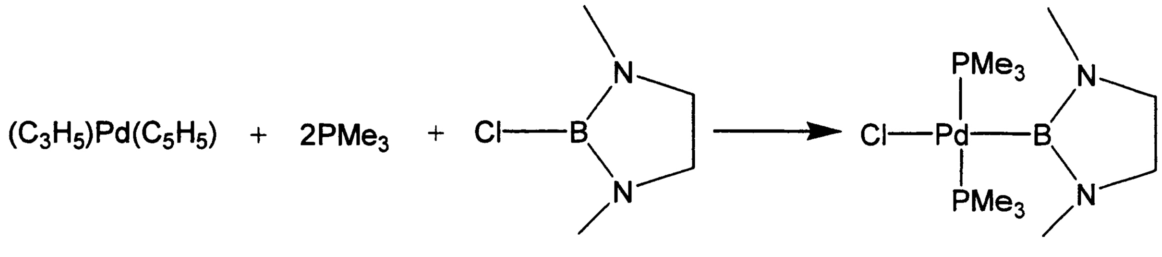
Scheme 1.14 Oxidative addition of Ph_2BCl to $CoH(dppe)_2$.

More recently the oxidative addition of XBCat (X = Cl, Br) to $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ to form the complexes *trans*-$(Ph_3P)_2Pt(X)BCat$ was reported, together with structural data for the Pt(II) products (Scheme 1.15).[49]



Scheme 1.15 Synthesis of *trans*-$(Ph_3P)_2Pt(X)BCat$ via the oxidative addition of XBCat (X = Cl, Br) to $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$

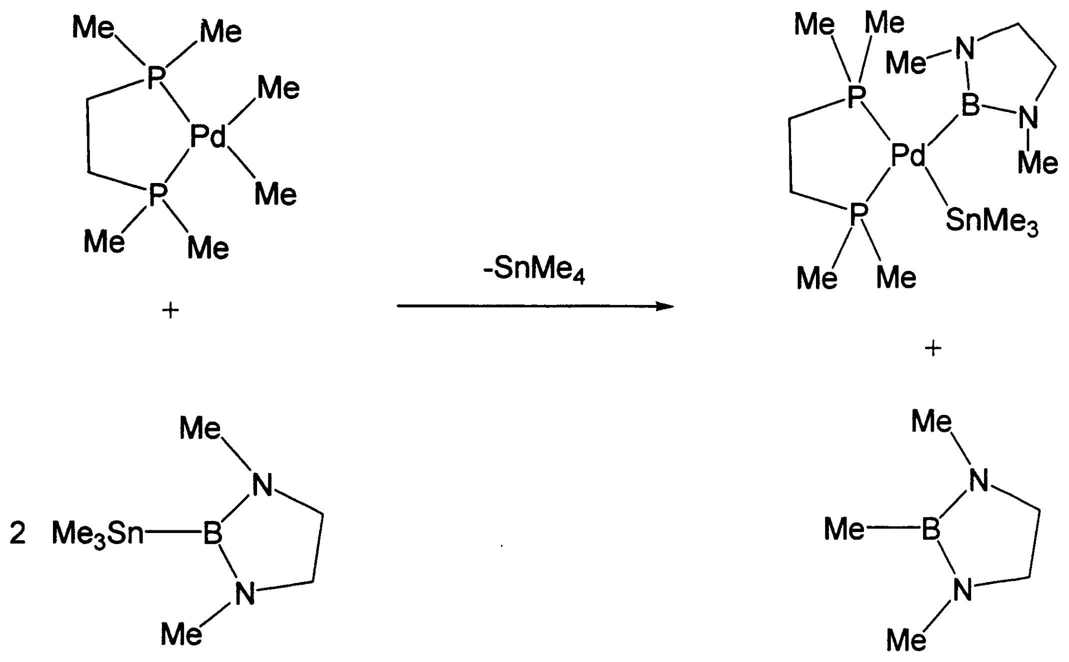
Palladium complexes have also been prepared by the oxidative addition of a B-Cl bond to Pd(0) intermediates derived from $(C_3H_5)Pd(C_5H_5)$ (Scheme 1.16).[56]



Scheme 1.16 Oxidative addition of a B-Cl bond to Pd(0) intermediates derived from $(C_3H_5)Pd(C_5H_5)$.

1.2.2.2.4 Oxidative addition of other borane reagents

Several boryl complexes have been synthesised via oxidative addition reactions that involve different bonds from those mentioned previously. For example, Tanaka et al. reported the oxidative addition of a stannylborane to form the cis-(stannyl)boryl complex $[1,2\text{-}(NMe_2)_2C_2H_4]PdSnMe_3(dmpe)$ (Scheme 1.17).[57] In addition, the silyl(boryl)Pt(II) complexes cis-$Pt(SiMe_2Ph)(BR_2)(PR'_3)_2$ (R' = Et, Me) have been prepared by the oxidative addition of the B-Si bond in $PhMe_2SiBR_2$ (R_2 = Pin, dmeda) to $Pt(cod)_2$ in the presence of PEt_3 or PMe_3.[58]

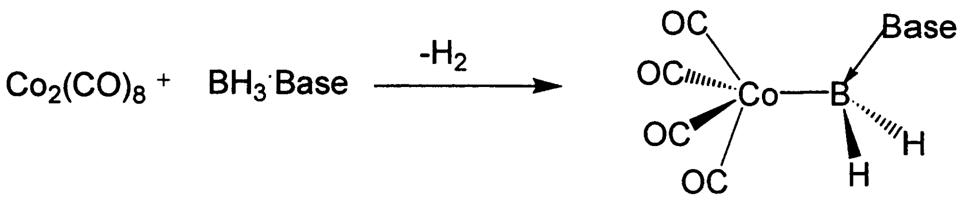


Scheme 1.17 Oxidative addition of a stannylborane to form the cis(stannyl)boryl complex $[1,2\text{-}(NMe_2)_2C_2H_4]PdSnMe_3(dmpe)$.

1.2.2.3 Miscellaneous syntheses

There are some boryl complexes which have not been synthesised by either the salt elimination or oxidative addition routes. For example, the base-stabilised complexes $(CO)_4CoBH_2\cdot base$ (base = THF, SMe_2), were synthesised by Fehlner et al. via the reaction of $Co_2(CO)_8$ with $BH_3\cdot base$, with concomitant loss of H_2 (Scheme 1.18). Due to their thermal instability, these complexes have only been characterised spectroscopically in solution at low temperature.[59,60]

A related phosphine adduct which is more stable has been synthesised by the reaction of $CoCl_2$ with $NaBH_4$ in the presence of dppm and crystallographically characterised.[61]



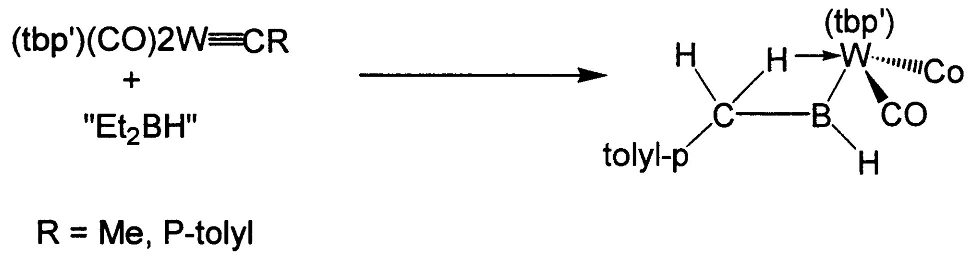
Scheme 1.18 Synthesis of the base-stabilised complexes $(CO)_4CoBH_2{\cdot}base$ (base = THF, SMe_2).

Kawano and co-workers have reported a number of base-stabilised boryl compounds. These include $(C_5Me_5)M(CO)_n(BH_2.PMe_3)$ (n = 2, M = Fe; n = 3, M = Mo, W) which were obtained by the photolysis of $(C_5Me_5)M(CO)_nMe$ in the presence of $BH_3{\cdot}PMe_3$ (Scheme 1.19).[62,63] The iron complex, together with its ruthenium analogue, were also accessible by salt elimination.

$$(\eta^5\text{-}C_5Me_5)M(CO)_nMe + BH_3{\cdot}PMe_3 \xrightarrow{h\nu} (\eta^5\text{-}C_5Me_5)M(CO)_n(BH_2{\cdot}PMe_3)$$

Scheme 1.19 Photolytic synthesis of iron and ruthenium complexes containing the $-BH_2{\cdot}PMe_3$ ligand.

Moreover, a novel mode of formation of boryl complexes has been reported by Wadepohl and co-workers from the reaction of a Fischer carbyne complex with "Et_2BH" (Scheme 1.20). This complex was stabilised by an agostic interaction between the tungsten centre and a methylene proton.[64]



Scheme 1.20 The synthesis of a tungsten boryl complex from a Fischer carbyne and "Et_2BH".

1.2.3 Spectroscopic and structural aspects of boryl complexes

1.2.3.1 Bonding in boryl complexes

Due to the sp^2 hybridization, boron atoms in boryl complexes have a trigonal-planar coordination in which the boron atom is directly bonded to a metal centre. The stability of the metal-boron bond is influenced strongly by the ligands attached to boron, the nature of those completing the coordination sphere of the metal, the metal itself, and its oxidation state. σ-Bonding between the boron and the metal centre can be described in a simplified manner as overlap between the filled sp^2-hybrid orbital centred on boron and an empty orbital of suitable σ-symmetry on the metal (Figure 1.5).

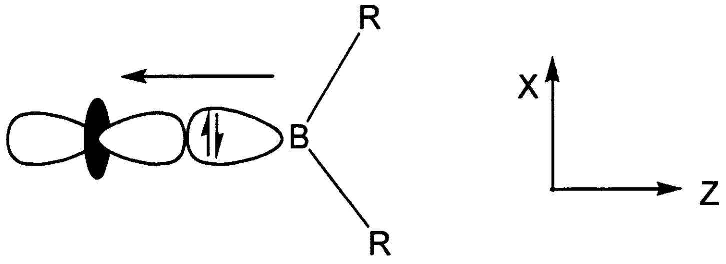


Figure 1.5 σ Donation from the (formal) BR_2^- ligand to a metal centre.

In addition, the possibility of a π back-bonding interaction between the boron centre and the metal exists as long as occupied d orbitals of appropriate symmetry on the metal are able to interact with the empty p_y, orbital on boron.. Stabilization of the boron atom can also be effected by π-donor substituents X, thus giving rise to the competitive π bonding model shown in Figure 1.6 and previously advanced for similar metal carbene complexes.

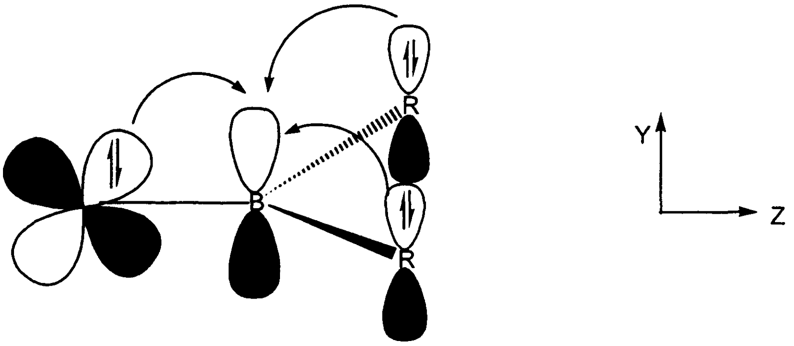


Figure 1.6 The "competitive π bonding model" of stabilisation of the boron $2p_y$ orbital.

1.2.3.2 Spectroscopic features of boryl complexes

1.2.3.2.1 ^{11}B NMR spectroscopy

^{11}B NMR has become one of the major physical tools for any researcher dealing with boron-transition metal complexes, since it offers much information concerning the composition, structure, and dynamics of such compounds. Although definitive proof, especially in cases of ambiguity, usually depends on X-ray methods, ^{11}B NMR nonetheless helps in the assignment of structures.

The shielding of the ^{11}B nucleus is influenced by the chemical nature of the adjacent atoms or groups. Therefore, the chemical shift may be characteristic of the B-E linkages (particularly if E is a transition metal) and if a certain chemical shift is observed this can in turn be used as to assign to this boron atom a certain chemical environment.[31] Boryl complexes display a wide range of ^{11}B NMR chemical shifts. For example three coordinate boryl complexes exhibit values ranging from δ_B 23.9 for $(C_5Me_5)IrH(BF_2)(PMe_3)$[65] to δ_B 141.2 for the complex $(C_5H_5)(CO)_2FeB(Cl)Si(SiMe_3)_3$.[41] Four coordinate boryl complexes typically exhibit upfield chemical shifts eg δ_B -31.7 for $(C_5H_5)_2W(BH_2.PMe_3)$.[63] The change in metal electron density is not necessarily reflected in change of the boron chemical shift. For example, the anionic species $Li[Fe(CO)_4(Bcat)]$, shows a single resonance in the ^{11}B NMR spectrum at δ_B 55; this resonance is downfield of the related neutral species, *cis*-$[Fe(CO)_4(Bcat)_2]$, (δ 45), which cannot be explained simply in terms of electron density on boron.[52] In addition, Hartwig et al., have noted that the interpretation of chemical shifts of metal-boryl compounds and in particular correlation with the degree of π-back-bonding should be approached with caution. This reflects the fact that paramagnetic shielding effects of the metal exert a dominant influence on the chemical shifts of atoms bound directly to that metal.[52]

1.2.3.2.2 Infrared spectroscopy (IR)

IR is useful tool to probe π back-bonding from the metal to boron in boryl complexes. The stretching frequencies of good π-acceptor ligands such as CO, CS, NO, and CNR are very sensitive to ancillary ligand effects. Replacement of CO by a better σ-donor, poorer π-acceptor phosphine ligand results in a lowering of the remaining carbonyl stretching frequencies, since the relative electron density on the metal increases.66,67 From a molecular orbital perspective, higher π acidity leads to reduced donation of electron density into the π* CO orbitals resulting in an increased C-O bond order, and a higher CO stretching frequency. Nőth and Schmid have compared boryl complexes with related compounds containing methyl ligands that are similarly strong σ-donors but incapable of π back-bonding. Comparison of the carbonyl stretching frequencies for $(C_5H_5)Mo(CO)_3(X)$ and $(C_5H_5)W(CO)_3(X)$ $(X=Me,BPh_2,BCl_2)$ indicated a shift to lower wave number for the methyl complex of tungsten, while the opposite trend was observed for the molybdenum derivatives, indicative of stronger back bonding to the carbonyl ligands in the tungsten boryl complexes.[68,3] Hartwig et al. have found that the CO stretching frequencies are higher for $(C_5H_5)Fe(CO)_2(BX_2)$ (X_2 = cat, Ph_2) complexes compared to the corresponding $(C_5H_5)Fe(CO)_2$(alkyl) compounds which are incapable of π interactions, and have attributed this to a small but significant Fe to B π interaction.[3]

1.2.3.3 Structural features of boryl complexes

To date, structurally characterised boryl complexes are the largest among transition metal complexes of boron. With respect to a simple model of the covalent bonding in general form complex L_nMBX_2 (Figures 1.5 and 1.6), the sp^2-hybridized boron atom adopts a trigonal planar geometry and forms a σ-bond to the metal fragment. Generally, the complexes to the left and centre of the periodic table (e.g. Nb, Ta, W, Mn, and Fe) contain M-B bond lengths longer than the sum of the covalent radii, whereas those to the right (e.g. Os, Co, Rh, Ir, Pt) display a shorter bond.[3]

As alluded to in section 1.2.2.2.1 hydrido-metal boryl complexes of the earlier transition metals can be described in at least two different ways: as boryl complexes or as hydroborate complexes. For example, the Nb-B distances for the complexes $(C_5H_5)Nb(H_2BC_8H_{14})$ [2.40(1) Å] and $(C_5H_5)Nb(BCat)$ [2.292(5) Å] suggest that the compound with the longer Nb-B bond is a hydroborate, while the other has been shown in solution to consist of a rapidly equilibrating mixture of the hydroborate and boryl complexes.[37]

In the case of tungsten boryl complexes, the complex $(tbp')W(CO)_2[BEt(CH_2\text{-}4\text{-}MeC_6H_4)]$ displays the shortest W-B distance [2.07(1) Å] (albeit supported by an agostic interaction) which indicates significant π back-bonding from the metal to the boron. Moreover, the complex $(C_5H_5)W(CO)_3\{B(NMe_2)B(NMe_2)Cl\}$ which was the first structurally characterised example of a diboran(4)yl complex has the longest W-B distance [2.370(8) Å].[66] thus, depending on boryl substituents and metal fragment there is considerable scope (ca. 15%) for variation in the W-B bond length.

For the Mn complex $(CO)_5MnBCat$, the Mn-B distance [2.108(6) Å] is shorter than expected from the sum of the covalent radii. Furthermore, there is some indication of π back-bonding from the manganese to the boron provided by the Mn-CO bond distances for the carbonyl ligands. The Mn-CO distance for the carbonyl ligand trans to the Bcat is within the range of other Mn-CO bond distances and not significantly lengthened as would be expected for a boryl ligand which is both a stronger σ donor and weaker π acceptor than CO.[21]

Among the structurally characterised cyclopentadienyl iron haloboryl complexes, there is significant variation not only in the Fe-B distance, but also in the torsion angle θ defined as that between the cyclopentadienyl centroid, the iron and boron atoms and the substituent X. As has been demonstrated both boryl isoelectronic cationic carbene systems, an angle θ of 0° is consistent with optimal π overlap between the a″ HOMO of the metal fragment and the vacant boron-centered p orbital.[13,137,121] For an angle, θ of 90° a less favourable π interaction involving the perpendicular a′ symmetry HOMO-2 orbital of the metal fragment is conceivable. The extent of the π interaction between the iron and boron centres is clearly influenced by both steric and electronic factors, as has been argued previously by Hartwig in his analysis of the compounds $(C_5H_5)Fe(CO)_2BX_2$ (X_2: cat, Ph_2).[13] Two series of compounds serve to highlight the effects on the Fe-B bond of changes in the electronic properties of the boryl ligand. Hence, examining the groups of compounds $(C_5H_5)Fe(CO)_2BX[Si(SiMe_3)_3]$ (X = Cl, F) and $(C_5Me_5)Fe(CO)_2BX(Mes)$ (X: Br, Cl, F), sequentially longer Fe-B bond lengths are achieved by replacement of weakly donor bromo and chloro substituents by the more strongly donating fluoride.[120,130,136] This seems to occur irrespective of the relative orientations of the boryl organometallic fragment. Thus the compounds $(C_5H_5)Fe(CO)_2BX[Si(SiMe_3)_3]$ are characterised by torsion angles approaching 90° (e.g. $\theta = 83.5°$ for X: F), whereas virtually all complexes of the type $(C_5R_5)Fe(CO)_2BX(Mes)$ (including halo and alkoxo derivatives) have $\theta = 0°$ (e.g. 2.3 for X = Br).[112,113,120,122,130,136]

Steric factors can also play a significant structural role, although not always in the manner expected. The structures of the mesityl and phenyl complexes $(C_5Me_5)Fe(CO)_2BCl(Ar)$ (Ar = Mes, Ph) display markedly different orientations of the boryl ligands. These dissimilarities at first inspection appear counter-intuitive, i.e. a significantly shorter Fe-B bond might have been expected for the less sterically demanding phenyl substituent. In fact the respective Fe-B distances are 1.985(2) and 2.006(10) Å for Ar = Mes and Ph, respectively. Examination of the structure of the mesitylboryl complex implies that the orientation of the mesityl group is largely determined by steric factors - the near zero torsion angle (θ) and near perpendicular arrangement of boryl and aryl planes are essentially fixed by the need to minimize steric repulsions between Mes and (C_5Me_5) moieties.[130,136] For $(C_5Me_5)Fe(CO)_2BCl(Ph)$ the smaller size of the phenyl substituent allows for significantly greater conformational freedom. By adopting a conformation with $\theta = 78.6(7)°$ and the angle between boryl and aryl planes set to 31.3(9)°, the phenyl ring takes on an orientation within the crystal lattice such that intermolecular stacking can occur without significant steric repulsion. That the geometry of the boryl complex is markedly influenced by such weak interactions in the solid state further testifies to the relatively small π component of the Fe-B bond.[113]

A good deal of evidence therefore suggests that the M-B bond distance in boryl complexes and the degree of back-bonding from the metal to the boron is influenced by substituents at boron. This is particularly well demonstrated by a series of osmium boryl complexes synthesised by Roper. Comparison of the Os-B length in the five-coordinate complexes $(R_2B)OsCl(CO)(PPh_3)_2$ [R_2 = Cat, Et_2O, 1,2-$(NMe)_2C_6H_4$] showed that the shortest bond was for [$(CatB)OsCl(CO)(PPh_3)_2$] [2.019(3) Å] which has the weakest effective π donor substituents on boron. Hence the Bcat ligand is the best π -acceptor of those examined. The longest bond was found for {[1,2-$(NMe)_2C_6H_4$]B}$OsCl(CO)(PPh_3)_2$ which has the strongest π donors at boron.[3,40,72] Comparison of two isomers of the six-coordinate complex $CatBOsI(CO)_2(PPh_3)_2$ also gives an indication of the π -acceptor ability of the BCat ligand. A much longer Os-CO distance was found for the carbonyl group when trans to BCat than when trans to I, p-tolyl or even CO, thus implying a strong acceptor role for the boryl ligand (Figure 1.8).[40]

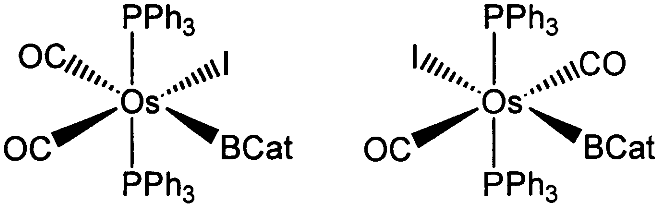


Figure 1.7 The two structurally characterised isomers of $CatBOsI(CO)_2(PPh_3)_2$.

The bis-boryl complex $(Me_3P)_3Co(BCat)_2$ has been reported to adopt a distorted square-pyramidal coordination geometry at cobalt with a phosphine ligand at the apical site (Figure 1.9). The B-Co-B angle is small [67.9(4)°] and the B-B distance, at 2.158 Å, although longer than that in B_2Cat_2 (1.678 Å) is indicative of some residual B--B interaction. The authors' explanation of this was that this complex lays part way along an oxidative addition reaction pathway for the B-B bond.[73]

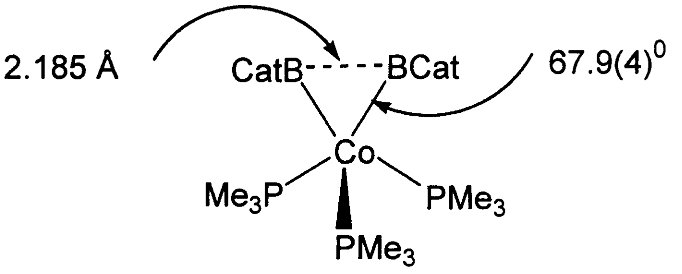


Figure 1.8 The structurally characterised complex $(Me_3P)_3Co(BCat)_2$.

The complex $RhCl(PPh_3)_2(BCat)_2$ has also been reported to display a square pyramidal geometry at the rhodium centre and has two BCat groups in different environments (Figure 1.10).[44] The BCat ligand trans to chloride has a significantly longer Rh-B distance (2.008(4) Å) longer than the BCat in the apical position (1.954(4) Å); this observation reflects how the absence of a trans ligand prevents competition for electron density.

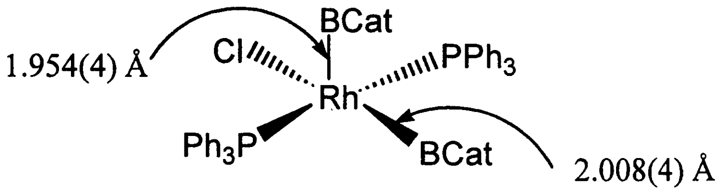


Figure 1.9. The structurally characterised complex $RhCl(PPh_3)_2(BCat)_2$.

Comparison between the two iridum complexes *mer*-$IrHCl(PMe_3)_3BCat$ and *mer,cis*-$Ir(PMe_3)_3Cl(BCat)_2$ (Figure 1.11) shows the differences in the trans influence of Cl, H and BCat.[46] The former has an octahedral geometry; the latter has a similar arrangement with hydride replaced by Bcat. The stronger trans influence of H compared to PMe_3 in *mer*-$IrHCl(PMe_3)_3BCat$ is clear from the longer trans Ir-P distances [Figure 1.11(a)], whereas in *mer,cis*-$Ir(PMe_3)_3Cl(BCat)_2$ the stronger trans influence of BCat compared to hydride is shown by a lengthening of the Ir-P bond trans to BCat compared to the analogous bond trans to hydride.

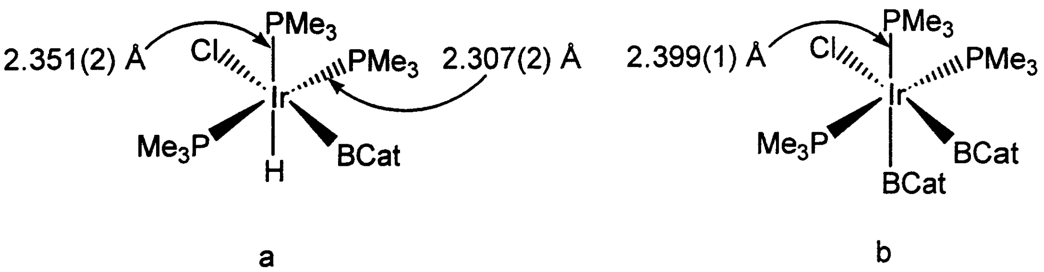


Figure 1.10. The structures of (a) *mer*-$IrHCl(PMe_3)_3BCat$; and (b) *mer,cis*-$Ir(PMe_3)_3Cl(BCat)_2$.

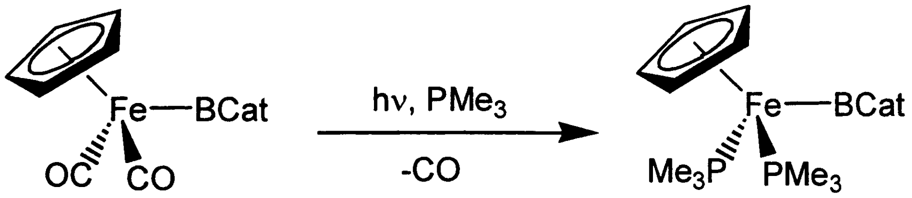
Most of the platinum complexes that have been reported to date adopt a square planar arrangement with cis dispositions of the boryl ligand. Exceptions to this include the complexes *trans*-$(PPh_3)_2Pt(Cl)BR_2$ [R_2 = Cat, $(NMe_2)Cl$] presumably due to the greater trans influence of the boryl ligand compared to PPh_3 and Cl. The Pt-P coupling constants measured for the cis complexes are in the range of 1500-1600 Hz, which is smaller than for typical Pt-aryl complexes and further demonstrates the strong trans influence of the boryl ligand.[74,75]

1.2.4 Reactivity of boryl complexes

The reactivity of boryl complexes has been under increasing investigation due to their important roles in the functionalization of carbon-carbon multiple bonds and in highly selective stoichiometric and catalytic hydrocarbon functionalisation under thermal and photolytic conditions. Reactions of boryl complexes can formally be divided into the following broad types.

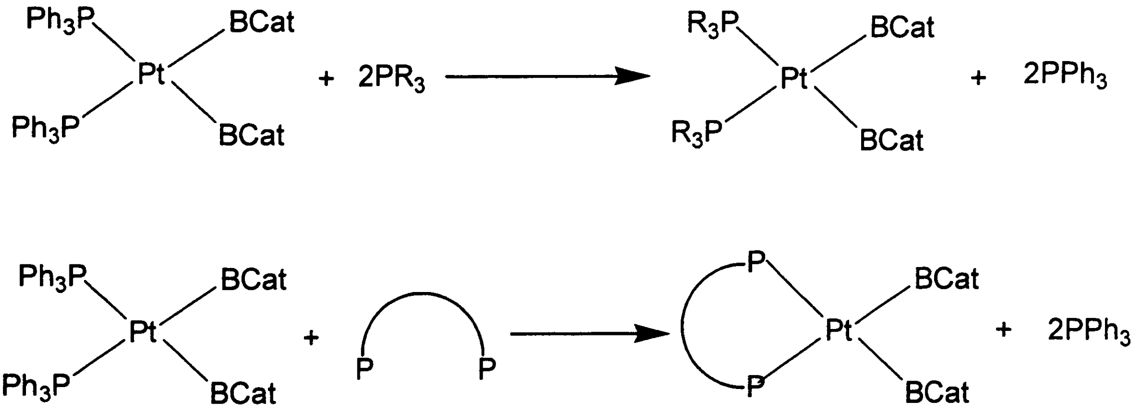
1.2.4.1 Reactions at the metal centre

Many of the reactions of boryl complexes that have been reported to date are ligand substitution at the metal by phosphines or coordination of incoming ligands to a vacant site at the metal. Reactivity of the metal centre is limited due to cleavage of the metal–boron bond under a broad range of experimental conditions. Several examples of substitution of carbonyls in iron and tungsten derivatives by PMe_3 have been reported by Hartwig to occur under photolytic conditions (e.g. Scheme 1.21).[16,76]



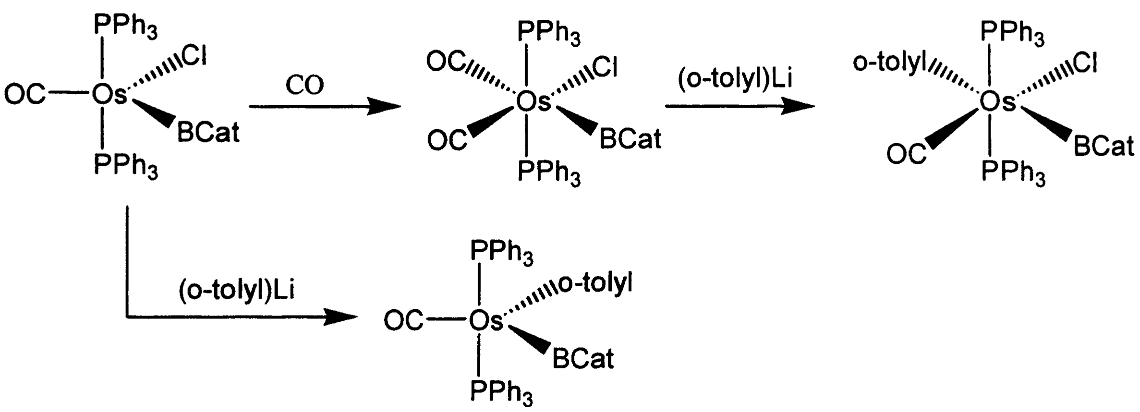
Scheme 1.21 Substitution of carbonyls under photolytic conditions.

Phosphine exchange reactions have also been reported. For example, substitution of the PPh_3 ligands in complex $RhCl(PPh_3)_2(BCat)_2$ by PEt_3 leads to the formation of the five-coordinate complex $RhCl(PEt_3)_2(BCat)_2$, while reaction with PMe_3, PMe_2Ph and $PMePh_2$ instead yields the six-coordinate complexes *cis,mer*-$RhCl(PR_3)_3(BCat)_2$ (R_3 = Me_3, Me_2Ph, $MePh_2$).[44] Exchange of PPh_3 with the bidentate phosphines dppe, dppb, and dcpe in *cis*-$Pt(PPh_3)_2(BCat)_2$ has been reported to form new boryl complexes containing a chelating phosphine ligand (Schemes 1.22 and 1.23).[48,77]



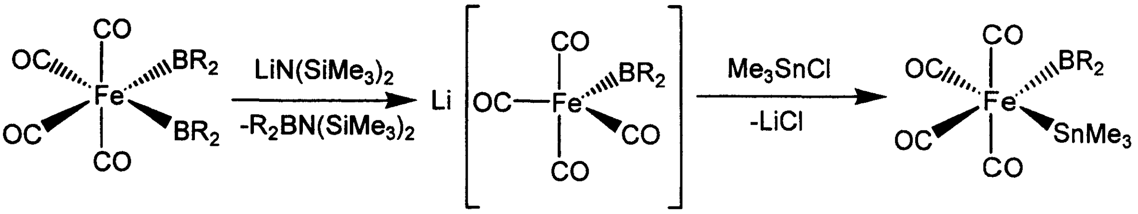
Schemes 1.22 and 1.23 Exchange reactions of PPh_3 with bidentate phosphines.

The reactivity of osmium and ruthenium boryl complexes has been investigated extensively by Roper et al. Five-coordinate osmium and ruthenium boryl complexes were found to react with Lewis bases to form coordinatively saturated complexes. Furthermore, both five- and six-coordinate osmium complexes react with ArLi (Ar = phenyl, o-tolyl) to form the corresponding aryl complexes (Scheme 1.24).[78]



Scheme 1.24 Reaction of both five- and six- coordinate osmium complexes with o-tolyllithium.

The anionic boryl complexes Li[$(CO)_4Fe(BR_2)$] which are themselves formed by abstraction of the boryl fragment from the bis-boryl complexes $(CO)_4Fe(BR_2)_2$ (R_2 = Cat, 1,2-O_2-3,5-$^tBu_2C_6H_2$) have been shown to react with Me_3SnCl to form *cis* stannyl-substituted complexes such as $(CO)_4Fe(SnMe_3)(B\{1,2\text{-}O_2\text{-}3,5\text{-}^tBu_2C_6H_2\})$ (Scheme 1.25).[52]



Scheme 1.25 Reaction of the bis-boryl complexes $(CO)_4Fe(BR_2)_2$ (R_2 = Cat, 1,2-O_2-3,5-$^tBu_2C_6H_2$) with Me_3SnCl.

1.2.4.2 Reaction at boron centre

Reactions at the boron centre reported to date are limited in number, this due to the lability of the M-B linkage and therefore most examples of this type of reaction occur with cleavage of the metal-boryl linkage. Indeed most of boryl complexes that undergo substutition reactions at boron centre with retention of the metal boryl linkage contain weakly π donor substituents such as halides (which are relatively labile).

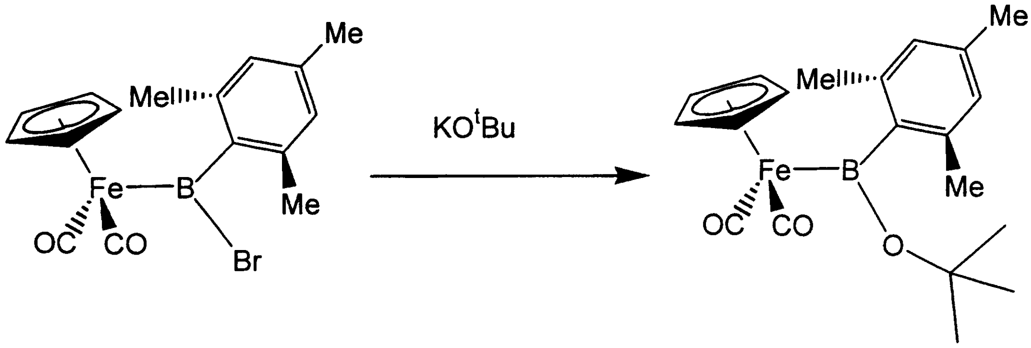
One of the most investigated boron-centered substitution systems is that involving the reactivity of five- and six-coordinate osmium complexes containing the BCl_2 ligand. In particular the boron-centred substitution reactions of $OsCl(CO)(PPh_3)_2(BCl_2)$ have been used to synthesise a number of boryl and base-stabilized borylene complexes. For example Roper et al. reported the controlled hydrolysis of both five- and six-coordinate osmium boryl complexes in the presence of methanol and ethanol to form the analogous dialkoxyboryl complexes (Scheme 1.26).[40]

$$OsCl(CO)(PPh_3)_2(BCl_2) \xrightarrow{ROH} OsCl(CO)(PPh_3)_2[B(OR)_2]$$

$(OR)_2 = (OH)_2, (OMe)_2, (OEt)_2,$
cat, $1,2\text{-}O_2C_6H_4$

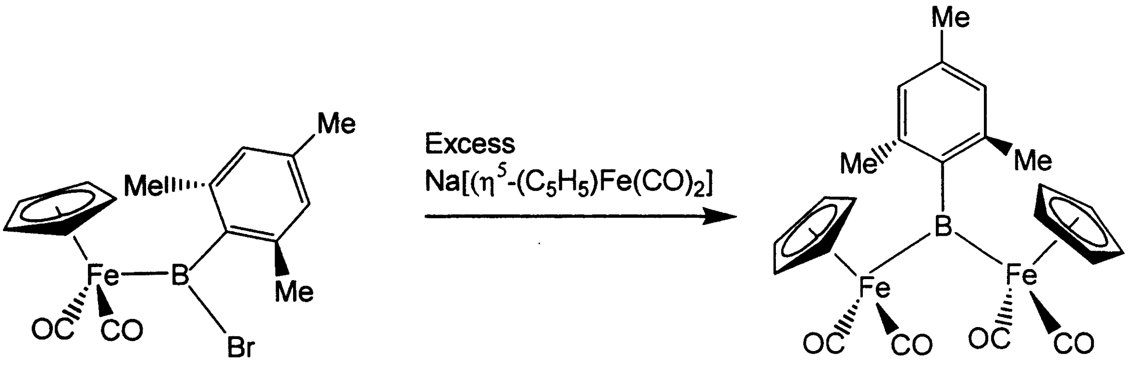
Scheme 1.26 Substitution reactions of a five-coordinate osmium complex with ROH.

A number of cyclopentadienyliron haloboryl complexes have been shown to be robust enough as to undergo substitution reactions at the boron centre with retention of the metal boron bond. For example the synthesis of $(C_5H_5)Fe(CO)_2B(O^tBu)Mes$ from its bromoboryl analogue has been achieved by substitution of the single remaining halide in the precursor boryl complex $(C_5H_5)Fe(CO)_2B(Br)Mes$ (Scheme 1.27).[122]



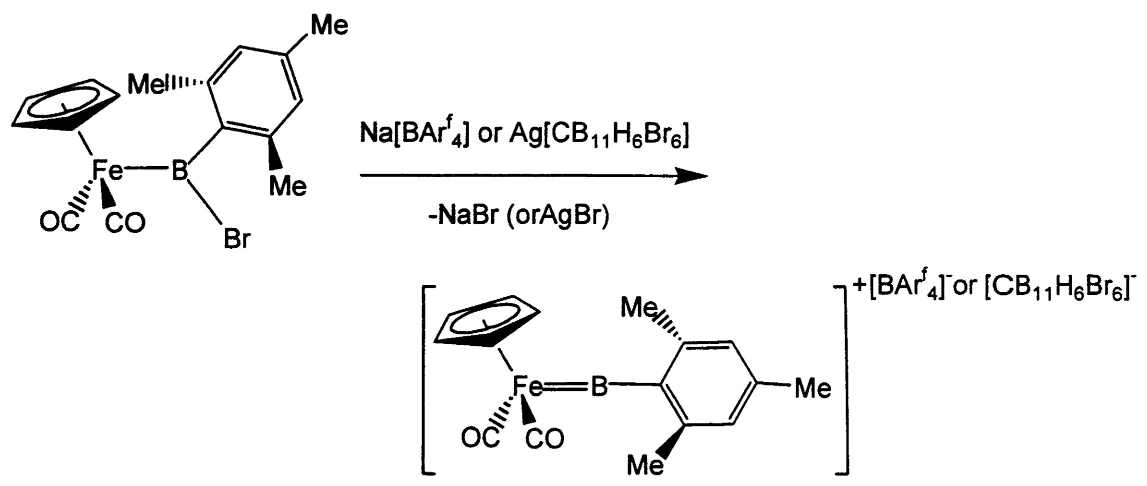
Scheme 1.27 A boron-centred substitution reaction of the boryl complex $(C_5H_5)Fe(CO)_2B(Br)Mes$.

In similar fashion, bridging borylene complexes can also be synthesised,in this case by substitution of the remaining halide by an organometallic nucleophile. One such example, is the synthesis of the unsupported bridging borylene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2BMes$ by the substitution of the Br ligand by an $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ fragment (Scheme 1.28).[112]



Scheme 1.28: The synthesis of the unsupported bridging borylene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2BMes$ by a substitution reaction at a boryl centre.

