

The Synthesis and Coordination Chemistry of Boranes and Boronium Reagents

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The Australian National University

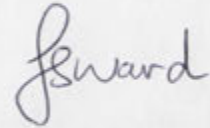
October 2014



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Declaration

The research described in this thesis is the author's own original work, with the exception of that to which reference is made in the text.

A handwritten signature in black ink, appearing to read 'J Stuart Ward', with a stylized, cursive script.

James (Jas) Stuart Ward

Acknowledgements

I think when I started my PhD I couldn't '*see the forest for the trees*', but now I see a little more of the forest I dare say, and I know this is thanks to Tony Hill, my unwavering supervisor and friend, who, in tandem with Mark Santos, has treated me like family from the very beginning. This whole endeavour has been so much more enjoyable than I suspect it should have been, and the credit for this must rightly be given to the two of them.

I would like to thank my family and friends, who have had the kindness to listen and nod to all my chemistry ramblings over the last few years. They were everything I could have asked for and have always been a great source of support; I can safely say that I would not be here if not for their patience and love.

The ever-changing *yet* ever-present Hill Group has had a loyal membership over the years I've been a part of it, and I would like to thank them all for their friendship: Ian Cade, Annie Colebatch, Richard (Spike) Cordiner, Lily Dixon, Amy Halcon, Yong-Shen Han, Vincent Huynh, Suprita Kaur, Sian Keys, Chenxi (Kathy) Ma, Richard (Ritchie) Manzano, Caitlin McQueen, Horst Neumann, Stephen Lee, Torsten Schwich, Rong Shang, Manab Sharma, Arup Sinha, Craig Stewart, Kassetra (Kass) von Nessi, Jorg Wagler, Jiao-Yu (Joseph) Wang, Yao Yao (Jane) Xiong and Rowan Young.

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Abstract

This thesis describes investigations into highly reactive boron-functionalised reagents and the reactions they undergo with appropriate organometallic precursors. Trifluoroborate-functionalised alkynes failed to yield isolable products on reaction with various organoruthenium substrates. However, *B*-ethynyl-*N*-methyliminoacetatoborane ($\text{HC}\equiv\text{CBMIDA}$) proved to be a more versatile reagent. The reaction of $\text{HC}\equiv\text{CBMIDA}$ with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ or $\text{Ru}(\text{C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2$ afforded the α -ethynyl hydrido complex $\text{Ru}(\text{H})(\text{C}\equiv\text{CBMIDA})(\text{CO})_2(\text{PPh}_3)_2$ via reversible C-H activation of the terminal alkyne. The reaction of the hydride complex with chloroform gave the corresponding chloro complex $\text{RuCl}(\text{C}\equiv\text{CBMIDA})(\text{CO})_2(\text{PPh}_3)_2$.

Reaction of $\text{HC}\equiv\text{CBMIDA}$ with $[\text{RuCl}(\text{dppe})_2][\text{PF}_6]$ (dppe = 1,2-bis(diphenylphosphino)ethane) yielded the vinylidene complex $[\text{Ru}(\text{C}=\text{CHBMIDA})\text{Cl}(\text{dppe})_2][\text{PF}_6]$, deprotonation of which with NEt_3 gave the α -alkynyl complex $[\text{Ru}(\text{C}\equiv\text{CBMIDA})\text{Cl}(\text{dppe})_2]$. The reaction of $\text{HC}\equiv\text{CBMIDA}$ with *mer*- $\text{Ru}(\text{H})\text{Cl}(\text{CO})(\text{PPh}_3)_3$ proceeded via alkyne hydrometallation to yield the 16-electron complex $\text{Ru}(\text{E}-\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ as the major product. Reaction of $\text{Ru}(\text{E}-\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with CO , $\text{CNC}_6\text{H}_2\text{Me}_{3-2,4,6}$ and NCMe afforded the coordinatively saturated derivatives $\text{Ru}(\text{E}-\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{L})(\text{PPh}_3)_2$ ($\text{L} = \text{CO}$, $\text{CNC}_6\text{H}_2\text{Me}_{3-2,4,6}$, NCMe), whilst treatment with $[\text{NH}_2\text{Et}_2][\text{S}_2\text{CNEt}_2]$ and $\text{K}[\text{Tp}]$ (Tp = hydrotris(pyrazol-1-yl)borate) provided $\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2$ and $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Tp}(\text{CO})(\text{PPh}_3)$, respectively. The reaction of $\text{HC}\equiv\text{CBMIDA}$ with $\text{Ru}(\text{H})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2$ afforded the α -alkynyl complex $\text{Ru}(\text{C}\equiv\text{CBMIDA})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2$.

The stabilisation of highly reactive boron halides was explored via the synthesis and structural characterisation of a range of new phosphine-borane adducts, $\text{R}_3\text{P}\cdot\text{BH}_n\text{X}_{3-n}$ ($n = 1, 2, 3$; $\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{Ph}, \text{Cy}$) via reactions of monodentate phosphines with labile dimethylsulphide borane adducts $\text{BH}_n\text{X}_{3-n}\cdot\text{SMe}_2$. Modifications of the procedure were conducted to include the use of multidentate heteroatom donors. The diphosphines dppe , dcpe (1,2-bis(dicyclohexylphosphino)ethane), dmpe (1,2-bis(dimethylphosphino)ethane) and dppf (1,1'-bis(diphenylphosphino)ferrocene) reacted with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ to afford chelated boronium salts, $[\text{H}_2\text{B}(\text{diphosphine})]\text{Br}$. Similarly, triphos (1,1,1-tris(diphenylphosphinomethyl)ethane) was found to react with

BH₂Br·SMe₂ to give [H₂B(κ²-*P,P'*-triphos)]Br, which featured a pendant phosphine arm. Whilst this pendant donor was found not to substitute the labile PPh₃ ligand in a range of organometallic precursors, halide bridge-splitting reactions ensued with Rh₂(μ-Cl)₂Cl₂Cp*₂, Ru₂(μ-Cl)₂Cl₂(η⁶-C₆H₄Me-1-*i*-Pr-4)₂ and Rh₂(μ-Cl)₂(η⁴-COD)₂ (COD = 1,5-cyclo-octadiene) to provide monomeric complexes [RhCl₂Cp*(κ¹-*P*-H₂B{triphos})]Br, [RuCl₂(η⁶-C₆H₄Me-1,4)(κ¹-*P*-H₂B{triphos})]Br and [RhCl(η⁴-COD)(κ¹-*P*-H₂B{triphos})]Br.

The mixed phosphine/arsine ligand arphos (Ph₂AsCH₂CH₂PPh₂) reacted with BH₂Br·SMe₂ to generate κ¹-*P*-arphos·BH₂Br. The pendant arsine arm of arphos·BH₂Br was potentially able to coordinate to suitable organometallic precursors, but was not observed to do so experimentally. Instead, loss of the BH₂Br substituent facilitated conventional bidentate fashion of the arphos ligand. Thus the reactions of arphos·BH₂Br with Rh₂(μ-Cl)₂Cl₂Cp*₂ afforded the complex [RhClCp*(κ²-As,*P*-arphos)]Cl, and reaction of arphos·BH₂Br with Ru(Ph)Cl(CO)(PPh₃)₂ afforded RuBr₂(CO)(κ²-As,*P*-arphos)(PPh₃) and RuBr₂(κ²-As,*P*-arphos)₂.

Synthetic routes to phosphine ligated *B*-bromo-boronium salts [BrHB(L)₂]Br were developed *via* the reactions of BHBr₂·SMe₂ with appropriate phosphines (L), though the formation of [BrHB(L)₂]⁺ boronium species proved much less general (*cf.* [H₂B(L)₂]⁺ salts) and was often accompanied by subsequent decomposition. The reactions of BHBr₂·SMe₂ with dcpe or PMe₂Ph provided [BrHB(dcpe)]Br and [BrHB(PMe₂Ph)₂]Br, respectively, whilst the heterodentate amine/phosphine donor compound amphos (*N,N*-dimethyl-2-diphenylphosphinoaniline) gave [BrHB(amphos)]Br.

Rare examples of borane adducts and boronium salts [H₂B(L)₂]Br (L = PHCy₂, PHPh₂, PH₂Cy, PH₂Mes, PMe₂Ph, PHEtPh, arphos) ligated by primary, secondary and tertiary phosphines were obtained *via* reactions of the phosphines PHCy₂, PHPh₂, PH₂Cy, PH₂Mes, PMe₂Ph, PHEtPh and arphos with BH₂Br·SMe₂. In contrast, the formation of [BrHB(L)₂]Br was never unequivocally observed upon reaction of PHCy₂ and PH₂Cy with BHBr₂·SMe₂ due to their facile decomposition to afford the respective phosphonium salts.

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Abbreviations

+I	A positive inductive effect
-I	A negative inductive effect
[9]aneS ₃	1,4,7-trithiacyclononane, C ₆ H ₁₂ S ₃
[14]aneS ₄	1,4,8,11-tetrathiacyclotetradecane, C ₁₀ H ₂₀ S ₄
amphos	<i>N,N</i> -dimethyl-2-(diphenylphosphino)aniline, C ₂₀ H ₂₀ NP
Ar ^F	3,5-bis(trifluoromethyl)phenyl, C ₆ H ₃ (CF ₃) ₂
arphos	1-diphenylarsino-2-diphenylphosphinoethane, C ₂₆ H ₂₄ AsP
Cat	catechol, 1,2-dioxybenzene, C ₆ H ₄ O ₂
COD	1,5-cyclooctadiene, C ₈ H ₁₂
COE	1-cyclooctene, C ₈ H ₁₄
Cp	cyclopentadienyl, [C ₅ H ₅] ⁻
Cp [*]	1,2,3,4,5-pentamethylcyclopentadienyl, [C ₅ Me ₅] ⁻
Cy	cyclohexyl, C ₆ H ₁₁
cymene	1-isopropyl-4-methylbenzene, C ₁₀ H ₁₄
DBU	1,8-diazabicycloundec-7-ene, C ₉ H ₁₆ N ₂
DBUH	protonated 1,8-diazabicycloundec-7-ene, [C ₉ H ₁₇ N ₂] ⁺
DCM	dichloromethane, CH ₂ Cl ₂
DMAD	dimethyl acetylenedicarboxylate, C ₆ H ₆ O ₄
DMS	dimethylsulphide, SMe ₂
DMSO	dimethylsulphoxide, S(O)Me ₂
dcpe	1,2-bis(dicyclohexylphosphino)ethane, C ₂₆ H ₄₈ P ₂
dcpm	1,2-bis(dicyclohexylphosphino)methane, C ₂₅ H ₄₆ P ₂
diphars	<i>meso</i> -1,2-bis(phenyl(diphenylarsinoethyl)phosphino)ethane, C ₄₂ H ₄₂ As ₂ P ₂
dmpe	1,2-bis(dimethylphosphino)ethane, C ₆ H ₁₆ P ₂
dpae	1,2-bis(diphenylarsino)ethane, C ₂₆ H ₂₄ As ₂
dppa	1,2-bis(diphenylphosphino)acetylene, C ₂₆ H ₂₀ P ₂
dppb	1,4-bis(diphenylphosphino)butane, C ₂₈ H ₂₈ P ₂
dppe	1,2-bis(diphenylphosphino)ethane, C ₂₆ H ₂₄ P ₂
dppethylene	1,2-bis(diphenylphosphino)ethylene, C ₂₆ H ₂₂ P ₂
dppf	1,1'-bis(diphenylphosphino)ferrocene, C ₃₄ H ₂₈ FeP ₂
dppm	1,2-bis(diphenylphosphino)methane, C ₂₅ H ₂₂ P ₂

dppp	1,2-bis(diphenylphosphino)propane, $C_{27}H_{26}P_2$
dppph	1,2-bis(diphenylphosphino)benzene, $C_{30}H_{24}P_2$
e.s.d.	estimated standard deviation
ESI-MS	electrospray ionisation mass spectroscopy
Et	ethyl, C_2H_5
<i>fac</i>	facial
glycol	glycolato, 1,2-dioxyethane, $C_2H_4O_2$
h	hour
ⁱ Pr	isopropyl, C_3H_7
IR	infrared
KHMDS	potassium bis(trimethylsilyl)amide, $K[N(SiMe_3)_2]$
LDA	lithium diisopropylamide, $Li[N^iPr_2]$
LDBB	lithium 4,4'-di- <i>tert</i> -butylbiphenylide, $C_{20}H_{26}Li_2$
<i>m/z</i>	mass/charge
Me	methyl, CH_3
<i>mer</i>	meridional
Mes	mesityl, 2,4,6-trimethylphenyl, C_9H_{11}
min	minute
MS	mass spectroscopy
mt	2-mercapto-1-methylimidazole, $C_4H_5N_2S$
<i>N</i> -Carb	<i>N</i> -carbazolyl, $C_{12}H_8N$
ⁿ Bu	butyl, C_4H_9
ⁿ <i>J</i> _{AB}	<i>n</i> -bond coupling between nuclei A and B, expressed in Hz
OTf	trifluoromethanesulfonate, $[OSO_2CF_3]^-$
Ph	phenyl, C_6H_5
pin	pinacolato, 2,3-dimethyl-2,3-dioxybutane, $C_6H_{12}O_2$
pip	piperidine, $C_5H_{11}N$
py	pyridyl, C_5H_4N
pz	pyrazolyl, $C_3H_3N_2$
pz*	3,5-dimethylpyrazolyl, $C_5H_7N_2$
^t Bu	<i>tert</i> -butyl, CMe_3
THF	tetrahydrofuran, C_4H_8O
THT	tetrahydrothiophene, C_4H_8S
TMS	trimethylsilyl, $SiMe_3$

Tp	hydrotris(pyrazolyl)borate, $[\text{C}_9\text{H}_{10}\text{BN}_6]^-$
Tp*	hydrotris(3,5-dimethylpyrazolyl)borate, $[\text{C}_{15}\text{H}_{22}\text{BN}_6]^-$
triphos	1,1,1-tris(diphenylphosphinomethyl)ethane, $\text{C}_{41}\text{H}_{39}\text{P}_3$
triphos-asym	bis(2-diphenylphosphinoethyl)phenylphosphine, $\text{C}_{34}\text{H}_{33}\text{P}_3$
triphos ^{Me}	1,1,1-tris(dimethylphosphinomethyl)ethane, $\text{C}_{11}\text{H}_{27}\text{P}_3$
vdW	Van der Waals

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Introduction

Amongst first row p-block elements, boron is unique in having fewer valence electrons (three) than the number of valence orbitals available ($2s$, $2p_x$, $2p_y$, $2p_z$). In its highest oxidation state (III), the formation of three σ -bonds does not satisfy the octet rule and accordingly the chemistry of boron(III) is dominated by either multi-centre bonding or adduct formation with Lewis bases. Hence, the widespread use of boron(III) reagents as Lewis acids and the wealth of polyborane cluster chemistry. If the 20th century was the golden age of organotransition metal chemistry, the early years of the new millennium suggest a similarly exciting period of development for metal-boron chemistry. Boryl, borylenes and borido ligands are already emerging from curiosity status to that of synthetically valuable reactive intermediates, though many gaps remain to be explored.

Thus whilst organic boron compounds have long been of interest as organic reagents,¹⁻⁶ in the last two decades it is the organometallic aspect of boron chemistry that has greatly increased in scope, so-called borometallic chemistry. Prior to 1990, several classes of transition metal-boron species involving multicentre ($nc-2e$, $n>2$) bonding, such as ceramic borides, metallaborane and metallacarboranes, were well established.⁷⁻¹¹ However, well-defined σ -boryl complexes which contained conventional $2c-2e$ metal-boron bonds, were relatively unknown, despite being first reported in 1963.¹² The early development of the field of σ -boryl complexes has been attributed to the groups of Baker, Marder, Hartwig, Roper and Merola,¹³ though it was Merola *et al.* who reported the first fully characterised (until then a crystallographically characterised metal σ -boryl complex had proven elusive) iridium boryl complex *mer*-[IrH(BO₂C₆H₄)(Cl)(PMe₃)₃] (Figure 1).¹⁴

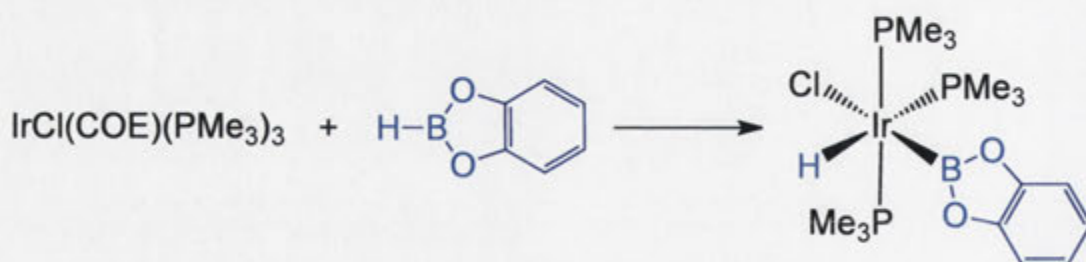


Figure 1: The first structurally characterised metal boryl complex, *mer*-[IrH(BCat)(Cl)(PMe₃)₃], reported by Merola *et al.* in 1990.¹⁴

As can be seen in Figure 1, the first fully characterised metal boryl complex had boron ligated by the catecholate group (phenylene-1,2-dioxy = 1,2-O₂C₆H₄). The actual first reported boryl complex involved a B(NMe₂)₂ ligand but was not structurally characterised.¹² It was not until decades later that catecholoboryl derivatives opened the door to this field. The catecholoboryl ligand (hereafter 'BCat') should be recognised as being pivotal to the development of this field, it having been noted in 1998 that of the approximately 30 metal boryl complexes known at the time, 20 of them were BCat complexes.⁷ The catecholato substituent is able to stabilise the neutral and electron-deficient boron atom *via* π -donation from the lone pairs of the two oxygen atoms, and also offers the kinetic stabilisation of being heterocyclic. The interest in σ -boryl complexes was, however, not only driven by fundamental interest. Other factors played an important and contemporaneous role:

- 1) The development of metal-catalysed hydroboration and diboration protocols that involved metal σ -boryl complexes, and
- 2) The activation of hydrocarbons, especially arenes, in processes that catalytically and often regioselectively afforded organoboranes.

Both of these streams of research were seen to address the increasing need for boronate esters, which through the increasing popularity of Suzuki-Miyaura cross-coupling protocols offered many practical and environmental advantages over more classical organometallic reagents.

After the deluge of new boryl complexes that followed the first fully characterised examples in 1990, more was yet to come, for in 1995 a new class of compounds was again discovered. Braunschweig *et al.*, on the rationale of equivalent metal alkylidene (M=CR₂) and imido (M=NR) complexes being known, synthesised and fully characterised the first bridging borylene complex [(μ -Me₂NB){Mn(CO)₂(η^5 -C₅H₅)}₂] (Figure 2).¹⁵ In the case of the first bridging borylene complex, and other early examples thereafter, the method of synthesising these complexes was performed using diborane compounds of the form B₂X₂Cl₂ (where X = NMe₂, ^tBu), which was a surprising result as the intended products were diborane(4)yl complexes, which were subsequently realised.¹⁶ More systematic approaches to bridging borylene complexes have appeared in the interim.¹⁷

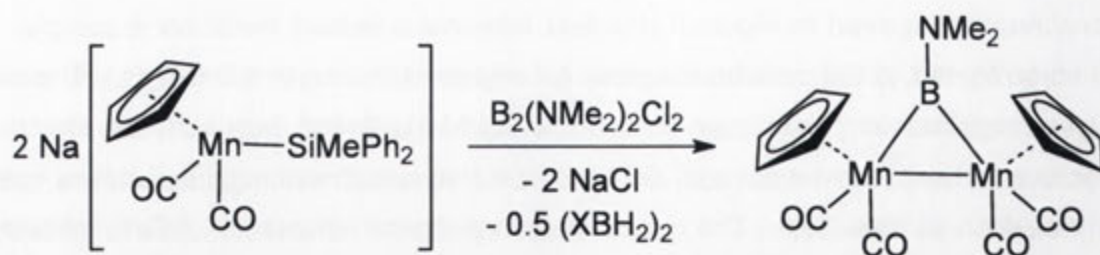


Figure 2: The first bridging borylene complex, $[(\mu\text{-Me}_2\text{NB})\{\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\}_2]$, reported in 1995 by Braunschweig *et al.*¹⁵

The use of diboranes to synthesise bridging borylene complexes was unfortunately greatly limited, and more general synthetic routes were therefore investigated. A systematic study of 2:1 mixtures of anionic transition metal species and aminodihaloboranes produced the first bridging borylene complexes synthesised without diborane, $[\text{M}_2\{\mu\text{-BN}(\text{SiMe}_3)_2\}(\mu\text{-CO})(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]$ (where $\text{M} = \text{Fe}, \text{Ru}$), from 2 equivalents of $\text{Na}[\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ and 1 equivalent of $(\text{Me}_3\text{Si})_2\text{NBCl}_2$.¹⁸ This salt-elimination type reaction has proven to be more general and more amenable to the production of related bridging borylene complexes.¹⁹

It should be noted that the same method does not allow the formation of hetero-dinuclear bridging borylene complexes by simply using 1 equivalent each of two different metal compounds, due to the difference in nucleophilicity of the carbonyl metalates.²⁰ However, a hetero-dinuclear bridging borylene complex was synthesised *via* the reaction of the boryl complex $[\text{Fe}(\text{BBr}_2)(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_5)]$ with the low-valent transition metal complexes $[\text{M}(\text{PCy}_3)_2]$ ($\text{M} = \text{Pd}, \text{Pt}$) to give $[\text{FeM}(\mu\text{-BBr})(\mu\text{-CO})(\text{CO})(\text{PCy}_3)_2(\eta^5\text{-C}_5\text{Me}_5)]$.²¹ Though of course interesting in their own right, perhaps one of the more intriguing aspects of these hetero-dinuclear bridging borylene complexes is that upon reaction with a further equivalent of $[\text{M}(\text{PCy}_3)_2]$ (where $\text{M} = \text{Pd}, \text{Pt}$), they can be converted to the novel trimetallic μ -borido species $[\text{FePtM}(\mu_3\text{-B})(\mu\text{-CO})(\mu\text{-Br})\text{Br}(\text{CO})(\text{PCy}_3)_2(\eta^5\text{-C}_5\text{Me}_5)]$ ($\text{M} = \text{Pd}, \text{Pt}$; Figure 3).²²

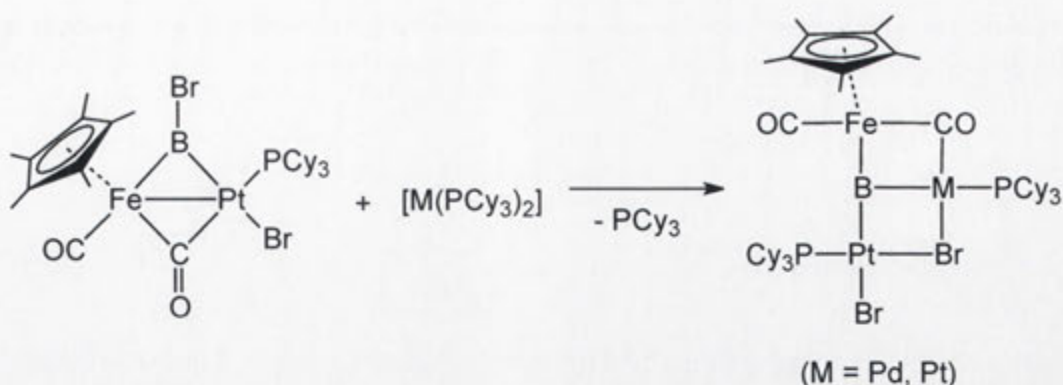


Figure 3: The structures of $[\text{FePtM}(\mu_3\text{-B})(\mu\text{-CO})(\mu\text{-Br})\text{Br}(\text{CO})(\text{PCy}_3)_2(\eta^5\text{-C}_5\text{Me}_5)]$ (M = Pd, Pt).²²

In 1998, Cowley and coworkers reported $(\text{CO})_4\text{Fe}(\text{BCp}^*)$ (Figure 4),²³ which may be considered a special example of a terminal borylene, followed later that year by Braunschweig discovering the first formal terminal borylene complexes involving two-coordinate boron. The reactions of dianionic transition metal complexes $\text{Na}_2[\text{M}(\text{CO})_5]$ (where M = Cr, W) with the aminodihaloborane $\text{Br}_2\text{BN}(\text{SiMe}_3)_2$ proceed *via* a double metathesis to yield the terminal borylene complexes $[(\text{CO})_5\text{M}=\text{BN}(\text{SiMe}_3)_2]$ (M = Cr, W; Figure 5).²⁴

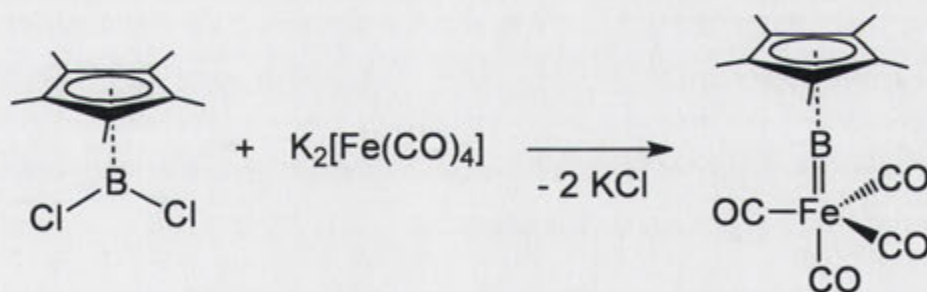


Figure 4: The synthesis of the unusual terminal borylene complex $[\text{Cp}^*\text{B}=\text{Fe}(\text{CO})_4]$.²³

Unlike the previously mentioned bridging borylenes, *terminal* borylenes possess 2-coordinate boron and are multiply bonded to the metal centre. In the interim, these reagents have been shown to serve as a borylene transfer agent to afford a range of other metal-borylene complexes. Remarkably, the species turned out to be relatively stable (considering the unsaturated nature of the boron atom within the complexes), with the crystalline solid being air tolerant for approximately an hour, whilst in solution

the complexes showed no sign of decomposition after a couple of days (under an inert atmosphere).

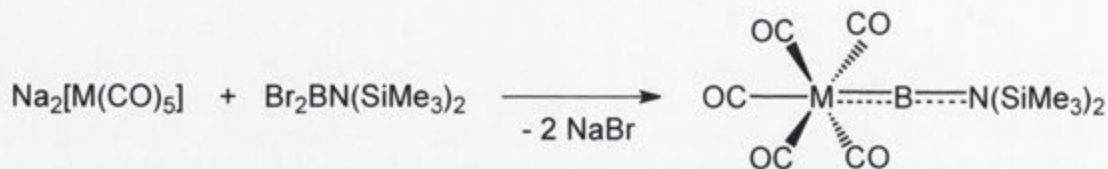


Figure 5: The synthesis of the first terminal borylene complex $[(\text{CO})_5\text{M}=\text{BN}(\text{SiMe}_3)_2]$ ($\text{M} = \text{Cr}, \text{W}$).²⁴

Metathesis reactions are not the only way that subsequent terminal borylene complexes have been synthesised. In 2008, Sabo-Etienne *et al.* reported the formation of a ruthenium terminal borylene, $[\text{Ru}(\text{H})\text{Cl}(\text{BMes})(\text{PCy}_3)_2]$, formed from mesitylborane (BH_2Mes) and the ruthenium dihydrogen complex $[\text{Ru}(\text{H})\text{Cl}(\text{H}_2)(\text{PCy}_3)_2]$.²⁵ The reaction proceeds at room temperature with the loss of two equivalents of hydrogen gas, which provides an entropic driving force for the reaction that is however reversible. Aldridge has subsequently demonstrated further examples of the dehydrogenative route to terminal borylenes.²⁶

The use of adducts of borane, *e.g.* $\text{L}\cdot\text{BH}_3$ ($\text{L} = \text{NMe}_3, \text{PMe}_3, \text{PPh}_3$), has been successful in coordinating the borane to metal centres *via* the photolysis of homoleptic $\text{M}(\text{CO})_6$ precursors ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$).²⁷ The highly labile nature of the borane coordination meant that species generated by this process were found to quickly decompose in solution or under vacuum, though isolation and crystallographic characterisation was in some cases possible.

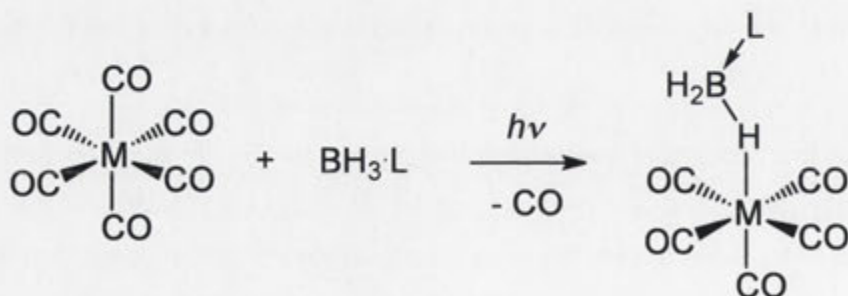


Figure 6: The coordination of borane adducts to chromium and tungsten hexacarbonyls *via* photolysis.²⁷

Polyhapto boracycles, most notably 'boratabenzene', have long been of interest due to their isoelectronic nature with benzene and the pyridinium ion. The first example of an anionic boratabenzene was generated through modification of a Cp ring already coordinated to a cobalt atom by reaction of cobaltocene with BBr_2Ph (and subsequently $[\text{NH}_4][\text{PF}_6]$) to give the salt $[\text{CoCp}(\text{PhBC}_5\text{H}_5)][\text{PF}_6]$ (Figure 7),²⁸ and the synthesis of the free $[\text{PhBC}_5\text{H}_5]^-$ anion was reported soon after by Ashe.²⁹ There are few examples of the hydrogen-substituted boratabenzene anion which was first observed in $\text{Fe}(\text{HBC}_5\text{H}_5)_2$,³⁰ and later characterised in itself as $\text{Li}[\text{HBC}_5\text{H}_5]$.³¹

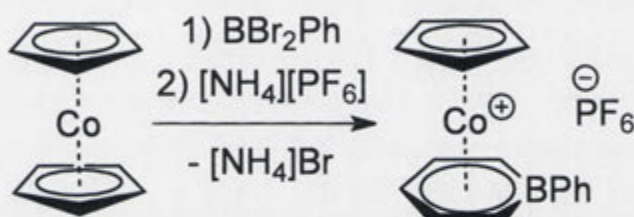


Figure 7: The synthesis of $[\text{CoCp}(\text{PhBC}_5\text{H}_5)][\text{PF}_6]$.²⁸

The preparation of neutral adducts of borabenzene have been demonstrated in recent years with a straightforward three step synthesis being reported by Fu *et al.* to a borabenzene precursor, which in effect enables the storage of a neutral masked 'borabenzene' delivery reagent (Figure 8).³²

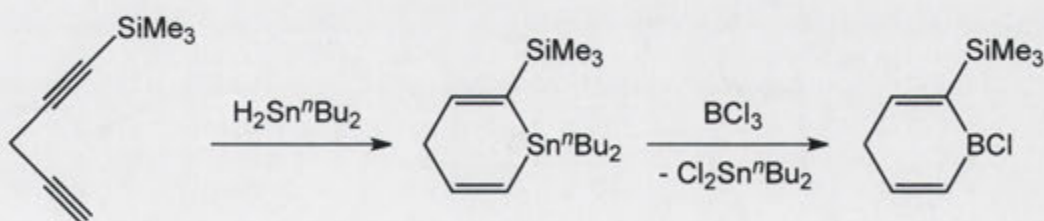


Figure 8: The synthesis of the borabenzene precursor reported by Fu *et al.*³²

Interestingly, a boron analogue of a ketenylidene was unintentionally synthesised by Shore *et al.* via insertion of a boron atom into an osmium carbonyl bond to give $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ (Figure 9).³³ The reactivity was probed and found to deviate from the ketenylidene species $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})$ in that the boron analogue did not react with proton sources or methylating agents.³⁴ However, it was demonstrated that

$(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ reacts with Lewis acidic BX_3 ($\text{X} = \text{Cl}, \text{Br}$) to produce vinylidene analogues $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CBX}_2)$, or with $\text{BH}_3\cdot\text{THF}$ to give $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCH}_2)$ in which the boron and carbon atoms do not swap positions.³⁴

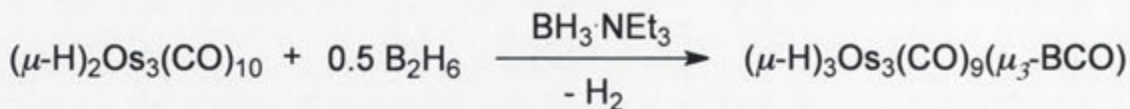


Figure 9: The accidental synthesis of $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-BCO})$ reported by Shore *et al.*³³

Metallaboratranes have enjoyed interest due to their potential as catalysts, but also because of their ability to exhibit novel coordination modes of the boron atom proximal to the metal centre, such as the rare example of pentacoordinate gold(I) in Figure 10.³⁵ An atrane is considered to consist of two bridgehead atoms bridged by three three-atom buttresses that support a transannular interaction between the bridgehead atoms, though non-traditional atrane constructs wherein one bridgehead is a metal and the other a boron with a transannular dative $\text{M}\rightarrow\text{B}$ bond have been demonstrated by Hill and coworkers.³⁶⁻³⁸ It has also been demonstrated that dinitrogen bonded to the iron centre in $\text{Fe}(\text{TPB})(\text{N}_2)$ (TPB = tris-[2-(diisopropylphosphino)phenyl]borane) can be functionalised, a process for which there are very few known examples, and has been attributed to the flexibility of the Fe-B linkage in the complex.^{39, 40}

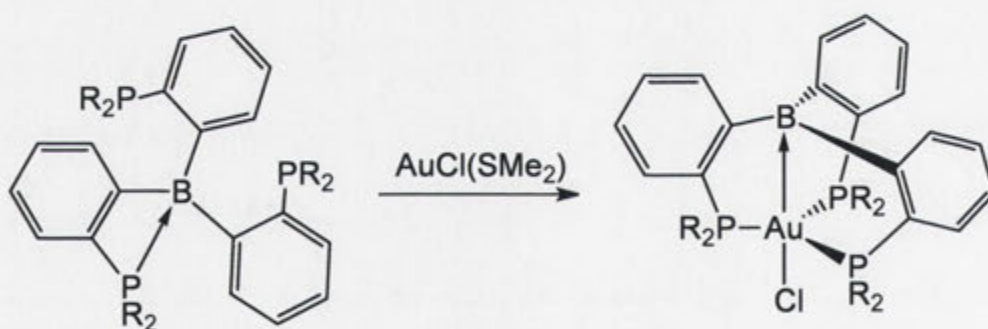


Figure 10: The synthesis of a gold chloride metallaboratrane.³⁵

Boron reagents have been utilised in the pursuit of selective C-H activation, where the combination of their strong σ -donor properties and an unoccupied p_z -orbital make such species ideal. This C-H activation has been demonstrated *via* rhodium catalysed

borylation of aliphatic compounds of the form $R-CH_3$ by reaction with B_2pin_2 (pin = pinacol; Figure 11).⁴¹

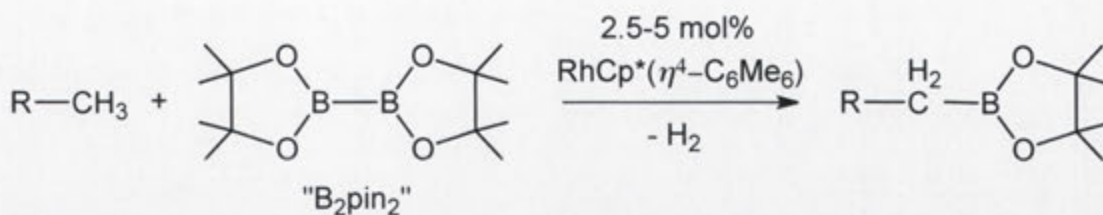


Figure 11: The rhodium catalysed borylation of alkanes.⁴¹

A similar process of borylation was performed *via* iridium catalysis on a range of alkylamines, which was followed by conversion of the newly introduced Bpin group to a BF_3 anion by reaction with $K[HF_2]$ (Figure 12), performed so as to simplify subsequent isolation.⁴²

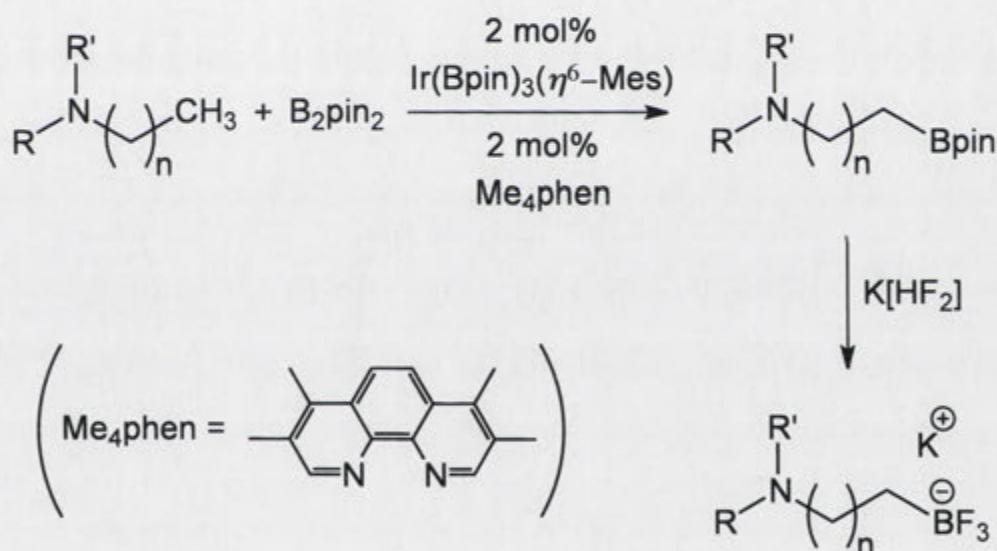


Figure 12: The iridium catalysed borylation of alkylamines by B_2pin_2 , followed by conversion to potassium trifluoroborate.⁴²

It should be noted that catalytic formation of B-B bonds using $PtBr_2$ by dehydrocoupling was also demonstrated in borane and carborane clusters.⁴³ More recently, the catalytic hydrogenolysis of diboranes such as B_2pin_2 and B_2cat_2 has been reported by reaction with dihydrogen at ~1-5 atm, where the catalysts were

immobilised group 10 metals (Raney Ni, Pd/C, Pt/C).⁴⁴ This process was conceptually developed after Hartwig *et al.* reported that elimination of B₂pin₂ from Rh(H)₂(Bpin)₂Cp* was disfavoured relative to the reductive elimination of HBpin.⁴⁵

The utility of BH₃·NH₃ for hydrogen storage has been mooted,⁴⁶ along with prior reports of the synthesis of B-N and B-P bonds from amine- and phosphine-borane adducts *via* dehydrocoupling (Figure 13).⁴⁷⁻⁵⁰

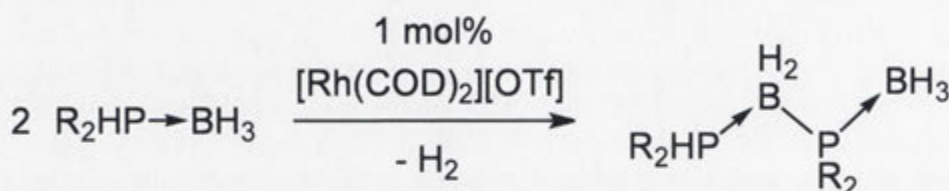


Figure 13: The dehydrocoupling of phosphine-borane adducts (R = ^tBu, Ph).^{48, 50}

Dehydrocoupling has also been demonstrated with other rhodium complexes such as [Rh(η^6 -C₆H₅F)(dppp)][BAR^F₄] (Ar^F₄ = C₆H₃(CF₃)_{3-3,5}).⁵⁰, though with [Rh(COD)₂][OTf] a number of cyclic oligomers and polymeric phosphine-boranes have been previously described (Figure 14).^{51, 52}

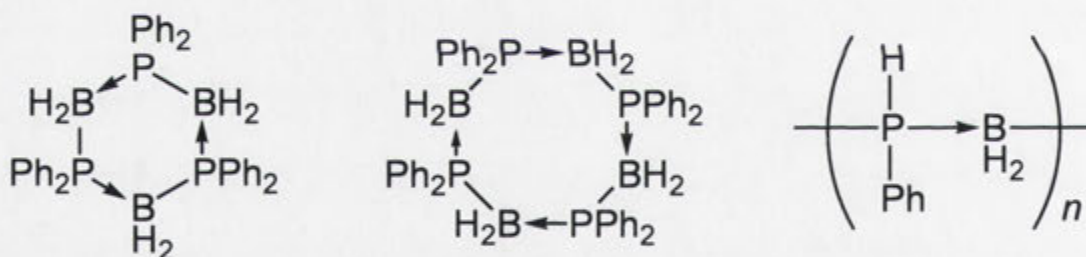


Figure 14: Cyclic oligomers derived from heating Ph₂HP·BH₃ as a melt (left, middle) and a polymer derived from heating PhH₂P·BH₃ as a melt (right).

With the target of new boron-containing organometallic complexes, the methods by which to tackle this goal can be envisioned. As discussed previously, alkylboranes and aminoboranes have played a major role in the development of the field of metal-boron chemistry.^{7, 13, 25} However, the organometallic potential of boron sources bearing a phosphorus substituent(s) are yet to be explored, especially with respect to phosphahaloboranes.

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Chapter 1

Boron- β -Functionalised σ -Organyl Ligands

1.1. Preamble

The metal-mediated transformations of alkynes, $\text{RC}\equiv\text{CR}$, are a technologically important area of organometallic chemistry. The coordination of compounds containing carbon-carbon multiple bonds to transition metal centres can affect their reactivities dramatically,¹ or simply protect the $\text{C}\equiv\text{C}$ bond whilst other functional groups are modified prior to deprotection. This vastly increases the potential scope of such reactions that can be performed. The interaction of acetylenes with transition metal complexes has proven invaluable for numerous carbon-carbon bond formation protocols in widely utilised processes such as couplings and oligomerisations leading to diynes, ene-ynes, arenes and cyclopolyolefins (Reppe chemistry) and polyacetylenes (precursors to conducting polymers). Whilst classical organic synthetic routes (alkene halogenation/dehydrohalogenation, acyl dehydration etc) continue to dominate the large scale industrial synthesis of alkynes, for high value-added fine chemicals the Sonogashira coupling protocol has proven extremely versatile and reliable (Figure 1).²⁻⁴ This involves the reaction of a terminal acetylene with an aryl or vinyl halide in the presence of palladium and copper catalysts to install $\text{C}(\text{sp})\text{-C}(\text{sp}^2)$ bonds. Whilst less developed, other transition metals have also been shown to offer promise as catalysts, though the intimate mechanistic details may vary.⁵

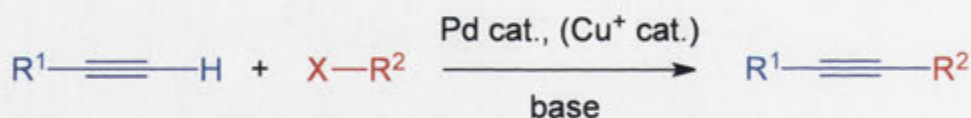


Figure 1: General reaction scheme for a Sonogashira cross coupling reaction. (R^1 = aryl, heteroaryl, vinyl; R^2 = aryl, heteroaryl, alkenyl, alkyl, silyl; X = I, Br, Cl, OTf).⁴

In instances where the Sonogashira coupling reaction is ineffective, other methodologies have been developed that involve organometallic acetylide intermediates such as the Stille reaction and the Negishi reaction, which require tin and zinc acetylene reagents respectively.^{6, 7} However, the Suzuki reaction, which involves the use of organoboron acetylene reagents, possesses several advantages over organometallic acetylene based reactions, for example a much lower toxicity which has important implications in areas such as the synthesis of pharmaceuticals.⁸

In processes such as the Sonogashira protocol, transient cuprous alkynyls are employed as the nucleophilic partner. In contrast, Suzuki-Miyaura cross couplings employ boronic esters, RB(OR')_2 , acids RB(OH)_2 , or their anhydrides $(\text{RBO})_3$ as the nucleophilic source of 'R'. In recent times, organotrifluoroborates $\text{K}[\text{RBF}_3]$ and *N*-methyliminodiacetate (MIDA) ester derivatives have been demonstrated to serve as effective alternatives,^{9, 10} however, the intermediates have in general not been pursued. The work described in this chapter therefore addresses the organometallic chemistry of such alkynyl-boron species in association with a variety of transition metal reagents.

1.2. Alkynyltrifluoroborates

Following the successful deployment of other organotrifluoroborates, $\text{K}[\text{RBF}_3]$, alkynyltrifluoroborates, $[\text{RC}\equiv\text{CBF}_3]^-$ (where $\text{R} = \text{H}, \text{Ph}, \text{TMS}, \text{etc.}$),¹¹ have been shown to be versatile synthetic reagents for use in, *e.g.*, Suzuki-Sonogashira hybrid coupling reactions.⁹ The relative ease of synthesis and purification of potassium alkynyltrifluoroborates in addition to their longevity upon storage are important factors that contribute to their general utility (Figure 2). Most useful, however, is the 4-coordinate boron centre, which obviates the need for extraneous base, which is otherwise required to activate more conventional 3-coordinate boron reagents such as boronic acids and esters.

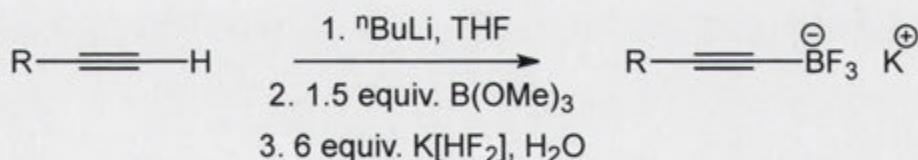


Figure 2: The general reaction scheme to synthesise substituted potassium alkynyltrifluoroborate salts from a substituted terminal acetylene (where $\text{R} = \text{alkyl}, \text{aryl}, \text{TMS}, \text{etc.}$).⁹

The carbocentric focus has previously, with impressive success, considered the boron component expendable; the intimate nature of the interaction with the metal centre has been of little interest. Intrigued by the observation by Stephan that

alkynylboranes may coordinate to nickel(0) in an $\eta^3\text{-C,C',B}$ manner,¹² a general exploration of the coordination chemistry of alkynyltrifluoroborates was undertaken.

The synthesis of the corresponding terminal ethynyltrifluoroborate was attempted according to reported procedures based on the commercially available $\text{BrMgC}\equiv\text{CH}$ as the starting material,⁹ bypassing the need to first lithiate ethyne using $n\text{BuLi}$. The reaction could never, however, be satisfactorily reproduced due to the variable but consistently poor quality of the $\text{BrMgC}\equiv\text{CH}$ reagent as received from Sigma-Aldrich (purported to be 0.5 M solution in THF). In contrast, no difficulties were encountered in obtaining the substituted derivative $\text{K}[\text{PhC}\equiv\text{CBF}_3]$.⁹ Given that structural data is not available for alkynylfluoroborates, the characterisation of $\text{K}[\text{PhC}\equiv\text{CBF}_3]$ included a crystallographic study (Figure 3), which revealed, in addition to the gross composition, a 3-dimensional extended network of $\text{K}\cdots\text{F}$ interactions (Figure 4) that presumably contribute to the stability of the compound.

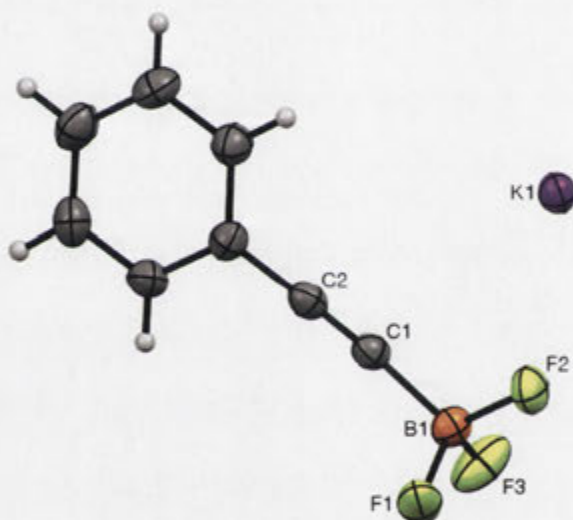


Figure 3: The molecular structure of $\text{K}[\text{PhC}\equiv\text{CBF}_3]$. (Solvent molecules omitted for clarity, 50% displacement ellipsoids).[§] Selected bond lengths (Å), angles (°) and intermolecular distances (Å): B1-F1 1.403(6); B1-F2 1.403(6); B1-F3 1.398(6); B1-C1 1.599(7); C1-C2 1.195(6); B1-C1-C2 174.6(5); F1 $\cdots$ K1 2.756(3); F2 $\cdots$ K1 3.069(3); F3 $\cdots$ K1 2.692(3).

[§] The molecular structure was previously unreported, though the compound was synthesised according to a literature procedure.⁹

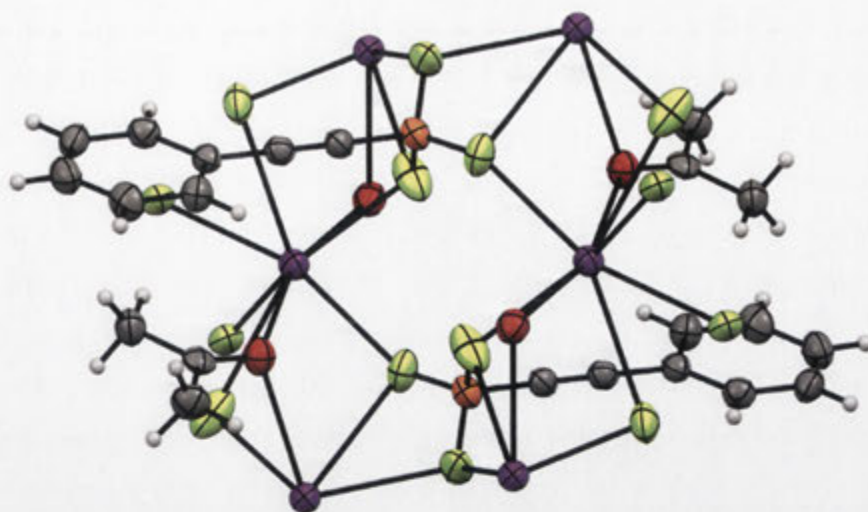


Figure 4: The molecular packing of $\text{K}[\text{PhC}\equiv\text{CBF}_3]\cdot\text{C}_3\text{H}_6\text{O}$ showing the extended system of intermolecular $\text{F}\cdots\text{K}$ and $\text{O}\cdots\text{K}$ interactions. Key: grey - carbon; white - hydrogen; orange - boron; green - fluorine; purple - potassium; red - oxygen. (50% displacement ellipsoids).

A remarkably general reaction of alkynes is their coordination to ' $\text{Co}_2(\text{CO})_8$ ' as a result of facile reactions with $\text{Co}_2(\text{CO})_8$. Indeed, the alkynylborane $\text{RC}\equiv\text{CBCat}$ has been shown to also form such an adduct.¹³

The reaction of $\text{K}[\text{PhC}\equiv\text{CBF}_3]$ with $\text{Co}_2(\text{CO})_8$ in DCM afforded a brown coloured solid which was found to have three strong absorptions in the solution IR spectrum (DCM) at ν_{CO} 2015, 2044 and 2083 cm^{-1} ,¹⁴ distinct from the starting material ($\text{Co}_2(\text{CO})_8$: ν_{CO} 2024, 2041, 2068 cm^{-1})¹⁴ and with a similar intensity profile to that observed for $\text{Co}_2(\mu\text{-HCCR})(\text{CO})_6$, though moved to lower frequency which is consistent with the overall negative charge of the complex.

No reaction, coordination or transalkynylation,² was observed for the equimolar combination of $\text{K}[\text{PhC}\equiv\text{CBF}_3]$ and Vaska's complex,⁸ though this reagent is known to only form stable adducts with electron-poor alkynes, *e.g.* DMAD.¹⁵ In contrast, the ' $\text{Pt}(\text{PPh}_3)_2$ ' fragment is known to coordinate to a range of alkynes. Stirring of $\text{K}[\text{PhC}\equiv\text{CBF}_3]$ with $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ in THF overnight failed to provide any indication of a reaction, as determined by ^{31}P NMR analysis, which confirmed the major component to be $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ (δ_{P} 35.2) accompanied by trace amounts of $\text{Pt}(\text{O}_2)(\text{PPh}_3)_2$ (δ_{P}

⁸ Heated to reflux in THF for 2 h; IR (THF) found only Vaska's complex (1967 cm^{-1}).