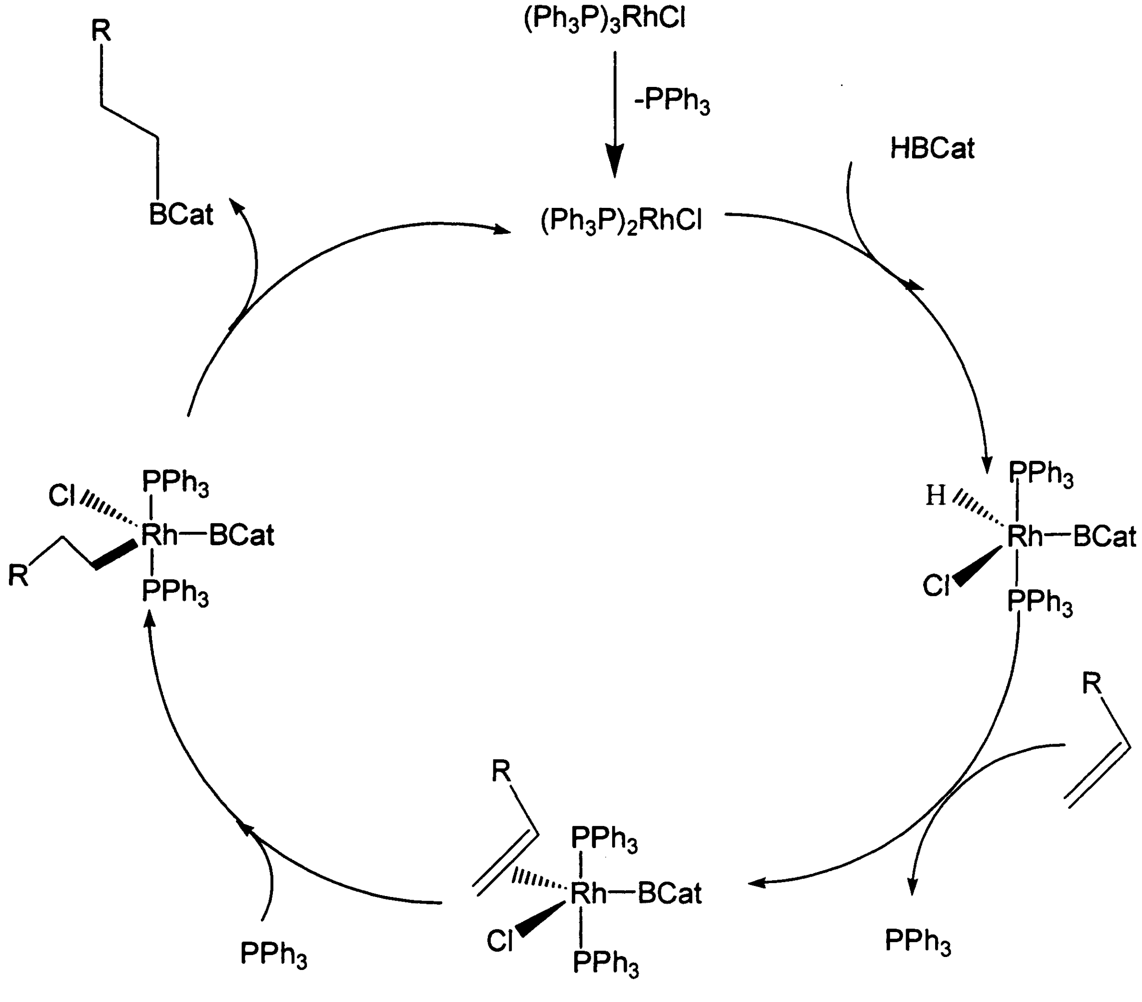
In a number of cases, substitution reactions have been reported to occur via initial abstraction of the boron-bound halide; these include, the 1,4 hydroboration of pyridine by $[(C_5H_4Me)Mn(CO)_2]_2(BCl)$ and certain substitution reactions of osmium boryl complexes reported by Roper.[111,123] In both cases the thermodynamic impetus for the halide abstraction is presumably provided by the precipitation of an insoluble (thallium or silver) halide salt. The synthesis of the terminal borylene complex $[(C_5Me_5)Fe(CO)_2(=BMes)]^+$ via bromide abstraction from $(C_5Me_5)Fe(CO)_2B(Br)Mes$ by either $Na[BAr^f_4]$ or $Ag[CB_{11}H_6Br_6]$ represents an explicit example of this type of chemistry (Scheme 1.29).[124]



Scheme 1.29 Synthesis of the terminal borylene complex [$(C_5Me_5)Fe(CO)_2(=BMes)$]$^+$ via bromide abstraction from the boron centre

1.2.4.3 Hydroboration catalysis

Boryl transition metal complexes play a decisive role in the catalyzed hydroboration of organic multiple bonds. Moreover, it has been found that catalyzed hydroboration can do more than simply activate less reactive boranes, by providing a means of controlling the selectivity of the reaction. For example, the C=C double bond in unsaturated ketones undergoes catalytic hydroboration, whereas the keto group does not.[16,17] Subsequent work has demonstrated not only differences in chemo-selectivity, but also in regio-, diastereo- and enantioselectivity. Early work on hydroboration catalysis was reported by Kono and Nagai in 1975.[79] However, the first example of catalytic hydroboration was discovered in 1980 when Sneddon described the cobalt catalyzed addition of B_5H_9; [80] catalytic hydroboration by Wilkinson's catalyst was reported in 1985 when Nőth described the addition of HBCat to alkenes.[30] The mechanism of hydroboration by Wilkinson's catalyst has been investigated extensively [31,34,81-85] but there still remain some differences in opinion over certain details of the mechanism. These address the question of whether the olefin inserts into the M-H or the M-B bond in the key step.[82,86,87] The most generally favoured mechanistic scheme, i.e. that involving insertion of the alkene into the Rh-H bond is shown in Scheme 1.30.[30]



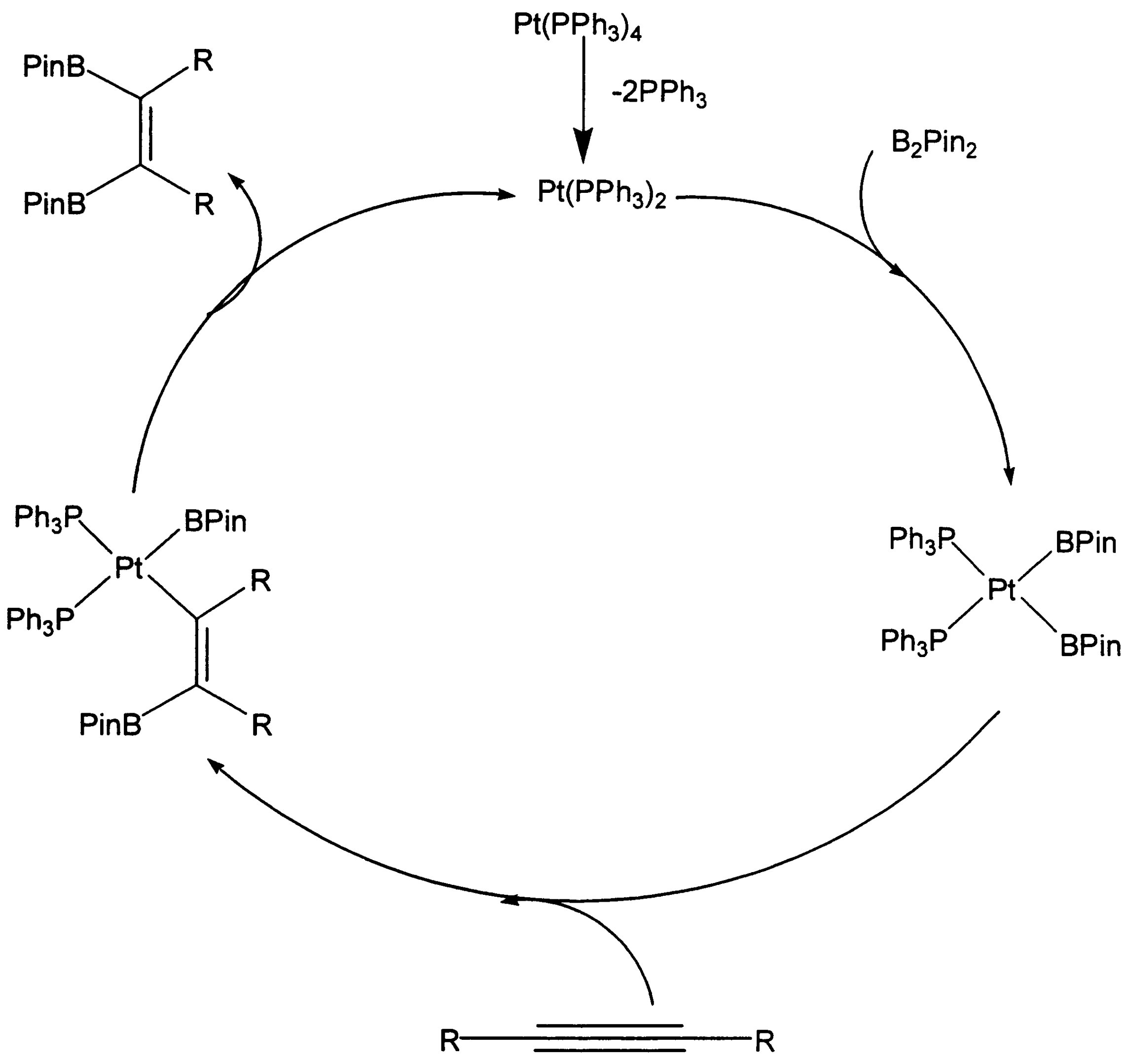
Scheme 1.30 One possible mechanism for the transition metal catalysed hydroboration of olefins.

A number of experimental studies have examined the nature of this mechanism.[31,34] When Wilkinson's catalyst $RhCl(PPh_3)_3$ is used a mixture of products is typically formed due to β-elimination. However, β-elimination can be controlled by the use of an electron rich Au(I) catalyst, made, for example, from $AuCl(PEt_3)$ and two equivalents of $(cHex_2PCH_2)_2$. However, this system only functions with a few activated alkenes, such as vinyl- or allylbenzene.[88,89] Moreover, iridium, palladium and nickel complexes with low oxidation states have also been shown to be active in hydroboration catalysis. Similar catalytic mechanisms to that shown in Scheme 1.30 have been suggested.

Organolanthanide and early transition metal complexes have also been used as hydroboration catalysts, although the proposed mechanism in these systems involves no M-B bonded intermediates.[48,90,91]

1.2.4.4 Diboration catalysis

Diboration of unsaturated organic substrates is related to hydroboration. The use of tetrahalodiboranes(4) to functionalize multiple bonds has been known for a long time.[92] However, the usefulness of this chemistry is limited due to the instability of the diborane precursors. The more stable oxygen substituted diboranes(4) such as B_2Pin_2 and B_2Cat_2, however, do not react with alkenes or alkynes under mild conditions in the absence of a catalyst. However, the synthesis of *cis*-1,2-bis(boryl)alkenes can be effected by diboration using B_2Pin_2 in the presence of $Pt(PPh_3)_4$ as a catalyst.[93] The mechanism of this diboration has been investigated and an outline of the key steps shown in Scheme 1.31.



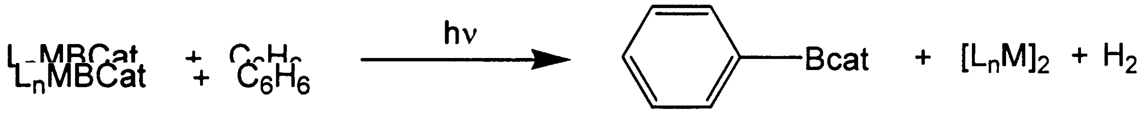
Scheme 1.31 Mechanism for the transition metal catalysed diboration of alkynes.

This reaction has been studied experimentally and theoretically by a number of groups providing data consistent with the mechanism shown in Scheme 1.31.As such the key steps are: firstly, oxidative addition of the B-B bond to the low valent platinum centre, then (rate-determining) alkyne insertion into one Pt-B bond and finally reductive elimination of the 1,2-bisborylalkene.[50,93,94,95] Corresponding addition of compounds with B-Si, B-Sn and B-S bonds to unsaturated organic substrates using platinum and palladium have also been reported.[75,85,93,96]

1.2.4.5 C-H activation by boryl complexes

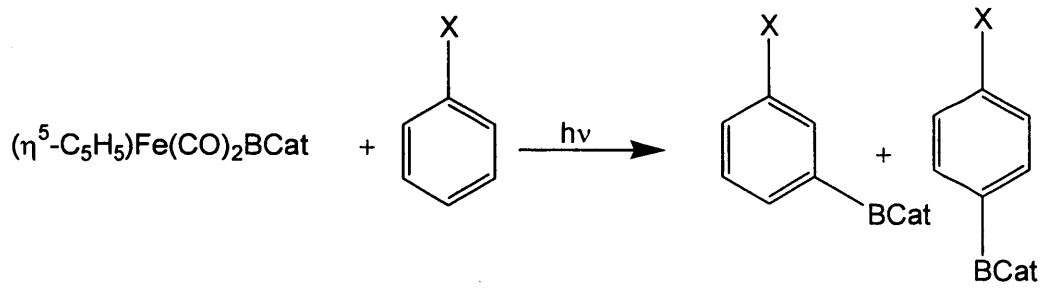
1.2.4.5.1 Arene functionalization

Irradiation of $(C_5R_5)Fe(CO)_2BCat$ (R = H, Me), $(CO)_5MnBCat$ and $(CO)_5ReBCat$ in benzene has been shown to yield PhBCat and the corresponding dinuclear metal complex. $(C_5R_5)Fe(CO)_2BCat$ (R = H, Me) gave PhBCat in quite high yield, while $(CO)_5MnBCat$ and $(CO)_5ReBCat$ gave significant amounts of side-products (Scheme 1.32).[22,76]



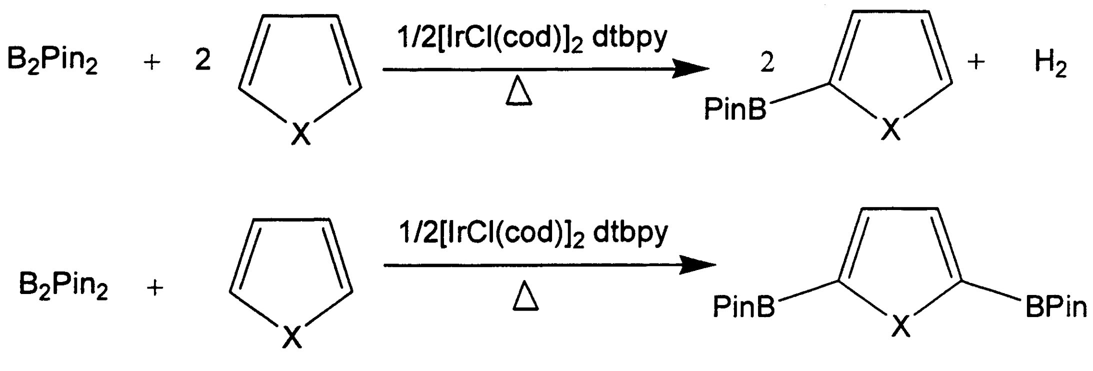
Scheme 1.32 Functionalization of benzene under photolytic conditions.

Photolysis of $(C_5H_5)Fe(CO)_2BCat$ in a variety of mono-substituted arene solvents (PhX) has been shown to form *meta-* and *para*-substituted arylboronate esters in different yields (Scheme 1.33). However, *ortho*-functionalization was observed when anisole (X = OMe) was used. Similar selectivities were seen for $(CO)_5ReBCat$.[76]



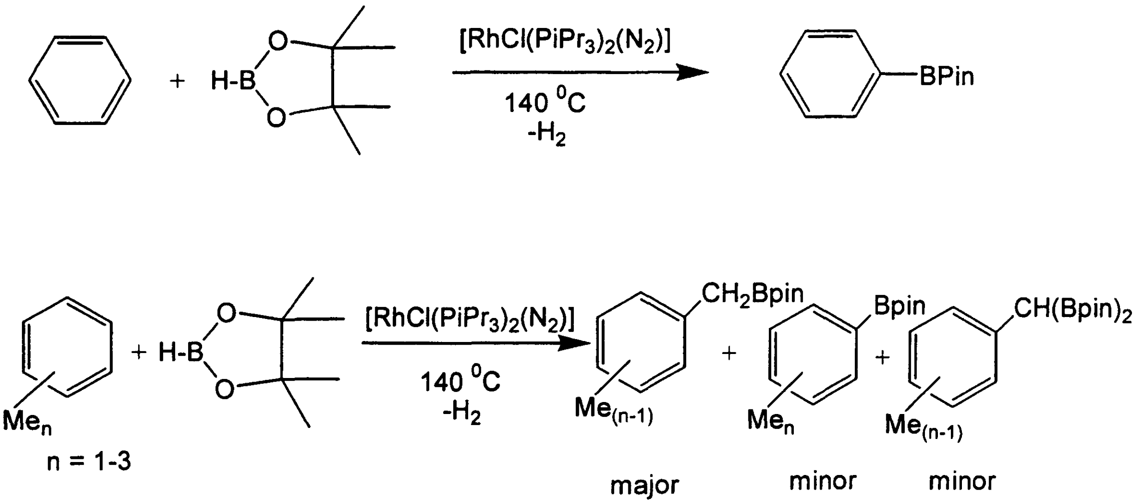
Scheme 1.33 Functionalization of PhX in the meta and para positions under photolytic conditions.

Functionalization of aromatic species using iridium boryl complexes has also been reported.[97-99] Smith et.al have investigated the highly selective functionalisation of a number of arenes using (η^6-mesitylene)Ir(BPin)$_3$ under thermal conditions. They found that the presence of PMe$_3$ is required for the reaction to proceed at temperature below 150°C.[98] The catalytic borylation of a number of heteroaromatic compounds has been reported using a IrCl(cod)$_2$(dtbpy) catalyst and B$_2$Pin$_2$ under thermal conditions (Scheme 1.34).



Scheme 1.34 Catalytic borylation of heteroaromatic compounds.

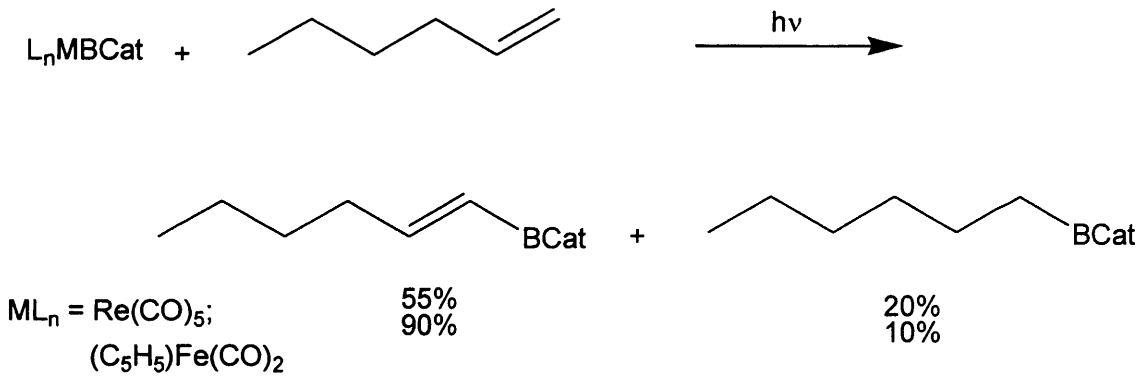
In the case of five membered heterocycles (e.g. furan, thiophene or pyrrole) and benzo-fused derivatives, 2-borylated products were formed. However, with six membered systems (e.g. pyridine or quinoline) the 3-borylated product was formed instead.[100] In related work, Marder et Al. have reported the functionalization of benzene and toluene by HBpin in the presence of $RhCl(P^iPr_3)_2(N_2)$ and found while the functionalization of benzene proceeds via aromatic C-H activation, the major product of toluene occur by benzylic C-H activation (Scheme 1.35).[125]



Scheme 1.35 Catalysed functionalization of benzene and methylarenes by HBpin.

1.2.4.5.2 Alkene functionalization

In addition to the arene functionalisation using $(C_5H_5)Fe(CO)_2BCat$, Hartwig has also use the same complex to functionalize alkenes.[22,76] The functionalization of 1-hexene by irradiation in the presence of an appropriate boryl complex formed the terminal hexenylboronate ester with high selectivity (Scheme 1.36).[76]

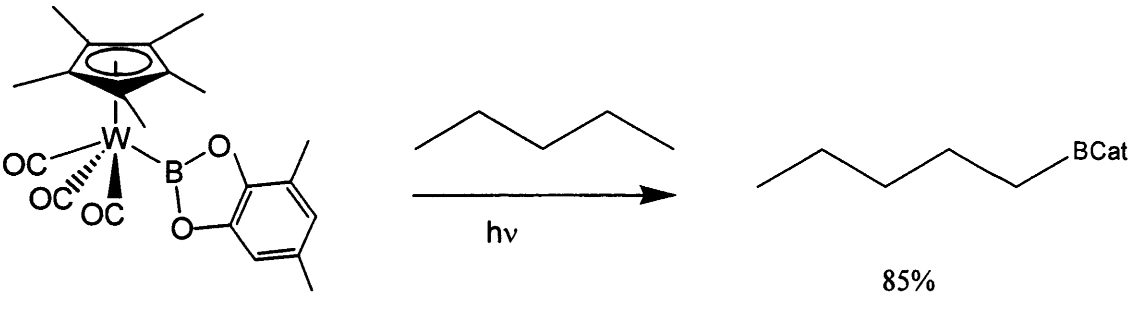


Scheme 1.36 Functionalization of 1-hexane under photolytic conditions.

A similar reaction was achieved using $(C_5H_5)Fe(CO)_2BCat$ with ethylene forming ethynylBCat in 88% yield. The reaction is considered to proceed via photochemical cleavage of a carbonyl ligand and subsequent C-H/C-B oxidative addition/ reductive elimination (or sigma bond metathesis chemistry) rather than through a radical mechanism.[76]

1.2.4.5.3 Alkane functionalization

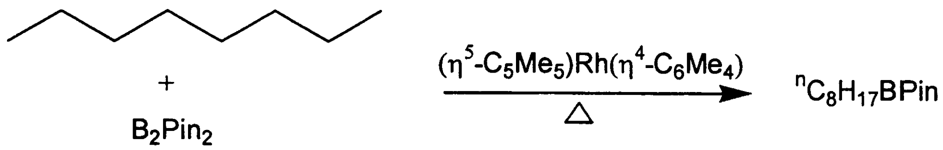
Transition metal boryl complexes can also be used in the functionalisation of alkanes. Hartwig has reported that irradiation of simple transition metal complexes of the formula $(C_5Me_5)M(CO)_nB(OR)_2$ [M = Fe, Ru, n = 2; M = W, n = 3; $(OR)_2$ = bulky catechol-type substituents] in alkane solvents yields products resulting from selective functionalization of the alkane at the terminal position (Scheme 1.37).[16,17]



Scheme 1.37 Selective functionalization of pentane at the terminal position using isolated transition metal boryl reagents.

There is much debate as to why piano-stool boryl complexes of this type should show such unusual reactivity especially with respect to alkane systems which are difficult to functionalize using other organometallics. Certainly the overall thermodynamics of this functionalization process are favourable (or neutral at the very worst), and the kinetics of B-C reductive elimination have been calculated to be very rapid.[16,17]

Hartwig et al. have also described a metal catalysed functionalization process yielding the 1-pentylboronate ester from pentane using B_2pin_2 under photolytic conditions.[101] The thermal, catalytic functionalization of alkanes has also been investigated. Reaction of octane with B_2pin_2 catalysed by 5 mol% $(C_5Me_5)Rh(\eta^4\text{-}C_6Me_4)$ at 150°C formed n-octylBpin in 88% yield (Scheme 1.38).[101]



Scheme 1.38 Metal catalysed functionalization of octane using B_2pin_2.

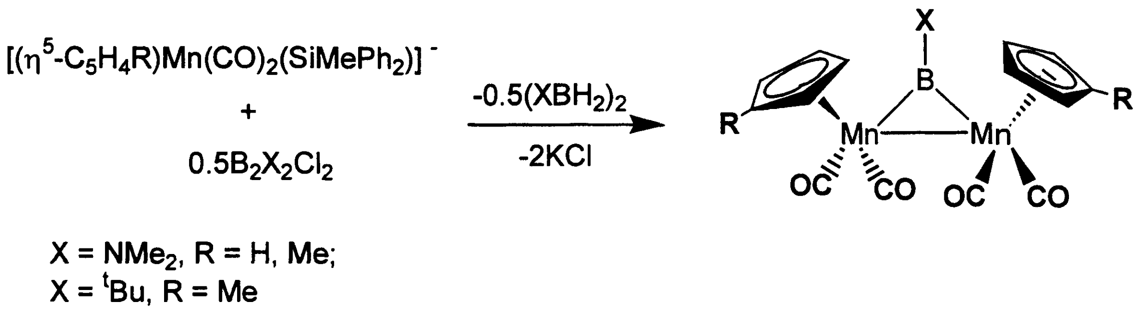
1.3 Borylene complexes

There are two predominant modes of coordination for transition metal complexes featuring the borylene ligand, BX; bridging between two metals, (featuring boron centres with coordination number of three), and terminally bound to one metal centre, with a coordination number of two. Borylene complexes featuring either bridging or terminal modes of coordination have been realised only recently.

1.3.1 Synthesis of borylene complexes

1.3.1.1 From diboranes(4)

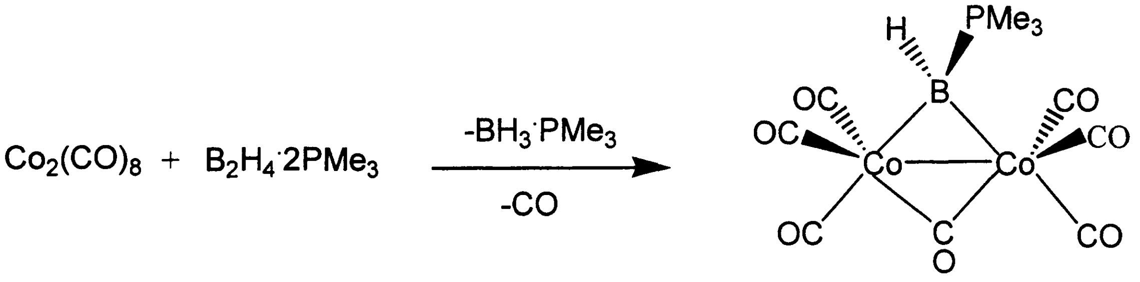
The first bridged borylene complexes $[(\mu\text{-BX})\{(\eta^5\text{-}C_5H_4R)Mn(CO)_2\}_2]$ were synthesised by Braunschweig et al. in 1995.[102] These complexes were formed by the reaction between the dianion synthetic equivalent $K[(C_5H_4R)Mn(CO)_2(SiMePh_2)]$ (R = H, Me) and a diborane(4) species $B_2X_2Cl_2$ (X = NMe_2, ^tBu), with cleavage of the B-B bond (Scheme 1.39).



Scheme 1.39 Syntheses of bridged borylene complexes (μ-BX){(η^5-C_5H_4R)Mn$(CO)_2$}$_2$ from diboranes(4).

Similar reaction with the corresponding anionic manganese hydride complex K[(η^5-C_5H_4R)HMn$(CO)_2$] has been found to improve the synthetic yield.[103] The same manganese hydride has also been used to synthesise two further borylene complexes (μ-BX){(η^5-C_5H_4Me)Mn$(CO)_2$}$_2$ (X = NC_4H_8, NC_5H_{10}).[104]

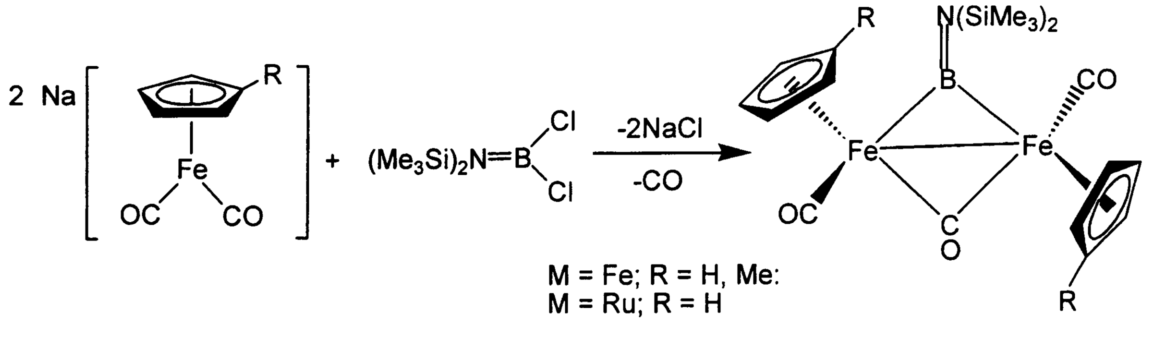
The first example of a base-stabilised bridged borylene complex [Co$(CO)_3$]$_2$(μ-CO)(μ-BH·PMe_3) was reported by Shimoi;[105] this complex was synthesised by the reaction of $Co_2(CO)_8$ with B_2H_4·2PMe_3 and involves fragmentation of the diboron(4) reagent into BH_3·PMe_3 and BH·PMe_3 and liberation of one of the cobalt-bound carbonyl ligands (Scheme 1.40).



Scheme 1.40 Syntheses of the base-stabilised bridged borylene complex [Co$(CO)_3$]$_2$(μ-CO)(μ-BH·PMe_3).

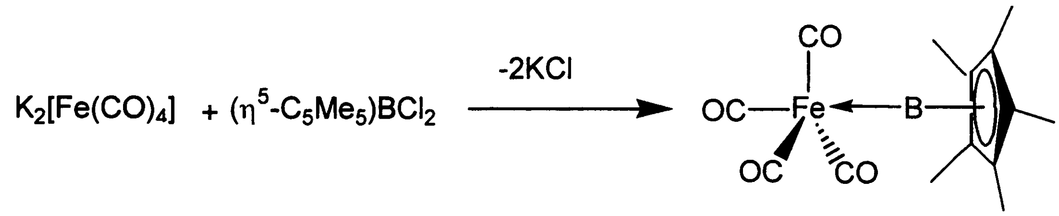
1.3.1.2 From dihaloboranes

The salt elimination reaction between transition metal anions and dihaloboranes affords a more generally applicable route to bridging borylene complexes.[106] The iron complexes $[(\eta^5\text{-}C_5H_4R)Fe(CO)]_2[\mu\text{-}BN(SiMe_3)_2]$ (R = H, Me) were the first bridging borylene complexes reported using this route. These complexes were synthesised by the reaction of $(Me_3Si)_2NBCl_2$ with two equivalents of $Na[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]$ (Scheme 1.41). It has been found that the reaction of Me_2NBCl_2 with $Na[(\eta^5\text{-}C_5H_4R)Fe(CO)_2$ formed exclusively a boryl complex with replacement of only one chlorine atom, whereas the reaction of the analogous (silylamino)borane $(Me_3Si)_2NBCl_2$ yields only the bridging borylene complex. This has been attributed to the electronic properties of the silyl group which make $[(Me_3Si)_2N]BCl_2$ more reactive by weakening the boron-nitrogen double bond. The analogous ruthenium complex $[(\eta^5\text{-}C_5H_4R)Ru(CO)]_2[\mu\text{-}BN(SiMe_3)_2]$ has also been synthesised by this route.[107]



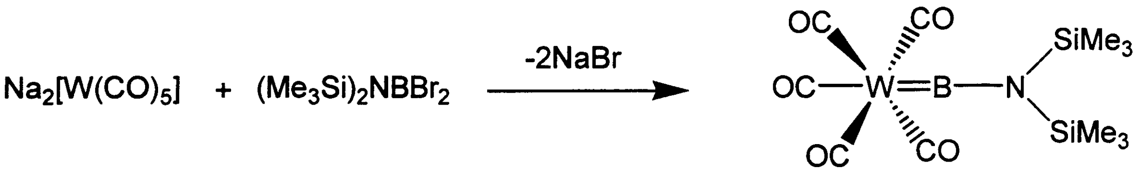
Scheme 1.41 Syntheses of the bridging borylene complexes $[(\eta^5\text{-}C_5H_4R)Fe(CO)]_2[\mu\text{-}BN(SiMe_3)_2]$ from dihaloboranes.

This methodology has also been used for the synthesis of terminal borylene complexes. Cowley et al. reported the synthesis of $(CO)_4FeB(\eta^5\text{-}C_5Me_5)$ by the salt elimination reaction between the dihaloborane $(\eta^5\text{-}C_5Me_5)BCl_2$ and the metal dianion $K_2[Fe(CO)_4]$ (Scheme 1.42).[126]



Scheme 1.42 Synthesis of the terminal borylene complex $(CO)_4FeB(\eta^5\text{-}C_5Me_5)$.

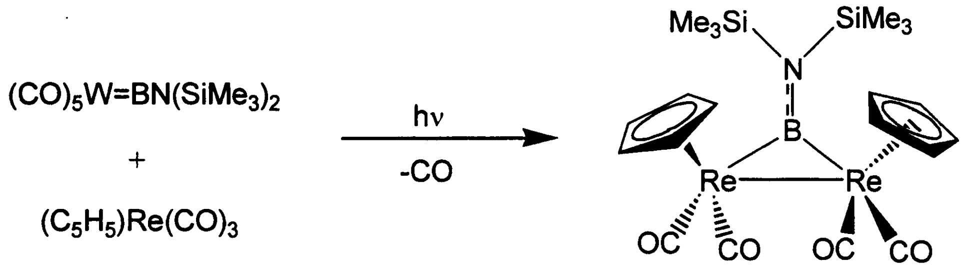
In similar fashion, Braunschweig et al. used the salt elimination reaction between the dihaloborane $(SiMe_3)_2NBBr_2$ and the metal dianion $Na_2[W(CO)_5]$ to synthesise the terminal borylene complex $(CO)_5W{=}BN(SiMe_3)_2$ (Scheme 1.43).[127]



Scheme 1.43 Synthesis of terminal borylene complex $(CO)_5W{=}BN(SiMe_3)_2$.

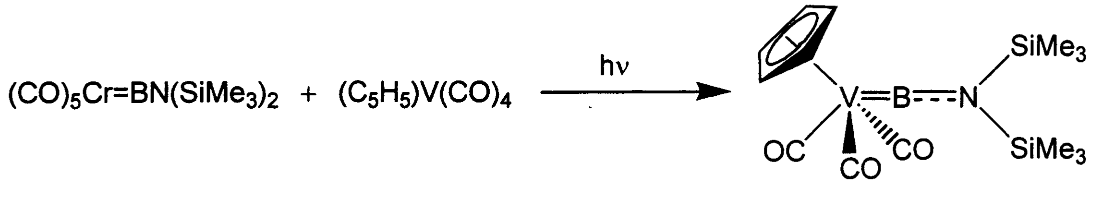
1.3.1.3 Photochemical borylene transfer

Photochemically induced borylene transfer is a new route for the synthesis of bridging borylene complexes reported by Braunschweig et al in 2001. Photolysis of the terminal borylene complex $(CO)_5W{=}BN(SiMe_3)_2$ in the presence of $(C_5H_5)Re(CO)_3$, for example, formed the bridging borylene $[(C_5H_5)Re(CO)_2]_2[\mu\text{-}BN(SiMe_3)_2]$ (Scheme 1.44).[108].



Scheme 1.44 Synthesis of $[(C_5H_5)Re(CO)_2]_2[\mu\text{-}BN(SiMe_3)_2]$ by photolysis of the terminal borylene $(CO)_5W{=}BN(SiMe_3)_2$ in the presence of $(C_5H_5)Re(CO)_3$.

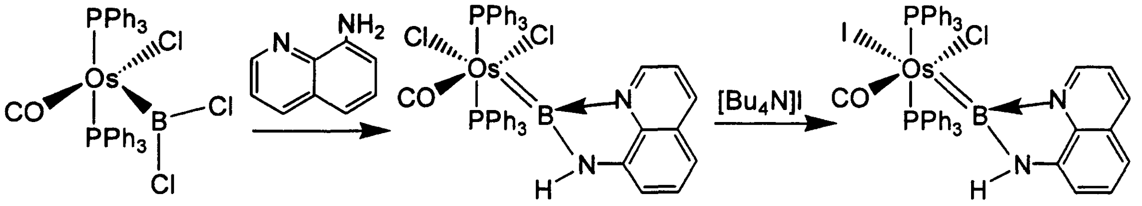
This method also enables the synthesis of a number of terminal borylene complexes e.g. $(C_5H_5)V(CO)_3BN(SiMe_3)_2$ formed by the photolysis of $(CO)_5Cr{=}BN(SiMe_3)_2$ in the presence of $(C_5H_5)V(CO)_4$ (Scheme 1.45).[128]



Scheme 1.45 Synthesis of the terminal borylene complex $(C_5H_5)V(CO)_3BN(SiMe_3)_2$.

1.3.1.4 Boron-centred substitution and abstraction chemistry

The terminal borylene complex $[(C_5Me_5)Fe(CO)_2(=BMes)]^+$ has been synthesised via the abstraction reaction between $(C_5Me_5)Fe(CO)_2B(Br)Mes$ and either $Na[BAr^f_4]$ or $Ag[CB_{11}H_6Br_6]$ (vide supra). The first intramolecular base-stabilised terminal borylene complex $Os{=}B(NHC_9H_6N)Cl_2(CO)(PPh_3)_2$ was synthesised by the boron centred substitution reaction of $OsCl(CO)(PPh_3)_2(BCl_2)$ with 8-aminoquinoline (Scheme 1.6) and then reacted with $[Bu_4N]I$ to form the iodide analogue which was crystallographically characterised.[129]



Scheme 1.46 Synthesis of the intramolecular base-stabilised terminal borylene complex $Os{=}B(NHC_9H_6N)Cl_2(CO)(PPh_3)_2$.

1.3.2 Structural and spectroscopic features

A significant deshielding of the ^{11}B NMR resonance is the most characteristic spectroscopic feature which all bridging borylene complexes have in common; this is due to the formation of two metal-boron bonds. The tert-butyl borylene complex $(\mu\text{-}B^tBu)\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2\}_2$ shows the most downfield chemical shift at δ_B 170.0, [102] due to the lack of π interaction with the ^tBu substituents. In the case of amino substituted complexes in which N-B π interaction is present, higher field ^{11}B NMR resonances ranging from δ_B 100.4 to 119.1 ppm are observed.[106,108] Due to the increased coordination number of the boron centre, the base-stabilised complex $[Co(CO)_3]_2(\mu\text{-}CO)(\mu\text{-}BH{\cdot}PMe_3)$ shows the most upfield chemical shift at δ_B 17.5.[105]

Most of the bridging borylene complexes that have been reported feature a borylene centre that is supported by a metal-metal bond (e.g $[(C_5H_4R)Fe(CO)]_2[\mu\text{-}BN(SiMe_3)_2]$, $[Co(CO)_3]_2(\mu\text{-}CO)(\mu\text{-}BH{\cdot}PMe_3)$ and $[(C_5H_5)Re(CO)_2]_2[\mu\text{-}BN(SiMe_3)_2]$.[102,106,105,109-111] On the other hand, examples of bridging borylene complexes that feature an unsupported bridging ligand have recently been reported e.g $[(C_5H_5)Fe(CO)]_2(BMes)$.[121] In the supported bridging borylene complexes the metal-metal and metal-boron distances are in the range expected for single bonds and thus can be considered as three-membered MBM metallacycles. The M-B bond distances in the unsupported complex $[(C_5H_5)Fe(CO)]_2(BMes)$ [(2.090(10) Å] are significantly longer than those found in similar complexes containing a M-M bond {e.g. $[(\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(BMes)$, 2003(3) Å}.[130] Significantly longer M-B distances have been reported for the base-stabilised complex $[Co(CO)_3]_2(\mu\text{-}CO)(\mu\text{-}BH{\cdot}PMe_3)]$ [2.110(10) Å].[102,105,106]

A number of crystallographically characterised terminal borylene complexes have recently been reported. The Fe-B bond in $(C_5Me_5)BFe(CO)_4$ [(2.010(3) Å],[126] for example, is very much longer than that in $[(C_5Me_5)Fe(CO)_2(BMes)]^+$ [1.792(8) Å]. [124] The latter linkage can be viewed as double bond similar to those found in tungsten and chromium amino- and silyl-borylenes, i.e. composed of a B to Fe donor/acceptor component supplemented by Fe to B back-bonding. This implies a significantly greater back-bonding component in $[(C_5Me_5)Fe(CO)_2(BMes)]^+$ than in $(C_5Me_5)FeB(CO)_4$, with the Fe-B bond in the latter being viewed as a simple B to Fe donor/acceptor linkage.

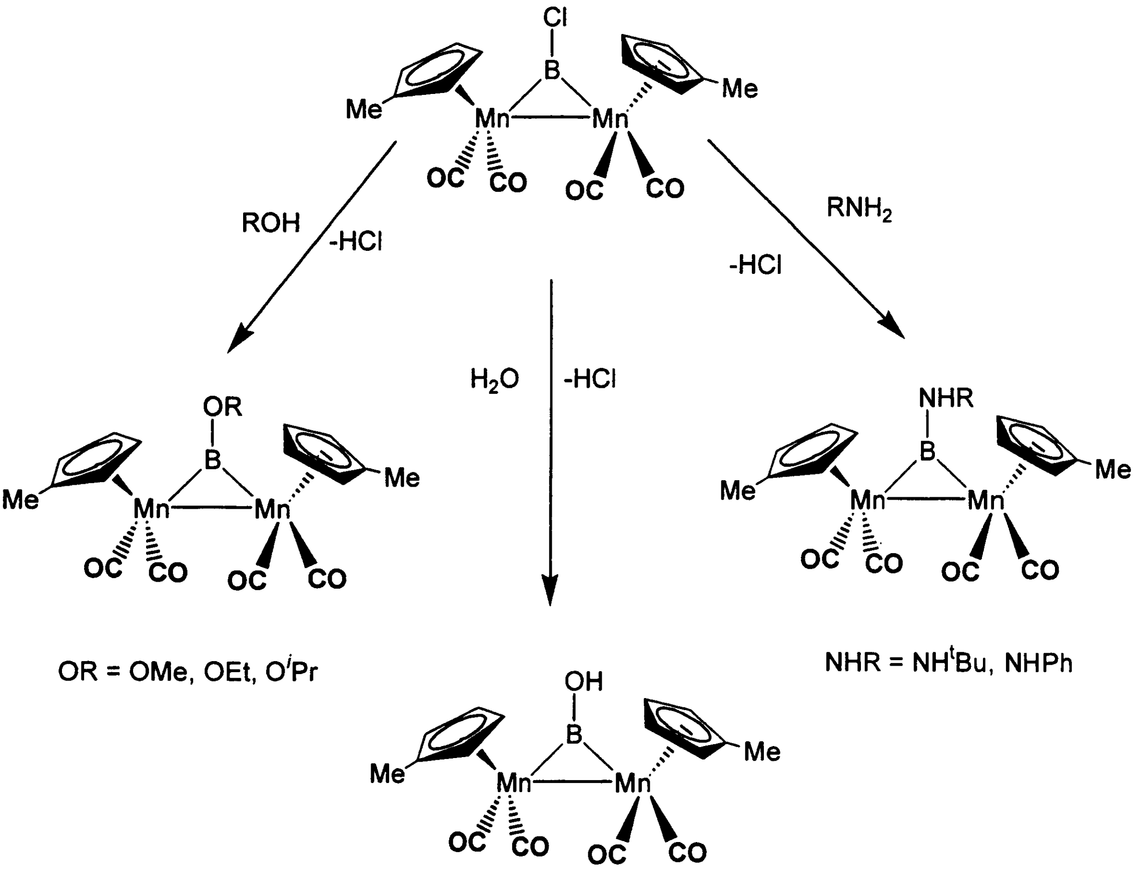
1.3.3 Theoretical studies

Recently, borylene complexes have been the subject of a number of computational investigations.[114,115] It has been found that borylene complexes should be thermodynamically stable due to the good σ donor and π acceptor properties of BX ligand.[116,117] However, studies on the uncoordinated borylene ligand suggested low kinetic stability due to high polarity and a small HOMO-LUMO gap. Kinetic stability should be increased by complexation which will increase the HOMO-LUMO gap. However, the imbalance between σ–donation and π–acceptance in these complexes is thought to lead to a positive charge on the boron atom of the borylene ligand and to lability to nucleophilic attack. The stability of borylene complexes can be enhanced by steric protection by using bulky substituents at the boron centre or by complexation in a binuclear transition metal fragment such as $Fe_2(CO)_8$ or $(C_5H_5)_2Mn_2(CO)_4$.

The bonding between the metal and the boron centre in terminal borylene complexes has also been examined by computational studies.[115,131,132,134] It has been found that the interaction of the metal and boron centres consists of a B to M donor/acceptor σ component, accompanied to a greater or lesser extent (depending on borylene and metal substituents) by an M to B π back-bond. The M to B π back-bond in homoleptic terminal borylene complexes is found to be greater than for terminal borylene containing carbonyl ligands. In addition, recent computational work by Frenking and co-workers has shown that the sum of the covalent interactions in terminal borylene complexes typically gives a bond order of less than one, leading to the conclusion that the bonding in terminal borylene complexes is mainly ionic.[115,132,133]

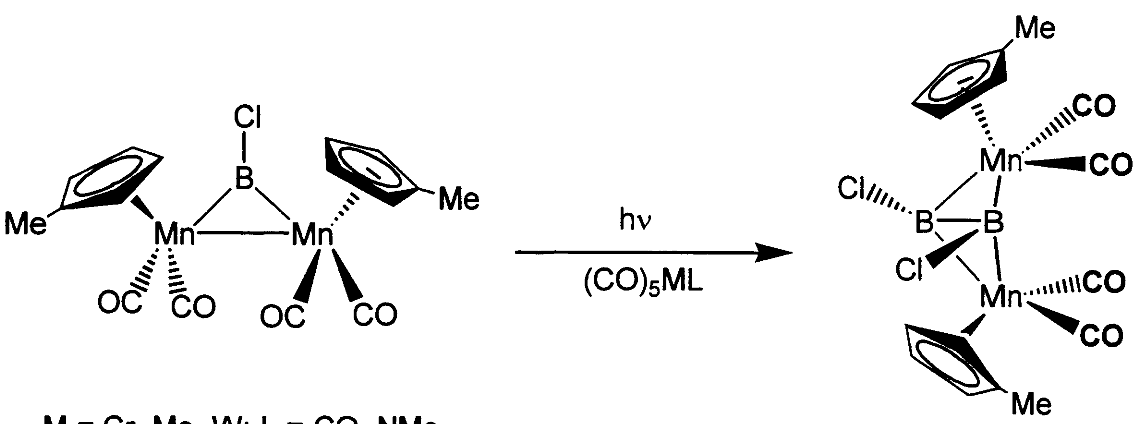
1.3.4 Reactivity

It has been found that the aminoborylene complexes $(\mu\text{-BX})\{(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn(CO)}_2\}_2$ (R = H, Me; X = NMe_2) display uniquely high stability toward air and moisture.[26,102] Moreover, these complexes display low reactivity towards nucleophilic substitution at the bridging boron centre. Reaction of $(\mu\text{-BNMe}_2)\{(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn(CO)}_2\}_2$ with an excess of HCl however generates the chloroborylene complex $[(\mu\text{-BCl})\{(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn(CO)}_2\}_2$ and, as expected, this complex displays much higher reactivity toward nucleophilic substitution at the borylene centre. It has therefore been utilised for further substitution chemistry (Scheme 1.47).[109]



Scheme 1.47: Substitution reactions at the borylene centre of a bridging chloroborylene complex.

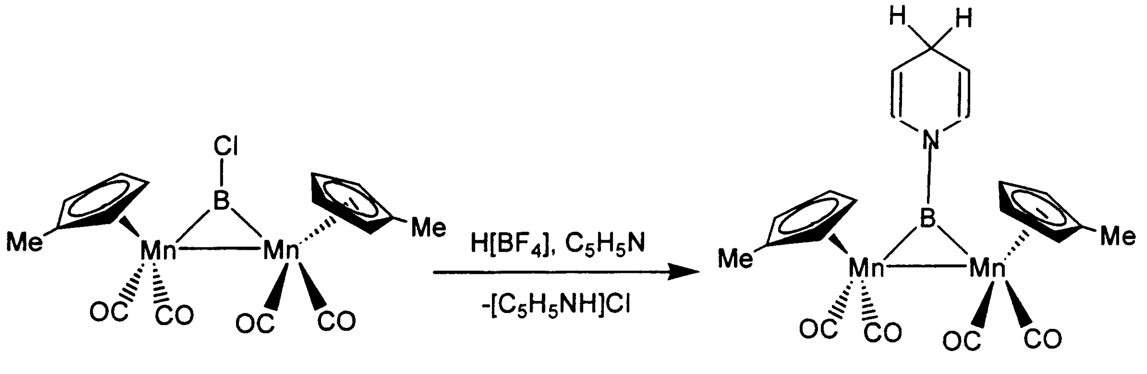
Very recently, Braunschweig has reported further studies on the reactivity of the chloroborylene complex [(μ-BCl){(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$. Photolysis in the presence of M(CO)$_6$ (M = Cr, Mo, W) formed not a terminal borylene complex via borylene transfer but a novel metallaborane complex. This metallaborane (Scheme 1.48) is thought to be formed via dimerisation of the putative intermediate terminal chloroborylene complex "(C_5H_4Me)Mn(CO)$_2$BCl".[110]



M = Cr, Mo, W; L = CO, NMe_3

Scheme 1.48 Synthesis of the metallaborane $[(\mu\text{-BCl})_2\{(C_5H_4Me)Mn(CO)_2\}_2$.