18.0) and $\text{Pt}(\text{PPh}_3)_3$ (δ_{P} 50.9), the latter generated through normal phosphine scrambling displayed by $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ over extended periods of time in solution.¹⁶

If a disubstituted alkyne is reacted with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$, for example diphenylacetylene, then *via* loss of PPh_3 an alkyne complex $\text{Ru}(\eta^2\text{-PhC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2$ can be synthesised (Figure 5).¹⁷ However, if a terminal alkyne is used instead of a disubstituted one, then the reaction can yield a ruthenium hydride complex *via* the same process of loss of a labile PPh_3 and formation of an alkyne complex, followed this time by insertion of the ruthenium centre into the terminal alkyne C-H bond. The formation of a ruthenium hydride complex requires by necessity a terminal alkyne to provide the hydrogen atom that will become the metal hydride and is therefore a more specialised reaction than those discussed previously. Examples of a variety of substituents at the opposite end of the acetylene do exist, such as an alkyne,¹⁸ carbyne,¹⁹ silane,²⁰ phosphonium salt,²¹ making the reaction useful for attaching alkynes to ruthenium whilst retaining the reactivity of the alkyne group and the substituent it bears.

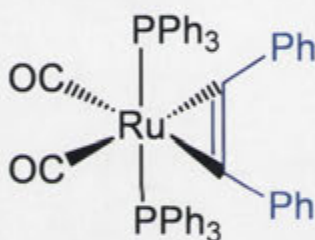


Figure 5: The structure of $\text{Ru}(\eta^2\text{-PhC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2$ synthesised by Hill *et al.*¹⁷

Treating $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ with a slight excess of $\text{K}[\text{PhC}\equiv\text{CBF}_3]$ in THF was found to generate a new compound after 1 h stirring at ambient conditions. The new compound, presumed to be the alkyne complex $\text{K}[\text{Ru}(\text{PhC}\equiv\text{CBF}_3)(\text{CO})_2(\text{PPh}_3)_2]$ (Figure 6), was evident in the IR spectrum (THF) with the development of two absorptions at 1857 and 1942 cm^{-1} [*cf.* ν_{CO} 1875, 1963 cm^{-1} for neutral $\text{Ru}(\eta^2\text{-PhC}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2$],¹⁷ though as a very minor product compared to unreacted $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ (1908 cm^{-1}). Further stirring, however, failed to result in further spectroscopic changes over an additional 11 days at room temperature. The mixture was therefore heated to near reflux for 30 min, but once again this caused no change to the product distribution. Addition of an equimolar amount of 18-crown-6 followed by 5 hours stirring afforded a new pair of

very weak stretches (ν_{CO} 1982, 2032 cm^{-1}) which correspond to those of the oxidative addition product $\text{Ru}(\text{H})(\text{C}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2$, which is also the product of the direct reaction of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ with $\text{HC}\equiv\text{CPh}$ [cf. ν_{CO} 1976, 2032 cm^{-1} for $\text{Ru}(\text{H})(\text{C}\equiv\text{C}\{\text{C}_6\text{H}_4\text{Me-4}\})(\text{CO})_2(\text{PPh}_3)_2$].^{†20} Whilst this most likely arose from hydrolysis of the C-BF₃ functional group, it should be recalled that the synthesis of $\text{K}[\text{PhC}\equiv\text{CBF}_3]$ involves an aqueous step, *i.e.*, the metal centre must in some way be mediating the hydrolysis relative to the free fluoroborate salt. Whether the hydrolysis proceeds whilst the alkyne is η^2 -coordinated or *via* an alkyne/vinylidene rearrangement is unclear, however, with some ion-pairing involved it may well be that the interaction with 18-crown-6 induces such a rearrangement and that the β -boronato-vinylidene (*vide infra*) is more prone to hydrolysis or protonation at the more accessible ruthenium(0) centre.

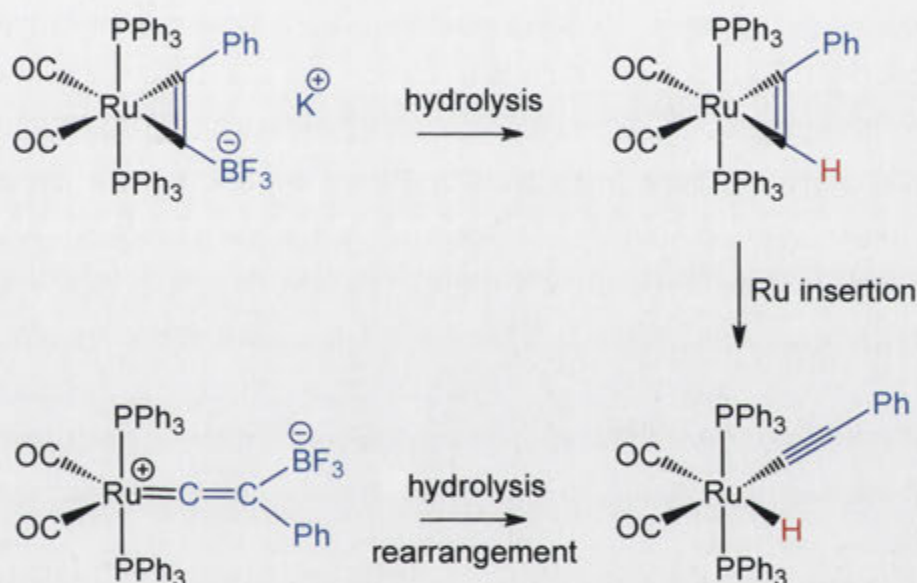


Figure 6: Proposed products for the reaction of $\text{K}[\text{PhC}\equiv\text{CBF}_3]$ with $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$, *via* alkyne-coordination (top) or β -boronato-vinylidene formation (bottom).

The inability to push the equilibrium to the desired $\text{K}[\text{Ru}(\text{PhC}\equiv\text{CBF}_3)(\text{CO})_2(\text{PPh}_3)_2]$ product is reminiscent of the failure of the reaction of the same precursor with $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ to proceed to completion. In both examples, it would appear that the substitution of one phosphine by an electron-rich alkyne competed with re-coordination

[†] $\text{Ru}(\text{H})(\text{C}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2$ has not been previously described in the literature, which is why comparison is made to the analogous tolyl derivative.

of the phosphine. The complex $\text{Ru}(\text{C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2$ serves as an alternate source of the " $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2$ " fragment with the advantage that gaseous ethane is lost from the system obviating any competition with the desired addend. However, after 24 hours stirring, no reaction between the ethane complex and $\text{K}[\text{PhC}\equiv\text{CBF}_3]$ was apparent (IR), the only two absorptions being those due to $\text{Ru}(\text{C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2$ (THF: ν_{CO} 1895, 1952 cm^{-1}). After a further 24 hours the starting materials had been completely consumed to yield only the hydrolysed product $\text{Ru}(\text{H})(\text{C}\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2$ (THF: ν_{CO} 1987, 2033 cm^{-1}).

In a similar manner, only an incomplete reaction ensued between $\text{K}[\text{Me}_3\text{SiC}\equiv\text{CBF}_3]$ and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ to provide the desired alkyne complex $\text{K}[\text{Ru}(\text{Me}_3\text{SiC}\equiv\text{CBF}_3)(\text{CO})_2(\text{PPh}_3)_2]$ (THF: ν_{CO} 1857, 1941 cm^{-1}) but only alongside a majority of unreacted starting complex $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ (THF: ν_{CO} 1909 cm^{-1}). Extended reaction times (10 days) saw the gradual development of the hydrolysis product $\text{Ru}(\text{H})(\text{C}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{PPh}_3)_2$ (THF: ν_{CO} 1986, 2024 cm^{-1}) without any discernible increase in the proportion of $\text{K}[\text{Ru}(\text{Me}_3\text{SiC}\equiv\text{CBF}_3)(\text{CO})_2(\text{PPh}_3)_2]$. As with $\text{K}[\text{PhC}\equiv\text{CBF}_3]$, the use of $\text{Ru}(\text{C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2$ did not facilitate formation of the $\text{K}[\text{Ru}(\text{Me}_3\text{SiC}\equiv\text{CBF}_3)(\text{CO})_2(\text{PPh}_3)_2]$ in the short term, whilst protracted (11 days) stirring eventually led to the formation of $\text{Ru}(\text{H})(\text{C}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{PPh}_3)_2$ alongside unreacted $\text{Ru}(\text{C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2$.

The repeated observation of hydrolysed side products in reactions involving $\text{K}[\text{PhC}\equiv\text{CBF}_3]$ and $\text{K}[\text{Me}_3\text{SiC}\equiv\text{CBF}_3]$ was curious given their synthesis under aqueous conditions such that it may be surmised that the metal plays a significant but inexplicable role.

1.3. Ethynyl-BMIDA, $\text{HC}\equiv\text{CB}(\text{O}_2\text{CCH}_2)_2\text{NMe}$

The susceptibility of the ethynyltrifluoroborates to lose the BF_3 moiety *via* hydrolysis as previously discussed called for a more hydrolytically stable boron-based substituent. The substituent selected was a relatively new advancement that involves a boron centre protected by a *N*-methylinodiacetate (MIDA) (Figure 7).¹⁰ The BMIDA substituent was pioneered primarily as a more stable alternative to the highly reactive polyenylboronic acids that were previously utilised for the Suzuki-Miyaura reaction.²² However, it should also be noted that the BMIDA group was similarly lauded for being

easily removed under mild aqueous basic conditions. A further feature is the transannular N $\rightarrow$ B interaction that renders the boron centre 4-coordinate, thereby polarising the B-C bond so as to facilitate transmetallation.

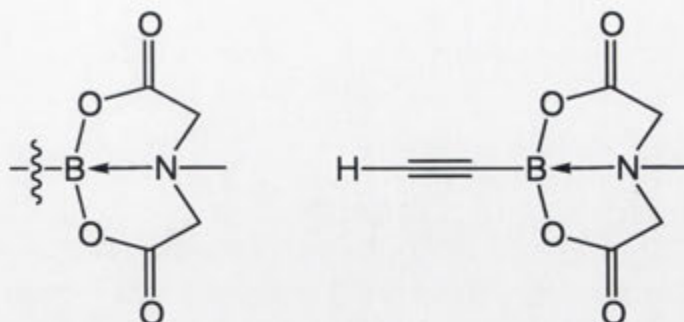


Figure 7: The boron protected *N*-methyliminodiacetate substituent (BMIDA) (left) and the ethynyl-BMIDA reagent (right).

Given that the BMIDA group had been primarily developed as an improved protecting group for cross-coupling reactions, its organometallic chemistry has yet to be explored. From an organometallic perspective, ethynyl-BMIDA is of interest in providing three potentially reactive sites, viz. the terminal C-H, the C $\equiv$ C bond and the polar B-C bond.

1.4. Alkynyl complexes derived from ethynyl-BMIDA

The reaction of equimolar amounts of ethynyl-BMIDA and $\text{Ru}(\text{C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2$ yielded the intended ruthenium hydride σ -alkynyl complex $\text{Ru}(\text{H})(\text{C}\equiv\text{CBMIDA})(\text{CO})_2(\text{PPh}_3)_2$ in which the ruthenium had inserted into the terminal alkyne C-H bond. The identity of the product was confirmed by the appearance of a hydride resonance in the ^1H NMR spectrum at -5.87 ppm (t, $\text{cis-}^2J_{\text{PH}}$ 20.0 Hz), as well as two new IR stretches appearing at ν_{CO} 1988 and 2032 cm^{-1} . Although a ν_{RuH} absorption could not be unambiguously identified, an absorption at 2081 cm^{-1} is assigned to the ν_{CC} absorption of the alkynyl ligand. The ^{31}P NMR spectrum revealed a

single doublet at 45.0 ppm (d, $^{cis-2}J_{PH}$ 4.5 Hz)[§] due to the *trans*-disposed chemically equivalent nature of the two phosphorus nuclei.

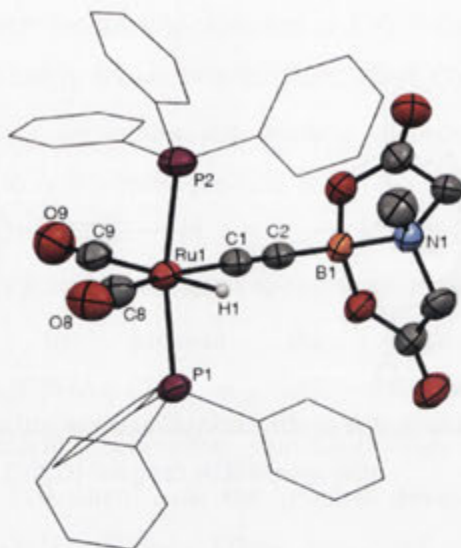


Figure 8: The molecular structure of $\text{Ru(H)(C}\equiv\text{CBMIDA)(CO)}_2\text{(PPh}_3\text{)}_2$. (Solvate molecules and some hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): Ru1-C1 2.060(7); Ru1-H1 1.560; Ru1-C8 1.899(8); Ru1-C9 1.955(8); C1-C2 1.21(1); B1-C2 1.54(1); B1-N1 1.666(9); C8-O8 115.6(9); C9-O9 1.131(9); Ru1-C1-C2 178.1(6); C1-C2-B2 171.5(8).

The solid-state structures[†] (Figure 8) revealed that the asymmetric unit cells contained two crystallographically distinct molecules of $\text{Ru(H)(C}\equiv\text{CBMIDA)(CO)}_2\text{(PPh}_3\text{)}_2$. The four Ru-C≡C angles were found to be near linear, as would be expected with the involvement of the sp-hybridised carbon triple bond, with values of 178.1(6), 175.7(6), 176.0(4) and 176.7(4) $^\circ$. However, for the four C≡C-B angles observed, three were found to be near linear with values of 171.5(8), 174.2(7) and 177.2(5) $^\circ$, whilst one was found to deviate significantly from linearity with a value of 164.5(5) $^\circ$ (Figure 9). The bond lengths of the atoms involved are

[§] Although measured in the $^{31}\text{P}\{^1\text{H}\}$ mode, coupling due to the hydride ligand is still observed as the hydride resonance falls outside the usual decoupling range.

[†] Two crystallographically distinct solid-state structures were determined and both found to be the desired product, though both solvated with DCM. Molecular metrical parameters of interest did not vary significantly between the two crystal forms except where discussed.

crystallographically the same between the linear and non-linear solid-state structures, eliminating the possibility that the non-linear $\text{C}\equiv\text{C}-\text{B}$ of $164.5(5)^\circ$ was due to a different chemical environment. This distortion is therefore most likely due to the intermolecular packing forces, given that the alkynyl ligand protrudes from the complex (Figure 10 & Figure 11).

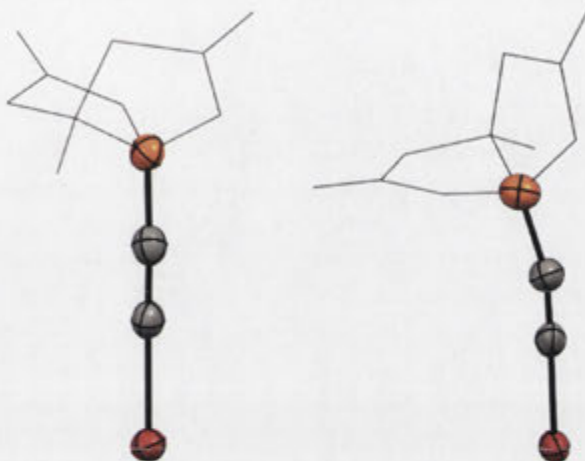


Figure 9: The $\text{Ru}-\text{C}\equiv\text{C}-\text{BMIDA}$ unit from the crystallographically distinct molecules of the $\text{RuH}(\text{C}\equiv\text{CBMIDA})(\text{CO})_2(\text{PPh}_3)_2$ crystal structure, illustrating the expected near linear form (left) and the non-linear form (right). (Solvate molecules, PPh_3 ligands, carbonyl ligand and hydrogen atoms omitted for clarity, MIDA groups simplified, 50% displacement ellipsoids).

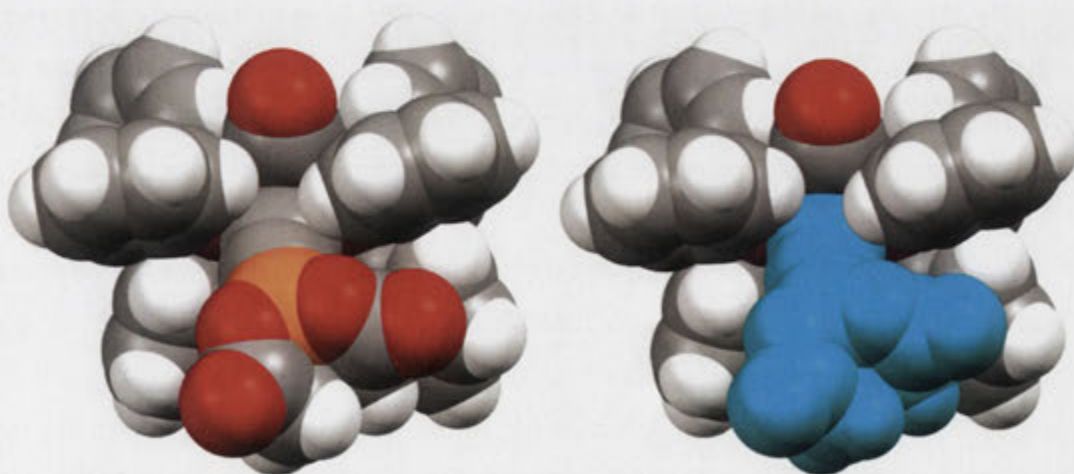


Figure 10: Spacefill representations of the non-linear $\text{Ru}(\text{H})(\text{C}\equiv\text{CBMIDA})(\text{CO})_2(\text{PPh}_3)_2$ molecule (left) and the same diagram with the $\text{C}\equiv\text{CBMIDA}$ ligand highlighted in turquoise (right). (Solvate molecules omitted for clarity, 50% displacement ellipsoids).

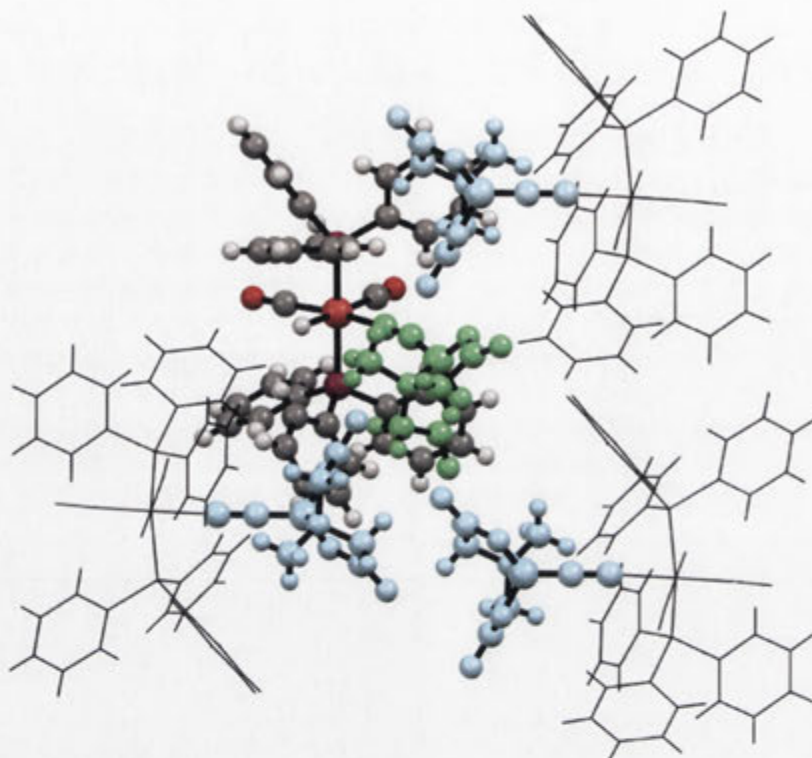


Figure 11: Four molecules of $\text{Ru}(\text{H})(\text{C}\equiv\text{CBMIDA})(\text{CO})_2(\text{PPh}_3)_2$, which illustrate the packing of a non-linear BMIDA substituent (green) surrounded by three near-linear BMIDA substituents (blue) in the solid-state. (Solvate molecules omitted for clarity, $\text{Ru}(\text{H})(\text{CO})_2(\text{PPh}_3)_2$ groups simplified).

The MS analysis for $\text{Ru}(\text{H})(\text{C}\equiv\text{CBMIDA})(\text{CO})_2(\text{PPh}_3)_2$, with a clearly observed $[\text{M} + \text{K}]^+$ (m/z 902) isotopic manifold, was unremarkable other than to note facile alkynyl cleavage indicated by a significant peak attributable to $[\text{M} + \text{NCMe} - \text{C}\equiv\text{CBMIDA}]^+$ (m/z 724). Notably, no peaks attributable to C-BMIDA fragmentations were identified.

The insertion of the ruthenium into the alkyne C-H bond was found to be reversible such that exposure of $\text{Ru}(\text{H})(\text{C}\equiv\text{CBMIDA})(\text{CO})_2(\text{PPh}_3)_2$ to air resulted in gradual formation of the dioxygen adduct $\text{Ru}(\text{O})_2(\text{CO})_2(\text{PPh}_3)_2$ (ν_{CO} 1945, 2005 cm^{-1}). The alkyne elimination process could, however, be prevented by conversion of the hydrido complex to the corresponding chloro derivative through reaction with chloroform over 2 hours. The $\text{RuCl}(\text{C}\equiv\text{CBMIDA})(\text{CO})_2(\text{PPh}_3)_2$ product was characterised by a significant shift of the PPh_3 groups to lower frequency in the ^{31}P NMR spectrum (δ_{P} 17.7)

compared to $\text{Ru(H)(C}\equiv\text{CBMIDA)(CO)}_2(\text{PPh}_3)_2$ (δ_{P} 45.0). The IR analysis showed a similar shift from the precursor (ν_{CO} 1988, 2032 cm^{-1})⁵ to higher frequency for the chloro complex (ν_{CO} 1995, 2058 cm^{-1}) as observed previously for the 4-tolyethynyl complex for $\text{RuCl(C}\equiv\text{C(C}_6\text{H}_4\text{Me-4))}(\text{CO)}_2(\text{PPh}_3)_2$ (ν_{CO} 1995, 2055 cm^{-1}).²³ The ν_{CC} absorption (2080 cm^{-1}) was surprisingly insensitive to hydride/chloro metathesis being unchanged from that of the precursor (2081 cm^{-1}).

The BMIDA methyl and two methylene protons were observed in the ^1H NMR spectrum at 3.08, 3.73 and 3.80, respectively, where the methylene protons had the characteristic $^2J_{\text{HH}}$ value of 16.4 Hz. Interestingly, for $\text{RuCl(C}\equiv\text{CBMIDA)(CO)}_2(\text{PPh}_3)_2$ a $^4J_{\text{HH}}$ coupling was observed between the methyl and methylene groups with a value of 4.0 Hz (Figure 12), which had not been observed for other complexes containing the BMIDA group. The resonance for the boron atom in the ^{11}B NMR spectrum was also observed to shift to slightly higher frequency from 4.7 ppm to 5.5 ppm, but given the broadness of these resonances, this is of borderline significance.

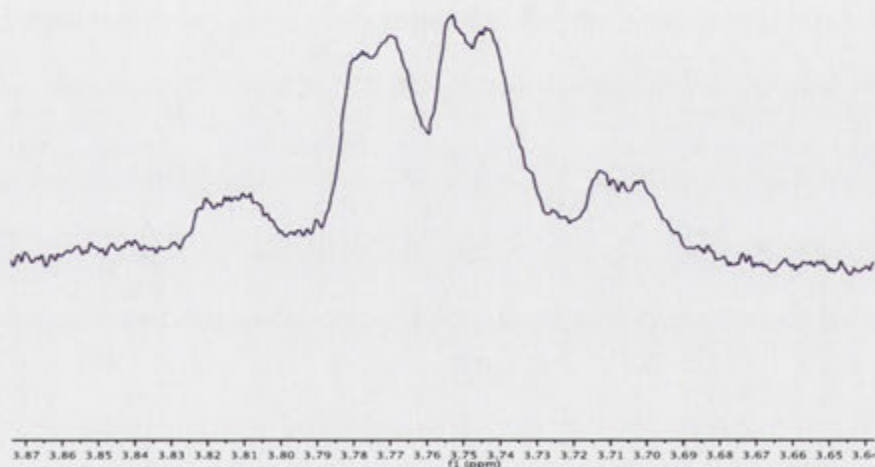


Figure 12: The ^1H NMR spectrum illustrating the pair of doublets of doublets due to the two NCH_2 groups that have inequivalent hydrogen atoms.

⁵ Caution is recommended when interpreting ν_{CO} data for hydrido-carbonyl complexes since coupling of the ν_{RuH} and ν_{CO} oscillators arises, especially when a *trans*-H-Ru-CO geometry is involved.

1.5. Vinylidene complexes of ethynyl-BMIDA

Another outcome of alkynes reacting with organometallic species is the synthesis of vinylidenes, which possesses a 'M=C=C' functional group. There have been two mechanisms suggested for this process: the first involves oxidative addition of the alkyne to the metal centre, as described previously for the formation of a ruthenium hydride complex, followed by a 1,3-hydrogen shift of the hydride to the β -carbon atom of the α -alkynyl substituent; the second mechanism involves the concomitant approach of the metal to the α -carbon as the α -hydrogen contorts itself toward the β -carbon (Figure 13).²⁴

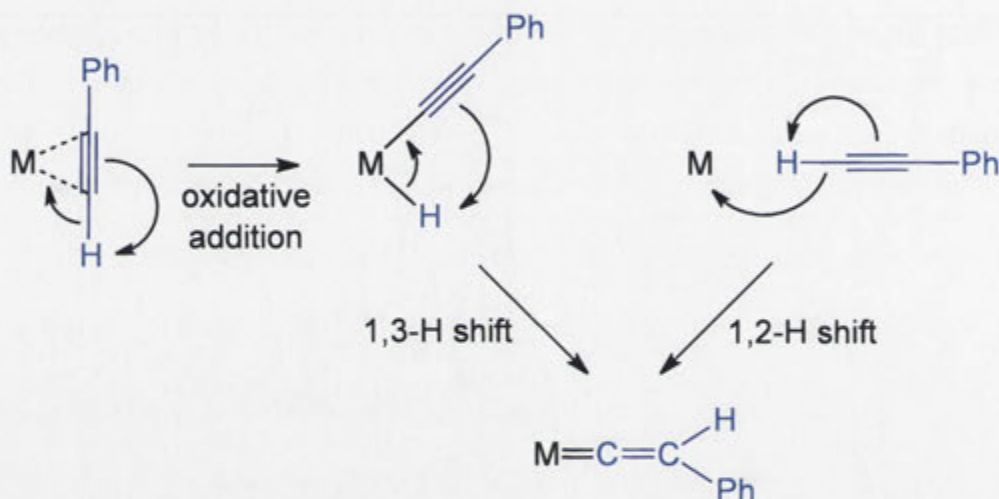


Figure 13: Two proposed mechanisms for the synthesis of a vinylidene from an alkyne: oxidative addition of the alkyne to the metal centre to give a metal hydride, followed by a 1,3-hydrogen shift (left) or directly from a simultaneous 1,2-hydrogen shift upon complexation of the alkyne (right).

Whilst the oxidative addition of the alkyne C-H bond to the electron rich d^8 - $\text{Ru}^0(\text{CO})_2(\text{PPh}_3)_2$ fragment is to be expected, the vast majority of alkyne ruthenium chemistry involves the metal in the divalent (d^6) state.[§] The simple Dewar-Chatt-Duncanson model,²⁵ in describing alkyne coordination, ignores the occupied π -orbital orthogonal to the MC_2 plane. For metal centres with low d -occupancies (d^n , $n < 6$), this

[§] For a complete review please see 'Comprehensive Organometallic Chemistry, Vol. I and II'.

orbital may serve as a π -donor towards vacant t_{2g} -type metal orbitals,^{26, 27} leading to so-called 4-electron alkyne coordination, which is especially prevalent for d^4 -octahedral alkyne complexes. For d^6 -octahedral metals (such as Ru^{II}), the t_{2g} orbitals are already fully occupied such that this interaction becomes destabilising. Accordingly, the reactions of $Ru(II)$ substrates with alkynes often proceed in such a way as to avoid, where possible, simple η^2 -coordination. By far the most common pathway involves rearrangement to a vinylidene ligand, which has no π -donor capacity but superlative π -acidity. The 1,2-substituent shift is most commonly encountered for the C-H of terminal alkynes,²⁴ however other groups (silyl,²⁸ stannyl,²⁹ thiolate,³⁰ selenolate³¹) are also able to undergo this rearrangement, albeit with less facility. The accepted mechanism involves a concerted 1,2-shift, though intermolecular proton transfer may be mediated by extraneous base in the case of a hydrogen shift.

There are only a few recent examples of vinylidene complexes bearing boron substituents (Figure 14), though all those reported possessed 3-coordinate boron centres. Interestingly, the osmium complexes were generated *via* a 1,3-shift of the boryl substituent from the Os centre to the β -carbon of the phenyl alkynyl substituent.³² ³³ The rhodium example was generated by a more traditional 1,3-H shift of the hydride in $[Rh(H)(C\equiv CBMes_2)Cl(P^iPr_3)_2]$ to the β -carbon of the alkynyl substituent.³⁴ Therefore, to explore the possibility of a vinylidene bearing a 4-coordinate boron centre, ethynyl-BMIDA and the salt $[RuCl(dppe)_2][PF_6]$ were utilised, given its extensive precedent for vinylidene formation.³⁵⁻³⁷

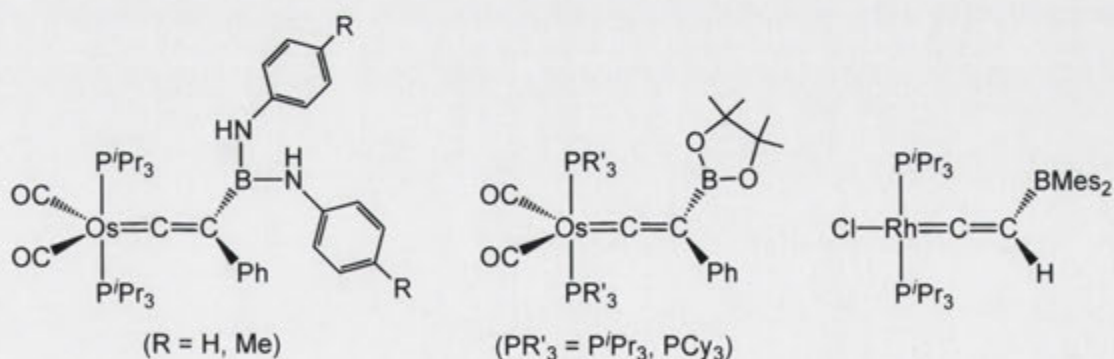


Figure 14: Prior examples of vinylidene functionalities bearing 3-coordinate boron centres.³²⁻³⁴

Addition of one equivalent of ethynyl-BMIDA to $[\text{RuCl}(\text{dppe})_2][\text{PF}_6]$ in DCM was found to proceed cleanly to the desired pale orange/red vinylidene complex, $[\text{RuCl}(=\text{C}=\text{CHBMIDA})(\text{dppe})_2][\text{PF}_6]$, over three days at room temperature. The formation of the complex was evinced by observation of a new resonance in the ^1H NMR spectrum at 3.08 ppm for the vinylidene proton (*cf.* 3.04 ppm^o for $[\text{RuCl}(=\text{C}=\text{CHPh})(\text{dppe})_2][\text{PF}_6]$).³⁸ In the ^{31}P NMR spectrum a singlet was now observed at 45.5 ppm, consistent with a *trans*-geometry, replacing the two triplets (δ_{P} 56.7, 84.7; $^2J_{\text{PP}}$ 12.6 Hz) for the AA'BB' spin system of the C_2 -symmetric precursor $[\text{RuCl}(\text{dppe})_2][\text{PF}_6]$.[†]

The ESI mass spectrum was devoid of a molecular ion for the cationic complex, but did include an isotopic manifold attributable to $[\text{M} + \text{NCMe} - \text{Cl}]^+$ ($m/z = 1119$) which further confirmed the identity of the complex, as well as suggesting a pronounced *trans* effect for the vinylidene ligand. The reversibility of the alkyne/vinylidene rearrangement means that under MS conditions, alkyne/vinylidene loss is commonly encountered, as in the present case with a predominant peak assigned as $[\text{M} - \text{Cl} - \text{C}=\text{CHBMIDA}]^+$ ($m/z = 899$). X-ray diffraction quality crystals were obtained *via* DCM/pentane solvent diffusion, crystallographic analysis of which confirmed the formulation of $[\text{RuCl}(=\text{C}=\text{CHBMIDA})(\text{dppe})_2][\text{PF}_6]$ (Figure 15). The molecular structure confirmed the octahedral geometry and the chemically equivalent phosphorus atoms of the mutually *trans* dppe ligands.[§]

^o Both NMR spectra were run in CD_2Cl_2 .

[†] The $[\text{PF}_6]^-$ anion was also evident ($\delta_{\text{P}} -143.8$, heptet, $^1J_{\text{PF}}$ of 711 Hz).

[§] This geometry ensures that the single π -donor ligand (Cl) is *trans* to the single π -acceptor ligand ($=\text{C}=\text{CHBMIDA}$).

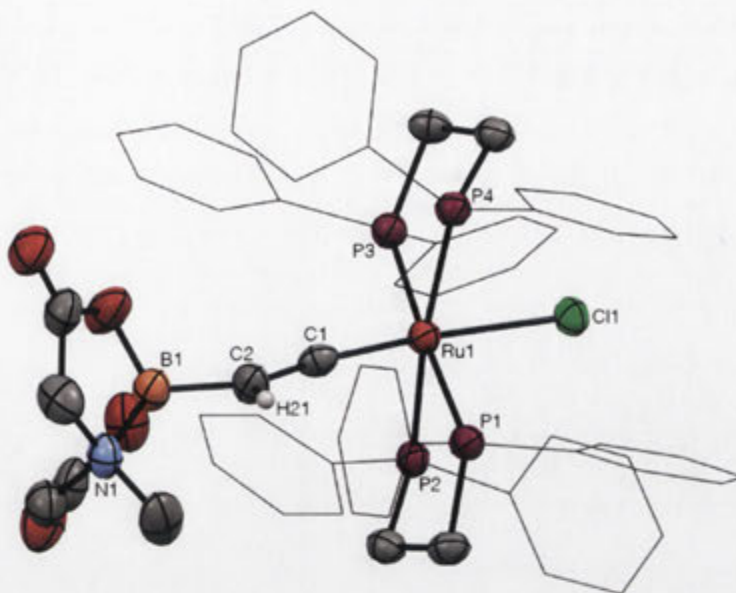


Figure 15: The molecular structure of $[\text{RuCl}(\text{=C=CHBMIDA})(\text{dppe})_2]^+$. (Anion, solvate molecules and some hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): Ru1-C1 1.844(5); Ru1-Cl1 2.466(1); C1-C2 1.310(7); B1-C2 1.589(9); B1-N1 1.663(8); Ru1-C1-C2 168.9(5); C1-C2-B1 138.5(6).

Despite the widespread use of $[\text{RuCl}(\text{dppe})_2][\text{PF}_6]$ in the formation of useful ruthenium vinylidene chemistry, there are few structurally characterised examples of the $[\text{RuCl}(\text{=C=CHR})(\text{dppe})_2]^+$ complexes in the literature,³⁹⁻⁴² the most relevant in the current context is $[\text{RuCl}(\text{=C=CH}\{4\text{-C}_6\text{H}_4\text{NPh}_2\})(\text{dppe})_2][\text{PF}_6]$.⁴² The Ru=C and C=C bond lengths for the BMIDA (1.844(5), 1.310(9) Å) and 4- $\text{C}_6\text{H}_4\text{NPh}_2$ (1.844(2), 1.313(3) Å) complexes were crystallographically indistinguishable suggesting similar steric and electronic properties for the vinylidene substituents. The Ru=C=C bond angles for the two complexes were similarly crystallographically indistinguishable with values of 168.9(5) and 168.5(2) $^\circ$ respectively, which further supported the electronic comparison of the two vinylidene substituents. The C=C-B bond angle was found to be significantly larger than the C=C-C bond angle with values of 138.5(6) and 133.2(2) $^\circ$ respectively, perhaps reflecting the steric hindrance of the more three-dimensionally bulky BMIDA substituent forcing the angle even further away from the ideal sp^2 value of 120 $^\circ$. The Ru-Cl bond length (2.466(2) Å) is somewhat shorter than that for the 4- $\text{C}_6\text{H}_4\text{NPh}_2$ example (2.4831(6) Å), which might suggest that the ruthenium centre is less electron rich, though this is not reflected in variations in the Ru=C bond length.

In contrast, the complex $[\text{RuCl}(\text{=C=CH}\{\text{C}(\text{O})\text{CH}_2\text{Ph}\})(\text{dppe})_2][\text{O}_3\text{SCF}_3]$ has a shorter Ru-Cl bond length (2.426(3) Å), though in that case the Ru=C bond length is considerably shorter (1.77(1) Å), perhaps reflecting increased Ru=C 'carbyne' character with an attendant lengthening of the C=C bond as it gains more C-C character in comparison to the BMIDA substituted complex (Figure 16).

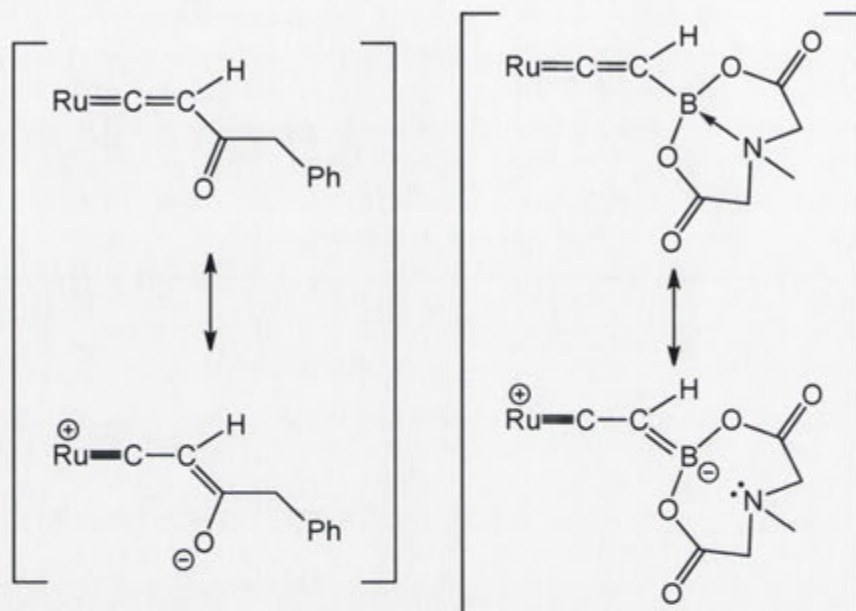


Figure 16: A potential resonance structure of $[\text{RuCl}(\text{=C=CH}\{\text{C}(\text{O})\text{CH}_2\text{Ph}\})(\text{dppe})_2][\text{O}_3\text{SCF}_3]$ (left) to explain the shortening of the Ru=C bond length and lengthening of the C=C bond length, in comparison to the analogous resonance form for $[\text{RuCl}(\text{=C=CHBMIDA})(\text{dppe})_2][\text{PF}_6]$ (right).

1.5.1. Deprotonation of vinylidene complexes of ethynyl-BMIDA

With the vinylidene complex successfully characterised, the next step was to deprotonate the vinylidene proton with a non-nucleophilic base (Figure 17). Initially DBU was utilised, as it is a strong non-nucleophilic base, though this resulted in a mixture of products being observed in the ^{31}P NMR spectrum. The side product $[\text{DBUH}][\text{PF}_6]$ was observed crystallographically, indicating that it had fulfilled its role of deprotonating the vinylidene. Therefore it was believed that the presence of minor water contamination in the DBU used led to cleavage of the BMIDA group; this was considered highly likely given that the BMIDA substituent was applauded for its clean

cleavage under mild, aqueous basic conditions.¹⁰ Resonances were observed in the ^{31}P NMR spectrum of the crude reaction filtrate at 41.9 and 48.2 ppm (amongst others),[§] which closely resembled those reported for $[\text{RuCl}(\text{=C=CH}_2)(\text{dppe})_2][\text{PF}_6]$ (δ_{P} 41.5) and $[\text{RuCl}(\text{C}\equiv\text{CH})(\text{dppe})_2]$ (δ_{P} 49.3),^{†38} which further confirmed the loss, *via* hydrolysis, of the BMIDA substituent.

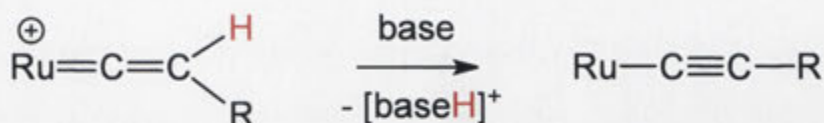


Figure 17: The conversion of a vinylidene into a terminal acetylene *via* the use of a non-nucleophilic base.

When the reaction was repeated with a large excess of dried and degassed NEt_3 it was found to proceed readily to the desired terminal acetylene complex $\text{RuCl}(\text{C}\equiv\text{CBMIDA})(\text{dppe})_2$ (Figure 18). The product was found to possess poor solubility in common solvents, but was characterised by a single resonance in the ^{31}P NMR spectrum at 47.8 ppm, that was shifted to slightly higher frequency compared to the precursor vinylidene (δ_{P} 45.5). The elimination of the $[\text{PF}_6]^-$ anion was evident in both the ^{31}P NMR and IR spectra. The latter included indicative absorptions at 1745, 1773 (ν_{CO}) and 2023 cm^{-1} (ν_{CC}). The MS analysis also confirmed the identity of the product with an isotopic envelope at m/z 1119 corresponding to the $[\text{M} - \text{Cl} + \text{NCMe}]^+$ ion. Unfortunately, due to the poor solubility of the complex, further purification and analysis was prevented.

[§] CDCl_3 , 25°C.

[†] CD_2Cl_2 , 25°C.

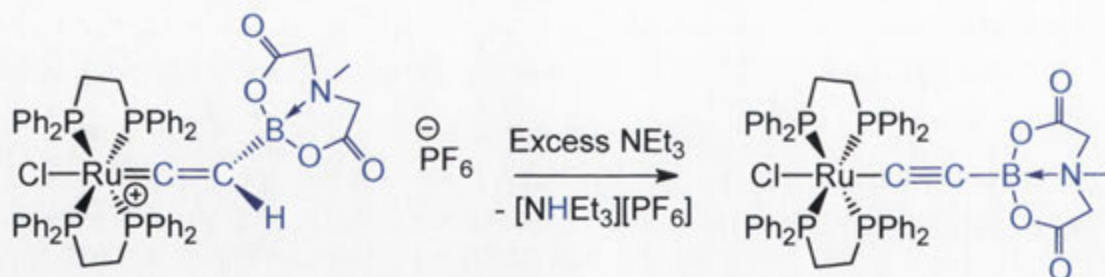


Figure 18: The conversion of the vinylidene, $[\text{RuCl}(\text{=C=CHBMIDA})(\text{dppe})_2][\text{PF}_6]$, into the terminal acetylene, $\text{RuCl}(\text{C}\equiv\text{CBMIDA})(\text{dppe})_2$, via deprotonation with an excess of NEt_3 .

Interestingly, washing of $\text{RuCl}(\text{C}\equiv\text{CBMIDA})(\text{dppe})_2$ with dry EtOH was found to almost exclusively decompose the complex to an unidentified product (δ_B 9.0, δ_P 37.5), along with a very minor peak attributed to $[\text{RuCl}(\text{=C=CH}_2)(\text{dppe})_2]$, caused by reprotonation of the σ -alkynyl complex.

1.6. Vinyl complexes of ethynyl-BMIDA

Whilst alkyne and alkynyl complexes are key intermediates in these catalytic processes, under favourable conditions stable examples may often be isolated, even to the point of being sufficiently robust for applications in materials research. Common organometallic precursors such as the ruthenium phenylvinyl complex $\text{Ru}(\text{E-CH=CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ are synthesised by reaction of *mer*- $\text{Ru}(\text{H})\text{Cl}(\text{CO})(\text{PPh}_3)_3$ and phenylacetylene (Figure 19).⁴³

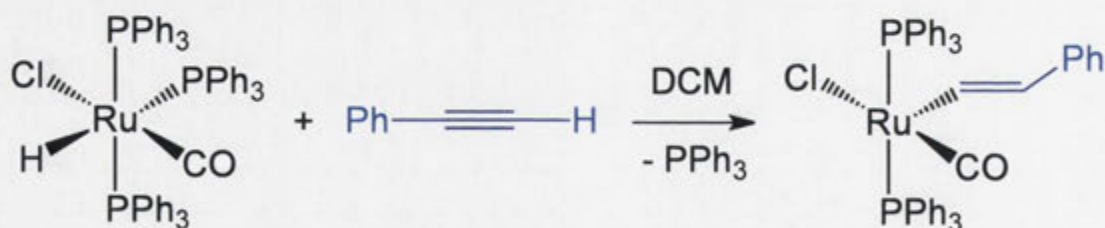


Figure 19: Reaction scheme for the synthesis of $\text{Ru}(\text{E-CH=CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$.⁴³

The reaction involves the loss of a labile PPh_3 ligand to create a vacant coordination site, coordination of the alkyne bond to the metal centre, followed by insertion of the phenylacetylene into the Ru-H bond, which is why the products of this process are in

an *E* stereochemistry. This reaction of *mer*-Ru(H)Cl(CO)(PPh₃)₃ is a general one with terminal alkynes (HC≡CR) and typically proceeds with regioselective hydorruthenation of the C≡C bond to afford *E*- β -substituted σ -vinyl complexes of the form Ru(*E*-CH=CHR)Cl(CO)(PPh₃)₂.¹ This reaction is not limited to terminal alkynes and can be extended to substituted alkynes as well, *e.g.* diphenylacetylene, which gives the analogous diphenyl substituted *E*-vinyl product.⁴³

The analogous synthesis of the ruthenium vinyl complex with ethynyl-BMIDA was therefore investigated. Combining equimolar amounts of the ethynyl-BMIDA and Ru(H)Cl(CO)(PPh₃)₃ resulted in rapid formation of a dark brown solution, the ¹H NMR spectrum of which indicated the formation of two ruthenium vinyl complexes, with the major (42%) vinyl complex being observed at 5.10 (³J_{HH} 16.5 Hz) and 8.44 ppm (³J_{HH} 16.5 Hz),⁸ and the minor vinyl species being observed at 5.57 (³J_{HH} 20.0 Hz) and 8.28 ppm (³J_{HH} 19.6 Hz).⁹ In each case, the low-field resonance showed apparent but poorly refined triplet structure indicating ³J_{PH} coupling to two phosphorus nuclei of the *trans*-disposed phosphines.

The most plausible inference is that the two different vinyl complexes correspond to the *E* and *Z* isomeric species (Figure 20), with the conventional *E* stereochemistry being favoured due to the concerted hydorruthenation mechanism and minimisation of the steric interactions between the bulky BMIDA substituent and ligands on the ruthenium centre. Traditionally the magnitude of ³J_{HH} coupling for *Z* isomers of 1,2-disubstituted alkenes falls in the range 5-10 Hz, whilst those for *E* isomers are typically larger (11-18 Hz).⁵ The major vinyl complex had a ³J_{HH} value of 16.5 Hz, which would suggest it possessed the *E* stereochemistry, as would be expected. However, the minor vinyl complex was observed to have an unusually large ³J_{HH} value of 19.8 Hz,⁹ falling outside these general indicative ranges.

⁸ For comparison purposes the vinyl resonances of the major vinyl complex were observed at $\delta_{\text{H}} = 5.09$ (d, ³J_{HH} 13.6 Hz, 1H, CH=CHBMIDA) and 8.57 (d, ³J_{HH} 13.2 Hz, 1H, CH=CHBMIDA) in CDCl₃.

⁹ The vinyl complexes were observed to be only partially soluble in CDCl₃, therefore NMR data was collected with the isolated major product in *d*₈-THF, which was not used for monitoring purposes due to its high cost. However, the minor impurity was never isolated and the values reported here were collected in CDCl₃.

⁵ The geminal arrangement, with a ³J_{HH} value of 0-3 Hz, was ignored because the mechanism for its formation would be greatly disfavoured given the bulk of the BMIDA group.

⁹ The average value of the two coupling constants observed experimentally.

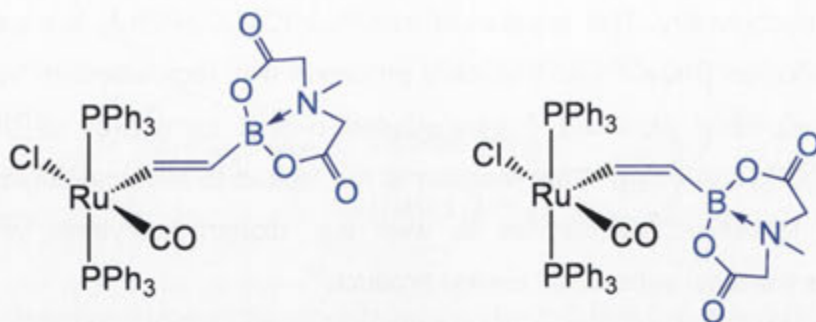


Figure 20: The two configurational isomers of the synthesised vinyl group: Ru(E-CH=CHBMIDA)Cl(CO)(PPh₃)₂ (left) and Ru(Z-CH=CHBMIDA)Cl(CO)(PPh₃)₂ (right).

The subsequent characterisation of the isolated major vinyl complex confirmed the identity of the species as Ru(CH=CHBMIDA)Cl(CO)(PPh₃)₂, with an isotopic manifold being observed at m/z 877 for $[M + \text{NCMe} - \text{Cl}]^+$, and at m/z 836 for $[M - \text{Cl}]^+$. The IR spectrum included strong absorptions at 1774 and 1930 cm^{-1} for the carboxylate and ruthenium carbonyl groups respectively (*cf.* ν_{CO} 1923 cm^{-1} for Ru(CH=CH{C₆H₄Me-4})Cl(CO)(PPh₃)₂).⁴⁴ The single ³¹P NMR resonance at 31.6 ppm was also nearly identical to those reported for the analogous complexes with hydrocarbon substituents in place of the BMIDA group (*cf.* δ_{P} 31.1 for Ru(CH=CH{C₆H₄Me-4})Cl(CO)(PPh₃)₂).⁴⁴

The minor vinyl complex was not successfully separated from the major vinyl product, therefore only the ¹H and ³¹P NMR data was available for characterisation. The lower frequency resonance of the ³¹P NMR shift at 22.6 ppm would suggest that the ruthenium centre had become more electron withdrawing than the ruthenium centre of the major vinyl complex, which was observed at 31.6 ppm. The singlet peak observed in the ³¹P NMR spectrum also indicated that there is a single phosphorus environment, either a single PPh₃ ligand or multiple PPh₃ ligands equivalent by symmetry.

An interesting possibility observed by Roper and co-workers was the analogous vinyl species bearing a BCat substituent instead of the BMIDA, but with the vinyl in a Z stereochemistry and with an 18-electron ruthenium centre, rather than a 16-electron ruthenium centre, due to coordination of one of the oxygen atoms of the catechol group to the vacant coordination site of the ruthenium (Figure 21).⁴⁵ Despite the resemblance of Ru(Z-CH=CHBCat)Cl(CO)(PPh₃)₂ to Ru(CH=CHBMIDA)Cl(CO)(PPh₃)₂, the BCat complex was generated by the insertion of acetylene into the Ru-B bond of

$\text{Ru}(\text{BCat})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, which accounts for the *Z* stereochemistry of the product (Figure 22).

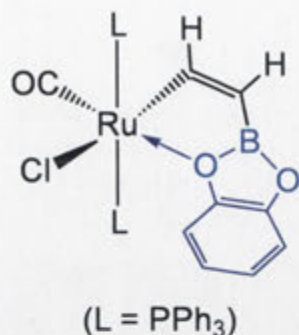


Figure 21: The structure of $\text{Ru}(\text{Z-CH=CHBCat})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ reported by Roper and co-workers.⁴⁵

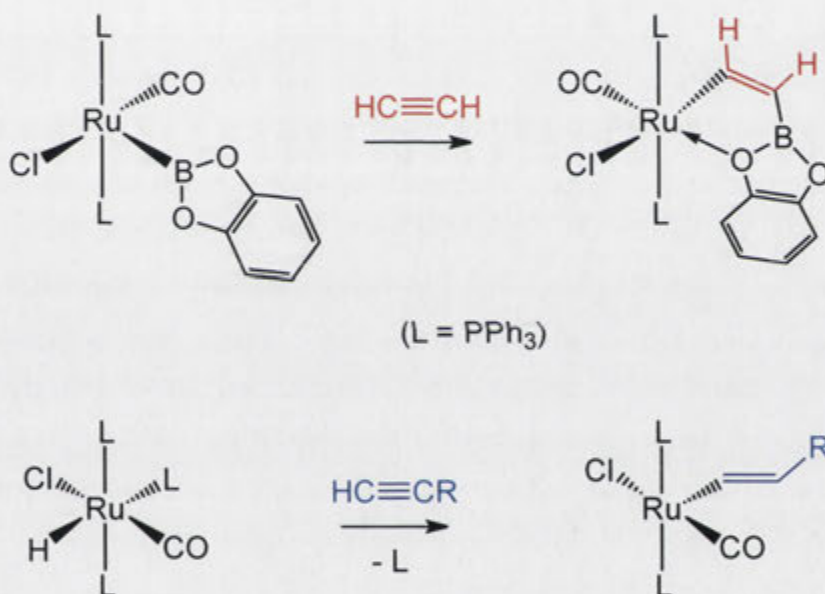


Figure 22: The alkyne insertion of $\text{HC}\equiv\text{CH}$ to give $\text{Ru}(\text{Z-CH=CHBCat})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (red) and the hydrometallation of $\text{HC}\equiv\text{CR}$ to give $\text{Ru}(\text{E-CH=CHR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (blue).