Additionally treatment of the same chloroborylene complex with pyridine formed not the expected base-stabilised borylene complex, but (in the presence of protic reagents) yielded $[(C_5H_4Me)Mn(CO)_2]_2[1\text{-}(\mu\text{-B})\text{-}4\text{-H-}(NC_5H_5)]$ (Scheme 1.49).[111] This complex, derived from the 1,4-hydroboration of pyridine was suggested to be formed via initial chloride abstraction and subsequent attack of pyridine at the boron centre.



Scheme 1.49 Reaction of $[(\mu\text{-BCl})\{(C_5H_4Me)Mn(CO)_2\}_2$ with pyridine in the presence of protic reagents.

1.4 Aims of the present research

The objectives for the research described in this thesis were as follows:

(i) To investigate further the nature of the transition metal boron bond in boryl systems, and in particular the scope for π back-bonding from the metal to the boron centre. This was to be accomplished by a combined synthetic and computational study, for example involving complexes containing the bis(pentafluorophenyl)boryl and related ligands, precursors to which have been reported by Chivers and Chambers in 1965.[135] Such ligands might offer greater potential for π back-bonding due to the strongly electron withdrawing C_6F_5 substituents. Using the precedented salt elimination route, the synthesis of a variety of metal complexes was to be attempted. Detailed investigation of the M-B bonding and comparison with previously reported complexes was then to be carried out by using spectroscopic, structural and the Density Functional studies.

(ii) To exploit the alternative oxidative addition route for the synthesis of related boryl complexes containing late transition metals such as platinum and rhodium.

(iii) Base-stabilised boryl and borylene complexes number significantly fewer than two- and three-coordinate systems. Therefore, it was planned to synthesise base-stabilised haloboranes, $R_nBX_{3-n}\cdot L$ (n = 0, 1, 2) which act as precursors to base-stabilised boryl and borylene complexes via salt elimination. The resultant complexes would provide useful comparison with two- and three-coordinate borylene and boryl complexes [and in particular with the strongly π acidic -B(C_6F_5)$_2$ containing systems synthesised under (i) and (ii)].

1.5 References

1. G Schmid, Angew. Chem. Int. Ed. Engl., 1970, 9, 819.
2. H. Wadepohl, Angew. Chem. Int. Ed. Engl., 1997, 36 2441.
3. G.J. Irvine, M.J.G. Lesley, T.B. Marder, N.C. Norman, C.R. Rice, E,G. Robins, W.R. Roper, G.R. Whittell, L.J. Wright, Chem. Rev., 1998, 98 2685.
4. H. Braunschweig, Angew. Chem. Int. Ed. Engl., 1998, 37, 1786.
5. M.R. Smith III, Prog. Inorg. Chem. ,1999, 48, 505.
6. B. Wrackmeyer, Angew. Chem. Int. Ed. Engl., 1999, 38, 771.
7. H. Braunschweig, M. Colling, J. Organomet. Chem., 2000, 18, 614.
8. H. Braunschweig, M. Colling, Coord. Chem. Rev., 2001, 1, 223.
9. H. Braunschweig, M. Colling, Eur. J. Inorg. Chem., 2003, 393.
10. H. Nőth, G. Schmid, Angew. Chem. Int. Ed. Engl., 1963, 2, 623.
11. G. Schmid, Angew. Chem. Int. Ed. Engl., 1970, 9, 819.
12. A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams, Angew. Chem. Int. Ed., 1999, 38, 2759.
13. J. F. Hartwig, S. Huber, J. Am. Chem. Soc., 1993, 115, 4908.
14. S. Aldridge, D. L. Coombs, Coord. Chem. Rev., 2004, 535.
15. C. N. Iverson and M. R. Smith, J. Am. Chem. Soc., 1999, 121, 7696.
16. K. M. Waltz, J. F. Hartwig, Science, 1997, 277, 211.
17. K. M. Waltz, J. F. Hartwig, J. Am. Chem. Soc., 2000, 122, 11358.
18. H. Chen, S. Schlecht, T. C. Semple, J. F. Hartwig, Science, 2000, 287, 1995.
19. K. Burgess, M. J. Ohlmeyer, Chem. Rev., 1991, 91, 1179.
20. I. Beletskaya, A. Petter, Tetrahedron, 1997, 53, 4957.

21. S. Shimada, A. S. Batsanov, J. A. K. Howard, T. B. Marder, Angew. Chem., Int. Ed., 2001, 40, 2168.

22. K. M. Waltz, X. He, C. Muhoro, J. F. Hartwig, J. Am. Chem. Soc., 1995, 117, 11357.

23. P. R. Rablen, J. F. Hartwig, S. P. Nolan, J. Am. Chem. Soc., 1994, 116, 4121.

24. D. R. Lantero, D. H. Motry, D. L. Ward, M. R. Simth III, J. Am. Chem. Soc., 1994, 116, 10811.

25. H. Braunschweig, C. Kollann, M. Müller, Eur. J. Inorg. Chem., 1998, 291.

26. H. Braunschweig, B. Ganter, M. Koster, T. Wagner, Chem. Ber., 1996, 129, 1099.

27. H. Braunschweig, M. Koster, R. Wang, Inorg. Chem., 1999, 38, 415.

28. H. Braunschweig, M. Koster, K. W. Klinkhammer, Angew. Chem. Int. Ed. Engl., 1999, 38, 2229.

29. H. Kono, K. Ito, Y. Nagai, Chem. Lett., 1975, 1095.

30. D. Männig, H. Nőth, Angew. Chem. Int. Ed. Engl., 1985, 24, 878.

31. S. A. Westcott, H. P. Blom, T. B. Marder, R. T. Baker, J. C. Calabrese, Inorg. Chem., 1993, 32, 2175.

32. K. Burgess, W. A. van der Donk, S. A. Westcott, T. B. Marder, R. T. Baker, J. C. Calabrese, J. Am. Chem. Soc., 1992, 114, 9350.

33. R. T. Baker, J. C. Calabrese, S. A. Westcott, P. Nguyen, T. B. Marder, J. Am. Chem. Soc., 1993, 115, 4367.

34. S. A. Westcott, N. J. Taylor, T. B. Marder, R. T. Baker, N. J. Jones and J. C. Calabrese, J. Chem. Soc., Chem. Commun., 1991, 304.

35. R. T. Baker, D. W. Ovenall, J. C. Calabrese, S. A. Westcott, N. J. Taylor, I. D. Williams, T. B. Marder, J. Am. Chem. Soc., 1990, 112, 9399.

36. J. R. Knorr, J. S. Merola, Organometallics, 1990, 9, 3008.

37. P. Nguyen, H. P. Bolm, S. A. Westcott, N. J. Taylor, T. B. Marder, J. Am. Chem. Soc., 1993, 115, 9329.

38. B. P. Cleary and R. Eisenberg, Organometallics, 1995, 14, 4525.

39. G. J. Irvine, W. R. Roper, J. L. Wright, Organometallics, 1997, 16, 2291.

40. G. R. Clark, G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, in Contemporary Boron Chemistry, eds. A. K. Hughes, T. B. Marder, K. Wade, MPG Book, Bodmin, 200, p 379.

41. J. F. Hartwig, S. R. De Gala, J. Am. Chem. Soc. 1994, 116, 3661.

42. D. R. Lantero, D. L. Ward, M. R. Smith III, J. Am. Chem. Soc., 1997, 119, 9699.

43. D. R. Lantero, S. L. Miller, J. Cho, D. L. Ward, M. R. Smith III, Organometallics, 1999, 18, 235.

44. W. Clegg, F. J. Lawlor, T. B. Marder, P. Nguyen, C. C. Norman, A. G. Orpen, M. J. Quayle, C. R. Rice, E. G. Robins, A. J. Scott, F. E. S. Souza, G. Stringer, G. R. Whittell, J. Chem. Soc., Dalton Trans., 1998, 301.

45. C. Dai, G. Stringer, T. B. Marder, A. J. Scott, W. Clegg, N. C. Norman, Inorg. Chem., 1997, 36, 272.

46. C. Dai, G. Stringer, T. B. Marder, R. T. Baker, A. J. Scott, W. Clegg, N. C. Norman, Can. J. Chem., 1996, 74, 2026.

47. C. N. Iverson, M. R. Smith III, J. Am. Chem. Soc., 1995, 117, 4403.

48. G. Lesley, P. Nguyen, N. J. Taylor, T. B. Marder, A. J. Scott, W. Clegg, N. C. Norman, Organometallics, 1996, 15, 5137.

49. W. Clegg, F. J. Lawlor, G. Lesley, T. B. Marder, N. C. Norman, A. G. Orpen, M. J. Qualye, C. R. Rice, A. J. Scott, F. E. S. Souza, J. Organomet. Chem., 1998, 550, 183.

50. T. Ishiyama, N. Matsuda, M. Murayta, F. Ozawa, A. Suzuki, N. Miyaura, Organometallics, 1996, 15, 713.

51. J. F. Hartwig, X. He, Angew. Chem. Int. Ed. Engl., 1996, 35, 315.

52. X. He, J. F. Hartwig, Organometallics, 1996, 15, 400.

53. G. Schmid and H. Nőth, Z. Naturforsch, 1965, 20b, 1008.

54. G. Schmid and H. Nőth, Chem. Ber., 1967, 100, 2899.

55. G. Schmid, Chem. Ber., 1969, 102, 191.

56. S. Ozonawa, M. Tanaka, Organometallics, 2001, 20, 2956.

57. S. Ozonawa, Y. Hatanaka, T. Sakakura, S. Shimada, M. Tanak, Organometallics, 1996, 15, 5450.

58. T. Sagawa, Y. Asano, F. Ozawa, Organometallics, 2002, 21, 5879.

59. J. D. Basil, A. A. Aradi, N. K. Bhattacharyya, N. P. Rath, C. Eigenbrot, T. P. Fehlner, Inorg. Chem., 1990, 29, 1260.

60. C. Jun, J. Halet, A. L. Rheingold, T. P. Fehlner, Inorg, Chem., 1995, 24, 2101.

61. D. J. Elliot, C. J. Levy, R. J. Puddephatt, D. G. Holah, A. N. Hughes, V. R. Magnuson, I. M. Moser, Inorg, Chem., 1990, 29, 5015.

62. T. Yasue, Y. Kawano, M. Shimoi, Chem. Lett., 2000. 58.

63. Y. Kawano, T. Yasue, M. Shimoi, J. Am. Chem. Soc., 1999, 121, 11744.

64. H. Wadepohl, U. Arnold. H. Pritzkow, Angew. Chem. Int. Ed. Engl., 1997, 36, 974.

65. T. H. Peterson, J. T. Golden, R. G. Bergamann, Organometallics, 1999, 18, 2005.

66. C. A. Tolman, J. Am. Chem. Soc., 1970, 92, 2953, 2956.

67. K. Nakamoto, Infared and Raman Spectra of Inorganic and Coordination Compound: Part B, 5th edn., Wiley-Interscience, New York, 1997, P. 127.

68. G. Schmid, H. Nőth, J. Organomet. Chem., 1967, 7, 129.

69. S. Helm, H. Nőth, Angew. Chem. Int. Engl., 1988, 27, 1331.

70. S. Channareddy, G. Linti, H. Nőth, Angew. Chem. Int. Engl., 1990, 29, 9, 199.

71. A. R. Rossi, R. Hoffmann, Inorg. Chem. 1975, 14, 365.

72. C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, Organometallics, 1998, 17, 4869.

73. C. Dai, G. Stringer, J. F. Corrigan, N. J. Taylor, T. B. Marder, N. C. Norman, J. Organomet. Chem., 1996, 513, 273.

74. R. K. Harris, I. J. McNaught, P. Reams and K. J. Packer, Magn. Reson. Chem., 1991, 29, 60.

75. T. Debaerdmaeker, K. Berhalter, C. Weisemann and H. A. Brune, Acta. Crystallogr. Sect. C, 1987, 43, 1253.

76. K. M. Waltz, C. N. Muhoro, J. F. Hartwig, Organometallics, 1999, 18, 3383.

77. D. Curtis, M. J. G. Lesley, N. C. Norman, A. G. Orpen, J. Starbuck, J. Chem. Soc., Dalton Trans., 1999, 1687.

78. C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, Organometallics, 2000, 19, 4344.

79. H. Kono, K. Ito, Y. Nagai, Chem. Lett., 1975, 1095.

80. R. Wilczynski and L. G. Sneddon, J. Am. Chem. Soc., 1980, 102, 2857.

81. D. A. Evans, G. C. Fu, A. H. Hoveyda, J. Am. Chem. Soc., 1988, 110, 6917.

82. D. A. Evans, G. C. Fu, B. A. Anderson, J. Am. Chem. Soc., 1992, 114, 6679.

83. D. A. Evans, G. C. Fu, A. H. Hoveyda, J. Am. Chem. Soc., 1992, 114, 6671.

84. K. Burgess, M. J. Ohlmeyer, Tetrahedron Lett., 1989, 30, 395, 5857, 5861.

85. K. Burgess, W. A. Van der Donk, A. M. Kook, J. Org. Chem., 1991, 56, 2949.

86. D. G. Musaev, A. M. Mebel, K. Morokuma, J. Am. Chem. Soc., 1994, 116, 10963.

87. A. E. Dorigo, P. vonR. Schleyer, Angew. Chem. Int. Ed. Engl., 1995, 34, 115.

88. R. T. Baker, P. Nguyen, T. B. Marder, S. A. Westcott, Angew. Chem. Int. Ed. Engl, 1995, 34, 1336.

89. H. Braunschweig, K. W. Klinkhammer, M. Koster, K. Radacki, Chem. Eur. J., 2003, 9, 1303.

90. M. Sato. Y. Nomoto, N. Miyaura, A. Suzuki, Tetrahedron Lett., 1989, 30, 3789.

91. I. D. Gridnev, N. Miyaura, A. Suzuki, Organometallics, 1993, 12, 589.

92. P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. D. Parsons, G. Urry, H. I. Schlesinger, J. Am. Chem. Soc., 1959, 81, 6368.

93. T. Ishiyama, N. Matsuda, N. Miyaura, A. Suzuki, J. Am. Chem. Soc., 1993, 115, 11018.

94. Q. Cui, D. G. Musaev, K. Morokuma, Organometallics, 1997, 16, 1355.

95. Q. Cui, D. G. Musaev, K. Morokuma, Organometallics, 1998, 17, 742.

96. M. Suginome, Y. Ohmori, Y. Ito, J. Organomet. Chem., 2000, 611, 403.

97. J. –Y. Cho, C. N. Iverson, M. R. Smith III, J. Am. Chem. Soc., 2000, 122, 12868.

98. J. –Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka Jr., M. R. Smith III, Science, 2002, 295, 305.

99. T. Ishiyama, J. Takagi, Ishida, N. Miyaura, N. R. Anastasi, J. F. Hartwig, J. Am. Chem. Soc., 2002, 124, 390.

100. J. Takagi, K. Sato, J. F. Hartwig, T. Ishiyama, N. Miyaura, Tetrahedron Lett., 2002, 43, 5649.

101. H. Chen, J. F. Hartwig, Angew. Chem. Int. Ed., 1999, 38, 3391.

102. H. Braunschweig, T. Wagner, Angew. Chem. Int. Ed. Engl., 1995, 34, 825.

103. H. Braunschweig, B. Ganter, J. Organomet. Chem., 1997, 545, 136.

104. H. Braunschweig, M. Koster, J. Organomet. Chem., 1999, 588, 231.

105. M. Shimoi, S. Ikubo, Y. Kawano, J. Am. Chem. Soc., 1998, 120, 4222.

106. H. Braunschweig, C. Kollann, U. Englert, Eur. J. Inorg. Chem., 1998, 465.

107. H. Braunschweig, C. Kollann, K. W. Klinkammer, Eur. J. Inorg. Chem., 1999, 1523.

108. H. Braunschweig, M. Colling, C. Kollann, H. G. Stammler, B. Neumann, B. Neumann, Angew. Chem. Int. Ed., 2001, 40, 2298.

109. H. Braunschweig, M. Müller, Chem. Ber., 1997, 130, 1295.

110. H. Braunschweig, M. Colling, C. Hu, K. Radacki, Angew. Chem. Int. Ed., 2002, 41, 1359.

111. H. Braunschweig, M. Colling, C. Hu, Inorg. Chem., 2003, 42, 941.

112. S. Aldridge, D. L. Coombs, C. Jones, Chem. Commun. 2002, 856.

113. D. L. Coombs, S. Aldridge, S. J. Coles, M. B. Hursthouse, Organometallics, 2003, 23, 4213.

114. A. W. Ehlers, E. J. Baerends, F. M. Bickelhaupt, U. Radius, Chem. Eur. J., 1998, 4, 210

115. J. Uddin, G. Frenking, J. Am. Chem. Soc., 2001, 123, 1683.

116. A. W. Ehlers, E. J. Baerends, F. M. Bickelhaupt, U. Radius, Chem. Eur. J., 1998, 4, 120.

117. U. Radius, F. M. Bickelhaupt, A. W. Ehlers, N. Goldberg, R. Hoffmann, Inorg. Chem., 1998, 37, 1080.

118. S. Aldridge, R. J. Calder, R. E. Baghurst, M. E. Light, M. B. Hursthouse, J. Organomet. Chem., 2002, 649, 9.

119. S. Aldridge, R. J. Calder, A. Rossin, A. A. Dickinson, D. J. Willock, C. Jones, D. J. Evans, J. W. Steed, M. E. Light, S. J. Coles, M. B. Hursthouse, J. Chem. Soc., Dalton Trans., 2002, 2020.

120. H. Braunschweig, M. Colling, C. Kollann, U. Englert, J. Chem. Soc., Dalton Trans., 2002, 2289.

121. B.E.R. Schilling, R. Hoffmann, D. Lichtenberger, J. Am. Chem. Soc., 1979, 101, 585.

122. D. L. Coombs, S. Aldridge, C. J. Coles, Appl. Organomet. Chem., 2003,17, 356.

123. C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, Organometallics., 2003, 21, 4862.

124. D. L. Coombs, S. Aldridge, C. Jones, D. J. Willock, J. Am. Chem. Soc., 2003, 125, 6356.

125. S. Shimada, A. S. Batsanov, J. A. K. Howard, T. B. Marder, Angew. Chem. Int. Ed., 2001, 40, 2168.

126. A. H. Cowley. V. Lomelf, A. Voigt, J. Am. Chem. Soc., 1998, 120, 6401.

127. H. Braunschweig, C. Kollann, U. Englert, Angew. Chem. Int. Ed., 1998, 37, 3179.

128. H. Braunschweig, M. Colling, C. Hu, K. Radacki, Angew. Chem. Int. Ed., 2003, 42, 205.

129. G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, Angew. Chem. Int. Ed., 2000, 39, 948.

130. D. L. Coombs, S. Aldridge, C. Jones, J. Chem. Soc., Dalton Trans., 2002, 3851.

131. C. L. Macdonald, A. H. Cowley, J. Am. Chem. Soc., 1999, 121, 12113.
132. J. Uddin, C. Frenking, Organometallics, 2000, 19, 571.
133. C. Boehme, J. Uddin, G. Frenking, Coord. Chem. Rev., 2000, 197, 249.
134. Y. Chen, G. Frenking, J. Chem. Soc., Dalton Trans., 2001, 434.
135. R. D. Chambers, T. Chivers, J. Chem. Soc., 1965, 3933.
136. S. Aldridge, D. L. Coombs, unpublished work.
137. A. A. Dickinson, D. J. Willock, R. J. Calder, S. Aldridge, Organometallics., 2000, 21, 1146.

Chapter two

Experimental techniques

2.1 Manipulation of air-sensitive compounds

Since the vast majority of compounds reported in this thesis are air and moisture sensitive, it was important that their synthesis and manipulation be carried out under an inert atmosphere. Therefore, the use of standard Schlenk line and high vacuum techniques were essential in the handling of these compounds. Accordingly, a brief discussion of these techniques is required. More detailed discussion of inert atmosphere techniques and apparatus can be found in the literature.[1,2]

2.1.1 Inert atmosphere techniques

Exclusion of air using an inert gas such as nitrogen or argon is one of the prevalent methods for the manipulation of air sensitive compounds. Two methods were utilised in this project: (i) Schlenk line techniques that afford a proper means for performing inert atmosphere reactions on the bench top through the use of specially designed equipment and (ii) glove box techniques, which facilitated the handling and storage of compounds under inert atmosphere.

Schlenk line techniques that were used in this project are ideally suited to the manipulation of large or small quantities of solids and liquids under an inert atmosphere. The Schlenk line used was constructed of Pyrex glass tube including a number of two-way stopcocks, which can be switched between inert gas and vacuum. The stopcocks were lubricated with 'Dow-Corning High Vacuum' grease to prevent leakiness. The glassware can be connected to the line via a number of heavy walled tubes, thus allowing several pieces of apparatus could be attached at once. Evacuation was achieved by a mechanical vacuum pump protected by a liquid nitrogen cooled trap to collect volatiles and obviate contamination of the pump. This enabled evacuation to pressure in the range 1-10^{-3} Torr, which was monitored by a Pirani pressure gauge. The inert gas used (generally argon) was introduced into the apparatus from a cylinder through a scavenger column packed with molecular sieves to observe any traces of moisture. A mercury bubbler was connected to the gas outlet to prevent any excess pressure. An inert atmosphere was attained by series of several cycles of pumping followed by filling with inert gas. Transferral of liquids and solutions between Schlenk apparatus was achieved by cannula and syringes using rubber septa.

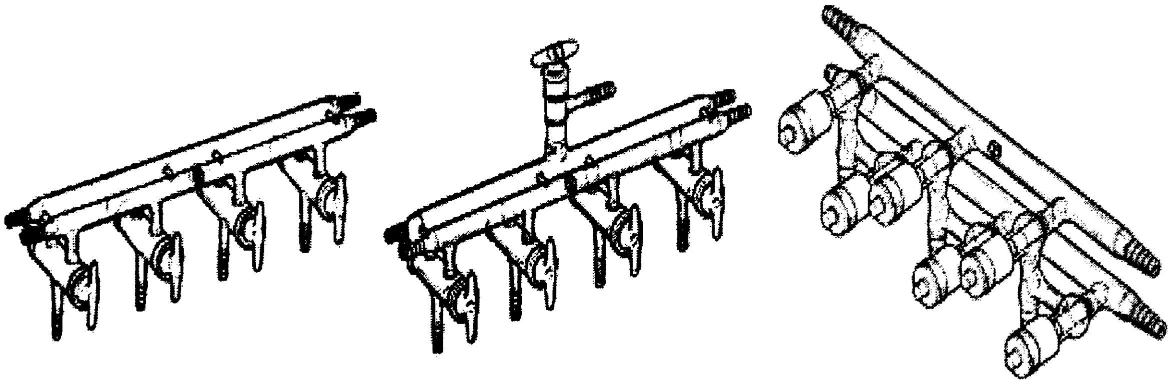


Figure 2.1 Typical Schlenk lines.

The ‘Saffron Scientific Omega’ glove box used in this study afforded a convenient means of manipulating air-sensitive solids. This consisted of a sealed stainless steel unit containing a toughened glass viewing panel, accessed via two neoprene gloves and an evacuable side-port which facilitated loading of equipment into the glove box. The inert atmosphere was introduced by a nitrogen cylinder, which was recirculated internally through catalyst, molecular sieve and solvent scrubbing columns accomplishing an atmosphere with oxygen and moisture levels of less than 5 ppm and 10 ppm respectively.[3]

2.1.2 High vacuum techniques

Processes such as vacuum sublimation and removal of trace solvent from compounds where the mechanical pump on a Schlenk line provides insufficient vacuum were achieved on a high vacuum line. This system was composed of a Pyrex glass tube including greaseless Young’s stopcocks. Evacuation was preformed by a combination of mercury diffusion and mechanical pump which provide a pressure of ca. 10^{-4} Torr, monitored by the use of a Tesla coil which produced a high frequency discharge at pressures above 10^{-3} Torr. A liquid nitrogen cooled trap prevented contamination of the pumps by volatile substances.

2.2 Physical measurements

2.2.1 NMR spectroscopy

NMR spectra were recorded on either Bruker AM-400 or Jeol Eclipse 300-plus FT-NMR spectrometers. Residual proton of solvents were used as reference for ^1H and ^{13}C NMR; a sealed tube containing a solution of $[^nBu_4N][B_3H_8]$ in $CDCl_3$ was used as an external reference for ^{11}B NMR; Me_4Sn was used as an external reference for ^{119}Sn NMR, $CFCl_3$ was used as an external reference for ^{19}F NMR; and an 85% solution of H_3PO_4 was used as an external reference for ^{31}P NMR. Samples were prepared by transferral of solution via cannula into a Young's NMR tube in a Schlenk which had previously been filled with inert atmosphere using several cycles of pumping followed by filling with inert gas.

2.2.2 Infrared spectroscopy

Infrared spectra were measured for each compound as a KBr disk or as a solution of benzene. Spectra were recorded on a Nicolet 500 FT-IR spectrometer. Disks of moisture sensitive solid samples were prepared in the glove box by compressing a powdered sample with a ten-fold excess of KBr. KBr was heated under continuous pumping prior to use.

2.2.3 Mass spectrometry

Mass spectra were measured at the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea and by the departmental service. Perfluorotributylamine and polyethylemimine were used as the standards for high resolution EI mass spectra.

2.2.4 Chemical analysis

Elemental analysis was performed by Warwick Analytical Services, University of Warwick and by the departmental service.

2.2.5 X-ray crystallography

Data collection was carried out on Enraf Nonius Kappa CCD diffractometers either in Cardiff or at the EPSRC Crystallography Service, University of Southampton. Structure solution and refinement for intermolecular base-stabilised species was carried out by Dr. L. Ooi (Cardiff University). Other structure solution and refinement procedures were carried out by Dr. S. J. Coles, University of Southampton.

2.2.6 Theoretical Calculations

Theoretical Calculations were performed by Dr. A. A. Dickinson and Dr. D. J. Willock (Cardiff University). Calculations were carried out, in part, using 'Glyndwr', a silicon Graphics multiprocessor Origin 2000 machine. A detailed computational methodology can be found in the reference 9.

2.3 Purification and preparation of essential solvents and reagents

Many of the compounds that have been synthesised in this research had themselves precursors which were not readily available. Therefore, they have been prepared from commercially available reagents, some of which it was necessary to purify before use. The preparations of these starting materials are included in this section. Table 2.1 lists the sources and procedures for the purification of the commercially available reagents.

Table 2.1 Sources of chemicals.

Compound	Source	Purity	Procedure
Reagents			
Cyclopentadienyl iron dicarbonyl dimer	Fluorochem	a	Used as supplied
BCl_3 (1.0 M in heptane)	Aldrich	a	Used as supplied
BBr_3	Aldrich	a	Used as supplied
$Fe(CO)_5$	Aldrich	>99%	Used as supplied
$Na[Mn(CO)_5]$	c	a	Used as supplied
$MoCl_5$	Aldrich	95%	Used as supplied
WCl_5	Aldrich	95%	Used as supplied
$TaCl_5$	Aldrich	95%	Used as supplied
$Na(\eta^5\text{-}C_5H_5)$	c	a	Used as supplied
$Na(\eta^5\text{-}C_5H_5)_2$	Strem	a	Used as supplied
$NaBH_4$	Lancaster	98%	Used as supplied
^nBuLi (1.6 M in Hexane)	Aldrich	a	Used as supplied
^nBuLi (2.5 M in Hexane)	Aldrich	a	Used as supplied
$(C_6F_5)Br$	Lancaster	99%	Used as supplied
Me_4Sn	Aldrich	99%	Used as supplied
Cl_4Sn	Aldrich	99%	Used as supplied
3,5-bis(trifluoromethyl)benzeneboronic acid	Aldrich	98%	Used as supplied
	Aldrich	98%	Used as supplied
$(C_6F_5)B(OH)_2$	Aldrich	99%	Used as supplied
PCl_5	Aldrich	98%	Used as supplied

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[a] Information not available. Courtesy of [b] Mr. A. Rossin, [c] Dr. R. J. Calder and respectively.

Compound	**Source**	**Purity**	**Procedure**
Reagents			
Phenyldichloroborane	Aldrich	97%	Used as supplied
Mercury	Johnson Matthey	99.998 %	Used as supplied
$(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$	b	a	Used as supplied
$(PPh_3)_3RhCl$	Aldrich	a	Used as supplied
Triphenylphosphine	Aldrich	99%	Used as supplied
Sodium	Lancaster	99%	Used as supplied
CaH_2	Aldrich	98%	Used as supplied
$Co_2(CO)_8$	Aldrich	99%	Used as supplied
[PPN]Cl	Aldrich	98%	Used as supplied
$Me_2Si(Cl)H$	Aldrich	98%	Used as supplied

Solvents			
Toluene	Fisher	>99%	Heated under reflux over sodium followed by distillation
Hexane	Fisher	>99%	Heated under reflux over potassium followed by distillation
Dichloromethane	Fisher	>99%	Heated under reflux over CaH_2 followed by distillation
Diethyl ether	Fisher	>99%	Heated under reflux over sodium followed by distillation
THF	Fisher	>99%	Heated under reflux over CaH2 followed by distillation
Acetonitrile	Fisher	>99%	Heated under reflux over sodium followed by distillation
4-picoline	Fisher	>99%	Heated under reflux over sodium followed by distillation
Chloroform	Fisher	>99%	Used as supplied
CCl_4	Fisher	>99%	Stored under argon over flamed-out molecular sieves
Benzene-d_6	Goss	>99.6%	Stored under argon over potassium
Toluene-d_8	Goss	>99.6%	Stored under argon over potassium
Gases			
Argon	B.O.C	a	Used as supplied
Nitrogen	B.O.C	a	Used as supplied

2.3.2 Preparation of metal reagents

Preparation of $Na[(C_5H_5)Fe(CO)_2]$

$[(C_5H_5)Fe(CO)_2]_2$ (8 g, 23 mmol) in THF (80 ml) was transferred via cannula onto sodium amalgam (1.8 g, 3 equivalents of Na) and the reaction mixture stirred for 24 h. Filtration of the mixture at this point and removal of solvent in vacuo gave crude $Na[(C_5H_5)Fe(CO)_2]$. Since the presence of THF in the reaction mixture leads to the decomposition of some boryl complexes and their precursors, it was important to remove all traces of this solvent. This was achieved by washing the product several times with hot toluene and drying by continuous pumping under high vacuum.[4]

Preparation of $Ta(C_5H_5)_2H_3$

$Ta(C_5H_5)_2H_3$ was prepared by minor modification of the method published by Green et al.[5] $TaCl_5$ (2.3 g, 6 mmol) in THF (20 ml) was transferred onto a mixture of $Na(C_5H_5)$ (4.4 g, 50 mmol) and $NaBH_4$ (0.7 g, 18.5 mmol) in THF (20 ml) at 0°C. The mixture was heated under reflux for 16 h and allowed to cool slowly to room temperature. The resulting dark brown solid was sublimed yielding $Ta(C_5H_5)_2H_3$ as a pale yellow powder in yields of ca. 40%. Purity was confirmed by ^1H NMR spectroscopy.[5]

Preparation of $Li[Ta(C_5H_5)_2H_2]$

$Li[Ta(C_5H_5)_2H_2]$ was prepared by minor modification of the method published by Green et al.[6] $Ta(\eta^5\text{-}C_5H_5)_2H_3$ (0.3 g, 0.95 mmol) in toluene (20 ml) was treated with ^tBuLi (1.85 ml of 1.7 M in heptanes). The mixture was heated for 45 min then allowed to cool slowly to room temperature. Filtration of the solvent to waste and drying gave the yellow-orange crystalline solid Li[Ta(C_5H_5)$_2$$H_2$] which was washed with toluene and dried under vacuum affording 90% yield.

Preparation of Mo(C_5H_5)$_2$$H_2$

Mo(C_5H_5)$_2$$H_2$ was prepared by minor modification of the method published by Green et al.[6] $MoCl_5$ (7 g, 53 mmol) in THF (20 ml) was transferred to mixture of Na(C_5H_5) (17 g, 130 mmol) and $NaBH_4$ (2.6 g, 68.7 mmol) in THF (20 ml) at 0^0C. The mixture was heated under reflux for 16 h and allowed to cool slowly to room temperature. The resulting dark brown solid was sublimed to form Mo(C_5H_5)$_2$$H_2$ as a yellow powder in yields of 60%. Purity was confirmed by ^{1}H NMR spectroscopy.[6]

Preparation of Li[Mo(C_5H_5)$_2$H]

Li[Mo(C_5H_5)$_2$H] was prepared by minor modification of the method published by Green et al.[6] [Mo(η^5-C_5H_5)$_2$$H_2$] (0.4 g, 1.7 mmol) in toluene (20 ml) was treated with ^{t}BuLi (2 ml of 1.7 M in heptanes). The mixture was heated for 45 min then allowed to cool slowly to room temperature. Filtration of the solvent to waste and drying resulted in the yellow powder Li[Mo(C_5H_5)$_2$H] which was washed with toluene and dried under vacuum (90% yield).

Preparation of W(C_5H_5)$_2$$H_2$

W(C_5H_5)$_2$$H_2$ was prepared by minor modification of the method published by Green et al.[6] WCl_5 (10 g, 27.6 mmol) in THF (20 ml) was transferred to mixture of Na(C_5H_5) (13 g, 147.7 mmol) and $NaBH_4$ (2.5 g, 66 mmol) in THF

(20 ml) at 0^oC. The mixture was heated under reflux for 16 h and allowed to cool slowly to room temperature. The resulting dark brown solid was sublimed to formed $W(\eta^5-C_5H_5)_2H_2$ as a yellow powder in yields of 60%. Purity was confirmed by ^1H NMR spectroscopy.[6]

Preparation of $Li[W(\eta^5-C_5H_5)_2H]$

$Li[W(\eta^5-C_5H_5)_2H]$ was prepared by the same method as its molybdenum analogues.

Preparation of $[PPN][Co(CO)_4]$

$[PPN][Co(CO)_4]$ was prepared according to the method of Ruff and Schlientz.[7] This process has two stages: firstly, $Co_2(CO)_8$ (6 g, 17 mmol) in THF (80 ml) was transferred via cannula onto sodium amalgam (2 g, 2 equivalents of Na) and the reaction mixture stirred for 24 h. Filtration of the mixture at this point and removal of solvent in vacuo gave crude $Na[Co(CO)_4]$. In the second step [PPN]Cl (2.68 g, 7.8 mmol) in CH_2Cl_2 (20 ml) was transferred to $Na[Co(CO)_4]$ (0.454 g, 2 mmol) in CH_2Cl_2 (20 ml) and the mixture stirred for 30 min. Filtration of the mixture at this point and slow addition of Et_2O initiated precipitation. The mixture was then stored at -30°C for 12 h. After precipitation appeared to be complete, the mixture was filtered, and the product $[PPN][Co(CO)_4]$ was dried under vacuum (yield 2.17 g, 75%).

Preparation of Me_2SnCl_2

A mixture of Me_4Sn (6.19 ml) and $SnCl_4$ (5.23 ml) was heated for 1 h then allowed to cool to room temperature during which time white crystals of

Me_2SnCl_2 were formed. Further cooling in ice induced further crystallisation of the product. Purity was confirmed by ^1H, ^{13}C and ^{119}Sn NMR spectroscopies.[8]

Preparation of $[(PPh_3)_2RhCl]_2$

A 6.5 g (9.8 mmol) sample of Wilkinson catalyst was dissolved in toluene (100 ml) and refluxed for 12 h. Filtration of the solid, washing with Et_2O (2 x 50 ml) and drying under high vacuum yield the dimer as an orange solid (80%).

2.4 References

1. D. F. Shriver, M. A. Drezdzon, The Manipulation of Air-Sensitive Compounds, 2nd edn., Wiley-Intersicence, New York, 1986.
2. R. E. Dodd, P. L. Robinson, Experimental Inorganic Chemistry, Elsevier, 1954.
3. Saffron Scientific Equipment Ltd., glove box operation manual.
4. R. B. King, Organometallic Syntheses, Vol. 1, Transition Metal Compounds, eds. J. J. Eisch, R. B. King, Academic Press, 1965.
5. M. L. H. Green, J. A. McCleverty, L. Pratt, G. Wilkinson, J. Chem. Soc. 1961, 4854.
6. B. R. Francis, M. L. Green, T. Luong-Thi, G. A. Moser, J. Chem. Soc., Dalton Trans., 1976, 1339.
7. J. K. Ruff, W. J. Schlientz, Inorg. Synth., 84.
8. N. W. Isaacs, C. H. L. Kennard, J. Chem. Soc. (A), 1970. 1257.
9. A. A. Dickinson, D. J. Willock, R. J. Calder, S. Aldridge, Organometallics, 2002, 21, 1146

Chapter three

Perfluorinated boryl and borylene complexes: synthesis and characterisation

3.1 Introduction

(a) Boryl complexes

Transition metal boryl complexes ($L_nM\text{-}BX_2$) have been the centre of intense recent research activity,[1] partly because of their involvement in the hydro- and diboration of carbon-carbon and carbon-oxygen multiple bonds,[2] but also because of their implication in highly selective stoichiometric and catalytic functionalisation of alkanes under either photolytic or thermal conditions.[3-5,7,9] One of the significant questions investigated by such studies is the potential for the extremely strongly σ donor boryl ligand also act as a π acid by utilizing the vacant boron-based orbital of π-symmetry (Figure 3.1).

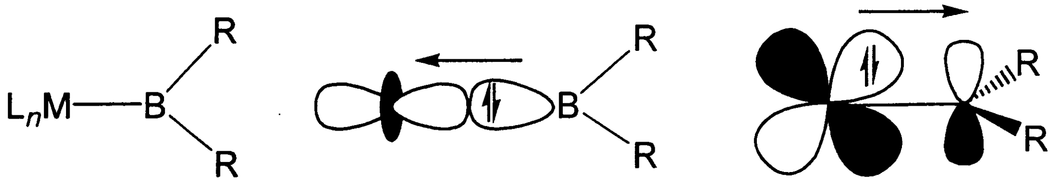
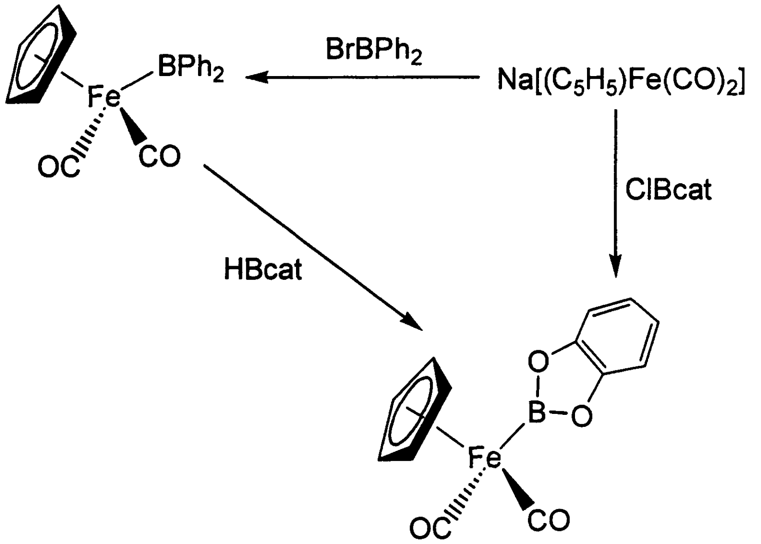


Figure 3.1 σ and π bonding in boryl complexes.

The π interaction between the metal and the boron atom can be influenced by several different factors: the nature of boryl substituent (R), metal (M), and the ligand framework L_n. The metal-boron bond length, together with the relative orientation of metal and boryl fragments and the IR stretching frequencies of ancillary carbonyl ligands have typically been used to probe the extent of back-bonding. For most of the complexes investigated to date it has been demonstrated that π interactions represent at most a relatively minor contribution to the overall metal boron bond. Such a result is not unexpected, given the strongly π donating boryl substituents (e.g. catecholate, 1,2-$O_2C_6H_4$) and π acceptor spectator ligands (e.g. CO) commonly employed in precedented synthetic routes. To date, the structure and reactivity of boryl complexes with a number of different substituents have been studied. Following the first structurally characterized boryl complexes reported by Marder et al. in 1990,[6] the majority (about 50%) of these complexes that have been reported in the literature feature the catecholboryl ligand. In part this reflects the stability and accessibility of this ligand. In an early study designed to probe the scope of σ and π bonding in iron boryl systems, Hartwig and Huber reported the syntheses and structures of $CpFe(CO)_2Bcat$ and $CpFe(CO)_2BPh_2$.[7] This chemistry is outlined in scheme 3.1.



Scheme 3.1 Syntheses of $(C_5H_5)Fe(CO)_2Bcat$ and $(C_5H_5)Fe(CO)_2BPh_2$.

These initial studies implied that a π back bond from the metal to the boron atom exists but that it is weak. Moreover, the π interaction in the diphenylboryl complex is weaker than in that featuring catechol substituent due to steric effects. Hoffmann and co-workers found that in order to optimize the π interaction between Fp$^+$ [Fp = $(C_5H_5)Fe(CO)_2$] (and isoelectronic metal fragments) and π acidic ligands such as carbenes and olefins, the Fp$^+$ HOMO should be aligned so as to overlap with the ligand LUMO, as in Figure 3.2 (a). A less effective metal to ligand π interaction could also be envisaged involving the perpendicular HOMO-2 orbital from Fp$^+$, as shown in Figure 3.2 (b).[8]

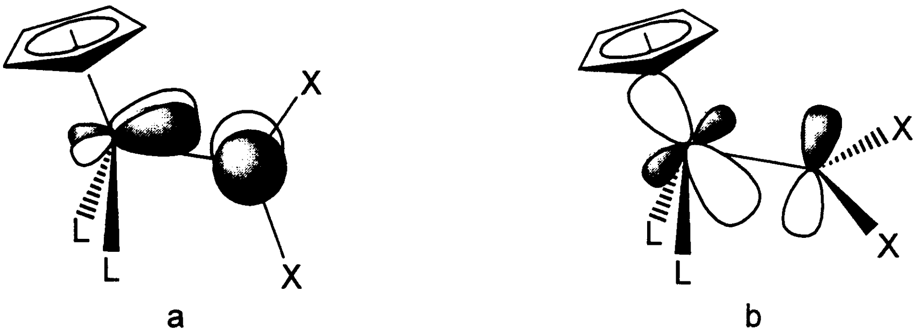


Figure 3.2 Two possible π interactions between $[(C_5R_5)ML_2]$ and $[BX_2]$ fragments: (a) the interaction between the HOMO of $[(C_5R_5)ML_2]$ and the LUMO of $[BX_2]$; (b) the interaction between the HOMO-2 of $[(C_5R_5)ML_2]$ and the LUMO of $[BX_2]$.

In the case of the catecholboryl complex, the solid state structure shows the possibility of a π-interaction involving the HOMO of Fp$^+$ since the catecholboryl ligand is oriented to allow overlap of the boron p-orbital with this orbital at iron (the dihedral angle between the Cp centroid-Fe-B and BO_2 planes is 7.9° which is close to zero). However, variable temperature NMR shows that there is no hint of restricted rotation at low temperature. Since the Fp^+ HOMO-2 has π-symmetry and is orthogonal to the HOMO, it is possible to achieve some degree of π bonding with a dihedral angle of 90°. Thus the rotational barrier as described by VT-NMR does not necessarily reflect the absolute magnitude of π bonding.

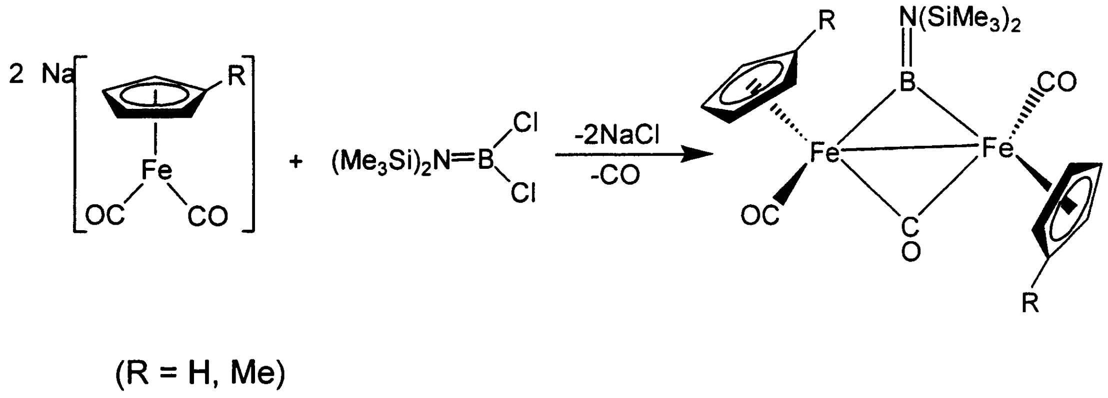
Since Hartwig and Huber's report in 1993[7], a number of Fp and Fp* complexes have been synthesised, featuring a range of boryl substituents. These have been tabulated below (Table 3.1).

Table 3.1 Known transition metal boryl complexes containing the Fp, Fp* and related organometallic fragments

Compound	d(M-B)A	δ_B ppm	ν(CO)cm^{-1}	Ref
[CpFe(BCat)(CO)$_2$]	1.959(6)	51.8	2024,1971	7
[Cp*Fe(Bcat)(CO)$_2$]	1.980(2)	54.3	1996, 1940	9
[CpFe(BPh$_2$)(CO)$_2$]	2.034(3)	121.0	2021,1951	7
[CpFe{Si(SiMe$_3$)$_3$}Cl}(CO)$_2$]	1.964(8)	141.2	2009,1956	10
[CpFe{Ge(SiMe$_3$)$_3$}Cl}(CO)$_2$]	1.985(11)	139.0	2009,1956	10
[CpFe{B(NMe$_2$)Cl}(CO)$_2$]	x	56.4	2006, 1946	11
[Cp*Fe{B(NMe$_2$)Cl}(CO)$_2$]	2.027(5)	59.1	1988,1928	11
[(C$_5$H$_4$Me)Fe{B(NMe$_2$)Cl}(CO)$_2$]	x	56.4	2002,1944	11
[CpFe{B(NMe$_2$)Br}(CO)$_2$]	x	54.5	x	12
[Cp*Fe{B(NMe$_2$)Br}(CO)$_2$]	x	57.2	1991, 1933	12
[(C$_5$H$_4$Me)Fe{B(NMe$_2$)Br}(CO)$_2$]	x	55.0	x	12
[CpFe{B(NMe$_2$)B(NMe$_2$)Cl}(CO)$_2$]	2.090(3)	69.5	1988,1932	13
[CpFe{B(NC$_4$H$_8$)B(NC$_4$H$_8$)Cl}(CO)$_2$]	x	38.4	1980, 1922	14
[CpFe{B(NC$_5$H$_{10}$)B(NC$_5$H$_{10}$)Cl}(CO)$_2$]	x	37.8	1981, 1927	14
[{CpFe(CO)$_2$}$_3$(B$_3$N$_3$H$_3$)]	x	49.7	1988, 1928	15
[Cp*Fe(B$_3$N$_3$H$_3$Cl$_2$)(CO)$_2$]	x	28.4	1995, 1935	15
[{(C$_5$H$_4$Me)Fe(CO)$_2$}$_2$(B$_3$N$_3$H$_3$Cl)]	2.041(1)	27.2	1996, 1937	15
[Cp*Fe{B(Mes)F}(CO)$_2$]	2.017(3)	90.4	1989,1931	17
[CpFe{B(Si(SiMe$_3$)$_3$F}(CO)$_2$]	1.983(9)	113.2	2001,1946	10
[Cp*Fe{B(Mes)Cl}(CO)$_2$]	1.985(2)	112.1	1996,1937	17
[CpFe{B(Ph)Cl}(CO)$_2$]	2.003(10)	111.0	1995,1929	17
[CpFe{B(Mes)Br}(CO)$_2$]	1.964(5)	111.4	2016,1962	18
[Cp*Fe{B(Mes)Br}(CO)$_2$]	1.972(2)	113.2	2006,1961	18
[(C$_5$H$_4$Me)Fe{B(Mes)Br}(CO)$_2$]	1.962(4)	111.3	2009,1961	18
[CpFe(BCl$_2$)(CO)$_2$]	1.942(3)	90.7	2022, 1963	16
[CpFe(BCl$_2$·4pic)(CO)$_2$]	2.13391	18.8	1976,1916	16

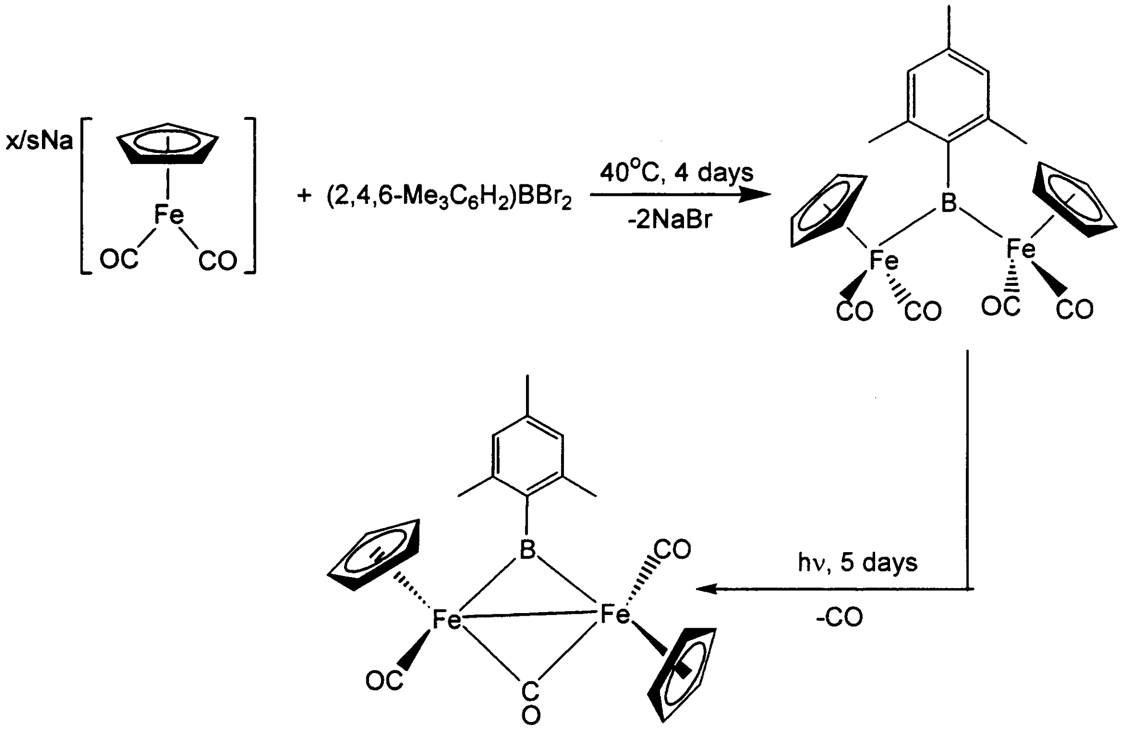
(b) Borylene complexes

Bridged and terminal borylene complexes have also been the subject of much recent investigation. Braunchweig et. al reported the first bridging borylene complexes of the type μ-BX{$(C_5R_5)Mn(CO)_2$}$_2$ (X=NMe_2, ^{t}Bu,) in 1995.[19] However, the number of bridged and terminal borylene that have been reported is significantly less than boryl complexes. The strongly nucleophilic compound $Na[(C_5R_5)Fe(CO)_2]$ (R= H, Me), was used to produce the first iron bridging borylene complexes, compounds which also feature Fe-Fe bonds and bridging carbonyl ligands. These were synthesised by Braunschweig et. al in 1998 by reacting bulky and electrophilic aminodichloroboranes such as $[(Me_3Si)_2N]BCl_2$ with 2 equivalents of $Na[(C_5H_5)Fe(CO)_2]$ or $Na[(C_5H_4Me)Fe(CO)_2]$ (Scheme 3.2).[12]



Scheme 3.2 Synthesis of $[(C_5H_4R)Fe(CO)]_2(\mu\text{-}CO)[\mu\text{-}BN(SiMe_3)_2]$.

Interestingly these authors found that in reacting $(Me_2N)BCl_2$ with either FpNa or Fp*Na the boryl complexes $[(C_5R_5)Fe(CO)_2B(Cl)NMe_2]$ were always obtained; however, using $[(Me_3Si)_2N]BCl_2$ bridging borylene complexes were obtained under all conditions even with an excess of $[(Me_3Si)_2N]BCl_2$. This was thought to be due to the electronic properties of the silyl group which make $[(Me_3Si)_2N]BCl_2$ more reactive by weakening the boron-nitrogen double bond. Unsupported iron bridging borylene complexes such as $[(C_5H_5)Fe(CO)_2]_2B(2,4,6\text{-}Me_3C_6H_2)$ have been synthesised by our group by reacting the bulky borane $(2,4,6\text{-}Me_3C_6H_2)BBr_2$ with $Na[(C_5H_5)Fe(CO)_2]$. Moreover, photolysis of $[(C_5H_5)Fe(CO)_2]_2B(2,4,6\text{-}Me_3C_6H_2)$ at room temperature for 5 days led to loss of CO and the formation of the supported bridging borylene complex (Scheme 3.3).[18,20]



Scheme 3.3 Synthesis of $[(C_5H_5)Fe(CO)_2]_2B(2,4,6\text{-}Me_3C_6H_2)$.

3.1.1 Aims of the present research

The broad aim of this body of work was to better define the structure and reactivity of the transition metal - boron bond in boryl complexes and in particular the possibility for π back bonding from the metal to the boron centre. This was to be accomplished by a combined synthetic and computational study for example involving complexes containing the bis(pentafluorophenyl)boryl and related ligands, precursors to which have been reported by Chivers and Chambers in 1965.[21] Such ligands might offer greater potential for π back-bonding due to the strongly electron withdrawing C_6F_5 substituents. Using salt elimination and oxidative addition routes, the synthesis of a variety of metal complexes was to be attempted. Detailed investigation of the M-B bonding and comparison with previously reported complexes was then to be carried out by using spectroscopic, structural and Density Functional studies.

3.2 Ligand Syntheses

3.2.1 Experimental

Synthesis of $(C_6F_5)_2BCl$

The known compound $(C_6F_5)_2BCl$ was prepared by minor modification of the method reported by Piers.[22] This method involves two stages: synthesis of $Me_2Sn(C_6F_5)_2$ from LiC_6F_5, followed by aryl transfer to create $(C_6F_5)_2BCl$ as shown in equations 3.1 and 3.2:

$$Me_2SnCl_2 + 2C_6F_5Br + 2{}^{n}BuLi \xrightarrow{-78\ {}^{0}C} Me_2Sn(C_6F_5)_2 \qquad (3.1)$$

$$Me_2Sn(C_6F_5)_2 + BCl_3 \longrightarrow ClB(C_6F_5)_2 + Me_2SnCl_2 \qquad (3.2)$$

8.7 ml of ^{n}BuLi in hexane (1.6M) was added dropwise to 5.4 g (21.8 mmol) of C_6F_5Br at -78°C and stirred at -78°C for 45 min. A solution of 2.4 g (11.5 mmol) of Me_2SnCl_2 in Et_2O was then transferred via cannula to the mixture and stirred for 15 min at -78°C. The mixture was then warmed to 20°C and stirred for a further 12 h. Wet hexane was added to the suspension to quench any unreacted C_6F_5Li and the solvent was then removed under reduced pressure. The resulting solid was then extracted with dry petrol or hexane (3 x 30 ml). The solvent was removed from the collected extracts, and the resulting oil distilled under reduced pressure at (10^{-3}mmHg) in a Kugelrohr apparatus at 100-130°C to give a colourless liquid which was analysed by NMR spectroscopy. NMR data were in good agreement with that reported in the literature.[22]

^{1}H NMR (C_6D_6, 300 MHz), δ 0.88 (s, 6H). ^{13}C NMR (C_6D_6, 76 MHz), δ -6.3 (CH_3), 127.2, 135.1, 138.5, (C_6F_5). ^{19}F NMR (C_6D_6, 282 MHz), δ -122.1 (dd, J = 8.7 Hz and J = 25.0 Hz, ortho-CF), -151.0 (tt, J = 2.3 Hz and J = 20.0 Hz, para-CF), and 160.6 (m, meta-CF). ^{119}Sn NMR (C_6D_6, 112 MHz), δ -60.

In the second stage $Me_2Sn(C_6F_5)_2$ (1.113 g, 2.3 mmol) was placed in high pressure tube and 2.7 ml of 1.0 M BCl_3 in heptane was transferred to the tube via syringe. 2.5 ml of hexane were also added via cannula. The solution was stirred for 1 h at room temperature then heated to 120°C for 48 h. After removal from the oil bath, subsequent cooling in an ice bath for 4 h caused white crystals of Me_2SnCl_2 to form. Under an increased flow of argon the supernatant liquid was decanted into a Schlenk tube and the remaining crystals in the high-pressure tube washed once with hexane. The solvent was removed from the combined extracts under reduced pressure to leave a white residue which was transferred to a sublimation apparatus. The remaining traces of Me_2SnCl_2 were removed by sublimation under an atmosphere of argon at an oil bath temperature of 35°C. Solid Me_2SnCl_2 was removed from the cold finger and the procedure was repeated until no more of Me_2SnCl_2 was obtained. Sublimation of the remaining white powder under full vacuum (10^{-3} mmHg) at an oil bath temperature of 60°C produced $ClB(C_6F_5)_2$ as a colourless waxy solid. NMR data were in a good agreement with that reported previously.[22]

^{13}C NMR (C_6D_6, 76 MHz), δ, 135.7, 138.9, 146.4, (C_6F_5). ^{11}B NMR (C_6D_6, 96 MHz), δ 58.7. ^{19}F NMR (C_6D_6, 282 MHz), δ -129.3 (tt, J = 4.9 Hz and J = 20.9 Hz, ortho-CF), -143.6 (tt, J = 6.6 Hz and J = 21.2 Hz, para-CF), and -160.4 (m, meta-CF).

Attempted Synthesis of $C_6F_5BCl_2$

(a) From $Me_3SnC_6F_5$ and BCl_3

Synthesis of the known compound $C_6F_5BCl_2$, first reported by Chambers and Chivers in 1965,[21] was attempted by a modification of the original method along similar lines to that reported by Piers for making $(C_6F_5)_2BCl$. This method was adapted by using hexane as a reaction solvent instead of reacting neat BCl_3 and tin reagents, and it also involves two stages: synthesis of $Me_3SnC_6F_5$ from LiC_6F_5 followed by aryl transfer to create $C_6F_5BCl_2$ as shown in equations 3.3 and 3.4:

$$Me_3SnCl + C_6F_5Br + {}^nBuLi \xrightarrow{-78\ ^0C} Me_3SnC_6F_5 \quad (3.3)$$

$$Me_3SnC_6F_5 + 2BCl_3 \xrightarrow[72\ h\ /\ hexane]{120\ ^0C} C_6F_5BCl_2 + Me_2SnCl_2 + MeBCl_2 \quad (3.4)$$

5 ml of ^nBuLi in hexane (1.6M) was added dropwise to 1.3 g (7.4mmol) of C_6F_5Br at -78°C and stirred at -78°C for 45 min. A solution of 2.0 g (10.03 mmol) of Me_3SnCl in Et_2O was then transferred via cannula to the mixture and stirred for 15 min at -78°C. The mixture was then warmed to 20^{0}C and stirred for a further 12 h. Wet hexane was added to the suspension to quench any unreacted C_6F_5Li and the solvent was then removed under reduced pressure. The resulting solid was then extracted with dry petrol or hexane (3 x 30 ml). The solvent was removed from the collected extracts to give a colourless liquid. NMR data were in good agreement with the literature values for $Me_3SnC_6F_5$.[21]

In the second stage $Me_3SnC_6F_5$ (2.79 g, 8.43 mmol) was placed in a high pressure tube and 20 ml of 1.0 M BCl_3 in heptane was transferred to the tube via syringe. 2.5 ml of hexane were also added via cannula. The solution was stirred for one night at room temperature. Under an increased flow of argon the supernatent liquid was decanted into a Schlenk tube. The solvent was removed from the combined extracts at -15°C under reduced pressure to leave a white residue which was then transferred to a sublimation apparatus. Me_2SnCl_2 was removed by sublimation under an atmosphere of argon at an oil bath temperature of 35°C. Solid Me_2SnCl_2 was then removed from the cold finger and the procedure was repeated until no more Me_2SnCl_2 was obtained.

Sublimation of the remaining white powder under full vacuum (10^{-3} mmHg) at room temperature produced a colourless waxy solid that melted on the sublimation finger. ^{11}B NMR spectra of this solid revealed it to be an intractable mixture.

^{11}B NMR (C_6D_6, 96 MHz), δ 68.5, 52.9 ($C_6F_5BCl_2$), 46.1 (BCl_3), 33.8, and 29.4.

^{119}Sn NMR (C_6D_6, 112 MHz), δ 156.3 (Me_2SnCl_2).

(b) From $C_6F_5B(OH)_2$ with PCl_5

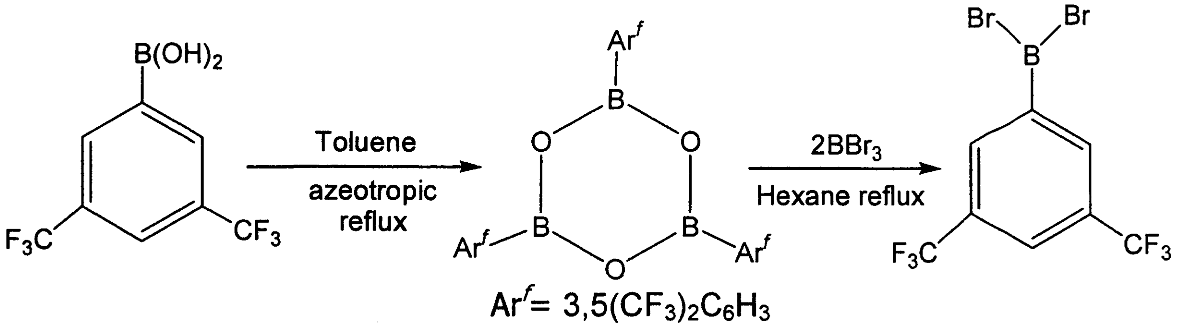
In this method a solution of (0.98 g, 4.7 mmol) of PCl_5 in 20 ml of CCl_4 was transferred to solution of (1.0 g, 4.72 mmol) of $C_6F_5B(OH)_2$ in 20 ml CCl_4. Examination of the ^{11}B NMR spectrum of the solution after 12 hours at room temperature revealed that the signal at δ 27.5 characteristic of $C_6F_5B(OH)_2$ was still present with no corresponding resonance being observed for the product. Therefore, the mixture was refluxed for 56 h, but ^{11}B NMR again revealed no conversion.

(c) From $C_6F_5B(OH)_2$ with $SOCl_2$

In this method an excess of $SOCl_2$ (0.8 ml, 11.0 mmol) was added via syringe to a solution of $C_6F_5B(OH)_2$ (0.5 g, 2.36 mmol) in 20 ml $CHCl_3$. Examination of the ^{11}B NMR spectrum of the solution after 12 h at reflux revealed that the signal at δ 27.5 characteristic of $C_6F_5B(OH)_2$ was still present with no corresponding resonance being observed for the product. Extended traction time led to no perceptible conversion by ^{11}B NMR.

Synthesis of $3,5\text{-}(CF_3)_2C_6H_3BBr_2$.

The ligand precursor $3,5\text{-}(CF_3)_2C_6H_3BBr_2$ was prepared by minor modification of the method reported by Yamamoto and his group.[23]



Scheme 3.4 Synthesis of $3,5\text{-}(CF_3)_2C_6H_3BBr_2$.

In this method (Scheme 3.4) a mixture of $3,5\text{-}(CF_3)_2C_6H_3B(OH)_2$ (3.6 g, 9.38 mmol) in toluene (100 ml) was heated at reflux for 12 h with removal of water (CaH_2 in Soxhlet thimble) at 100 -110°C. After the solution was cooled to room temperature, the solvent was removed under reduced pressure to give the trimeric anhydride as a white solid in yield of ca. 80%. This was then taken to a high pressure tube and dissolved in hexane; 3ml of neat BBr_3 was added to the reaction mixture at room temperature under argon. After the reaction mixture was heated for 48 h at 75–90°C, solvent was removed under reduced pressure to give the $3,5\text{-}(CF_3)_2C_6H_3BBr_2$ as pale yellow oil in 50% yield. NMR data were in good agreement with that reported in the literature.[23]

^1H NMR (C_6D_6, 300 MHz) δ 8.42 (s, para-H), 8.41(s, ortho-H). ^{13}C NMR (C_6D_6, 76 MHz), δ 123.3 (CF_3), 127.6, 131.4, 136.5, (aromatic CH). ^{11}B NMR (C_6D_6, 96 MHz) δ 56.1. ^{19}F NMR (C_6D_6, 282 MHz) δ -64.2.

3.2.2 Results and discussion

3.2.2.1 Chloroborane ligand precursors

The synthesis of $ClB(C_6F_5)_2$ is somewhat involved and tedious. Care should be taken using this method since it involves the use of the very reactive reagent C_6F_5Li. Under no circumstances should this reagent isolated or warmed above -30°C. In addition, it is difficult to collect the product from the sublimation finger since its melting point is very close to room temperature. One advantage of this method is recycling of the tin source Me_2SnCl_2, since it is an isolable by-product of the sublimation part of the process. $ClB(C_6F_5)_2$ is an air and moisture sensitive solid, however it can be stored as a stock toluene solution under argon at -30°C for an indefinite period. Use of a similar process for $Cl_2B(C_6F_5)$ did not yield a clean product. Examination of the crude product by ^{11}B shows many boron-containing species, including the starting material. It was not possible to separate these boron containing products from each other and from Me_2SnCl_2 by sublimation as the ^{11}B and ^{119}Sn NMR spectra of the sublimate showed. Very recent work by Britovsek has shown that the use of Bu_3SnCl as the tin source gives a much cleaner product.[24] Unfortunately, the two attempted reactions using $C_6F_5B(OH)_2$ and the chlorinating/dehydrating reagents PCl_5 or $SOCl_2$ did not proceed at all even when heating the reaction mixture for 56 hours. This contrasts with the use of these chlorinated reagents in the synthesis of other boranes.[25]

3.2.2.2 3,5-$(CF_3)_2C_6H_3BBr_2$

In order to gain access to a ligand precursor with two boron-halogen bonds, and since it is very difficult to obtain $Cl_2B(C_6F_5)$ as a pure substance the 3,5-$(CF_3)_2C_6H_3BBr_2$ ligand precursor has been investigated instead. The strongly electron–withdrawing nature of two CF_3 groups has been reported to be similar to that of five fluorine atoms. This moisture-sensitive ligand precursor has been made by dehydration of 3,5-$(CF_3)_2C_6H_3B(OH)_2$ to the trimeric anhydride and subsequent halogenation of the trimer with 2 equivalents of boron tribromide. Although it is air and moisture sensitive it can, however, be stored in toluene solution under argon at -30°C for indefinite period.

3.3 Syntheses and characterisation of boryl and bridging borylene complexes

3.3.1 Experimental

Synthesis of $(C_5H_5)Fe(CO)_2B(C_6F_5)_2$

Dropwise addition of a solution of $ClB(C_6F_5)_2$ (0.4 g,1.05 mmol) in 12 cm^3 toluene to 1 equivalent of $Na[(C_5H_5)Fe(CO)_2]$ suspended in toluene at 20^0C led to the generation of an orange-red solution and an off-white precipitate. Examination of the ^{11}B NMR spectrum of the solution after three hours revealed that the signal at δ_B 58.7 characteristic of $ClB(C_6F_5)_2$ had disappeared, the sole resonance observed being at δ_B 121.5. Filtration of the reaction mixture at this point, removal of volatiles under reduced pressure and recrystallisation from hexanes at -30°C afforded golden yellow crystals of $(C_5H_5)Fe(CO)_2B(C_6F_5)_2$ in yields of ca. 42%. Spectroscopic data: MS (EI): M^+ = 522 (weak) ,isotopic pattern corresponding to 1 B and 1 Fe atom, strong fragment ion peaks at m/z 494 [(M-CO)$^+$, 60%] and 466 [(M-2CO)]$^+$, 18%]. ^{1}H NMR (C_6D_6, 300 MHz), δ 3.91 (s, C_5H_5). ^{13}C NMR (C_6D_6, 76 MHz), δ 86.3 (C_5H_5), 137.3, 139.9, 140.7 (aromatic CF), 211.0 (CO). ^{11}B NMR (C_6D_6, 96 MHz), δ 121.5 (br). ^{19}F NMR (toluene, 282 MHz), δ -132.9 (dq, ortho-CF, J = 21.26, 6.1Hz), δ -153.7 (tt, para-CF, J = 20.8, 6.1 Hz), δ -161.5 (m, meta-CF, J = 23.36, 6.1 Hz). IR (KBr disk, cm^{-1}) ν(CO) 2014 s, 1968 s. Elemental analysis: calc. for $C_{19}H_5BF_{10}FeO_2$: C, 43.72; H, 0.97%. Found: C, 43.55; H, 0.97%. No significant changes in the ^{19}F NMR spectrum were observed on cooling to -110°C due to the barrier to rotation about the Fe-B bond being very small.

Synthesis of $(C_5Me_5)Fe(CO)_2B(C_6F_5)_2$

Dropwise addition of solution of $ClB(C_6F_5)_2$ (0.56 g,1.47 mmol) in 40cm^3 toluene to 1 equivalent of Na[$(C_5Me_5)Fe(CO)_2$] suspended in toluene at 20°C led to the generation of an dark orange-red solution and an off-white precipitate. Examination of the ^{11}B NMR spectrum of the solution after 1 h our revealed that the signal at δ 58.7 characteristic of $ClB(C_6F_5)$ had disappeared, the sole resonance observed being at δ 121.3. Filtration of the reaction mixture at this point removal of volatiles in vacuo and recrystallisation from hexanes at -30°C afforded golden yellow crystals in yields of ca 40%. Spectroscopic data: MS (EI): M$^+$ = 592 (weak), isotopic pattern corresponding to1 B and 1 Fe atom, strong fragment ion peaks at *m/z* 563.1 [M-(CO)],100% and 564.5 (M-(CO), 60%]. ^{1}H NMR (C_6D_6, 300 MHz), δ 1.20 (s, CH_3).^{13}C NMR (C_6D_6, 76 MHz), δ 8.7 (CH_3), δ 98.0 ($C_5(CH_3)_5$), 137.5, 138.0, 140.4 (aromatic CF), 212.3 (CO).^{11}B NMR (C_6D_6, 96 MHz), δ 121.3. ^{19}F NMR (C_6D_6, 282

MHz), δ -133.1 (dq, ortho CF, J = 21.26, 6.1Hz) δ -154.5 (tt, para CF, J = 20.8, 6.1 Hz),δ -162.2 (m, meta CF, J = 23.36, 6.1 Hz). IR (KBr disk, cm^{-1}) ν(CO) 2004 s, 1953 s. Elemental analysis: calculated for $C_{24}H_{15}BF_{10}FeO_2$, C 48.69 %, H 2.55 %; observed, C 48.92 %, H 2.71 %.

Synthesis of $(CO)_5MnB(C_6F_5)_2$

Dropwise addition of solution of $ClB(C_6F_5)_2$ (0.34 g, 0.789 mmol) in $40cm^3$ toluene to 1 equivalent of $Na[Mn(CO)_5]$ suspended in toluene at 20°C led to the generation of an yellow solution and an off-white precipitate. Examination of the ^{11}B NMR spectrum of the solution after a two hours revealed that the signal at 58.7 characteristic of $ClB(C_6F_5)_2$ had disappeared, the sole resonance observed being at δ130.7. Filtration of the reaction mixture at this point, concentration and layering with hexane at -30°C for crystallisation, yielded a yellow microcrystalline material in yields of ca. 54%. Spectroscopic data: MS (EI): M^+ = 540 (weak) , isotopic pattern corresponding to 1B and 1Mn atom, strong fragment ion peaks at *m/z* 512 [$(M-CO)^+$, 12%], 484 [$(M-2CO)^+$, 5%], 456 [$(M-3CO)^+$,12%], 428 [$(M-4CO)^+$, 17%], and 400 [$(M-5CO)^+$, 100%]. ^{13}C NMR (C_6D_6, 76 MHz), δ 141.3, 139.3, 138.4, 135.7, (aromatic CF), 208.6, 207.9, (CO). ^{11}B NMR (C_6D_6, 96 MHz), δ 130.7. ^{19}F NMR (C_6D_6, 282 MHz), δ -132.1 (d, ortho-CF, J = 22.26, Hz), -150.9 (t, para-CF, J = 19.7, 6.1 Hz), -160.6 (m, meta-CF, J = 22.36, 6.1 Hz). IR (KBr disk, cm^{-1}) ν(CO) 2049 s, 2136 s, and 2014 m. Elemental analysis: calculated for $C_{17}BF_{10}MnO_5$, C 37.82 %, H 0 %; observed, C 38.05 %, H 0.12 %.

Reaction of [PPN][Co(CO)$_4$] with ClB(C$_6$F$_5$)$_2$

Dropwise addition of solution of ClB(C$_6$F$_5$)$_2$ (0.2 g, 2.5 mmol) in 40 cm^3 toluene to 1 equivalent of [PPN][Co(CO)$_4$] in toluene led to yellow solution and a blue-green precipitate. Examination of the ^{11}B NMR spectrum of the solution after two hours revealed that the signal at δ 58.7 characteristic of ClB(C$_6$F$_5$)$_2$ had disappeared with no corresponding resonance being observed. Moreover, examination of the ^{1}H, ^{31}P NMR and IR spectrum of the precipitate showed that it was principally unreacted [PPN][Co(CO)$_4$].

Reaction of Na[Co(CO)$_4$] with ClB(C$_6$F$_5$)$_2$

Dropwise addition of solution of ClB(C$_6$F$_5$)$_2$ (0.78 g, 2.05 mmol) in 40 cm^3 toluene to 1 equivalent of Na[Co(CO)$_4$] lead to the formation of dark brown solution and a white precipitate. Examination of the ^{11}B NMR spectrum of the solution after three hours revealed that the signal at δ 58.7 characteristic of ClB(C$_6$F$_5$)$_2$ had disappeared with no corresponding resonance being observed to have grown in. The mixture was filtered, concentrated and stored at -30°C for crystallization but no homogenous product was isolated.

Reaction of Li[(C$_5$H$_5$)$_2$TaH$_2$] with ClB(C$_6$F$_5$)$_2$

Dropwise addition of solution of ClB(C$_6$F$_5$)$_2$ (0.33 g, 0.86 mmol) in 40 cm^3 toluene to 1 equivalent of Li[(C$_5$H$_5$)$_2$TaH$_2$] led to a colour change of the solution from orange to dark brown. Examination of the ^{11}B NMR spectrum of the solution after three hours revealed that the signal at δ 58.7 characteristic of ClB(C$_6$F$_5$)$_2$ had disappeared with no corresponding resonance being observed to have grown in. The mixture was filtered, concentrated and stored at -30°C for crystallisation but no homogenous product was isolated.

Reaction of Li[$(C_5H_5)_2$MoH] with ClB$(C_6F_5)_2$

Dropwise addition of solution of ClB$(C_6F_5)_2$ (0.65 g, 1.70 mmol) in 40 cm^3 toluene to 1 equivalent of Li[$(C_5H_5)_2$MoH] led to a colour change of the solution from yellow to dark brown . Examination of the ^{11}B NMR spectrum of the solution after two days revealed that the signal at δ 58.7 characteristic of ClB$(C_6F_5)_2$ had disappeared, with new resonances being observed at δ -12. The mixture was filtered, concentrated and stored at -30°C for crystallisation but no homogenous product was isolated.

Reaction of [$(C_5H_5)_2$WH]Li with ClB$(C_6F_5)_2$

Dropwise addition of solution of ClB$(C_6F_5)_2$ (0.44 g, 1.17 mmol) in 40 cm^3 toluene to 1 equivalent of [$(C_5H_5)_2WH_2$]Li led to a colour change of the solution from orange to dark brown. Examination of the ^{11}B NMR spectrum of the solution after three hours revealed that the signal at δ 58.7 characteristic of ClB$(C_6F_5)_2$ had disappeared with no corresponding resonance being observed to have grown in. The mixture was filtered, concentrated and stored at -30°C for crystallization but no homogenous product was isolated.

Synthesis and spectroscopic characterization of $(C_5H_4Me)(CO)_2$HMnB$(C_6F_5)_2$

A solution of ClB$(C_6F_5)_2$ (0.026 g, 0.068 mmol) in toluene (10 ml) was added to suspension of K[$(C_5H_4Me)_2Mn(CO)_2H$] (0.020 g, 0.086 mmol) in toluene (10 ml) at -50°C causing the colour changed immediately to dark red. Examination of the ^{11}B NMR spectrum of the solution after 30 min revealed that the signal at 58.7 characteristic of $ClB(C_6F_5)$ had disappeared, the sole resonance observed being at δ 82.3. Removal of volatiles under reduced pressure at -10°C and recrystallisation from hexanes at -50°C afforded microcrystalline material in yield of ca. 35 %. Warming the reaction mixture to room temperature leads to decomposition of the product as judged by ^{11}B NMR. ^{1}H NMR (C_6D_6, 300 MHz), δ -16.81, 1.11 (s, 1H, Mn-H), (s, 3H, $C_5H_4\mathit{Me}$), 3.68 (s, 2H, $C_5\mathit{H}_4Me$), 3.85 (s, 2H, $C_5\mathit{H}_4Me$). ^{13}C NMR (76 MHz, C_7D_8, -30°C), δ 12.4 ($C_5H_4\mathit{Me}$), 87.1, 87.8 (CHs of C_5H_4Me), 225.8 (CO). ^{11}B NMR (C_6D_6, 96 MHz), δ 82.3. ^{19}F NMR (C_6D_6, 282 MHz), δ -122.0 (s, ortho-CF), -132.7 (d, ortho-CF, J = 22.26, Hz), -149.9 (d, para-CF, J = 19.7, Hz), -159.18 (d, meta-CF, J = 121 Hz), -161.5 (d, meta-CF, J = 491 Hz). IR (hexanes solution, cm^{-1}) 1986 [ν(CO), st], 1922 [ν(CO), st], 1648 [ν(MnH), md].

Synthesis of $[(C_5H_5)Fe(CO)_2]_2B[3,5-(CF_3)_2C_6H_3]$

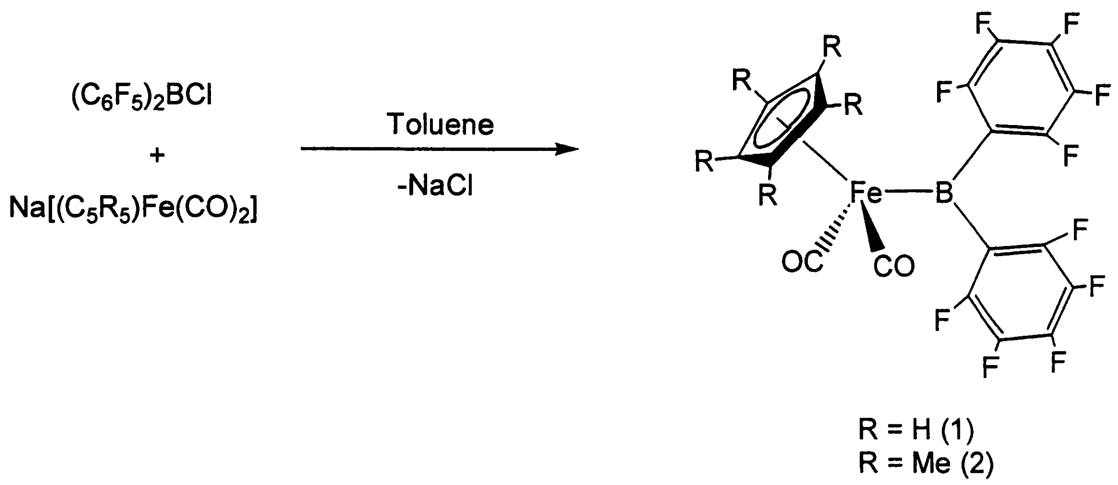
A solution of (0.3 g, 0.78 mmol) of $Br_2B[3,5-(CF_3)_2C_6H_3]$ in toluene (10 ml) was added to a suspension of (0.3 g, 1.5 mmol) of $Na[(C_5H_5)Fe(CO)_2]$ in toluene (20 ml) and the mixture stirred at room temperature for 12 h. Filtration, removal of volatiles in *vacuo* and recrystallisation from hexane at -50°C yielded $[(C_5H_5)Fe(CO)_2]_2B[3,5-(CF_3)_2C_6H_3]$ as yellow crystals in yields of ca. 65%. ^{1}H NMR (C_6D_6, 300 MHz), δ 4.14 (C_5H_5), 7.91 (meta, aromatic), 8.24 (para, aromatic). ^{13}C NMR (C_6D_6, 76 MHz), 87.3 (C_5H_5), 123.4 (CF3, JCF = 274 Hz), 128.2 (para, aromatic), 130.8 (meta, aromatic), 137.2 (ortho, aromatic), 218.9 (CO). ^{11}B NMR (C_6D_6, 96 MHz), δ 167.7. ^{19}F NMR (toluene, 282 MHz), δ -62.3. IR (KBr disk, cm^{-1}) ν(CO) st 2002, m 1976, st 1933, st

1929. Mass spec. (EI): M^+ = 577 (weak), fragment ion peaks at *m/z* 550 [$(M\text{-}CO)^+$, 22%], 521 [$(M\text{-}2CO)^+$, 13%], 494 [$(M\text{-}3CO)^+$, 14%], 465 [$(M\text{-}4CO)^+$, weak].

3.3.2 Results and Discussion

3.3.2.1 Pentafluorophenyl-based boryl complexes of iron

The iron boryl complexes $(C_5R_5)Fe(CO)_2B(C_6F_5)_2$ (**1**, R = H; **2** R = Me) were prepared by addition of $ClB(C_6F_5)_2$ to a suspension of $Na[(C_5R_5)Fe(CO)_2]$ in toluene (Scheme 3.5) to form **1** and **2** as air-, moisture-and photolytically sensitive golden yellow crystals in yields of up to 42%. The reaction of $ClB(C_6F_5)_2$ with $Na[(C_5H_5)Fe(CO)_2]$ was monitored by ^{11}B NMR spectroscopy; the resonance due to the chloroborane at δ_B 58.7 was replaced by a low-field signal at δ_B121.5, in the region characteristic of alkyl and aryl substituted transition metal boryl complexes. ^1H, ^{13}C, and ^{19}F NMR and IR spectroscopic data support the proposed formulation. Peaks in the EI mass spectrum corresponding to the M^+ ion, and to the $(M\text{-}CO)^+$, and $(M\text{-}2CO)^+$ fragments also support the proposed formulation for **1**.



Scheme 3.5 The synthetic route to complexes **1** and **2**.

The formulation of **1** as $(C_5H_5)Fe(CO)_2B(C_6F_5)_2$ is further supported by the results of a single crystal X–ray diffraction study, the crystals being obtained by cooling a concentrated toluene solution of **1** to -30°C. The molecular structure of **1** is illustrated in Figure 3.3 and relevant bond lengths and angles are listed in Table 3.2. Single crystals of **1** could also be isolated by cooling a concentrated solution in hexane to -30°C. In this case a different polymorph was obtained [monoclinic, a = 14.2397(2), b = 19.0947(5), c = 27.1321(5) Å, β= 90.418(3)° vs. triclinic, a = 10.6895(2), b = 13.4060(2), c = 13.6885(2) Å, α = 93.628(3), β = 93.588(3), γ = 113.060(3)°]. In this case the compound crystallises with four molecules in the asymmetric unit (Figure 3.4), although the quality of the data is such that the uncertainties in derived bond lengths and angles (Table 3.3) are significantly larger than for the triclinic polymorph. As such, discussion of structural data is based around the polymorph obtained from toluene solution.

Table 3.2 Selected bond lengths [Å] and angles [°] for one of the two crystallographically independent molecules in the triclinic polymorph of **1**.

Fe2-B2	1.965(5)	B2-C33	1.598(5)
Fe2-Cp centroid	1.739(4)	04-C26	1.157(4)
Fe2-C25	1.760(4)	03-C25	1.145(4)
Fe2-C26	1.751(4)	C38-F20	1.354(3)
B2-C27	1.595(5)	C33-C38	1.395(5)

C25-Fe2-C26	95.0(2)	C27-B2-C33	111.4(3)
Fe2-B2-C27	122.7(3)	Centroid-Fe2-B2-C27	28.4(3)
Fe2-B2-C33	125.8(2)		

Table 3.3 Selected bond lengths [Å] and angles [°] for one of the four crystallographically independent molecules in the monoclinic polymorph of **1**.

Fe1-B1	1.92(2)	B1-C14	1.59 (2)
Fe2-Cp centroid	1.739(4)	O1-C1	1.21(2)
Fe1-C1	1.758(17)	O2-C2	1.139(16)
Fe1-C2	1.751(4)	C9-F1	1.325(17)
B1-C8	1.62(2)	C8-C9	1.37(2)
C1-Fe1-C2	94.5(8)	C8-B2-C14	107.2(14)
Fe1-B1-C8	125.8(11)	Centroid-Fe1-B1-C8	28.4(3)
Fe2-B2-C14	126.6(13)		

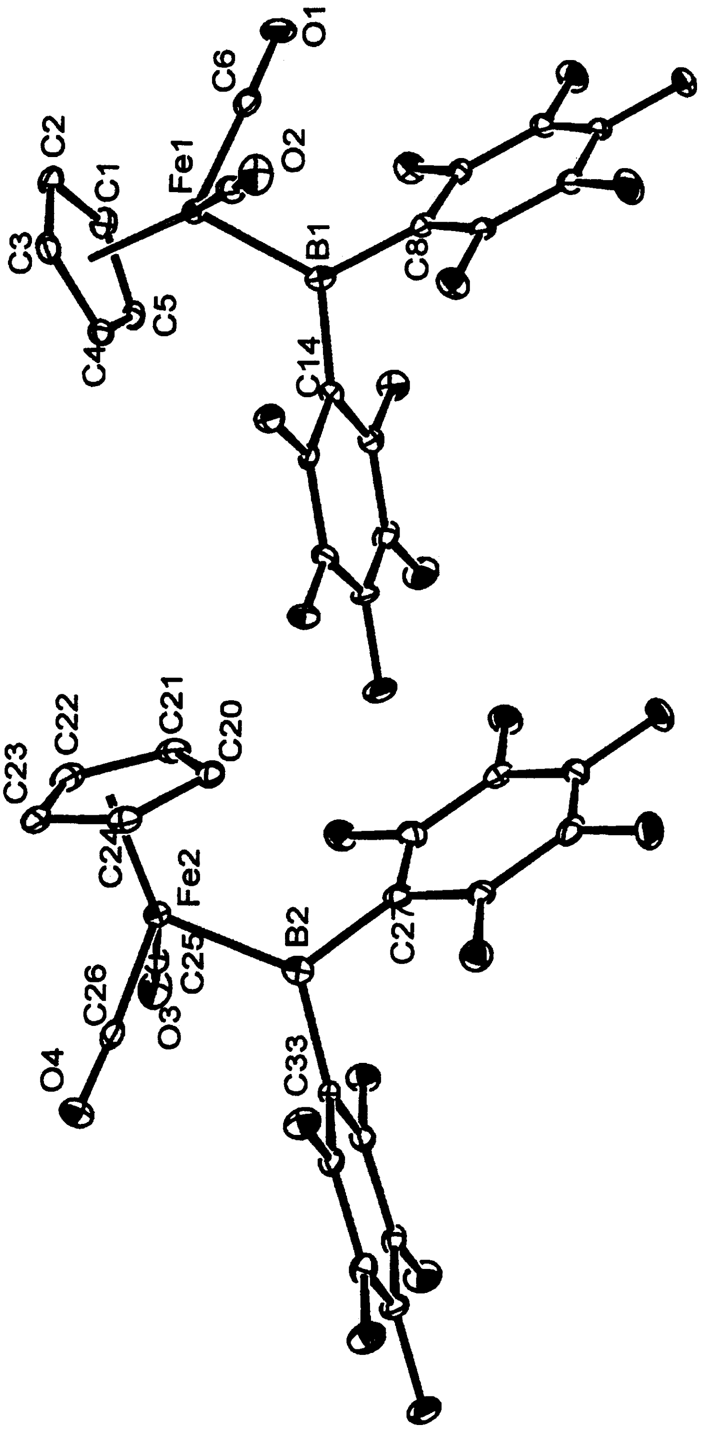


Figure 3.3 Molecular structure of the two crystallographically independent molecules in the asymmetric unit of the triclinic polymorph of $(C_5H_5)Fe(CO)_2B(C_6F_5)_2$, **1**. Hydrogen atoms omitted for clarity; ORTEP ellipsoids set at the 50% probability level.