It was also demonstrated that $\text{Ru}(\text{Z-CH=CHBCat})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ could be used to prepare $\text{Ru}(\text{Z-CH=CHB(glycol)})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ *via* transesterification with ethylene glycol (Figure 23). The product was observed to reform the same oxygen coordination as had been exhibited for the BCat starting material. The $\kappa^2\text{-C,O}$

coordination mode displayed by these two complexes raises the possibility of an analogous complex being formed by chelation of the BMIDA substituent (Figure 24).

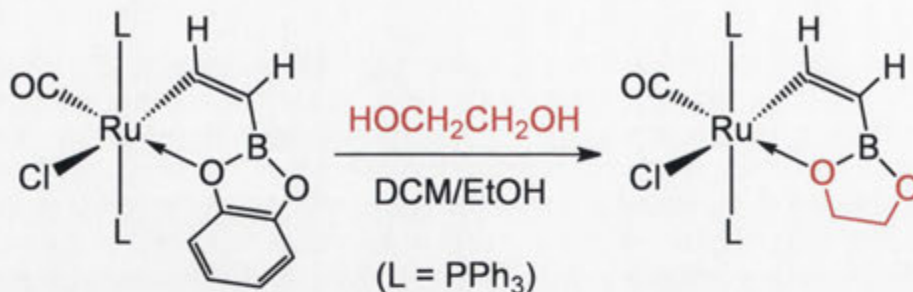


Figure 23: The synthesis of Ru(CH=CHB{glycol})Cl(CO)(PPh₃)₂ by reaction of ethylene glycol and Ru(CH=CHBCat)Cl(CO)(PPh₃)₂.⁴⁵

The two vinyl proton resonances for Ru(Z-CH=CHBCat)Cl(CO)(PPh₃)₂ were observed in the ¹H NMR spectrum at 5.40 ppm (³J_{HH} 11.1 Hz) and 9.31 ppm (³J_{HH} 11.0 Hz), and similarly at 5.79 ppm (³J_{HH} 11.7 Hz) and 9.71 ppm (³J_{HH} 11.7 Hz) for Ru(Z-CH=CHB{glycol})Cl(CO)(PPh₃)₂. Whilst the resonances of the β-protons approximated the analogous shift of 5.57 ppm for the minor vinyl complex observed for the ethynyl-BMIDA reaction, the α-proton chemical shifts were both substantially larger than the 8.28 ppm observed. The coupling constants observed for the BCat and B(glycol) complexes, though at the higher end of the general range, were both still indicative of a Z arrangement around the carbon-carbon double bond, unlike the very large coupling constant of 19.8 Hz for the minor vinyl complex of the BMIDA. This would strongly indicate that it was not from a Z stereochemistry, which is a necessary requirement for an oxygen atom of the BMIDA to coordinate to the ruthenium centre.

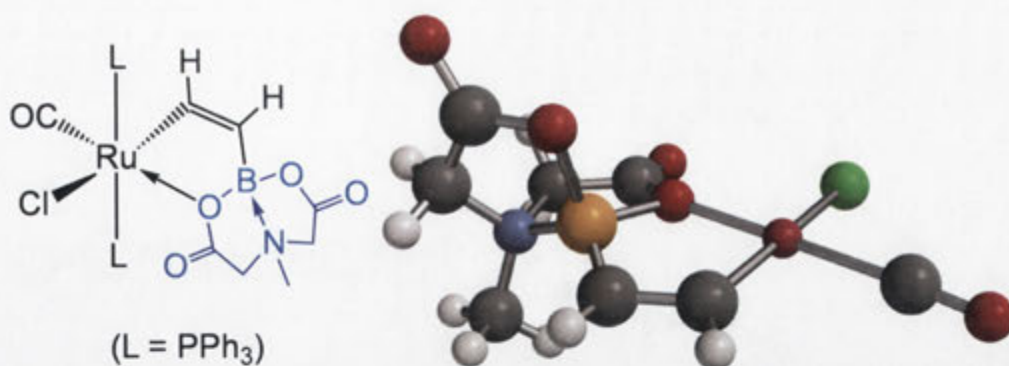


Figure 24: The potential structure for the BMIDA analogue of Ru(CH=CHBCat)Cl(CO)(PPh₃)₂ (left) and the simplified Ru(CH=CHBMIDA)Cl(CO) core illustrating the asymmetry of the BMIDA substituent when coordinating to the ruthenium centre *via* an oxygen.

The essentially planar nature of the BCat (Figure 25) and B(glycol) substituents due to the sp^2 hybridised boron atoms would cause the two PPh₃ ligands to remain equivalent by symmetry and produce a single resonance in the ^{31}P NMR spectrum.[†] However, chelation by a BMIDA substituent containing an sp^3 hybridised boron atom removes the equatorial plane of symmetry rendering the two PPh₃ ligands (as well as the two esters) chemically inequivalent (an AB system with $^2J_{AB} \approx 200\text{--}300\text{ Hz}$ for a *trans*-Ru(PPh₃)₂ arrangement) unless dissociation of the oxygen donor was rapid on the ^{31}P NMR timescale. Therefore, the single resonance observed in the ^{31}P NMR spectrum at 22.6 ppm is inconsistent with the static theoretical species drawn in Figure 24, as this would give rise to two inequivalent phosphine resonances that would presumably also couple to one another and be observed as a pair of doublets.

[†] The ^{31}P NMR shifts were not reported in the journal article in which they were synthesised. Therefore, these values were not available for comparison.

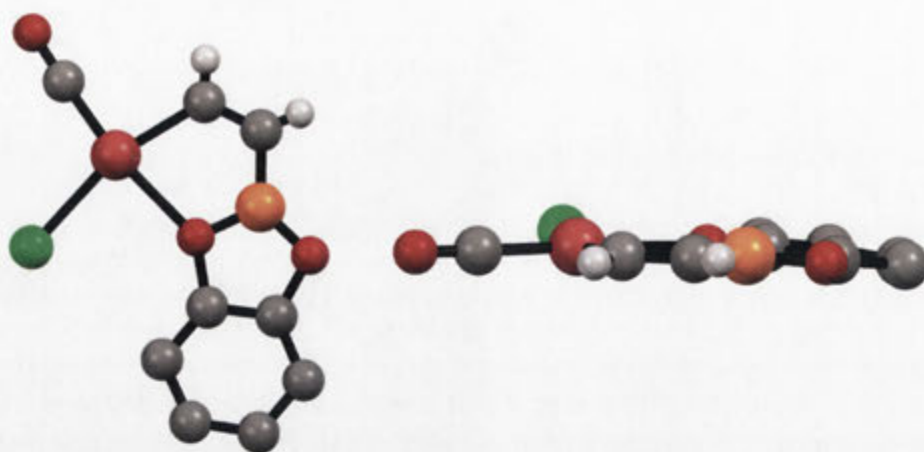


Figure 25: The plane and side view of the $\text{Ru}(\text{Z-CH=CHBCat})\text{Cl}(\text{CO})$ plane of $\text{Ru}(\text{Z-CH=CHBCat})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, illustrating its essentially planar nature. (Triphenylphosphine ligands and some hydrogen atoms omitted for clarity).⁴⁵

Another possibility might involve coordination of the amine group directly to the ruthenium in such a way as to maintain an equatorial plane of symmetry that renders both the phosphines and the ester groups chemically equivalent (Figure 26). However, this seems less likely given the inherent ring strain and also the relative bond strengths associated with coordination of trialkylamines to boron and ruthenium, which strongly favour the former.

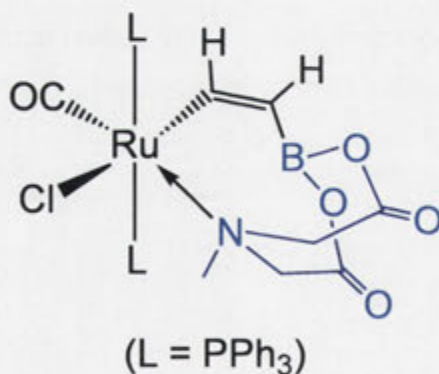


Figure 26: Another potential structure for the BMIDA analogue of $\text{Ru}(\text{CH=CHBCat})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, in which the nitrogen atom of the BMIDA substituent is coordinated to the ruthenium centre as opposed to an oxygen atom.

Unfortunately, despite multiple attempts to obtain crystallographic analysis of the solid-state structure of the major vinyl complex, efforts were ultimately unsuccessful,

being hindered by poor solubility of the product in common solvents (DCM, chloroform, benzene, toluene, Et₂O). The complex was found to have good solubility in THF, though the resulting black solution indicated the decomposition of the species leading to *inter alia* yellow crystals of the curious 2-chloroacrylate complex Ru(O₂CCH=CHCl-*E*)Cl(CO)(PPh₃)₂ (Figure 27).

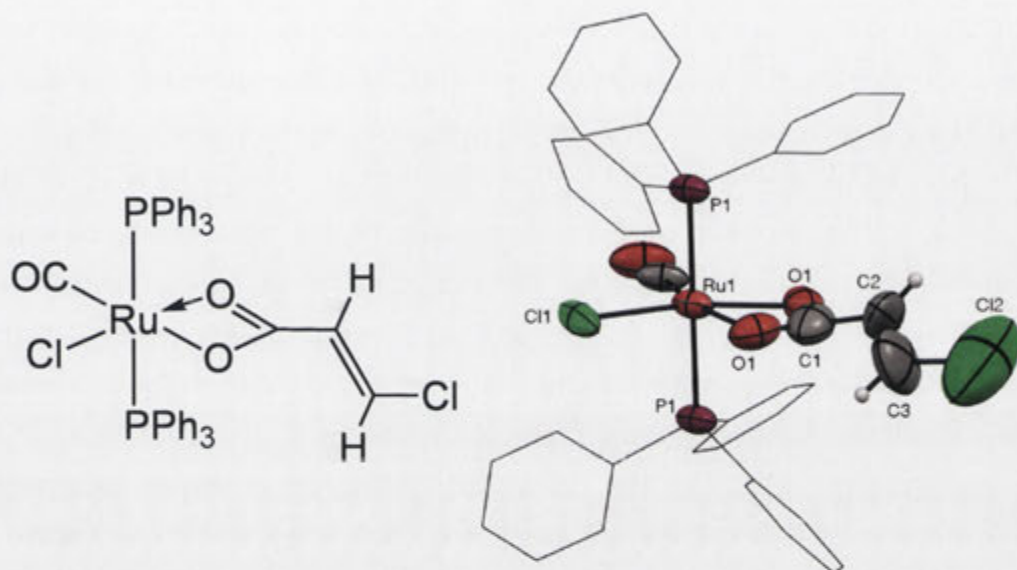


Figure 27: The molecular structure of Ru(O₂CCH=CHCl-*E*)Cl(CO)(PPh₃)₂. (Some hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Ru1-Cl1 2.354(4); Ru1-O1 2.148(3); O1-C1 1.277(5); C1-C2 1.53(1); C2-C3 1.30(2); C3-Cl2 1.81(2); Ru1-O1-C1 91.4(4); O1-C1-O1ⁱ 116.5(7); O1-C1-C2 127(2); C1-C2-C3 111(1); C2-C3-Cl2 118(1).

The C-monoclinic crystal system of the compound meant that a symmetry operation was present, causing positional disorder between the chlorine and carbonyl ligands, as well as two overlapping orientations, both with *E* stereochemistry of the carbon-carbon double bond, of the chlorovinyl group of the acetochlorovinyl ligand. The chlorine atom of the acetochlorovinyl ligand was also only partially occupying its position, with an occupancy of 80%, which indicated that 20% of the time the chlorine was replaced by a proton. The C-Cl bond length of 1.81(2) Å supported the identity of the chlorine atom, but the electron density at this position was insufficient to be a chlorine of complete occupancy, hence the refinement with partial occupancy.

Despite complications encountered in the crystallographic model,[†] refinement yielded sufficiently satisfactory residuals ($R = 0.047$) to confirm the formulation of the product with confidence as being $\text{Ru}(\text{O}_2\text{CCH}=\text{CHCl-}E)\text{Cl}(\text{CO})(\text{PPh}_3)_2$. The origins of the product are somewhat more difficult to reconcile. Whilst insertion of adventitious and extraneous atmosphere CO_2 into a transition metal σ -organyl bond is commonplace, the exchange of the BMIDA substituent for chloride is curious since $\text{B-C}(\delta^-)$ bond polarisation would appear to call for an electrophilic halogen source. In the absence of such, it seems likely that the B-C cleavage arises *via* a radical process involving the halocarbon solvent DCM from which it was recovered.

There are several anomalies to reconcile in the structure of $\text{Ru}(\text{O}_2\text{CCH}=\text{CHCl-}E)\text{Cl}(\text{CO})(\text{PPh}_3)_2$, but the most troubling would be the aceto group bonded to the ruthenium centre. Aceto groups are well known as bidentate organometallic ligands, and though representatively displayed as one conventionally bonded oxygen atom and an additional dative bond from the carbonyl group, the reality is a resonance delocalised bond between the two potential orientations.

The structure of $\text{Ru}(\text{O}_2\text{CCH}=\text{CHCl-}E)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ is of interest because it is the only example of an *E*-3-chloroacrylate ligand coordinated to a metal centre, though there is a single solid-state example of an *E*-2-chlorofumarato $[\text{O}_2\text{CCH}=\text{C}(\text{CO}_2)\text{Cl-}E]$ coordinated to a samarium centre which contains the same motif, but with one of the hydrogen atoms replaced by a CO_2 group.⁴⁶

1.7. Reactions of vinyl BMIDA complexes

The inability to definitively assign the stereochemistry of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ *via* analysis led to the pursuit of the characterisation based on its reactivity. The complex $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ is coordinatively

[†] The C-monoclinic crystal system of the compound meant that a symmetry operation was present, causing the commonly encountered positional disorder between the chlorine and carbonyl ligands, as well as two overlapping orientations, both with *E* stereochemistry of the carbon-carbon double bond, of the chlorovinyl group of the chloroacrylate ligand. The chlorine atom of the chloroacrylate was also partially occupying its position, with an occupancy of 80%, which indicated that 20% of the time the chlorine was replaced by a proton. The C-Cl bond length of 1.81(2) Å supported the identity of the chlorine atom, but the electron density at this position was insufficient to be a chlorine of complete occupancy, hence the refinement with partial occupancy.

unsaturated and might therefore be expected to enter into ligand addition and substitution reactions which might in turn moderate the reactivity of the σ -vinyl ligand.

1.7.1. Acetonitrile

The MS analysis of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ conducted in the ESI (+ve ion) mode using acetonitrile as the matrix resulted in the observation of a significant peak attributable to $[\text{M} - \text{Cl} + \text{NCMe}]^+$ and accordingly the synthesis of this complex was explored (Figure 28).

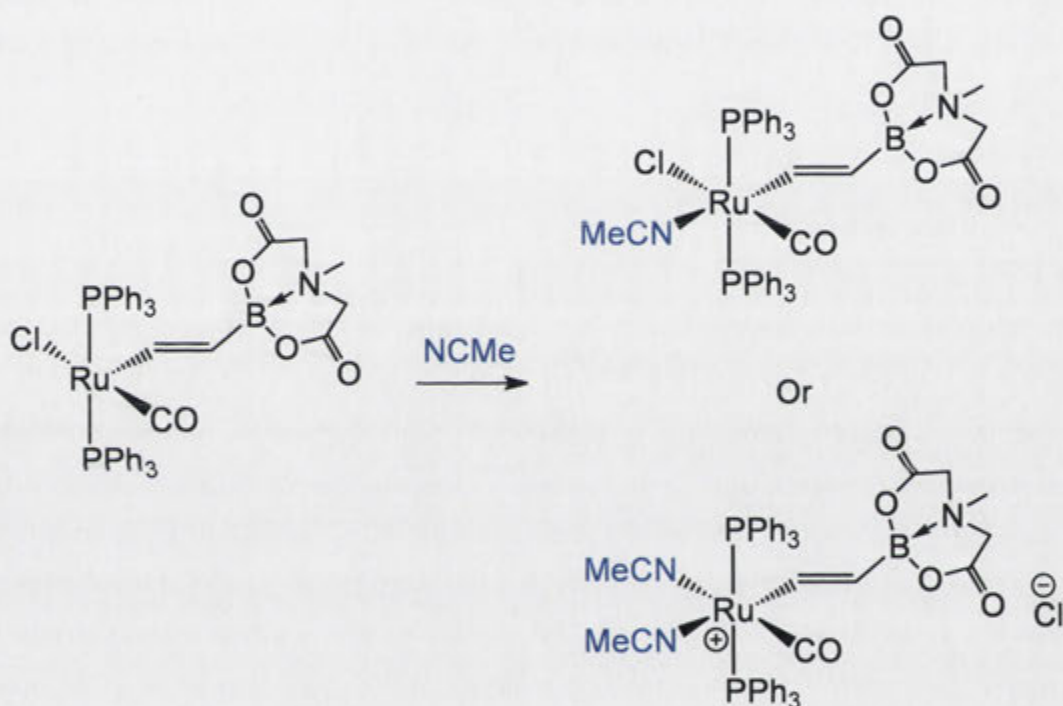


Figure 28: The reaction scheme for the synthesis of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{NCMe})(\text{CO})(\text{PPh}_3)_2$ or $[\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{NCMe})_2(\text{CO})(\text{PPh}_3)_2]^+\text{Cl}^-$.

Immediate decolourisation of the mustard colour of the complex $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ was observed upon dissolution in NCMe , from which a grey solid could be isolated. Characterisation, however, proved difficult because dissolution in solvents other than acetonitrile (chloroform, DCM , THF) resulted in regeneration of the mustard coloured precursor. Solutions in these solvents were decolourised upon addition of acetonitrile (excess), with this behaviour being clearly

indicative of reversible coordination of the nitrile, a common feature of nitriles that are employed as labile ligands.

The MS analysis of the grey product confirmed the presence of $[\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{NCMe})(\text{CO})(\text{PPh}_3)_2]^+$, though as previously discussed this could arise under MS conditions from any of the complexes $[\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2(\text{NCMe})_x]$ ($x = 0, 1$) or $[\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2(\text{NCMe})_2]^+$ and is therefore not definitive. The solid-state IR spectrum included two strong absorptions at ν_{CO} 1757 and 1923 cm^{-1} (KBr) for the ester and ruthenium bound carbonyl groups and given the similarity of the latter to that observed in the neutral precursor (1921 cm^{-1}) it seems most likely that the complex is also the neutral one, *i.e.*, $[\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2(\text{NCMe})]$, as supported by microanalytical data. The demonstrable lability of the nitrile ligand points towards a significant *trans* effect being exerted by the σ -vinyl ligand.

1.7.2. Isonitriles

Isonitriles (isocyanides, CNR ; R = alkyl, aryl) are isoelectronic with CO but are stronger σ -donors, less π -acidic and typically bind strongly to divalent ruthenium.⁴⁷ The reaction of related 16-electron σ -organyl ruthenium complexes with isocyanides have been shown to take one of three courses.⁴⁸ The reaction of $\text{Ru}(\text{R})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (R = $\text{C}_6\text{H}_4\text{Me-4}$) with CNR affords the complex $\text{Ru}(\text{R})\text{Cl}(\text{CO})(\text{CNR})(\text{PPh}_3)_2$ in which the isonitrile coordinates *trans* to the σ -toyl ligand. Heating this kinetic product presumably results in an isomer with the σ -toyl ligand *cis* to the isonitrile, however this is not observed directly but inferred from the nature of the final product in which migratory insertion has ensued to provide an iminotolyl ligand $\text{Ru}\{\eta^2\text{-C(=NR)R}\}\text{Cl}(\text{CO})(\text{PPh}_3)_2$.⁴⁹ In contrast, the σ -styryl complex $\text{Ru}(\text{CH}=\text{CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ reacts with CN^tBu to first afford the simple adduct $\text{Ru}(\text{CH}=\text{CHPh})\text{Cl}(\text{CO})(\text{CN}^t\text{Bu})(\text{PPh}_3)_2$ which, however, reacts with further isonitrile to afford the salt $[\text{Ru}\{\text{C(=O)CH}=\text{CHPh}\}(\text{CN}^t\text{Bu})_3(\text{PPh}_3)_2]\text{Cl}$ in which migratory insertion involves the carbonyl rather than isonitrile ligand.⁵⁰ The reaction of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with CNMe was investigated and found to provide the neutral 18-electron species $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{CNMe})(\text{PPh}_3)_2$ (Figure 29).

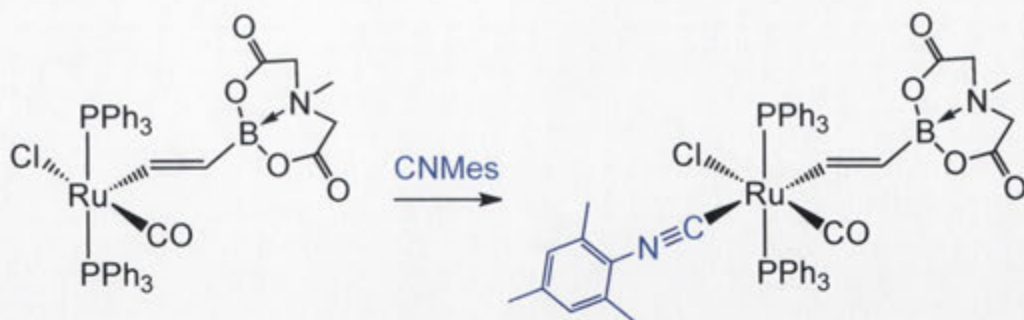


Figure 29: The reaction scheme for the synthesis of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$.

The formation of the desired product was found to be complete after 30 minutes as determined by ^{31}P NMR spectroscopy with the observation of a new peak at 24.9 ppm (*cf.* 31.6 ppm for the precursor). The product was found to be stable in solution for at least up to 8 hours as again determined by ^{31}P NMR spectroscopy. Isolation of the brown product yielded microanalytical data consistent with the $\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{CNMe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ complex and MS analysis revealed a $[\text{M} - \text{Cl}]^+$ ion at m/z 981, along with various NCMe and CNMe adducts at higher values of m/z . The ^1H NMR spectrum revealed that the methyl groups at the 2 and 6 positions of the mesityl group were equivalent (δ_{H} 1.96) indicating free CN-aryl rotation. The vinylic AB system (δ_{H} 5.69, 8.59) showed a large $^3J_{\text{AB}}$ value (20.0 Hz) thereby removing the regiochemical uncertainty discussed above for the precursor. The coupling of the α -proton to the two equivalent phosphorus nuclei ($^3J_{\text{PH}}$ 2.6 Hz) was also observed in this complex though unresolved in the starting material. The infrared spectrum showed three characteristic stretches, with the BMIDA carbonyl and the ruthenium carbonyl stretches being observed (DCM: ν_{CO} 1762, 1959 and ν_{CN} 2118 cm^{-1} ; KBr: 1762, 1952 and 2117 cm^{-1}) the frequencies of which are consistent with the neutral formulation.

1.7.3. Carbon Monoxide

In a similar manner to the reaction with CNMe₂, treating a DCM solution of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with CO (1 atm) results in the formation of a colourless precipitate over a period of 1 hour, formulated as $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ (Figure 30).

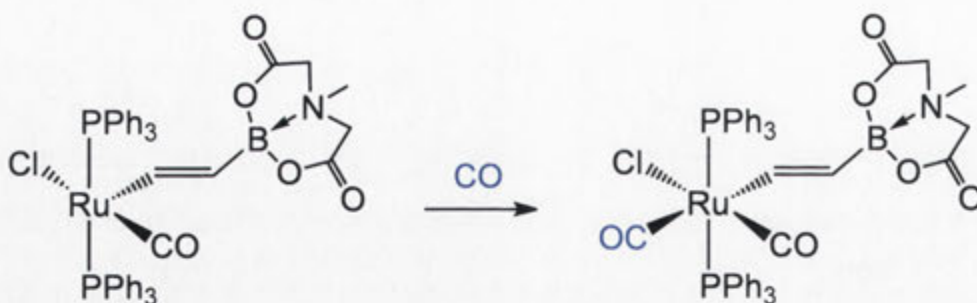


Figure 30: The reaction scheme for the synthesis of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$.

The complex was found to have poor solubility in common solvents, which prevented observation of the ^{11}B NMR signal of the BMIDA substituent. However, satisfactory ^1H and ^{31}P NMR spectra were obtained. The ^{31}P NMR spectrum, comprising a single resonance, confirmed the presence of chemically equivalent PPh_3 groups (δ_{P} 22.5; cf. 31.6 for the precursor). The ^1H NMR spectrum confirmed the presence of the MIDA substituent and the vinylic AB system (δ_{H} 5.57, 8.29; $^3J_{\text{AB}}$ 19.6 Hz).

In addition to the characteristic BMIDA ester absorption (DCM: 1763 cm^{-1}), the infrared spectrum included two ν_{CO} peaks at 1974 and 2037 cm^{-1} confirming the *cis*- $\text{Ru}(\text{CO})_2$ geometry [cf. IR (KBr): ν_{CO} 1974 , 2032 cm^{-1} for $\text{Ru}(\text{CH}=\text{CH}^t\text{Bu})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$].⁵¹ A satisfactory microanalysis was also obtained for the desired complex, which supported its successful formation.

The reduced solubility of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ confounded the obtention of crystallographic grade crystals through subsequent recrystallisation. Good quality crystals were obtained by slow diffusion of CO into a solution of the precursor in DCM which, however, rapidly desolvated (<15 s) upon removal from the supernatant preventing good quality measurements.⁵ Despite the rapid desolvation that was observed, a low precision molecular structure of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ was obtained, though the low precision precluded the interpretation of the geometrical parameters. However, the connectivity of the structure was clearly established and confirmed the *cis*- $\text{Ru}(\text{CO})_2$ geometry (Figure 31).

⁵ Under an atmosphere of DCM, the colourless crystals were found to persist for weeks without any signs of decomposition.

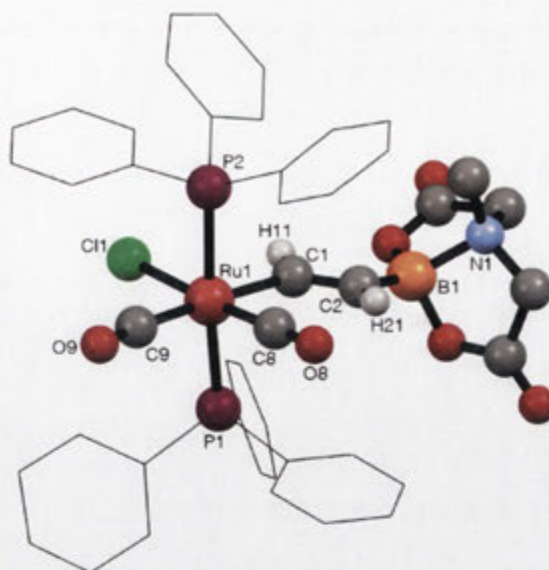


Figure 31: The molecular structure of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$. The connectivity and gross geometry were confirmed, but the low precision of the data precluded detailed interpretation of the geometrical parameters.

The availability of the complex $\text{RuCl}(\text{C}\equiv\text{CBMIDA})(\text{CO})_2(\text{PPh}_3)_2$ (*vide infra*) with an identical ligand set to that of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ provides an ideal basis for comparison of the vinyl BMIDA substituent *versus* the terminal acetylene substituent.

Immediately apparent was the similarity of poor/partial solubility of both complexes in common solvents, especially chlorinated solvents such as DCM and chloroform, to the point that a ^{11}B NMR resonance could not be observed for $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$.[†] However, the ^{31}P NMR resonances for each of the complexes was observed and were found to be 22.5 ppm for the vinyl BMIDA complex, and 17.7 ppm for the σ -alkynyl BMIDA complex.

Each complex displays coupled ν_{sym} and ν_{asym} modes for the *cis*- $\text{Ru}(\text{CO})_2$ unit which are presented in Table 1 along with comparative data for related complexes. The derived Cotton-Kraihanzel force constant[§] indicates that the alkynyl ligand is more electron-withdrawing than the vinyl, but not a perfluoromethyl group. The differential

[†] A quartz NMR tube was used to run the ^{11}B NMR sample.

[§] Because the coupling of oscillators can vary between complexes, the Cotton-Kraihanzel force constant provides a more convenient single parameter for comparison, $k_{\text{CK}} = 2.0191 \times 10^{-6} (\nu_{\text{sym}}^2 + \nu_{\text{asym}}^2) \text{ Ncm}^{-1}$.

effect of the BMIDA group relative to a simple aryl substituent is not significantly transmitted to the metal centre.

Table 1: Selected infrared data for dicarbonyl σ -organyl complexes $\text{Ru(R)Cl(CO)}_2(\text{PPh}_3)_2$ in ^aDCM, ^bNujol or ^cKBr Plate.

R	$\nu_{\text{sym}} (\text{cm}^{-1})$	$\nu_{\text{asym}} (\text{cm}^{-1})$	$k_{\text{CK}} (\text{Ncm}^{-1})$
^c H ⁵²	2040	1965	16.20
^b CH=CHPh ⁵³	2031	1970	16.16
^b C ₆ H ₄ Me-4 ⁵⁴	2055	1952	16.22
^a CH=CHBMIDA	2037	1974	16.24
^a C $\equiv$ C(C ₆ H ₄ Me-4) ²³	2055	1995	16.56
^a C $\equiv$ CBMIDA	2058	1995	16.59
^b CF ₃ ⁵⁵	2061	2005	16.69
^b Cl ⁵⁶	2064	2001	16.69

Interestingly, the methyl and methylene protons of the BMIDA group were also noticeably shifted between the two complexes, even though they are somewhat removed from the carbon-carbon multiple bond in both instances. The *N*-methyl groups were observed in the ¹H NMR spectra at 2.11 and 3.08 ppm for the vinyl BMIDA and σ -alkynyl BMIDA complexes, respectively. The corresponding values of 2.71 and 3.11 ppm for H₂C=CHBMIDA (*vide infra*) and HC $\equiv$ CBMIDA suggest that this is a result of the magnetic anisotropy of the C=C (or C $\equiv$ C) bond to which the NMe group is directed, rather than any through-bond inductive effect. Similarly, the methylene groups were observed at 3.04 and 3.40 ppm for RuCl(C $\equiv$ CBMIDA)(CO)₂(PPh₃)₂, and at 3.73 and 3.80 ppm for Ru(CH=CHBMIDA)Cl(CO)₂(PPh₃)₂, though with comparable ²J_{HH} coupling values of 16.0 and 16.4 Hz for the two pairs of doublets, respectively.

1.7.4. Hydrotris(pyrazolyl)borate

Trofimenko's eponymous pyrazolylborate ligands permeate numerous fields of chemistry, with organometallic chemistry perhaps benefitting the most.^{57, 58} The comparatively general use of the parent Tp ligand [Tp = hydrotris(pyrazol-1-yl)borato]

(Figure 32) to support ruthenium centres bearing σ -vinyl substituents has been previously described.^{59, 60}

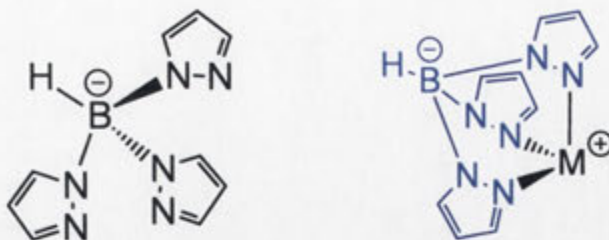


Figure 32: Trofimenko's eponymous hydrotris(pyrazolyl)borate ligand, $[Tp]^-$ (left) and a general example of its tridentate coordination to metal centres.

The reaction of $K[Tp]$ with the complex $Ru(CH=CHBMIDA)Cl(CO)(PPh_3)_2$ provided the colourless complex $Ru(CH=CHBMIDA)Tp(CO)(PPh_3)$ *via* metathesis of KCl and loss of a PPh_3 (Figure 33). The product gives rise to a single resonance in the ^{31}P NMR spectrum at 49.7 ppm and two strong stretches in the IR spectrum at 1770 and 1939 cm^{-1} for the BMIDA and ruthenium carbonyl groups respectively [*cf.* ν_{CO} 1942 cm^{-1} for $Ru(CH=CH\{C_6H_4Me-4\})Cl(CO)(PPh_3)_2$].⁶¹

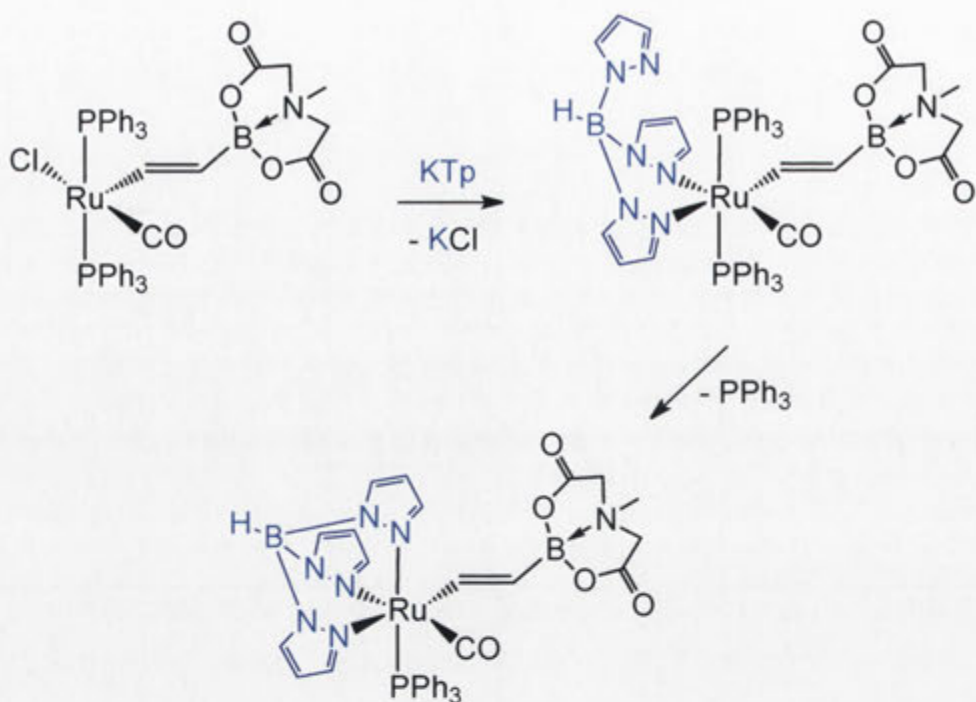


Figure 33: The reaction scheme for the synthesis of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Tp}(\text{CO})(\text{PPh}_3)$, analogous to that reported by Hill et al. as a general synthetic route,⁵⁹ via the $\kappa^2\text{-Tp}$ intermediate $\text{Ru}(\text{CH}=\text{CHBMIDA})(\kappa^2\text{-Tp})(\text{CO})(\text{PPh}_3)_2$.

In the early stages of reaction, an intermediate formulated as $\text{Ru}(\text{CH}=\text{CHBMIDA})(\kappa^2\text{-Tp})(\text{CO})(\text{PPh}_3)_2$ could be observed en route to the formation of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Tp}(\text{CO})(\text{PPh}_3)$. The boat geometry of the $\kappa^2\text{-Tp}$ ligand renders the two phosphine environments distinct as indicated by the appearance of an AB system in the ^{31}P NMR spectrum (δ_{P} 42.6, 47.0) with a $^2J_{\text{AB}}$ coupling (304 Hz) indicative of *trans*-disposed phosphines. A similar structurally characterised intermediate, $\text{Ru}(\text{H})(\kappa^2\text{-Tp})(\text{CO})(\text{PPh}_3)_2$,⁶² has been observed in the synthesis of $\text{Ru}(\text{H})\text{Tp}(\text{CO})(\text{PPh}_3)$ from $\text{K}[\text{Tp}]$ and $\text{Ru}(\text{H})\text{Cl}(\text{CO})(\text{PPh}_3)_3$ (δ_{P} 42.6, 47.0; $^2J_{\text{AB}}$ 301.8 Hz).

The ^1H NMR spectrum confirmed the chirality of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Tp}(\text{CO})(\text{PPh}_3)$, which manifested as three chemically distinct pyrazolyl environments. The vinylic group gave rise to doublet resonances at 5.78 and 8.55 ppm ($^3J_{\text{HH}}$ 18.6 Hz) with that to lower field being broadened, so as to be unable to observe the anticipated $^3J_{\text{PH}}$ coupling.

Surprisingly, in contrast to the usual stability of the complexes $\text{Ru}(\text{CH}=\text{CHR})\text{Tp}(\text{CO})(\text{PPh}_3)$,⁵⁹ on standing, solutions of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Tp}(\text{CO})(\text{PPh}_3)$ deposit crystals of $\text{HC}\equiv\text{CBMIDA}$. Given the

coordinative saturation of $\text{Ru}(\text{CH}=\text{CHR})\text{Tp}(\text{CO})(\text{PPh}_3)$, it must be presumed that hemilabile coordination of one pyrazole arm allows a vacant site to be revealed for subsequent β -Ru-H elimination. Though not previously observed for related complexes, one might surmise that the 3-dimensional steric bulk of the BMIDA group perhaps favours de-insertion of the alkyne.

1.7.5. Dithiocarbamate

The reaction of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with the strongly chelating pro-ligand salt $[\text{NH}_2\text{Et}_2][\text{S}_2\text{CNEt}_2]$ afforded the anticipated 18-electron complex $\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2$ (Figure 34).

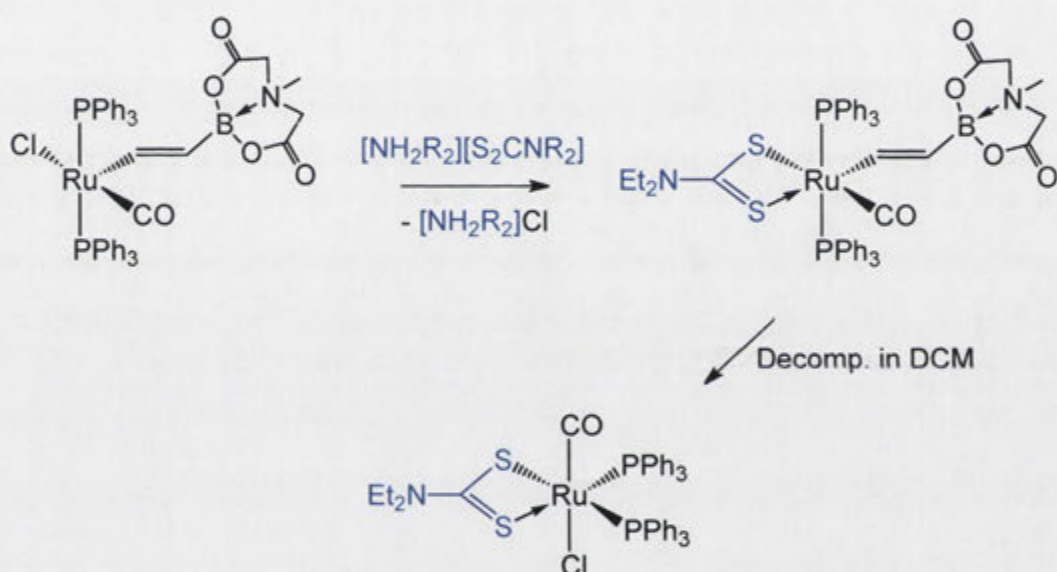


Figure 34: The reaction scheme for the synthesis of $\text{Ru}(\text{CH}=\text{CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ from $\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2$, and the observed decomposition product in chlorinated solvents.

The gross composition was indicated by microanalytical data and the observation of a strong $[\text{M} + \text{Na}]^+$ ion ($m/z = 1006$) in the ESI-MS spectrum. The comparatively electron-rich nature of the ruthenium centre is reflected both in the shift to higher frequency ($\delta_{\text{P}} 38.4$) of the single resonance in the ^{31}P NMR spectrum and the shift to lower frequency for the metal carbonyl ν_{CO} absorption (1912 cm^{-1}). The ^1H NMR

spectrum indicated that the two ethyl substituents of the thiocarbamate ligand were inequivalent with the observation of two triplets and two quartets at 0.57, 0.74, 2.76 and 2.87 ppm, respectively, all with $^3J_{\text{HH}}$ values of 6.8 Hz, allowing a *cis*-Ru(PPh₃)₂ geometry to be excluded (*vide infra*). The two vinyl protons were observed at δ_{H} 5.18 and 7.31 ($^3J_{\text{HH}}$ 18.0 Hz) for the β - and α -protons respectively, which was a significant shift to lower frequency for the α -proton when compared to the precursor (δ_{H} 8.56), which has similarly been observed previously (*cf.* δ_{H} 5.55, 8.35 for Ru(CH=CH{C₆H₄Me-4})Cl(CO)(PPh₃)₂ and δ_{H} 5.55, 7.74 for Ru(CH=CH{C₆H₄Me-4})(S₂CNEt₂)(CO)(PPh₃)₂).^{44, 63}

The complex Ru(CH=CHBMIDA)(S₂CNEt₂)(CO)(PPh₃)₂ was observed to quickly decompose over several hours in chlorinated solvents (DCM, chloroform), the product of the decomposition being Ru(S₂CNEt₂)Cl(CO)(PPh₃)₂, arising from complete cleavage of the ethenyl-BMIDA group. The product gives rise to a single resonance (δ_{P} 36.0) in the ^{31}P NMR spectrum, however in contrast to previous examples, the chemically equivalent phosphine ligands are mutually *cis*-disposed as indicated by a single ethyl environment (δ_{H} 1.15, 2.97; $^3J_{\text{HH}}$ 7.0 Hz). This geometry (Figure 35) was confirmed on numerous occasions for a range of solvates inadvertently observed during unsuccessful attempts to obtain crystals of Ru(CH=CHBMIDA)(S₂CNEt₂)(CO)(PPh₃)₂ for crystallographic analysis.

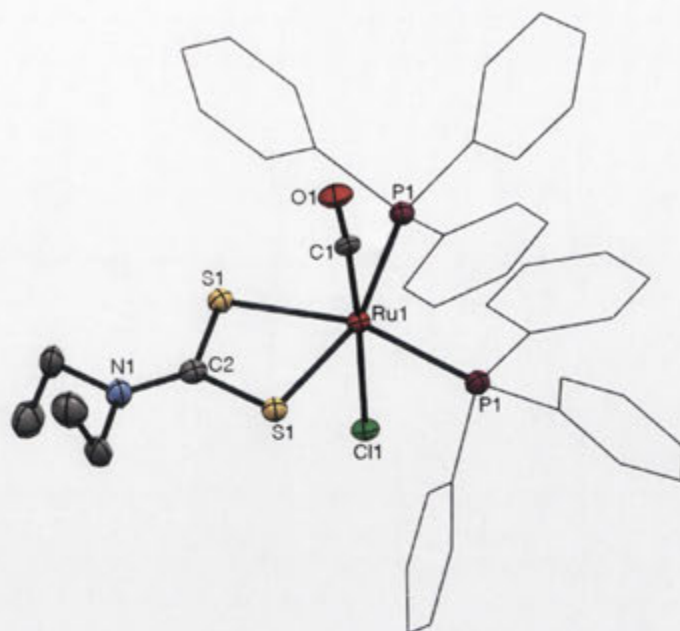


Figure 35: The molecular structure of $\text{Ru}(\text{S}_2\text{CNET}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ in a crystal of $\text{Ru}(\text{S}_2\text{CNET}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2 \cdot \text{DCM}$. (Solvate molecules and hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): Ru1-Cl1 2.461(3); Ru1-C1 1.821(9); Ru1-S1 2.4268(5); C1-O1 1.165(8); S1-C2 1.722(2); P1-Ru1-P1' 106.81(3); Cl1-Ru1-C1 176.2(2); S1-Ru1-S1' 72.11(2); S1-C2-S1' 112.1(2).

The complex $\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)_2$ was (eventually) structurally characterised with crystals obtained *via* vapour diffusion of pentane into an acetone solution of the compound, providing the first solid-state characterisation of a ruthenium vinyl complex bearing a boron substituent in a *trans* geometry (Figure 36).⁶ Interestingly, the solid-state structure had three crystallographically independent molecules of $\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)_2$ and similarly three molecules of acetone solvate. The identity and *trans* geometry of the vinyl bond was clearly established by the C=C bond lengths of 1.32(1), 1.33(1) and 1.28(1) Å for the three crystallographically independent molecules, Ru-C=C angles of 128.6(6), 129.9(7) and 132.4(7) $^\circ$, and lastly C=C-B angles of 126.4(8), 126.1(9) and 125.0(8) $^\circ$.

⁶ There is only one previous solid-state example of a ruthenium vinyl complex bearing a boron substituent, which was the chelated borocatechol described in Figure 21 of this chapter reported by Roper *et al.*, though the vinyl group was in a *cis* geometry.⁴⁵

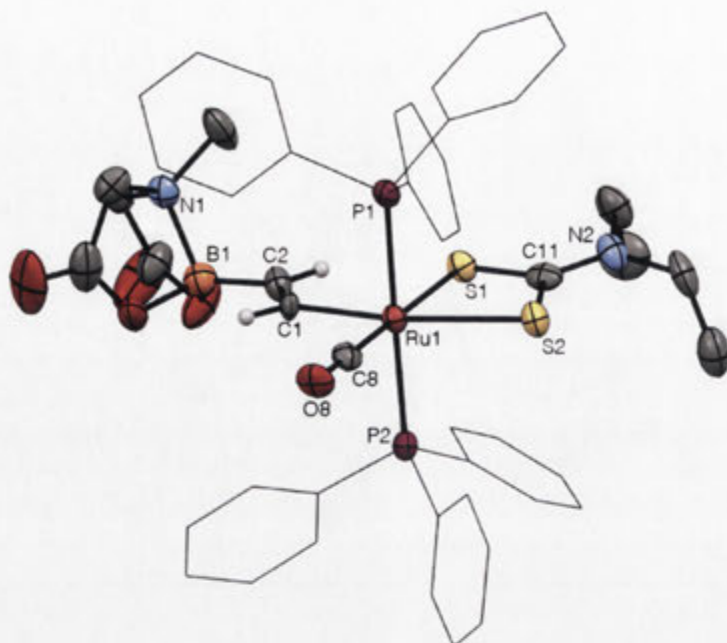


Figure 36: The molecular structure of $\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)_2$. (Solvate molecules and some hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Ru1-C1 2.123(8); Ru1-C8 1.856(8); Ru1-S1 2.440(2); Ru1-S2 2.517(2); C1-C2 1.32(1); B1-C2 1.55(2); B1-N1 1.68(1); C8-O8 1.157(9); Ru1-C1-C2 128.6(6); C1-C2-B1 126.4(8); S1-Ru1-S2 70.49(8).

The ruthenium vinyl, Ru-C, bond lengths of 2.123(8), 2.094(9) and 2.101(8) Å were crystallographically indistinguishable from that observed (2.085(2) Å) for the complex $\text{Ru}(\text{CH}=\text{CH}\{\text{C}_6\text{H}_4\text{Me}-4\})(\text{S}_2\text{CN}\{\text{CH}_2\text{CH}_2\text{OMe}\}_2)(\text{CO})(\text{PPh}_3)_2$,⁶⁴ indicating that the steric and electronic nature of the BMIDA substituent has minimal effect on the vinyl group's interaction with the ruthenium centre. The two distinct (39 e.s.d.) Ru-S bond lengths provide an internally referenced comparison of the relative *trans* influence of the σ -vinyl and carbonyl ligands, the former displaying the stronger influence.[§]

The Ru-C bond of the dithiocarbamate complex proved to be unusually reactive towards cleavage, which would seem consistent with both the strongly π -basic ruthenium and the inductively electron releasing boryl substituent both contributing to make the vinyl unit especially electron rich and prone to electrophilic cleavage.

[§] By '*trans* influence' it is meant the thermodynamic ground-state destabilisation (bond lengthening) which may contribute to a kinetic '*trans* effect' by lowering the ground-state/transition state separation (activation energy), though other factors, e.g. transition state stabilisation may provide an alternative contribution to the kinetic *trans* effect.⁶⁵

Given that the reaction of $\text{Ru(H)Cl(CO)(PPh}_3)_3$ with ethynyl-BMIDA afforded more than one species, calling for extensive purification, an alternate synthetic route to $\text{Ru(CH=CHBMIDA)(S}_2\text{CNEt}_2\text{)(CO)(PPh}_3)_2$ was considered involving hydrometallation of the alkyne by the complex $\text{Ru(H)(S}_2\text{CNR}_2\text{)(CO)(PPh}_3)_2$ ($\text{R} = \text{Me, Et}$). Although these complexes, being coordinatively saturated, are far less active in hydrometallation requiring phosphine loss/recoordination, it was presumed that once formed the products would be more thermodynamically stable in a suitably inert solvent. In practice, the desired ruthenium vinyl complexes were not observed, but rather the alkynyl complexes $\text{Ru(C}\equiv\text{CBMIDA)(S}_2\text{CNR}_2\text{)(CO)(PPh}_3)_2$ were the major recovered products. For complete conversion to $\text{Ru(C}\equiv\text{CBMIDA)(S}_2\text{CNR}_2\text{)(CO)(PPh}_3)_2$, a second equivalent of ethynyl-BMIDA was required to serve as a proton donor to generate one equivalent of ethenyl-BMIDA, $\text{H}_2\text{C=CHBMIDA}$ (Figure 37). Once the process of the reaction was appreciated, adjustment of stoichiometry resulted in the alkynyl complexes being obtained in 23% ($\text{R} = \text{Me}$) and 63% ($\text{R} = \text{Et}$) yields, respectively.

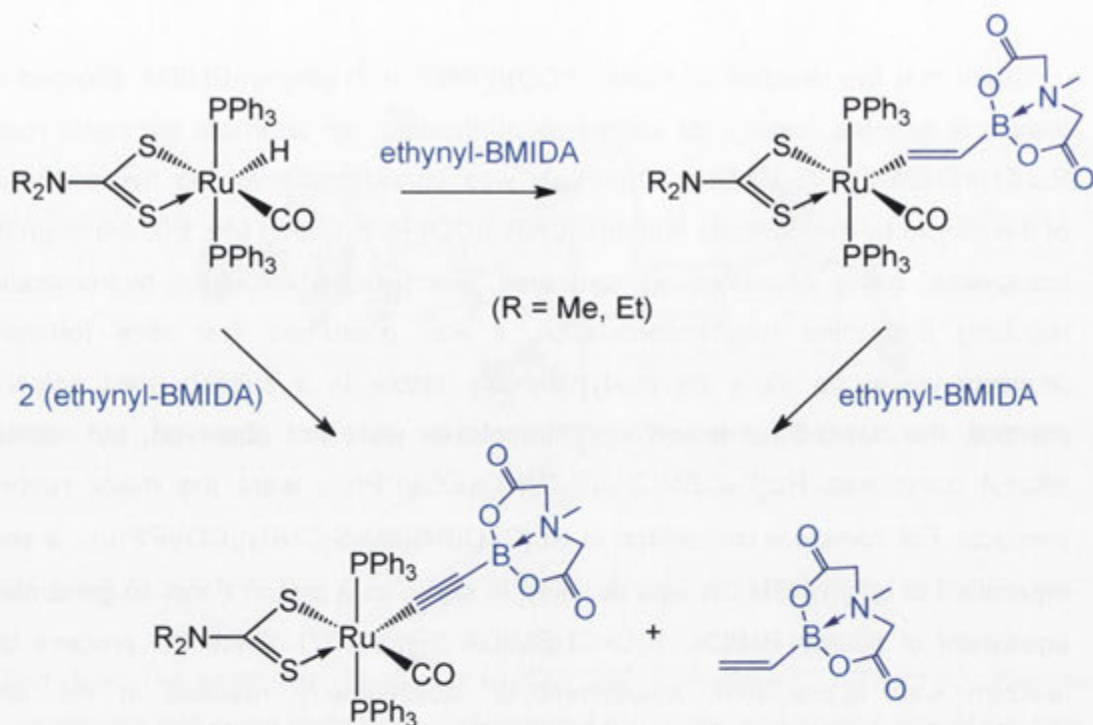


Figure 37: The intended reaction scheme for the synthesis of $\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{S}_2\text{CNR}_2)(\text{CO})(\text{PPh}_3)_2$ from $\text{Ru}(\text{H})(\text{S}_2\text{CNR}_2)(\text{CO})(\text{PPh}_3)_2$, and the reaction that was observed to actually occur to form $\text{Ru}(\text{C}\equiv\text{CBMIDA})(\text{S}_2\text{CNR}_2)(\text{CO})(\text{PPh}_3)_2$ and $\text{H}_2\text{C}=\text{CHBMIDA}$.