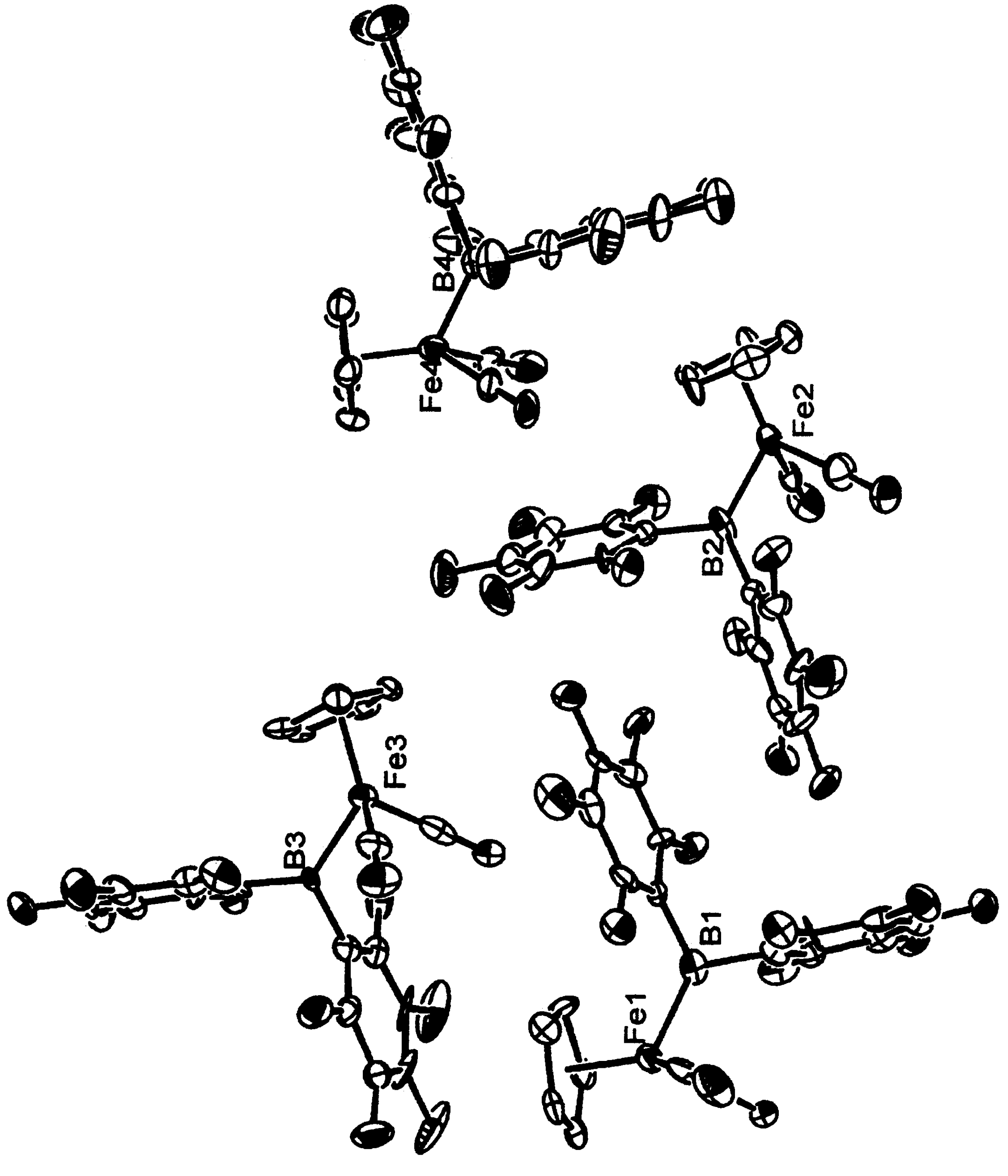


Figure 3.4 Molecular structure of the four crystallographically independent molecules in the asymmetric unit of the monoclinic polymorph of $(C_5H_5)Fe(CO)_2B(C_6F_5)_2$, **1**. Hydrogen atoms omitted for clarity; ORTEP ellipsoids set at the 50% probability level.

The solid state structure of **1** (triclinic polymorph) is based around an asymmetric unit consisting of two very similar but independent molecules. The two molecules adopt the expected half–sandwich geometry at the iron centre with the coordination sphere being completed by two carbonyls and one bis(pentafluorophenyl) boryl ligand (Figure 3.3). The geometry of the $B(C_6F_5)_2$ ligand shows that the planes of the C_6F_5 and BC_2 units are inclined at an average angle of 67.1(3)° to one another. This compares to an average value of 34.3° for $ClB(C_6F_5)_2$, and almost certainly reflects the greater steric demands of $(C_5H_5)Fe(CO)_2$ compared to Cl. Fe-B distances for the two independent molecules are 1.965(5) and 1.964(4) Å ,values which are comparable to the distances found in $(C_5H_5)Fe(CO)_2B(cat)$[7], **3,** [1.959(6) Å], $(C_5H_5)Fe(CO)_2BPhCl$[17] [2.003(10) Å], and $(C_5H_5)Fe(CO)_2BO_2C_6H_2O_2BFe(CO)_2(C_5H_5)$ [25] [1.971(2) Å]. This compares to an average value of 2.015(6) Å found for related boryl complexes, and the significantly longer bond found in the analogous diphenylboryl complex, $(C_5H_5)Fe(CO)_2BPh_2$, **4,** [2.034(3) Å][7]. Despite the larger steric demands of the $B(C_6F_5)_2$ ligand compared to $B(C_6H_5)_2$, the shorter Fe-B distance in **1** (compared to **4**) almost certainly reflects the greater Lewis acidity of the boron centre. The carbonyl stretching frequencies for **1** (2014 and 1968 cm^{-1}) are also comparable to those for **3** and **4** (2024, 1971 and 2021, 1951 cm^{-1}), and somewhat higher than the average values for $(C_5H_5)Fe(CO)_2$ boryl complexes (2007 and 1949 cm^{-1}).[5,11,13,15,25]

The torsion angle (θ) between the Cp centroid-Fe-B and BC_2 planes is significantly smaller in **1** [average value of 28.2(3)° for **1** vs. 75° for **4**]. This angle can be defined pictorially as that between the C_5R_5 centroid-Fe-B and BX_2 planes shown in Figure 3.5. Hoffmann and coworkers have concluded that the pseudo-isoelectronic $(C_5H_5)Fe(CO)_2CH_2^+$ system should have a value of 0° for best overlap between the filled $[(C_5R_5)Fe(CO)_2]^+$ HOMO and the empty boron p-orbital (Figure 3.2); moreover, the deeper lying HOMO-2 for Fp^+ can also interact with the empty boron p-orbital.[8]

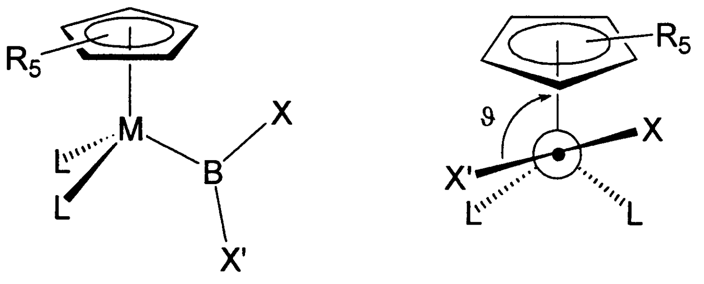


Figure 3.5 Definition of the torsion angle θ between the C_5R_5 centroid-Fe and BX_2 planes.

As was shown by Hoffmann, both of these molecular orbitals have the appropriate energy for Fe to B π interaction. However, due to the smaller energy difference between the Fp^+ HOMO and the higher lying boron-centred p orbital, π donation from the HOMO is more effective than from the HOMO-2. Therefore, a torsion angle close to 0° provides better π interaction than a value of 90^0. The torsion angle measured for **1** [28.2(3)] may therefore also be indicative of a stronger π interaction than in **4** [for which θ = 78°], although almost certainly the high steric demands of the $B(C_6F_5)_2$ ligand prevent the attainment of a virtually coplanar arrangement such as that found in **3** (7.9°). Further investigation of the bonding in $(C_5H_5)Fe(CO)_2B(C_6F_5)_2$ and comparison with related species such as **3** and **4** was carried out by the use of Density Functional Theory (DFT). The results of these analyses are included in Section 3.4 below.

Given that the more strongly electron-donating Na[$(C_5Me_5)Fe(CO)_2$] fragment might be expected to lead to a more electron-rich iron centre and hence to greater Fe to B π back bonding, the synthesis of the permethylated complex $(C_5Me_5)Fe(CO)_2B(C_6F_5)_2$ was also attempted. The reaction of $ClB(C_6F_5)_2$ with Na[$(C_5Me_5)Fe(CO)_2$] was monitored by ^{11}B NMR spectroscopy; the resonance due to the chloroborane at δ_B 58.7 was replaced by a low-field signal at δ_B121.3. ^1H, ^{13}C, and ^{19}F NMR and IR spectroscopic data support the proposed formulation as $(C_5Me_5)Fe(CO)_2B(C_6F_5)_2$ (**2**) and peaks in the EI mass spectrum corresponding to the M^+ ion, $(M\text{-}CO)^+$, and $(M\text{-}2CO)^+$ ions also support this assertion.

The formulation of **2** as $(C_5Me_5)Fe(CO)_2B(C_6F_5)_2$ is further supported by the result of a single crystal X–ray diffraction study, the crystals being obtained by cooling a concentrated hexane solution to -30°C. The molecular structure of **2** is illustrated in Figure 3.6 and relevant bond lengths and angles are listed in Table 3.5.

Table 3.5 Selected bond lengths [Å] and angles [°] for **2**.

Fe1-B1	1.968(5)	B1-C19	1.588(6)
Fe1-Cp centroid	1.739(4)	O1-C11	1.155(5)
Fe1-C11	1.750(5)	O2-C12	1.149(4)
Fe1-C12	1.749(5)		
B1-C13	1.599(6)		

C11-Fe1-C12	94.74(19)	C13-B1-C19	110.2(3)
Fe1-B1-C13	126.9(3)	Centroid-Fe1-B1-C13	43.1(3)
Fe1-B1-C19	122.8(3)		

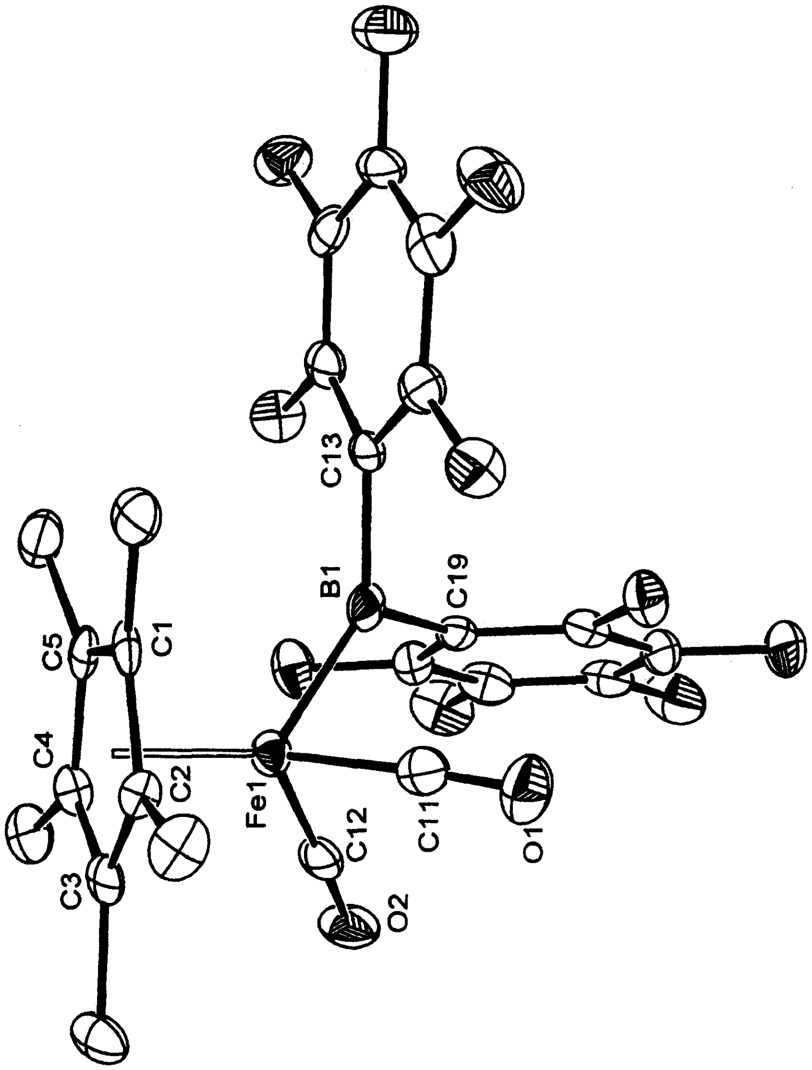
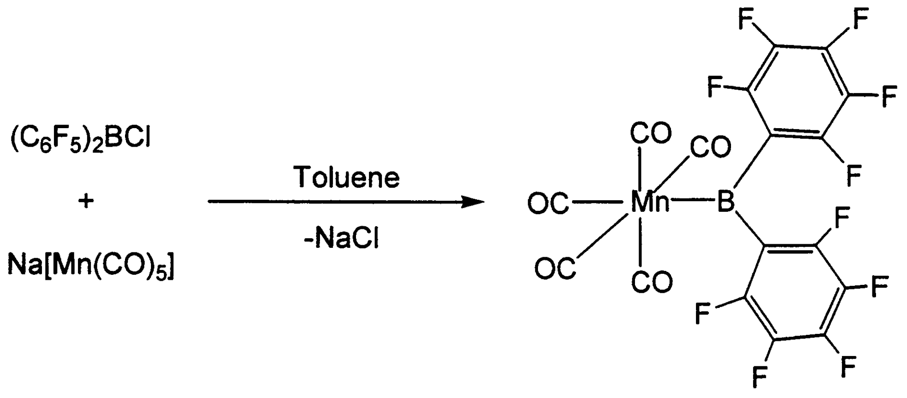


Figure 3.6 The molecular structure of $(C_5Me_5)Fe(CO)_2B(C_6F_5)_2$, **2**. Hydrogen atoms omitted for clarity; ORTEP ellipsoids set at the 50% probability level.

Here too, the molecule adopts the expected half sandwich geometry at the iron center with the coordination sphere being completed by two carbonyls and one bis(pentaflurophenyl)boryl ligand. The Fe–B distance in **2** is 1.968(5) Å which is comparable to the distance in (**1**) [1.964(4) Å], and to that in $(C_5Me_5)Fe(CO)_2B(cat)^9$ (**3**) [1.980(2) Å]. The carbonyl stretching frequencies for **2** (2004, 1953 cm^{-1}) are slightly lower than those for **1** and **3** (2024, 1968 and 1996, 1939cm^{-1}), as expected for permethylation of the cyclopentadienyl ligand. A similar red shift is observed on going from $(C_5H_5)Fe(CO)_2B(cat)^7$ (2024, 1971 cm^{-1}) to $(C_5Me_5)Fe(CO)_2B(cat)^9$ (1996, 1940 cm^{-1}) . The larger steric demands of the (C_5Me_5) ligand compared to (C_5H_5) cause the torsion angle (θ) between the (C_5Me_5) centroid-Fe-B and BC_2 planes to be 43.1 (3) ° i.e. significantly larger than the value of 28.2(3)° for the (C_5H_5) centroid-Fe-B and BC_2 in **1**.

3.3.2.2 Pentafluorophenyl-based boryl complexes of manganese

Salt elimination chemistry can also be performed with manganese anions such as $Na[Mn(CO)_5]$ to form a pentafluorophenyl boryl complex. Reaction of $ClB(C_6F_5)_2$ with $Na[Mn(CO)_5]$ in toluene for 2 h produces $(CO)_5MnB(C_6F_5)_2$ in yields of ca. 30 % (Scheme 3.6).



Scheme 3.6 Synthetic route to $(CO)_5MnB(C_6F_5)_2$

The ^{11}B NMR signal due to the chloroborane at δ_B 58.7 was replaced by a low-field signal at δ_B130.7, (c.f. values of 121.5 and 121.3 for **1** and **2** respectively). ^{13}C and ^{19}F NMR and IR spectroscopic data support the proposed formulation with ^{13}C the spectrum showing two broad carbonyl resonances at δ 207.9 and 208.6 ppm, assigned to the cis and trans CO ligands respectively. Additionally, features in the EI mass spectrum corresponding to the M^+ ion, and to the fragment ions $(M-CO)^+$, $(M-2CO)^+$, $(M-3CO)^+$, $(M-4CO)^+$, and $(M-5CO)^+$ also support the proposed formulation. Comparison of the carbonyl stretching frequencies of $(CO)_5MnB(C_6F_5)_2$ (2136, 2049, 2014 cm^{-1}) to other complexes containing this metal fragment e.g. $(CO)_5MnBcat$ (2112 and 2009 cm^{-1})[9] and $(CO)_5MnBO_2C_6Cl_4$ (2120, 2036, 2014, 1990 and 1972 cm^{-1})[27] reveals somewhat higher stretching frequencies for $(CO)_5MnB(C_6F_5)_2$ which may be indicative greater Mn to B π back bonding. Similar reactions with sources of $[Co(CO)_4]^-$ have been attempted, but did not lead to the isolation of any products containing Co-B bonds. In the case of $[PPN][Co(CO)_4]$ the organometallic starting material was recovered essentially unchanged. It is possible that the weakly nucleophilic nature of the $[Co(CO)_4]^-$ ion is responsible for this lack of reactivity, and indeed the only example of a cobalt boryl species reported in the literature has been made by an oxidative addition route.

3.3.2.3 Reactions of $ClB(C_6F_5)_2$ with organometallic hydrides

In contrast to metal carbonylate anions, the reactions of $ClB(C_6F_5)_2$ with metal hydrides proved to be less fruitful. Thus, no tractable products were isolated from the reactions with $Li[(C_5H_5)_2TaH_2]$, $Li[(C_5H_5)_2WH]$, or $Li[(C_5H_5)_2MoH]$. A clue to the possible cause of these reactions can be obtained from literature precedent and from the reaction with $K[(C_5H_4Me)_2Mn(CO)_2H]$. Hydrido-metal boryl complexes and σ-borane complexes have been shown to be differentiated in effect by the position of the hydrogen ligand (Figure 3.7) with the two canonical forms shown representing the extremes of oxidative addition of the B-H bond.

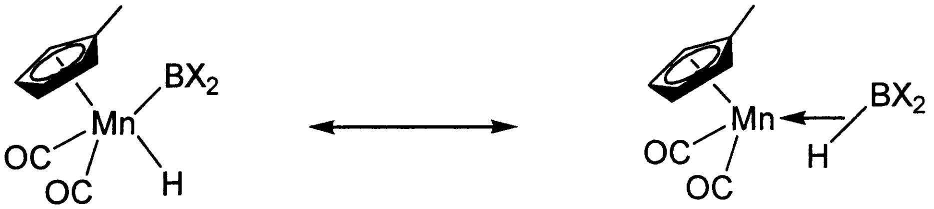


Figure 3.7 Hydridoboryl and σ-borane representations.

Reaction of $K[(C_5H_4Me)_2Mn(CO)_2H]$ with $ClB(C_6F_5)_2$ at -50°C proceeds quickly and cleanly to give a highly labile species which decomposes rapidly at temperatures above -10°C. It is characterised by broad resonances at δ_B 82.3 and δ_H -16.4 which sharpen markedly on appropriate decoupling (^1H or ^{11}B respectively). The position of the ^{11}B resonance is shifted significantly upfield from iron boryl complexes containing the $B(C_6F_5)_2$ ligand and this together with the B-H coupling revealed by ^1H and $^1H\{^{11}B\}$ measurements indicates a degree of quaternization at boron through direct B-H interaction (Figure 3.8).

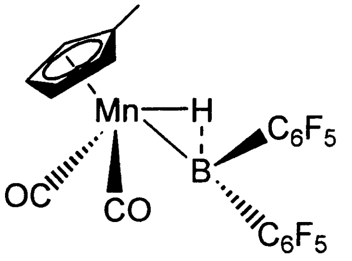


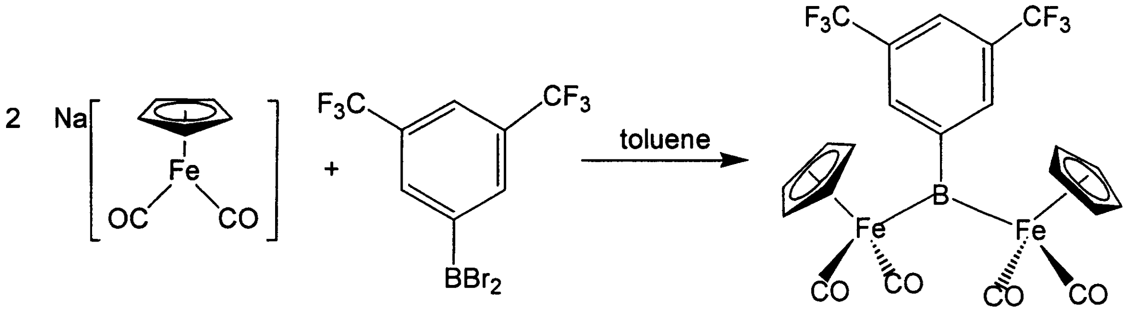
Figure 3.8 Partial quaternization at boron through direct B-H interaction.

Such a structure is consistent with that found for the corresponding BCy_2 derivative by Hartwig and its lability is also in agreement with that observed for $(C_5H_4Me)Mn(CO)_2(H)BMe_2$ and $(C_5H_4Me)Mn(CO)_2(H)BCy_2$.[41] Although structural data for this compound were not accessible, the ^{19}F NMR spectrum does give some information: inequivalent C_6F_5 groups are observed at -20°C, implying that the barrier to their interconversion through rotation along the B-H bond is significant. Similar phenomena have been observed previously for $(C_5H_4Me)Mn(CO)_2(H)B(cat)$.[41]

Finally, although the products of the thermal decomposition of $(C_5H_4Me)_2Mn(CO)_2HB(C_6F_5)_2$ were not definitively characterised, warming a solution in toluene-d_8 to room temperature does result in the complete loss of the signal at δ_B 82.3 and the formation of a predominant resonance at δ_B -25.5 which gives a doublet (J = 79 Hz) on ^{1}H coupling. The position and multiplicity of the signal implies a boron adduct of the type [$HB(C_6F_5)\cdot L$] or [$HB(C_6F_5)\cdot X]^-$ (c.f. -25.5 for [$HB(C_6F_5)_3]^-$).[42] As such it seem likely that decomposition of the hydrido manganese boryl system (C_5H_4Me) $Mn(CO)_2HB(C_6F_5)_2$ proceeds via loss of the borane unit $HB(C_6F_5)_2$. Conceivably this mode of decomposition could operate for other putative boryl species of the type $L_nM(H)B(C_6F_5)_2$, and might therefore explain the lack of success in isolating further complexes of this type.

3.3.2.4 A bridging borylene complex of iron

The alternative bis(trifluoromethyl) substituent was used prepare a bridging borylene complex $[(C_5H_5)Fe(CO)_2]_2B[3,5\text{-}(CF_3)_2C_6H_3]$ **5** via the reaction of $Br_2B[3,5\text{-}(CF_3)_2C_6H_3]$ with $Na[(C_5H_5)Fe(CO)_2]$ in toluene (Scheme 3.7). After a period of 12 h, the reaction was judged to be complete by the replacement of the peak in the ^{11}B NMR spectrum of the reaction mixture due to $Br_2B[3,5\text{-}(CF_3)_2C_6H_3]$ (δ_B 56.1) with a peak at δ_B 167.7, a chemical shift which is consistent with the replacement of both B-Br bonds with B-Fe bonds. The ^{11}B NMR chemical shift is within the range of those reported previously for other bridging borylene complexes e.g. $[(C_5H_5)Fe(CO)]_2B(2,4,6\text{-}Me_3C_6H_2)$ (δ_B 158.0)[18,20], $[(C_5H_5)Fe(CO)]_2(\mu_2\text{-}CO)[\mu_2\text{-}B(2,4,6\text{-}Me_3C_6H_2)]$ (δ_B 161.9) [18,20], and $[(C_5H_4Me)Fe(CO)]_2(\mu_2\text{-}CO)[\mu_2\text{-}BN(SiMe_3)_2)]$ (δ_B 119.1)[12].



Scheme 3.7 Synthetic route to complex **5**.

The formulation of **5** is also implied by the ^{1}H, ^{13}C, and ^{19}F NMR spectra; in particular the carbonyl ligands give a single resonance at δ_C 218.9. There are four terminal CO stretches in the IR spectra for **5**, as would be expected for the formulation proposed, with no bands corresponding to the stretching motions of bridging carbonyls observed (1700-1800 cm^{-1}). This inference is further supported by the mass spectrum, which shows the parent M^+ ion, with additional peaks corresponding to fragment ions $(M-CO)^+$, $(M-2CO)^+$, $(M-3CO)^+$, and $(M-4CO)^+$ also being evident. Hence it seems that an unsupported structure is most likely for borylene **5**, with alternative $[(C_5H_5)Fe(CO)]_2(\mu-CO)(\mu-BX)$ formulation formed by loss of CO being ruled out by IR, ^{13}C NMR and mass spectral evidence. **5** therefore represent a very rare example of this type of borylene coordination. Complex **5** was recrystallised from hexanes to form yellow crystals in 65% yield. However, the crystals did not diffract sufficiently strongly for complete structural characterisation.

3.4 Density Functional Theory studies

3.4.1 Introduction

Recently, the use of DFT methods to analyse the nature of the interaction between a transition metal centre and a low-coordinate group 13 ligand has received considerable interest, most notably in diyl complexes of the type $L_nM \leftarrow EX$ (E = B, Al, Ga, In, Tl).[28-30] Calculation of the electrostatic (ΔE_{elstat}) and orbital (ΔE_{orb}) contributions to the overall attractive metal ligand interaction has shown the importance of considering ionic terms in the bonding of such ligands to transition elements.[31] Until recently computational studies involving boryl complexes, however, had focussed almost exclusively on reactivity and mechanism, rather than on issues of structure and bonding. The mechanisms of group 10 metal catalysed di- and thio-boration of carbon-carbon multiple bonds, for example, have been investigated by Sakaki[32] and by Musaev and Morokuma;[33] in addition the key mechanistic steps of Rh(I) catalysed hydroboration of alkenes have been the subject of several computational studies.[34] In 2001 Frenking *et al.* reported the results of DFT studies[35] of five- and six-coordinate osmium boryl complexes originally synthesised by Roper and Wright.[36] Despite this, computational studies of structural and thermodynamic properties of metal boryl complexes have remained relatively few in number,[37]

Computational studies on half-sandwich boryl complexes of the type $[(C_5R_5)FeL_2(BX_2)]$ offer several advantages over octahedral or square pyramidal complexes as model compounds. Firstly, the molecular orbital configuration of the $C_5R_5ML_2$ fragment is such that the relative orientation of $(C_5R_5)ML_2$ and BX_2 units can be used as a probe of π-type interactions, as has been demonstrated by Hoffmann *et al.* in their analysis of the pseudo-isoelectronic $CpFe(CO)_2CH_2^+$ cation.[8] In theory π-type interactions are conceivable involving the vacant boryl-based π orbital and either the $(C_5R_5)ML_2$ HOMO of *a″* symmetry [Figure 3.2(a)] or the deeper lying perpendicular HOMO-2 orbital of *a′* symmetry [Figure 3.2(b)]. The relative importance of these possible interactions is thought to be dependent on the steric and electronic properties of the boryl ligand.[7] Secondly, comparison of calculated structural parameters with those obtained for crystallographically characterized compounds of the type $[(C_5R_5)ML_2(BX_2)]$ (M = Fe) allows some measure of the validity of the DFT method to be made.[7,9,13-15,26,38,39] Wide variation in Fe-B bond lengths [1.942(3) – 2.195(14) Å] and in CO stretching frequencies (*e.g.* 2024 and 1971 cm^{-1} *vs.* 1932 and 1869 cm^{-1}) are observed for $(C_5H_5)Fe(CO)_2$ boryl derivatives, with the role of π interactions being described as anywhere between 'modest'[7] and 'non-existent'.[15] Reproduction of structural parameters over such breadth would therefore lend credence to the DFT method, and allow an analysis of the calculated density to shed light on the origins of the observed variation.

3.4.2 Results and discussion

(i) Comparison of calculated structural and spectroscopic parameters with experimentally observed values.

In order to evaluate the accuracy of the gradient-corrected DFT method for complexes of this type a series of calculations was carried out involving compounds for which crystallographically determined structural data are available. The range of compounds investigated allows for wide variation in the nature of the Fe-B bond, by altering (i) the π-donor capacity of the boryl substituent, X [*e.g.* BX_2 = Bcat (**3, 5**), BPh_2 (**4**), $B(Cl)NH_2$ (**7**) and $B(C_6F_5)_2$ (**1**)]; (ii) the electronic and steric requirements of the cyclopentadienyl ligand [*e.g.* Cp, C_5H_5, (**3**, **6**, **4**); Cp*, C_5Me_5, (**5**, **7**, **8**)]; (iii) the mode of coordination of the boryl ligand [*e.g.* terminal Bcat (**3**, **5**) *vs.* bridging $BO_2C_6H_2O_2B$ (**6**)] and (iv) the availability of the boryl-based π orbital for back-bonding (*e.g.* using the base-stabilised boryl **8**, incorporating a four-coordinate boron center). Satisfactory agreement with experimentally determined structural parameters and reproduction of observed trends of over such a range of compounds would then provide a strong indication of the reliability of the DFT method. The results of these calculations are reproduced in Table 3.6, which compares calculated and experimentally observed bond lengths and angles. There is a good agreement between theoretically predicted and experimentally observed geometries. The calculated Fe-B distances for all complexes are typically 2-3% greater than those obtained crystallographically; such an over-estimate in bond lengths involving heavier atoms by DFT is well precedented.[40] Frenking et al., for example, in their recent study of osmium boryl complexes found a similar over-estimation of Os-B distances [*e.g.* 2.046 Å (exp.) vs 2.104 Å (calc.) for the five-coordinate species $(R_3P)_2OsCl(CO)B(OH)_2$, a discrepancy which has been attributed among other things to solid-state effects which leads to the shortening of donor-acceptor bonds.[35] It is interesting to note, however, that the differences between observed and calculated Fe-B distances are reasonably constant, and therefore that the DFT method reproduces well observed trends in this parameter. In particular the shorter Fe-B lengths found for **1**, and boryl ligands bearing oxygen substituents and the somewhat longer distances found for BPh_2, $B(Cl)NH_2$ and especially $BH_2{\cdot}PR_3$ ligands are reflected in the corresponding calculated values.

The geometries of $Fe(CO)_2$ and BX_2 units are extremely well reproduced computationally, and there is also reasonable agreement between observed and calculated values for θ, defined in Figure 3.5 as the angle between Cp centroid-Fe-B and BX_2 planes. As has been noted previously,[7] the magnitude of θ is dependent on several factors, notably the π acceptor capacity and steric requirements of the BX_2 ligand. In fact, rotation about the Fe-B bond represents motion across a very shallow potential energy surface, with the difference in energy for several rotamers often being very small. It is reassuring therefore, that despite such small energy differences, the calculations do reproduce with reasonable accuracy the experimentally observed torsion angles. In particular, the contrasting near coplanar (7.9° and 26.7°) and near perpendicular (82.2°) geometries determined experimentally for the superficially similar complexes of terminal Bcat (**3** and **5**)[7,9] and bridging $BO_2C_6H_2O_2B$ ligands (**6**)[26] are reproduced well by these calculations (1.4°, 28.1° and 83.4°, respectively).

Table 3.6 Calculated (*in italics*) and crystallographically determined structural parameters for iron boryl complexes **1**-**8**.

	Distance (Å)				Angle (°)		
	Fe-B	Fe-Cp centroid	Mean Fe-L	Mean B-X	L-Fe-L	X-B-X	ϑ[a]
1[f]	1.965(5) *2.006*	1.734(4) *1.823*	1.755(4) *1.776*	1.596(5) *1.597*	94.5(2) *93.3*	111.5(3) *114.0*	28.2(3) *40.5*
2	-	-	-	-	-		-
	2.002	*1.772*	*1.767*	*1.414*	*94.6*	*108.3*	*2.7*
3	1.959(6) *2.009*	1.716(1) *1.809*	1.731(6) *1.765*	1.411(7) *1.420*	92.9(3) *94.6*	108.0(5) *109.4*	7.9 *1.4*
4	2.034(3)	1.729(1)	1.748(3)	1.577(3)	90.8(1)	116.6(2)	75
	2.107	*1.824*	*1.762*	*1.582*	*89.0*	*118.2*	*66.8*
5	1.980(2)	1.72(1)	1.746(3)	1.407(3)	96.3(1)	108.8(2)	26.7
	2.027	*1.802*	*1.767*	*1.420*	*95.3*	107.6	*28.1*
6	1.971(2)	1.721(2)	1.755(2)	1.406(2)	94.0(8)	109.2(1)	82.2(1)
	2.015	*1.804*	*1.773*	*1.415*	*94.2*	*109.7*	*83.4*
7[b]	2.027(5)	1.735(1)	1.746	1.377(6) N 1.834(5) Cl	93.6	112.0(3)	87.4
	2.058	*1.823*	*1.763*	*1.409 N* *1.855 Cl*	*94.3*	*111.7*	*75.2*
8[c]	2.195(14)	[d]	[d]	1.924(15) P	[d]	[d]	[e]
	2.215	*1.820*	*1.758*	*1.211 H* *1.971 P*	*94.7*	*114.7*	[e]

[a] Angle θ as defined in Figure 3.5. [b] Calculations employed the simplification of using the B(Cl)NH_2 ligand, rather than B(Cl)NMe_2. [c] Calculations employed the simplified ligands PH_3 and C_5Me_5 rather than PMe_3 and C_5Me_4Et. [d] Data not available. [e] Not applicable. [f] Crystallographically determined values for **1** are the mean values for the two independent molecules within the asymmetric unit of the triclinic polymorph.

(ii) Analysis of Fe-B bond in complexes 1-8

Comparison by computational studies between different boryl ligands in the generic complexes $(C_5H_5)Fe(CO)_2BX_2$ was undertaken for the specific species listed in Table 3.7. In general, π and σ contributions to the Fe-B bond are influenced by the σ/π acceptor properties of the substituents on the boryl ligand and by the ancillary ligands at the iron centre. In comparison with **3** and **4**, the Fe-B bond in **1** shows significantly increased contributions not only from π symmetry covalent interactions but also from electrostatic attraction between the organometallic and boryl fragments. This is probably due to the replacement of the H atoms on the phenyl rings in complex **4** with highly electronegative F atoms in complex **1** thus making the boron centre more Lewis acidic. Furthermore, the results in Table 3.7 show that replacement of a poor π donor boryl substituent (X = H, Cl) with one which is appreciably more π donating (X = F) effects the π contribution to an appreciable degree. As expected the smallest π contribution is found for the BF_2 complex with the correspondingly longest Fe-B length, due to the strong π donor properties of fluorine. Comparison to the chloroboryl (X = Cl) and hydridoboryl (X = H) complexes shows that the π contribution is increased due to the greater π acceptor properties of BCl_2 and BH_2. On first inspection, the BH_2 ligand should be a better π acceptor than BCl_2 and also a better σ donor due to the lower electonegativity of H vs. Cl. The calculated relative percentage σ/π contributions for the two systems are essentially the same. However, the higher bond dissociation energy (66.8 vs 58.1 Kcal mol^{-1}) shows that the overall orbital contribution to bonding is higher in the case of BH_2. Finally, in comparing the calculated relative π contributions for the BF_2, BCl_2, and BH_2

ligands with $B(C_6F_5)_2$ we can see that the $B(C_6F_5)_2$ ligand has among the highest percentage π contribution (18.0) of the four (6.0, 17.8, 1, and 15.8 respectively). Consequently the $B(C_6F_5)_2$ ligand offers one of the better test systems of the ability of strongly σ donor boryl ligands to also act as π acids.

(iii) Analyses of molecular orbital compositions for model compounds 10 and 11.

A molecular orbital (MO) analysis has been carried out to compare descriptions of bonding in the isoelectronic pair of molecules $(C_5H_5)Fe(CO)_2BH_2$ (**10**) and $(C_5H_5)Fe(CO)_2CH_2^+$ (**11**).[8] Sigma bonding between iron and boryl fragments in **10** is represented by the HOMO-3, which, like its counterpart for Fischer carbene **11**, contains significant contributions from Fe $3d_{z^2}$ and B $2p_z$. The differences between the bonding in these molecules revolve around the use of the Fe $3d_{yz}$ orbital. In the case of the carbene **11** this atomic orbital plays a major role in the HOMO-4 bonding molecular orbital between Fe and cyclopentadienyl ligand (HOMO-4: 31.8% Fe $3d_{yz}$) and also in π bonding to the carbene fragment (HOMO-2 contains 22.4 % Fe $3d_{yz}$). These two orbitals are separated by some 0.6 eV. In boryl complex **10** the Fe $3d_{yz}$ orbital is also involved in π type interactions with both cyclopentadienyl and boryl ligands, as evidenced by significant contributions to HOMO-1 and HOMO-2. In contrast to the situation in **11**, however, these two orbitals are nearly degenerate ($\Delta E = 0.02$ eV) and both contain significant Fe-Cp and Fe-B π bonding character. Most significant, however, is the observation that the total contribution of the B $2p_y$ orbital to both of these MOs (7.8%) is markedly less than the contribution of the C $2p_y$ orbital to the analogous MO in molecule **11** (21.0% to HOMO-2). Likewise, the MOs for **10** which represent the Fe-B π* antibonding interaction (LUMO and LUMO+2) contain smaller amounts of Fe 3d_{yz} character (19.4% in total) than does the corresponding FeC π* MO in **11** (23.5% Fe 3d_{yz} in the LUMO). In addition, the energy difference between orbitals of π and π* character (4.1 eV) is somewhat greater than in the case of the carbene (3.2 eV).

Table 3.7 Analysis of Bonding in Complexes 1-11.

Compound	Calculated r(M-E) / Å[a]	Breakdown of orbital contribution to bond / %		Mayer bond order	BDE (D_o) / kcal mol^{-1}	ΔE_{elstat}[b] / kcal mol^{-1}	ΔE_{orb}[b] / kcal mol^{-1}	ΔE_{Pauli}[b] / kcal mol^{-1}	ΔE_{elstat} / ΔE_{orb}
		σ	π						
1	2.006	81.9	18.0	0.999	53.6	-112.9	-194.2	228.0	0.58
2	2.002	87.6	12.3	0.920	64.8	-93.0	-201.3	208.8	0.46
3	2.009	89.2	10.7	0.957	66.1	-110.5	-224.5	247.6	0.49
4	2.107	90.4	9.5	0.888	45.5	-60.8	-322.4	107.5	0.19
5	2.027	87.0	12.9	0.856	65.2	-112.1	-225.7	250.0	0.50
6	2.015	87.2	12.1	0.935	65.2	-115.5	-227.6	256.5	0.51
7	2.058	86.9	13.0	0.904	55.3	-118.4	-204.6	240.8	0.58
8	2.215	97.2	2.9	0.694	40.0	-85.9	-157.3	173.6	0.55
9	2.007	85.0	14.8	1.016	68.5	-121.8	-233.2	261.7	0.52
10	1.988	84.1	15.8	0.995	66.8	-136.2	-239.6	285.6	0.57
11	1.818	63.8	36.3	0.995	80.0	-179.3	-121.1	201.9	1.48

As expected these observations confirm that the π interaction between $[(C_5H_5)Fe(CO)_2]$ and carbene/boryl fragments is weaker in the case of boron. This is primarily due to the higher energy of the $2p_y$ orbital required for π bonding in the case of the boryl ligand (3.65 eV for the BH_2^- fragment, compared to –4.80 eV for CH_2). This results in a larger energy difference between the Fe $3d_{yz}$ and E $2p_y$ orbitals in the case of E = B and therefore in less efficient orbital mixing (as reflected by smaller B $2p_y$ contributions to MOs with Fe-B π bonding character and smaller Fe $3d_{yz}$ contributions to MOs with FeB π* character).

The significance of π contributions to Fe-B bonding can be seen to further diminish on replacement of the H substituents of the boryl ligand by π donor oxygen-based substituents, for example in the model system $BO_2C_2H_2$. For the $[(C_5H_5)Fe(CO)_2]$ complex of this ligand the expected strong σ interaction between metal and $BO_2C_2H_2$ fragments is represented by the HOMO-4 which again features significant contributions from Fe $3d_{z^2}$ and B $2p_z$ and 2s orbitals. However, the HOMO-2 orbital which, as in the case of carbene **11**, represents the predominant Fe-B π bonding interaction, notably has a much smaller contribution from B $2p_y$ (5.3%) than do the corresponding MOs for **10** (7.8% B $2p_y$) and **11** (21.0% C $2p_y$). Furthermore it is possible to identify orbitals at *ca.* –8.0 and +0.9 eV (LUMO+12) which have significant character as (filled) B-O π and (unfilled) B-O π* MOs, respectively. The contribution of Fe $3d_{yz}$ to either of these orbitals is negligible. DFT-calculated molecular orbital analysis for model compound $(C_5H_5)Fe(CO)_2BO_2C_2H_2$ (**12**) is therefore consistent with a boryl ligand which acts as a strong σ donor, but which interacts to a much smaller degree with Fe-based orbitals of π symmetry due to competing O-B π interaction. Examining the molecular orbital make-up for the fragment $BO_2C_2H_2^-$,reveals that, in effect, the available π symmetry orbital at boron has been shifted to much higher energy (5.41 *vs.* 3.65 eV for BH_2^-), as it is now a B-O π* orbital (the filled orbital with B-O bonding character being found at – 5.20 eV). A simplified description of the π-type interactions between metal and boryl/carbene fragments in molecules, **10**, **11** and **12** is reproduced in Figure 3.7, and is fully consistent with the calculated orbital energies for the CH_2, BH_2^- and $BO_2C_2H_2^-$ fragments The vacant orbital of appropriate (π) symmetry on the boryl/carbene fragment is found at –4.80, 3.65 and 5.41 eV, respectively.

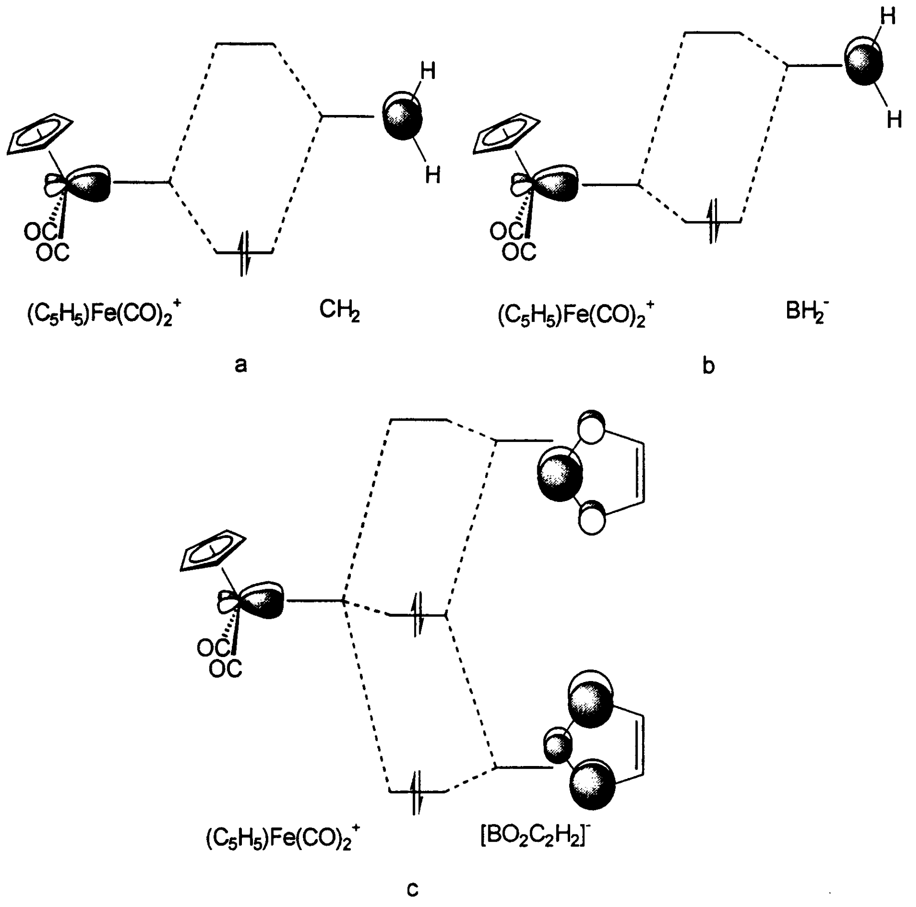


Figure3.7 Simplified omparison of π orbital interactions for compounds **10**, **11** and **12**.

To summarize, therefore, bonding in transition metal boryl complexes of the type $(C_5R_5)Fe(CO)_2BX_2$ has been investigated by density functional methods, in order to quantify the relative contributions to the metal boryl linkage from ionic and covalent interactions. Covalent (orbital) terms account for 60-70% of the overall attractive interaction between metal and boryl fragments, with σ donation from the boryl ligand being predominating over π back donation even in the most favourable cases [*e.g.* 84.1 : 15.8 and 81.9 : 18.0 for $(C_5H_5)Fe(CO)_2BH_2$ and $(C_5H_5)Fe(CO)_2B(C_6F_5)_2$, **1**, respectively].

3.5 Conclusions

The synthesis, spectroscopic and structural characterisation of the first transition metal complexes containing the bis(pentafluorophenyl)boryl ligand, $(C_5H_5)Fe(CO)_2B(C_6F_5)_2$, $(C_5Me_5)Fe(CO)_2B(C_6F_5)_2$, and $(CO)_5MnB(C_6F_5)_2$ have been accomplished in reasonable yields by the salt elimination reaction between the $ClB(C_6F_5)_2$ and appropriate organometallic anions. Furthermore, reaction of $ClB(C_6F_5)_2$ with hydride-containing organometallics can be accomplished at low temperature (< -10°C) to generate $(C_5H_4Me)_2Mn(CO)_2HB(C_6F_5)_2$, although the propensity of such complexes to eliminate $[HB(C_6F_5)_2]_n$ appears to preclude the isolation of related examples from groups 5 and 6. As expected the electron withdrawing nature of the pentafluorophenyl substituents leads to enhanced π interaction with the metal centre, although even here this still represents only a small contribution to the overall metal ligand bond.

On the other hand, the preparation of unsupported bridging borylene complexes $[(C_5H_5)Fe(CO)_2]_2B[3,5\text{-}(CF_3)_2C_6H_3]$ can also be achieved in reasonable yields via salt elimination between the appropriate fluorinated borane $Br_2B[3,5\text{-}(CF_3)_2C_6H_3]$ and organometallic anions.

3.6 References for chapter three

1. (a) H. Wadepohl, Angew. Chem. Int. Ed. Engl., 1997, 36, 2441; G.J. Irvine, M.J.G. Lesley, T.B. Marder, N.C. Norman, C.R. Rice, E,G. Robins, W.R. Roper, G.R. Whittell, L.J. Wright, Chem. Rev., 1998, 98, 2685; (b) H. Braunschweig, Angew. Chem., Int. Ed. Engl., 1998, 37, 1786; (c) M.R. Smith III, Prog. Inorg. Chem., 1999, 48, 505.
2. See, for example: K. Burgess, M. J. Ohlmeyer, Chem. Rev., 1991, 91, 1179.
3. (a) H. Chen, J. F. Hartwig, Angew. Chem. Int. Ed., 1999, 38, 3391; (b) H. Chen, S. Schlecht, T. C. Semple, J. F. Hartwig, Science, 2000, 287, 1995.
4. C. N. Iverson, M. R. Smith, J. Am. Chem. Soc., 1999, 121, 7696.
5. (a) K. M. Waltz, J.F. Hartwig, Science, 1997, 277, 211.
6. R. T. Baker, D. W. Ovenall, J. C. Calabrese, S. A. Westcott, N. J. Taylor, I. D. Williams, T. B. Marder, J. Am. Chem. Soc., 1990, 112, 9399.
7. J. F. Hartwig, S. Huber, J. Am. Chem. Soc., 1993, 115, 4908.
8. B. E. R. Schilling, R. Hoffmann, D. Lichtenberger, J. Am. Chem. Soc., 1979, 101, 585.
9. K. M. Waltz, C. N. Muhoro, J. F. Hartwig, Organometallics, 1999, 18, 3383.
10. H. Braunschweig, M. Colling, C. Kollann, U. Englert, J. Chem. Soc., Dalton Trans., 2002, 2289.
11. H. Braunschweig, C. Kollann, U. Englert, Eur. J. Inorg. Chem., 1998, 465.

12. H. Braunschweig, C. Kollann, K. W. Klinkammer, Eur. J. Inorg. Chem., 1999, 1523.
13. H. Braunschweig, B. Ganter, M. Koster, T. Wagner, Chem. Ber., 1996, 129, 1099.
14. H. Braunschweig, M. Koster, J. Organomet. Chem., 1999, 588, 231.
15. H. Braunschweig, C. Kollann, M. Müller, Eur. J. Inorg. Chem., 1998, 291.
16. (a) D. L. Coombs, S. Aldridge, S. J. Coles, M. B. Hursthouse, Organometallics, 2003, 22, 4213; (b) D. L. Coombs, S. Aldridge, A. Rossin, C. Jones, D.J. Willock, Organometallics, 2004, 23, 2911.
17. H. Braunschweig, K. Radacki, F. Seeler, G.R. Whittell, Organometallics, 2004, 23, 4178.
18. D. L. Coombs, S. Aldridge, C. Jones, J. Chem. Soc. Dalton Trans., 2002, 3851.
19. H. Braunschweig, T. Wagner, Angew. Chem. Int. Ed. Engl., 1995, 34, 825.
20. S. Aldridge, D. L. Coombs, C. Jones. Chem. Commun., 2002, 856.
21. R. D. Chambers, T. Chivers, J. Chem. Soc., 1965, 3933.
22. D. J. Parks, W. E. Piers, G. P. A. Yap, Organometallics, 1998, 17, 5492.
23. K. Ishihara, S. Kondo, H. Yamamoto, J. Org. Chem., 2000, 65, 9125.
24. G. J. P. Britovsek, personal communication.
25. S.S. Al-Juaid, C. Eaborn, M.N.A. El-Kheli, P.B. Hitchcock, P.D. Lickiss, E.M. Molla, D.J. Smith, J.A. Zora, J. Chem. Soc., Dalton Trans., 1989, 447.

26. S. Aldridge, R. J. Calder, A. A. Dickinson, D. J. Willock, J. W. Steed, Chem. Commun., 2000, 1377.

27. R. J. Calder, PhD thesis, Cardiff University, 2002.

28. (a) G. Frenking, N. Fröhlich, Chem. Rev. 2000, 100, 717. (b) J. Uddin, C. Boehme, G. Frenking, Organometallics., 2000, 19, 571. (c) C. Boehme, J. Uddin, G. Frenking, *Coord. Chem. Rev.* 2000, 197, 249. (e) Y. Chen, G. Frenking, Dalton Trans. 2001, 434.

29. (a) F.M. Bickelhaupt, U. Radius, A.W. Ehlers, R. Hoffmann, E.J. Baerends, New. J. Chem. 1998, 1. (b) U. Radius, F.M. Bickelhaupt, A.W. Ehlers, N. Goldberg, R. Hoffmann, Inorg. Chem. 1998, 37, 1080. (c) A.W. Ehlers, E.J.Baerends, F.M. Bickelhaupt, U. Radius, Chem. Eur. J. 1999, 4, 210.

30. (a) J. Weiss, D. Stetzkamp, B. Nuber, R.A. Fischer, C.Boehme, G. Frenking, Angew. Chem. Int. Ed. Engl., 1997, 36, 70. (b) F.A. Cotton, X. Feng, Organometallics., 1998, 17, 128. (c) C. Boehme, G. Frenking, Chem. Eur. J. 1999, 5, 2184. (d) C.L.B. Macdonald, A.H. Cowley, J. Am. Chem. Soc. 1999, 121, 12113. (e) G. Linti, H. Schnöckel, H. Coord. Chem. Rev. 2000, 206-207, 285.

31. J. Uddin, G. Frenking, J. Am. Chem. Soc. 2001, 123, 1683.

32. (a) S. Sakaki, T. Kikuno, Inorg. Chem. 1997, 36, 226. (b) S. Sakaki, S. Kai, M. Sugimoto, Organometallics., 1999, 18, 4825.

33. (a) Cui, Q. Musaev, D. G. Morokuma, K. Organometallics., 1997, 16, 1355. (b) ibid, 1998, 17, 742. (c) ibid, 1998, 17, 1383.

34. (a) D. G. Musaev, A. M. Mebel, K Morokuma,. J. Am. Chem. Soc. 1994, 116, 10693. (b) A. E. Dorigo, P. v. R. Schleyer,. Angew. Chem.

Int. Ed. Engl. 1995, 34, 115. (c) D. G.Musaev, T. Matsubara, A. M. Mabal, N. Koga, K. Morokuma, Pur. Appl. Chem. 1995, 67, 257. (d) C.Widauer, H. Grützmacher, T. Ziegler, Organometallics, 2000, 19, 2097.

35. K. T.Giju, M. Bickelhaupt, G.Frenking, Inorg. Chem. 2000, 39, 4776.

36. (a) G. J.Irvine, W. R. Roper, L. J. Wright, Organometallics., 1997, 17, 4869. (b) C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, Organometallics., 1998, 17, 4869. (c) C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, Angew. Chem. Int. Ed. Engl. 1999, 38, 1110. (d) G. J. Irvine,, C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, Angew. Chem. Int. Ed. Engl. 2000, 39, 948. (e) C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, Organometallics., 2000, 19, 4344.

37. (a) P. R. Rablen, J. F. Hartwig, S. P. Nolan, J. Am. Chem. Soc. 1994, 116, 4121. (b) P. R. Rablen, J. F. Hartwig., J. Am. Chem. Soc. 1996, 118, 4648. (c) M. Wagner, N. J. R. v. E. Hommes, H. Nöth, P. v. R. Schleyer., Inorg. Chem. 1995, 34, 607.

38. (a) K. M. Waltz, X. He, C. Muhoro, J. F.Hartwig, J. Am. Chem. Soc. 1995, 117, 11357. (b) K. M. Waltz, J. F. Hartwig., J. Am. Chem. Soc. 2000, 122, 11358. (c) K. Kawamura, J. F. Hartwig, J. Am. Chem. Soc. 2001, 123, 8422.

39. (a) H. Braunschweig, M. Koster, R. Wang, Inorg. Chem. 1999, 38, 415. (b) H. Braunschweig, C. Kollann, K. W. Klinkhammer., Eur. J. Inorg. Chem. 1999, 1523. (c) T. Yasue, Y. Kawano, M. Shimoi, Chem. Lett. 2000, 58.

40. See, for example, E. A. Jr. McCullough, E. Aprà, J. Nichols, J. Phys. Chem. A., 1997, 101, 2502.

41. S. Schlecht, J. F. Hartwig, J. Am. Chem. Soc., 2000, 122, 9435.

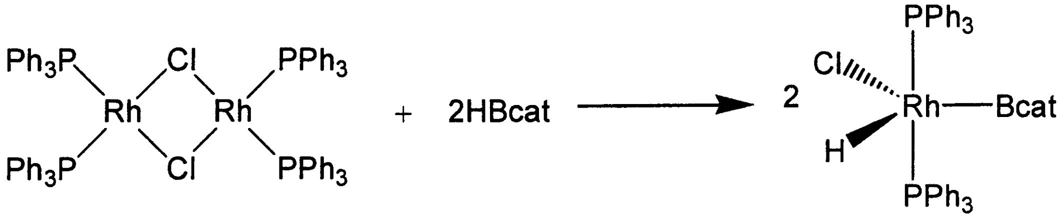
42. See chapter four of this thesis.

Chapter four

Late transition metal boryl complexes of rhodium and platinum

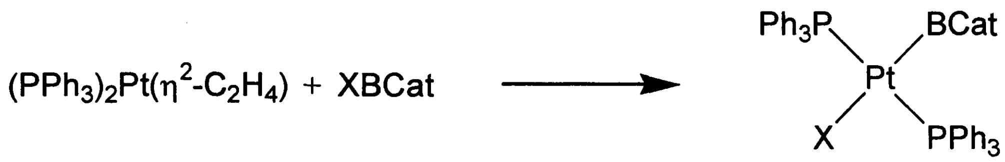
4.1 Introduction

Oxidative addition of B-X (X = H, Cl, Br, B, Sn) bonds to low valent transition metal centres has received much attention since 1960, in part due to the importance of such steps in the metal catalysed hydroboration and diboration of carbon-carbon multiple bonds and in the stoichiometric and catalytic functionalisation of alkanes under either photolytic or thermal conditions.[1] B-H oxidative addition is considered to be the initial step in catalytic hydroboration,[28] and the oxidative addition of HBCat to Wilkinson's catalyst, for example, has been investigated in great depth. Moreover, Marder and co-workers have reported the oxidative addition of HBcat to the related Rh(I) dimer $[(Ph_3P)_2RhCl]_2$ to form $RhHCl(PPh_3)_2(Bcat)$.[2] This reaction occurs more cleanly than that with Wilkinson's catalyst due the absence of competing reactions of free PPh_3 with the borane (Scheme 4.1). Moreover, reaction of $RhHCl(PPh_3)_2(Bcat)$ with excess HBcat, or of $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ with B_2cat_2 generates the bis(boryl) complex $RhCl(PPh_3)_2(Bcat)_2$.



Scheme 4.1 Oxidative addition of HBcat to $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$.

Particularly relevant to the work undertaken in this chapter, is the oxidative addition of XBCat (X = Cl, Br) to $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ to form the complexes *trans*-$(Ph_3P)_2Pt(X)BCat$, which was reported by Marder and Norman, together with structural data for the Pt(II) products (Scheme 4.2).[3]

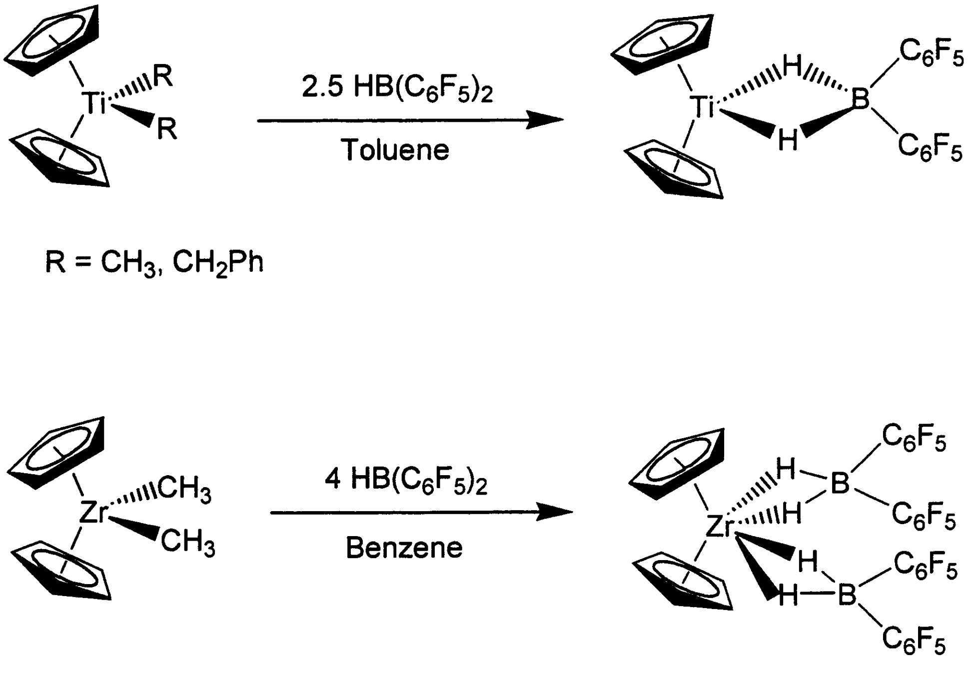


Scheme 4.2 Synthesis of *trans*-$(Ph_3P)_2Pt(X)BCat$ via the oxidative addition of XBCat (X = Cl, Br) to $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$.

While initial investigations of B-H oxidative addition concentrated on the late transition metals, it has subsequently been found that early transition metal fragments such as $[(C_5H_5)_2TaH]$ and $[(C_5H_5)_2W]$ can also display similar chemistry. Thus photolytically generated $[(C_5H_5)_2W]$ will oxidatively add the B-B bond in $B_2cat'_2$ (cat' = 3-^{t}Bu catecholate) to give $(C_5H_5)_2W(Bcat')_2$.[4]

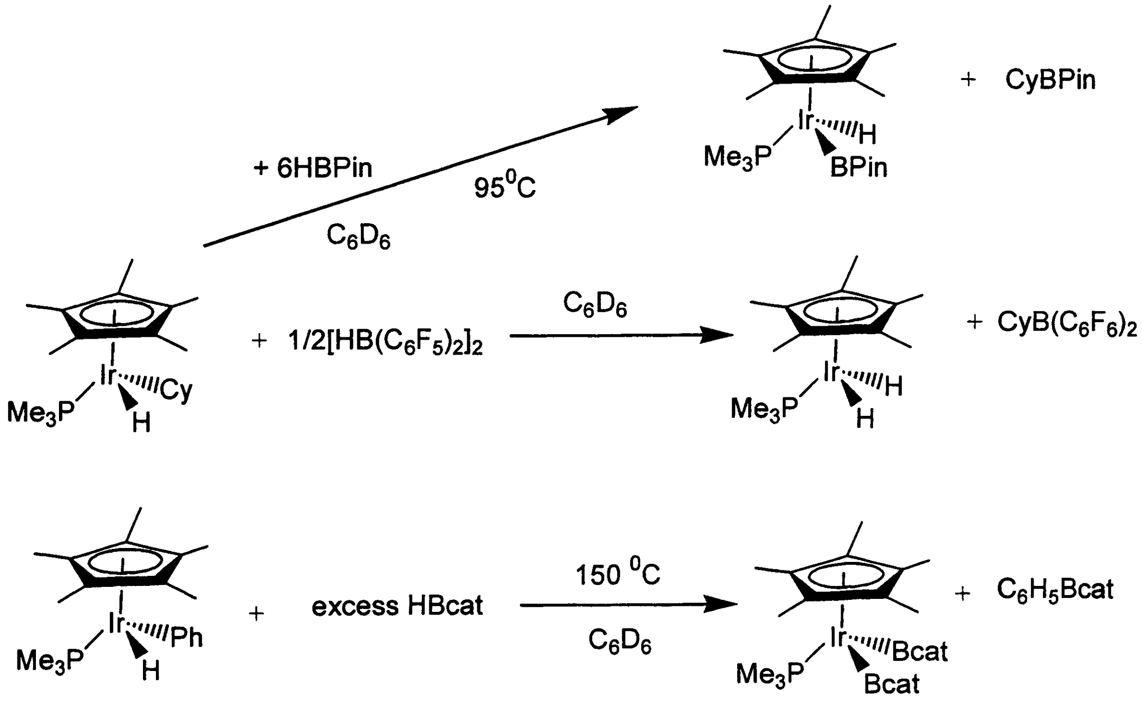
Other modes of reactivity of boranes with early transition metal reagents have also been demonstrated. Piers et al., for example, have examined the reactivity of the highly electrophilic borane $[HB(C_6F_5)_2]_n$ with early transition metal (organozirconium and organotantalum) compounds.[5] They found that while the reaction of $[HB(C_6F_5)_2]_n$ with $(C_5H_5)_2ZrR_2$ (R = CH_3, CH_2SiMe_3, $CH_2C_6H_5$) is highly sensitive to variation in reaction stoichiometry and solvent, a clean reaction with the analogous dialkyl titanocenes $(C_5H_5)_2TiR_2$ (R = CH_3, CH_2Ph) was observed when 2.5 equivalents of borane were used (Scheme

4.3). Furthermore, the reaction of $[HB(C_6F_5)_2]_n$ with titanocene reagents varies significantly from the corresponding reaction with HBcat. While the latter gives the Ti(II) σ–complex $(C_5H_5)_2Ti[HBcat]_2$, the reaction with $[HB(C_6F_5)_2]_n$ forms the Ti(III) η^2-hydroborate complex $(C_5H_5)_2Ti[\eta^2\text{-}H_2B(C_6F_5)_2]$.[6] There are several factors suggested for the different chemistry of $HB(C_6F_5)_2$ compared to HBcat: first is the poor solubility of the borane in toluene. Second, the B-H bond in $[HB(C_6F_5)_2]_n$ is less polarized than in other boranes and would be a poorer σ-donor than HBcat. Finally, the steric effects of the nonplanar $-C_6F_5$ substituents would tend to disfavour the geometry required at boron for maximal overlap of the acceptor orbitals on the borane with the metallocene orbitals in the σ–complex structure.



Scheme 4.3 Syntheses of $(C_5H_5)_2Ti[\eta^2\text{-}H_2B(C_6F_5)_2]$ and $(C_5H_5)_2Zr[(\mu\text{-}H)_2B(C_6F_5)_2]_2$.

Very interesting reactivity between $[HB(C_6F_5)_2]_n$ and $(C_5Me_5)Ir(PMe_3)H(Cy)$ has been reported by Smith and co-workers.[7] They found that $[HB(C_6F_5)_2]_n$ reacted with $(C_5Me_5)Ir(PMe_3)H(Cy)$ to form the alkylborane derivative, $CyB(C_6F_5)_2$ and the iridium hydride complex $(C_5Me_5)Ir(PMe_3)H_2$, while $(C_5Me_5)Ir(PMe_3)H(Cy)$ and $(C_5Me_5)Ir(PMe_3)H(Ph)$ reacted with HBPin or HBcat to give the boryl complexes $(C_5Me_5)Ir(PMe_3)H(BPin)$ and $(C_5Me_5)Ir(PMe_3)(Bcat)_2$ (Scheme 4.4). Given that the hydrido-iridium alkyl/aryl derivatives $(C_5Me_5)Ir(PMe_3)H(R)$ (R = Cy or Ph) are known to be formed by oxidative addition of RH to '$(C_5Me_5)Ir(PMe_3)$', their subsequent reactivity towards $[HB(C_6F_5)_2]_n$ offers a route to completion of the alkane functionalisation process linking RH with $RB(C_6F_5)_2$.



Scheme 4.4 B-C bond forming chemistry for the archetypal C-H activation products, $(C_5Me_5)Ir(PMe_3)H(R)$.

4.1.1 Aims of the present research

Due to the prevalence of oxidative addition chemistry in the synthesis of metal boryl complexes, it was decided to exploit this route in an attempt to complement the salt elimination methodology outlined in chapter 3 and thereby synthesise rhodium and platinum complexes containing the $-B(C_6F_5)_2$ ligand. This was to be attempted by considering the reactions of $(C_6F_5)_2BCl$ and $[HB(C_6F_5)_2]_n$ with low valent precursors such as $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ and $[(PPh_3)_2Rh(\mu\text{-}Cl)]_2$.

4.2 Experimental

Reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with $ClB(C_6F_5)_2$: isolation of platinum phosphine products.

To a solution of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (0.100 g, 0.13 mmol) in toluene (15 cm^3) at room temperature was added 10 cm^3 of a toluene solution containing one equivalent of $ClB(C_6F_5)_2$. After stirring for 12 h, the reaction mixture was examined by ^{11}B and ^{31}P NMR, revealing complete consumption of the starting materials, and the appearance of resonances at δ_B 73.5 and at δ_P 24.3 ($^1J_{Pt\text{-}P}$ = 3169 Hz) and 15.1 ($^1J_{Pt\text{-}P}$ = 3680 Hz). Removal of volatiles in vacuo, re-extraction into toluenes and cooling to -30°C for ca. 1 week led to the isolation of trans-$(Ph_3P)_2Pt(C_6F_5)Cl$ as colourless crystals suitable for X-ray diffraction (yield ca. 33 %). Spectroscopic data are in agreement with those reported previously,[8] and confirm trans-$(Ph_3P)_2Pt(C_6F_5)Cl$ as the phosphorus-containing species giving rise to the resonance at δ_P 24.3. The second phosphorus-containing product (δ_P 15.1) was shown to be cis-

$(Ph_3P)_2PtCl_2$ by comparison with literature data.[9] Selected spectroscopic data for trans-$(Ph_3P)_2Pt(C_6F_5)Cl$:[8] ^1H NMR (C_6D_6, 300 MHz), δ 6.96 (m, 18H, PPh_3), 7.43 (m, 12H, PPh_3). ^{31}P (C_6D_6, 122 MHz), 24.3 (J_{Pt-P} = 3769 Hz). ^{19}F NMR (C_6D_6, 282 MHz), δ -122.0 (ortho CF, J = 21, 6Hz), -147.4 (para CF, J = 21, 6 Hz), -161.0 (meta CF, J = 23, 6 Hz). IR (KBr disk, cm^{-1}) 3078 m, 1645 m, 1574w, 1513s, 1478 s, 1433s, 1095s, 730 s. MS (EI): [M^+ = 921, 80%], 885 [$(M-Cl)^+$, 55%], 755 [$(M-C_6F_5)^+$, 60%], 719 [$(M-(C_6F_5 + Cl))^+$, 55%], 262 [(PPh_3), 100%].

Reaction of $(Ph_3P)_2Pt(\eta^2-C_2H_4)$ with $ClB(C_6F_5)_2$: multinuclear NMR monitoring of the reaction.

To a solution of $(Ph_3P)_2Pt(\eta^2-C_2H_4)$ (0.050g, 0.07 mmol) in toluene-d_8 (ca. 1 cm^3) at room temperature contained in a J. Young's NMR tube, was added a solution containing one equivalent of $ClB(C_6F_5)_2$ in toluene-d_8 (ca. 1 cm^3). After agitation, the reaction mixture was monitored periodically (at 2 h intervals) over a period of 24 h. The volatile boron-containing product giving rise to the signal at δ_B 73.5 was confirmed as $EtB(C_6F_5)_2$,[10] by comparison of ^1H, ^{13}C, ^{11}B and ^{19}F NMR data with the literature values. In addition to confirming the identities of the platinum phosphine products trans-$(Ph_3P)_2Pt(C_6F_5)Cl$ and cis-$(Ph_3P)_2PtCl_2$, a number of intermediates species were also identified, these being (sequentially), trans-$(Ph_3P)_2Pt[CH_2CH_2B(C_6F_5)_2]Cl$, $[(Ph_3P)_3PtH]^+$,[11] and $[HB(C_6F_5)_2]_n$.[10] NMR data for trans-$(Ph_3P)_2Pt[CH_2CH_2B(C_6F_5)_2]Cl$: ^1H NMR (300 MHz, C_7D_8, 21°C), δ 1.99 (m, $PtCH_2CH_2B$). ^{11}B NMR (96 MHz, C_7D_8, 21°C), δ 35.0. ^{19}F NMR (283 MHz, C_7D_8, 21°C), δ -131.2 (m, ortho CF,), -159.5 (t, J = 21 para CF), -

165.2 (m, meta CF). ^{31}P NMR (121 MHz, C_7D_8, 21°C) δ 23.6 ($^1J_{PtP}$ = 5137 Hz, $^2J_{PP}$ = 12 Hz) 28.1 ($^1J_{PtP}$ = 1769 Hz, $^2J_{PP}$ = 12 Hz).

Reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with $[HB(C_6F_5)_2]_n$.

To a solution of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (0.050 g, 0.07 mmol) in toluene (5 cm^3) at room temperature was added 10 cm^3 of a toluene solution containing 0.100 g of $[HB(C_6F_5)_2]_n$ {0.144 mmol of $[HB(C_6F_5)_2]_2$ dimer}. After stirring for 15 min., a colourless solution and a finely divided black precipitate were formed. Comparison of spectroscopic data with authentic samples showed the toluene soluble products to be $EtB(C_6F_5)_2$[10] and $Ph_3P{\cdot}HB(C_6F_5)_2$ (vide infra).

Reaction of $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ with $[HB(C_6F_5)_2]_n$.

To a suspension of $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ (0.060 g, 0.05 mmol of dimer) in toluene (5 cm^3) at room temperature was added 5 cm^3 of a toluene solution containing 0.100g of $[HB(C_6F_5)_2]_n$ {0.144 mmol of $[HB(C_6F_5)_2]_2$ dimer}. The reaction mixture was stirred for 72 h, during which time the pale red $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ dissolved generating a red-brown solution. Examination of the reaction mixture by ^{31}P NMR at this point revealed two signals, a sharp doublet (δ_P 44.7, $^1J_{RhP}$ = 208 Hz) and a broader resonance (δ_P 12.0, fwhm = ca. 140 Hz), whereas the corresponding ^{11}B spectrum displayed signals at δ_B -23.9 (broad doublet, $^1J_{BH}$ = 48 Hz) and -2.5. Removal of volatiles in vacuo, extraction with hexanes (ca. 10 cm^3) and cooling to -50°C for 1 week led to the isolation of $Ph_3P{\cdot}HB(C_6F_5)_2$ as a colourless crystalline solid (yield ca. 45 %). $Ph_3P{\cdot}HB(C_6F_5)_2$ has been characterized by ^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMR, IR, mass spectrometry and single crystal X-ray diffraction, and was shown to give identical spectroscopic data to samples prepared independently from $[HB(C_6F_5)_2]_n$ and PPh_3. ^1H NMR (300 MHz, C_6D_6, 21°C), δ 4.64 (b, fwhm ca. 150Hz, 1H, BH),6.88 - 7.02 and 7.32 - 7.44 (m, 15H, PPh_3). ^{13}C NMR (76 MHz, C_6D_6, 21°C), δ 127.6, 131.4, 133.2 (aromatic CH), 138.9, 141.7, 150.2 (aromatic CF). ^{11}B NMR (96 MHz, C_6D_6, 21°C), δ -23.9 (b d, $^1J_{BH}$ = 47 Hz). ^{19}F NMR (283 MHz, C_6D_6, 21°C), δ -127.4 (d, J = 21 Hz, ortho CF), -157.6 (t, J = 21 Hz, para CF), -163.8 (m, meta CF). ^{31}P NMR (121 MHz, C_6D_6, 21°C) δ_P 12.0 (b, fwhm ca. 140 Hz). IR (KBr disk, cm^{-1}) ν(BH) 2610 md. MS(EI): M^+ = 608 (100 %), isotopic pattern corresponding to 1 B atom. Reliable elemental analysis was precluded by the air-sensitivity of $Ph_3P{\cdot}HB(C_6F_5)_2$. The residual hexane insoluble red-brown oily solid was shown by comparison of spectroscopic data with those reported previously,[12] to be the known cation $[(Ph_3P)_2Rh(\eta^6\text{-}C_6H_5Me)]^+$ (δ_P 44.7, $^1J_{RhP}$ = 208 Hz), present as the $[ClB(C_6F_5)_3]^-$ salt (δ_B -2.5).[13] The same compound was identified as the product from the reaction of $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ with $ClB(C_6F_5)_2$.

4.3 Results and discussion

4.3.1 Reactivity

4.3.1.1 Reactivity of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ towards bis(pentafluorophenyl)-boranes

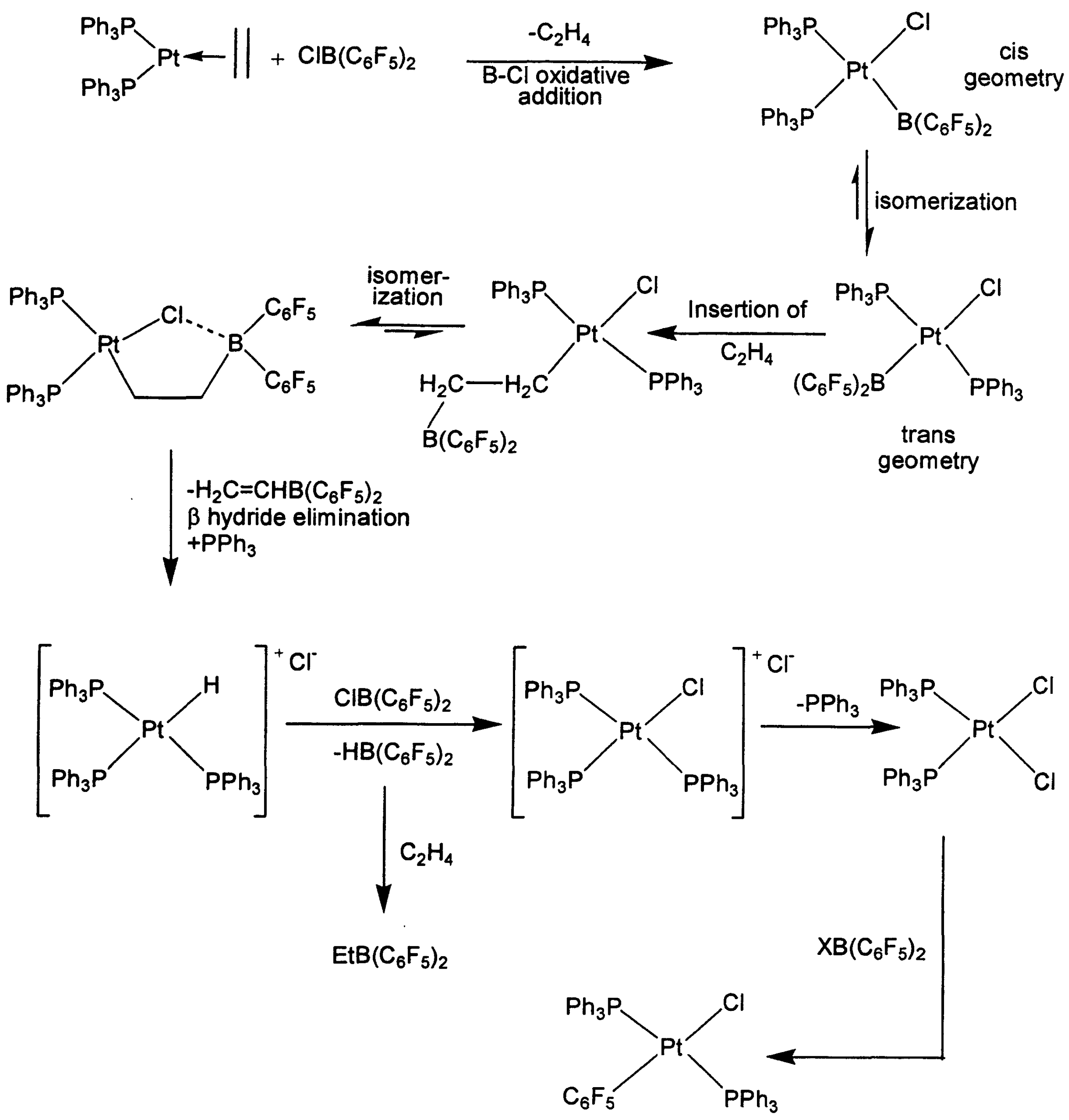
The reactivity of $ClB(C_6F_5)_2$ (**1**) towards anionic organometallic reagents has been shown to mirror that of related diaryl, dialkyl and bis(heteroatom) stabilised boranes [e.g. Ph_2BCl, (9-BBN)Br and ClBcat (cat = catecholate, $O_2C_6H_4$-1,2)] in generating complexes containing metal-boron bonds.[1] Given that another precedented route to complexes containing such linkages is the oxidative addition of B-H or B-Cl bonds, the reactivity of **1** and $[HB(C_6F_5)_2]_n$ (**2**) towards low-valent rhodium and platinum complexes was to be a second area of investigation. Initial studies focussed on the reaction of **1** with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ as this reagent has previously been employed to great effect in the synthesis of boryl species of types cis-$(Ph_3P)_2Pt(BX_2)_2$ and trans-$(Ph_3P)_2Pt(Y)BX_2$ by oxidative addition of B-B or B-Y bonds (Y = Cl or Br).[1,14] In the case of **1**, however, reaction with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ does not appear to proceed to the isolation of a platinum boryl complex, but rather to the formation of two main platinum-containing species, cis-$(Ph_3P)_2PtCl_2$ (**3**) and trans-$(Ph_3P)_2Pt(C_6F_5)Cl$ (**4**). The formation of **4**, originally reported by Rosevear and Stone in 1965,[8] and of **3** was implied by spectroscopic data obtained for the crude (pumped down) reaction mixture (δ_P 15.1, $^1J_{PtP}$ 3680 Hz; δ_P 24.3, $^1J_{PtP}$ 3169 Hz for **3** and **4**, respectively) and subsequently confirmed crystallographically for **4**. No boron-containing products were detected by ^{11}B NMR analysis of the same reaction mixture.

In order to determine the nature of the boron-containing product(s) and in an attempt to shed light on the mechanism for the formation of **3** and **4** (Scheme 4.5), the reaction was repeated in toluene-d_8 with periodic monitoring by multinuclear (^1H, ^{11}B, ^{19}F and ^{31}P) NMR. ^{11}B NMR measurements revealed predominant conversion of **1** to a single boron-containing compound giving rise to a signal at δ_B 73.5, which was subsequently shown by further comparison of spectroscopic data with the literature values reported by Piers and co-workers, to be the volatile borane $EtB(C_6F_5)_2$ (**5**).[10] Conversion of **1** to

5 was accomplished over a period of ca. 24 h at room temperature and was ultimately accompanied by only minor quantities (< 10% by NMR) of boron-containing side/decomposition products. **5** presumably results from the formal hydroboration of the ethylene ligand of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ by $[HB(C_6F_5)_2]_n$ (**2**). Indeed NMR monitoring of the course of the reaction reveals that $[HB(C_6F_5)_2]_2$ (δ_B 17.0, δ_H 4.2, δ_F -134.5, -149.1, -161.4) is in fact an intermediate present at relatively low concentrations at t = ca. 90 min. The concentration of $[HB(C_6F_5)_2]_2$ subsequently falls, such that there is no trace detectable by NMR once the reaction reaches completion.

The feasibility of the proposed hydroboration reaction is amply justified by literature precedent, and readily demonstrated by independent reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with excess **2**, which (admittedly under different reaction conditions) rapidly generates $EtB(C_6F_5)_2$[10] (together with $Ph_3P{\cdot}HB(C_6F_5)_2$ (**6**) and insoluble platinum black).

Although the origins of the borane **2** cannot be stated unequivocally, one possibility with significant literature precedent[10] is chloride/hydride exchange between **1** and a metal hydride species.[15] Indeed, one of the literature methods for the preparation of **2** involves the reaction of hydride sources such as silanes, stannanes or $[(C_5H_5)_2Zr(Cl)H]_n$ with **1**. Consistent with this hypothesis is the observation in the reaction mixture of ^{31}P (δ_P 23.2, $^1J_{PtP}$ = 2810 Hz, $^2J_{PP}$ = 18 Hz; δ_P 23.7, $^1J_{PtP}$ = 2290 Hz, $^2J_{PP}$ = 18 Hz) and ^1H NMR resonances (δ_H -5.69, $^1J_{PtH}$ = 776 Hz, $^2J_{PH,trans}$ = 160 Hz, $^2J_{PH,cis}$ = 13 Hz) associated with the known hydride $[(Ph_3P)_3PtH]^+$ (**7**). The concentration time profile for **7**, determined by ^1H and ^{31}P NMR data, indicates that it reaches detectable concentrations at short reaction times ($t < 90$ min), and that it too is an intermediate in the reaction sequence. Given the known chemistry of complexes of the types $(R_3P)_2Pt(Y)(CH_2CH_2X)$ and $(R_3P)_2Pt(Y)(H)$,[11] it is plausible that the Pt-H linkage in **7** is formed by a β hydride elimination process, originating from a complex such as cis-$(Ph_3P)_2Pt[CH_2CH_2B(C_6F_5)_2]Cl$ **8**, itself produced by insertion of ethylene into the Pt-B bond of an initially formed platinum boryl complex $(Ph_3P)_2Pt(Cl)B(C_6F_5)_2$. Although such a premise is necessarily speculative, both the initial B-Cl oxidative addition step and the subsequent alkene insertion into the Pt-B bond are well precedented in the literature.[1,14,16] Furthermore, ^{11}B and ^{31}P NMR resonances consistent with an intermediate such as **8** are detected at very short reaction times (t = ca. 30 min.) prior to the appearance of signals associated with **7** or **2**. The ^{11}B resonance (δ_B 35) is shifted markedly upfield compared to that expected for a three-coordinate $(alkyl)B(C_6F_5)_2$ derivative [e.g. ca. 40 ppm compared to $EtB(C_6F_5)_2$, **5**, (δ_B 73.5)][10] consistent with partial quaternization of the boron centre. Similar upfield shifts (ca. 50 ppm) have been observed by Bochmann and co-workers for intramolecular coordination of a metal-bound chloride ligand to a $-B(C_6F_5)_2$ containing Lewis acid {e.g. δ_B 59.8 and 4.5, respectively, for $[C_5H_4B(C_6F_5)_2]TiCl_3$[17] and $(C_5H_5)[C_5H_4B(C_6F_5)_2](\mu\text{-}Cl)TiCl$}. The presence of a similar intramolecular $Cl \rightarrow B$ interaction in **8** would also explain the observed cis geometry of the intermediate (δ_P 23.6, $^1J_{PtP} = 5137$ Hz, $^2J_{PP} = 12$ Hz; δ_P 28.1, $^1J_{PtP} = 1769$ Hz, $^2J_{PP} = 12$ Hz) and the very high Pt-P coupling constant for the PPh_3 ligand trans to the $Pt\text{-}Cl\cdots B$ linkage.

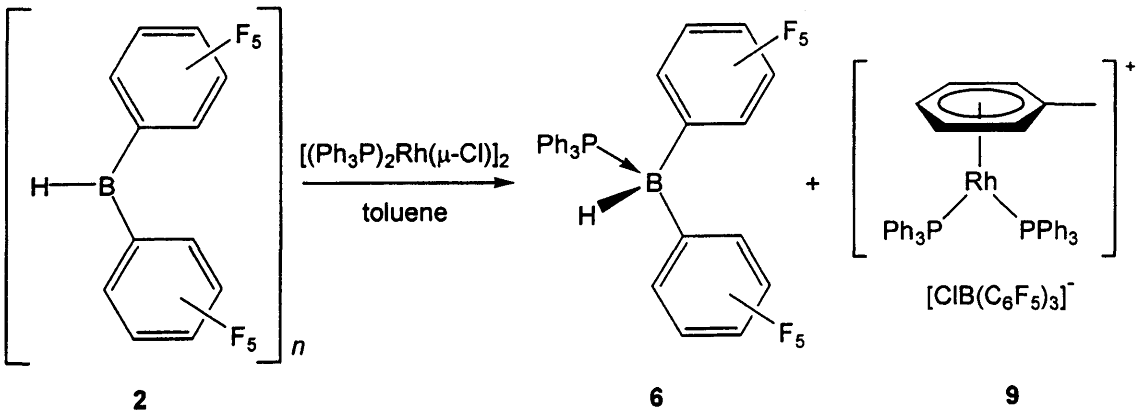


Scheme 4.5 A possible mechanism for the reaction of **1** with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$.

From the spectroscopically identified platinum hydride intermediate $[(Ph_3P)PtH]^+$ (**7**), therefore, the proposed chloride/hydride exchange step, followed by phosphine loss would generate one of the final products, in cis-$(Ph_3P)_2PtCl_2$ (**3**), with subsequent chloride/aryl exchange between boron and platinum accounting for the formation of trans-$(Ph_3P)_2Pt(C_6F_5)Cl$ (**4**). Finally, implicit in the proposal of a β-hydride elimination step for the formation of **7**, is the formation of a vinyl-containing co-product. Although weak ^1H resonances associated with a vinyl group (δ_H 5.92, 6.25, 6.72; J_{HH} = 3, 12, 19 Hz) were detected early in the reaction, the ultimate fate of this unit is unclear. Small amounts of platinum/phosphine containing species (other than **3** or **4**) are observed in the final product mixture, but none of these has the spectroscopic properties associated with a vinyl-platinum complex.[18]

4.3.1.2 Reactivity of $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ towards bis(pentafluorophenyl)-boranes

At first inspection the reaction of the borane $[HB(C_6F_5)_2]_n$ (**2**) with $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ (B:Rh 3:1) in toluene (Scheme 4.6) also appears to diverge from the oxidative addition based chemistry delineated for other boranes of the type HBX_2.[1]



Scheme 4.6 Ligand abstraction from $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ by $[HB(C_6F_5)_2]_n$, **2**; generation of $Ph_3P{\cdot}HB(C_6F_5)_2$, **6** and $[(Ph_3P)_2Rh(\eta^6\text{-}C_6H_5Me)]^+$, **9**.

The ^{31}P and ^{11}B NMR spectra of the crude (pumped down) reaction mixture each display two signals, the former showing a sharp doublet ($^{1}J_{RhP}$ = 208 Hz) at δ_P 44.7 and a broad resonance at δ_P 11.9 (fwhm = ca. 140 Hz), the latter signals at δ_B -2.5 and δ_B -24.0 (broad doublet, $^{1}J_{BH}$ = 48 Hz). Recrystallisation from hexanes yields a colourless crystalline solid subsequently shown by spectroscopic and crystallographic analysis (and by comparison with a sample prepared independently from **2** and PPh_3) to be $Ph_3P{\cdot}HB(C_6F_5)_2$, **6** (δ_P 11.9, δ_B -24.0). The rhodium/phosphine containing component of the residual (hexane insoluble) red-brown oily solid was shown, by comparison of multinuclear NMR data with those reported previously, to be the known cation $[(Ph_3P)_2Rh(\eta^6\text{-}C_6H_5Me)]^+$, isolated as the $[ClB(C_6F_5)_3]^-$ salt.[12-13] The same compound is identified as the product from the reaction of $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ with $ClB(C_6F_5)_2$, **1**.