The alkynyl complexes $\text{Ru}(\text{C}\equiv\text{CBMIDA})(\text{S}_2\text{CNR}_2)(\text{CO})(\text{PPh}_3)_2$ were clearly differentiated from the desired complex $\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2$ on the basis of IR spectroscopy (ν_{CO} 1938 (R = Me), 1945 (R = Et) cm^{-1} cf. 1912 cm^{-1} for $\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2$) and by comparison with data for the previously reported phenyl analogue, $\text{Ru}(\text{C}\equiv\text{CPh})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2$ (ν_{CO} 1942 cm^{-1}).^{*,66} Absorptions attributable to ν_{CC} were also conspicuous (2057 (R = Me), 2062 (R = Et) cm^{-1}) though moved to lower frequency compared to that observed for the phenyl analogue (ν_{CC} 2091 cm^{-1}).

The ^{31}P NMR resonance was comparatively insensitive to the change in α -organyl substituent with a shift of only 1 ppm to higher frequency accompanying conversion of

* The cited journal article did not state in what medium the IR spectra were recorded, so it is unknown whether the data reported were from solid-state or solution IR measurements, somewhat compromising direct comparison.

the vinyl (δ_p 38.4) to alkynyl (δ_p 39.5) complex. The ESI-MS analysis revealed an envelope (m/z 982) corresponding to $[M + H]^+$ which is consistent with the facile protonation of alkynyl ligands to afford vinylidene complexes.

The solid-state structures of both the methyl- and ethyl-substituted dithiocarbamate alkynyl complexes were determined (Figure 38), with the ethyl-substituted analogue having two crystallographically independent molecules in the asymmetric unit cell. The three molecules each display essentially linear geometries for the alkynyl group ($Ru1-C1-C2 = 178.0(2)$, $171.3(3)$ and $172.2(4)^\circ$; $C1-C2-B2 = 172.9(3)$, $172.3(4)$ and $172.9(5)^\circ$) with the C1-C2 bond lengths being typical of ruthenium(II) alkynyls ($C1-C2 = 1.202(4)$, $1.189(6)$ and $1.199(6)$ Å).

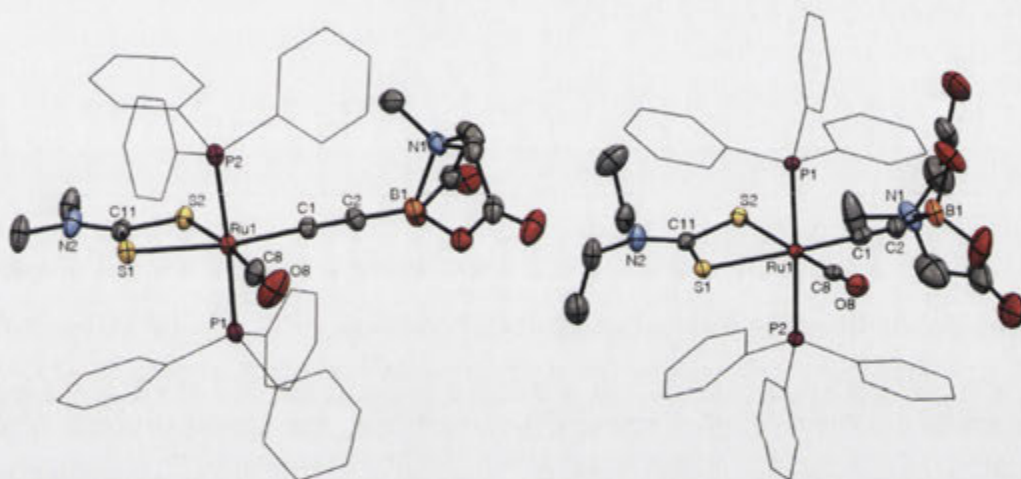


Figure 38: The molecular structures of $Ru(C\equiv CBMIDA)(S_2CNMe_2)(CO)(PPh_3)_2$ (left) and $Ru(C\equiv CBMIDA)(S_2CNEt_2)(CO)(PPh_3)_2$ (right). (Solvate molecules and hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$) for $Ru(C\equiv CBMIDA)(S_2CNMe_2)(CO)(PPh_3)_2$: $Ru1-C1$ 2.030(3); $Ru1-C8$ 1.842(3); $Ru1-S1$ 2.4549(6); $Ru1-S2$ 2.4734(7); $C1-C2$ 1.202(4); $B1-C2$ 1.539(4); $B1-N1$ 1.674(4); $C8-O8$ 1.126(4); $Ru1-C1-C2$ 178.0(2); $S1-Ru1-S2$ 71.32(2); $C1-C2-B1$ 172.9(3). Selected bond lengths (Å) and angles ($^\circ$) for $Ru(C\equiv CBMIDA)(S_2CNEt_2)(CO)(PPh_3)_2$: $Ru1-C1$ 2.044(4); $Ru1-C8$ 1.857(4); $Ru1-S1$ 2.4688(8); $Ru1-S2$ 2.4566(8); $C1-C2$ 1.189(6); $B1-C2$ 1.540(6); $B1-N1$ 1.665(6); $C8-O8$ 1.147(5); $Ru1-C1-C2$ 171.3(3); $S1-Ru1-S2$ 71.17(3); $C1-C2-B1$ 172.3(4).

As noted above for the dicarbonyl complexes (Table 1), the greater electron-withdrawing nature of the alkynyl (*cf.* alkenyl) ligand is reflected in the increase in ν_{CO}

on going from $\text{Ru}(\text{CH}=\text{CHBMIDA})(\text{S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)_2$ (1912 cm^{-1}) to $\text{Ru}(\text{C}\equiv\text{CPh})(\text{S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)_2$ (1945 cm^{-1}).

The formation of ethenyl-BMIDA was confirmed by the appearance of a second set of characteristic *N*-methyl (δ_{H} 2.71) and methylene resonances (δ_{H} 3.68, 3.79; $^2J_{\text{HH}}$ 16.4 Hz) in the ^1H NMR spectrum in addition to the vinylic resonances and associated couplings indicated (Figure 39).

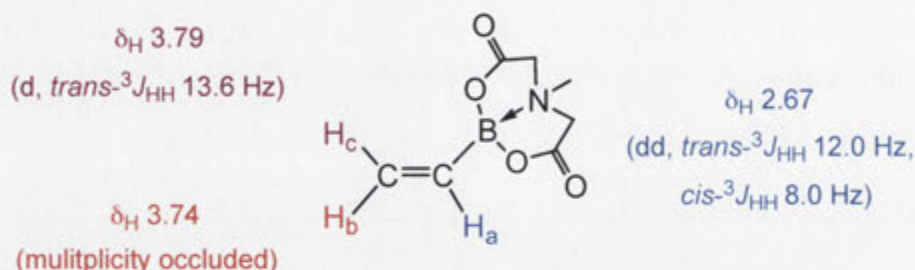


Figure 39: A diagram of ethenyl-BMIDA annotated with the ^1H NMR data for the vinylic protons.[Ⓢ]

The ethenyl-BMIDA was also structurally characterised (Figure 40) revealing that the substitution of one alkene hydrogen atom for $\text{Ru}(\text{S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)_2$ did not lead to any significant crystallographic differences in the bond lengths or C-C-B angle associated with the C=C-B spine. Comparison with the crystal structure of ethynyl-BMIDA reveals a marginally (7 e.s.d.) lengthened B1-C2 bond, consistent with the increased coordination number at C2.

[Ⓢ] 'cis' and 'trans' will be used in the discussion instead of 'Z' and 'E', given that proton-proton coupling values will be described in relation to one another. The use of priority rules in the case of ethylene BMIDA would be confusing, given that the boron is higher priority than a proton, and for example would make a *cis*- $^3J_{\text{HH}}$ coupling value the *E* stereochemistry coupling.

[Ⓣ] The geminal $^2J_{\text{HH}}$ coupling between H_b and H_c was not observed, though this coupling would be expected to be the smallest of the three types (geminal, *cis* and *trans*) demonstrated by the carbon-carbon double bond of the ethylene BMIDA, and therefore it was unsurprising that it was not observed.

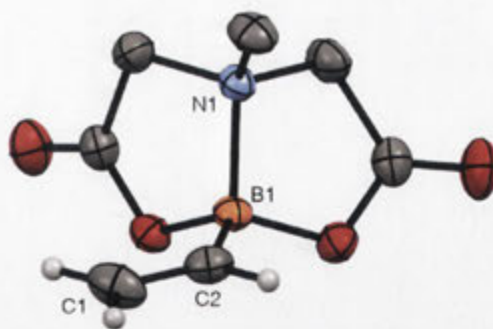


Figure 40: The molecular structure of $\text{H}_2\text{C}=\text{CHBMIDA}$. (Some hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): C1-C2 1.299(3); B1-C2 1.577(3); B1-N1 1.648(2); C1-C2-B1 127.3(2); C2-B1-N1 115.3(1).

1.8. Atrane character of BMIDA

An atrane is considered to consist of two bridgehead atoms bridged by three three-atom buttresses that support a transannular interaction between the bridgehead atoms. The degree of this interaction may be quantitatively measured *via* the bond length between the two bridgehead atoms (Figure 41), or in some cases by 1J scalar couplings in the event that the bridgehead atoms have NMR active isotopes.⁶⁷ Non-traditional constructs,⁶⁸ wherein one bridgehead is a metal and the other a boron with a transannular dative $\text{M} \rightarrow \text{B}$ bond have also been described as (*metallabor*)atranes. A motif in which two bridgehead atoms (N, B) are buttressed by two three-atom tethers underpins the stability of the BMIDA group allowing for the operation of a transannular $\text{N} \rightarrow \text{B}$ bond.

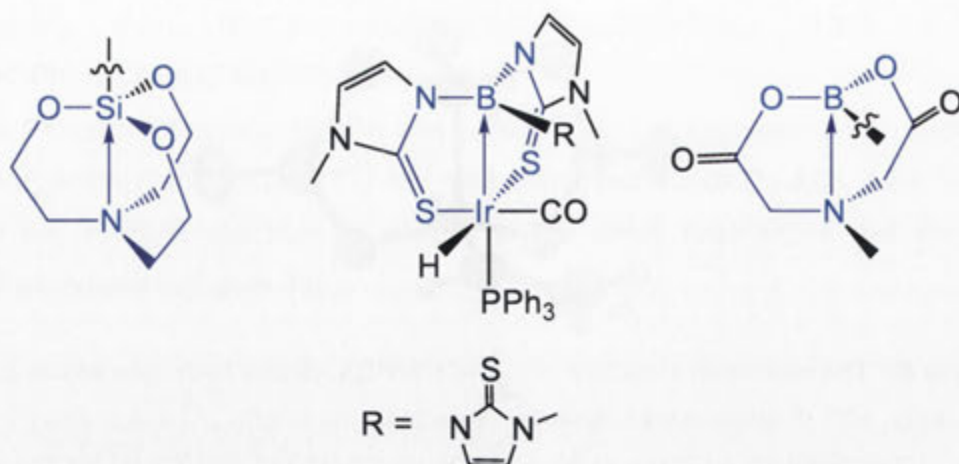


Figure 41: A general atrane type (tricyclo-[3.3.3.0]) type construct, in this instance a silatrane (left), a non-classical (bicyclo-[3.3.0]) atrane reported by Hill *et al.* (middle), and the same non-classical (bicyclo-[3.3.0]) atrane topology found in the BMIDA group (right). The atrane moiety is highlighted in blue in all three diagrams.

Looking at the BMIDA as an atrane-type construct is of interest because of the potential information garnered from the length of the N-B bond in the solid-state structures of different complexes, as has been previously described for the aptly named silicon examples of such, silatranes.⁶⁹ However, an overview of all the solid-state structures described in this chapter, which were usually organometallic type species, and of those reported in the literature, which were mainly organic in nature, found that nearly all the N-B bonds were of comparable length and for the most part were crystallographically indistinguishable from one another, with the exception of a couple outliers that were still very similar.[†]

1.9. Conclusion

In conclusion, the stable anionic alkynylfluoroborates, $[\text{RC}\equiv\text{CBF}_3]^-$ ($\text{R} = \text{Ph}, \text{SiMe}_3$), were found to be recalcitrant reagents for exploring the organometallic chemistry of boron functionalised alkynes for the substrates investigated. The intended products, such as the ruthenium alkyne salt, $\text{K}[\text{Ru}(\text{PhC}\equiv\text{CBF}_3)(\text{CO})_2(\text{PPh}_3)_2]$, were formed, though were observed to decompose before the reaction had gone to completion.

[†] See Appendix 1.

In contrast, ethynyl-BMIDA proved to be a versatile species for the synthesis of a range of organometallic complexes including rare examples of σ -alkenyl, σ -alkynyl and vinylidene complexes in which the organometallic ligand featured a boratrane substituent β - to the metal centre. In addition, the interconversion of these ligands could be demonstrated.

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Chapter 2

Reactions of Mixed Haloboranes

2.1. Preamble

Phosphine-borane adducts are far from new, the first compound of this class being the phosphine-stabilised haloborane $\text{H}_3\text{P}\cdot\text{BCl}_3$ reported in 1890.¹ However, it was not until $\text{Me}_3\text{P}\cdot\text{BH}_3$ was reported in 1953 that the surprising stability of these phosphine-stabilised boranes was appreciated, the synthetic potential thereby kindling interest in the field. Applications for these compounds were quickly discovered and reactions such as the treatment of $\text{Me}_3\text{P}\cdot\text{BH}_3$ with $^t\text{BuLi}$, followed by subsequent reaction with $\text{Me}_2\text{ClP}\cdot\text{BH}_3$ to afford the coupled product $\text{H}_2\text{C}(\text{PMe}_2\text{BH}_3)_2$ (Figure 1). However, as this example illustrates, attention was frequently focused on the phosphine substituents, or at the phosphorus centre itself, rather than the boron centre; the boron substituent was in essence used as a protecting group for the phosphine.¹⁻³

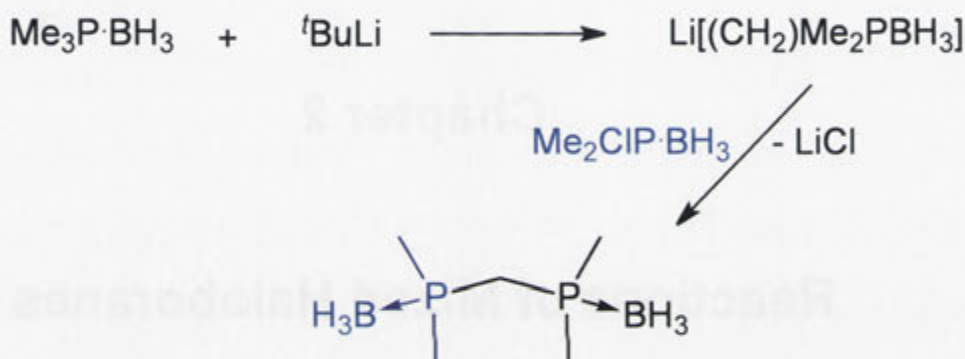


Figure 1: Reaction scheme showing early uses of phosphine-stabilised boranes.

Utilising the stability of these new $\text{P}\rightarrow\text{B}$ compounds, a method of synthesising phosphine-stabilised mixed haloborane species was developed *via* the reaction of the parent phosphine borane adduct with the corresponding halogen gas.^{4, 5} This process worked effectively for both electron-donating and electron-withdrawing (Me and Ph, respectively) phosphine substituents, even though it had been previously determined that varying the substituents on the phosphine had, as expected, a discernible effect on the reactivity of the boron atom.¹ At the same time, it was realised that phosphine-stabilised mixed haloborane species could be synthesised in an analogous fashion to phosphine-stabilised boranes *via* direct reaction of the parent phosphine with the desired mixed haloborane freshly generated *in situ*. Phosphine adduct formation was found to stabilise the mixed haloborane with respect to otherwise facile

disproportionation and gave the desired product.⁵ This method allowed the use of anhydrous hydrohalic acids instead of the corresponding halogen gases, making the process both easier and safer with comparable yields.

2.1.1. Haloboranes and Mixed Haloboranes

Whilst the pursuit of phosphine-borane adducts has continued, attention has focused primarily on their use as phosphine protecting groups such that substituted haloborane and mixed haloborane substituents have been somewhat neglected. Binary haloboranes of the form BX_3 (where X = halogen) are highly reactive and therefore useful, albeit hydrolytically sensitive reagents. Mixed haloboranes of the form $\text{BH}_n\text{X}_{3-n}$ ($n = 1, 2$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) also share the highly reactive nature of haloboranes, but with an added dimension, the ability to selectively functionalise at a hydrogen or halogen atom. Unfortunately, mixed haloboranes are prone to spontaneous disproportionation to yield boranes and trihaloboranes (Figure 2). A small number of mixed haloboranes are commercially available as dimethylsulphide (SMe_2) stabilised solutions, however, these also suffer from disproportionation, albeit at a much slower rate. The reagents $\text{Me}_2\text{S} \rightarrow \text{BH}_n\text{X}_{3-n}$ ($n = 1, 2$; $\text{X} = \text{Cl}, \text{Br}$) were therefore the reagents of choice in the work to be described.

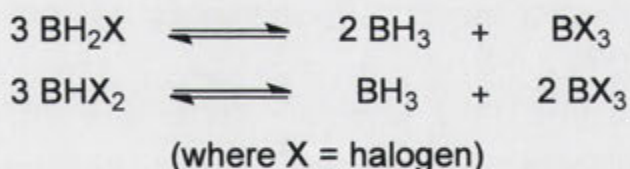


Figure 2: Disproportionation of mixed haloboranes.

Mixed haloborane adducts of conventional phosphines such as triphenylphosphine were synthesised in the mid 1980's, but with limited characterisation by today's standards.^{4, 6} Infrared and elemental microanalytical data were common, NMR data (^1H , ^{13}C , ^{31}P) less so, and the techniques that might provide the most insight into the nature of the $\text{P} \rightarrow \text{B}$ dative bond, ^{11}B NMR spectroscopy or single X-ray diffraction, were less expedient and infrequently employed.

2.2. Phosphine-Stabilised Mixed Haloborane Adducts

The initial objective was to develop convenient and general synthetic procedures for these key species based on ligand substitution reactions involving SMe_2 adducts of mixed haloboranes as opposed to the problematic generation of mixed haloboranes *in situ*.⁴ Reactions of equimolar amounts of triphenylphosphine and $\text{BHCl}_2\cdot\text{SMe}_2$ or $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ afforded the phosphine-stabilised mixed haloboranes $\text{Ph}_3\text{P}\cdot\text{BHCl}_2$ and $\text{Ph}_3\text{P}\cdot\text{BH}_2\text{Br}$ in good yields. Both compounds exhibited good stability with no decomposition upon brief exposure to (moist) air. The analogous tricyclohexylphosphine adducts were also synthesised, with the products showing the same air/moisture tolerance as noted for the triphenylphosphine adducts.

The success of reactions between mixed haloboranes and the common phosphines, PPh_3 and PCy_3 , was followed by variations of the phosphine substituents. A comprehensive study was therefore conducted to examine the steric and electronic threshold for these two mixed haloboranes, $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ and $\text{BHCl}_2\cdot\text{SMe}_2$. For the purposes of benchmarking results, the Tolman steric (cone angle, θ_T) and electronic parameters (ν_T) were employed in addition to the percent buried volume ($\%V_{\text{Bur}}$), which is beginning to enjoy wider use.*

The compact and strongly σ -basic trialkyl phosphines PMe_3 and PEt_3 have been previously prepared,^{7, 8} but the other end of the steric/electronic spectrum involving bulkier and more weakly σ -basic phosphines has yet to be explored. To fulfil this role, $\text{P}(\text{C}_6\text{H}_4\text{F-4})_3$, $\text{P}(\text{C}_6\text{F}_5)_3$, $\text{P}(\text{C}_6\text{H}_4\text{Me-2})_3$ and $\text{P}(\text{N-Carb})_3$ (where N-Carb = N-carbazolyl , $\text{C}_{12}\text{H}_8\text{N}$) were employed. The fluoroaryl examples were chosen to mimic the very similar steric features of PPh_3 , whilst greatly curtailing the σ -basicity of the phosphine. The 2-tolyl derivative exemplified an increase in the steric congestion about phosphorus with minimal change in basicity; the use of $\text{P}(\text{N-Carb})_3$ allowed the effects of a very bulky, electron-withdrawing substituent to be studied. Perhaps unsurprisingly, $\text{P}(\text{C}_6\text{F}_5)_3$ failed to react with either $\text{BHCl}_2\cdot\text{SMe}_2$ or $\text{BH}_2\text{Br}\cdot\text{SMe}_2$. This reticence to react may be attributed to the very strong electron-withdrawing effect of the C_6F_5 substituents, given that $\text{P}(\text{C}_6\text{F}_5)_3$ sterically approximates to $\text{P}(\text{C}_6\text{H}_5)_3$ (which readily forms $(\text{C}_6\text{H}_5)_3\text{P}\cdot\text{BH}_2\text{Br}$ and $(\text{C}_6\text{H}_5)_3\text{P}\cdot\text{BHCl}_2$). Similarly, $\text{P}(\text{N-Carb})_3$ failed to react to any appreciable extent with $\text{BH}_3\cdot\text{SMe}_2$ as evinced by ^{31}P NMR spectroscopy, the cause of

* Please see Appendix 2.

which is most likely electronic in origin given the existence of $\text{Se}=\text{P}(\text{N-Carb})_3$ and $\text{AuCl}(\text{P}[\text{N-Carb}]_3)$.^Ω For neither of these phosphines has there been any reports of adduct formation with boron electrophiles (of any description),^{*} leading to the inference that the Lewis basicity of $\text{P}(\text{C}_6\text{F}_5)_3$ and $\text{P}(\text{N-Carb})_3$ is insufficient for stable adduct formation.

Given that $\text{P}(\text{C}_6\text{H}_4\text{F-4})_3$ has been shown to form adducts with trihaloboranes $(\text{C}_6\text{H}_4\text{F-4})_3\text{P}\cdot\text{BX}_3$ (where $\text{X} = \text{F}, \text{Cl}, \text{Br}$), this phosphine provided a case intermediate between $\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{P}(\text{C}_6\text{F}_5)_3$ in terms of basicity whilst presenting a nearly identical steric profile to the former. This was indeed found to be the case with the successful formation of $(\text{C}_6\text{H}_4\text{F-4})_3\text{P}\cdot\text{BH}_2\text{Br}$ and $(\text{C}_6\text{H}_4\text{F-4})_3\text{P}\cdot\text{BHCl}_2$ in 25% and 52% purified yields,[§] respectively (Figure 3). These compounds showed limited air/moisture tolerance in the solid state, but decomposed over several weeks of exposure. It may be surmised that as the more Lewis basic phosphine $\text{P}(\text{C}_6\text{H}_4\text{F-4})_3$ was found to react to give the corresponding mixed haloborane adducts, that only the weakest σ -donating phosphines, resulting from extremely electron-withdrawing substituents, are unable to form adducts with electron deficient boranes and mixed haloboranes.

^Ω $\text{AuCl}(\text{P}[\text{N-Carb}]_3)$ - unpublished results.

^{*} SciFinder search - 28/09/14

[§] cf. $(\text{C}_6\text{H}_5)_3\text{P}\cdot\text{BH}_2\text{Br}$ and $(\text{C}_6\text{H}_5)_3\text{P}\cdot\text{BHCl}_2$ were recovered in 97% and 64% yields, respectively.

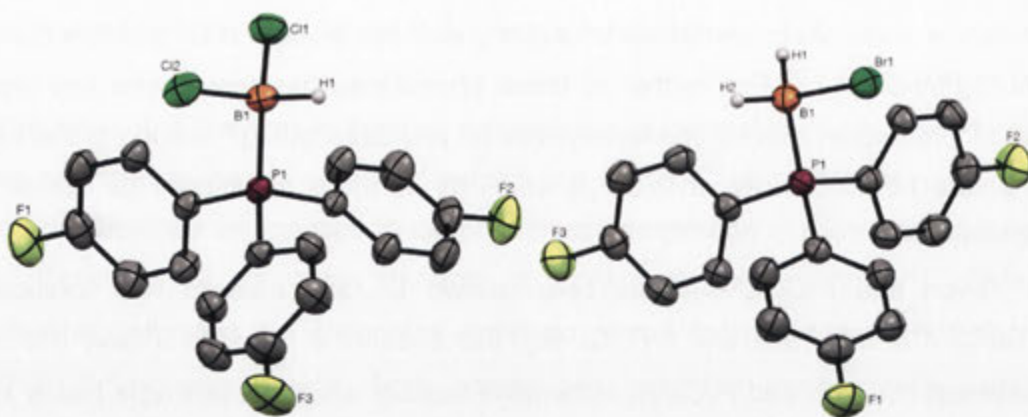


Figure 3: The molecular structures of $(\text{C}_6\text{H}_4\text{F-4})_3\text{P}\cdot\text{BHCl}_2$ (left) and $(\text{C}_6\text{H}_4\text{F-4})_3\text{P}\cdot\text{BH}_2\text{Br}$ (right) in the solid-state. (Aryl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°) for $(\text{C}_6\text{H}_4\text{F-4})_3\text{P}\cdot\text{BHCl}_2$: B1-Cl1 1.841(3); B1-Cl2 1.851(3); B1-P1 1.978(3); Cl1-B1-Cl2 111.1(1); Cl1-B1-P1 110.9(1); Cl2-B1-P1 107.2(1). Selected bond lengths (Å) and angles (°) for $(\text{C}_6\text{H}_4\text{F-4})_3\text{P}\cdot\text{BH}_2\text{Br}$: B1-Br1 2.054(3); B1-P1 1.945(3); Br1-B1-P1 106.8(1).[†]

The steric limitations of reactions between boranes and phosphines were also tested. The ability of both PPh_3 ($\theta_{\text{T}} = 145^\circ$; $\%V_{\text{Bur}} = 34.5$) and PCy_3 ($\theta_{\text{T}} = 170^\circ$; $\%V_{\text{Bur}} = 37.1$) to form adducts with $\text{BHCl}_2\cdot\text{SMe}_2$ and $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ suggested that traditional bulky substituents were readily accommodated in the formation of mixed haloborane adducts. Therefore, the use of $\text{P}(\text{C}_6\text{H}_4\text{Me-2})_3$ ($\theta_{\text{T}} = 194^\circ$; $\%V_{\text{Bur}} = 46.7$) was chosen to examine the steric threshold, given its modest basicity ($\nu_{\text{T}} = 2066.6 \text{ cm}^{-1}$; cf. $\nu_{\text{T}} = 2068.9 \text{ cm}^{-1}$ for PPh_3). Reaction of equimolar amounts of $\text{P}(\text{C}_6\text{H}_4\text{Me-2})_3$ and $\text{BHCl}_2\cdot\text{SMe}_2$ yielded a mixture of products that could not be separated due to decomposition attending subsequent purification attempts, though presumably the desired product $(\text{C}_6\text{H}_4\text{Me-2})_3\text{P}\cdot\text{BHCl}_2$ was among these products, as suggested by ^{11}B NMR spectroscopy with peaks observed at -14.9, -3.6, 5.2 and 6.4 ppm. However, the reaction of $\text{P}(\text{C}_6\text{H}_4\text{Me-2})_3$ with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ did proceed, at least partially, and cleanly to the desired product which was observed by NMR spectroscopy (δ_{B} -19.9; δ_{P} 13.7), in addition to resonances due to the mixed haloborane educt (δ_{B} -12.1), the sharpness of

[†] The hydrogen atoms for most solid-state structures were placed artificially based on the geometry present in the model and restrained to ride on their respective parent atom. As a result of this approximation, the bond lengths and angles relating to these hydrogen atoms do not possess e.s.d.'s and will not be reported herein.

which suggested that adduct formation is not rapidly reversible on these NMR timescales. The successful isolation of the desired adduct $(\text{C}_6\text{H}_4\text{Me-2})_3\text{P}\cdot\text{BH}_2\text{Br}$ was hindered by the continual decomposition of the product even under an inert atmosphere of dinitrogen during recrystallisation attempts. The increased steric hindrance of three methyl groups surrounding the phosphorus atom would be expected to disfavour adduct formation with bulkier mixed dihaloboranes such as BHCl_2 .¹⁰ The decomposition of $(\text{C}_6\text{H}_4\text{Me-2})_3\text{P}\cdot\text{BH}_2\text{Br}$ was interesting and indicated that the P-B bond was significantly more labile, and therefore longer, than those for the other previously synthesised phosphines bearing less bulky substituents. The steric origin of this lability might have been confirmed in the solid-state but unfortunately the obtention of suitable crystals was confounded by the continual decomposition observed with each subsequent recrystallisation. However, it was possible to infer the weakness of the B-P interaction from the ^{11}B NMR chemical shift of -19.9 ppm for $(\text{C}_6\text{H}_4\text{Me-2})_3\text{P}\cdot\text{BH}_2\text{Br}$, which was at a slightly higher frequency than those for $\text{Ph}_3\text{P}\cdot\text{BH}_2\text{Br}$ (δ_{B} -23.2) and $(\text{C}_6\text{H}_4\text{F-4})_3\text{P}\cdot\text{BH}_2\text{Br}$ (δ_{B} -23.9). A space-filling representation derived from the computationally optimised geometry of $\text{P}(\text{C}_6\text{H}_4\text{Me-2})_3$ is shown in Figure 4, which reflects the steric congestion about phosphorus.

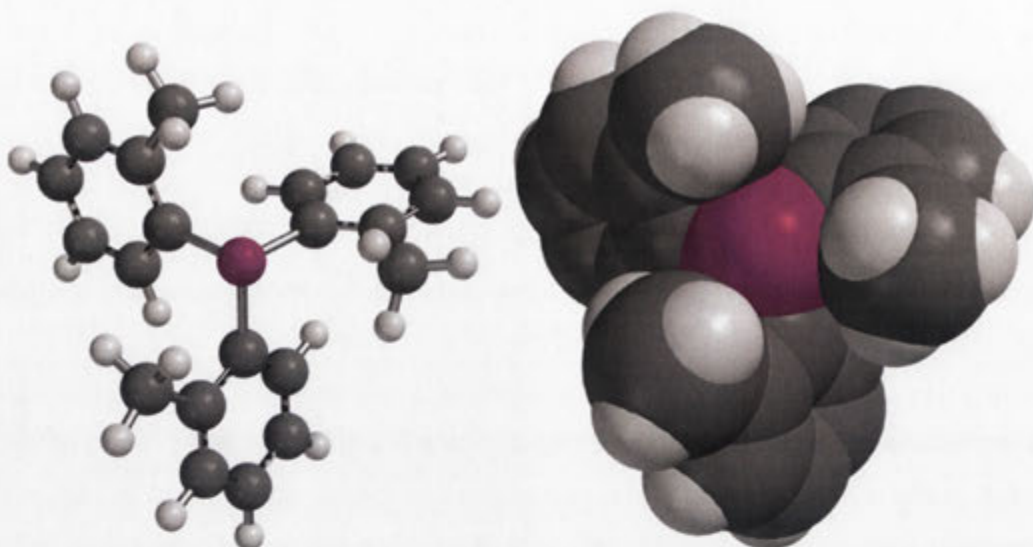


Figure 4: The computational ground state configuration^a of $P(C_6H_4Me-2)_3$ to illustrate the steric hindrance around the phosphorus centre.

2.2.1. Spectroscopy of Phosphine-Stabilised Mixed Haloboranes Adducts

The most notable observation to emerge from the resulting adducts that were formed was the remarkable similarity in their spectroscopic data. The solid-state structures of the BH_2Br and $BHCl_2$ adducts for each of the tertiary phosphines, PPh_3 , PCy_3 and $P(C_6H_4F-4)_3$ were determined crystallographically (Table 1). The BH_2Br adducts are particularly useful with their near identical values for the $P \rightarrow B$ bond length, as they present a striking example of how, despite the greatly altered electronics of the phosphine substituents, the resulting strength of the $P \rightarrow B$ dative bond is unaffected. Similarly, the values for the $BHCl_2$ adducts are well within the 6σ margin of error traditionally allowed for crystallographic data.

^a Performed with Spartan 10 using Hartree-Fock level of theory, 3-21G basis set and simulated as if in a vacuum.

Table 1: P→B bond lengths (Å) for tertiary phosphine mixed haloborane adducts.

	BH ₂ Br	BHCl ₂	BH ₂ Cl
PCy ₃	1.945(2)	2.02(1)	-
PPh ₃	1.943(3)	1.979(2)	-
P(C ₆ H ₄ F-4) ₃	1.945(3)	1.978(3)	-
Ph ₂ PBH ₂ PClPh ₂ ¹¹	-	-	1.9518(8)
Me ₂ PPMe ₂ ¹²	1.97(1)	-	-
^t Bu ₂ HPBH ₂ P ^t Bu ₂ ¹³	-	-	1.955(3)

This trend was seen to extend to the solution state, as ¹¹B NMR spectra for these compounds supported the solid-state data. All the resonances for the BHCl₂ adducts lie within a narrow 2-3 ppm range, as do the corresponding BH₂Br adducts (Table 2). The single outlier is the BH₂Br adduct of P(C₆H₄Me-2)₃, the lability of which is attributed to steric pressures. As expected, the ³¹P NMR values vary significantly between compounds due the differing electronic properties of the phosphine substituents.

Table 2: ¹¹B NMR data (ppm; referenced to external BF₃·Et₂O) for tertiary phosphine mixed haloborane adducts.

	θ _T (°)	ν _T (cm ⁻¹)	% V _{Bur}	BH ₂ Br	BHCl ₂
PCy ₃	170	2056.4	37.1	-26.2	-6.2
PPh ₃	145	2068.9	34.5	-23.2	-4.4
P(C ₆ H ₄ F-4) ₃	145	2071.3	34.5	-23.9	-6.0
P(C ₆ H ₄ Me-2) ₃	194	2066.6	46.7	-19.9	- [§]

2.3. Organometallic Potential of Phosphine-Stabilised Mixed Haloboranes Adducts

There has been considerable success in coordinating borane adducts, *e.g.* L·BH₃ (L = NMe₃, PMe₃, PPh₃), to metal centres with the use of homoleptic metal hexacarbonyls (where metal = Cr, Mo, W) (Figure 5).¹⁴ However, to synthesise these species

[§] (C₆H₄Me-2)₃P·BHCl₂ could not be isolated, therefore the ¹¹B NMR resonance could not be definitively assigned and will not be included here.

photolysis was often required to first create a vacant coordination site around the metal centre and generate the highly reactive, 16-electron $M(CO)_5$ species, to which borane adducts could then coordinate *via* 3-centre, 2-electron B-H-M bonds. Reflecting the weakness of this interaction, such species were often found to quickly decompose in solution or under vacuum due to the highly labile nature of the coordination, though isolation and crystallographic resolution in some cases was possible. Nevertheless, the goal of synthesising more stable analogues of σ -alkane metal complexes was achieved, as phosphine-stabilised adducts are isoelectronic with alkanes (Figure 6). In contrast to this lability, B-H-M interactions which form part of a chelate are commonplace and date back to the early studies of Trofimenko and Kosky who observed such interactions in the complex $Mo(\eta^3-C_3H_5)(CO)_2\{\kappa^3-H,N,N'-H_2B(pz^*)\}$.¹⁵⁻¹⁷ Three-centre, 2-electron B-H-M interactions are also a recurrent feature of metallapolyborane chemistry, where inclusion within (or *exo* to) a polyhedral cluster framework confers stability.

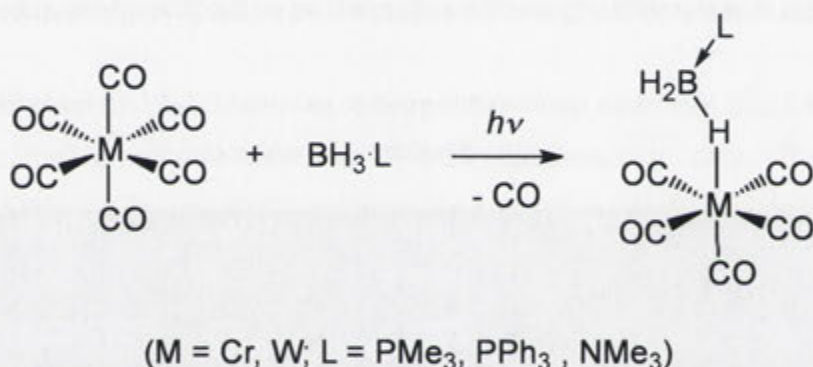


Figure 5: The coordination of borane adducts to chromium and tungsten hexacarbonyls *via* photolysis.¹⁴



Figure 6: An ammonia-borane adduct and ethane, which illustrates the isoelectronic nature of the borane adduct and the methyl groups, as both have the same structure and number of electrons.

This intrinsic lability of an unsupported borane adduct when coordinated to a metal centre led Weller *et al.* to synthesis a tethered 1,2-bis(diphenylphosphino)methane (dppm) monochloroborane adduct as a precursor to a chelate stabilised B-H-M interaction (Figure 7).^{18, 19} The pendant phosphine remained free to bind to metal centres whilst proximally positioning the mixed haloborane in the vicinity of the metal centre for subsequent ring-closure chelation.

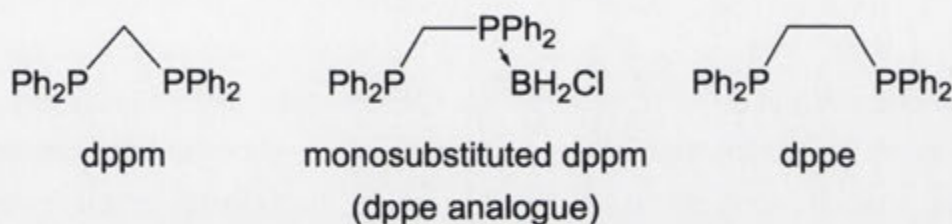


Figure 7: A comparison of the structures of diphosphines.¹⁹

As a demonstration of this ability, the ruthenium salt $[\text{RuCp}^*(\kappa^3\text{-H,H,P-H}_2\text{ClB-dppm})][\text{BAR}^{\text{F}}_4]$ was prepared, wherein the BH_2 group occupies two coordination sites *via* two 3c-2e B-H-Ru interactions (together comprising a 4c-4e association) (Figure 8). The chelated structure thereby enjoys kinetic stabilisation not observed for untethered complexes, *e.g.*, of the form $[\text{M}(\text{CO})_5(\kappa^1\text{-BH}_3\text{-L})]$ (where $\text{M} = \text{Cr}, \text{W}$ and $\text{L} = \text{PMe}_3, \text{PPh}_3$).¹⁴

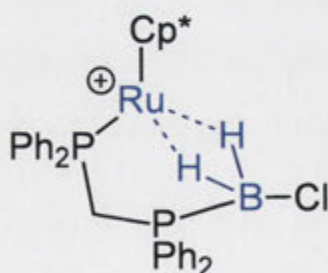


Figure 8: The molecular structure of the cation $[\text{RuCp}^*(\kappa^3\text{-H,H,P-H}_2\text{ClB-dppm})]^+$ in a crystal of $[\text{RuCp}^*(\kappa^3\text{-H}_2\text{ClB-dppm})][\text{BAR}^{\text{F}}_4]$, showing the two hydrogen atoms of the BH_2Cl adduct coordinating to the ruthenium centre.¹⁹

2.3.1. Mono- and Di-Substituted Diphosphine Mixed Haloborane Adducts

The syntheses of $\text{dppm} \cdot \text{BHCl}_2$ and $\text{dppm} \cdot \text{BH}_2\text{Br}$ were investigated in an analogous fashion to the reported protocol for $\text{dppm} \cdot \text{BH}_2\text{Cl}$.¹⁹ Unfortunately, stoichiometric reactions of dppm and the mixed haloboranes were found to produce approximately equal mixtures of the mono- and disubstituted products (the disubstituted product being ineffective for the intended purpose of complexing a free phosphine donor to a metal centre), along with unreacted dppm. The same reactions were performed using dppe in place of dppm, but similarly failed to exclusively produce the monosubstituted product, along with the additional complication of the possibility of a ring-closed product with the mixed bromoboranes BH_2Br and BHBr_2 .⁶ Given the disparity of these results, the published procedure was revisited, but was also found by ^{31}P NMR spectroscopy to yield a mixture of mono- and disubstituted products. Whilst the formation of the $\text{dppm} \cdot \text{BH}_2\text{Cl}$ mono-adduct was supported by its subsequent coordination to a ruthenium centre, it might be surmised that the bis adduct $\text{dppm} \cdot (\text{BH}_2\text{Cl})_2$, which appears to also form, would not be expected to coordinate to the ruthenium, *i.e.* this impurity might not have interfered with the subsequent coordination chemistry. For both dppm and dppe, the similar physical properties of the mono- and disubstituted products hindered attempts to cleanly isolate the desired monosubstituted product, and accordingly, these species were not pursued further.

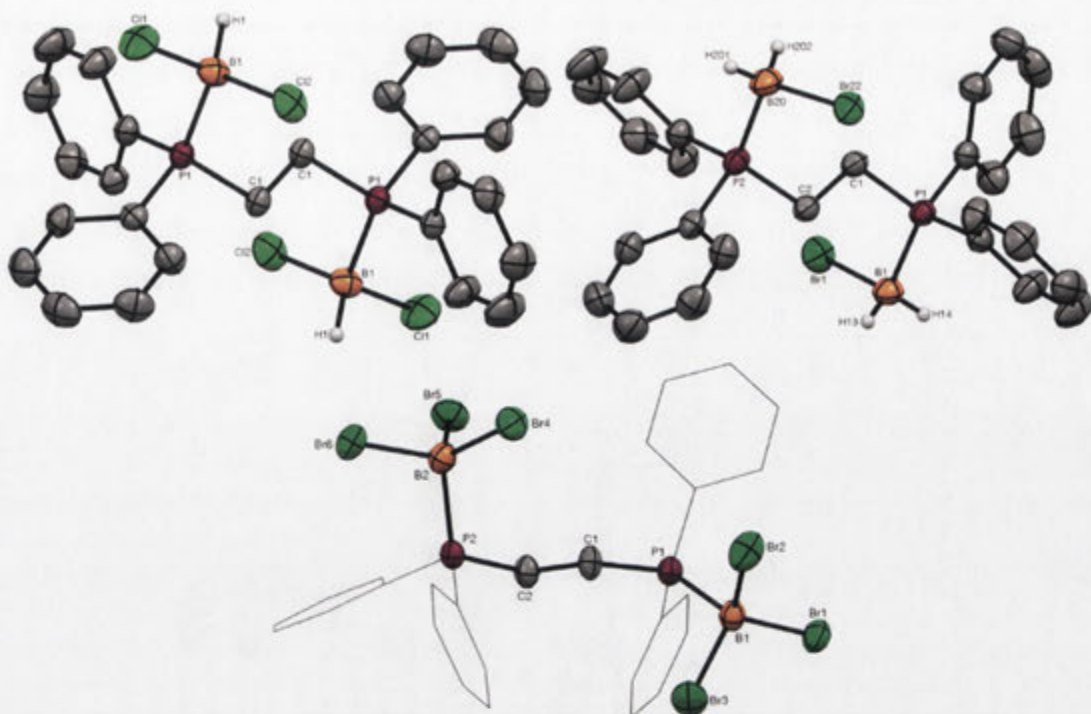


Figure 9: The molecular structures of $\text{dppe} \cdot (\text{BHCl}_2)_2$ (top left), $\text{dppe} \cdot (\text{BH}_2\text{Br})_2$ (top right) and $\text{dppe} \cdot (\text{BBr}_3)_2$ (bottom). (Carbon-bound hydrogen atoms omitted for clarity, some aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°) for $\text{dppe} \cdot (\text{BHCl}_2)_2$: B1-Cl1 1.841(2); B1-Cl2 1.869(2); B1-P1 1.970(2); P1-C1 1.825(2); C1-C1ⁱ 1.535(3); Cl1-B1-Cl2 111.8(1); Cl1-B1-P1 107.4(1); Cl2-B1-P1 105.86(9); B1-P1-C1 110.10(8); P1-C1-C1ⁱ 111.3(1). Selected bond lengths (Å) and angles (°) for $\text{dppe} \cdot (\text{BH}_2\text{Br})_2$: B1-Br1 2.055(3); B1-P1 1.940(3); B20-Br22 2.053(5); B20-P2 1.948(4); P1-C1 1.828(3); P2-C2 1.825(3); C1-C2 1.526(4); Br1-B1-P1 105.4(2); B1-P1-C1 111.5(1); Br22-B20-P2 108.3(2); B20-P2-C2 113.1(2); P1-C1-C2 112.5(2); P2-C2-C1 113.8(2). Selected bond lengths (Å) and angles (°) for $\text{dppe} \cdot (\text{BBr}_3)_2$: B1-Br1 1.983(5); B1-Br2 2.026(5); B1-Br3 2.005(5); B1-P1 1.972(4); B2-Br4 2.012(5); B2-Br5 2.006(5); B2-Br6 2.004(5); B2-P2 1.973(5); P1-C1 1.835(4); P2-C2 1.825(4); C1-C2 1.533(5); Br1-B1-Br2 112.4(2); Br1-B1-Br3 110.9(2); Br2-B1-Br3 110.2(2); Br1-B1-P1 109.3(2); Br2-B1-P1 105.6(2); Br3-B1-P1 108.2(2); B1-P1-C1 107.2(2); Br4-B2-Br5 111.2(2); Br4-B2-Br6 110.5(2); Br5-B2-Br6 110.2(2); Br4-B2-P2 111.7(2); Br5-B2-P2 105.0(2); Br6-B2-P2 108.0(2); B2-P2-C2 110.8(2); P1-C1-C2 117.9(3); P2-C2-C1 112.6(3).

The bis adducts of dppe with BHCl_2 , BH_2Br and BBr_3 could be obtained using an excess of the haloborane or its dimethylsulphide adduct. Thus the disubstituted dppe species were deliberately synthesised with both BHCl_2 and BH_2Br as the substituents, and the disubstituted BBr_3 analogue was isolated from a failed attempt to ring-close

dppe around a single boron centre (Figure 9). For completeness, the corresponding *E*-C₂H₂(PPh₂)₂ species with BHCl₂ and BH₂Br substituents were synthesised. The reaction of *Z*-C₂H₂(PPh₂)₂ with BH₂Cl·SMe₂ had already been reported to yield the ring-closed species [H₂B{C₂H₂(PPh₂)₂}]Br,²⁰ but reactions of the *E*-C₂H₂(PPh₂)₂ have not been reported and were of interest to establish whether the unsaturated C=C bond would present a further site for reactivity, given the inability to readily form a ring-closed boronium product.

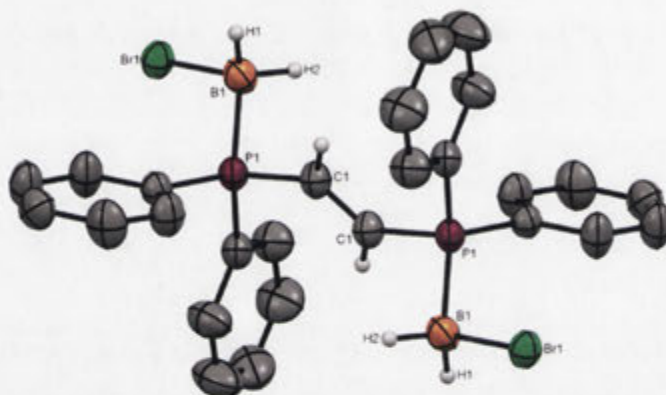


Figure 10: The molecular structure of C₂H₂(PPh₂)₂·(BH₂Br)₂ in a crystal. (Aryl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): B1–Br1 2.037(3); B1–P1 1.945(3); P1–C1 1.806(2); C1–C1' 1.323(5); Br1–B1–P1 110.6(1); B1–P1–C1 103.4(1); P1–C1–C1' 124.2(3).

2.3.2. Novel Reactions of Mixed Haloboranes

The reaction of *E*-C₂H₂(PPh₂)₂ with two equivalents of BH₂Br·SMe₂ proceeded as expected to form the disubstituted product *E*-C₂H₂(PPh₂)₂·(BH₂Br)₂ (Figure 10). However, the disubstituted BHCl₂ product could not be isolated from the corresponding reaction of *E*-C₂H₂(PPh₂)₂ with two equivalents of BHCl₂·SMe₂ due to unexpected reactivity. The anticipated product was appeared to form initially, as confirmed by ¹¹B (δ_B -6.0) and ³¹P (δ_P -2.7) NMR analysis, however, subsequent recrystallisation of the crude mixture separated an unknown minor side-product. A small number of X-ray diffraction quality colourless crystals formed during a prolonged period of crystallisation at -15°C, but not in sufficient quantity for the acquisition of spectroscopic data.

Diffraction analysis however revealed the compound to be the very unusual heterocycle $[\text{Cl}_2\text{B}(\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{BCl}_3)\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]$ (Figure 11).

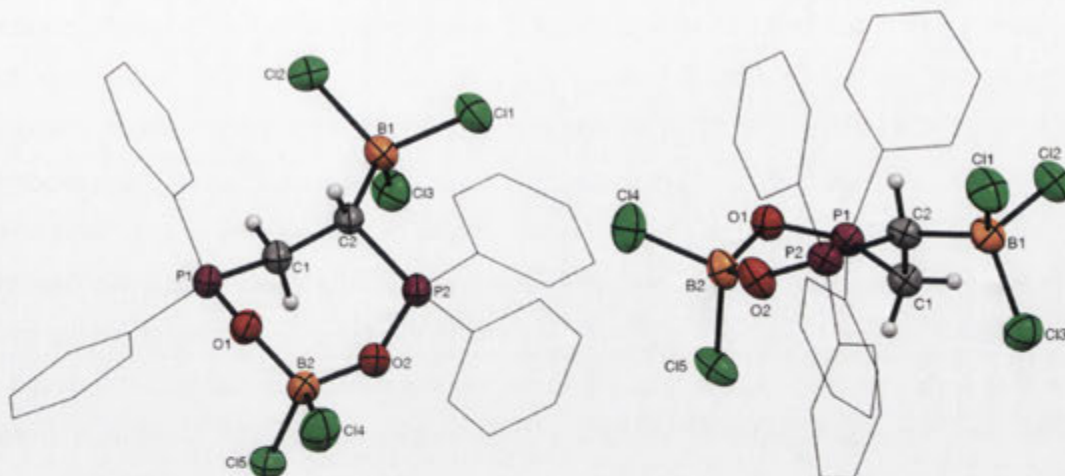


Figure 11: The plane and side-on view of the molecular structure of $[\text{Cl}_2\text{B}(\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{BCl}_3)\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]$ in a crystal. (Aryl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): B1-Cl1 1.848(3); B1-Cl2 1.883(3); B1-Cl3 1.843(3); B1-C2 1.649(4); B2-Cl4 1.823(3); B2-Cl5 1.887(3); B2-O1 1.464(3); B2-O2 1.443(3); P1-O1 1.552(2); P1-C1 1.798(3); P2-O2 1.544(2); P2-C2 1.810(2); C1-C2 1.548(3); Cl1-B1-Cl2 108.7(2); Cl1-B1-Cl3 109.5(2); Cl2-B1-Cl3 108.2(2); Cl1-B1-C2 112.4(2); Cl2-B1-C2 106.9(2); Cl3-B1-C2 111.2(2); Cl4-B2-Cl5 110.2(2); Cl4-B2-O1 109.1(2); Cl4-B2-O2 110.3(2); Cl5-B2-O1 108.9(2); Cl5-B2-O2 106.0(2); O1-B2-O2 112.3(2); B2-O1-P1 127.5(2); B2-O2-P2 145.6(2); O1-P1-C1 109.9(1); O2-P2-C2 109.9(1); P1-C1-C2 112.8(2); P2-C2-C1 110.7(2).

The structural model included a small amount of positional disorder associated with the BCl_2 group (two conformers: 88:12 ratio), but was otherwise definitive ($R = 0.044$). The structural model revealed that not one, but two, haloborane moieties had been incorporated into the heterocycle, assuming endo- (BCl_2) and exocyclic (BCl_3) positions, accompanied by a reduction of the diposphine ethene spine. A BCl_3 substituent had been added across the unsaturated double bond, but a second BCl_2 substituent had been installed between the two oxygen atoms of adventitiously oxidised phosphine oxides. As such, the heterocycle is best viewed as a zwitterion in which a dichloroboronium group is bonded by an anionic $[\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{BCl}_3)\text{CH}_2\text{P}(\text{O})\text{Ph}_2]^-$ chelate (Figure 12).

The small amount of the heterocycle obtained and the slow growth (2-3 months) of crystals under clearly less than scrupulously anaerobic conditions renders mechanistic conjecture highly dubious. Nevertheless, a couple of incontrovertible points may be noted. Firstly, sufficient observations discussed previously point towards phosphine-mixed haloborane adduct formation being reversible, such that whilst the initially formed $E\text{-C}_2\text{H}_2(\text{PPh}_2)_2\cdot(\text{BHCl}_2)_2$ no doubt predominates in the bulk sample, dissociation to regenerate free 'HBCl₂' would allow a slower conventional hydro-dichloroborylation of the PCH=CHP backbone.²¹ It might reasonably be surmised that this occurs *via* the free diphosphine rather than its dichloroborane adducts which would be deactivated (both sterically and electronically) with respect to the electrophilic attack on the olefin. It is only once this *E*-configured double bond has been reduced that rotation would allow the two phosphine groups to chelate to a single Lewis acid to form a boronium heterocycle.²⁰ Adventitious oxygen and moisture then accounts for both the oxidation of the phosphine groups and the availability of the additional halide for the exocyclic BCl₃ group, given that alkene hydro-dichloroborylation of alkenes usually affords the corresponding neutral dichloroboranes as SMe₂ adducts which may be freed of the thioether by additional BCl₃.²¹ The weakly stabilising SMe₂ quite possibly prolongs the longevity of the BHCl₂ reagent. Routine assays of samples of BHCl₂·SMe₂ (including that used here) reveals that over a period of 2-3 months, significant amounts of BH₃·SMe₂, BH₂Cl·SMe₂ and BCl₃·SMe₂ arise through disproportionation.

Mechanistic vagaries aside, the structure itself also presents some points of note. Firstly, whilst organotrifluoroborate salts are increasingly studied as partners in modified Suzuki-Miyaura cross-coupling protocols,²² structural data for organotrichloroborates are surprisingly scarce, being limited to two cyclopentadienyl examples.

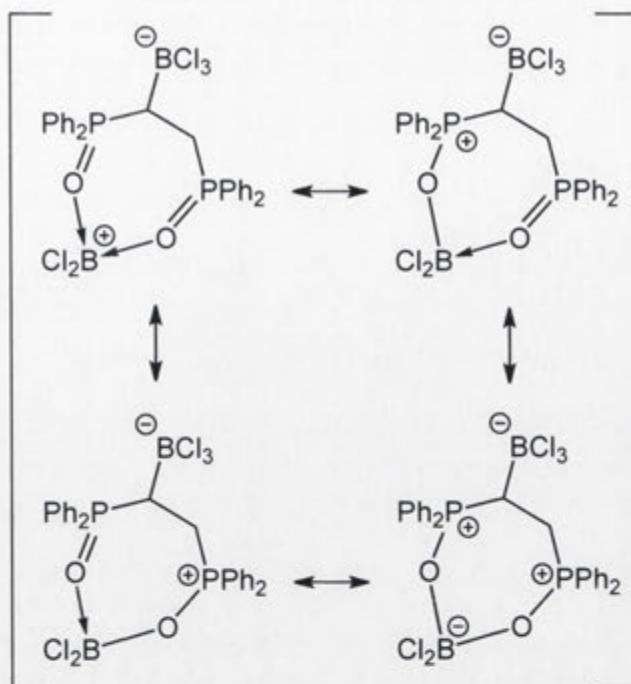


Figure 12: Canonical descriptions of the bonding in $[\text{Cl}_2\text{B}(\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{BCl}_3)\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]$, illustrating charge delocalisation.

The first example was generated by reaction of $\text{Na}[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ with BCl_3 to give $\text{Fe}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_3\text{Me}(\text{BCl}_3))$ as a minor product (< 5%).²³ The second example was synthesised by reaction of SiCp^*_2 and three equivalents of Cl_2BCp^* to give $[\text{SiCl}_2(\eta^1\text{-Cp}^*)(\text{BCp}^*)][\text{Cl}_3\text{BCp}^*]$ and ClBCp^*_2 .²⁴ However, the anion of interest, $[\text{Cl}_3\text{BCp}^*]^-$, was found to decompose rapidly in the presence of chlorinated solvents such as CD_2Cl_2 and CDCl_3 , which unfortunately were the only solvents the product was found to be soluble in. A small number of neutral *N*-heterocyclic carbene adducts of BCl_3 and BBr_3 have also been described, for which a degree of zwitterionic trihaloborato-imidazolium character might be envisaged.²⁵⁻²⁸

The boronium centre in $[\text{Cl}_2\text{B}(\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{BCl}_3)\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]$ is of particular interest, not least because structural data for a BO_2Cl_2 connectivity was not previously available. Nevertheless, a range of anionic groups have been observed to bind through two oxygen donors to the BCl_2 group including oxalate,²⁹ β -diketonates, malonamides,³⁰ benzoines,³¹ and Lukehart's 'rhenadiketonate' $[(\text{OC})_4\text{Re}(\text{MeCO})_2\text{BCl}_2]$.³²⁻³⁴ Dichloroboronium etherate cations $[\text{Cl}_2\text{B}(\text{OR}_2)_2]^+$ ($\text{OR}_2 = \text{Et}_2\text{O}$, THF) have also been spectroscopically observed,^{35, 36} though again no structural data is available. Consistent with the canonical forms depicted in Figure 12,

coordination of the two phosphoryl donors to the electrophilic BCl_2^+ unit results in elongation of the (statistically equivalent: 1.544(2), 1.552(2) Å) P-O bonds relative to those of $\text{dppe}(\text{O})_2$ (1.463(8), 1.50(1) Å) and its corresponding conjugate diacid $[\text{dppe}(\text{OH})_2]\text{Br}_2$ (1.641(6) Å) (Figure 13).^{37, 38}

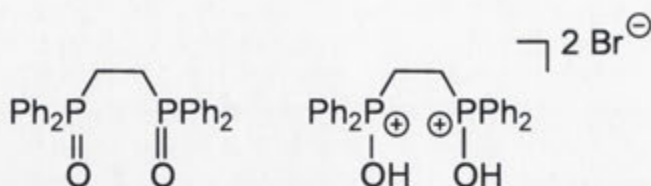


Figure 13: The two crystallographic comparison compounds used to analyse the charge delocalisation of $[\text{Cl}_2\text{B}(\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{BCl}_3)\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]$.^{37, 38}

In the absence of comparative structural data for the BCl_2O_2 donor set a small number of reported data for the analogous fluoride motif, $\text{BF}_2(\text{OPR}_3)_2$, might be considered and these also serve to illustrate the way this motif has been synthesised previously (Figure 14).^{39, 40} In both cases the BF_2 group was generated from a more halogenated boron source *via* halide-abstraction, and more importantly, both were synthesised from their respective phosphinous acid or acids, perhaps lending insight into the formation of $[\text{Cl}_2\text{B}(\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{BCl}_3)\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]$.

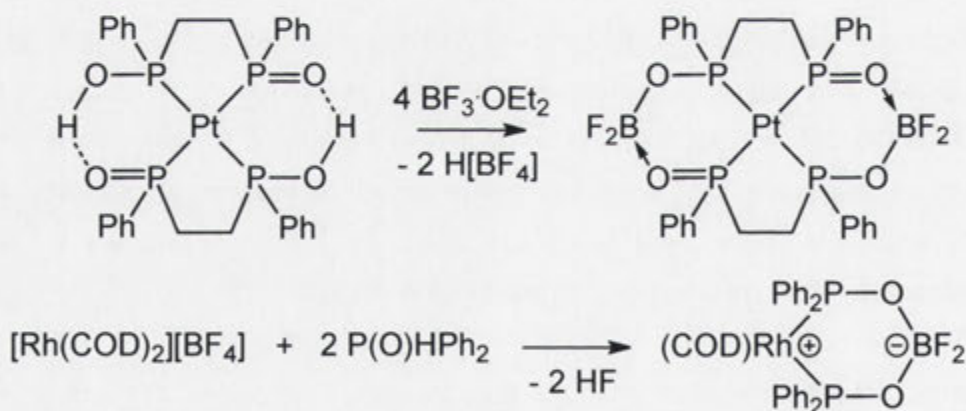


Figure 14: Synthesis of two complexes featuring a $\text{BF}_2(\text{OPR}_3)_2$ donor set.^{39, 40}

2.4. Haloborane adducts of dppa

As a prelude to the next chapter, three disubstituted phosphine-borane adducts were synthesised from 1,2-bis(diphenylphosphino)acetylene (dppa) and mixed haloboranes. These species were generated by reaction of two equivalents of the relevant SMe_2 stabilised borane or mixed haloborane and dppa in benzene to give $\text{dppa} \cdot (\text{BH}_3)_2$ (Figure 15), $\text{dppa} \cdot (\text{BHCl}_2)_2$ and $\text{dppa} \cdot (\text{BH}_2\text{Br})_2$ (Figure 16). The combination of the acetylene and phosphine-stabilised mixed haloborane groups presented a potentially interesting family of compounds to investigate.

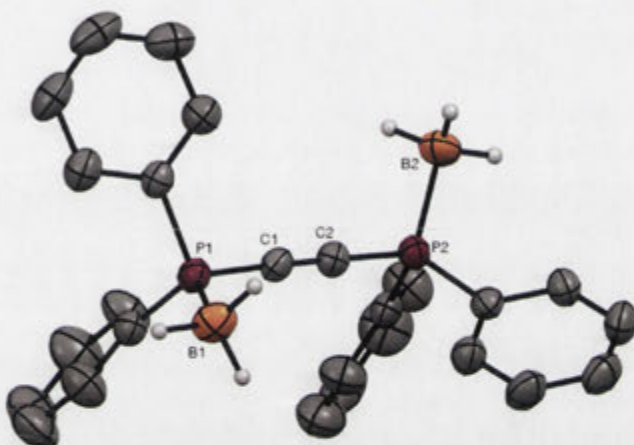


Figure 15: The molecular structure of $\text{dppa} \cdot (\text{BH}_3)_2$. (Alkyl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): B1-P1 1.912(5); B2-P2 1.924(5); P1-C1 1.757(3); P2-C2 1.770(3); C1-C2 1.198(4); B1-P1-C1 113.7(2); B2-P2-C2 113.2(2); P1-C1-C2 178.4(3); P2-C2-C1 178.6(3).

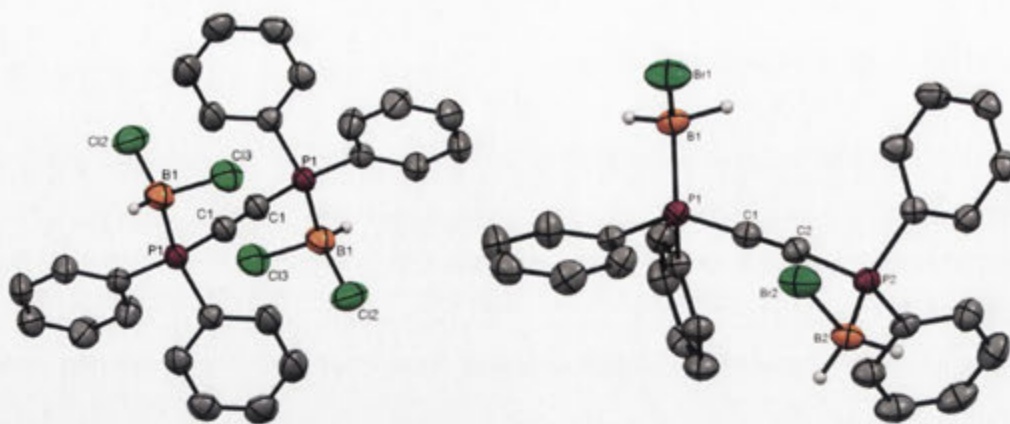


Figure 16: The crystal structure of $\text{dppa} \cdot (\text{BHCl}_2)_2$ (left) and $\text{dppa} \cdot (\text{BH}_2\text{Br})_2$ (right). (Alkyl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°) for $\text{dppa} \cdot (\text{BHCl}_2)_2$: B1-Cl2 1.832(4); B1-Cl3 1.834(4); B1-P1 1.970(4); P1-C1 1.754(3); C1-C1[†] 1.195(6); Cl2-B1-Cl3 111.3(2); B1-P1-C1 106.3(2); P1-C1-C1[†] 175.6(4). Selected bond lengths (Å) and angles (°) for $\text{dppa} \cdot (\text{BH}_2\text{Br})_2$: B1-Br1 2.014(3); B1-P1 1.936(3); B2-Br2 2.025(3); B2-P2 1.938(3); P1-C1 1.762(3); P2-C2 1.761(3); C1-C2 1.196(4); B1-P1-C1 112.6(1); B2-P2-C2 111.7(1); P1-C1-C2 177.7(2); P2-C2-C1 174.4(2).

2.5. Reactions of $\text{dppa} \cdot (\text{BH}_2\text{Br})_2$

The major organometallic products of the reaction of acetylenes with $\text{Co}_2(\text{CO})_8$ are well known (Figure 17), though can potentially be low-yielding due to competition with other side products.⁴¹ The formation of an organometallic tetrahedrane cluster under mild reaction conditions makes this reaction synthetically useful. The tetrahedrane cluster can also be viewed as the alkyne adding across the cobalt-cobalt bond in an η^2 fashion, which lends itself to a more visually apparent understanding of the reaction. The $\text{Co}_2(\text{CO})_8$ reagent has been shown to demonstrate a wide functional group tolerance for the substituents on the alkyne, which has also been extended to include other main group elements such as boron and silicon.⁴²

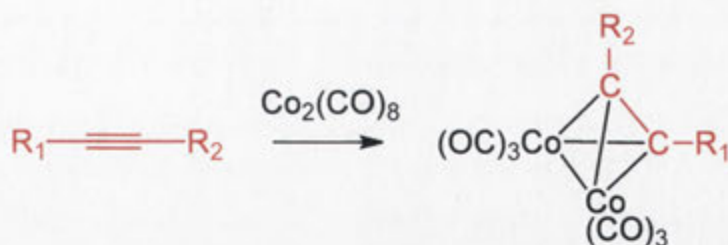


Figure 17: The general organometallic tetrahedrane cluster that is synthesised from reaction of alkynes and $Co_2(CO)_8$ ($R_1/R_2 = H, Me, Ph, B(NEt_2)_2, SiMe_3$, etc).⁴²

With this functionality in mind, the same tetrahedrane product was envisioned for reaction with one of the potentially more reactive mixed haloborane adducts of dppa. The reaction of $Co_2(CO)_8$ and unsubstituted dppa had already been reported, though not isolated nor any characterisation performed.^{43, 44} The presumed identity of the $Co_2(CO)_6(\mu-Ph_2PC\equiv CPh_2)$ product was inferred by subsequent reaction of the species with a second equivalent of $Co_2(CO)_8$ to give the parent cluster bridging across another $Co_2(CO)_6$ fragment *via* the two phosphine groups (Figure 18). The dppm tethered analogue of the dicobalt backbone has been used to coordinate the two phosphine groups to metal fragments such as $Mo(CO)_4$, $W(CO)_4$ and $PdCl_2$.⁴⁵

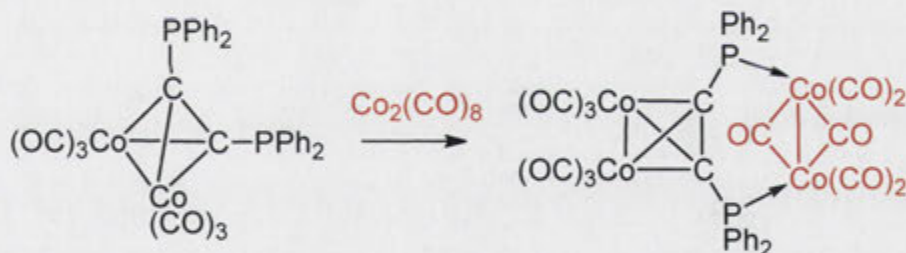


Figure 18: The reaction of the *in situ* species $Co_2(CO)_6(\mu-Ph_2PC\equiv CPh_2)$ with $Co_2(CO)_8$ to give $Co_2(CO)_4(\mu-CO)_2\{\mu-P,P-(\mu-Ph_2PC\equiv CPh_2)-Co_2(CO)_6\}$.⁴⁴

The bromoborane adduct, $dppa \cdot (BH_2Br)_2$, was chosen for reaction with $Co_2(CO)_8$ to attempt to generate $Co_2(CO)_6(\mu-Ph_2PC\equiv CPh_2)$ mixed haloborane adduct analogue $Co_2(CO)_6(\mu-C_2(PPh_2)_2 \cdot (BH_2Br)_2)$. The reaction was performed under similar conditions to those reported (THF solvent, 5-8 hours at ambient conditions), though no discernible signals could be detected from the crude reaction mixture in the ^{31}P NMR spectrum. The failure to observe any resonances in the ^{31}P NMR spectrum was even more perplexing given the two weak peaks observed in the ^{11}B NMR at -35.4 and -38.4 ppm,

which might possibly have been a doublet though was unlikely due to the large coupling constant that would be associated with it (~295 Hz). The ^{11}B NMR resonances were in the region for boronium type compounds, which are 4-coordinate borocations, the observation of which would imply degradation of the carbon-carbon triple bond in order to form such cyclic boronium species, accompanied by loss of one of the BH_2Br groups (Figure 19).

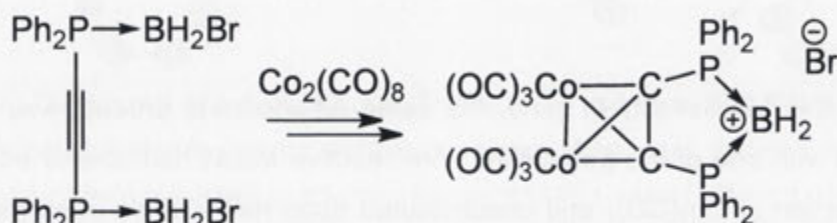


Figure 19: A potential product as suggested by the ^{11}B NMR spectrum of the crude reaction of $\text{Co}_2(\text{CO})_8$ and $\text{dppa} \cdot (\text{BH}_2\text{Br})_2$.

An underlying theme of this work is the development of boron-phosphorus reagents for subsequent investigations of transition metal coordination chemistry. A reverse approach would involve prior addition of phosphines to metal centres followed by their reactions towards haloboranes, which will be discussed further in later chapters.

2.6. References

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Chapter 3

Reactions of Mixed Haloboranes with Heterodentate Ligands

3.1. Alternate Synthetic Route to Mono-Substituted Mixed Haloboranes

In an attempt to circumvent the issue of mono- *versus* bis(adduct) formation when mixed haloboranes react with diphosphines such as dppm and dppe, the mixed coordination dppm molybdenum complex *fac*-[Mo(κ^1 -dppm)(κ^2 -dppm)(CO)₃] was investigated. This complex, previously reported by Shaw and structurally characterised here (Figure 1), features one dppm molecule in the normal bidentate coordination mode, but more importantly a second dppm coordinates in a monodentate coordination mode leaving one pendant phosphine group poised for *subsequent* mixed haloborane installation. It was envisaged that if the carbonyl co-ligands were labile (or labilised) this might then allow an interaction of the boron fragment with the molybdenum to result.

The reaction of BH₂Br·SMe₂ and *fac*-[Mo(κ^1 -dppm)(κ^2 -dppm)(CO)₃] was investigated, however NMR analysis of the recovered crude products indicated that cleavage of the molybdenum phosphine coordination had occurred, the major product being identified by ¹¹B (δ_B -23.6) and ³¹P (δ_P 1.8) as dppm·(BH₂Br)₂ with no evidence for free dppm (δ_P -27) or its monoborane adduct. Surprisingly, despite a stoichiometric 1:1 ratio of reagents being used, a significant amount of unreacted BH₂Br·SMe₂ was detected (¹¹B NMR) though numerous, markedly less intense ³¹P NMR resonances were observed between 18-37 ppm. Whilst the *fac*-[Mo(κ^1 -dppm)(κ^2 -dppm)(CO)₃] starting material was no longer present and other molybdenum phosphine complexes had been generated in the process, none predominated sufficiently to allow isolation.

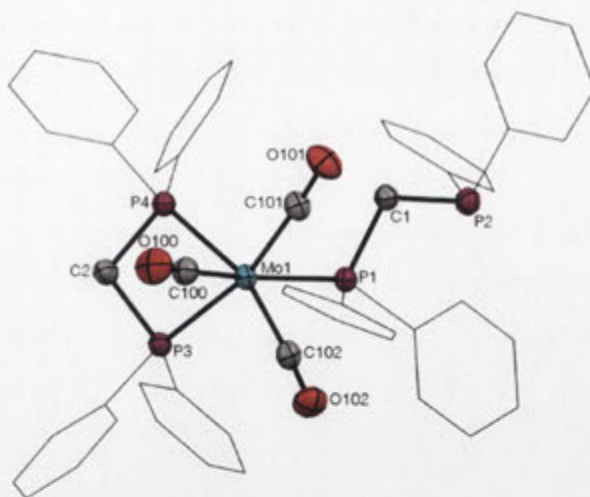


Figure 1: The molecular structure of *fac*-[Mo(κ^1 -dppm)(κ^2 -dppm)(CO)₃]. (Hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Mo1-P1 2.5644(4); Mo1-P3 2.5207(4); Mo1-P4 2.5133(4); P1-C1-P2 114.00(8); P3-C2-P4 98.80(8); P3-Mo1-P4 67.83(1).

3.2. Phosphine-Stabilised Mixed Haloboranes of Arsenic Heterochelates

An alternative approach to the issue of mono- *versus* bis(borane) adduct formation was considered which relies on the difference in Lewis basicity between phosphorus and arsenic. Descending group 15 is accompanied by a marked decrease in σ -basicity ($N > P > As$)[†] where hard and soft acid and base factors (*i.e.*, orbital overlap) become relevant for Lewis acid/base interactions. For the extremely electrophilic boron trihalides (and organoboranes), adducts with the corresponding arsines AsR₃ (where R = Me, Ph) are known by analogy with the corresponding phosphine species,²⁻⁴ though in general the former are less stable. For example, the enthalpy of reaction between diborane and PPh₃ (-160.4 kJmol⁻¹) and AsPh₃ (-76.1 kJmol⁻¹) indicate a pronounced preference for P→B *versus* As→B bond formation. The corresponding mixed haloborane arsine adducts have, however, not been previously reported. When AsPh₃ was treated with BHCl₂·SMe₂ no reaction was found to occur, even with heating (~55°C), the major effect of which was simply to promote disproportionation of the mixed haloborane reagents. Treating AsPh₃ with BH₂Br·SMe₂ similarly failed to result in

[†] *e.g.*, AsH₃ can only be protonated *via* the use of superacids.¹

any appreciable reaction, though upon heating a very small amount of $\text{Ph}_3\text{As}\cdot\text{BH}_2\text{Br}$ appeared to form, as inferred from the *in situ* ^{11}B NMR spectrum (δ_{B} -20.4). Reactions did ensue, however, between AsEt_3 and both of the mixed haloboranes $\text{BHCl}_2\cdot\text{SMe}_2$ and $\text{BH}_2\text{Br}\cdot\text{SMe}_2$, to form their respective arsine adducts, $\text{Et}_3\text{As}\cdot\text{BHCl}_2$ and $\text{Et}_3\text{As}\cdot\text{BH}_2\text{Br}$, which were observed in the ^{11}B NMR spectra at -4.4 and -23.4 ppm, respectively. Adducts arising from disproportionation such as $\text{Et}_3\text{As}\cdot\text{BH}_2\text{Cl}$ (δ_{B} -17.9, t, $^1J_{\text{BH}}$ 124.5 Hz), $\text{Et}_3\text{As}\cdot\text{BCl}_3$ (δ_{B} 2.8, s) and $\text{Et}_3\text{As}\cdot\text{BH}_3$ (δ_{B} -40.5, q, $^1J_{\text{BH}}$ 95.1 Hz)⁴ were also observed in trace amounts in the ^{11}B NMR spectra (Figure 2).^{*}

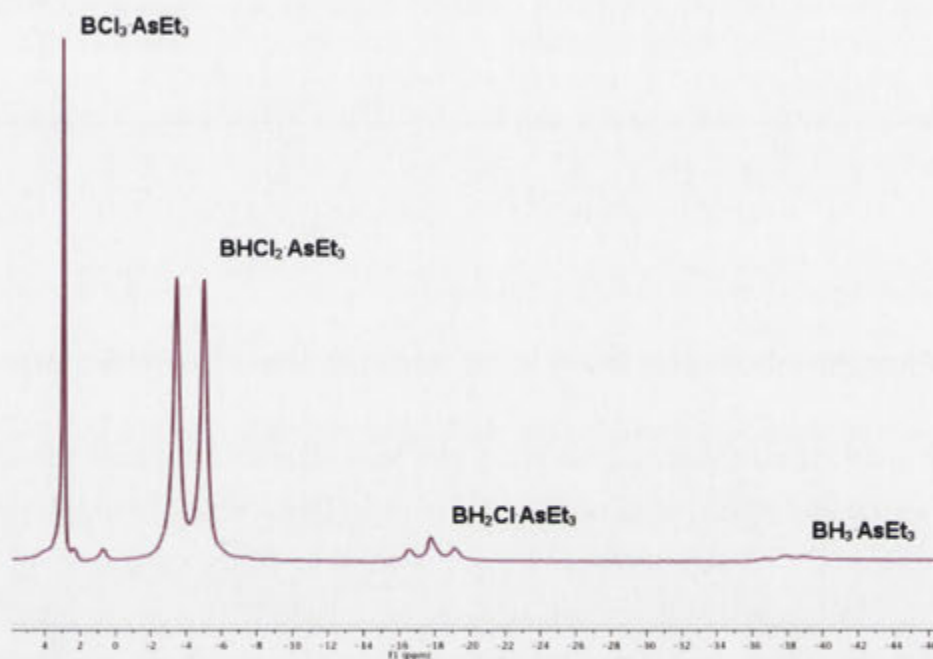


Figure 2: The proton-coupled ^{11}B NMR spectrum for the crude reaction of AsEt_3 with $\text{BHCl}_2\cdot\text{SMe}_2$.

These observations, coupled with a previous report describing the sequential addition of diborane first to the phosphorus and then to the arsenic donors of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$ (arphos),⁴ suggested that the reduced σ -basicity of arsines versus their phosphine analogues could be utilised to selectively coordinate a mixed haloborane such as BH_2Br to one donor of a heterotopic bi- or polydentate ligand containing both arsenic and phosphorus donor atoms.

^{*} Assignments of arsine-haloborane adducts made based on the multiplicity of the $^{11}\text{B}\{^1\text{H}\}$ NMR resonances.

This was confirmed by reaction of the dppe analogue $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$ (arphos) with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$. In contrast to dppe, which yields a mixture of mono- and bis-adducts as well as ring-closed products, the reaction selectively yielded only the phosphine adduct in a good yield of 82% (Figure 3). The arphos- BH_2Br adduct showed reasonable air and moisture tolerance but was found to be thermally unstable, converting *via* intermolecular interaction with itself in both non-polar benzene and polar DCM solutions over a relatively short period of time (approximately 24 hours). The new product was determined to be a boronium salt that will be discussed in more detail in a later chapter. The ^{11}B NMR peak for the mono-adduct was evident at -24.9 ppm (*cf.* δ_{B} -25.4 for $[\text{CH}_2\text{PPh}_2\cdot\text{BH}_2\text{Br}]_2$), which further confirmed that there was no interaction between the boron atom and the arsenic donor even in solution. This agreed with the crystallographically determined solid-state structure (Figure 4), in which the alkyl backbone adopted an antiperiplanar As-C-C-P conformation with no short intra- or intermolecular contacts of note. The B-P bond length was found to be 1.935(7) Å, which was once again not statistically different to those for other tertiary phosphine- BH_2Br adducts described in the previous chapter. As a solid the compound was found not to suffer from decomposition and was therefore thought to be an ideal candidate for further reaction with organometallic precursors.

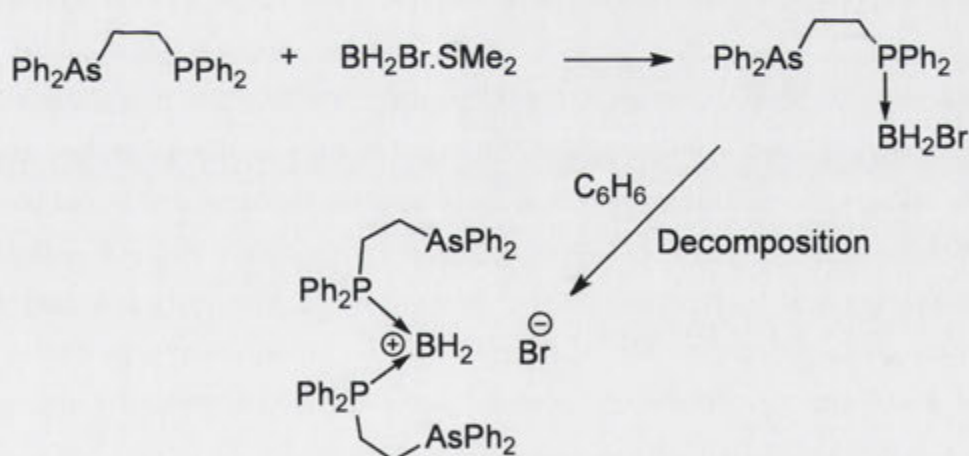


Figure 3: The reaction of arphos with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ and subsequent evolution to a boronium salt.

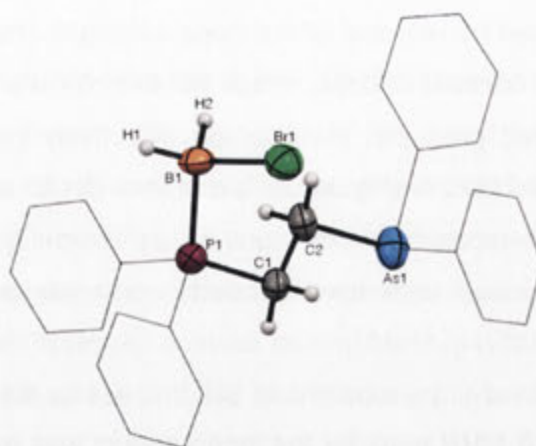


Figure 4: The molecular structure of arphos·BH₂Br. (Aryl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): B1-Br1 2.025(8); B1-P1 1.935(7); P1-C1 1.811(6); As1-C2 1.973(6); C1-C2 1.529(9); Br1-B1-P1 105.3(3); B1-P1-C1 111.8(3); P1-C1-C2 110.1(4); As1-C2-C1 112.3(5).

3.2.1. Reactions of arphos·BH₂Br with Metal Centres

In principle two modes of reactivity with transition metal reagents might be envisaged: (i) B-Br oxidative addition or salt elimination *via* bromide displacement by a nucleophilic metal carbonylate, each resulting in direct metal-boron bond formation; (ii) Simple arsine coordination to a coordinatively unsaturated metal centre (possibly followed by chelation through a B-H-M interaction). The first avenue explored was using the molybdenum anion, K[MoTp⁺(CO)₃], following previous literature approaches to metal-boron bond formation *via* the reaction of haloboranes and mixed haloboranes with metal salts,⁵⁻⁷ though not with this particular carbonylate. However, reaction of the molybdenum salt proved to yield a mixture of starting materials and boronium decomposition products. It was suspected that the halide metathesis driving force *via* loss of KBr also led to the decomposition of arphos·BH₂Br described above, effectively sequestering liberated BH₂Br as perhaps K[H₂BBr₂].

It was hoped that moving away from the potentially very reactive species generated *via* metathesis type reactions would reduce the possibility of decomposition to the arphos·BH₂Br starting material. Accordingly, Co₂(CO)₈ was investigated, in part because of the known existence of the complex [Co(κ^2 -B,P-BH₂PPh₂CH₂PPh₂)(κ^1 -dppm)(CO)₂].⁸ Whilst this unusual compound was only observed in low "hand-picked"

yield from the reduction of cobalt chloride by $\text{Na}[\text{BH}_4]$ in the presence of dppm and CO, its structure attests to the viability of such a chelate system (Figure 5). The reactions of $\text{Co}_2(\text{CO})_8$ with conventional phosphines might proceed *via* simple CO substitution, retaining the binuclear zerovalent state, or alternatively redox disproportionate with heterolytic cleavage of the $\text{Co}^0\text{-Co}^0$ bond ($[\text{Co}^{\text{I}}][\text{Co}^{\text{I}}]$) depending on the nature of the phosphine.⁹ The reaction was envisioned to proceed with the arphos- BH_2Br acting as a straightforward Lewis base at the arsenic atom, possibly followed by chelate-assisted activation of the BH_2Br group. In practice, the reaction proceeded very differently.

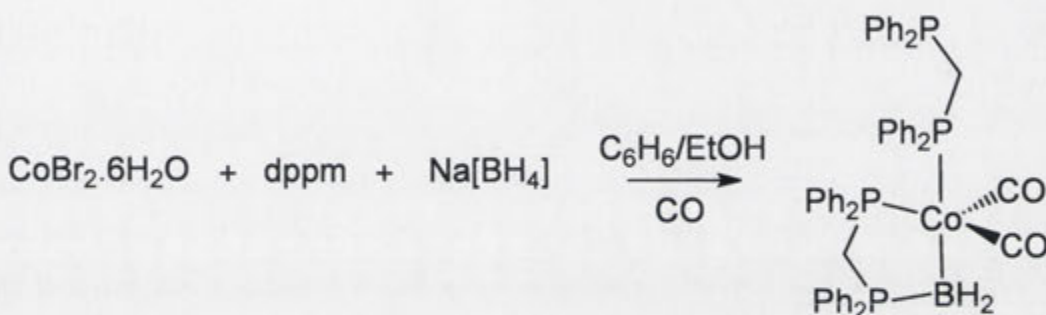


Figure 5: The reaction scheme for the formation of $[\text{Co}(\kappa^2\text{-B,P-BH}_2\text{PPh}_2\text{CH}_2\text{PPh}_2)(\kappa^1\text{-dppm})(\text{CO})_2]$.⁸

Under relatively mild conditions in DCM (ambient temperature, stirred overnight) the stoichiometric reaction of $\text{Co}_2(\text{CO})_8$ and arphos- BH_2Br does not proceed to completion, the major species present being unreacted arphos- BH_2Br (δ_{B} -25.5; δ_{P} 5.0). The arphos- BH_2Br that is consumed becomes replaced by a mixture of at least five other detected compounds, two of which displayed the characteristic peak-broadening characteristic of direct B-P bonding at 33.1 and 65.8 ppm in the ^{31}P NMR spectrum. Unfortunately, all five peaks were of comparable low intensities and the corresponding ^{11}B NMR peaks attributable to the two broadened ^{31}P NMR resonances were not observed (the only observed ^{11}B NMR peak being that for unreacted arphos- BH_2Br), though their absence may be attributed to the low sensitivity of ^{11}B NMR spectroscopy and the borosilicate glass background.

Reaction of arphos- BH_2Br with a Au(I) source was attempted, though with the intention of confirming a foreseen negative result. Despite the good stability of arphos- BH_2Br , it was expected that it would cause the Au(I) to reduce to Au(0), which was readily observed by the precipitation of elemental gold from the reaction. However,

if the $\text{arphos}\cdot\text{BH}_2\text{Br}$ starting material did not cause the Au(I) to reduce, then it was possible it would instead act as a Lewis base *via* the arsino group.

The reaction of $\text{arphos}\cdot\text{BH}_2\text{Br}$ with the labile Au(I) source $[\text{AuCl(THT)}]$ did indeed result in the rapid reduction to Au(0) as indicated by the almost instantaneous deposition of colloidal gold. The ^{11}B NMR spectrum of the resulting supernatant showed the unreacted starting material (unsurprising, as the very small scale of the reaction may have caused inaccuracy in terms of stoichiometry), the boronium decomposition product $[\text{H}_2\text{B(arphos)}_2]\text{Br}$ and a new peak at -20.5 ppm. However, the peak at $\delta_{\text{B}} -20.5$ was attributed to some slight modification of the starting material such as scrambling of the boron substituents, due to the relatively minor shift of less than 5 ppm.

The square-pyramidal 16-electron ruthenium complex $\text{Ru(Ph)Cl(CO)(PPh}_3)_2$ has been used in a number of instances for the chelate assisted activation of B-H bonds or the installation of polyboronate ligands.¹⁰ The activation of B-H relies on the σ -phenyl co-ligand serving as a hydrogen sink *via* benzene elimination, a reaction that might in principle ensue with $\text{arphos}\cdot\text{BH}_2\text{Br}$. After stirring a mixture of $\text{arphos}\cdot\text{BH}_2\text{Br}$ and $\text{Ru(Ph)Cl(CO)(PPh}_3)_2$ for 18 hours in benzene at room temperature, the ^{11}B and ^{31}P NMR spectra indicated the presence of only the two starting materials, along with free PPh_3 . As no reaction had taken place, the reaction mixture was heated to reflux in benzene overnight. Analysis of the resulting yellow solution revealed two peaks in the ^{11}B NMR spectrum at -17.9 and -23.4 ppm, and 22 peaks in the ^{31}P NMR spectrum, ranging from 70 to -5 ppm. The spread out range of peaks in the ^{31}P NMR spectrum, combined with the lack of matching ^{11}B NMR peaks immediately suggested the loss of the BH_2Br group upon heating. The peak at $\delta_{\text{B}} -23.4$ was found to be $\text{Ph}_3\text{P}\cdot\text{BH}_2\text{Br}$ (described previously), and was presumably formed by addition of the liberated BH_2Br with the labile PPh_3 . The high frequency nature of a significant number of the phosphorus peaks observed indicated that they were bonded to the ruthenium centre, but could not be assigned further. Fractional crystallisations from a mixture of DCM/pentane were moderately successful, however, in isolating crystals of two decomposition products from the reaction, which supported the NMR data.

The first product separated in a trace amount was $\text{RuBr}_2(\text{arphos})_2$ (Figure 6), which indicated that not only had the boron group been lost, but it had somehow managed to transfer its bromine atom to the ruthenium centre, perhaps suggesting that at some point the BH_2Br substituent had been coordinated in some way to the ruthenium.

However, as this product had only been recovered in a trace amount, it was not considered mechanistically significant.[†]

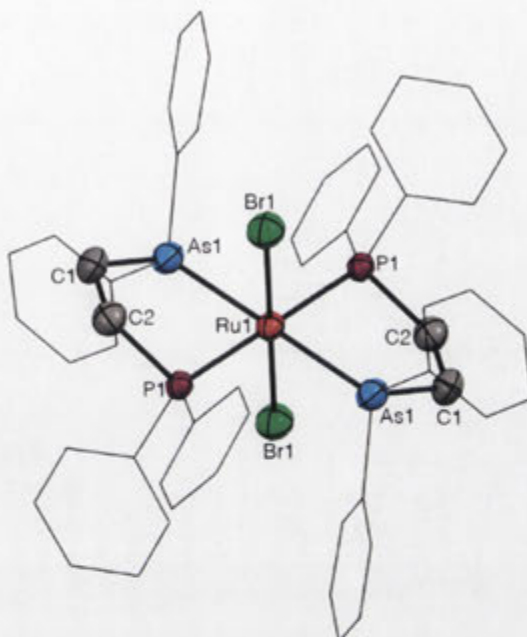


Figure 6: The molecular structure of $\text{RuBr}_2(\text{arphos})_2$. (Hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). The molecule lies on an inversion centre at ruthenium. Selected bond lengths (Å) and angles (°): Ru1-Br1 2.5504(5); Ru1-P1 2.369(1); Ru1-As1 2.4466(5); Br1-Ru1-P1 93.13(3); Br1-Ru1-As1 98.59(2); P1-Ru1-As1 81.60(3).

The second product was found to be $\text{RuBr}_2(\text{CO})(\text{PPh}_3)(\text{arphos})$ (Figure 7), which was recovered in a moderate yield of 53% (with $\text{arphos-BH}_2\text{Br}$ as limiting reagent). The fact that a major product was not observed in the post-reflux NMR spectra also suggested that this second product was either the thermodynamically most stable product, where more reactive species had decomposed to eventually end up as $\text{RuBr}_2(\text{CO})(\text{PPh}_3)(\text{arphos})$, or more likely, that the product existed as a mixture of stereoisomers. The satisfactory microanalysis obtained for the recovered product crystals supported the idea of a single product consisting of multiple isomers. Crystallographically, the arsenic and phosphorus atoms of the arphos ligand in

[†] $\text{RuBr}_2(\text{arphos})_2$ was intentionally synthesised by reaction of $\text{RuBr}_2(\text{PPh}_3)_3$ and two equivalents of arphos.

$\text{RuBr}_2(\text{CO})(\text{PPh}_3)(\text{arphos})$ were found to be disordered with respect to the location of one another,¹¹ which would already account for potentially 4 ^{31}P NMR peaks (2 from each possible orientation of the arphos ligand), as well as the discernibly different $^2J_{\text{PP}}$ coupling values for a *cis* versus a *trans* relationship between the two phosphines. Further rearrangement of the ligand set, easily plausible due to the labile nature of PPh_3 , could therefore be imagined to generate more stereoisomers, which would account for the numerous ^{31}P NMR peaks observed, though this would not adequately explain the wide range of ppm values.

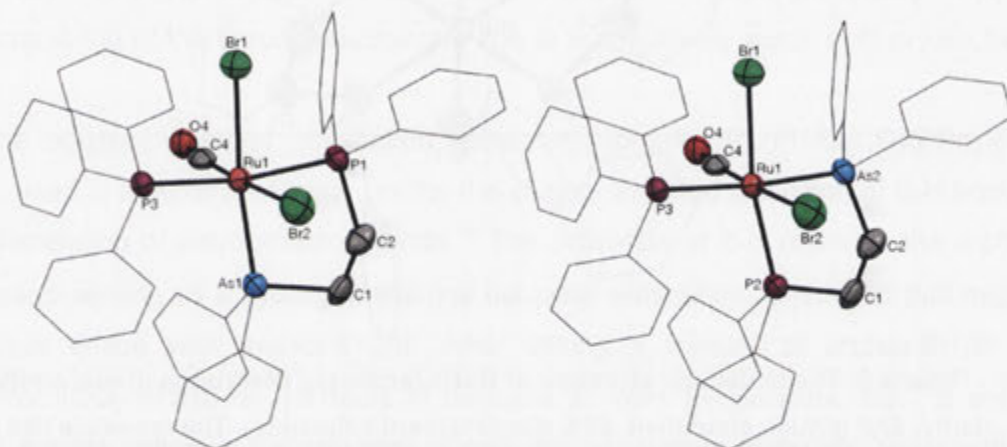


Figure 7: The molecular structures of $\text{RuBr}_2(\text{CO})(\text{PPh}_3)(\text{arphos})$. (Hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Dominant orientation of arphos ligand shown on left (58% occupancy), minor orientation on right (42% occupancy). Selected bond lengths (Å) and angles (°) for major orientation: Ru1-Br1 2.573(2); Ru1-Br2 2.576(2); Ru1-P1 2.50(2); Ru1-P3 2.426(4); Ru1-As1 2.41(2); Br1-Ru1-Br2 96.36(7); Br1-Ru1-P1 85.0(7); Br1-Ru1-P3 86.5(1); Br1-Ru1-As1 172.6(3); Br2-Ru1-P1 89.0(4); Br2-Ru1-P3 92.6(1); Br2-Ru1-As1 83.6(3); P1-Ru1-P3 171.4(7); P1-Ru1-As1 87.6(7); P3-Ru1-As1 101.0(3).

Potentially there are 10 possible stereoisomers of $\text{RuBr}_2(\text{CO})(\text{PPh}_3)(\text{arphos})$; four of which have the PPh_3 ligand occupying a meridional geometry with respect to the arphos, minimising steric hindrance and presumably resulting in lower energy structures, as apparently confirmed by the solid-state structures. These four likely low energy structures would give rise to 8 doublet ^{31}P NMR resonances, which when combined with the observation of other species found to be present such as

$\text{RuBr}_2(\text{arphos})_2^\dagger$ would amply begin to explain the high number of peaks observed experimentally. Notably, the absence of a σ -phenyl ligand in any of the products does suggest that the intended process (chelate assisted B-H activation *via* benzene elimination) had indeed occurred, but that the product(s) were not stable under the reaction conditions. Furthermore, since $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ is known to undergo clean reaction with free dppe to afford thermally stable $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)(\text{dppe})$, it may be surmised that free arphos does not accumulate in significant amounts whilst unreacted $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ remains. Accordingly, the reaction was repeated in C_6D_6 keeping the temperature at 50°C , monitoring its course by ^{31}P NMR spectroscopy, however, at this temperature no reaction was observed to occur other than decomposition of the $\text{arphos}\cdot\text{BH}_2\text{Br}$ to $[\text{H}_2\text{B}(\text{arphos})_2]\text{Br}$.

The ultimate disruption of the P-B bond observed in the reaction of $\text{arphos}\cdot\text{BH}_2\text{Br}$ with $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ suggested that perhaps an organometallic reagent with less options for reactivity might prove more amenable to study. The binuclear complex $\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2\text{Cp}^*_2$ is readily cleaved by a variety of monodentate ligands (L) to afford coordinatively saturated complexes $[\text{Rh}(\text{L})\text{Cl}_2\text{Cp}^*]$ in which the co-ligands are typically innocent.¹³ Most relevant, the reaction of $\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2\text{Cp}^*_2$ with AsPh_3 proceeds rapidly at room temperature to afford the dark red complex $[\text{RhCl}_2(\text{AsPh}_3)\text{Cp}^*]$ in high yield.¹⁴ In contrast, no reaction was observed between the dirhodium complex and $\text{arphos}\cdot\text{BH}_2\text{Br}$ over 1.5 hours of stirring at room temperature in benzene, therefore the mixture was heated to reflux for 16 hours to encourage reaction. Subsequent NMR analysis of the mixture revealed two relatively sharp peaks in the ^{11}B NMR spectrum at 6.32 and 7.42 ppm, which suggested that they might be B-O type decomposition products. This was supported by the fact that after all volatiles had been removed under vacuum, the remaining solid was found to contain no identifiable boron, suggesting the two ^{11}B NMR resonances were volatile substances removed along with the solvent.

A crystal structure determination of the recovered solid revealed it to be the boron free salt $[\text{RhCl}_{0.88}\text{Br}_{0.12}(\text{arphos})\text{Cp}^*]\text{Br}_{0.5}\text{Cl}_{0.5}$ (Figure 8), the asymmetric unit of which

[†] A *trans* arrangement of the two Br atoms would give rise to a singlet ^{31}P NMR resonance for the two phosphine groups in a *cis* or in a *trans* relationship to one another. A *cis* arrangement of the two Br atoms would give rise to a singlet when the phosphines were equivalent to one another, and a pair of doublets when they were inequivalent due to $^2J_{\text{PP}}$ coupling.¹²

contained two independent metal complexes, each displaying positional disorder with respect to the arsenic and phosphorus sites. Both the metal-bound halide and the free counter anion were best modelled on the basis of partial Cl/Br exchange with the occupancies being refined.[§]

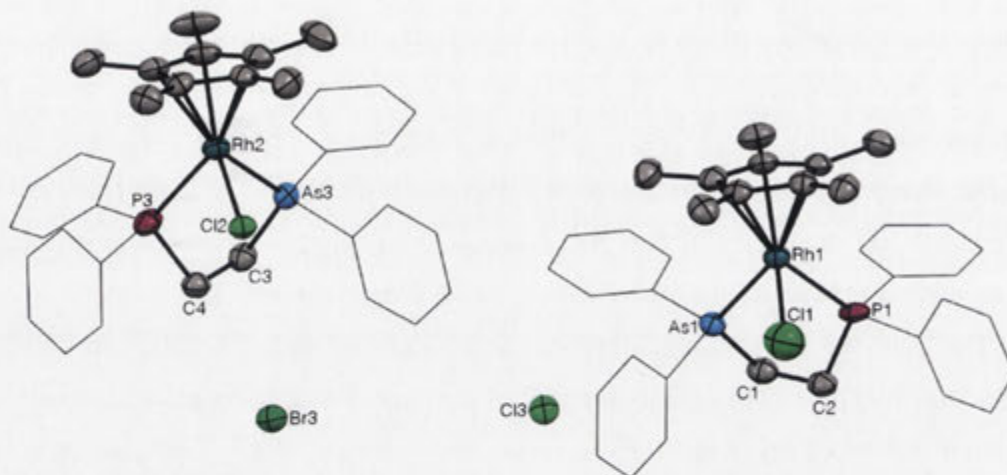


Figure 8: The molecular structure of $[\text{RhXCp}^*(\text{arphos})]\text{Cl}.[\text{RhXCp}^*(\text{arphos})]\text{Br}$ (where $\text{X} = \text{Cl}, \text{Br}$ in 88/12% and 56/44% occupancies respectively). (Hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Dominant orientation of arphos ligands (70/30% in left molecule and 65/35% in right molecule) and metal halides ($\text{X} = \text{Cl}$ with occupancy of 88% in left molecule and 56% in right molecule) are shown. **Minor orientations omitted for clarity.** Selected bond lengths (Å) and angles (°) for major orientation: Rh1-Cl1 2.46(1); Rh1-P1 2.341(8); Rh1-As1 2.400(7); Rh2-Cl2 2.423(3); Rh2-P3 2.361(9); Rh2-As3 2.413(7); Cl1-Rh1-P1 81.5(4); Cl1-Rh1-As1 85.6(3); P1-Rh1-As1 83.2(3); Cl2-Rh2-P3 83.2(3); Cl2-Rh2-As3 87.2(2); P3-Rh2-As3 84.0(3).

The final investigation of $\text{arphos} \cdot \text{BH}_2\text{Br}$ involved the rhodium dimer $\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2$, which was perhaps the most successful but least well understood of those attempted. As with $\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2\text{Cp}^*_2$, this reagent readily undergoes halide-bridge cleavage with various monodentate ligands (L) to afford $[\text{RhCl}(\text{L})(\text{COD})]$ or with bidentate ligands (LL') to provide salts of the cationic species $[\text{Rh}(\text{LL}')(\text{COD})]^+$.¹⁵

[§] $\text{RhCl}_2\text{Cp}^*(\kappa^1\text{-arphos})$ and $[\text{RhClCp}^*(\kappa^2\text{-arphos})]\text{Cl}$ were intentionally synthesised by reaction of half an equivalent of $[\text{RhCl}_2\text{Cp}^*]_2$ and one equivalent of arphos. In addition, $[\text{RhClCp}^*(\kappa^2\text{-arphos})][\text{AsF}_6]$ was intentionally synthesised by the stoichiometric reaction of $\text{RhCl}_2\text{Cp}^*(\kappa^1\text{-arphos})$ or $[\text{RhClCp}^*(\kappa^2\text{-arphos})]\text{Cl}$ with $\text{K}[\text{AsF}_6]$.

Stirring a mixture of $\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2$ and $\text{arphos}\cdot\text{BH}_2\text{Br}$ in DCM resulted in decomposition of the $\text{arphos}\cdot\text{BH}_2\text{Br}$ into $[\text{H}_2\text{B}(\text{arphos})_2]\text{Br}$ over a period of 16 hours. In contrast, heating a benzene solution of the two reagents to reflux for 16 hours, followed by removal of volatiles provided a residue which revealed a very high frequency shift of 57.1 ppm in the ^{11}B NMR spectroscopic analysis of the major product, in a region perhaps suggestive of a direct metal-boron connectivity (*cf.* δ_{B} 30-70 for M-BCat complexes).⁶ However, the ^{31}P NMR spectrum comprised of approximately 10 significant resonances, all of similar intensities. An ESI-MS spectrum was obtained, but few envelopes could be assigned unambiguously besides expected decomposition fragments such as $[\text{Rh}(\text{H})\text{Br}(\text{arphos})_2]^+$ and $[\text{Rh}(\text{arphos})_2]^+$.