Superficially, therefore the ultimate products of the reaction of **2** with $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ appear to be derived from abstraction of either the rhodium-bound chloride or triphenylphosphine ligands by the strongly Lewis acidic borane (with the anion $[ClB(C_6F_5)_3]^-$ presumably resulting from subsequent exchange of aryl substituents with the excess of **2** used). Previous studies have examined the reactivity of four-coordinate Rh(I) phosphine- and halide-containing complexes with a variety of Lewis acids. On the basis of spectroscopic data, possible interactions of BX_3 with the metal itself or with the phosphine or chloride ligands were postulated, although no definitive structural data were reported.[19a] In addition, phosphine abstraction from low valent ruthenium and iridium complexes by highly electrophilic boranes such as $[(9\text{-BBN})H]_2$ has previously been reported.[19b,c]

Closer examination of the course of the reaction of **2** with $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ in toluene-d_8 was attempted by multinuclear NMR. This study reveals the presence (i) of a Rh(III) intermediate present in low concentrations at $t > 30$ min.; and (ii) of the volatile borane $C_6D_5CD_2B(C_6F_5)_2$ in the final product mixture. The Rh(III) intermediate is characterized by ^{31}P (δ_P 38.4, $^1J_{RhP}$ = 116 Hz), ^{11}B (δ_B 71.0) and ^1H NMR resonances (δ_H -16.38, $^1J_{RhH}$ = 27 Hz, $^2J_{PH}$ = 12 Hz) characteristic of a trigonal bipyramidal hydrido-rhodium boryl complex, $(Ph_3P)_2RhH(Cl)BX_2$, [c.f. δ_P 39.9, $^1J_{RhP}$ = 117 Hz and δ_H -14.96, $^1J_{RhH}$ = 27 Hz, $^2J_{PH}$ = 14 Hz for $(Ph_3P)_2RhH(Cl)Bcat]$[20] and is tentatively assigned as $(Ph_3P)_2RhH(Cl)B(C_6F_5)_2$. The ^{11}B resonance due to $C_6D_5CD_2B(C_6F_5)$ (δ_B 67.4), on the other hand, represents a sizeable proportion (approximately 20 %) of the final boron-containing products and is presumably the result of a rhodium mediated toluene C-D functionalization process. Such processes have been the subject of considerable recent attention and previous examples of toluene C-H borylation processes mediated by $(^iPr_3P)_2RhCl(N_2)$, and of C-H activation processes involving $[HB(C_6F_5)_2]_n$ (**2**) have been reported by Marder and by Smith.[2,7] An in depth investigation of arene C-H functionalization processes involving **2** mediated by rhodium(I) bisphosphine complexes will make an exciting topic for future investigation.

4.3.2 Structural studies

4.3.2.1 X-ray crystal structure of trans-$(Ph_3P)_2Pt(C_6F_5)Cl$, 4

Single crystals suitable for X-ray diffraction of trans-$(Ph_3P)_2Pt(C_6F_5)Cl$ **4** were accessible by cooling a saturated solution of the complex in toluene to -30 °C. The subsequent single crystal X-ray diffraction study confirms the inferences made by comparison with literature spectroscopic data and the structure is illustrated in Figure 4.1. Relevant bond lengths and angles for **4** are listed in Table 4.1. The structure of **4** confirms the square-planar coordination for the central Pt atom and trans disposition of the two phosphine ligands implied spectroscopically. The Pt-P bond lengths [2.3069(10) and 2.3023(10) Å] are almost equal and consistent with the values found in trans-$(Ph_3P)_2Pt(C_6H_5)Cl$, **10**[21] [2.303(6) and 2.297(6) Å] and in trans-$[Ph_2P(CH_2)_{14}PPh_2]Pt(C_6F_5)Cl$ **11**[22] [2.3139(11) and 2.3075(11) Å]. The Pt-Cl bond length [2.3695(11) Å] also falls in the expected range [e.g. 2.3778(11) Å for **11**]. Although the Pt-C distance in **4** appears to be somewhat longer than that in **10** [2.071(4) vs. 2.00(2) Å], as might be expected on steric grounds, the relatively large esd associated with the latter value makes detailed comparison impossible. The P-Pt-P bond angle [176.59(4)°] is essentially the same as that in **10** [176.0(2)°], and the orientation of the aryl ligand with respect to the P_2PtCl plane (as defined by the P-Pt-C_{ipso}-C_{ortho} torsion angles) is also similar to that found in **10** [72.0 (mean) vs. 72.8°].

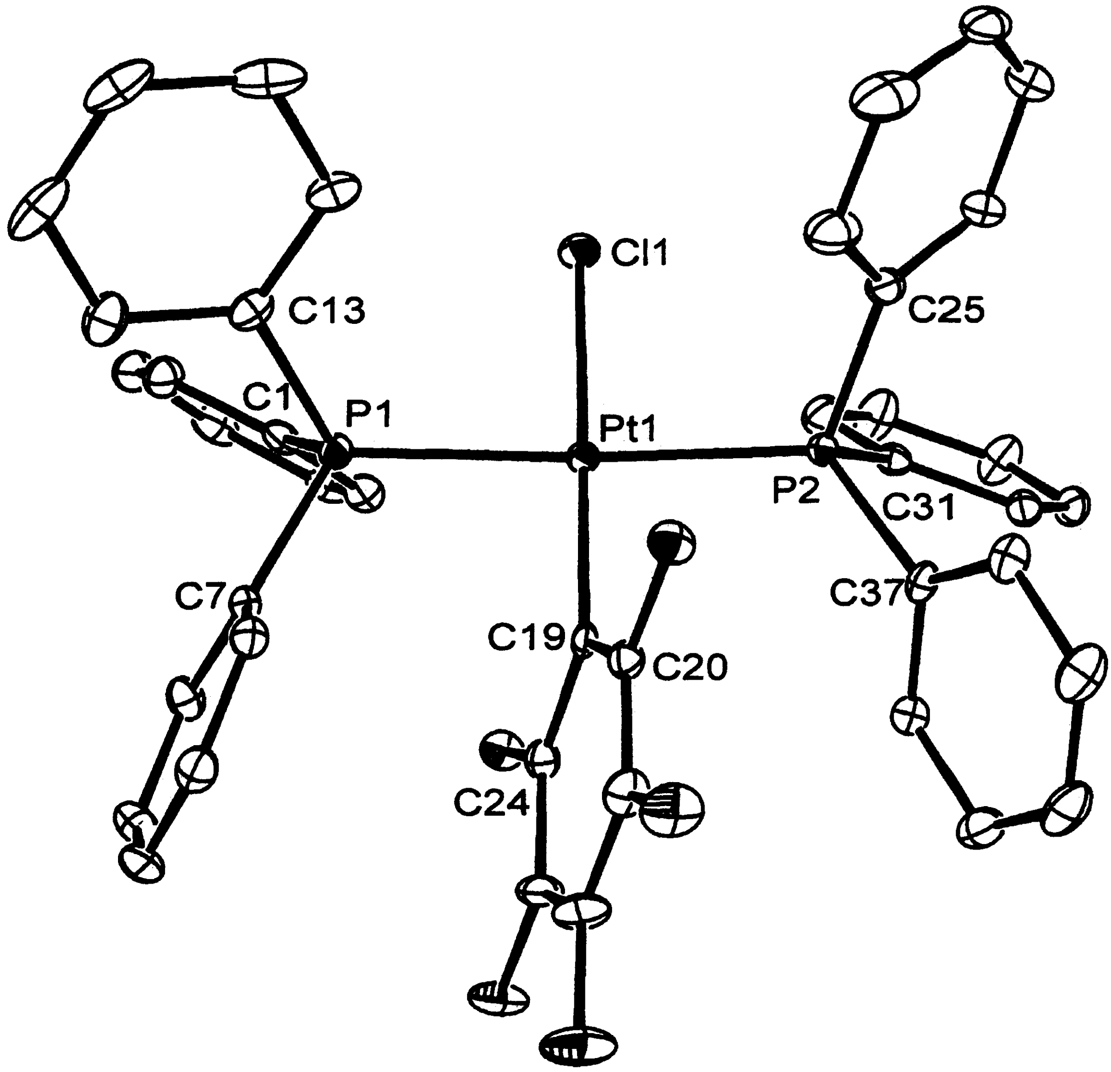


Figure 4.1: Molecular structure of *trans*-$(Ph_3P)_2Pt(C_6F_5)Cl$, **4**. Hydrogen atoms omitted for clarity; ORTEP ellipsoids set at the 50% probability level.

Table 4.1: selected bond lengths (Å) and angles (°) for **4**

Pt-P1	2.3069(10)
Pt-P2	2.3023(10)
Pt-Cl	2.3695(11)
Pt-C19	2.017(4)
P2-Pt-P1	176.59(4)
C19-Pt-Cl	179.52(10)
C19-Pt-P1	91.73(9)
C19-Pt-P2	91.59(9)
P1-Pt-Cl	87.82(4)
P2-Pt-Cl	88.85(4)
P(1)-Pt(1)-C(19)-C(24)	71.8(2)

4.3.2.2 X-ray crystal structure of $Ph_3P{\cdot}BH(C_6F_5)_2$ 6

The formulation of **6** as $Ph_3P{\cdot}BH(C_6F_5)_2$ is further supported by the results of a single crystal X-ray diffraction study conducted on the hexane hemi-solvate; the crystals being obtained by cooling saturated solutions of the complex in hexane to -30 °C. The molecular structure of **6** is illustrated in Figure 4.2 and relevant bond lengths and angles are listed in Table 4.2. The molecules of **6** adopt the expected tetrahedral geometry at the four coordinated boron centre and the adduct as whole adopts an effectively staggered orientation about the B-P coordinate bond, presumably to minimize steric interactions between vicinal substituents (mean C_{ipso}-P-B-C_{ipso} torsion angle = 61.6°). A similar orientatation ios found in the solid state structure of $Ph_3P{\cdot}B(C_6F_5)_3$. The B-P bond length in **6**, at [1.986(2) Å], is significantly shorter than that found in $Ph_3P{\cdot}BPhCl_2$,[24] [2.031(4) Å], and in $(SiMe_3)_3P{\cdot}BCl_3$[23] [2.022(2) Å],presumably reflecting the high acidity of the boron centre due to the $(C_6F_5)_2$ rings. Furthermore, the P-B distance in **6** is significantly shorter than that found in $Ph_3P{\cdot}B(C_6F_5)_3$[25] [2.180(6) Å], being more consistent with that found in $Me_2PhP{\cdot}HB(CN)(ipc)$[26] [1.958(4) Å, ipc = isopinocamphenyl, $C_{10}H_{17}$] and significantly longer than that found in $Ph_3P{\cdot}BH_3$[27] (mean 1.917 Å). Presumably this trend reflects the reduction in steric repulsion on increasing the number of boron-bound hydride substituents.

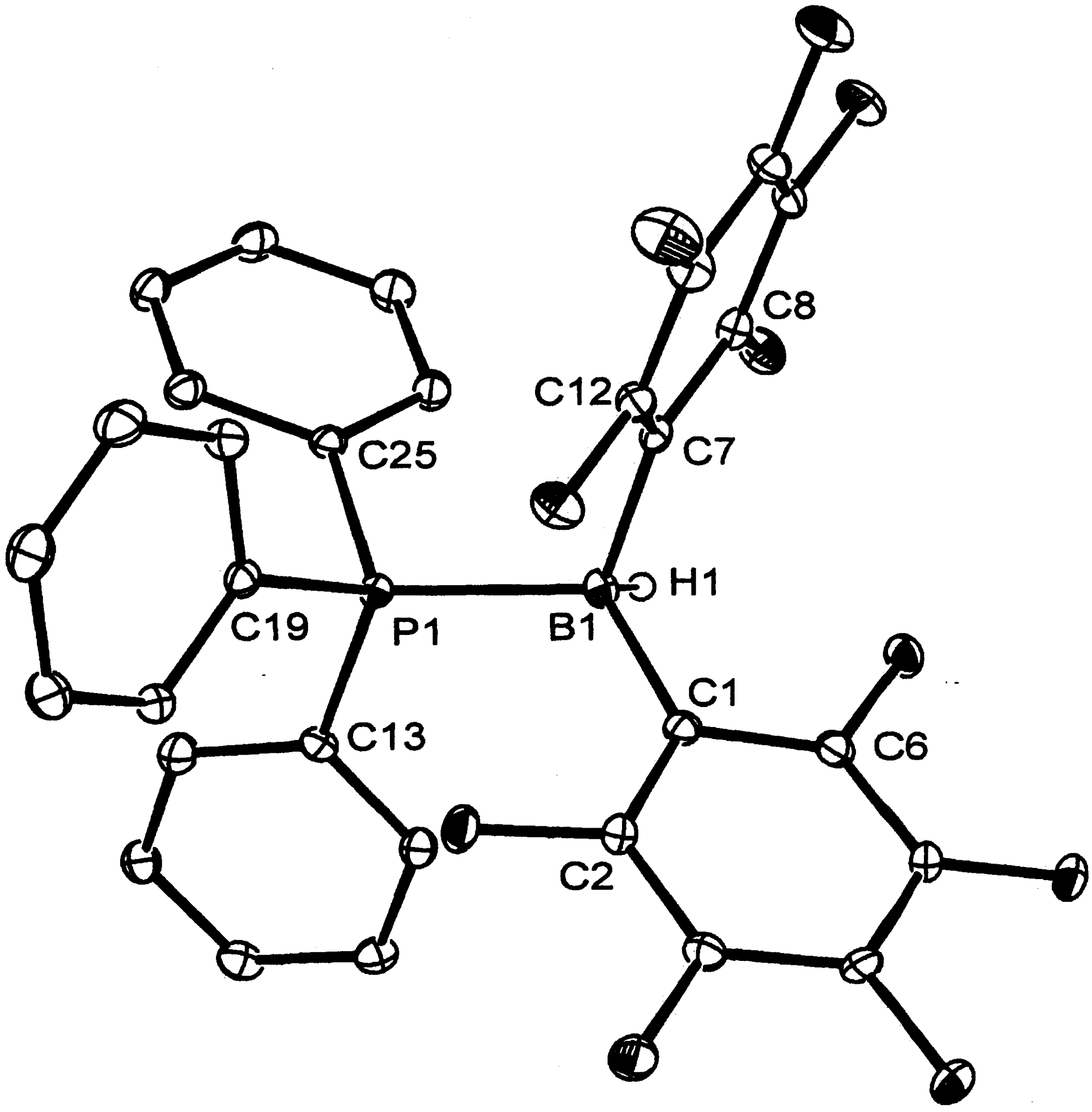


Figure 4.2: Molecular structure of $Ph_3P \cdot HB(C_6F_5)_2$, **6**. Hydrogen atoms (except that attached to B1) and half molecule of hexane omitted for clarity; ORTEP ellipsoids set at the 50% probability level.

Table 4.2: Selected bond lengths (Å) and angles (°) for **6**

P1-B1	1.986(2)
B1-C1	1.625(3)
B1-C7	1.627(3)
B1-H1	1.00
P1-B1-C1	118.1(1)
P1-B1-C7	110.3(2)
P1-B1-H1	105.8

4.4 Conclusions and suggestions for further research

Although the reactivity of the strongly Lewis acidic chloroborane $ClB(C_6F_5)_2$, **1**, towards anionic organometallic reagents mirrors that of other monohaloboranes in providing access to transition metal complexes containing M-B bonds via salt elimination, attempts to generate similar bonds from **1** or $[HB(C_6F_5)_2]_n$, **2**, via B-Cl or B-H oxidative addition illustrate how the chemistries of these boranes diverge from less electrophilic systems such as XBcat (X = Cl, H). Thus the reaction of **1** with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ ultimately generates $EtB(C_6F_5)_2$ and chloro-platinum(II) species, whereas the reaction of **2** with $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ generates products resulting from ligand abstraction from rhodium by the highly electrophilic borane. In both of these reactions there are hints that oxidative addition chemistry may well feature to some degree. Thus in the reaction of **1** with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$, the identification of the platinum hydride intermediate $[(Ph_3P)_3PtH]^+$ implies that β hydride elimination may be crucial mechanistic step. The mechanism proposed involves the generation of the preceeding intermediate, $(Ph_3P)_2Pt[CH_2CH_2B(C_6F_5)_2]Cl$, by insertion of ethylene into a M-B bond. Although this step finds ample precedent in rhodium hydroboration and platinum diboration chemistry, it should be noted that the analogous Bcat complexes trans-$(Ph_3P)_2Pt(Bcat)X_3$ (X = Cl, Br) do not undergo similar further chemistry. Conceivably this might reflect the differing propensities of Bcat and $B(C_6F_5)_2$ complexes to undergo M-B insertion reactions.

The reaction of **2** with $[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2$ appears to proceed predominantly via ligand abstraction from rhodium by the highly electrophilic borane.

However, traces of a Rh(III) intermediate are detected in the reaction mixture, and hints of interesting C-H activation chemistry (akin to that reported by Marder and by Smith for similar systems) are detected. An in depth investigation of the reactivity of $[HB(C_6F_5)_2]_n$ with low-valent transition metal including rhodium(I) bisphosphine complexes would be an exciting focus of future work.

4.5 References for chapter four

1. (a) G.J. Irvine, M.J.G. Lesley, T.B. Marder, N.C. Norman, C.R. Rice, E.G. Robins, W.R. Roper, G. Whittell, L.J. Wright, *Chem. Rev.*, 1998, **98**, 2685. (b) H. Braunschweig, Angew. Chem., Int. Ed. Engl., 1998, **37**, 1786. (c) M.R. Smith, III, Prog. Inorg. Chem., 1999, **48**, 505. (d) H. Braunschweig, M. Colling, *Coord. Chem. Rev.*, 2001, **223**, 1. (e) S. Aldridge, D.L. Coombs, Coord. Chem. Rev., 2004, **248**, 535.
2. S. A. Westcott, H. P. Blom, T. B. Marder, R. T. Baker, J. C. Calabrese, Inorg. Chem., 1993, **32**, 2175.
3. W. Clegg, F. J. Lawlor, G. Lesley, T. B. Marder, N. C. Norman, A. G. Orpen, M. J. Qualye, C. R. Rice, A. J. Scott, F. E. S. Souza, J. Organomet. Chem., 1998, 550, 183.
4. X. He, J. F. Hartwig, Organometallics, 1996, **15**, 400.
5. R. E. v. H. Spence, W. E. Piers, Y. Sun. M. Parvez, L. R. MacGillivray, M. J. Zaworotko, Organometallics., 1998, **17**, 2459.
6. P. A. Chase, W. E. Piers, M. Parvez, Organometallics., 2000, **19**, 2040.
7. C. N. Iverson, M. R. Smith (III), J. Am. Chem. Soc., 1999, **121**, 7696.
8. (a) D.T. Rosevear, F.G.A. Stone, J. Chem. Soc., 1965, 5275. (b) A.J. Mukhedkar, M. Green, F.G.A. Stone, J. Chem. Soc., A, 1970, 947.
9. O.J. Scherer, H. Jungmann, K. Hussong, J. Organomet. Chem., 1983, **247**, C1.
10. (a) D. J. Parks, R.E.v.H Spence, W.E. Piers, *Angew.* Chem., Int. Ed. Engl., 1995, **34**, 809. (b) D. J. Parks, W.E. Piers, G.P.A. Yap, Organometallics, 1998, **17**, 5492.

11. (a) K. Thomas, J.T. Dumler, B.W. Renoe, C.J. Nyman, D.M. Roundhill, Inorg. Chem., 1972, **11**, 1795. (b) R.G. Goel, R.C. Srivastava, J. Organomet. Chem., 1983, **244**, 303.

12. A. Rifat, N.J. Patmore, M.F. Mahon, A.S. Weller, Organometallics, 2002, **21**, 2856.

13. S. Courtenay, D.W. Stephan, Organometallics, 2001, **20**, 1442.

14. For representative examples see: (a) T. Ishiyama, N. Matsuda, M. Murata, F. Ozawa, A. Suzuki, N. Miyaura, Organometallics, 1996, **15**, 713. (b) G. Lesley, P. Nguyen, N.J. Taylor, T.B. Marder, A.J. Scott, W. Clegg, N.C. Norman, Organometallics, 1996, **15**, 5137. (c) C.N. Iverson, M.R. Smith, III, Organometallics, 1996, **15**, 5155. (d) W. Clegg, F.J. Lawlor, G. Lesley, T.b. Marder, N.C. Norman, A.G. Orpen, M.J. Quayle, C.R. Ricem A.J. Scott, F.E.S. Souza, J. Organomet. Chem., 1998, 550, 183. (e) D. Curtis, M.J.G. Lesley, N.C. Norman, A.G. Orpen, J. Starbuck, Dalton Trans., 1999, 1687.

15. Chloride/hydride exchange converting **1** to **2** using a silane is one of the established routes to **2** (reference 10). In addition, analogous exchange reactions using metal hydrides {e.g. stannanes or $[(C_5H_5)_2Zr(Cl)H]_n$} have also been reported (W.E. Piers, T. Chivers, Chem. Soc. Rev., 1997, 345.).

16. See, for example: (a) R.T. Baker, J.C. Calabrese, S.A. Westcott, P. Nguyen, T.B. Marder, J. Am. Chem. Soc., 1993, **115**, 4367. (b) Q. Cui, D.G. Musaev, K. Morokuma, Organometallics, 1997, **16**, 1355. For related insertion reactions of alkynes into M-B bonds see, for example,

references 25a,b, (c) G.R. Clark, G.J. Irvine, W.R. Roper, L.J. Wright, Organometallics, 1997, **16**, 5499.

17. S.J. Lancaster, S. Al-Benna, M. Thornton-Pett, M. Bochmann, Organometallics, 2000, **19**, 1599.

18. (a) C.J. Cardin, D.J. Cardin,, M.F. Lappert, J. Chem. Soc., Dalton Trans., 1977, 767. (b) A. Ohtaka, H. Kuniyasu, M. Kinomoto,, H. Kurosawa, J. Am. Chem. Soc., 2002, **124**, 14324.

19. (a) D.D. Lehman,, D.F. Shriver, Inorg. Chem., 1974, **13**, 2203; (b) R.T. Baker, D.W. Ovenall, J.C. Calabrese, S.A. Westcott, N.J. Taylor, I.D. Williams, T.B. Marder, J. Am. Chem. Soc., 1990, 112, 9399; (c) K. Essalah, J.-C. Barthelat, V. Montiel, S. Lachaize, B. Donnadieu, B. Chaudret, S. Sabo-Etienne, J. Organomet. Chem., 2003, 680, 182.

20. K. Burgess, W.A. van der Donk, S.A. Westcott, T.B. Marder, R.T. Baker,, J.C. Calabrese, J. Am. Chem. Soc., 1992, **114**, 9350.

21. W. Conzelmann, J. D. Koola, U. Kunze, J. Strahle, Inorganica Chimica Acta, 1984, **89**, 147.

22. E. B. Bauer, J. Ruwwe, J. M. Martin-Alvarez, T. B. Peters, J. C. Bohling, F. A. Hampel, S. Szafert, T. Lis, J. A. Gladysz, Chem. Commun., 2000, 2261.

23. M. S. Lube, R. L. Wells, Inorg. Chem., 1996, **35**, 2007.

24. Chapter five of this thesis.

25. H. Jacobsen, H. Berke, S. Doring, G. Kehr, G. Erker, R. Frohlich, O. Meyer, Organometallics, 1999, **18**, 1724.

26. P. Vedrenne, V. LeGuen, L. Toupet, T. LeGall, C. Mioskowski, J. Am. Chem. Soc., 1999, 121, 1090.

27. J.C. Huffman, W.A. Skupinski, K.G. Caulton, Cryst. Struct. Commun., 1982, **11**, 1435.

28. K. Burgess, M. J. Ohlmeyer, Chem. Rev., 1991, **91**, 1179.

Chapter five

Synthesis and reactivity of base-stabilised haloboranes

5.1 Introduction

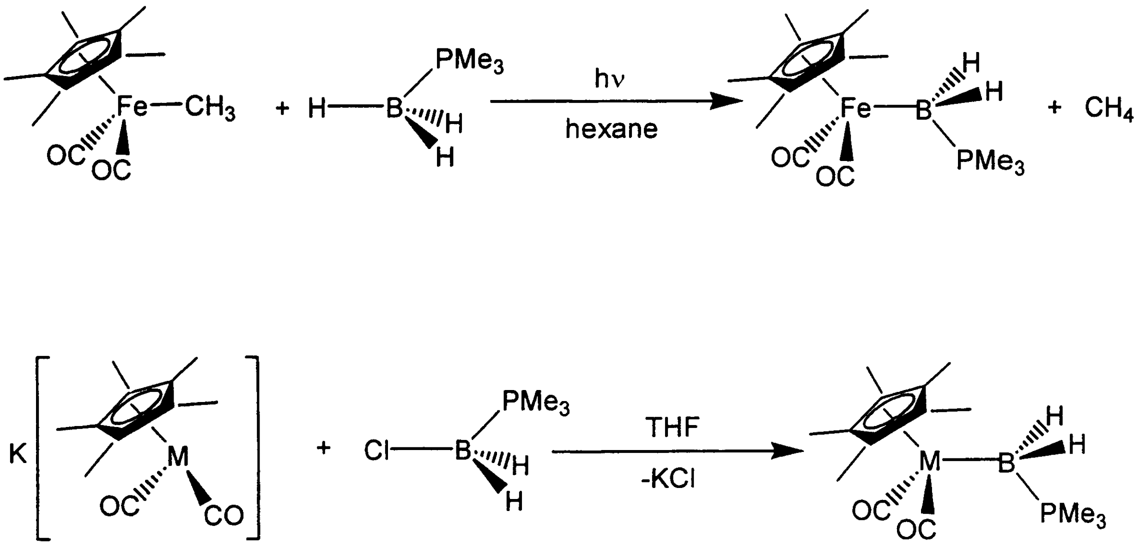
The chemistry of Lewis-base adducts is driven by the fact that boron has only three valence electrons, but four valence orbitals available for bonding.[1] Moreover, the use of Lewis bases for the stabilisation of complexes containing electronically unsaturated centres, unusual oxidation states or reactive bonds has been widely used.[2-4] Thus for example, the use of tethered intramolecular bases (especially alkoxo and amido ligands containing pendant donors[5,6]) has been exploited extensively in the synthesis of non-metallocene olefin polymerisation catalysts.[7,8] Within main group chemistry recent work, for example, has examined the use of amido-tethered picoline donors with respect to boron and tin centres. However much better known, and of some relevance to the work described in this chapter are borane adducts $BX_3{\cdot}L$ featuring intermolecular coordination of the base. Adducts of this type bearing one or more halogen substituents [i.e. $(BX_nR_{3-n}){\cdot}L$, $n \geq 1$] are potential precursors to complexes containing M-B bonds via salt elimination chemistry. This type of reactivity has recently been reported by Kawano (vide infra) and a representative listing of potentially useful (and structurally characterized) N-, P- and O-stabilized borane halides is given in Table 5.1.

Table 5.1 A listing of representative structurally characterized N- ,P- and O-donor stabilized borane halides

Compound	**r(B-X)/ Å, (X = O, P, N)**	**Reference**
Oxygen donors		
$CH_3OH{\cdot}BF_3$	1.524	16
$(PhO)_3P{=}O{\cdot}BCl_3$	1.511	17
$2,5\text{-}(SiMe_3)_2(C_4H_2)S{=}O{\cdot}BF_3$	1.494	18
$(C_8H_6)BCl{\cdot}Et_2O$	1.569	19
$(C_{12}H_8)O{\cdot}BCl_3$	1.514	20
$PPh_3{=}O{\cdot}BF_3$	1.516	21
$AsPPh_3{=}O{\cdot}BF_3$	1.486	21
$H_2O{\cdot}BF_3$	1.509	22
$THF{\cdot}Ph_2BCl$	1.569	23
$Me_2N{=}CH{=}O{\cdot}BCl_3$	1.482	24
Me2NCH=O·BF3	1.47	24
$Me_2N{=}CH{=}O{\cdot}BBr_3$	1.475	24
$Me_2N{=}CH{=}O{\cdot}BI_3$	1.456	24
Phosphorus donors		
$Ph_3P{\cdot}BBr_3$	1.988	25
$(C_2H_3)_3P{\cdot}BCl_3$	1.970	26
$(C_2H_3)_3P{\cdot}BBr_3$	1.952	26
$(C_2H_3)_3P{\cdot}BI_3$	1.944	26
$Et_3P{\cdot}BF_3$	2.028	26
$Me_3P{\cdot}BCl_3$	1.961	27

$Me_3P{\cdot}BBr_3$	1.920	27
$Me_3P{\cdot}BI_3$	1.919	27
$(SiMe_3)_3P{\cdot}BCl_3$	2.022	28
$(SiMe_3)_3P{\cdot}BBr_3$	1.988	28
$(SiMe_3)_3P{\cdot}BCl_3$	1.949	28
$(^nPr)_3P{\cdot}BBr_3$	1.949	29
Nitrogen donors		
$Py{\cdot}BF_3$	1.602, 1.604	30
$Py{\cdot}BCl_3$	1.593	31
$Py{\cdot}BBr_3$	1.593	32
$(C_5Me_5)BCl_2{\cdot}Py$	1.607	33
$(C_5Me_5)BCl_2{\cdot}$(isoquin)	1.601	33
$NMe_2Py{\cdot}BF_3$	1.589	34
4Pic·B(cat)Me	1.661, 1.644	35
4Pic·B(cat)Ph	1.651, 1.654	35
$4Pic{\cdot}(BPhS_2)_2$	1.647	36
$Cl_2(Me_3P)_3ReN{\cdot}BPhCl_2$	1.549	37

Kawano et al. have reported the synthesis of a range of boryl complexes $(C_5Me_5)M(CO)_n(BH_2.PMe_3)$ (n = 2, M = Fe, Ru; n = 3, M = Mo, W) stabilised by coordination of a trimethylphosphine ligand at the boron centre (Scheme 5.1).[9,10] The iron and ruthenium complexes are prepared either by photolysis or via salt elimination routes and the iron complex exhibits the longest Fe-B bond amongst structurally characterised iron (II) boryl complexes. Similarly the tungsten complex also has the longest W-B bond reported for any tungsten boryl complex.



Scheme 5.1 Two routes to base stabilised boryl complexes of iron and ruthenium (M = Fe, Ru).

Furthermore, Kawano and his group have used the trimethylphosphine ligand to base-stabilise the first BH containing bridging borylene complex, produced from the reaction of $B_2H_4{\cdot}PMe_3$ with $Co_2(CO)_8$ (Figure 5.1).[11]

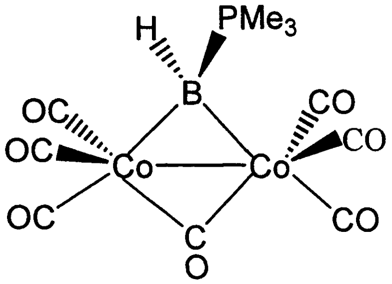


Figure 5.1 $(CO)_3Co(\mu\text{-}CO)(\mu\text{-}BH{\cdot}PMe_3)Co(CO)_3$: a dinuclear cobalt complex bridged by a nonsubstituted borylene-trimethylphosphine ligand.

In addition, the first fully characterised complex containing a BH_2 ligand was reported from a similar approach. In this complex the stabilisation of the boron centre is afforded by coordination of a PPh_2 moiety of the bridging dppm ligand (Figure 5.2).[12]

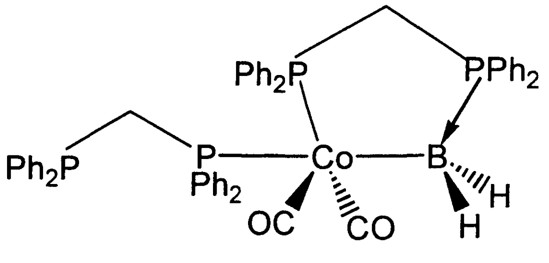
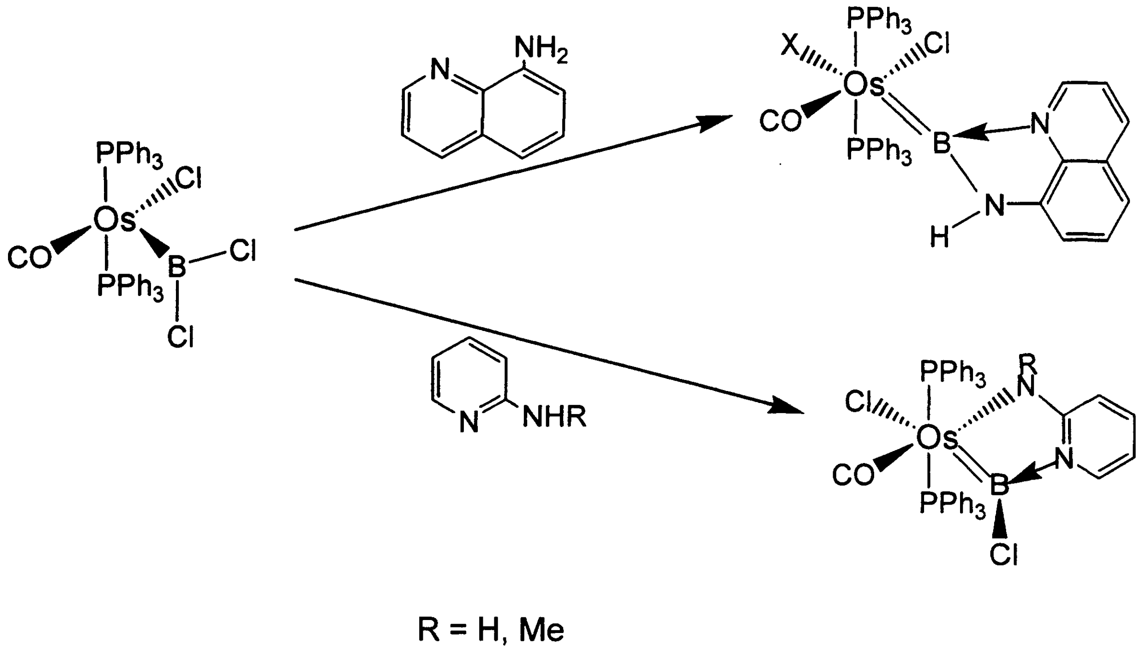


Figure 5.2 The first fully characterised non-substituted boryl complex of cobalt.

The use of nitrogen containing bases has also been exploited; Roper synthesised the first intramolecular base-stabilised terminal borylene species by reacting an osmium dichloroboryl complex with 8-aminoquinoline (Scheme 5.2).[13] This group also used 2-aminopyridines and 2-hydroxypyridines to form similar base-stabilised complexes.[14] The pyridine based ligands can however, exhibit a different mode of coordination to avoid creating the less favourable four-membered chelate ring.[15] In this case the alternative five-membered chelate ring is achieved by adopting an Os,B bridging mode of coordination.

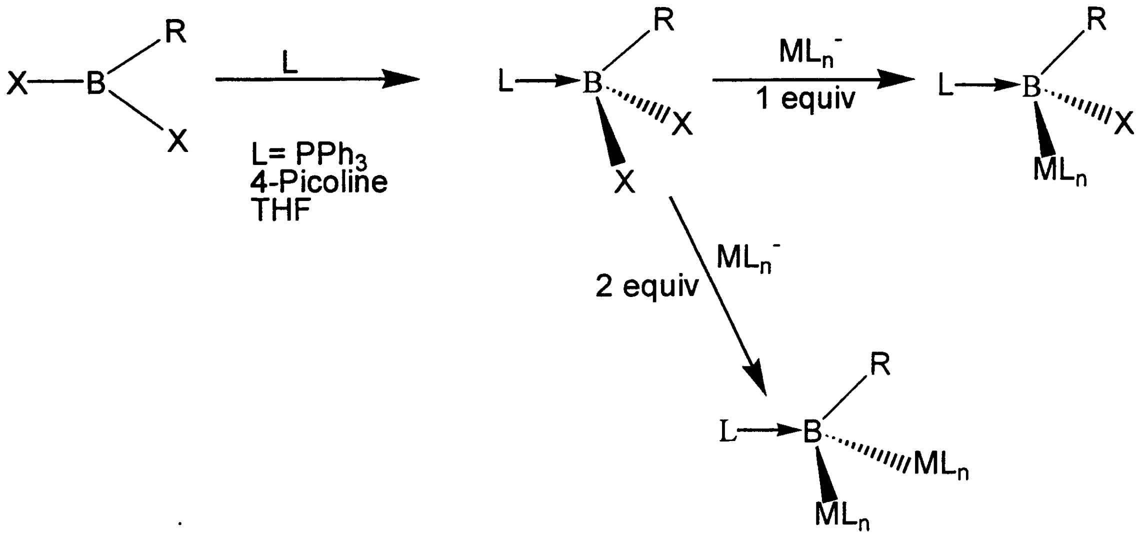


Scheme 5.2 Syntheses of intramolecular base-stabilised terminal borylene complexes of osmium using 8-aminoquinoline and –pyridine.

Very recently Braunschweig et al reported the novel base-stabilised boryl complex [$(C_5H_5)Fe(CO)_2BCl_2 \cdot 4$-pic]. This reaction represents the first demonstration of the synthesis of a base-stabilised boryl complex from an existing three-coordinate boryl ligand system, i.e. $(C_5H_5)Fe(CO)_2BCl_2$.[45]

5.1.1 Aims of the present research

Using triphenylphosphine, picoline and THF bases it was decided to synthesise a number of base-stabilised haloborane species. The successful synthesis of these new haloborane derivatives would then offer a route to base-stabilised boryl and borylene complexes via salt elimination reactions with metal anions (Scheme 5.3). If this latter aim were fulfilled a direct comparison with two and three coordinate borylene and boryl complexes would then afford an instructive probe for studying the bonding in transition metal complexes of boron. In particular the minimal π acceptor properties expected for base-stabilised boryl ligands $-BX_2.L$ might be expected to offer a useful contrast with the $-B(C_6F_5)_2$ systems examined in chapters 3 and 4.



Scheme 5.3 Potential routes to base-stabilised boryl and bridging borylene complexes via salt elimination chemistry.

5.2 Experimental

Synthesis of $Ph_3P{\cdot}BPhCl_2$ (**1**)

To a suspension of Ph_3P (0.3 g, 1.1 mmol) in toluene (15 ml) was added a solution of $PhBCl_2$ (0.18 g, 1.1 mmol) in toluene (1.5 ml). The reaction mixture was stirred at room temperature for two days during which time a white precipitate was formed. Filtration of the reaction mixture at this point and removal of volatiles in vacuo yielded **1** as a white solid (crude yield: 0.32 g, 67%). Recrystallisation by layering a toluene solution with hexanes yielded **1** as colourless crystals suitable for X-ray analysis. ^1H NMR (C_6D_6, 300 MHz), δ 6.89-7.2 (m, 12 H, meta and para CH of $PhBCl_2$ and PPh_3), 7.66 (t, 6H, ortho CHs of PPh_3, $J_{H\text{-}P}$ = 9 Hz), 7.87 (m, 2H, ortho of CHs of, $PhBCl_2$). ^{13}C NMR (C_6D_6, 76 MHz), δ 126.9 (PhB), 128.5 (PhB), 128.7 (PPh_3), 131.7 (ipso-C(B)), 134.6 (PPh_3), 134.7 (PPh_3), 134.8 (PhB). ^{11}B NMR (C_6D_6, 96 MHz), δ 3.8 (br). ^{31}P (C_6D_6, 122 MHz), δ -1.5 (br). IR (KBr disk, cm^{-1}) 3120 w, 2910 w, 1602 s, 1582 w, 1474 s, 1441 s, 1347 br, 1307 s, 1260 s, 1088 s, 1024 s. Mass spec. (EI): m/z 262 [$(PPh_3)^+$, 100%], 183 [$(PPh_2)^+$, 52%], 152 [$(M\text{-}PPh_3)^+$, 7%], 108 [$(PPh)^+$, 17%].

Synthesis of $Ph_3P{\cdot}BCl_3$ (**2**)

To a suspension of Ph_3P (0.3 g, 1.1 mmol) in toluene (15 ml) was added a solution of BCl_3 (1.1 mmol, 1.1 ml of a 1.0 M BCl_3 in heptane). The reaction mixture was concentrated and 20 ml of hexane was added. Filtration of the reaction mixture at this point removal of volatiles in vacuo yielded crude **2** as a white solid (0.32 g, 71%). ^1H NMR (C_6D_6, 300 MHz), δ 6.89 (m, 9H, meta and para of PPh_3), 7.76 (m, 6H,ortho of PPh_3). ^{13}C NMR (C_6D_6, 76 MHz), δ 129.0

(para-PPh_3), 132.3 (meta-PPh_3), 134.5 (ortho-PPh_3). ^{11}B NMR (C_6D_6, 96 MHz), δ 4.2 ($J_{B\text{-}P}$ = 150 Hz). ^{31}P (C_6D_6, 122 MHz), δ 1.0 ($J_{P\text{-}B}$ = 150 Hz). IR (KBr disk, cm^{-1}) 3120 w, 2910 w, 1602 s, 1582 w, 1474 s, 1441 s, 1347 br, 1307 s, 1260 m, 1088 s, 1024 s. Mass spec. (EI): m/z 379 [$(M)^+$, weak], 262 [$(PPh_3)^+$, 100%], 183 [$(PPh_2)^+$, 50%], 117 [$(M\text{-}PPh_3)^+$, 8%], 108 [$(PPh)^+$, 17%].

Synthesis of (4-Pic)·BCl_3 (**3**)

A solution of BCl_3 (10.6 mmol, 10.6 ml of a 1.0 M BCl_3 in heptane) was added to dried and distilled 4-picoline (1.0 g, 10.7 mmol) in toluene (4 ml). The reaction mixture was stirred at room temperature for 12 h during which time a white precipitate was formed. Filtration of the reaction mixture at this point and removal of volatiles in vacuo yielded crude **3** as a white powder (1.56 g, 69%). Recrystallisation by layering a toluene solution with hexanes yielded **3** as colourless crystals suitable for X-ray analysis. ^1H NMR (C_6D_6, 300 MHz), δ 1.40 (s, 3H, CH_3), 6.06 (m, 2H, 4-Pic), 8.66 (s, 2H, 4-Pic). ^{13}C NMR (C_6D_6, 76 MHz), δ 22.8 (CH_3), 129.3 (para-4-Pic), 132.6 (meta-4-Pic), 144.5 (ortho-4-Pic). ^{11}B NMR (C_6D_6, 96 MHz), δ 7.8. IR (KBr disk, cm^{-1}) 3106 w, 2965 w, 1945 md, 1841 md, 1794 w, 1634 s, 1558 md, 1484 s, 1332 md, 1262 s, 1237 s, 1212 md, 1096 s, 1031 w. Mass spec. (EI): m/z 208 [M^+ (weak)], 174 [$(M\text{-}Cl)^+$, 100%], 138 [$(M\text{-}2Cl)^+$, 9%], 93 [$(Pic)^+$, 43%].

Synthesis of (4-Pic)·$BPhCl_2$ (**4**)

Dried and distilled 4-picoline (0.25 g, 2.6 mmol) in toluene (1 ml) was added to a solution of $PhBCl_2$ (0.4 g, 2.5 mmol) in toluene (3.3 ml). The reaction mixture was stirred at room temperature for 12 h during which time a white precipitate was formed. Filtration of the reaction mixture at this point removal of volatiles in vacuo yielded **4** as a white crystalline powder (0.35 g, 54%). ^{1}H NMR (C_6D_6, 300 MHz), δ 1.27 (s, 3H, CH_3), 5.91 (m, 3H, 4-Pic), 7.33 (t, 2H, Ph), 7.31 (m, 3H, Ph), 8.46 (m, 2H, 4-Pic). ^{13}C NMR (C_6D_6, 76 MHz), δ 22.5 (CH_3) 125.4 (Ph), 132.9 (meta-4-Pic), 144.2 (ortho-4-Pic). ^{11}B NMR (C_6D_6, 96 MHz), δ 8.8. IR (KBr disk, cm^{-1}) 3079 md, 3042 md, 2615, 2522, 1950 s, 1862 s, 1779 s, 1681 s, 1616, 1551 s, 1449 s, 1388 s, 1328 s, 1258 s, 1088 s, 1024 s. Mass spec. (EI): m/z 251 [(M)$^+$, 4%], 216 [(M-Cl)$^+$, 23%], 174 [(M-Ph)$^+$, 20%], 158 [(M-Pic)$^+$, 38%], 123 [(M-Pic-Cl)$^+$, 38%], 93 [(Pic)$^+$, 100%].

Synthesis of BCl_3·THF (**5**)

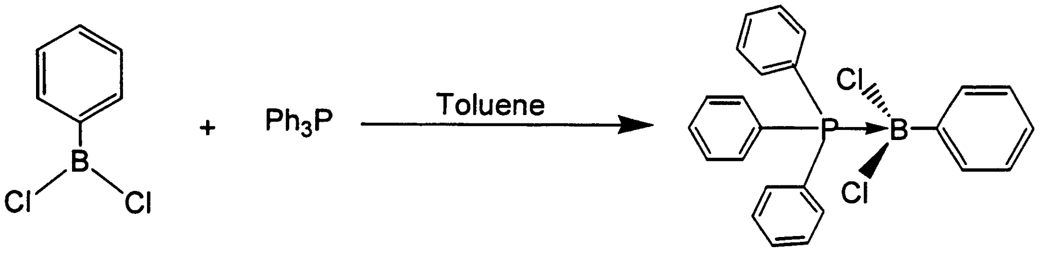
BCl_3·THF **5** was prepared according to the method of Grimley and Holliday.[38] Recrystallisation from hexane at -30°C afforded **5** as colourless crystals in yields of ca 65 %.

5.3 Results and Discussion

5.3.1 Syntheses of base-stabilised chloroboranes using triphenylphosphine

The synthesis of $Ph_3P{\cdot}BPhCl_2$ (**1**) was achieved via the reaction of Ph_3P with $PhBCl_2$ in toluene (Scheme 5.4). The ^{11}B NMR chemical shift of $PhBCl_2$ at δ 54.0 has been replaced by a high-field signal at δ 3.8 which is typical of four coordinate base-stabilised boranes [e.g $(SiMe_3)_3P{\cdot}BCl_3$ δ_B 5.0, $(C_2H_3)_3P{\cdot}BCl_3$ δ_B 1.9].[26,28] The ^{31}P NMR chemical shift of Ph_3P at δ -4.2 has been replaced by a single signal at δ -1.5 which is typical of PPh_3 borane adducts. ^{31}P and ^{11}B NMR signals were broad with no apparent coupling constant resolved.