It was suspected that the partial decomposition of the $\text{arphos}\cdot\text{BH}_2\text{Br}$ starting material from being stirred overnight in (polar) DCM may have had a domino effect to the purity of the product. Therefore, the reaction was repeated to exclude this step and the solution was immediately heated to reflux overnight in benzene. The result was a slightly cleaner ^{11}B NMR spectrum with only 3 resonances at 21.0, 32.1 and the previously noted resonance at 56.5 ppm (57.1 above). The ^{31}P NMR spectrum was considerably simplified, with only two strong doublets observed at 55.4 ($^1J_{\text{RhP}}$ 92.0 Hz) and 59.0 ppm ($^1J_{\text{RhP}}$ 108.8 Hz), both displaying coupling constants within the range expected for a direct Rh-P bond. However, unlike for the previous instance, the peak of interest at δ_{B} 56.5 was no longer the major product, but instead was of similar intensity to the other two resonances observed. The reaction had been effectively 'reacting' for two days when the δ_{B} 56.5 resonance was found to be the major product (stirred overnight in DCM, then heated to reflux overnight in benzene), so the reaction was again heated to reflux in benzene to match the previous reaction time. The result was for the peak at δ_{B} 32.1 to become the major observed product, along with the doublet at δ_{P} 59.0. These resonances were of interest because they did not coincide with those reported for $[\text{Rh}(\text{arphos})(\text{COD})]\text{ClO}_4$ (δ_{P} 59.8, $^1J_{\text{RhP}}$ 142.6 Hz) or $[\text{Rh}(\text{arphos})_2]\text{ClO}_4$ (*cis*: δ_{P} 62.6, $^1J_{\text{RhP}}$ 124.5 Hz; *trans*: δ_{P} 64.6, $^1J_{\text{RhP}}$ 150.9 Hz), both of which had larger $^1J_{\text{RhP}}$ coupling values.^{15, 16} The complex $[\text{RhCl}(\kappa^1\text{-P-arphos})(\text{COD})]$ was a possibility, but unfortunately had not been previously reported in the literature and therefore a comparison could not be made.

3.2.2. Alternative Phosphine-Stabilised Mixed Haloborane Heterochelates

The dibromoborane adduct $\text{arphos} \cdot \text{BHBr}_2$ was synthesised in an attempt to moderate the recalcitrant reactivity displayed by $\text{arphos} \cdot \text{BH}_2\text{Br}$. In contrast to $\text{arphos} \cdot \text{BH}_2\text{Br}$, which was found to be stable as a solid, $\text{arphos} \cdot \text{BHBr}_2$ decomposes over a relatively short period of time (approximately 48 h) in the solid state, even when stored under an inert atmosphere. However, its identity was clearly established by NMR analysis (δ_{B} -17.0, δ_{P} -1.5) and ESI-MS with an isotopic envelope being observed at 651 for $[\text{M} + \text{K}]^+$. The decomposition, even as a solid, was the main reason no subsequent reactions were undertaken with $\text{arphos} \cdot \text{BHBr}_2$.

3.3. Reactions of Mixed Haloboranes with Nitrogen and Phosphorus Heterochelates

Given the selective coordination of haloboranes to the phosphine donor of arphos , similar selectivity might have been anticipated for 2-pyridylphosphines, especially since amines are generally used to decomplex boranes from phosphine-borane adducts. A further potential advantage of diphenyl-2-pyridylphosphine, $\text{Ph}_2\text{P}(\text{py})$, is that bidentate chelation is somewhat disfavoured,¹⁷⁻²⁰ though not excluded,^{21, 22} in part due to the necessarily small ligand-metal bite angle ($<70^\circ$, Figure 9)

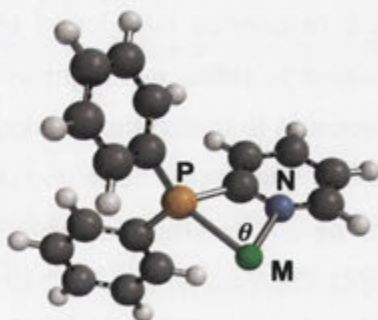


Figure 9: Computationally generated diagram showing the ligand bite angle (θ) of $\text{Ph}_2\text{P}(\text{py})$ when it acts in a bidentate fashion.

A boron- $\text{Ph}_2\text{P}(\text{py})$ adduct would provide a four atom backbone to the potential chelate, analogous to dppe and the $\text{dppm} \cdot \text{BH}_2\text{Cl}$ adduct reported by Weller *et al.* (Figure 10).²³ As a potential chelate, the adduct $\text{Ph}_2\text{P}(\text{py}) \cdot \text{BH}_2\text{Br}$ would perhaps benefit

from the rigidity of the pyridyl ring which would help secure the BH_2Br group in close proximity to the metal centre. The heterotopic nature of $\text{Ph}_2\text{P}(\text{py})$ would also theoretically enable the boron substituent to be chemoselectively added to one of the two potential Lewis basic positions available in the form of the pyridyl and phosphine functional groups (denoted $N\text{-Ph}_2\text{P}(\text{py})$ and $P\text{-Ph}_2\text{P}(\text{py})$ respectively). Schmidbaur has reported that the reaction of $\text{Ph}_2\text{P}(\text{py})$ with $\text{BH}_3\cdot\text{THF}$ affords $P\text{-Ph}_2\text{P}(\text{py})\cdot\text{BH}_3$ rather than $N\text{-Ph}_2\text{P}(\text{py})\cdot\text{BH}_3$, though this was based on limited spectroscopic data.²⁴ Haloboranes were not considered, though being somewhat 'harder' in nature an increase in proclivity towards nitrogen over phosphorus might be anticipated.

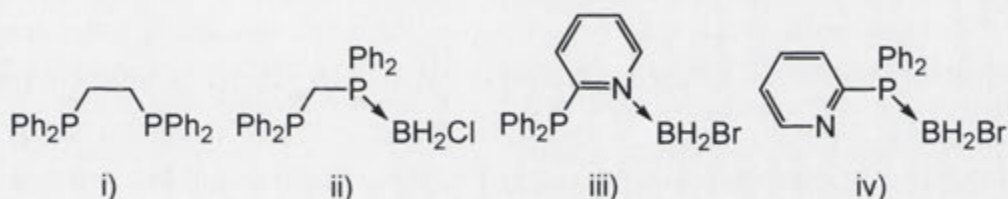


Figure 10: Diagram comparing potential chelating ligands comprising diphosphines and mixed haloborane phosphine adducts. i) dppe, ii) dppm·BH₂Cl, iii) $N\text{-Ph}_2\text{P}(\text{py})\cdot\text{BH}_2\text{Br}$, iv) $P\text{-Ph}_2\text{P}(\text{py})\cdot\text{BH}_2\text{Br}$.

The combination of equimolar amounts of $\text{Ph}_2\text{P}(\text{py})$ and $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ in DCM under the conditions used for the preparation of other mixed haloborane tertiary phosphine adducts resulted in a solution, the ^{11}B NMR spectroscopic analysis of which revealed the presence of three species in similar proportions (δ_{B} -39.2, -24.5, -7.5). By comparison with $\text{Ph}_3\text{P}\cdot\text{BH}_2\text{Br}$ (δ_{B} -23.2), the peak at δ_{B} -24.5 was attributed to $P\text{-Ph}_2\text{P}(\text{py})\cdot\text{BH}_2\text{Br}$. The low frequency nature of phosphine-boronium salts in the ^{11}B NMR spectrum leads to the tentative assignment of -39.2 ppm as $[\text{H}_2\text{B}\{P\text{-Ph}_2\text{P}(\text{py})\}_2]\text{Br}$. The final peak at -7.5 ppm was therefore thought to be $N\text{-Ph}_2\text{P}(\text{py})\cdot\text{BH}_2\text{Br}$, which was supported by the reported resonance compound for the related compound pyridine·BH₂Br (δ_{B} 5.5).[§] Addition of a second equivalent of

[§] In the literature, the ^{11}B NMR data reported for pyridine·BH₂Br (δ_{B} 23.7) was referenced to $\text{B}(\text{OMe})_3$.²⁵ $\text{B}(\text{OMe})_3$ is observed at δ_{B} 18.2 when referenced to $\text{BF}_3\cdot\text{Et}_2\text{O}$ (the species to which all ^{11}B NMR data reported herein is referenced), which is how the value of pyridine·BH₂Br referenced to $\text{BF}_3\cdot\text{OEt}_2$ was determined (δ_{B} 23.7 - δ_{B} 18.2 = δ_{B} 5.5).

BH₂Br.SMe₂ failed to isolate even the disubstituted version of Ph₂P(py) at both the nitrogen and phosphorus atoms.

The reaction was repeated at -78°C in an attempt to implement kinetic control and favour one product over the others. Care was taken to isolate the product as a precipitate before warming the reaction back up to ambient temperature, but unfortunately NMR analysis revealed the same mixture of products as had been achieved without cooling. The final methodology used was to implement thermodynamic control on the reaction by heating to reflux in benzene. Benzene was used instead of DCM as for the previous reactions, not only for its moderately high boiling point, but also because a non-polar solvent would favour the precipitation of any boronium salt side products formed. However, the result was largely unsuccessful with a mixture of products again being found in the product solution. A solid did precipitate out of the solution during the reflux and was found to consist of one product by ¹¹B and ³¹P NMR spectroscopy (δ_B -6.97 and δ_P -6.24), but subsequent MS analysis showed the species present to be a protonated salt of the Ph₂P(py) starting material[†] and characterisation was hindered by the precipitate's poor solubility in common solvents.

3.3.1. Reactions of Mixed Haloboranes with Metal Centres Bearing Nitrogen and Phosphorus Heterochelates

The combination of BH₂Br.SMe₂ and Ph₂P(py) was clearly proceeding, but the inability to cleanly synthesise a Ph₂P(py)·BH₂Br species prevented its use as a potential boron source toward organometallic compounds. However, Ph₂P(py) has a long established history, developed by Balch and co-workers, of reacting analogously to PPh₃ toward metal centres *via* the phosphorus lone pair, leaving the pyridyl nitrogen atom free to coordinate to other species.²⁶⁻²⁹ Prior installation of the Ph₂P(py) ligand on a metal centre by the phosphorus atom would selectively leave the pyridyl ring exclusively free to react with a Lewis acid, without fear of intervention by the phosphine.

[†] Possibly misleading, as an already positively charged compound would bypass the need to become charged in the chamber and would therefore be more abundantly detected than other species that first required ionisation.

Metal compounds with two $P\text{-Ph}_2\text{P}(\text{py})$ groups have been reacted with a wide range of transition metal Lewis acids to form heterobinuclear complexes.^{28, 30, 31} It seemed plausible that similar reactivity might ensue with main group Lewis acids, e.g., BH_2Br , with complexes in which the phosphorus of $\text{Ph}_2\text{P}(\text{py})$ was already associated with a metal. To this end, $\text{Fe}(\text{CO})_2(\eta^2\text{-CS}_2)\{P\text{-Ph}_2\text{P}(\text{py})\}_2$ was treated with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ to see if an adduct could be formed with the pendant pyridyl groups (Figure 11).

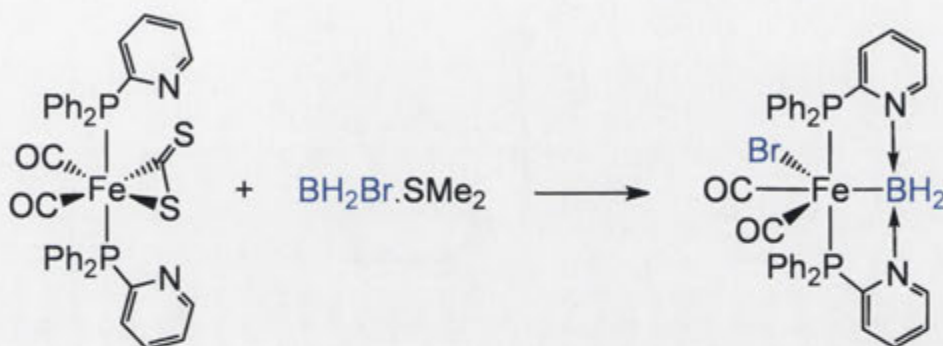


Figure 11: Possible reaction scheme for reaction of $\text{Fe}(\text{CO})_2(\eta^2\text{-CS}_2)\{P\text{-Ph}_2\text{P}(\text{py})\}_2$ with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$.

On combining the reagents no visible change was observed. Analysis of the product thus obtained was hampered by its poor solubility in chloroform or DCM, with no observed resonances in the ^{31}P NMR spectrum and only one peak found in the ^{11}B NMR spectrum at -39.9 ppm, which was presumed to be $[\text{H}_2\text{B}\{P\text{-Ph}_2\text{P}(\text{py})\}_2]\text{Br}$,[†] formed through decomposition of the iron precursor. Acetone was found to be a better solvent, but NMR analysis in d_6 -acetone revealed a new predominant peak at δ_{B} 21.1, which suggested possible decomposition caused by the acetone. Crystallisation of the acetone NMR sample with pentane seemed to confirm this finding, as orange crystals were produced and solved to be $\text{FeBr}_2\{\kappa^2\text{-Ph}_2\text{P}(\text{O})(\text{py})\}_2$ (Figure 12). Given that a small number of crystallographic studies of $\kappa^2\text{-O,N-Ph}_2\text{P}(\text{O})(\text{py})$ transition metal complexes have already been described,³²⁻³⁵ the crystal structure was of limited interest other than to confirm decomposition (oxidation to Fe^{II}) from air exposure. This would appear to have been mediated by the haloborane in that this had not been an issue for

[†] Assignment as $[\text{H}_2\text{B}\{P\text{-Ph}_2\text{P}(\text{py})\}_2]\text{Br}$ was made on the basis of previously observed boronium salts with similar ^{11}B NMR resonances, which will be discussed in chapter 4.

heterodinuclear complexes produced previously, though the trace yield did not justify mechanistic conjecture beyond this.

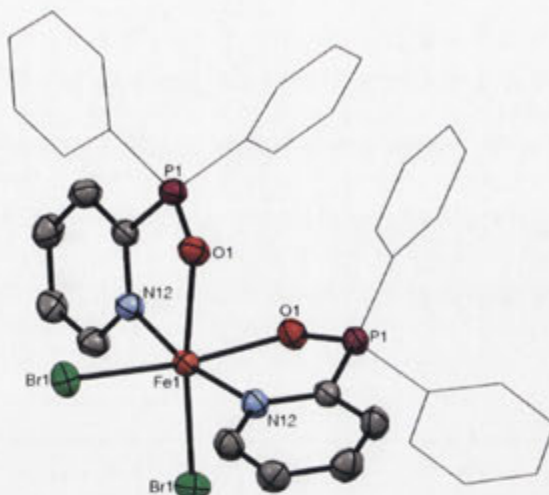


Figure 12: The molecular structure of $\text{FeBr}_2\{\kappa^2\text{-Ph}_2\text{P}(\text{O})(\text{py})\}_2$. (Hydrogen atoms omitted for clarity, phenyl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Fe1-Br1 2.5465(6); Fe1-N12 2.227(3); Fe1-O1 2.174(3); P1-O1 1.488(3); Br1-Fe1-Br1ⁱ 99.16(3); Br1-Fe1-N12 91.28(8); Br1-Fe1-N12ⁱ 95.11(8); Br1-Fe1-O1 90.79(7); Br1-Fe1-O1ⁱ 169.17(7); N12-Fe1-N12ⁱ 170.2(2); N12-Fe1-O1 80.3(1); N12-Fe1-O1ⁱ 92.1(1); O1-Fe-O1ⁱ 79.7(1); Fe1-O1-P1 117.9(1).

3.4. Reactions of Phosphine-Stabilised Mixed Haloboranes with Metal Centres

Some of the problems encountered with the use of arphos·BH₂Br were due to the heterodentate nature of the arphos once liberated from the BH₂Br group, as reflected in the numerous examples of stereoisomers (and crystallographic disorder) encountered for the resulting metal complexes of the arphos ligand. The use of a bidentate heterotopic ligand had been a design feature intended to facilitate chelate-assisted B-H activation. However, there are many examples of simple borane coordination to metal centres without the additional support of buttressing chelation.³⁶ The reactions of simple PPh₃ adducts of BH₃ and BH₂Br with organometallic precursors were therefore explored.

No reaction was observed to occur between Ru(Ph)Cl(CO)(PPh₃)₂ and Ph₃P·BH₃ over a period of 24 hours in DCM at room temperature, nor after being subsequently heated to reflux in benzene for 24 hours. In contrast, this organometallic reagent is

known to react with simple boranes, $\text{HBX}_2\text{C}_6\text{H}_4$ ($\text{X} = \text{O}, \text{S/NH}, \text{NH}$), in reflux benzene with formation of the σ -boryl complexes $\text{Ru}(\text{BX}_2\text{C}_6\text{H}_4)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and elimination of benzene.³⁷ The corresponding osmium analogue has also been shown to react with $\text{BHCl}_2\cdot\text{Et}_2\text{O}$ to afford the dichloroboryl derivative $[\text{Os}(\text{BCl}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$.³⁸ Addition of $\text{Na}[\text{PF}_6]$ to encourage halide abstraction and generate the more reactive species $[\text{Ru}(\text{Ph})(\text{CO})(\text{PPh}_3)_2][\text{PF}_6]$ still failed to induce a reaction with $\text{Ph}_3\text{P}\cdot\text{BH}_3$, and only facilitated decomposition of the metal centre as illustrated by the multiple ^{31}P NMR peaks observed. When the reaction was repeated using a polar solvent of similar boiling point, dichloroethane (b.p.: benzene = 80°C , 1,2-dichloroethane = 84°C), the outcome was again decomposition of the ruthenium species, of which only $\text{Ru}(\text{H})\text{Cl}(\text{CO})(\text{PPh}_3)_3$ could be identified from the mixture crystallographically,³⁹ and by its characteristic ^1H and ^{31}P NMR resonances.

Analogous to the previously discussed reaction of $\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2$ with $\text{arphos}\cdot\text{BH}_2\text{Br}$, the simpler monodentate phosphine mixed haloborane adduct, $\text{Ph}_3\text{P}\cdot\text{BH}_2\text{Br}$, was reacted with the rhodium reagent, and by comparison of these two reactions the effect of the arsenic tether of $\text{arphos}\cdot\text{BH}_2\text{Br}$ could be evaluated. After being stirred for 1 hour in benzene, ^{11}B and ^{31}P NMR analysis showed that the reaction consisted of mostly starting materials and $\text{RhCl}(\text{PPh}_3)(\text{COD})$, the latter as a doublet at $\delta_{\text{P}} 31.40$ ($^1J_{\text{PRh}} 151.6 \text{ Hz}$),⁴⁰ presumably generated by loss of the BH_2Br group to liberate PPh_3 . The mixture was heated to reflux for 2 hours and found by NMR spectroscopy to include five additional peaks in the ^{11}B NMR spectrum. Interestingly a new doublet was observed in the ^{31}P NMR spectrum at $\delta_{\text{P}} 33.1$ ($^1J_{\text{PRh}} 151.1 \text{ Hz}$), along with the previous doublet of $\text{RhCl}(\text{PPh}_3)(\text{COD})$, as well as $\text{Ph}_3\text{P}\cdot\text{BH}_2\text{Br}$, which was still the major phosphorus containing product present. After heating to reflux for 16 hours, there was effectively only a single ^{11}B NMR peak at 6.7 ppm, which was significantly less broad than those typically observed for directly bonded P-B type species. The ^{31}P NMR spectrum indicated complete consumption of $\text{Ph}_3\text{P}\cdot\text{BH}_2\text{Br}$ and the presence of only the two doublets at $\delta_{\text{P}} 31.4$ ($^1J_{\text{PRh}} 150.8 \text{ Hz}$) and $\delta_{\text{P}} 33.1$ ($^1J_{\text{PRh}} 151.1 \text{ Hz}$). The newly emerged doublet at 33.1 ppm had now surpassed that of the $\text{RhCl}(\text{PPh}_3)(\text{COD})$, which led to the summation the peak could be attributed to $\text{RhBr}(\text{PPh}_3)(\text{COD})$, generated by halogen-exchange of bromine liberated from the decomposition of $\text{Ph}_3\text{P}\cdot\text{BH}_2\text{Br}$, as had been observed previously with species such as $\text{RuBr}_2(\text{CO})(\text{PPh}_3)(\text{arphos})$ and $\text{RuBr}_2(\text{arphos})_2$ (*vide supra*). Unfortunately a literature value of δ_{P} could not be found for $\text{RhBr}(\text{PPh}_3)(\text{COD})$, but the identity was supported by

the very similar shift of δ_P 33.1 compared to that for $\text{RhCl}(\text{PPh}_3)(\text{COD})$ of δ_P 31.4, and their near identical $^1J_{\text{PRh}}$ coupling constants (151.1 and 151.6 Hz, respectively).

3.5. Cyclophosphinoboranes

The recurrent cleavage of BH_2Br from a variety of phosphine adducts in the previous discussion suggested that more robust haloborane phosphine adducts might be required for investigating reactions with organometallic substrates to obviate undesired fragmentation. Dimeric dihaloborylphosphines, first synthesised by Burg *et al* in 1953,⁴¹ are known to be comparatively stable and were considered to be promising candidates. In this respect, the known compound $[\text{Br}_2\text{BPPH}_2]_2$ was chosen as a viable species and synthesised without issue *via* deprotonation of $\text{Ph}_2\text{HP}\cdot\text{BBr}_3$.⁴² In addition, the synthesis of the cyclohexyl analogue, $[\text{Br}_2\text{BPCy}_2]_2$, was attempted through modification of the procedure for $[\text{Br}_2\text{B-PPh}_2]_2$, but the desired product could not be obtained due to the inability of the NEt_3 to deprotonate the $\text{Cy}_2\text{HP}\cdot\text{BBr}_3$ intermediate. Available structural data for dimeric dihaloborylphosphines are limited to those for $[\text{I}_2\text{BPPH}_2]$,⁴³ $[\text{X}_2\text{BP}^t\text{Bu}_2]$ ($\text{X} = \text{Cl}$,⁴⁴ Br),⁴⁵ $[\text{X}_2\text{BP}(\text{SiMe}_3)_2]$, ($\text{X} = \text{Cl}$, Br),⁴⁶ and the unusual metallated example $[\text{Cl}_2\text{BPPPh}\{\text{FeCp}(\text{CO})_2\}]$.⁴⁷ Accordingly $[\text{Br}_2\text{BPPH}_2]_2$ was structurally characterised (Figure 13), confirming a slightly puckered four-membered ring structure which possessed P-B bonds in the range 1.999(3)-2.007(3) Å, which are somewhat longer than those found in the acyclic haloborane-phosphine adducts described above. A space-filling representation reveals considerable steric congestion, which in part accounts for the stability of the heterocycle.

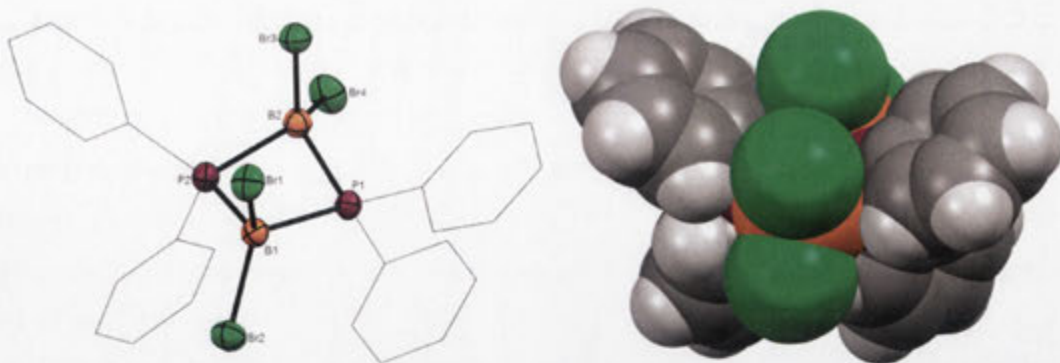


Figure 13: The molecular structure of $[\text{Br}_2\text{B-PPh}_2]_2$ (left) and a space filling representation (right). (Hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): B1-Br1 2.004(2); B1-Br2 1.990(3); B2-Br3 2.000(3); B2-Br4 1.988(3); B1-P1 2.007(3); B1-P2 2.006(3); B2-P1 1.999(3); B2-P2 2.002(3); Br1-B1-Br2 110.2(1); Br1-B1-P1 108.6(1); Br1-B1-P2 112.5(1); Br2-B1-P1 120.1(1); Br2-B1-P2 116.6(1); Br3-B2-Br4 110.7(1); Br3-B2-P1 109.7(1); Br3-B2-P2 107.2(1); Br4-B2-P1 118.7(1); Br4-B2-P2 120.7(1); P1-B1-P2 87.1(1); P1-B2-P2 87.4(1); B1-P1-B2 88.7(1); B1-P2-B2 88.6(1).

3.5.1. Reactions of Cyclophosphinoboranes with Metal Centres

The reaction of $[\text{Br}_2\text{BPPH}_2]_2$ with the iron dianion $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$ was explored in the hopes of observing salt elimination to afford the μ -borylene species $[(\text{CO})_8\text{Fe}_2\text{BPPH}_2]_2$, though no reaction was apparent over two days (room temperature, acetone) as was confirmed by the almost exclusive presence of starting materials observed by NMR analysis. A minor peak was observed in the ^{31}P NMR spectrum (δ_{P} 38.1), the narrow line width of which however indicated that this phosphorus was no longer bound to quadrupolar boron. Infrared analysis proved inconclusive due to the large number of carbonyl groups present, whilst TLC analysis indicated that no product amenable to chromatographic purification had arisen.

The reaction of $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$ towards $\text{dppm} \cdot (\text{BH}_2\text{Br})_2$ was also investigated but led only to a complex mixture containing free dppm (δ_{P} 13.7), unidentified dppm complexes of iron (δ_{P} 61.8, 63.1, 63.1) and the known complex $\text{Fe}(\text{CO})_4(\kappa^1\text{-dppm})$ (δ_{P} -26.3, 64.8, $^3J_{\text{PP}}$ 89.5 Hz).⁴⁸

3.6. Reactions of Main-Group Substituted Haloboranes with Metal Centres

The first structurally characterised metal σ -boryl complex *mer*-Ir(H)(BO₂C₆H₄)Cl(PMe₃)₂ involved the BO₂C₆H₄ ('BCat') group,⁴⁹ which has in the interim been extensively investigated in metal-mediated C-B bond forming reactions.⁴⁹ The utility of the BCat group and related dioxaboryl groups, e.g. BO₂C₂Me₄ ('Bpin'), may be traced to the reduction in electrophilicity of the boron centre due to the two chelated and positively mesomeric alkoxy substituents. A corollary of this reduced electrophilicity is the preference for the three-coordinate boron. The majority of synthetic approaches for installing the BCat group involve B-H activation, however, *B*-halo-BCat derivatives have also been employed in salt elimination reactions with carbonyl metallates.⁵⁰ In an attempt to prepare the unknown σ -boryl complex [Mo(BCat)Tp*(CO)₃], the reaction of K[MoTp*(CO)₃] and ClBCat was investigated.⁵ The target σ -boryl complex was of interest for two reasons. Firstly, the Tp* ligand has a strong tendency to favour octahedral rather than 7-coordinate geometries.⁵¹ Secondly, the hydroboration of carbyne complexes [M(CR)Tp*(CO)₂] (M = Mo, W; R = Me, C₆H₄Me-4) by 'EtBH₂' has been shown to afford the unusual agnostic σ -boryl dicarbonyl complexes [M{B(CH₂R)Et}Tp*(CO)₂].^{52, 53} After 48 hours, the ¹¹B NMR spectrum of the reaction mixture (DCM, ambient temperature) comprised a major peak (δ_B 6.6) in addition to a resonance of comparable intensity attributable to the Tp* ligand (δ_B -10.7) and three very minor peaks (δ_B -31.7, 12.9, 21.4). The chemical shift of the major resonance appeared at a lower frequency than the range (δ_B 21-141) characteristic of transition metal σ -boryl complexes.⁶

Aerobic crystallisation of the hexane-insoluble residue afforded X-ray quality crystals which were identified as the unusual salt [pz*H][Mo(O)(O₂C₆H₄)(μ -O)₂Mo(O)Tp*] (Figure 14), the result of significant degradation of both the molybdenum and boron reagents. Poly(hydroxyl)phenols have a rich molybdenum chemistry which may be traced to the ability of the ligands to stabilise a variety of oxidation states through non-innocent redox behaviour.^{54, 55} Thus, although the salt is novel, its structural features

⁵ The closest known analogue of this complex would be [W(BCat)Cp*(CO)₃] described by Hartwig and co-workers.⁵⁰

reflect many of the coordination environments previously encountered in $L_nMo_x(O)_y(O_2C_6H_4)_z$ complexes.*

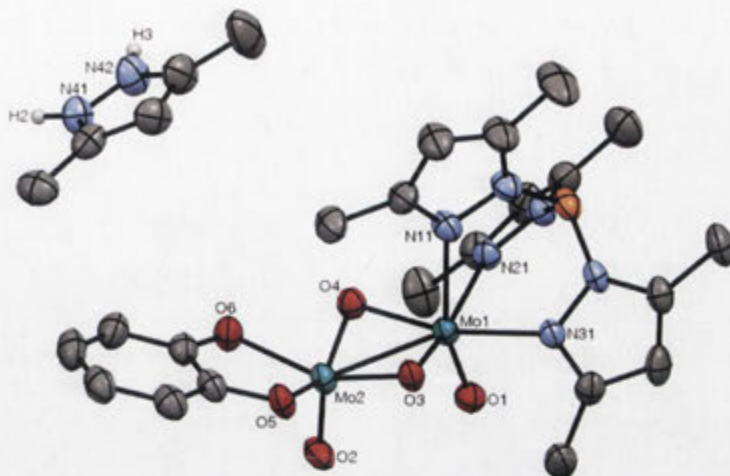


Figure 14: The molecular structure of $[pz^*H][Mo(O)(Cat)(\mu-O)_2Mo(O)Tp^*]$. (Solvate molecules and some hydrogen atoms omitted for clarity, 50% displacement ellipsoids).

Selected bond lengths (Å) and angles (°): Mo1-Mo2 2.581(2); Mo1-O1 1.679(3); Mo1-O3 1.946(3); Mo1-O4 1.941(3); Mo2-O2 1.676(3); Mo2-O3 1.930(3); Mo2-O4 1.918(3); Mo2-O5 2.038(3); Mo2-O6 2.010(3); O1-Mo1-Mo2 98.1(1); O1-Mo1-O3 106.1(2); O1-Mo1-O4 106.8(2); Mo1-O3-Mo2 83.5(1); Mo1-O4-Mo2 83.9(1); O3-Mo1-O4 91.5(1); O3-Mo2-O4 92.7(1); O2-Mo2-Mo1 102.2(1); O2-Mo2-O3 109.5(2); O2-Mo2-O4 108.7(2); O3-Mo2-O5 83.8(1); O3-Mo2-O6 143.8(1); O4-Mo2-O5 144.6(1); O4-Mo2-O6 84.0(1); O5-Mo2-O6 78.7(1).

3.6.1. Accidental Synthesis of Boron Cages with $[Tp^*]$

The reaction of $K[MoTp^*(CO)_3]$ (prepared *in situ* from $K[Tp^*]$ and $Mo(C_7H_8)(CO)_3$) with BCl_2Ph was undertaken so as to compare it with the reaction of $ClBCat$ with $K[MoTp^*(CO)_3]$. The reactions of the less sterically constrained anions containing, *e.g.*, Cp and Cp^* ligands, with haloboranes have been described previously by Hartwig and Braunschweig.^{7, 50, 56-58} After being stirred for an hour and left to settle, an orange precipitate was separated from the red supernatant. The ^{11}B NMR spectrum of each showed that both the precipitate and filtrate contained peaks at ~ -32 and ~ 0 ppm. The precipitate also contained two strong peaks at -10.5 and -3.5 ppm, in an area typical of

* Cambridge Crystallographic Data Centre (CCDC).

the Tp^* cage, although this could not be confirmed by ^1H coupled ^{11}B NMR spectroscopy due to the broad signals overlapping one another.

Fortuitously, a small number of pale red crystals were deposited during a purification attempt from a mixture of DCM/pentane of the orange precipitate, and found to be the salt $[\text{Tp}^*\text{BPh}][\text{MoTp}^*(\text{CO})_3]$ (Figure 15), in which the BPh substituent was coordinated to a second equivalent of Tp^* .

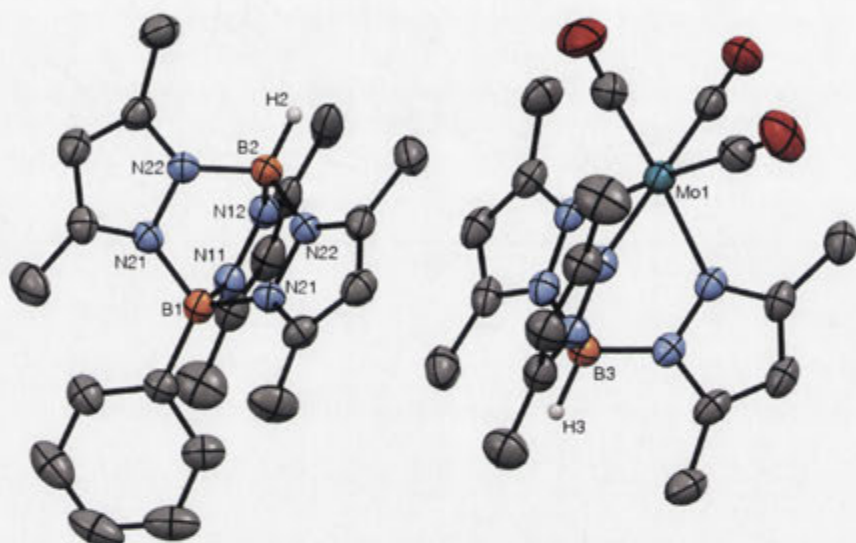


Figure 15: The molecular structure of $[\text{Tp}^*\text{BPh}][\text{MoTp}^*(\text{CO})_3]$. (Alkyl and aryl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): B1-N11 1.606(5); B1-N21 1.583(3); B2-N12 1.531(6); B2-N22 1.546(3); N11-B1-N21 104.4(2); N21-B1-N21ⁱ 101.1(3); N12-B2-N22 104.4(2); N22-B2-N22ⁱ 105.6(3).

The $[\text{MoTp}^*(\text{CO})_3]^-$ group is an anion, so the $[\text{Tp}^*\text{BPh}]^+$ must be a mono-cation for the salt to be neutral overall. The simplest way in which to view the $[\text{Tp}^*\text{BPh}]^+$ cage would be as a $[\text{Tp}^*]^-$ anion complexed *via* three dative bonds to a $\{\text{BPh}\}^{2+}$, which would make this a dicationic boronium species, though this is a conceptual artifice since both the boron centres will in practice bear similar actual charges (Figure 16).

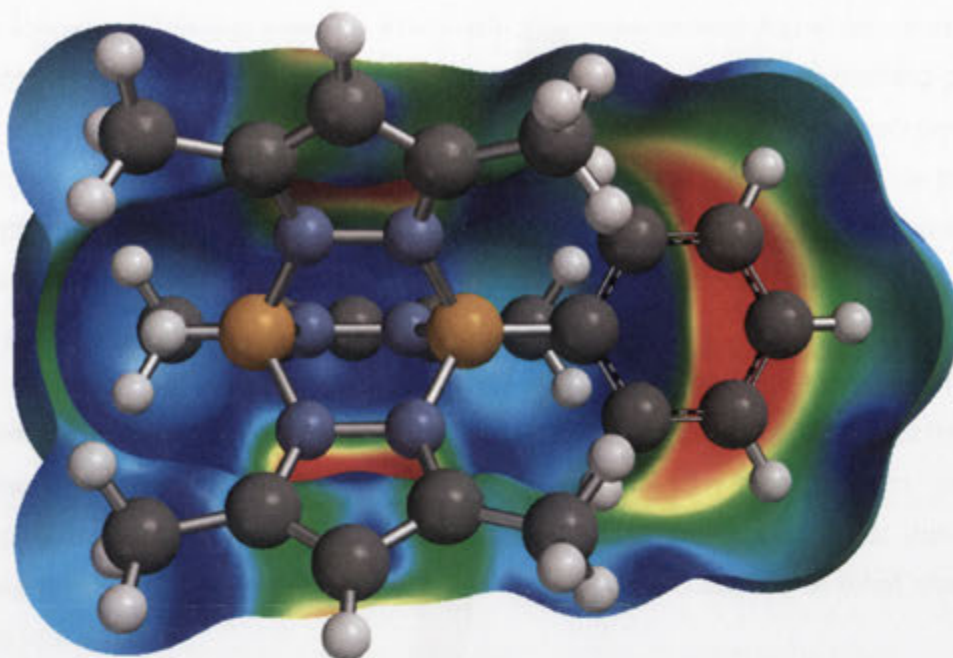


Figure 16: A cross-sectional diagram of the calculated ionisation potential map of $[\text{Tp}^*\text{BPh}]^*$.

The crystallographically distinguishable longer bond lengths between the BPh and its three bonded nitrogen atoms as opposed to the BH and its three surrounding nitrogen atoms [1.606(5), 1.583(3) and 1.583(3) Å *versus* 1.546(3), 1.546(3) and 1.531(6) Å, respectively] would primarily be accounted for by steric considerations, with an inability for the BPh phenyl ring to approach any closer to the pz^* methyl groups due to steric hindrance. The evidence for unfavourable steric interactions between the phenyl and methyl groups can be found by an angle of 79.9° between the calculated least-square planes for the phenyl ring and the plane of the three nitrogen atoms also bound to this boron (Figure 17), which can be seen as a 10.1° deviation* from ideal orthogonality.

* $90^\circ - 79.9^\circ = 10.1^\circ$

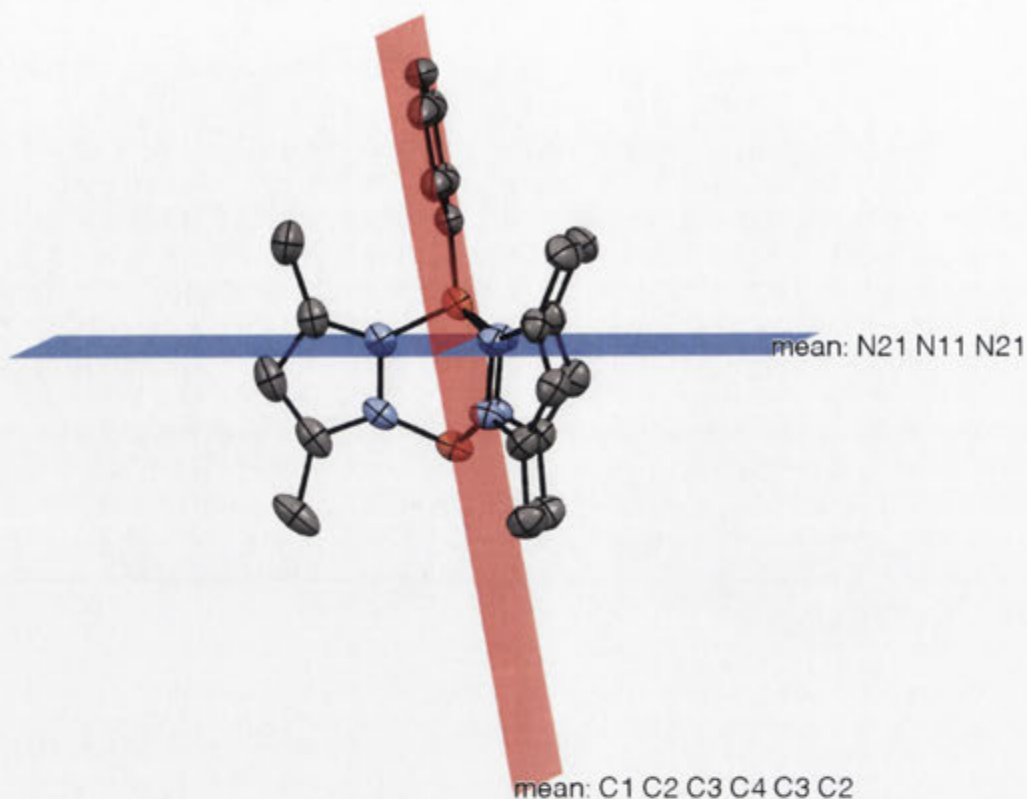


Figure 17: The molecular structure of $[\text{Tp}^*\text{BPh}]^+$ with calculated planes for the BPh phenyl ring (red) and the BPh bonded nitrogen atoms (blue). ($[\text{MoTp}^*(\text{CO})_3]^-$ and hydrogen atoms omitted for clarity, 50% displacement ellipsoids).

If the *in situ* generation of $\text{K}[\text{MoTp}^*(\text{CO})_3]$, from $\text{K}[\text{Tp}^*]$ and $\text{Mo}(\text{C}_7\text{H}_8)(\text{CO})_3$, was allowed to proceed for 96 (instead of 2.5) hours, the ^{11}B NMR spectrum consisted of a different mixture of peaks at -10.6, 6.5 and 29.0 ppm. The observation of a single peak around the Tp^* region (δ_{B} -10.6) suggested the *in situ* generation of $\text{K}[\text{MoTp}^*(\text{CO})_3]$ may not have proceeded to completion in the previous attempt, which allowed free $\text{K}[\text{Tp}^*]$ to react directly with BCl_2Ph (*vide infra*), as opposed to abstraction of the $[\text{Tp}^*]^-$ anion from $\text{K}[\text{MoTp}^*(\text{CO})_3]$ as was initially suspected.

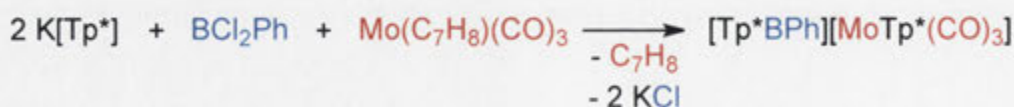


Figure 18: Proposed reaction stoichiometry for formation of $[\text{Tp}^*\text{BPh}][\text{MoTp}^*(\text{CO})_3]$.

The longer generation time for $K[MoTp^*(CO)_3]$ was indeed found to prevent the formation of $[Tp^*BPh][MoTp^*(CO)_3]$. The only other non- Tp^* boron-containing product was the boroxine $(PhBO)_3$ (Figure 19), most likely arising from hydrolysis by adventitious moisture during extended purification efforts. A second side-product, $MoCl_2(pz^*H)Tp^*$ (Figure 19), which had not been previously described, was also obtained during purification attempts of the crude product. The presence of a free dimethylpyrazole (confirmed absent in the $K[Tp^*]$ employed) indicated that the pro-ligand had been degraded by the Lewis-acidic BCl_2Ph accompanied by oxidation of the molybdenum(0) centre. On standing, further yellow crystals of $MoCl_2Tp^*(pz^*H)$ were also found to form from the reaction mixture, possibly the product of slow decomposition from another species. Useful NMR data was not obtained due to the paramagnetic molybdenum(III) centre, making it difficult to assess at what stage this species forms.

The isolation of $[Tp^*BPh][MoTp^*(CO)_3]$ from the reaction of BCl_2Ph and $K[MoTp^*(CO)_3]$ showed that unsymmetrical compounds of the form $[Tp^*BR]^+$ are viable species, as only the $[Tp^*BH]^+$ species had been previously reported, stabilised by various counterions such as $[OTf]^-$, $[NbCl_6]^-$ or $[TaCl_6]^-$,⁵⁹⁻⁶¹ usually as a side product from attempts to introduce the Tp^* ligand onto electrophilic metal centres. A diethyl analogue, $[EtB(pz)_3BEt][PF_6]$, had been synthesised by Trofimenko with less sterically bulky pyrazole bridges.⁶²

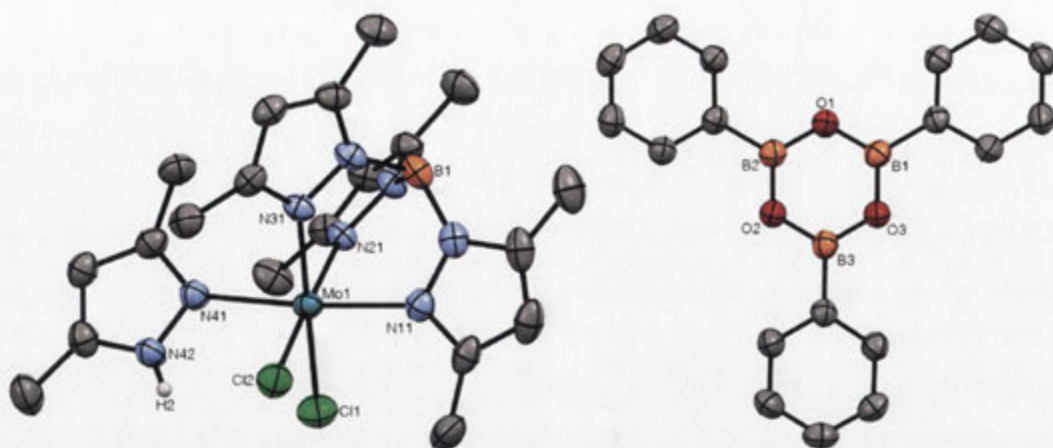


Figure 19: The recovered side products for the reaction of BCl_2Ph with $\text{K}[\text{MoTp}^*(\text{CO})_3]$. The molecular structures of $\text{MoCl}_2(\text{pz}^*\text{H})\text{Tp}^*$ (left) and $[\text{PhBO}]_3$ (right). (Solvate molecules and alkyl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected bond lengths (Å), angles ($^\circ$) and intramolecular distances (Å) for $\text{MoCl}_2(\text{pz}^*\text{H})\text{Tp}^*$: Mo1-Cl1 2.433(1); Mo1-Cl2 2.425(9); Mo1-N11 2.162(3); Mo1-N21 2.185(3); Mo1-N31 2.179(3); Mo1-N41 2.189(3); Cl1-Mo1-Cl2 89.85(3); Cl1-Mo1-N11 94.39(8); Cl1-Mo1-N21 91.56(7); Cl1-Mo1-N31 177.25(7); Cl1-Mo1-N41 90.54(8); Cl2-Mo1-N11 93.04(7); Cl2-Mo1-N21 177.49(7); Cl2-Mo1-N31 92.78(7); Cl2-Mo1-N41 88.63(7); N11-Mo1-N21 84.8(1); N11-Mo1-N31 86.3(1); N11-Mo1-N41 174.8(1); N21-Mo1-N31 85.84(9); N21-Mo1-N41 93.4(1); N31-Mo1-N41 88.7(1); N42-H2...Cl1 2.7213(9). Selected bond lengths (Å) and angles ($^\circ$) for $[\text{PhBO}]_3$: B1-O1 1.381(2); B1-O3 1.379(2); B2-O1 1.379(2); B2-O2 1.378(2); B3-O2 1.382(2); B3-O3 1.376(2); O1-B1-O3 119.0(2); O1-B2-O2 118.9(1); O2-B3-O3 119.2(2); B1-O1-B2 120.6(1); B2-O2-B3 120.5(1); B1-O3-B3 120.9(1).

A computational geometry optimisation of $[\text{Tp}^*\text{BH}]^+$ and $[\text{Tp}^*\text{BPh}]^+$ was carried out at the B3LYP/6-311++G** level of theory. The analysis of $[\text{Tp}^*\text{BH}]^+$ was of particular interest because the HOMO-6 orbital was found to include a degree of transannular boron-boron bonding interaction (Figure 20). The respective analysis of $[\text{Tp}^*\text{BPh}]^+$ was less fruitful in that a related MO orbital to that underpinning the boron-boron interaction in $[\text{Tp}^*\text{BH}]^+$ could not be found.[§] However, the same structural motif of the phenyl substituent being significantly deviated from orthogonality by 12.3° (*cf.* 10.1° found experimentally for $[\text{Tp}^*\text{BPh}][\text{MoTp}^*(\text{CO})_3]$) was calculated (Figure 21).[§]

[§] Down to the HOMO-30 orbital.

[§] $90^\circ - 77.7^\circ = 12.3^\circ$

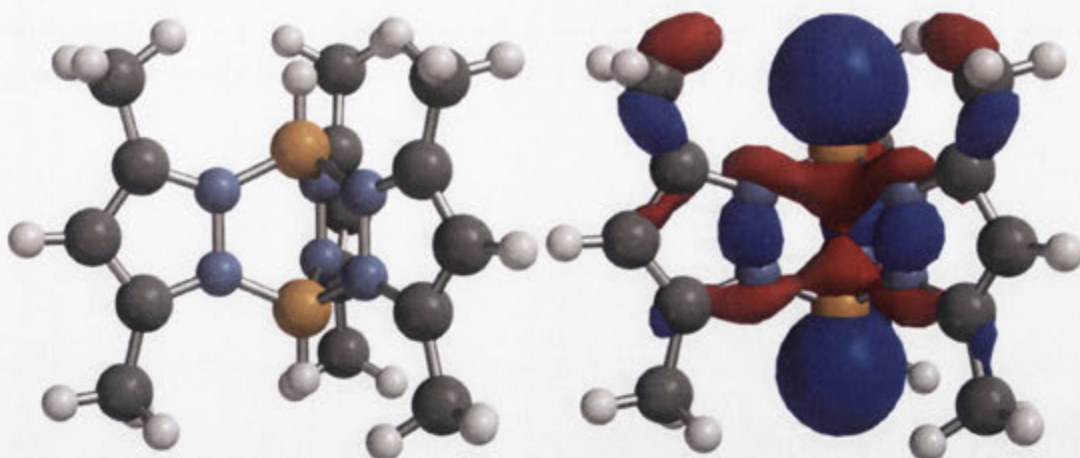


Figure 20: Computationally optimised (B3LYP/6-311++G**) structure of $[\text{Tp}^*\text{BH}]^+$ (left) and the HOMO-6 orbital (right).

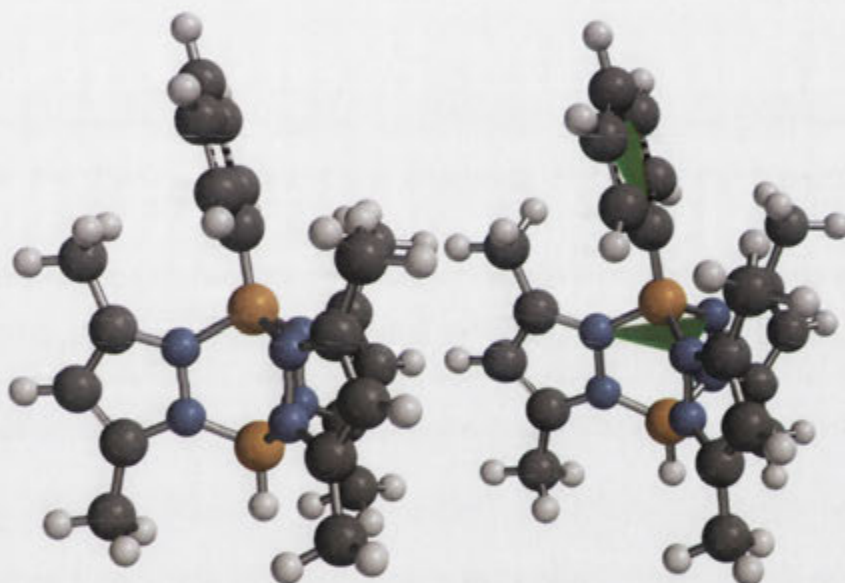


Figure 21: Computationally optimised (B3LYP/6-311++G**) structure of $[\text{Tp}^*\text{BPh}]^+$ indicating an angle of 12.3° between the N_3 and phenyl planes (shown in green).

3.6.2. Intentional Synthesis of Boron Cages with $[\text{Tp}^*]^-$

In an attempt to deliberately synthesise the $[\text{Tp}^*\text{BPh}]^+$ cation, $\text{K}[\text{Tp}^*]$, BCl_2Ph and $\text{Na}[\text{PF}_6]$ were combined (Figure 22) so as to potentially afford a simpler salt than $[\text{Tp}^*\text{BPh}][\text{MoTp}^*(\text{CO})_3]$. The recovered white solid was found to be insoluble for chlorinated solvents and DMSO. Despite the very poor solubility, three peaks were

found in the ^{11}B NMR spectrum at -0.9, 19.6 and 28.0 ppm and one peak in the ^{31}P NMR spectrum at -1.2 ppm, but none attributable to the anticipated $[\text{PF}_6]^-$ anion (δ_{P} -143.8; $^1J_{\text{PF}}$ 711.1 Hz).[§]

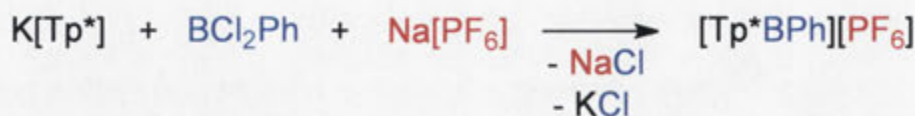


Figure 22: Proposed reaction stoichiometry for formation of $[\text{Tp}^*\text{BPh}][\text{PF}_6]$.

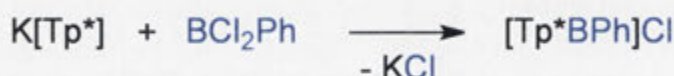


Figure 23: Proposed reaction stoichiometry for formation of $[\text{Tp}^*\text{BPh}]\text{Cl}$.

Given the essentially complete insolubility of the PF_6 derivative, the reaction of $\text{K}[\text{Tp}^*]$ and BCl_2Ph (Figure 23) was repeated without any attempt at anion metathesis. The white solid recovered from DCM was also found to have very poor solubility, even in DMSO, precluding the observation of resonances in the ^{11}B NMR spectrum. The ^1H NMR spectrum revealed numerous inequivalent pz^* environments. The MS analysis of the solid found that the major fragment present was $[\text{Tp}^* + \text{Na} + \text{H}]^+$, though there was a small but distinct envelope at m/z 386 corresponding to the desired $[\text{Tp}^*\text{BPh}]^+$ cation. Further characterisation and purification was hindered by the poor solubility of the product mixture.

The neutral thallium(I) substituted Tp^* analogue, TITp^* , is an effective, albeit toxic, ligand transfer reagent^{63, 64} due to its molecular nature rendering it more soluble than salts such as $\text{K}[\text{Tp}^*]$ ⁶⁵ and the complete insolubility of thallium halide co-products. The reaction of BCl_2Ph with TITp^* in DCM appeared to proceed as expected forming $[\text{Tp}^*\text{BPh}]\text{Cl}$, with the immediate precipitation of TlCl at 0°C . The ^{11}B NMR spectrum was equally encouraging, with two resonances at δ_{B} -7.3 (*cf.* δ_{B} -9.0 for TITp^* in the same solvent) and δ_{B} 0.3 (*cf.* δ_{B} 0.2 (BEt), -8.4 (BH) for $[\text{HB}(\text{pzMe})_3\text{BEt}]^+$).⁵⁹ The ^1H NMR spectrum proved to be cluttered, indicating several dimethylpyrazole environs. Purification was hindered by the initially DCM soluble product mixture becoming increasingly insoluble in DCM after a short period of time.

[§] In CD_2Cl_2 .

Addition of the BCl_2Ph to the TiTp^* at a lower temperature (-78°C rather than 0°C), followed by an identical work-up, still found the product to be a mixture of numerous pz^* resonances in the ^1H NMR spectrum. The ^{11}B NMR spectrum was similar to that observed in the previous reaction with resonances at -6.9 and 0.2 ppm, but with two new peaks at -8.3 and 1.5 ppm, all four of which were in the appropriate region for $[\text{Tp}^*\text{BR}]^+$ type compounds. Subsequent manipulation of the product mixture was again hindered by its loss of solubility in chlorinated solvents, presumed to be a result of decomposition. It therefore seems that the isolation of small amounts of $[\text{Tp}^*\text{BPh}][\text{MoTp}^*(\text{CO})_3]$ reflects a fortuitous combination of the favourable crystallisation with a bulky counter-anion and the high dilution of the reagents. Targeted synthesis of $[\text{Tp}^*\text{BPh}]^+$ salts with more conventional counter-anions, in all cases, contrastingly afforded materials which are most likely polymeric in nature. These materials contain bimolecular bridge-forming processes kinetically accessing oligomeric species, which all contain similar BPh and BH environments but with various chelated and bridging dimethylpyrazole environments. Pyrazaboles, e.g., $\text{H}_2\text{B}(\text{pz}^*)_2\text{BH}_2$, once formed are remarkably robust, such that redistribution to eventually form $[\text{Tp}^*\text{BPh}]^+$ cages would be kinetically precluded.

The reaction between TiTp^* and $\text{BCl}(\text{O}_2\text{C}_6\text{H}_4)$ was investigated to explore whether such polymer forming processes might be subverted. The reaction proceeded with immediate precipitation of TiCl and whilst the ^1H NMR analysis indicated only two different pz^* environments and two major ^{11}B NMR resonances at -6.8 and 6.3 ppm, crystallographic analysis indicated that the product was not the anticipated $\text{Tp}^*\text{B}(\text{O}_2\text{C}_6\text{H}_4)$. Rather, partial Tp^* cleavage had occurred to afford the pyrazabole $\text{HB}(\text{OC}_6\text{H}_4\text{OH}-2)(\mu\text{-pz}^*)_2\text{B}(\text{O}_2\text{C}_6\text{H}_4)$ (Figure 24). Trofimenko has previously reported the symmetrical pyrazabole, $(\text{C}_6\text{H}_4\text{O}_2)\text{B}(\mu\text{-pz}^*)_2\text{B}(\text{O}_2\text{C}_6\text{H}_4)$, but ^{11}B NMR data for comparison were not presented.^{66, 67} However, the more recently reported pyrazabole $(\text{CF}_3\text{CO}_2)_2\text{B}(\mu\text{-pz}^*)_2\text{B}(\text{O}_2\text{CCF}_3)_2$ was observed at $\delta_{\text{B}} -0.8$ (CDCl_3).⁶⁸

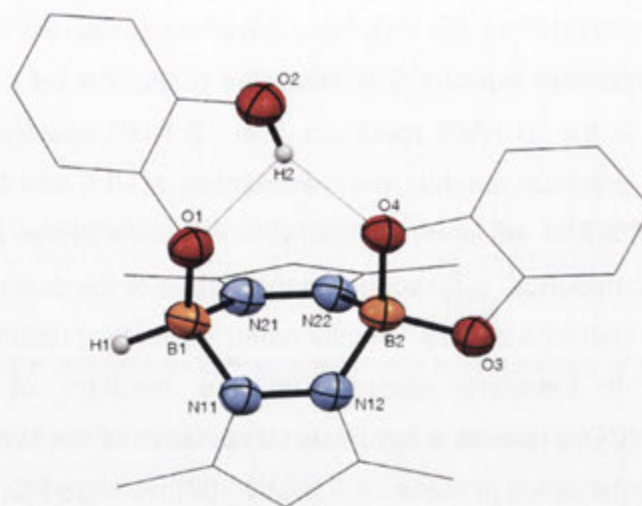


Figure 24: The molecular structure of $\text{HB}(\text{OC}_6\text{H}_4\text{OH-2})(\mu\text{-pz}^*)_2\text{B}(\text{O}_2\text{C}_6\text{H}_4)$. (Alkyl and aryl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å), angles (°) and intramolecular hydrogen bonds (Å): B1-N11 1.553(5); B1-N21 1.571(5); B1-O1 1.457(5); B2-N12 1.553(5); B2-N22 1.556(5); B2-O3 1.451(4); B2-O4 1.489(4); N11-B1-N12 104.9(3); N11-B1-O1 104.3(3); N21-B1-O1 110.3(3); N12-B2-N22 106.1(3); N12-B2-O3 111.0(3); N12-B2-O4 111.4(3); N22-B2-O3 110.4(3); N22-B2-O4 111.7(3); O3-B2-O4 106.3(3); O2-H2...O1 2.176(2); and O2-H2...O4 2.102(3).

An interesting feature of the solid state structure of $\text{HB}(\text{OC}_6\text{H}_4\text{OH-2})(\mu\text{-pz}^*)_2\text{B}(\text{O}_2\text{C}_6\text{H}_4)$ was the pendant hydroxyl group from the monodentate catecholate group lying almost equidistant between the two nearest intramolecular hydrogen bond acceptors (Figure 24: O2-H2...O1 2.176(2); O2-H2...O4 2.102(3) Å), which may explain the unusual pseudo-cage like arrangement assumed in the solid state.

3.7. Reactions of Mixed Haloboranes with Phosphidometallates

The predisposition of diphosphines towards ring-closure (chelation) processes in the formation of boronium centres[†] raised the question as to whether diphosphines in which the phosphine donors were bridged by a transition metal might perform similarly. The salt $\text{Li}_2[(\text{CO})_4\text{Mo}(\text{PPh}_2)_2]^{69}$ (readily prepared by deprotonation of

[†] Discussed in greater detail in the following chapter.

$\text{Mo(CO)}_4(\text{PPh}_2)_2$ ^{70, 71}), might be viewed as an analogue of dppe , with the possible advantage of salt elimination in reactions with haloboranes.

Initial reactions of $\text{Li}_2[(\text{CO})_4\text{Mo(PPh}_2)_2]$ with haloborane adducts of the form $\text{BHX}_2\cdot\text{SMe}_2$ (where $\text{X} = \text{Cl, Br}$) primarily afforded the reprotonated starting material $\text{Mo(CO)}_4(\text{PPh}_2)_2$ (δ_{P} 16.7). For the reaction with $\text{BHCl}_2\cdot\text{SMe}_2$, an unidentified minor additional peak was also observed (δ_{P} 7.0), which did not display any broadening caused by bonding to ^{11}B nuclei. The ^{11}B NMR spectrum for the $\text{BHBr}_2\cdot\text{SMe}_2$ reaction indicated formation of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (ca. 25%) which was absent in the reagent, however, the other partners in the usual disproportionation of $\text{BHBr}_2\cdot\text{SMe}_2$, *i.e.*, $\text{BH}_3\cdot\text{SMe}_2$ (δ_{B} -25.5) and $\text{BBr}_3\cdot\text{SMe}_2$ (δ_{B} 29.5),⁷² were absent, suggesting the operation of another mechanism for the formation of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$.^{72, 73}

In the reaction of BCl_2Ph with $\text{Li}_2[(\text{CO})_4\text{Mo(PPh}_2)_2]$, the ^{31}P NMR spectrum of the crude reaction mixture again revealed that $\text{Mo(CO)}_4(\text{PPh}_2)_2$ was by far the predominant phosphorus containing species present in addition to three minor signals appearing at δ_{P} 131.0, 134.0 and 136.2, which were absent from reactions involving $\text{BHCl}_2\cdot\text{SMe}_2$ and $\text{BHBr}_2\cdot\text{SMe}_2$. These resonances were sharp, which excluded the possibility of being B-P bonded products. In addition to peaks attributable to BCl_3 (δ_{B} 46.4), BCl_2Ph (δ_{B} 52.3) and B^nBu_3 (δ_{B} 85.7),⁷³⁻⁷⁵ the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum contained a further resonance at 77.0 ppm which on the basis of data for BClR_2 ($\text{R} = \text{Me, Et, } ^i\text{Pr, } ^n\text{Bu} = 77\text{--}78$) most likely corresponds to BCl^nBu_2 .⁷⁴

3.8. Conclusion

In conclusion, a wide range of phosphine haloborane adducts have been synthesised and were found to exhibit good thermal stability, especially when compared to their thioether precursors. Improved stability with respect to disproportionation is likely to be a useful feature in their subsequent use. The limitations of forming such adducts was tested and the electronic and steric thresholds were found with the successful synthesis of $(\text{C}_6\text{H}_4\text{F-4})_3\text{P}\cdot\text{BH}_2\text{Br}$ and $(\text{C}_6\text{H}_4\text{Me-2})_3\text{P}\cdot\text{BH}_2\text{Br}$, respectively, though both these compounds were observed to decompose over time, unlike with $\text{Ph}_3\text{P}\cdot\text{BH}_2\text{Br}$ and $\text{Cy}_3\text{P}\cdot\text{BH}_2\text{Br}$ where no decomposition ensues under ambient conditions.

The unremarkable differences between the P-B bond lengths of adducts with wildly varying phosphine substituents, in both their electronic and steric properties, combined with the narrow range of ^{11}B NMR values observed for these species, suggest that the strength of the newly generated $\text{P}\rightarrow\text{B}$ bonds were similar regardless of the nature of the phosphine.

Unfortunately an analogue of the literature compound $\text{dppm}\cdot\text{BH}_2\text{Cl}$ could not be synthesised due to the inability to ensure mono-substitution of diphosphines such as dppe , which led to a range of disubstituted diphosphines being synthesised. However, unexpected and intriguing side products were still observed occasionally, such as $[\text{Cl}_2\text{B}(\text{Ph}_2\text{P}(\text{O})\text{CH}(\text{BCl}_3)\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]$. In the case of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$, a third product was possible with these diphosphines *via* bromide ionisation to generate a boronium salt, which will be discussed in more detail in the following chapter.

The problem of mono-substitution was resolved by use of the heterochelate arphos, which possesses both phosphorus and arsenic Lewis bases. The preference of the monobromoborane for the phosphorus was expected due to the increased Lewis basicity of the phosphine group and was always observed experimentally. The reaction of $\text{arphos}\cdot\text{BH}_2\text{Br}$ with organometallic precursors led to the decomposition of the adduct with loss of boron and transfer of the chelate to various metals.

Direct reaction of haloboranes, such as BCl_2Ph , $\text{BHCl}_2\cdot\text{SMe}_2$ and $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ with metal centres were found to proceed unpredictably, often to a myriad of unexpected products *via* the decomposition of the organometallic reagent. One such decomposition led to the recovery of $[\text{Tp}^*\text{BPh}][\text{MoTp}^*(\text{CO})_3]$, featuring a rare unsymmetrical diboron cage. Computational calculations suggest that the previously known B-H analogue, $[\text{Tp}^*\text{BH}]^+$, possessed a degree of transannular boron-boron interaction, though this same interaction could not be identified computationally for $[\text{Tp}^*\text{BPh}]^+$.

The rational synthesis of the $[\text{Tp}^*\text{BPh}]^+$ and other related species, stabilised by differing anions, was attempted through various means, but was hindered by the insoluble nature of the presumably oligomeric products produced.

3.9. References

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Chapter 4

Borocations with Tertiary, Secondary and Primary Phosphines

4.1. Preamble

Cationic boron species may be divided into three subgroups: borinium, borenium and boronium (Figure 1) ions.¹ Each of the three subgroups can be viewed as a cationic boron bearing two σ -bound substituents, with borenium bearing an additional stabilising dative-bound substituent and boronium bearing two additional substituents.

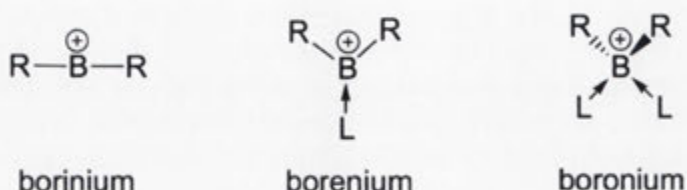


Figure 1: The three types of borocations.¹

The two coordinate nature of borinium cations coupled with their drastic electron deficiency makes them a very highly reactive species normally only inferred in gas phase reactions. Only four crystal structures of borinium cations have been reported (Figure 2),²⁻⁵ all bearing very bulky positively mesomeric amino groups that are able to stabilise the cationic boron centre *via* π -interactions. Three coordinate borenium cations are also coordinatively unsaturated, but if the dative substituent (L) is sufficiently basic, this will assist in stabilising the electron-deficient boron. Boronium cations are coordinatively saturated with a full octet, making them by far the most stable and common of the three classes of borocations.

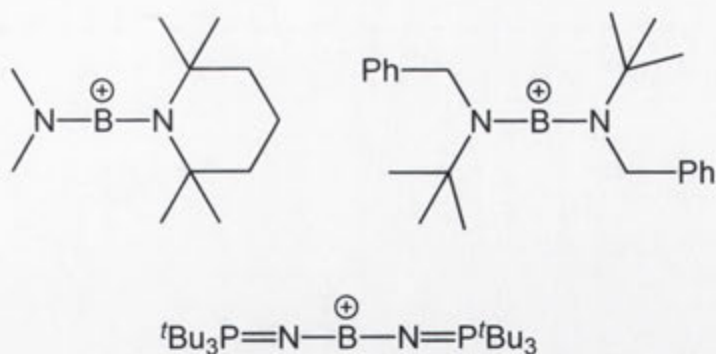


Figure 2: The molecular structures of the crystallographically characterised examples of boronium cations.¹²⁻⁵

Interest in stabilising boronium species has been consistent, however, a large proportion of these endeavours have involved nitrogen based substituents.¹ A notable exception is the recent isolation by Bertrand of a bis(*N*-heterocyclic carbene)boronium salt.⁶ With an ever-increasing number of phosphines becoming available, offering variations in both steric and electronic properties, the pursuit of phosphorus-based boronium species appears particularly attractive.

4.2. Borocations

As mentioned in chapter 2, a possible contaminant in the synthesis of $\text{BH}_2\text{Br}\cdot\text{dppe}$ was a ring-closed product. After initial formation of the mono-substituted adduct, the remaining non-coordinated phosphine could attack the bound boron, causing the substitution of the bromide to generate a salt. The resulting boronium salt contained a cationic 4-coordinate boron centre stabilised by dative bonds from both of the phosphine donors.

Tertiary phosphine ligated boronium salts synthesised in this way had already been reported by Schmidbaur *et al.* in the 1980's, where dppe was found to react with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ to give the ring-closed boronium product $[\text{H}_2\text{B}(\text{dppe})]\text{Br}$ (Figure 3).⁷ They found that boronium salts could also be synthesised by reaction of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ with the small tertiary phosphines PMe_3 ($\theta_T = 118^\circ$) and PEt_3 ($\theta_T = 132^\circ$),⁸ but that larger

[†] Though there are only three boronium cations shown, there are four examples due to the solid-state structures of both the Cl^- and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions having been reported for $[\text{B}(\text{N}=\text{P}{}^t\text{Bu}_3)_2]^+$.

tertiary phosphines such as P^iPr_3 ($\theta_T = 160^\circ$) and PPh_3 ($\theta_T = 145^\circ$) would only form simple mono-adducts, regardless of stoichiometry.

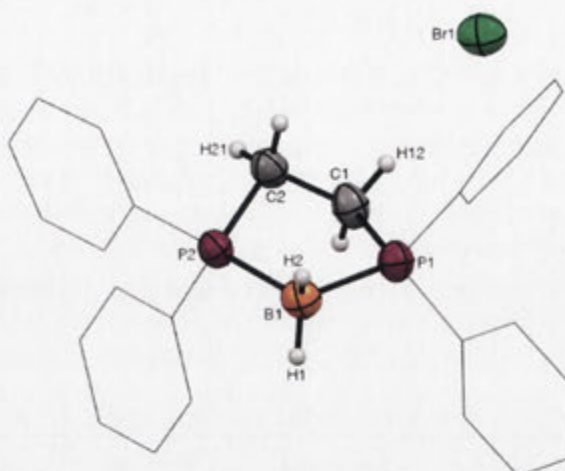


Figure 3: The molecular structure of $[H_2B(dppe)]Br$. (Alkyl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids).[†] Selected bond lengths (Å), angles ($^\circ$) and intermolecular distances (Å): B1-P1 1.955(4); B1-P2 1.933(4); P1-C1 1.830(3); P2-C2 1.815(3); C1-C2 1.540(5); P1-B1-P2 98.6(2); B1-P1-C1 104.1(2); B1-P2-C2 102.9(2); P1-C1-C2 107.3(2); P2-C2-C1 106.4(2); C1-H12 $\cdots$ Br1 2.9120(3); C2-H21 $\cdots$ Br1 2.9652(4).

Interestingly, a dicationic boron cage, $[HB(\kappa^3-P(Me_2)CH_2)_3CMe]Br_2$ (Figure 4), arose from the reaction of 1,1,1-tris(dimethylphosphinomethyl)ethane with $BHBr_2 \cdot SMe_2$, where both bromine atoms are lost in favour of phosphine coordination. Employing the per-phenylated analogue, 1,1,1-tris(diphenylphosphinomethyl)ethane, however resulted in only two of the three phosphines coordinating to the boron atom to give a ring-closed $[BHBBr]^+$ complex. Despite the more electron releasing nature of the methyl groups when compared to the weakly electron withdrawing phenyl groups, the difference in products obtained for the two analogues was attributed to the steric hindrance imposed by the phenyl groups not permitting a third PPh_2 group to coordinate to the boron atom.

[†] Though $[H_2B(dppe)]Br$ is a literature compound, the solid-state structure had not been previously reported.

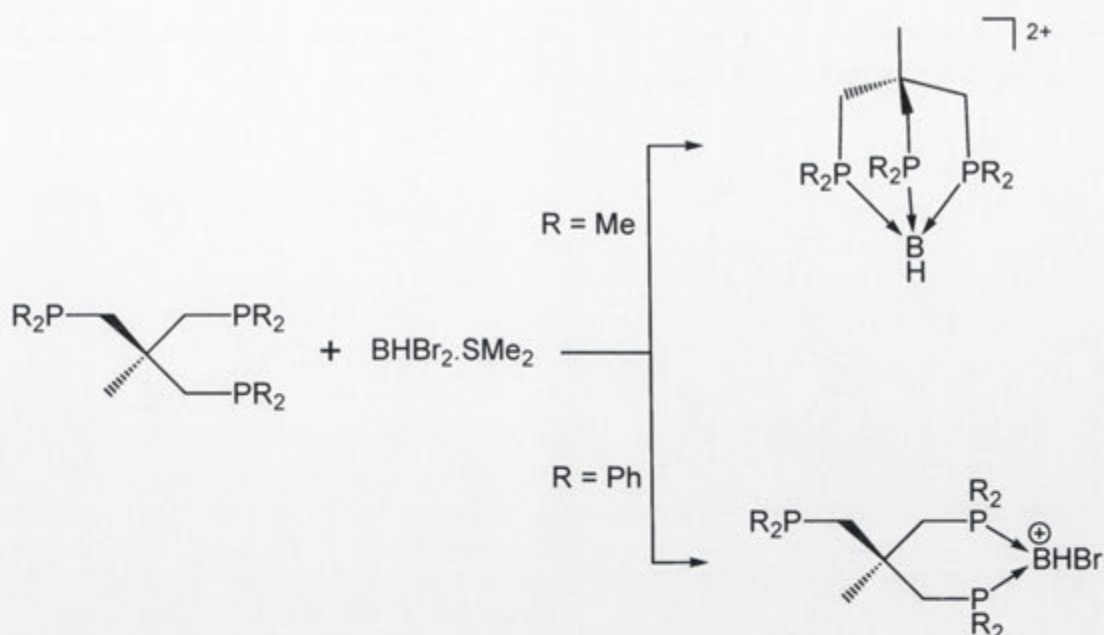


Figure 4: The dicationic boron cage $[HB(\kappa^3-P(Me)_2CH_2)_3CMe]^{2+}$ and the boronium cation $[BrHB(\kappa^2-P(Ph)_2CH_2)_3CMe]^+$ reported by Schmidbaur *et al.* in 1988.⁷

4.3. Boronium Salts of Secondary Phosphines

Whilst attempting to synthesise the secondary phosphine-stabilised mixed haloborane $Cy_2HP \cdot BH_2Br$ via reaction of stoichiometric amounts of the parent phosphine with $BH_2Br \cdot SMe_2$ (benzene or DCM, ambient temperature), the final product was instead found to be $[H_2B(PHCy_2)_2]Br$ (Figure 5).^{*} Monitoring the reaction by ^{11}B NMR spectroscopy showed first the consumption of the $BH_2Br \cdot SMe_2$ starting material ($\delta_B -12.0$) to form the adduct $Cy_2HP \cdot BH_2Br$ ($\delta_B -27.9$), followed by its conversion to $[H_2B(PHCy_2)_2]Br$ ($\delta_B -45.2$). The boronium salt was found to be the favoured product, even when a 1:1 stoichiometry of reagents was employed, with the reaction proceeding completely to the boronium salt within 10 minutes at ambient temperature. The ^{11}B NMR data illustrated the shift to lower frequency as the boron went from being the SMe_2 adduct, to the phosphine adduct, to the boronium salt, as it was progressively acquiring more electron density around itself in the form of first one, then two subsequent dative bonds from the phosphorus donors. Isolated $Cy_2HP \cdot BH_2Br$ (with

^{*} Whilst this work was undertaken another group reported this compound.⁹ However, the solid state structure was not reported.

some boronium salt contamination) was also found to completely decompose in solution to $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ over a period of 10 minutes at 0°C .

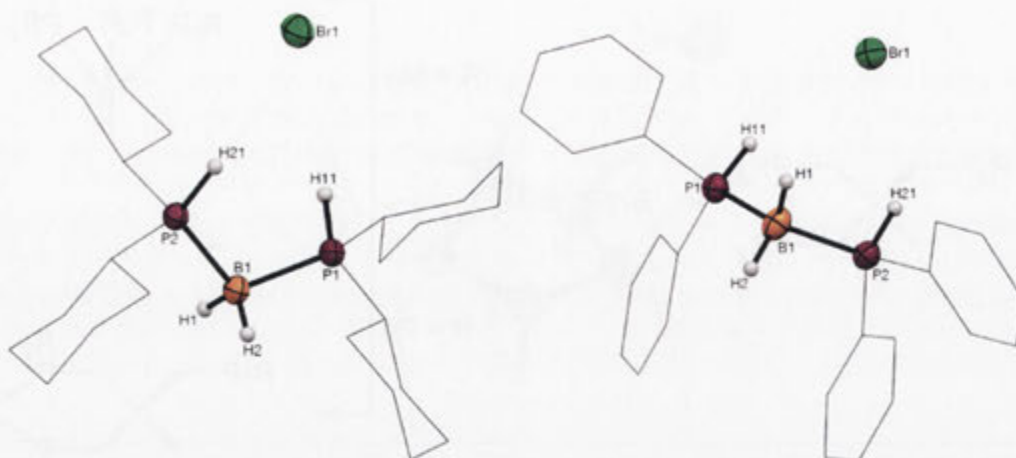


Figure 5: The molecular structures of $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ (left) and $[\text{H}_2\text{B}(\text{PHPh}_2)_2]\text{Br}$ (right). (Alkyl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å), angles ($^\circ$) and intermolecular distances (Å) for $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$: B1-P1 1.928(2); B1-P2 1.935(2); P1-B1-P2 112.4(1); P2-H21...Br1 2.9473(2). Selected bond lengths (Å), angles ($^\circ$) and intermolecular distances (Å) for $[\text{H}_2\text{B}(\text{PHPh}_2)_2]\text{Br}$: B1-P1 1.928(2); B1-P2 1.923(2); P1-B1-P2 111.0(1); P1-H11...Br1 2.8681(2); P2-H21...Br1 2.9243(2).

Encouraged by the serendipitous synthesis of $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$, the rational syntheses of other analogous boronium salts were explored in the same straightforward fashion. Diphenylphosphine (PHPh_2) and cyclohexylphosphine (PH_2Cy) were also found to preferentially proceed to the corresponding boronium salts (Figure 6), $[\text{H}_2\text{B}(\text{PHPh}_2)_2]\text{Br}$ (Figure 5) and $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$ (Figure 7), respectively, without isolation of the neutral stabilised mixed haloborane, even with a 1:1 stoichiometry of reactants. As before, the phosphine-stabilised mixed haloborane may be observed (^{11}B NMR) to form first, but then readily converts to the corresponding boronium salt (Table 1). Thus, isolated samples of the stabilised mixed haloboranes $\text{Ph}_2\text{HP}\cdot\text{BH}_2\text{Br}$ and $\text{Cy}_2\text{HP}\cdot\text{BH}_2\text{Br}$ were observed to decompose, both neat and in solution, to their corresponding boronium salts over a period of 2 hours.

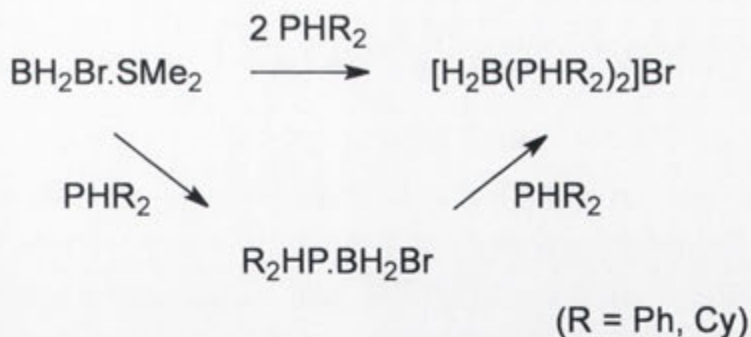


Figure 6: The general reaction scheme for the synthesis of boronium cations by reaction of monobromoborane and secondary phosphines.

Table 1: ^{11}B NMR data (ppm) in CD_2Cl_2 for secondary and primary boronium salts and their intermediate phosphine-stabilised mixed haloborane adducts.

PR_3	$\text{BH}_2\text{Br} \cdot \text{SMe}_2$	$\text{R}_3\text{P} \cdot \text{BH}_2\text{Br}$	$^1J_{\text{BH}}$ (Hz)	$[\text{H}_2\text{B}(\text{PR}_3)_2]\text{Br}$	$^1J_{\text{BH}}$ (Hz)
PPh_2	-13.5	-25.3	(unresolved)	-38.1	69.6
PHCy_2	-13.5	-27.9	76.9	-45.2	91.6
PH_2Cy	-13.5	-28.0	120.8	-44.5	90.3



Figure 7: The molecular structure of $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$. (Alkyl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): B1-P1 1.918(1); P1-B1-P1 i 117.0(1).

4.4. Boronium Salts of Tertiary Phosphines

Whilst the formation of $[\text{H}_2\text{B}(\text{PCy}_2)_2]\text{Br}$ readily occurred, the reaction of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ with two equivalents of PCy_3 failed to produce the boronium salt $[\text{H}_2\text{B}(\text{PCy}_3)_2]\text{Br}$, being consistent with previous observations of the inability to isolate $[\text{H}_2\text{B}(\text{PPh}_3)_2]\text{Br}$ by reaction of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ with two equivalents of PPh_3 .⁷ Simple semi-empirical (PM6) calculations suggest accommodation of two PCy_3 donors by $[\text{BH}_2]^+$ would require a P-B-P angle of 120 (PM6) to 138° (PM3), a significant deviation from the *ideal* tetrahedral bond angle of 109°. In these cases, the reaction only proceeded as far as the corresponding stabilised mixed haloborane species $\text{R}_3\text{P}\cdot\text{BH}_2\text{Br}$ ($\text{R} = \text{Ph}, \text{Cy}$). The readiness of PHCy_2 and PPh_2 to form boronium salts, coupled with the reluctance of PCy_3 and PPh_3 to do the same, would indicate that the formation of these salts was somewhat independent of the σ -donor ability of the parent phosphine and more dependent on steric considerations (two features of phosphine ligands that have traditionally been quantified with the Tolman electronic parameter and Tolman cone angle, respectively).^{§10, 11}

A steric limit was found with the inability to produce a boronium type species with bulky tertiary phosphines, but being able to with secondary and primary phosphines. This led to a fine-tuning of the steric limitations of the phosphines that would readily form boronium salts by reaction with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$. The reaction of two equivalents of PMePh_2 with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ did result in the formation of the boronium salt $[\text{H}_2\text{B}(\text{PMePh}_2)_2]\text{Br}$ ($\delta_{\text{B}} -34.8$), however the reaction did not go to completion and existed as a minor product alongside the stabilised adduct $\text{Ph}_2\text{MeP}\cdot\text{BH}_2\text{Br}$ ($\delta_{\text{B}} -23.3$), which was the major species present in the crude reaction product. Another stabilised adduct type species was also found to be present by NMR analysis ($\delta_{\text{B}} -15.6$). Although this species could not be definitively identified, it was estimated by ^{11}B NMR spectroscopy to be in an approximately equimolar quantity as the boronium product. The three broad ^{31}P NMR peaks present could not be assigned to the individual species due to the non-predictive shift of the B-P bonding for adducts and boronium salts, especially as the peaks were within 10 ppm of one another at -1.7, 3.6 and 8.2 ppm, in an approximately 2:2:1 ratio by integration, respectively. Notably, in electronic and steric terms two

[§] See Appendix 2 for the Tolman electronic parameter and Tolman cone angle values for various common phosphines.

PMePh_2 ligands should approximate one dppe, therefore the ready formation of $[\text{H}_2\text{B}(\text{dppe})]\text{Br}$ may be attributed to a chelate effect.

In steric terms, the tertiary phosphine PMe_2Ph was found to be the limit to successfully produce a boronium species, whereupon reaction of two equivalents of PMe_2Ph and $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ cleanly yielded the associated boronium salt $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$ (Figure 8) in an 85% yield.

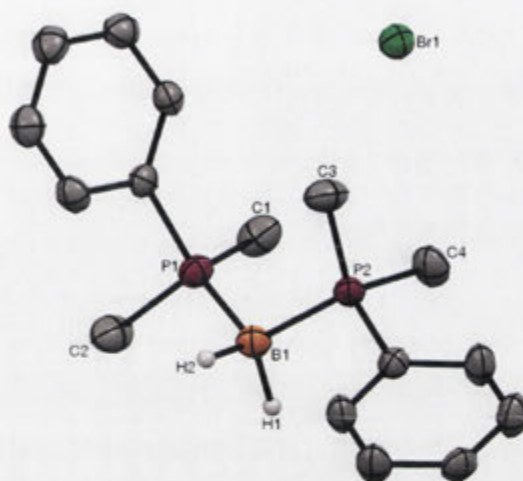


Figure 8: The molecular structure of $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$. (Alkyl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): B1-P1 1.924(3); B1-P2 1.918(3); P1-C1 1.796(3); P1-C2 1.814(3); P2-C3 1.798(3); P2-C4 1.794(3); P1-B1-P2 115.1(2); B1-P1-C1 115.1(2); B1-P1-C2 106.8(2); B1-P2-C3 114.1(2); B1-P2-C4 111.9(2).

4.5. Boronium Salts of Primary Phosphines

Having established the steric limitations of phosphines capable of forming boronium salt, the electronic limits were probed using a range of primary and secondary phosphines. The unexpected ease with which $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$ forms naturally led to the reaction of two equivalents of PH_2Ph with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$. The reaction appeared to proceed as expected, but the product was found to be only sparingly soluble, preventing the acquisition of useful NMR analysis. Attempts to obtain ESI-MS data were similarly unsuccessful. The insolubility of the salt was surprising but may be due to the presence of more sterically accessible P-H groups allowing hydrogen-bonding networks in the solid-state.

Reaction of two equivalents of PH_2Mes with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ in toluene proceeded to straightforwardly yield the stabilised adduct with a characteristic peak at -26.0 ppm, as determined by ^{11}B NMR spectroscopy. The desired boronium salt $[\text{H}_2\text{B}(\text{PH}_2\text{Mes})_2]\text{Br}$ was detected in a trace amount at δ_{B} -40.8, therefore forcing conditions were implemented in an attempt to favour the formation of the boronium product. After heating at 100°C for 16 hours* the boronium salt had decomposed and a new peak at δ_{B} -38.0 had appeared, again only as a minor product. Finally, being heated to reflux in toluene overnight appeared to provide a boronium type species as the major product (δ_{B} -35.9), though the corresponding ^{31}P NMR spectrum showed numerous P-B type compounds were present.

Treating two equivalents of the secondary phosphine *rac*-PHEtPh with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ fared the same as for PH_2Mes , where the desired boronium species $[\text{H}_2\text{B}(\text{PHEtPh})_2]\text{Br}$ was observed in the ^{11}B NMR spectrum at -41.7 ppm, but only in a trace amount, with the phosphine-stabilised mixed haloborane being the dominant product by far at -25.7 ppm. The typically broad resonances (^{11}B , ^{31}P NMR) precluded the resolution of peaks attributable to the *meso* (RS and SR) and diastereomers (RR and SS) for the boronium salt.

The ability to only cleanly synthesise a boronium species with PH_2Cy , the most σ -basic of the three primary phosphines attempted, suggested that electronic considerations were also an important factor dictating the formation of boronium salts. In contrast, PPh_2 proceeded relatively cleanly and with a good yield of 87%, whilst PHEtPh, a less sterically bulky and more σ -basic phosphine, seemed unwilling to proceed past the intermediate adduct. This counter-intuitive observation suggested that the factors behind successful boronium synthesis were especially subtle. Insight might have been provided by examination of the $^1J_{\text{PH}}$ values for the phosphine stabilised monobromoborane adducts, but given the aforementioned inability to prevent these species rapidly proceeding to their respective boronium salts, the $^1J_{\text{PH}}$ values could only be obtained for the boronium salts and not for many of the intermediate adducts. However, the $^1J_{\text{PH}}$ values for the series of free PHCy_2 , $\text{Cy}_2\text{HP}\cdot\text{BH}_2\text{Br}$ and $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ were determined by ^{31}P NMR spectroscopy to be 195.5, 400.3 and 407.3 Hz respectively. The dramatic increase (>200 Hz) in the $^1J_{\text{PH}}$ coupling going from

* No change was observed when the reaction was heated at lower temperatures for similar lengths of time.

the free PHCy_2 to the intermediate adduct $\text{Cy}_2\text{HP}\cdot\text{BH}_2\text{Br}$ was to be expected, given the donation of electron density from the phosphorus atom to the boron centre. Interestingly, the difference between $\text{Cy}_2\text{HP}\cdot\text{BH}_2\text{Br}$ and the boronium salt $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ was minor (7 Hz). A similar trend was seen for free PPh_2 and $[\text{H}_2\text{B}(\text{PPh}_2)_2]\text{Br}$ which were observed to have $^1J_{\text{PH}}$ values of 218.3 and 376.2 Hz respectively, as well as with free PH_2Cy and $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$ which had values of 191.6 and 414.7 Hz respectively.

4.6. Calculations on Simple Borane Adducts and Boronium Cations

Calculations on the simple borane adducts $\text{Me}_3\text{P}\cdot\text{BH}_2\text{Br}$ and $\text{Me}_2\text{HP}\cdot\text{BH}_2\text{Br}$, as well as their corresponding bis(phosphine) boronium cations $[\text{H}_2\text{B}(\text{PMe}_3)_2]^+$ and $[\text{H}_2\text{B}(\text{PMe}_2)_2]^+$, were performed using DFT.[†] Trimethylphosphine was chosen as a computationally more economic simplification of larger phosphines used in this study so as to isolate steric factors, which nevertheless were found to play a substantive role.

The similarity of the frontier orbitals for the borane adducts $\text{Me}_3\text{P}\cdot\text{BH}_2\text{Br}$ (Figure 9) and $\text{Me}_2\text{HP}\cdot\text{BH}_2\text{Br}$ (Figure 10) highlights the minimal difference in reactivity predicted for the two species, with both adducts having their HOMO and HOMO-1 being essentially 'lone pairs' centred on the bromine substituent. The LUMO for both adducts is also very similar, and whilst the orbital is diffused over the entire molecule in each case, it is predominantly B-Br σ^* in nature, *i.e.*, nucleophilic attack at boron is likely to proceed in much the same way as for simple alkyl halides ($\text{S}_{\text{N}}2$) with inversion at boron and displacement of bromide.

Relative to their constituents PMe_3 , PMe_2 and BH_2Br , thermodynamic data associated with the formation of adducts $\text{Me}_3\text{P}\cdot\text{BH}_2\text{Br}$ ($\Delta H = -131.3 \text{ kJmol}^{-1}$) and $\text{Me}_2\text{HP}\cdot\text{BH}_2\text{Br}$ ($\Delta H = -105.1 \text{ kJmol}^{-1}$) suggest that the tertiary trialkylphosphine forms a stronger interaction which may be traced to the increased basicity of tertiary phosphine *versus* secondary phosphines (*e.g.*, Tolman electronic parameter for PPh_3 and PPh_2 are 2068.9 and 2073.3).⁸

[†] Performed using Spartan 14; B3LYP, 6-31G**.

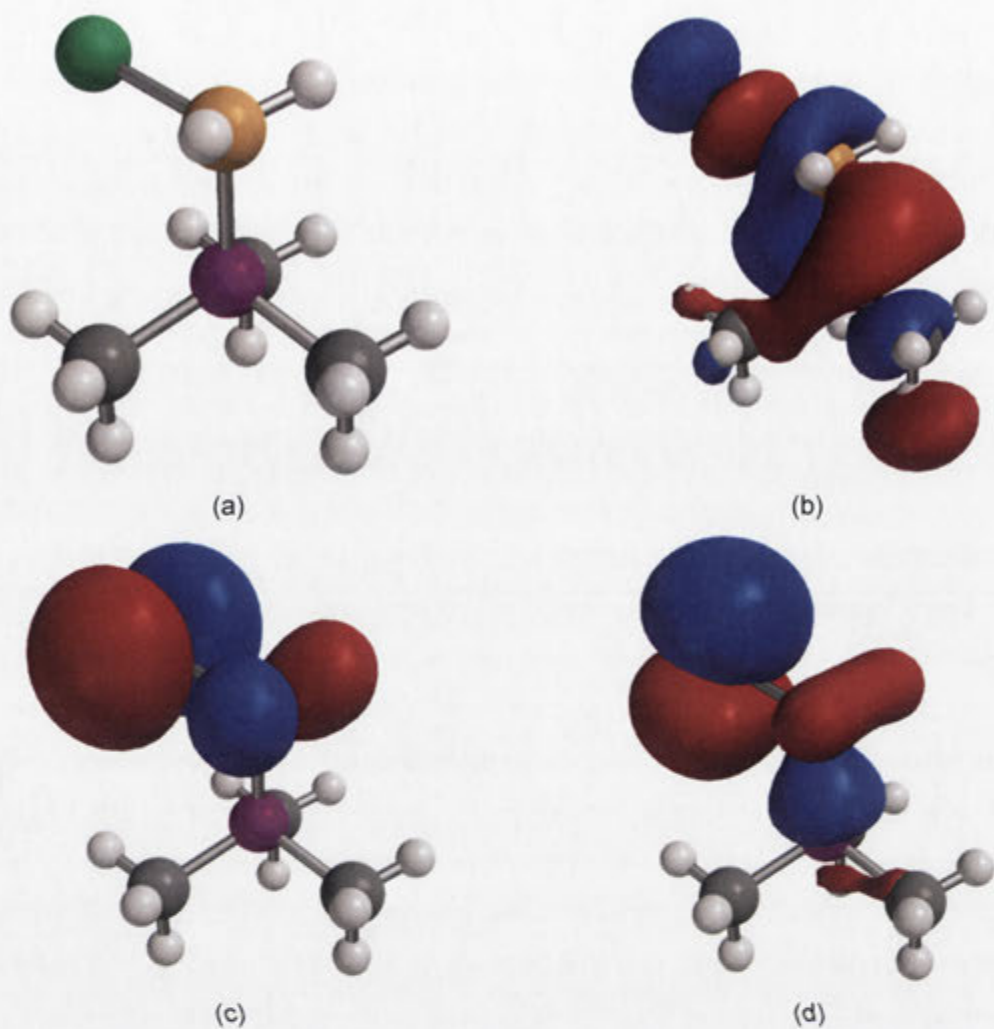


Figure 9: Optimised geometry of $\text{Me}_3\text{P}\cdot\text{BH}_2\text{Br}$ (a), along with its LUMO (b), HOMO (c) and HOMO-1 (d).

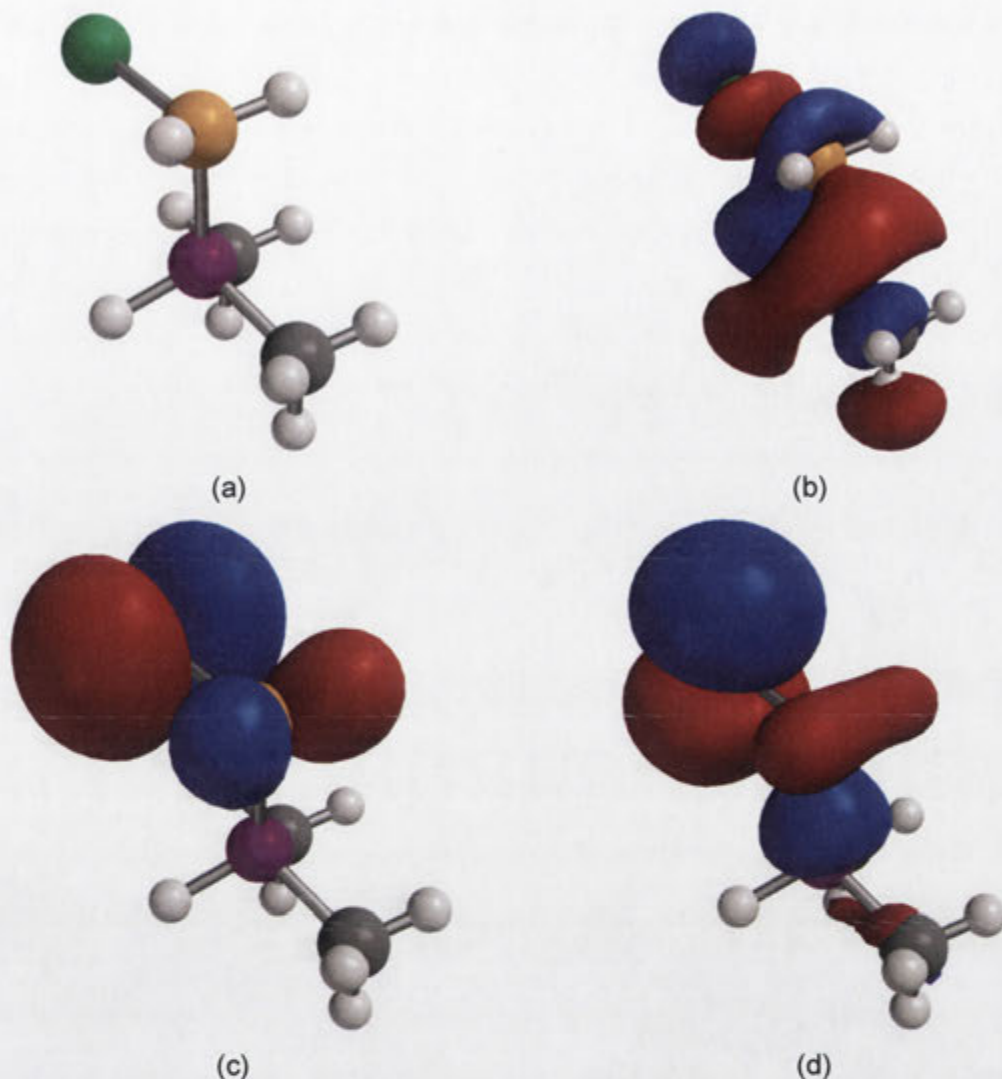


Figure 10: Optimised geometry of $\text{Me}_2\text{HP}\cdot\text{BH}_2\text{Br}$ (a), along with its LUMO (b), HOMO (c) and HOMO-1 (d).

The similarity of the frontier orbitals as previously discussed for the borane adducts was again observed for the comparison of the tertiary phosphine borocation $[\text{H}_2\text{B}(\text{PMe}_3)_2]^+$ (Figure 11) and the secondary phosphine borocation $[\text{H}_2\text{B}(\text{PHMe}_2)_2]^+$ (Figure 12). The LUMO orbital of both borocations was diffused over the entire molecule, whilst the HOMO orbitals were centred on the H_2BP_2 core of the molecule, but predominantly localised in the area between the two phosphine donors. Given the majority of boronium salts prepared in this study involved more sterically cumbersome phosphines than PMe_3 , the comparatively low reactivity towards nucleophiles may be

rationalised in terms of steric shielding of this otherwise reactive site. In both cases, the HOMOs were centred primarily on the BH_2 core of the molecule, indicating the retention of 'hydridic' character for the B-H bonds, which is curtailed by the positive charge. The HOMOs-1 were found to differ for the two borocations, with the HOMO-1 in $[\text{H}_2\text{B}(\text{PMe}_3)_2]^+$ primarily associated with B-P σ -bonding, whilst the HOMO-1 in $[\text{H}_2\text{B}(\text{PHMe}_2)_2]^+$ was centred on the BH_2 unit.[§] Relative to their constituents PMe_3 , $[\text{Me}_3\text{PBH}_2]^+$, PHMe_2 and $[\text{Me}_2\text{HPBH}_2]^+$, thermodynamic data associated with the formation of the boronium salts $[\text{H}_2\text{B}(\text{PMe}_3)_2]^+$ ($\Delta\text{H} = -262.5 \text{ kJmol}^{-1}$) and $[\text{H}_2\text{B}(\text{PHMe}_2)_2]^+$ ($\Delta\text{H} = -262.6 \text{ kJmol}^{-1}$) was comparable.

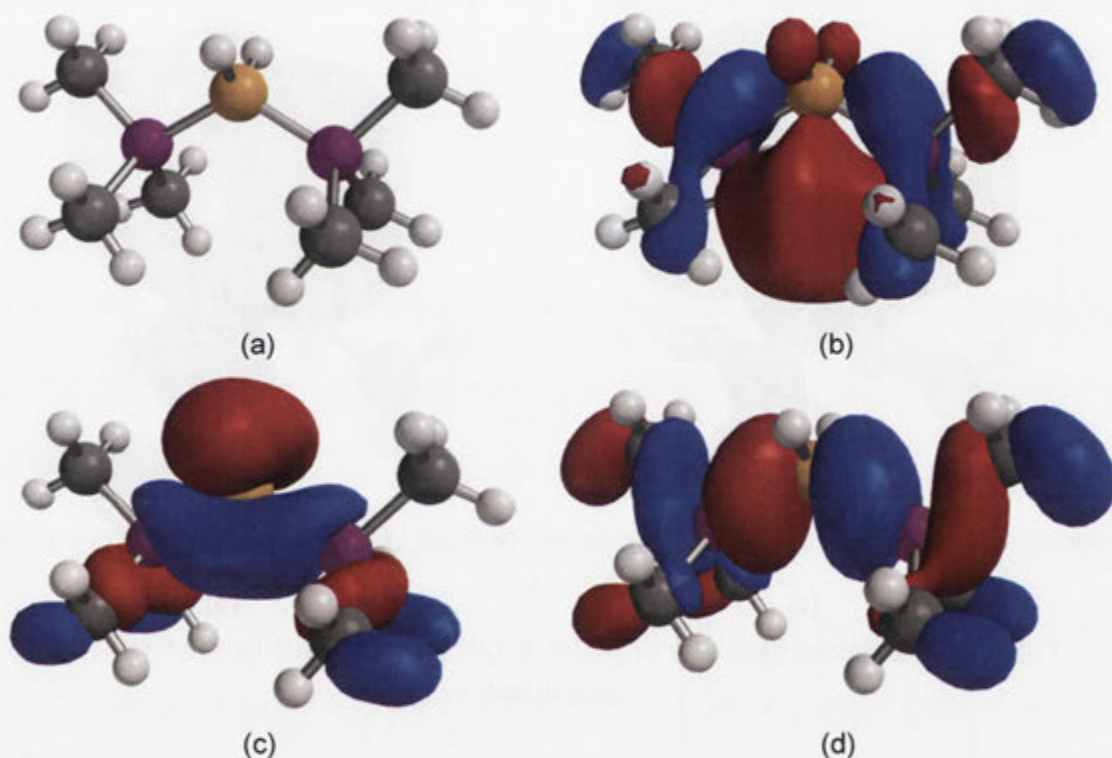


Figure 11: Optimised geometry of $[\text{H}_2\text{B}(\text{PMe}_3)_2]^+$ (a), along with its LUMO (b), HOMO (c) and HOMO-1 (d).

[§] However, the HOMO-2 of $[\text{H}_2\text{B}(\text{PHMe}_2)_2]^+$ was very near in energy to its HOMO-1 and was found to be very similar to that calculated for the HOMO-1 of $[\text{H}_2\text{B}(\text{PMe}_3)_2]^+$.

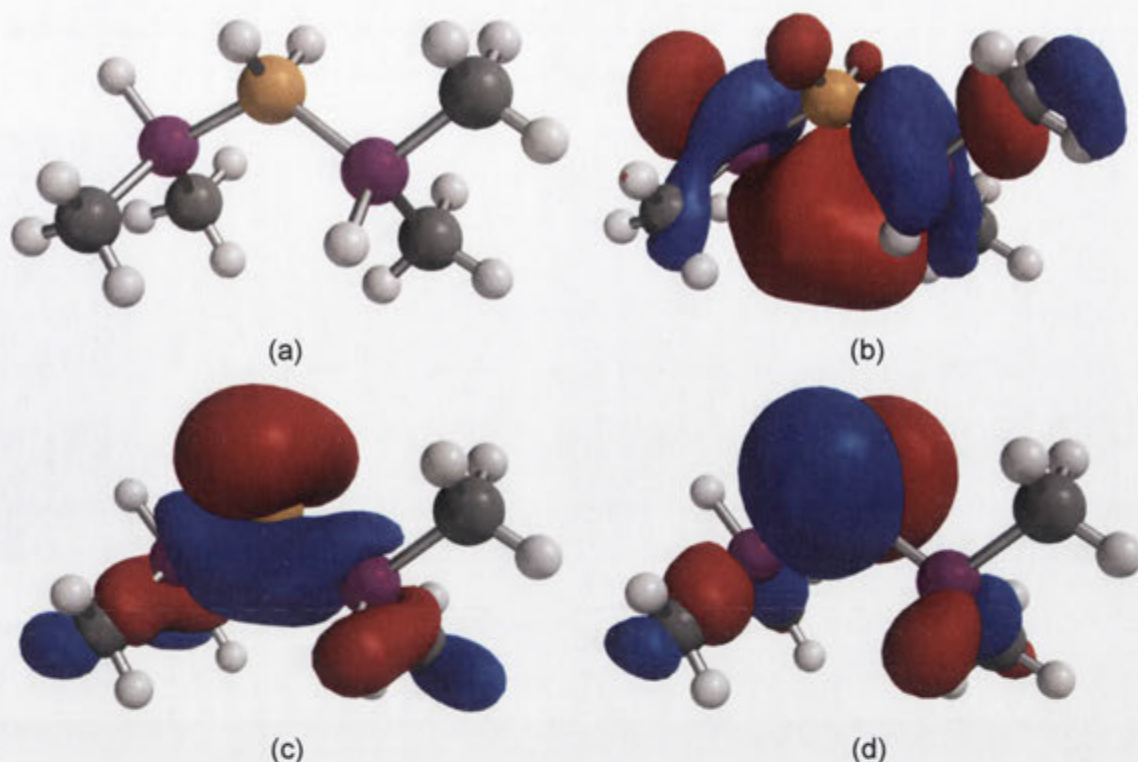


Figure 12: Optimised geometry of $[\text{H}_2\text{B}(\text{PHMe}_2)_2]^+$ (a), along with its LUMO (b), HOMO (c) and HOMO-1 (d).