This is almost certainly due to the low symmetry at the boron centre, as the corresponding complex $Ph_3P{\cdot}BCl_3$ does give rise to reasonably well resolved multiplets (vide infra). The ^1H and ^{13}C NMR data are consistent with the presence of triphenylphosphine and phenyl moieties. The EI mass spectrum also supports the proposed formulation for **1**.



Scheme 5.4 Synthetic route to $Ph_3P{\cdot}BPhCl_2$ (**1**).

The formulation of **1** as $Ph_3P{\cdot}BPhCl_2$ is further supported by the results of a single crystal X-ray diffraction study; the crystals were obtained by layering a toluene solution with hexane. The molecular structure of **1** is illustrated in Figure 5.3 and relevant bond lengths and angles are listed in Table 5.2. The molecules of **1** adopt the expected approximately tetrahedral geometry at the four coordinate boron centre. The adduct as whole adopts an effectively staggered orientation about the B-P coordinate bond, presumably to minimize steric interactions between vicinal substituents. Hence the torsion angles Cl1-B1-P1-C6 (44.8°) and Cl1-B1-P1-C12 (76.7°) compare with idealised values of 60^0. The B-P bond length in **1**, at 2.031(4) Å, is significantly longer than that found in $Ph_3P{\cdot}B(C_6F_5)_2H$ [**2**, 1.986(2) Å],[39] but comparable to that found in $(SiMe_3)_3P{\cdot}BCl_3$[28] [2.022(2) Å]. The significantly shorter B-P distance found in $Me_3P{\cdot}BCl_3$ [27](1.961 Å) compared to **1**, presumably reflects both the increased sigma donor strength of PMe_3 over PPh_3, and reduced steric integrations. On the other hand, the mean B-Cl distance in **1** [1.872(4) Å] is comparable to the mean B-Cl value (1.905 Å) found in four-coordinate neutral Lewis base adducts of diorganochloroboranes.

Table 5.2 Selected bond lengths [Å] and angles [°] for **1**.

B(1)-Cl(1)	1.886(4)	B(1)-C(19)	1.591(5)
B(1)-Cl(2)	1.872(4)	P(1)-C(12)	1.814(3)
B(1)-P(1)	2.031(4)	P(1)-C(13)	1.386(5)
C(19)-B(1)-Cl(2)	112.4(2)	Cl(2)-B(1)-P(1)	104.11(18)
C(19)-B(1)-Cl(1)	111.9(2)	Cl(1)-B(1)-P(1)	104.57(18)
Cl(2)-B(1)-Cl(1)	109.4(2)	C(13)-P(1)-B(1)	110.77(15)
C(19)-B(1)-P(1)	113.9(2)	C(12)-P(1)-B(1)	114.53(15)
Cl1-B1-P1-C6 centroid	44.8	Cl1-B1-P1-C12 centroid	76.7

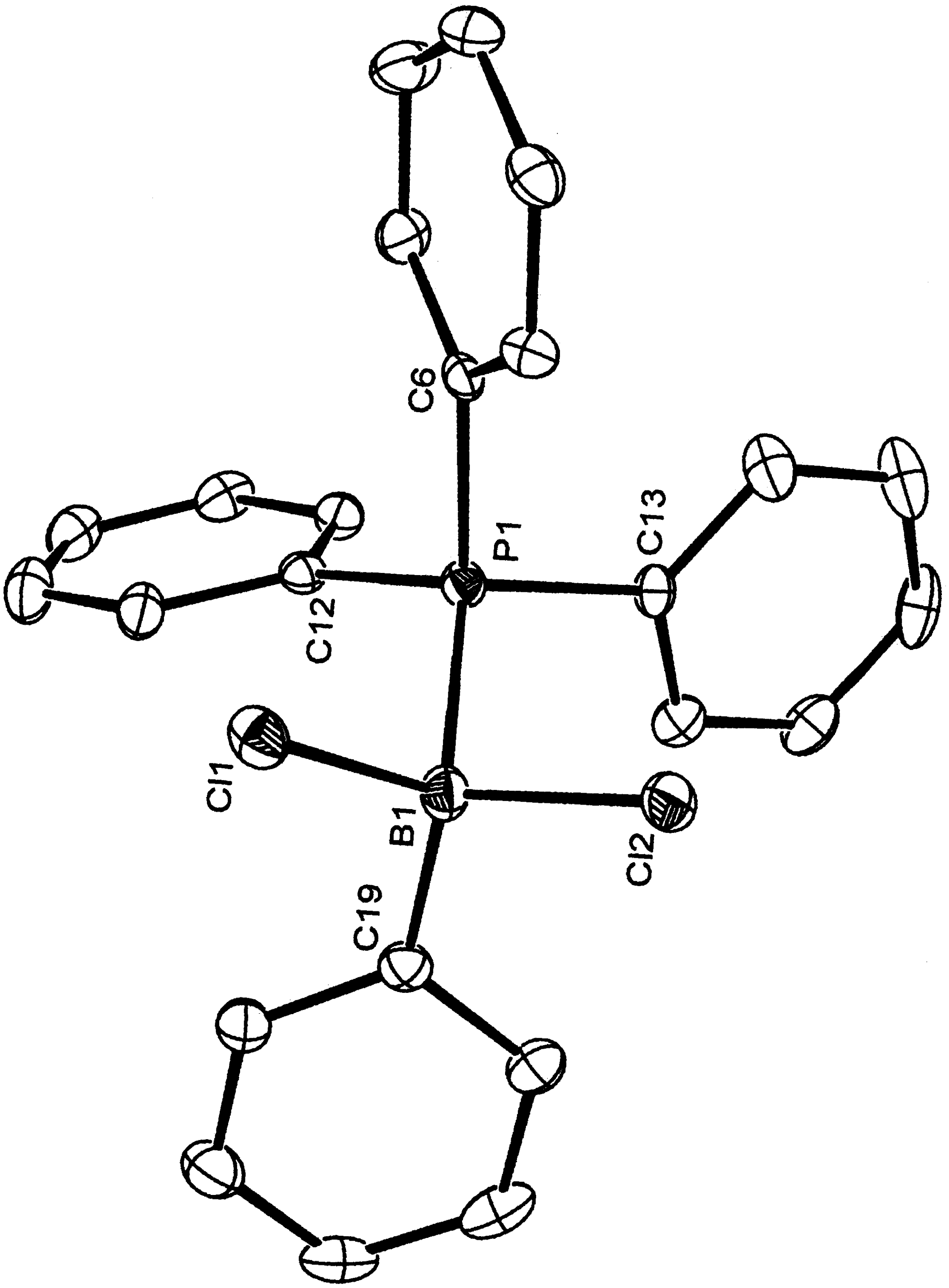
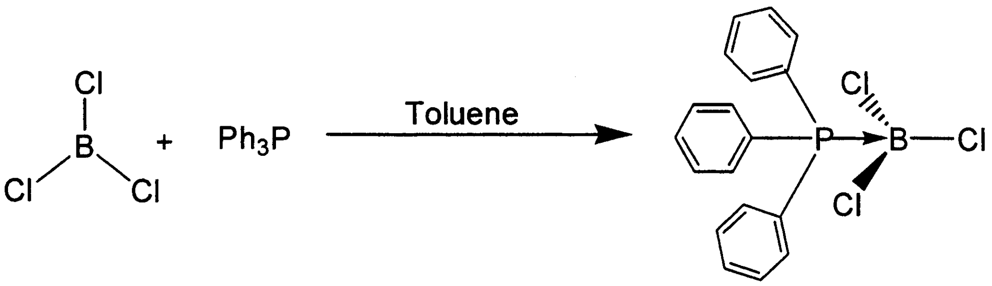


Figure 5.3 Molecular structure of $Ph_3P{\cdot}BPhCl_2$, **1**. Hydrogen atoms omitted for clarity; ORTEP ellipsoids set at the 50% probability level.

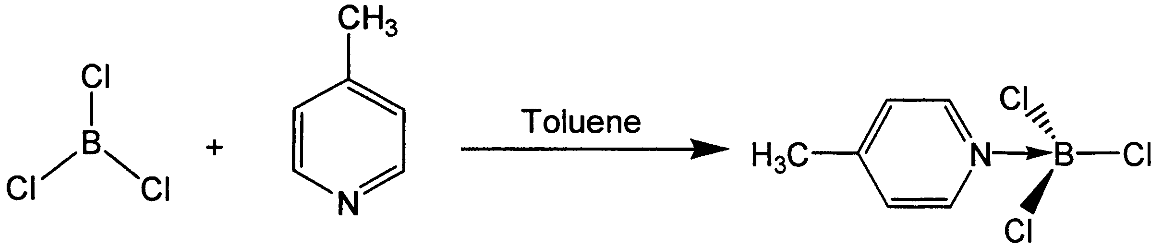


Scheme 5.5 Synthetic route to $Ph_3P{\cdot}BCl_3$ (**2**).

Similarly, triphenylphosphine also reacts with BCl_3 in toluene to form $Ph_3P{\cdot}BCl_3$ (**2**) (Scheme 5.5). The ^{11}B NMR chemical shift of BCl_3 at δ 48.0 has been replaced by a high-field signal at δ 4.2 with coupling constant, $J_{B\text{-}P}$ = 150 Hz, which is typical of a four coordinate boron species. The measured chemical shift is comparable to **1** (δ_B 3.8), $(SiMe_3)_3P{\cdot}BCl_3$ (δ_B 5.04, $J_{B\text{-}P}$ = 102.4 Hz), and $(C_2H_3)_3P{\cdot}BCl_3$ (δ_B = 1.99, $J_{B\text{-}P}$ = 162.62 Hz). The ^{31}P NMR chemical shift of **2** δ 1.0 is also consistent with a four coordinate phosphine borane species [c.f. $Ph_3P{\cdot}BPhCl_2$, **1**, δ_P -1.5] and the EI mass spectrum also supports the proposed formulation of **2**. Despite several attempts single crystals of **2** suitable for X-ray diffraction were not forthcoming.

5.3.2 Syntheses of base-stabilised chloroboranes using 4-picoline

The synthesis of 4-Pic$\cdot BCl_3$ (**3**) was accomplished via the reaction of BCl_3 with 4-picoline in toluene yielding **3** as colourless crystals in yields of ca. 65% (Scheme 5.6).



Scheme 5.6 Synthetic route to 4-Pic·BCl_3 (**3**).

The ^{11}B NMR chemical shift of δ 7.8 is typical of a four coordinate boron species and it is comparable to complexes **1** and **2** (δ_B 3.8, 4.2 respectively). The ^1H and ^{13}C NMR data are consistent with the presence of 4-picoline moieties and the EI mass spectrum also supports the proposed formulation of **3**. Single crystals of **3** were accessible via cooling to -30^{0}C of a concentrated toluene solution and the crystal structure (Figure 5.4 and Table 5.3) shows that the compound is monomeric. Although the final R-factor is high (20%) due to poor crystal quality, the crystallographic results do confirm the overall connectivity implied by the spectroscopic data. An approximately tetrahedral geometry at the boron centre is observed [angles range from 105.2(7)-111.4(7)^o] and the B-N length [1.585(14) Å] is comparable to those found in Py·BCl_3 (1.593 Å),[31] (C_5Me_5)BCl_2·Py (1.607 Å),[33] and (4-Pic)·B(cat)Me (1.661 Å).[35]

Table 5.3 Selected bond lengths [Å] and angles [°] for **3**.

Cl1-B1	1.846(13)	N1-B1	1.585(14)
Cl2-B1	1.849(14)	N1-C6	1.358(11)
Cl3-B1	1.825(13)	N1-C1	1.365(13)
N1-B1-Cl3	111.4(7)	N1-B1-Cl1	105.2(7)
N1-B1-Cl2	108.6(8)	Cl3-B1-Cl1	110.0(7)
Cl3-B1-Cl2	110.4(7)	Cl2-B1-Cl1	111.1(6)

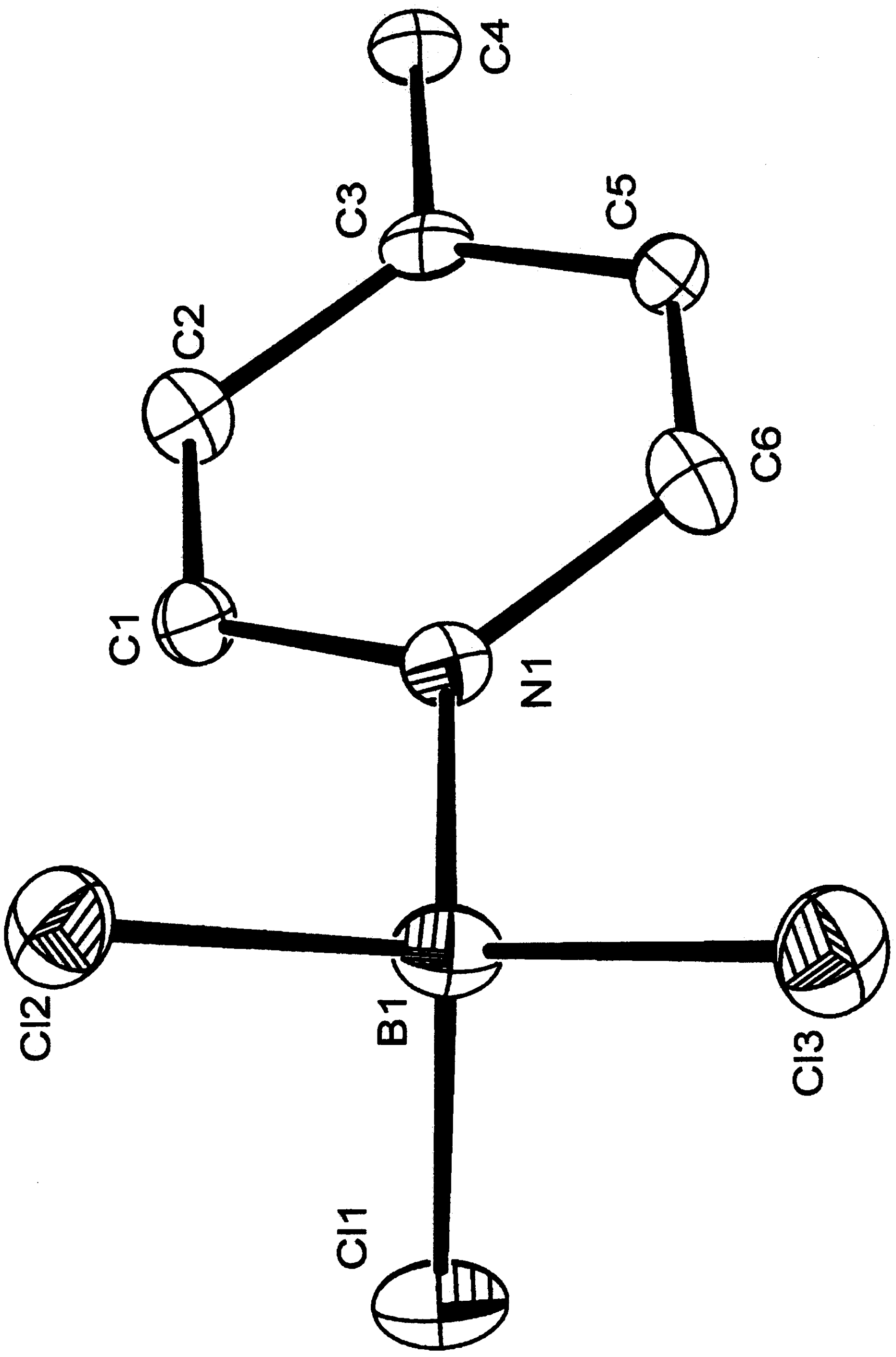
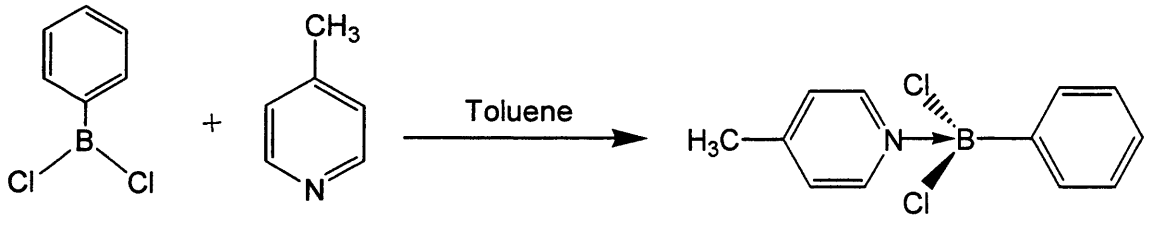


Figure 5.4 Molecular structure of (4-pic)·BCl_3, **3**. Hydrogen atoms omitted for clarity; ORTEP ellipsoids set at the 50% probability level.

Additionally, the 4-picoline base has also been reacted with $PhBCl_2$ in toluene to form 4-pic·$BPhCl_2$ (**4**) (Scheme 5.7).



Scheme 5.7 Synthetic route to 4-Pic·$BPhCl_2$ (**4**).

The ^{11}B NMR chemical shift (δ 8.8) is typical for a four coordinate boron species and comparable to **3** (δ_B 7.8). The ^1H and ^{13}C NMR data are consistent with the presence of 4-Pic moieties and the EI mass spectrum also supports the proposed formulation for **4**. Unfortunately, despite repeated attempts single crystals of **4** were not forthcoming.

5.3.3 Structure of BCl_3·THF

Single crystals of the known compound **5**[38] were obtained for comparative purposes via cooling to -30°C of concentrated hexane solution and the crystal structure (Figure 5.5 and Table 5.4) shows that the compound is monomeric. The B-O bond in **5** [1.519(17) Å] is shorter than those found in THF·BPh_2Cl [1.569(19) Å],[23] and THF·BPh_3 [1.660(4) Å][40], presumably due to the steric effects of the phenyl ring in the latter two compounds. It is also shorter than that in Me_2O·BCl_3 (1.633 Å),[41] presumably because the oxygen atom in the cyclic ether THF is a better electron donor than the oxygen in dimethyl ether.

Table 5.4 Selected bond lengths [Å] and angles [°] for **5**.

B1-Cl1	1.8382(15)		
B1-Cl2	1.8310(15)		
B1-Cl3	1.8480(15)		
B1-O1	1.5190(17)		
O1-B1-Cl2	106.95(9)	Cl2-B1-Cl3	111.37(8)
O1-B1-Cl1	107.58(9)	Cl1-B1-Cl3	110.79(8)
Cl2-B1-Cl1	111.27(7)		
O1-B1-Cl3	108.70(9)		

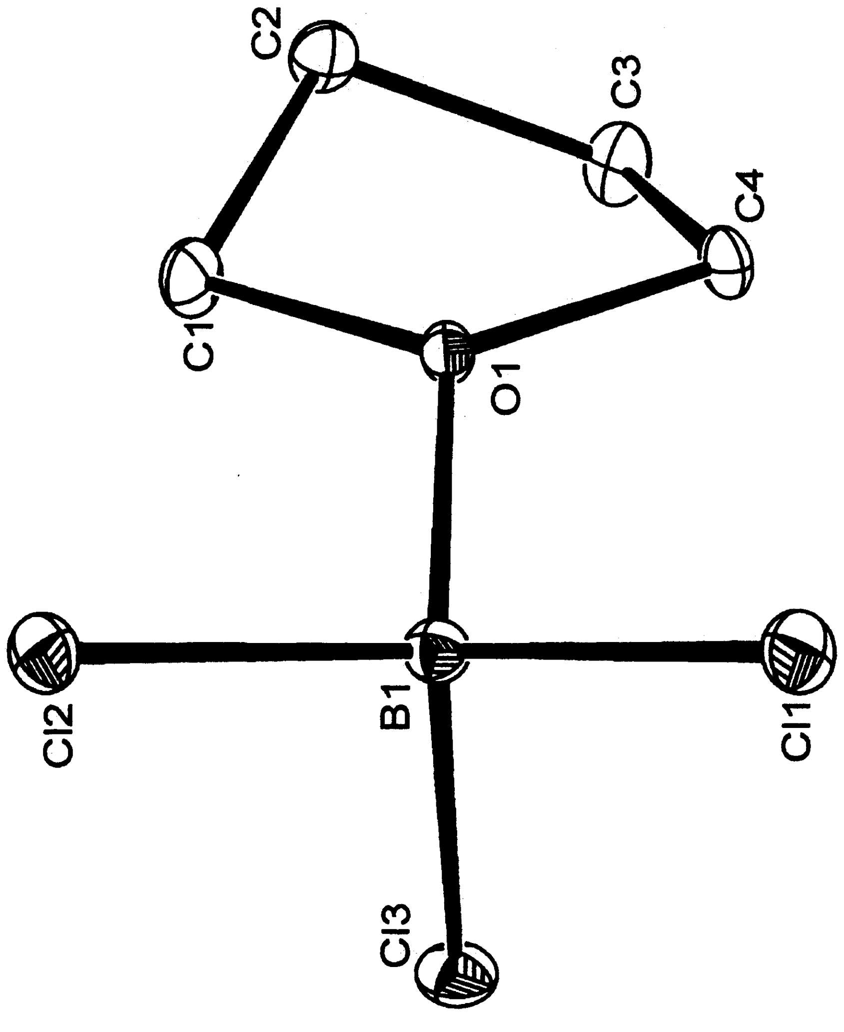


Figure 5.5 Molecular structure of THF·BCl_3, **5**. Hydrogen atoms omitted for clarity; ORTEP ellipsoids set at the 50% probability level.

5.4 Reaction of intermolecular base-stabilised chloroboranes with metal anions

5.4.1 Experimental

Reaction of $Ph_3P{\cdot}BPhCl_2$ (**1**) with $Na[(C_5H_5)Fe(CO)_2]$ in THF

A solution of (0.32 g, 0.76 mmol) of $Ph_3P{\cdot}BPhCl_2$ in THF (10 ml) was added to a solution of (0.15 g, 0.76 mmol) of $Na[(C_5H_5)Fe(CO)_2]$ in THF (20 ml). Examination of the ^{11}B and ^{31}P NMR spectra of the solution after one hour revealed that the signal at δ 3.8 characteristic of $Ph_3P{\cdot}BPhCl_2$ had disappeared, the sole resonance observed being at δ 12.6, characteristic of $THF{\cdot}BPhCl_2$. Examination of the ^{31}P NMR spectrum at this point showed a new resonance δ -4.2, characteristic of Ph_3P.

Reaction of **1** with $Na[(C_5H_5)Fe(CO)_2]$ (1:3) in toluene

A solution of (0.7 g, 1.66 mmol) of $Ph_3P{\cdot}BPhCl_2$ in toluene (10 ml) was added to a suspension of (0.99 g, 4.95 mmol) of $Na[(C_5H_5)Fe(CO)_2]$ in toluene (20 ml) and the reaction mixture stirred for 24 h. Examination of the ^{11}B and ^{31}P NMR spectra of the solution at this point revealed that the signal at δ 3.8 characteristic of $Ph_3PB{\cdot}PhCl_2$ had disappeared, the sole resonance observed being at δ 164.8. Examination of the ^{31}P NMR spectrum revealed a new resonance at δ -4.2 which is characteristic of Ph_3P. Filtration, removal of volatiles in *vacuo* and recrystallisation from hexane at -50^{0}C yielded $[(C_5H_5)Fe(CO)_2]_2BPh$ (**6**) as pale yellow powder in yields of ca. 53%. ^1H NMR (C_6D_6, 300 MHz), δ 4.2 (s, 10H, C_5H_5), 7.23 (t, $^3J_{HH}$ = 7.2 Hz, 1H, aromatic para-CH), 7.37 (t, $^3J_{HH}$ = 7.4 Hz, 2H, aromatic meta-CH), 7.79 (d, $^3J_{HH}$ = 7.2 Hz, 2H, aromatic ortho-CH). ^{13}C NMR (C_6D_6, 76 MHz), δ 85.3 (C_5H_5), 127.4, 127.7, 128.1 (aromatic CH). ^{11}B NMR (C_6D_6, 96 MHz), δ 164.8. IR (KBr disk, cm^{-1}) ν(CO) 1995, 1930. Mass spec. (EI): M^+ = 441.5 (weak), fragment ion peaks at *m/z* 413.5 [$(M-CO)^+$, 9%], and 385.5 [$(M-2CO)^+$, 80%].

Reaction of $Ph_3P\cdot BCl_3$ (**2**) with $Na[(C_5H_5)Fe(CO)_2]$

A solution of **2** (0.32 g, 0.84 mmol) in toluene (15 ml) was added to a suspension of $Na[(C_5H_5)Fe(CO)_2]$ (0.15 g, 0.76 mmol) in toluene (20 ml) and the resulting mixture was stirred at room temperature. Examination of the ^{11}B NMR spectrum of the reaction mixture after 1h revealed that it consisted solely of the starting material **2**. The reaction mixture stirred at room temperature for a further 48 h, after which examination by ^{11}B NMR revealed that a weak new signal had grown in at δ_B 58.3. Extensive variation of the reaction conditions (elevated temperature, reaction time) and the use of a 2-fold excess of $Na[(C_5H_5)Fe(CO)_2]$ were employed to encourage the reaction to proceed to completion. However, no change was observed by ^{11}B NMR spectroscopy in the intensity of the two peaks at δ_B 58.3 and 4.2. The solution was filtered, volatiles removed in vacuo and recrystallisation from hexane was attempted. However, the product found to decompose if stored for extended periods at -30°C in solution, as judged by the ^{11}B NMR spectrum of the hexane solution.

Reaction of 4-Pic$\cdot BCl_3$ (**3**) with $Na[(C_5H_5)Fe(CO)_2]$

A solution of **3** (0.32 g, 1.5 mmol) in toluene (15 ml) was added to a suspension of $Na[(C_5H_5)Fe(CO)_2]$ (0.28 g, 1.4 mmol) in toluene (20 ml) and the resulting mixture was stirred at room temperature. Examination of the ^{11}B

NMR spectrum of the reaction mixture after one hour revealed that new signal had begun to grow in at δ_B 2.3. Extensive variation of the reaction conditions (elevated temperature, reaction time) and a 2-fold excess of $Na[(C_5H_5)Fe(CO)_2]$ were employed to encourage the reaction to proceed to completion. However, no change was observed by ^{11}B NMR spectroscopy in the intensity of the two peaks at δ_B 2.3 and 7.8. The solution was filtered, volatiles removed in vacuo and recrystallisation from hexane was attempted. However, no homogenous product was isolated.

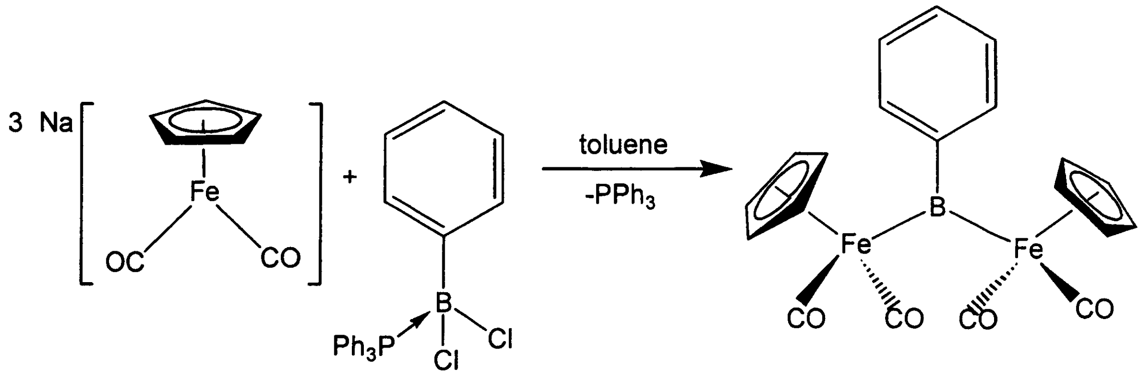
Reaction of 4-Pic·$BPhCl_2$ (**4**) with $Na[(C_5H_5)Fe(CO)_2]$

Reaction of a solution of **4** (0.2 g, 0.79 mmol) in toluene (15 ml) with a suspension of $Na[(C_5H_5)Fe(CO)_2]$ (0.15 g, 0.75 mmol) in toluene (20 ml) was also attempted. The course of the reaction proceeded in a similar fashion to that reported above for **3** yielding two boron containing species (δ_B 3.5 and starting material at 8.7), such that the reaction proved impossible to drive to completion. Attempts to separate the product by fractional crystallisation proved impossible.

5.4.2 Results and discussion

5.4.2.1 Reactions of metal anions with $Ph_3P{\cdot}BPhCl_2$ (1) and $Ph_3P{\cdot}BCl_3$ (2)

Base-stabilised chloroborane $Ph_3P{\cdot}BPhCl_2$ was used to synthesise the bridging borylene complex **6** by reaction with three equivalents of $Na[(C_5H_5)Fe(CO)_2]$ in toluene (Scheme 5.6).



6

Scheme 5.6 Synthetic route to complex **6**

After a period of 12 h, the reaction was judged to be complete by the replacement of the peak in the ^{11}B NMR spectrum of the reaction mixture due to $Ph_3P{\cdot}BPhCl_2$ (δ_B 3.8) with a peak at δ_B 164.8, which is consistent with the replacement of both B-Cl bonds with B-Fe bonds. Similar ^{11}B resonances have been reported for bridged iron borylene complexes, such as $[(C_5H_5)Fe(CO)_2]_2BMes$ (δ_B158.0) which also contain aryl substituents at boron.[43] The formulation of **6** is also supported by the ^1H and ^{13}C NMR spectra. Terminal CO stretches are observed in the IR spectrum of **6**, at (1995, 1930 cm^{-1}) as would be expected for the formulation proposed, with no stretching frequencies corresponding to bridging carbonyls being seen. This is further supported by the EI mass spectrum, which shows peaks due to the parent M^+ ion, and to the fragment ions $(M\text{-}CO)^+$, $(M\text{-}2CO)^+$, $(M\text{-}3CO)^+$, and $(M\text{-}4CO)^+$. Therefore, although crystals suitable for X-ray diffraction could not be obtained, the available spectroscopic evidence point to an unsupported structure for bridging borylene **6**, similar to the corresponding mesitylborylene complex, $[(C_5H_5)Fe(CO)_2]_2BMes$.[43] By contrast, reaction of $BPhCl_2$ with the bulkier permethylated reagent Na[(C_5Me_5)Fe(CO)$_2$] generates an Fe-Fe bonded species by loss of CO. As has been previously discussed,[42] steric factors are very important in determining the structures of borylene systems such as these. Presumably the smaller bulk of (C_5H_5) as opposed to (C_5Me_5) allows the adoption of the unsupported architecture, whereas the bulkier permethylated ligand drives the reaction through to the Fe-Fe bonded product in which there is considerably less steric crowding at boron (Figure 5.6).

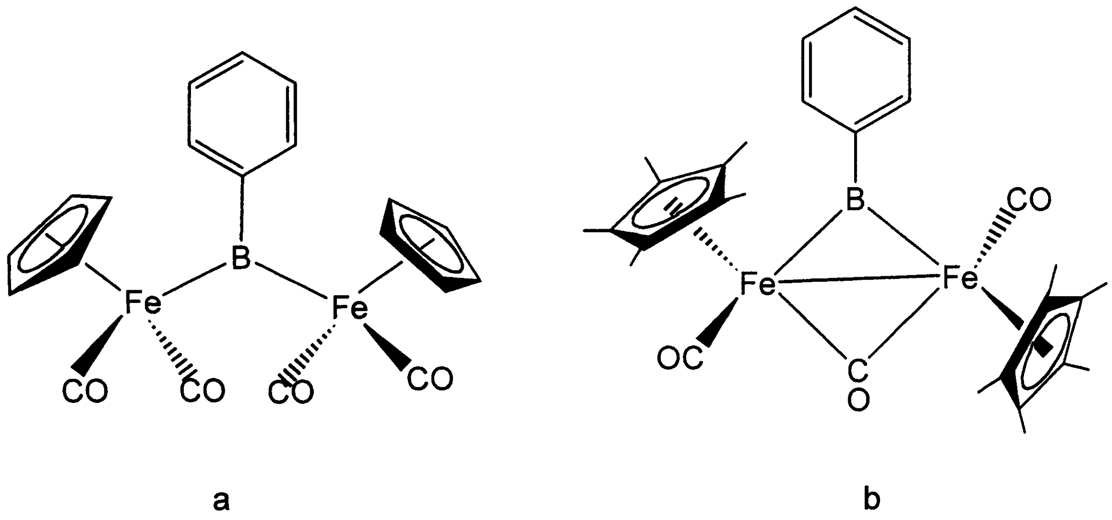


Figure 5.6 The two precedented structures of diiron bridging borylene systems: (a) unsupported architecture; and (b) Fe-Fe bonded structure.

On the other hand, if THF used as solvent instead of toluene the reaction generates THF·BPhCl$_2$ and PPh$_3$ as shown by multinuclear NMR. The ^{11}B NMR data for THF·BPhCl$_2$ are comparable to those for the authentic complex that has been synthesised previously.[44] This reactivity results from the fact that the THF is a stronger electron donor than PPh$_3$ towards boron.

Presumably coordination of the THF molecule then prevents completion of the subsequent reaction with $Na[(C_5H_5)Fe(CO)_2]$:

$$\mathrm{Ph_3P.BPhCl_2} \xrightleftharpoons{\mathrm{-PPh_3\backslash THF}} \mathrm{THF.BPhCl_2} \xrightarrow[\text{not to completion}]{\mathrm{Na[(C_5H_5)Fe(CO)_2]}} \mathrm{(C_5H_5)Fe(CO)_2BPhCl.THF}$$

Addition of the corresponding boron trichloride adduct $Ph_3P.BCl_3$ **2** to $Na[(C_5H_5)Fe(CO)_2]$ in toluene formed a very small amount of the product $[(\eta^5\text{-}C_5H_5)Fe(CO)_2][BCl_2{\cdot}THF]$.[44] Even though the reaction conditions were varied, by heating to 60°C for up to two weeks and by the use of excess $Na[(C_5H_5)Fe(CO)_2]$, the resonance observed in the ^{11}B NMR at δ_B 58.3 (due to the product) was always dwarfed by the starting material **2.** Unfortunately, the product was extremely prone to decomposition, even at -30 ^0C in solution and was not able to be isolated as a pure substance by recrystallisation.

5.4.2.2 Reactions of metal anions with 4-Pic·BCl$_3$ (3) and 4-pic·BPhCl$_2$ (4)

In an attempt to synthesise chloroboryl and bridging borylene complexes, the reactions of 4-Pic·BCl_3 **3** and 4-Pic·$BPhCl_2$ **4** with one and two equivalents of $Na[(C_5H_5)Fe(CO)_2]$ were carried out. In both cases, the reactions generated new species giving rise to a single high-field resonance (δ_B 2.3 for **3**; δ_B 3.5 for **4**) which indicates that four coordinate boron centres are retained and no metal boron bonds have been formed. In particular no signal at δ_B 18.8 characteristic of the complex $(C_5H_5)Fe(CO)_2BCl_2{\cdot}$4pic, recently synthesized by Braunschweig [by an alternative route from $(C_5H_5)Fe(CO)_2BCl_2$ and 4-picoline] could be detected.[45] In both cases the reaction could not be forced to completion as the ^{11}B NMR spectra showed that the resonance for the starting material (**3** or **4**) was still observed, even after changing the reactions conditions {solvent (toluene, and THF), heating to 60°C for up to two weeks and the use of excess $Na[(\eta^5–C_5H_5)Fe(CO)_2]$}. Unfortunately, no homogenous product was isolated in either case to allow further characterisation. It is worth to mention that using THF as a solvent in both reactions did not cause substitution of the 4-picoline, unlike the situation with PPh_3. This is as expected since the pyridyl base is a strong electron donor and forms a very stable B-N bond. Presumably this reduces substantially the electrophilicity of the boron centre and render the adducts $4\text{-Pic}\cdot BRCl_2$ inert to attack by organometallic nucleophiles such as $Na[(C_5H_5)Fe(CO)_2]$.

The aim of this particular section was to investigate reactions of base-stabilised boranes with $Na[(C_5H_5)Fe(CO)_2]$ in order to form boryl and borylene complexes (Scheme 5.3). It has been found that the reaction of 4-picoline stabilised boranes cannot driven to completion presumably because the coordination of an N-donor base makes the boron centre less electrophilic and hence not so reactive toward metal-centred nucleophiles. By contrast, weaker phosphorus donors can dissociate from the boron centre thereby allowing coordination by a stronger O-donor, or in the absence of a donor solvent, facilitating salt elimination chemistry typical of the base-free borane $PhBCl_2$.

Conventional salt elimination synthesis of metal boron bonds (i.e. boryl and borylene complexes) has been reported to require the use of weakly coordinating solvents since it has been thought that the presence of significantly Lewis basic reagents leads to rupture of the M-B bond. Hence, for example the synthesis of $(C_5H_5)Fe(CO)_2B(C_6F_5)_2$ (chapter 3) requires the use of $Na[(C_5H_5)Fe(CO)_2]$ from which all traces of THF had been rigorously removed. In the presence of THF, the product is known to decompose. The synthesis of the borylene complex $[(C_5H_5)Fe(CO)_2]_2BPh$ (**6**) from $Na[(C_5H_5)Fe(CO)_2]$ and $Ph_3P.BPhCl_2$ (**1**) is therefore somewhat surprising on first inspection, since ^{31}P NMR data are consistent with the generation of free PPh_3. In this case the reaction is clearly facilitated by the lability of the B-P bond, since the reaction of uncomplexed $BPhCl_2$ with $Na[(C_5Me_5)Fe(CO)_2]$ has previously been shown to lead to the formation of iron boryl and borylene products.[42,43] Presumably the large steric bulk of PPh_3, and the high degree of crowding the boron centre known to be a feature of unsupported bridging borylene complexes of the type $[(C_5R_5)Fe(CO)_2]_2BR$, prevents any appreciable coordination of the phosphine to the borylene product. Since this coordination step is thought to promote decomposition in related systems its prevention on steric grounds may be a decisive factor here.

5.5 Conclusions

The intermolecular base-stabilised haloboranes $Ph_3P{\cdot}BPhCl_2$ (**1**), $Ph_3P{\cdot}BCl_3$ (**2**), 4-Pic·BCl_3 (**3**), and 4-Pic·$BPhCl_2$ (**4**) represent examples of haloborane complexes containing the PPh_3 and 4-Pic ligands with potential for M-B bond formation. The structures of **1** and **3** have been determined by single crystal

X-ray diffraction and the structure of THF·BCl_3 (**5**) has also been obtained for comparative purposes.

A bridging borylene complex $[(\eta^5-C_5H_5)Fe(CO)_2]_2BPh$ **6** has been synthesised starting from a base-stabilised borane **1**. In the case of base-stabilised borane **2,** similar reaction leads to the complex $(C_5H_5)FeBCl_2$·THF and free PPh_3, as indicated by ^{11}B and ^{31}P NMR but to due decomposition, it could not be characterised by further analysis. Attempts to utilise the N-stabilised species **3** and **4** for the syntheses of boryl and borylene complexes have proved unsuccessful. This might be due to the strong electron donating properties of the 4-picoline donor which retards nucleophilic attack by metal anions.

5.6 References for chapter five

1. H.Braunschweig and M.Colling, Coord. Chem. Rev., 2001, 223, 4
2. L.H. Gade, Chem. Commun., 2000, 173.
3. R.R. Schrock, Acc. Chem. Res., 1997, 30, 9.
4. J. G. Verkade, Acc. Chem. Res., 1993, 26, 483.
5. M. H. Chisholm and I.P. Rothwell, in Comprehensive Coordination Chemistry, eds. G. Wilkinson, R. D. Gillard and R. J. McCleverty, Pergamon, Oxford, 1987, Vol. 2, P. 161.
6. (a) R. C. Mehrota, in Advances in Inorganic Chemistry and Radiochemistry, eds. H. G. Emedus and A. G. Sharpe, Academic Press, London, 1963, Vol. 26, p. 269. (b) D. C. Bradley, Chem. Rev., 1989, 89, 1317.
7. G. J. P. Britovsek, B. C. Gibson and D. F. Wass, Angew. Chem. Intl. Ed., 1999, 38, 428.
8. J. D. Scollard and D. H. McConville, J. Am. Chem. Soc., 1996, 118, 10008.
9. Y. Kawano, T. Yasue, M. Shimoi, J. Am. Chem. Soc., 1999, 121, 11744.
10. T. Yasue, Y. Kawano, M. Shimoi, Chem. Lett., 2000, 58.
11. M. Shimoi, S. Ikubo, Y. Kawano, J. Am. Chem. Soc., 1998, 120, 4222.
12. D. J. Elliot, C. J. Levy, R. J. Puddephatt, D. G. Holah, A. N. Hughes, V. R. Magnuson, I. M. Moser, Inorg. Chem., 1990, 29, 5015.
13. G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, Angew. Chem. Intl. Ed., 2000, 39, 948.

14. C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, Organometallics, 2002, 21, 4862.

15. C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, Organometallics, 2002, 21, 1714.

16. D. Mootz, M. Steffen, Z. Anorg. Allg. Chem., 1981, 483, 171.

17. M. L. Levin, J. W. Fieldhouse, H. R. Allcock, Acta Cryst B, 1982, 38, 2284.

18. S. Z. Zhang, S. Sato, E. Horn, N. Furukawa, Heterocycles, 1998, 48, 227.

19. T. Wagner, U. Eigendorf, G. E. Herberich, U. Englert, Struct. Chem., 1994, 5, 233.

20. C. G. Branch, S. G. Bott, AR Barron, J. organomet. Chem, 2003, 666, 23.

21. N. Burfork, R. E. V. H. Spence, A. Linder, T. S. Cameron, Acta Cryst C, 1990, 46, 92.

22. Y. A. Simonov, V. O. Gelmbdddt, E. V. Granin, A. A. Dvovkin, M. S. Fonar, L. V. Ostapchuk, Y. Lipkovsky, Koord. Khim., 1995, 21, 760.

23. W. I. Cross, M. P. Lightfoot, F. S. Mair, R. G. Pritchard, Inorg. Chem., 2000, 39, 2690.

24. E. J. Corey, J. J. Rohde, A. Fischer, M. D. Azimioara, Tetrahedron Lett., 1992, 33, 6945.

25. F. Weller, M. Mohlen, K. Dehnicke, Z. Kr. Stallogr., 1997, 212, 159.

26. U. Monkowius, S.Nogai, H. Schmidbaur, Dalton Trans, 2003, 987.

27. D. L. Black, R. C. Taylor, Acta Cryst B, 1975, 31, 1116.

28. M. S. Lube, R. L. Wells, Inorg. Chem., 1996, 35, 2007.

29. C. Aubauer, K. Davidge, T. M. Klapotka, P. Mayer, H. Piotrowski, A. Schulz, Z. Anorg. Aug. Chem. 2000, 626, 2373.
30. K. Topel, K. Hensen, J. W. Bats, Acta Cryst C, 1984, 40, 828.
31. K. Topel, K. Hensen, M. Tromel, Acta Cryst C, 1981, 37, 969.
32. K. Iijima, I. Oonishi, Chem. Lett, 1983, 251.
33. P. Jutzi, B. Krato, M. Hursthouse, A. J. Hases, Chem. Ber., 1987, 120, 1091.
34. MJG Lesley, A Woodward, NJ Taylor, T. B. Marder, I. Cazenobe, I. Ledoux, J. Zyss, A. Thornton, D. W. Bruce, A. K. Kakkar, Chem. Mater., 1998, 10, 1355.
35. W. Clegg, AJ Scott, FES Souza, TB Marder, Acta Cryst C, 1999, 55, 1885.
36. W. Clegg, Ch. Dai, F. J. Lawlor, T. B. Marder, P. Nguyen, N. C. Norman, N. L. Pickett, W. P. Power, A. J. Scott, J. Chem. Soc., Dalton Trans., 1997, 839.
37. U. Abram, A. Hagenbach, A. Voigt, R. Kirmse, Z. Anorg. Allg. Chem., 2001,627, 955.
38. J. Grimley, A. K. Holliday, J. Chem. Soc., 1954, 1212.
39. Chapter four of this thesis.
40. W. J. Evans, J. L. Shreeve, J. W. Ziller, Acta Crystallogr., Sect. C 1996, 52, 2571.
41. B. D. Roswell, R. J. Gillespie, G. L. Heard, Inorg. Chem., 1999, 38, 4659.
42. D. L. Coombs, S. Aldridge, S. J. Coles, M. B. Hursthouse, Organometallics, 2003, 22, 4231.

43. S. Aldridge, D. L. Coombs, C. Jones, Chem. Commun., 2002, 856.

44. Andrea Rossin, PhD thesis, Cardiff University, 2004.

45. H. Braunschweig, K. Radacki, F. Seeler, G. R. Whittell, Organometallics., 2004, 23, 4178.