4.7. NMR Comparisons for Boronium Salts Bearing Phosphine Ligands

The failure to cleanly synthesis more primary and secondary phosphine boronium salts was not a wasted effort, as the ^{11}B NMR data provided a definite trend as to the region of phosphine-stabilised monobromoboranes and phosphine-based boronium salts (Table 2). The data was especially helpful given the lack of ^{11}B NMR data in the literature for the admittedly few compounds of this type that were already known. An overview of the collected ^{11}B NMR data revealed that all of the observed phosphine-stabilised monobromoborane adducts were found within a narrow (5 ppm) range between -23 to -28 ppm, whilst all of the boronium salts were found within the slightly wider (10 ppm) range of -35 to -45 ppm. These values therefore provide a general analytical tool through which products in subsequent related reactions can more quickly be assigned based on empirical evidence.

Table 2: ^{11}B and ^{31}P NMR data for boronium salts and their intermediate phosphine-stabilised monobromoborane adducts.[†]

PR_3	$\text{R}_3\text{P}\cdot\text{BH}_2\text{Br}$		$[\text{H}_2\text{B}(\text{PR}_3)_2]\text{Br}$	
	δ_{B}	δ_{P}	δ_{B}	δ_{P}
PMePh_2 (C_6D_6)	-23.3	(unresolved)	-34.8	(unresolved)
PHPh_2 (CD_2Cl_2)	-25.3	-10.5	-38.1	-16.2
PMe_2Ph (C_6D_6)	-23.2	-8.0	-38.4	-3.5
PH_2Mes (C_6D_6)	-26.0	-72.4	-38.0	(unresolved)
PHEtPh (C_6D_6)	-25.7	-8.0	-41.7	1.5
PH_2Cy (CD_2Cl_2)	(not observed)	(not observed)	-44.5	-38.6
PHCy_2 (CD_2Cl_2)	-27.4	5.9	-45.2	-0.5

The ability to use ^{11}B NMR data to discriminate between the classes of compound has proven invaluable, especially given that a survey of the ^{31}P NMR data for the four fully characterised acyclic boronium salts failed to identify any obvious correlation (Table 3). As expected, the resonances were all shifted to higher frequencies upon ionisation to form the boronium products and broadened due to coupling with the 3/2 spin of the NMR active ^{11}B nuclei. However, the difference in chemical shift relative to those for the free phosphines provided no additional information by which to unequivocally identify the nature of products within the crude mixture, in contrast to the ^{11}B NMR data.

Table 3: ^{31}P NMR data for boronium salts, their uncoordinated parent phosphines and the difference in shift caused by boronium salt formation.

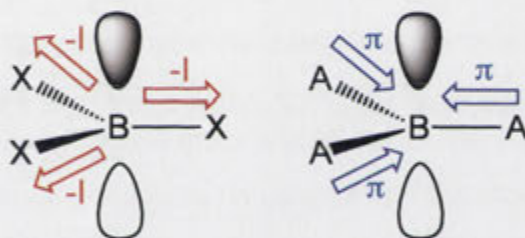
PR_3	Parent Phosphine	Boronium	Difference
PH_2Cy (CD_2Cl_2)	-111.2	-38.6	72.6
PMe_2Ph (C_6D_6)	-45.0	-3.5	41.5
PHPh_2 (CD_2Cl_2)	-39.4	-16.2	23.2
PHCy_2 (CD_2Cl_2)	-27.4	-0.4	27.0

[†] The use of deuterobenzene was initially preferred from an entirely economical point of view as chloroform was intentionally avoided in case unwanted side reactions occurred. However, some boronium salts were found to be insoluble in benzene, which necessitated that CD_2Cl_2 be used in these instances.

4.8. Electronic Stability of Boronium Salts

In contrast to the pronounced air and moisture sensitivity of their precursors, the acyclic boronium salts synthesised were found to possess remarkable stability in these respects. The salts could be handled in air without appreciable decomposition, were thermally stable, and resistant in the short term towards hydrolysis under ambient conditions, eventually degrading only over longer periods.

The chemistry of neutral boranes is governed by the electron deficient nature of boron. Whilst positively mesomeric heteroatom substituents can help stabilise the central boron atom *via* π -donation from filled p-orbitals (Figure 13), the addition of a dative (polar covalent) bond from a Lewis base causes boron to reach its octet, accounting for the stability of phosphine-borane adducts. In contrast, halogens are rather poor π -donors whilst also exerting a negative inductive effect (-I) due to their high electronegativity,^{*} thereby increasing the Lewis acidity of the boron (Figure 13).[§] The result of this increased Lewis acidity is that haloboranes and mixed haloboranes are far more reactive with respect to Lewis bases such as amines and phosphines.



(where X = halogen; A = N, O, P, etc)

Figure 13: Diagram showing a borane destabilising negative inductive effect from high electronegativity substituents (left) and borane stabilising π -donation from heteroatoms which possess filled p-orbitals (right).

The stability of boronium salts can be explained by going one step further than the case of stabilised mixed bromoboranes, in that the bromide ion is ejected from the boron centre to accommodate another dative bond from a second Lewis base. The loss of the bromine atom, which has a detrimental -I effect, in combination with the

^{*} A similar argument can be made for nitrogen and oxygen which also have high electronegativities.

[§] An exception to this is fluorine, which is a good π -donor with boron.

acquisition of a new dative bond, results in a very strong central boron atom that still has a full octet. It is unknown whether an S_N2 mechanism is responsible for boronium formation, or if boronium salts are formed through a borenium (a cationic boron centre bearing only one dative bond) intermediate. However, it can be stated that no evidence has been observed for the presence of borenium type species for any of the boronium salts synthesised thus far. Consideration may also be placed on the stability of not only the boronium cation, but also the bromide counterion that is simultaneously generated.

A look at the bond strengths for B-Br and B-P bonds, which are 435(21) and 347(17) kJmol^{-1} respectively, imply that it would take more energy to break the B-Br bond than would be gained by forming a B-P bond. However, the formation of $[\text{H}_2\text{B}(\text{NH}_3)_2][\text{BH}_4]$ by reaction of ammonia and diborane similarly illustrates the disproportionation of a hydride between the two boron atoms,¹² even though the B-H and B-N bond strengths are 330(4) and 389(21) kJmol^{-1} respectively.[†]

4.9. Anion Coordination of Boronium Salts

As mentioned (*vide supra*), the solid-state structures were obtained for several of the primary and secondary phosphine boronium salts. The molecular structures of some of the isolated boronium salts reveal short contacts between the cationic molecules and the anionic counterions that are less than the van der Waals (vdW) radii of the respective elements. The boronium salts of primary and secondary phosphines interact with the bromide *via* $\text{P-H}\cdots\text{Br}$ hydrogen bonding, *e.g.*, the $\text{P-H}\cdots\text{Br}$ distances in $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$ range from 2.84-3.16 Å, with all four of the P-H hydrogen atoms in each molecule oriented so as to interact with the bromide counterion, along with two additional P-H hydrogen atoms from neighbouring molecules (Figure 14).

[†] It should be noted that B-X bond strengths from studies of tertiary haloboranes, BX_3 , will contain a π -donation component (albeit minor) in their bonding and therefore care should be taken when comparing these values.

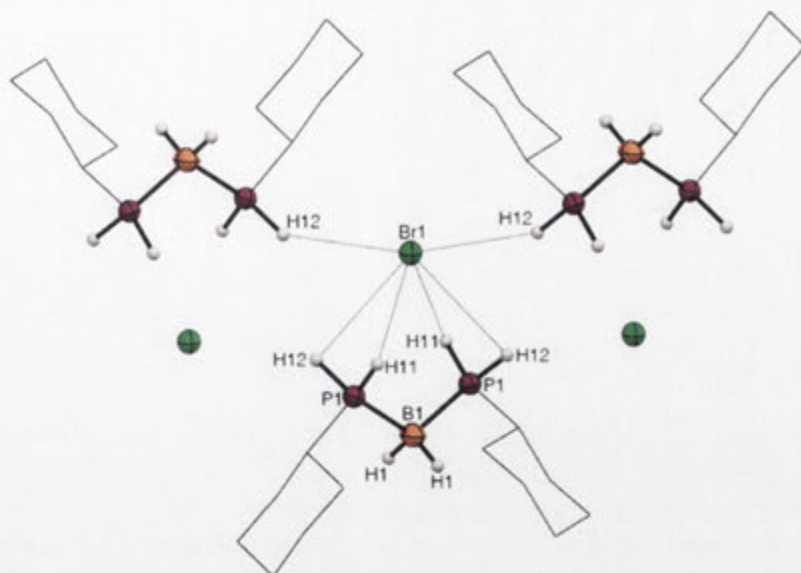


Figure 14: The molecular packing structure of three molecules of $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$ showing the coordination sphere around a single bromide counterion. (Alkyl hydrogen atoms, except those coordinating, omitted for clarity, cyclohexyl groups simplified, 50% displacement ellipsoids). Selected intermolecular hydrogen bonds ($\text{\AA}$): $\text{P1-H11} \cdots \text{Br1}$ 3.0081(2); $\text{P1-H12} \cdots \text{Br1}$ 3.1550(2); $\text{P1}^{\text{I}}\text{-H12}^{\text{I}} \cdots \text{Br1}$ 2.8418(1).

The solid-state structure of $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ (Figure 15) was similar to that for $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$, in that the structure had oriented itself so that the bromide interacted with both P-H hydrogen atoms ($\text{P-H} \cdots \text{Br}$ 2.9473(2), 3.8060(2) $\text{\AA}$), as well as a methine proton ($\text{C-H} \cdots \text{Br}$ 2.7741(2) $\text{\AA}$) and one methylene proton ($\text{C-H} \cdots \text{Br}$ 3.0103(3) $\text{\AA}$) from the same molecule (forming a four atom cradle as before). It was also oriented to interact with a methylene ($\text{C-H} \cdots \text{Br}$ 3.0409(2) $\text{\AA}$) and a methine ($\text{C-H} \cdots \text{Br}$ 3.0093(2) $\text{\AA}$) hydrogen atom from a second neighbouring molecule and a methine ($\text{C-H} \cdots \text{Br}$ 2.9236(2) $\text{\AA}$) hydrogen atom from a third neighbour. Whilst no single hydrogen bonding interaction is particularly short, the collective ensemble accounts for the well-ordered bromide position within the solid-state structure.

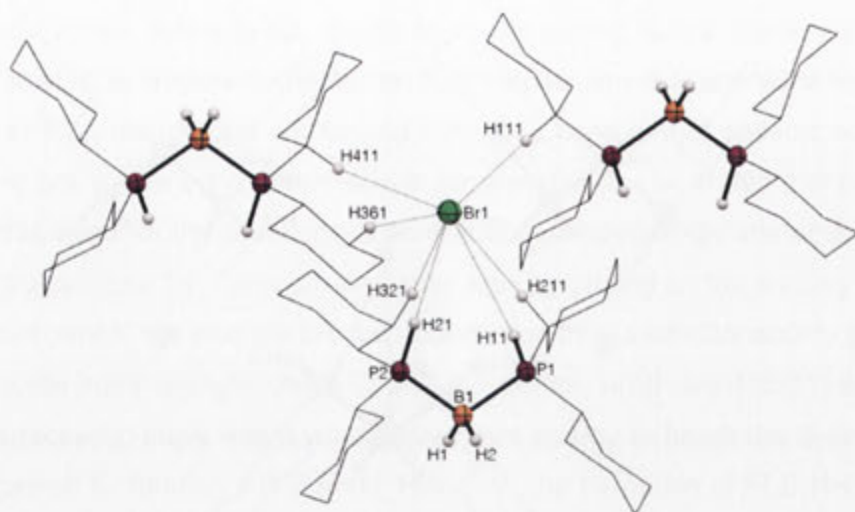


Figure 15: The molecular packing structure of three $[\text{H}_2\text{B}(\text{PHCy}_2)_2]^+$ cations showing the coordination sphere around a single bromide counterion. (Some hydrogen atoms, except those coordinating, omitted for clarity, cyclohexyl groups simplified, 50% displacement ellipsoids). Selected intermolecular hydrogen bonds (Å): P1-H11 $\cdots$ Br1 3.8060(2); P2-H21 $\cdots$ Br1 2.9473(2); C21-H211 $\cdots$ Br1 2.7741(2); C32-H321 $\cdots$ Br1 3.0103(3); C36ⁱ-H361ⁱ $\cdots$ Br1 3.0409(2); C41ⁱ-H411ⁱ $\cdots$ Br1 3.0093(2); C11ⁱⁱ-H111ⁱⁱ $\cdots$ Br1 2.9236(2).

The crystal packing structure around the bromide counterion was less complex for $[\text{H}_2\text{B}(\text{PPh}_2)_2]\text{Br}$ and the tertiary phosphine boronium salt $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$ in comparison to those discussed previously. For $[\text{H}_2\text{B}(\text{PPh}_2)_2]\text{Br}$, the two P-H protons align so as to provide effectively equidistant hydrogen bonds of 2.8681(2) and 2.9243(2) Å, but otherwise the anion was largely enveloped within a pocket faced by phenyl ring protons with distances of 3.10–3.77 Å (Figure 16). For $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$, the molecule was found to coordinate to the bromide *via* hydrogen bonding from the methyl and *ortho*-phenyl protons with distances of 2.9023(7) Å and 2.9531(5) Å, respectively. Whether these solid-state interactions persist whilst in solution will be discussed later (*vide infra*), though depending on the solvent, a degree of ion-pairing might be expected.

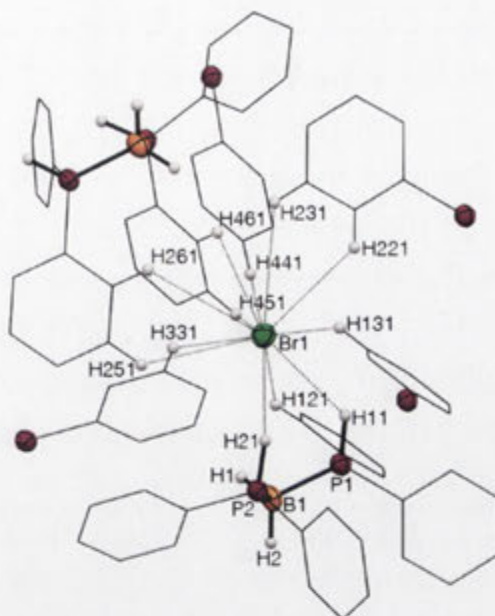


Figure 16: The molecular packing structure of three $[\text{H}_2\text{B}(\text{PHPh}_2)_2]^+$ cations of showing the coordination sphere around a single bromide counterion. (Alkyl hydrogen atoms, except those coordinating, omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected intermolecular hydrogen bonds (Å): P1-H11...Br1 2.8681(2); P2-H21...Br1 2.9243(2); C12-H121...Br1 3.5710(2); C25^I-H251^I...Br1 3.1491(2); C26^I-H261^I...Br1 3.2391(2); C45^I-H451^I...Br1 3.5108(2); C46^I-H461^I...Br1 3.5690(2); C22^{II}-H221^{II}...Br1 3.1243(2); C23^{II}-H231^{II}...Br1 3.2272(2); C33^{III}-H331^{III}...Br1 3.1076(2); C13^{IV}-H131^{IV}...Br1 3.1460(2); C44^V-H441^V...Br1 3.1041(2).

These intermolecular interactions presumably contribute in part to the stability found for the boronium salts in the solid state. The intermolecular P-H...Br interactions, however, do not appear to be limited to just the solid-state, but may also be inferred to persist in solution. Both ^1H and ^{31}P NMR data for the boronium salts change markedly when the bromide anion is exchanged for a weakly coordinating counterion. The operation of P-H...Br hydrogen bonding would be expected to result in a higher frequency shift of the ^1H NMR P-H resonance, concomitant with a corresponding shift in the frequency of the ^{31}P NMR resonance, when compared to the shifts observed for a weakly coordinating counterion.⁹

The bromide counterion of $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ was exchanged for the weakly coordinating counterion $[\text{SbF}_6]^-$ by metathesis with $\text{Ag}[\text{SbF}_6]$ to give the new salt $[\text{H}_2\text{B}(\text{PHCy}_2)_2][\text{SbF}_6]$. Notably, the ^1H and ^{31}P NMR signals for the unchanged $[\text{H}_2\text{B}(\text{PHCy}_2)_2]^+$ cation were significantly altered by the simple exchange of the anion

present. The ^1H NMR peak for $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ was observed at 6.04 ppm, whilst for $[\text{H}_2\text{B}(\text{PHCy}_2)_2][\text{SbF}_6]$ it was observed at 4.89 ppm.* The shift to lower frequency illustrated that the phosphorus protons were significantly more deshielded in $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$, suggesting an interaction with the bromide counterion. Similarly, the ^{31}P NMR peak of -1.2 ppm for $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ and -3.3 ppm for $[\text{H}_2\text{B}(\text{PHCy}_2)_2][\text{SbF}_6]$ also point toward a degree of ion-pairing with the bromide counterion in this solvent. The solid-state structure of $[\text{H}_2\text{B}(\text{PHCy}_2)_2][\text{SbF}_6]$ (Figure 17) was found to possess the same coordination of the anion by the two PH groups as observed for $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$, which indicated that the $[\text{H}_2\text{B}(\text{PHCy}_2)_2]^+$ cation was still able to coordinate to the larger $[\text{SbF}_6]^-$ anion, however any such interaction in solution, were it to persist, must be dynamic since there was no indication of enduring coupling between the ^{31}P - ^1H and ^{19}F nuclei.

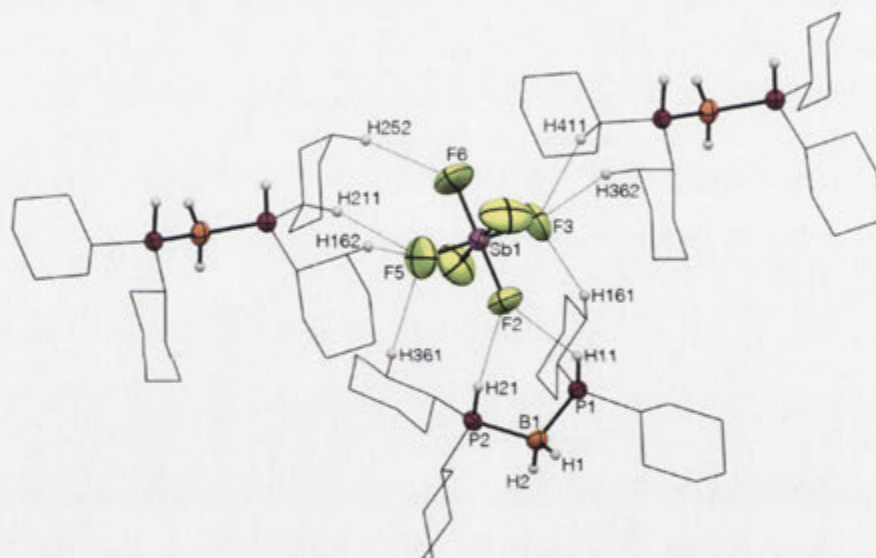


Figure 17: The molecular packing structure of three $[\text{H}_2\text{B}(\text{PHCy}_2)_2]^+$ cations showing the coordination sphere around a single $[\text{SbF}_6]^-$ counterion. (Alkyl hydrogen atoms, except those coordinating, omitted for clarity, cyclohexyl groups simplified, 50% displacement ellipsoids). Selected intermolecular hydrogen bonds (Å): P1-H11...F2 2.500(5); P2-H21...F2 2.687(5); C16-H161...F3 2.673(6); C36-H361...F5 2.790(7); C16-H162...F5 2.578(6); C21-H211...F5 2.642(6); C25-H252...F6 2.662(7); C36-H362...F3 2.513(5); C41-H411...F3 2.791(5).

* It should be noted that $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ and $[\text{H}_2\text{B}(\text{PHCy}_2)_2][\text{SbF}_6]$ were both recorded in CDCl_3 to eliminate differences caused by solvent effects.

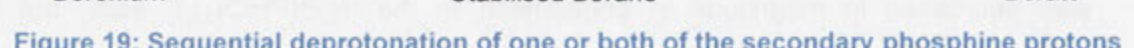
The $[\text{H}_2\text{B}(\text{PHCy}_2)_2][\text{SbF}_6]$ salt was found to be less stable than its bromide counterion analogue and decomposed in the solid-state over the comparatively short period of a week (*cf.* $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ showed no appreciable decomposition in solution[†] after several weeks). The ^{31}P and ^{11}B NMR spectra of the resulting mixture did not reveal any resonances that might suggest P-F or B-F bond formation, *i.e.*, fluoride abstraction does not appear to have ensued. It was not determined as to whether the differences in solid-state intermolecular hydrogen bonding of the Br^- or $[\text{SbF}_6]^-$ anions related to the observed differences in stability of the two species.

Similarly, $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2][\text{AsF}_6]$ was prepared by metathesis of $[\text{H}_2\text{B}(\text{Pme}_2\text{Ph})_2]\text{Br}$ with $\text{K}[\text{AsF}_6]$. The change of weakly coordinating counterion from $\text{Ag}[\text{SbF}_6]$ to $\text{K}[\text{AsF}_6]$ was due to the observed decomposition of some boronium salts when treated with $\text{Ag}[\text{SbF}_6]$. It was found that the reaction did not always proceed as expected with $\text{Ag}[\text{SbF}_6]$, and that sometimes what was believed to be a silver phosphine species (δ_{P} 42.2) was the major product recovered. This decomposition of the boronium cation was not observed when $\text{K}[\text{AsF}_6]$ was used instead, and it therefore became the preferred reagent for introducing a weakly coordinating counterion. Although silver salts are powerful halide sequestering agents, the attendant caveat is that they are also prone to single electron redox processes (to form silver metal) such that their use in the presence of $\text{B}(\delta^+)-\text{H}(\delta^-)$ bonds, *i.e.*, classical reductants, is likely to be problematic on occasion.

The tertiary phosphine boronium salts $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$ and $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2][\text{AsF}_6]$ were found to present the same trend of anion coordination as previously discussed for the $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ and $[\text{H}_2\text{B}(\text{PHCy}_2)_2][\text{SbF}_6]$ salts. However, the hydrogen bonding observed in the solid state for $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$ was understandably found to be less pronounced than for the secondary phosphine analogue, directly due to the lack of P-H bonds. The ^1H and ^{31}P NMR peaks for $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$ were δ_{H} 2.00 (methyl groups) and δ_{P} -3.5, whilst for $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2][\text{AsF}_6]$ they were found to be δ_{H} 1.68 and δ_{P} -3.6.[‡] Therefore, the difference of the NMR resonances caused by changing the counterion was decreased in magnitude in comparison to the $[\text{H}_2\text{B}(\text{PHCy}_2)_2]^+$ salts, but still

[†] Under an inert atmosphere.

[‡] It should be noted that $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$ and $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2][\text{AsF}_6]$ were both recorded in CDCl_3 to eliminate differences caused by solvent effects.



Experimentally, the proposed deprotonation was found to proceed, but not cleanly, with the desired product being only one of a myriad of products observed. Initially a single deprotonation was attempted to produce a stabilised borane using one equivalent of the strong base $n\text{BuLi}$. Despite the use of $n\text{BuLi}$, starting material was found to be present in the crude reaction mixture (δ_{B} -45.3; δ_{P} -1.3). However, the desired product was found to have formed with an ^{11}B NMR peak at δ_{B} -41.9 and two ^{31}P NMR peaks at δ_{P} -17.9 and 6.7, due to the now inequivalent nature of the two phosphorus atoms. The presence of free PHCy_2 in the ^{31}P NMR spectrum at -27.4 ppm also indicated that the starting material had decomposed to some extent (ca. 20%). The two species were found to be present in approximately equal amounts in the crude reaction mixture, in addition to half an equivalent of free PHCy_2 .

A similar attempt to form the symmetrical borate *via* double deprotonation of both the secondary phosphines in $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ resulted in a greater mixture of observed products. The ^{11}B NMR spectrum revealed that all the starting material had been consumed, but that the singly deprotonated product $\text{Cy}_2\text{HP}\cdot\text{BH}_2(\text{PCy}_2)$ remained (δ_{B} -42.2). The peak at δ_{B} -37.9 was thought to be the desired product $\text{Li}[\text{H}_2\text{B}(\text{PCy}_2)_2]$, which was similarly shifted to higher frequency as had been observed for $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ (δ_{B} -45.2) and $(\text{PCy}_2)_2\text{H}_2\text{B}\cdot\text{PHCy}_2$ (δ_{B} -42.2). The ^{31}P NMR spectrum comprised a myriad of resonances, with at least six of the peaks being broadened, presumably due to direct coordination to ^{11}B .

It was believed that the strong base $n\text{BuLi}$ was interacting with the BH_2 group of the boronium cation, possibly by acting as a nucleophile toward the boron. The disparity of Pauling electronegativities between boron (2.04) and hydrogen (2.20) means that the hydrogen is generally hydridic in nature, which would make the resulting electrophilic boron centre susceptible to nucleophilic attack. However, it has been recently reported that B-H groups bearing other electron-withdrawing substituents can be deprotonated with the boron group unusually acting as a nucleophile (Figure 20).¹⁵ The possibility of the boronium centre acting as both an electrophile and a Brønsted acid might explain the plethora of products observed by reaction of $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ with strong bases such as $n\text{BuLi}$. Furthermore, in addition to the expected site of kinetic deprotonation being the P-H bonds, the possibility of subsequent intramolecular hydrogen transfer between boron and phosphorus could not be excluded.

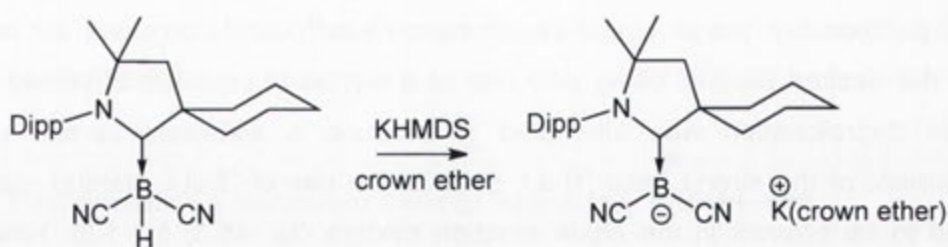


Figure 20: Deprotonation of a carbene stabilised borane as reported by Bertrand and co-workers [Dipp = diisopropylphenyl and KHMDS = potassium bis(trimethylsilyl)amide].¹⁵

4.11. Alternate Route to Functionalising Boronium Salts of Secondary Phosphines

In response to the indiscriminate deprotonation reactions discussed above, the reaction methodology was inverted to first form the phosphide anion, followed by addition of the monobromoborane (Figure 21). It was presumed that this approach would obviate complications arising from $n\text{BuLi}$ interacting with the borocation, having been consumed prior to introduction of the $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ reagent.



Figure 21: Deprotonation of a secondary phosphine to form a phosphide anion, followed by reaction with monobromoborane to form a borate salt (where R = Ph, Cy).

The lithiation of $\text{Cy}_3\text{P}\cdot\text{BH}_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OSO}_2\text{CF}_3$) with an excess of LDBB (LDBB = lithium 4,4'-di-*tert*-butylbiphenylide) followed by reaction with a range of electrophiles has been reported previously,¹⁶ which suggested that lithiation of the $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ precursor was a possible side reaction.

In practice, treating $\text{Li}[\text{PCy}_2]$ (generated *in situ*) with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ led to the formation of a mixture. Free PHCy_2 was again observed in the ^{31}P NMR spectrum ($\delta_{\text{P}} -27.5$) in addition to the boronium salt $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ ($\delta_{\text{B}} -45.4$; $\delta_{\text{P}} -0.5$) as the major product. Furthermore, the proton-coupled ^{31}P NMR spectrum indicated that the

remaining significant unidentified species at 55.6 ppm displayed direct P-H bonding with a $^1J_{\text{PH}}$ coupling value of 461.4 Hz, indicating that it was not the desired product.[§]

The reaction of $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ with two equivalents of a strong, non-nucleophilic base, lithium diisopropylamine (LDA), was also investigated. Similar to the reaction with two equivalents of $^n\text{BuLi}$, the reaction produced a range of products. The ^{11}B NMR spectrum appeared relatively clean with only two peaks, which were attributable to the starting material $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ (δ_{B} -45.1) and the singly deprotonated compound $\text{Cy}_2\text{HP}\cdot\text{BH}_2(\text{PCy}_2)$ (δ_{B} -41.8). The ^{31}P NMR spectrum was, however, more complex and revealed the presence of free PHCy_2 (δ_{P} -27.4), $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ (δ_{P} -1.5) and $\text{Cy}_2\text{HP}\cdot\text{BH}_2(\text{PCy}_2)$ (δ_{P} -17.8, 6.2). There were also two resonances at much higher frequency (δ_{P} 56.2, 77.6), with the former showing $^1J_{\text{PH}}$ of 440.9 Hz, though these could not be obtained in pure form, which compromised their identification. The greater number of ^{11}B broadened peaks in the ^{31}P NMR spectrum did suggest that there were additional ^{11}B NMR resonances that had not been observed, perhaps due to poor intensity of the signal or being obscured beneath other stronger resonances in the spectrum.

The final reagent used to attempt to deprotonate $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ was the milder non-nucleophilic base DBU,[†] however, the crude reaction mixture was found to contain four ^{11}B NMR peaks and four ^{31}P NMR peaks, including free PHCy_2 and the $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ starting material. Subsequent extraction of the products, away from the $[\text{DBUH}]\text{Br}$ side product, further complicated the ^{31}P NMR spectrum with eleven peaks being observed, eight of which displayed the distinctive broadening due to B-P coupling. Despite being a milder and non-nucleophilic base in comparison to $^n\text{BuLi}$ and LDA, the use of DBU proved to be disadvantageous to the goal of cleanly deprotonating $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$.

From the preceding discussion, it would appear that whilst the boronium salt $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ is stable with respect to dissociation, attempts to deprotonate it do lead to the neutral borane adduct $\text{Cy}_2\text{HP}\cdot\text{BH}_2(\text{PCy}_2)$, though not in a clean manner.

[§] The compound $(\text{Cy}_2\text{PBH}_2)_3$ was reported by Burg in 1959 (A. B. Burg and P. J. Slota, 1959, US 2877272 19590310),¹⁷ and subsequently its radiolytic ring-opening polymerisation was discussed,¹⁸ however, these studies pre-dated the now common use of ^{11}B NMR spectroscopy such that comparative data are not available. The possibility that oligomeric or polymeric $(\text{Cy}_2\text{PBH}_2)_3$ species are formed can not be excluded.

[†] 1,8-diazabicycloundec-7-ene.

Once formed it appears far more prone to dissociation than its precursor, suggesting that coordination of dicyclohexylphosphine to a cationic boron centre is more favourable than when the complex is neutral. It therefore seems likely that free H_2BPCy_2 forms, but is then prone to oligomerisation. Neither H_2BPCy_2 nor its dimer $(\text{H}_2\text{BPCy}_2)_2$ have been reported previously, whilst the trimer $(\text{H}_2\text{BPCy}_2)_3$ and its isomer $(\text{H}_3\text{BPHCy}_2)_3$ have been suggested in the early patent literature without recourse to spectroscopic data. Cyclic trimers based on less sterically congested phosphine substituents are, however, well known,^{9, 19} as are the oligomeric $\text{R}_2\text{HP}\cdot\text{BH}_2\text{PR}_2\cdot\text{BH}_3$ ($\text{R} = \text{'Bu, Ph}$) species,¹⁹ though the cyclohexyl analogue has not been reported and therefore a comparison can not be made.

An attempt was made to generate the desired borate species $[\text{DBUH}][\text{H}_2\text{B}(\text{PCy}_2)_2]$ *in situ* and immediately trap it with an organometallic precursor. For this purpose, the complex $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ was chosen due to its coordinative unsaturation, labile halide and track-record with respect to chelate-assisted B-H activation.^{20, 21} The combination of $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ with $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ in the absence of a base were found not to react, allowing combination of the two reagents prior to subsequent activation with base (DBU). If formed, it was anticipated that $[\text{DBUH}][\text{H}_2\text{B}(\text{PCy}_2)_2]$ would act as a diphosphine chelate.[§]

The ^{11}B NMR spectrum of the crude reaction indicated complete consumption of $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ whilst PPh_3 was observed in the ^{31}P NMR spectrum. However, the ^{31}P NMR spectrum also included up to fourteen additional resonances, many of which were within the characteristic $\text{Ru}(\text{II})\text{-PPh}_3$ (δ_{P} 30-50) region and none of which corresponded to free PHCy_2 (δ_{P} -27). This could indicate that the substitution of PPh_3 by PHCy_2 was a possible cause for the large number of similar resonances, due to the presence of closely interrelated species in the ^{31}P NMR spectrum. The reactions of $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ with PHCy_2 or DBU alone were performed in order to eliminate products that were not caused as a result of the boronium salt, *i.e.*, reactions which occurred independently of $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ being present. From these reactions two peaks (δ_{P} 39.9, 49.0) could be eliminated from the crude mixture as a result of an independent reaction between $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and PHCy_2 . Similarly, an additional four peaks (δ_{P} 27.9, 29.8, 38.0, 40.2) could be excluded as they originated

[§] The reactions of this complex with chelating diphosphines have been previously described, albeit employing less sterically demanding substituents, *e.g.*, dppm .²²

from an independent reaction between $\text{Ru(Ph)Cl(CO)(PPh}_3)_2$ and DBU, along with a further four peaks (δ_{P} -14.3, 10.4, 22.1, 50.4) that could be excluded as arising from a side reaction between $[\text{H}_2\text{B(PHCy}_2)_2]\text{Br}$ and DBU (*vide supra*). The large number of side products detected for this reaction was discouraging and led to alternate methodologies being considered.

The metal carbonylates $\text{K[MTp}^*(\text{CO})_3]$ ($\text{M} = \text{Mo, W}$) are not particularly basic but do display a rich chemistry in reactions with electrophiles, though none based on boron have been reported to date. These were therefore explored with a view to nucleophilic phosphine substitution with $[\text{H}_2\text{B(PHCy}_2)_2]\text{Br}$, though reactions were found not to proceed as cleanly as anticipated. It was hoped that simple counter-ion metathesis would first afford the salts $[\text{H}_2\text{B(PHCy}_2)_2][\text{MTp}^*(\text{CO})_3]$, followed by decarbonylative condensation. The product of the reaction between $[\text{H}_2\text{B(PHCy}_2)_2]\text{Br}$ and $\text{K[WTp}^*(\text{CO})_3]$ had poor solubility which hindered its characterisation, though the two peaks in the ^{11}B NMR spectrum at -45.2 and -10.2 ppm most likely correspond to the boronium and Tp^* borate nuclei, respectively. Furthermore, a single broad resonance was observed in the ^{31}P NMR spectrum (δ_{P} 1.5, *cf.* -0.4 for $[\text{H}_2\text{B(PHCy}_2)_2]\text{Br}$), all of which support the identity as the desired initial product $[\text{H}_2\text{B(PHCy}_2)_2][\text{WTp}^*(\text{CO})_3]$. Attempts to thermally induce further transformations were hindered by an inability to isolate the product.

The reaction of $[\text{H}_2\text{B(PHCy}_2)_2]\text{Br}$ and $\text{K[MoTp}^*(\text{CO})_3]$ was found to proceed in a similar manner as for $\text{K[WTp}^*(\text{CO})_3]$. The NMR analysis showed that the desired product predominated with two peaks in the ^{11}B NMR spectrum at -45.2 and -10.6 ppm and a broad peak at -0.6 ppm in the ^{31}P NMR spectrum. However, minor peaks were also observed at δ_{B} -31.8 and δ_{P} 12.7, 66.9, which would indicate at least one additional unidentified B-P type compound was present along with the desired product. The unassigned minor peaks in the ^{11}B and ^{31}P NMR spectra did not correspond to any peaks observed in any other reaction of the $[\text{H}_2\text{B(PHCy}_2)_2]\text{Br}$ precursor, and therefore can be assumed to be from reaction of $[\text{H}_2\text{B(PHCy}_2)_2]\text{Br}$ and not from decomposition. A single IR stretch observed at 1984 cm^{-1} suggested that not all of the Mo(CO)_6 had been converted to $\text{K[MoTp}^*(\text{CO})_3]$, which might explain the difference in products observed compared to the reaction of $[\text{H}_2\text{B(PHCy}_2)_2]\text{Br}$ with $\text{K[WTp}^*(\text{CO})_3]$. Protracted attempts to isolate the product by fractional crystallisation eventually only produced

decomposition products, $\text{Tp}^*(\text{O})_2\text{Mo}(\mu\text{-O})\text{Mo}(\text{O})_2\text{Tp}^*$ and $\text{Mo}(\text{O})\text{Cl}_2\text{Tp}^*$ [†] (Figure 22),^{23, 24} from adventitious oxidation. As with the tungsten analogue, attempts to thermally induce further reactivity were hindered by the inability to isolate the product.

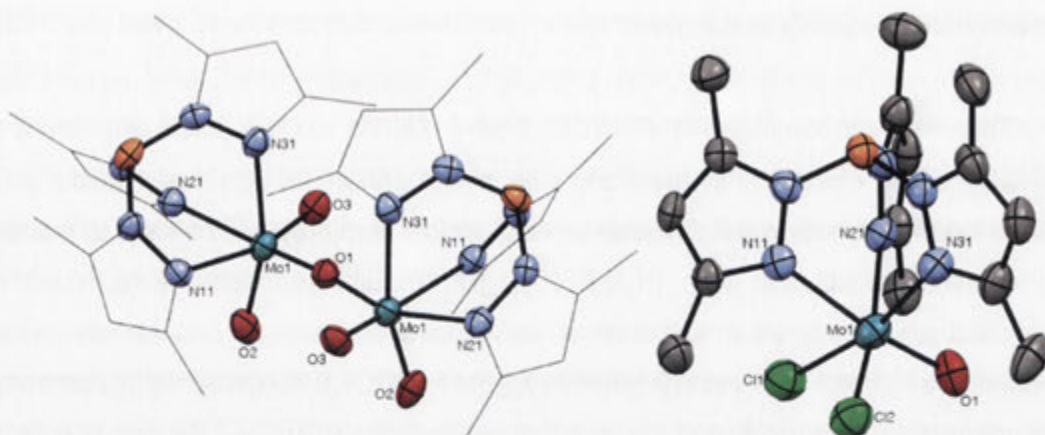


Figure 22: The molecular structures of $\text{Tp}^*(\text{O})_2\text{Mo}(\mu\text{-O})\text{Mo}(\text{O})_2\text{Tp}^*$ (left) and $\text{Mo}(\text{O})\text{Cl}_2\text{Tp}^*$ (right). (Solvate molecules and hydrogen atoms omitted for clarity, some aryl groups simplified, 50% displacement ellipsoids).

4.12. Unsymmetrical Boronium Salts Bearing Phosphine Ligands

The previous discussion has focused on the synthesis of symmetrically substituted boronium salts, however the intermediate formation of mono(phosphine)boranes followed by slower halide ionisation raises the possibility of sequentially introducing two different phosphines.

Several combinations of the various phosphines were attempted, and the results are summarised in Figure 23. Notably, in all cases, the symmetrically substituted boronium salts were preferentially formed. For highly nucleophilic phosphines, this might be accounted for by the rapidity of the second substitution being too rapid to allow sequential introduction. However, initial formation of the stable, albeit sterically congested tertiary phosphine adducts, $\text{R}_3\text{P}\cdot\text{BH}_2\text{Br}$ ($\text{R} = \text{Ph}, \text{Cy}$), followed by addition of a primary or secondary phosphine still led to the isolation of the symmetrical primary or secondary phosphine boronium salt and half an equivalent of tertiary phosphine adduct. It was unclear whether these reactions proceeded *via* ionisation to afford the

[†] Previously characterised as a chlorobenzene solvate.

desired mixed phosphine boronium salt from which the bulky tertiary phosphine rapidly dissociated, or if initial substitution of the bulky phosphine afforded the intermediate primary phosphine haloborane adduct, where it has already been demonstrated earlier that these rapidly react with further primary/secondary phosphine. Utilising this methodology, in no instance did a mixed phosphine boronium salt accumulate in sufficient quantity to be spectroscopically isolated.[§] Neither were appreciable amounts of primary or secondary phosphine haloborane adducts observed.

By cooling the reaction of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$, PH_2Cy and PHCy_2 down to -78°C , a small amount of the unsymmetrical boronium salt $[\text{H}_2\text{B}(\text{PHCy}_2)(\text{PH}_2\text{Cy})]\text{Br}$ was observed by NMR analysis. Specifically, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum included a broadened AB system (δ_{P} -41.6, 0.4, $^2J_{\text{AB}}$ 72.5 Hz; cf. δ_{P} -38.6 for $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$ and δ_{P} -1.2 for $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$) that was notably altered in chemical shift and discernibly different from the $^1J_{\text{BP}}$ coupling which typically fell within the range of 84-94 Hz for $[\text{H}_2\text{B}(\text{PR}_3)_2]\text{Br}$ ($\text{PR}_3 = \text{PH}_2\text{Cy}, \text{PHCy}_2, \text{PPh}_2, \text{PMe}_2\text{Ph}$), whilst a resonance was observed in the ^{11}B NMR spectrum (δ_{B} -45.1) which was effectively unchanged compared to either of the two symmetrical boronium salts (cf. δ_{B} -44.5 for $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$ and δ_{B} -45.2 for $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$).

However, the product was found to fully disproportionate to its two respective symmetrical boronium salts, $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$ and $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$, after a short period of time (~ 30 min at room temperature), confounding isolation for further study. A reaction between $\text{BH}_2\text{Br}\cdot\text{SMe}_2$, PH_2Cy and PHCy_2 at 0°C also produced the desired product, $[\text{H}_2\text{B}(\text{PHCy}_2)(\text{PPh}_2)]\text{Br}$ (δ_{P} -21.2, -3.2, $^2J_{\text{AB}}$ 261.5 Hz; cf. δ_{P} -16.2 for $[\text{H}_2\text{B}(\text{PPh}_2)_2]\text{Br}$ and δ_{P} -1.2 for $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$), but once again this was found to completely disproportionate during work-up to the two respective symmetrical boronium salts, $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ and $[\text{H}_2\text{B}(\text{PPh}_2)_2]\text{Br}$, eliminating it as a viable target for further studies.

[§] This would have been apparent as an AB system in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

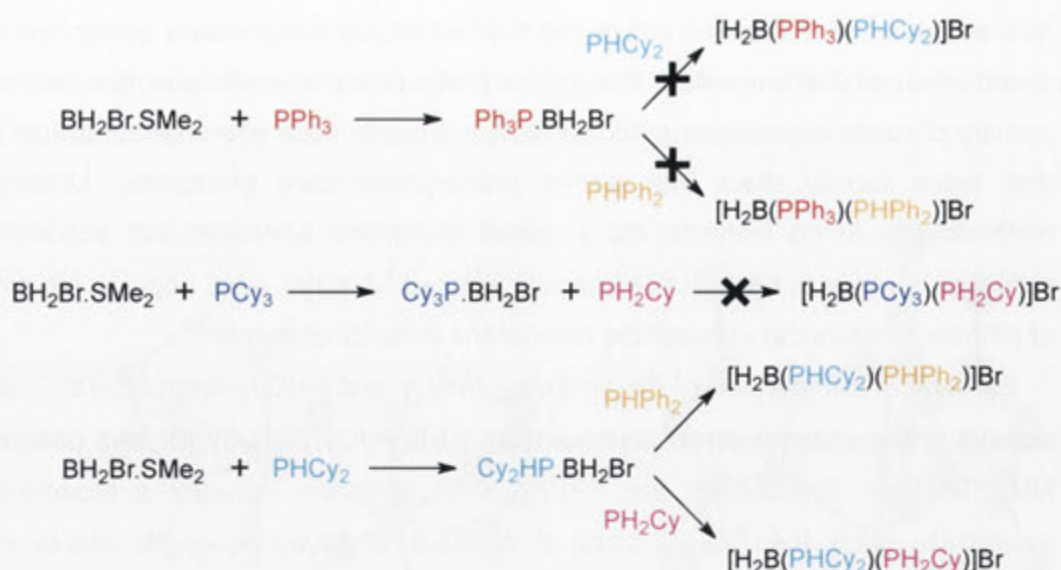


Figure 23: Reaction scheme showing the successful and unsuccessful combinations of phosphines attempted to form unsymmetrical boronium salts.

4.13. Boronium Salts of Chlorophosphines

A slight modification of the secondary phosphine boronium salts previously described was attempted, with the generation of $[\text{H}_2\text{B}(\text{PClPh}_2)_2]\text{Br}$ by reaction of $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ with two equivalents of PClPh_2 . It was hoped that a chlorinated analogue would be more susceptible to subsequent functionalisation than the secondary phosphine boronium salts. However, the reaction did not proceed past the phosphine stabilised monobromoborane, $\text{Ph}_2\text{ClP} \cdot \text{BH}_2\text{Br}$ (δ_{B} -22.4, δ_{P} 69.9; cf. 82.9 for PClPh_2). The ^{31}P NMR spectrum included a resonance at 73.3 ppm due to PBrPh_2 ,²⁵ arising from slow halogen exchange of chlorine for bromine, as previously observed in the reactions of HBr with chlorophosphines.²⁶ Notably, although numerous BH_3 and BX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) adducts of chlorophosphines are known, there appear to be no published examples of mixed haloborane ($\text{BH}_n\text{X}_{3-n}$) chlorophosphine adducts. Schmidbaur has, however, reported the reaction of $\text{Me}_3\text{P} \cdot \text{BH}_2\text{Cl}$ with PClMe_2 to provide $[\text{H}_2\text{B}(\text{PMe}_3)(\text{PMe}_2\text{Cl})]\text{Cl}$.²⁷

4.14. Cyclic Boronium Salts from Diphosphines

The modification of acyclic secondary phosphine boronium salts often resulted in the liberation of free secondary phosphine. Presuming chelation might offer some degree of kinetic stabilisation, a series of cyclic boronium salts were investigated, *cf.* $[\text{H}_2\text{B}(\text{dppe})]\text{Br}$ reported by Schmidbaur *et al.* previously.⁷

The new cyclic boronium salt $[\text{H}_2\text{B}(\text{dcpe})][\text{BHBr}_3]$ (Figure 24) readily formed upon reaction of equimolar amounts of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ and *dcpe* in a 71% yield.[†] The product was unusually isolated as the $[\text{BHBr}_3]^-$ salt rather than the simple bromide. The tribromoborate anion presumably arises from the reaction of the liberated bromide with a second equivalent of haloborane, which would need to be $\text{BHBr}_2\cdot\text{SMe}_2$, itself most likely generated from disproportionation of the $\text{BH}_2\text{Br}\cdot\text{SMe}_2$.[§] Whilst the $[\text{BHBr}_3]^-$ anion might appear simple, it has only been encountered on two previous instances from reactions of polyboronate salts $[\text{NR}_4][\text{B}_x\text{H}_y]$ ($\text{R} = \text{Me}, ^n\text{Bu}$; $x/y = 1/4, 3/8, 4/9, 9/14$) with BBr_3 and characterised on the basis of its ^{11}B NMR data ($\delta_{\text{B}} -13.1$, $^1J_{\text{BH}} = 175 \text{ Hz}$) alone.

The salt $[\text{H}_2\text{B}(\text{dcpe})][\text{BHBr}_3]$ therefore provides the first structural data for this anion, which adopts a near tetrahedral geometry with Br-B-Br angles in the conventional range (107.6 to 110.6°) that is surprisingly devoid of any significant distortions arising from the disparity in the size of the substituents. The BPCCP heterocycle is slightly non-planar, *i.e.* chiral (space group $P2_1/n$, Λ enantiomer shown, Δ enantiomer generated by crystallographic symmetry), with a slightly contracted P1-B1-P2 angle of $101.2(2)^\circ$ reflecting the constraints of chelation.

[†] Yield based on the number of moles of *dcpe* used, as the $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ was later found to be impure.

[§] Disproportionation is commonly observed to occur over time for these reagents.

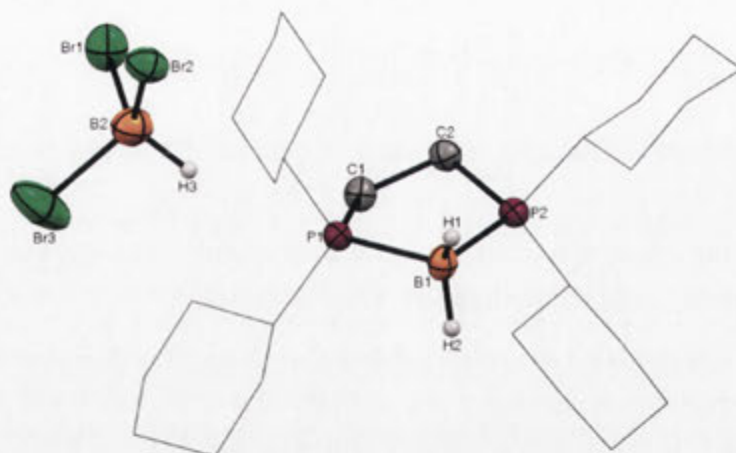


Figure 24: The molecular structure of $[\text{H}_2\text{B}(\text{dcpe})]\text{Br}$. (Alkyl hydrogen atoms omitted for clarity, cyclohexyl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): B1-P1 1.942(3); B1-P2 1.945(3); B2-Br1 2.030(5); B2-Br2 2.038(4); B2-Br3 2.008(5); P1-B1-P2 101.2(2); B1-P1-C1 104.1(1); B1-P2-C2 104.1(1); Br1-B2-Br2 109.7(2); Br1-B2-Br3 110.6(2); Br2-B2-Br3 107.6(2).

The methylated analogue, $[\text{H}_2\text{B}(\text{dmpe})]\text{Br}$, was also readily prepared by reaction of $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ with dmpe in 73% yield. However, unlike the dppe and dcpe analogues, the dmpe boronium salt was found to be insoluble in most common solvents. Partial solubility in d_6 -DMSO or D_2O allowed limited spectroscopic data to be acquired (^1H , ^{11}B , ^{31}P , but not ^{13}C NMR data) however neither proved suitable for growing crystallographic grade crystals. The identity of the salt was nevertheless confirmed conclusively by microanalysis, mass spectroscopy and NMR (^1H , ^{11}B and ^{31}P) spectroscopy. The satisfactory elemental microanalytical data confirmed the presence of a single equivalent of BH_2Br to the dmpe, whilst the single peak in the ESI-MS (m/z 163.1) matched precisely the isotope pattern of the desired product. The ^{11}B NMR resonance (δ_{B} -34.5) was similar to that observed for $[\text{H}_2\text{B}(\text{dppe})]\text{Br}$ (δ_{B} -35.7) previously prepared by Schmidbaur.⁷

The limitation of synthesising cyclic boronium salts was quickly met when reaction of diphosphines with longer backbone chains failed to provide ring-closed heterocycles. Reaction of $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ with dppb in equimolar quantities yielded a mixture of unreacted dppb and the disubstituted monobromoborane adduct $\text{dppb} \cdot (\text{BH}_2\text{Br})_2$. The same analogous side product $\text{dppm} \cdot (\text{BH}_2\text{Br})_2$ was recovered when equimolar quantities of $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ and dppm were reacted. The inability to produce cyclic boronium

species of a ring size other than 5 or 6 atoms (e.g., $[\text{H}_2\text{B}(\text{triphos})]\text{Br}$, *vide infra*), led to alternative methods being explored.

Whilst $\text{BH}_2\text{Cl}\cdot\text{SMe}_2$, in contrast to $\text{BH}_2\text{Br}\cdot\text{SMe}_2$, is ineffective with respect to boronium salt formation due to the failure to ionise the B-Cl bond, $\text{BH}_2\text{I}\cdot\text{SMe}_2$ has been reported to ring close longer and shorter diphosphine species (e.g., dppm, dppb) into the desired cyclic boronium salts,^{28, 29} although characterisation was based entirely on microanalytical (C, H, N; not B, I, P) and IR spectroscopy data. The reported protocol for preparing $[\text{H}_2\text{B}(\text{dppm})]\text{I}$ was repeated so as to further characterise the strained structure of a 4-membered boronium salt, but was found to yield the disubstituted phosphine stabilised monoiodoborane product $\text{dppm}\cdot(\text{BH}_2\text{I})_2$ (δ_{B} -35.0; δ_{P} 0.9), which was definitively confirmed by an X-ray crystallographic study.

Whilst cyclic boronium salts were found to possess comparable, if not better, stability to their acyclic counterparts, this also limited their reactivity toward metal centres. Simple addition of the cyclic boronium salts to a range of selected organometallic precursors, such as $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, failed to result in any reaction, or alternatively, rupture of the boronium salts themselves, consistent with the excessive stability conferred by chelation.

One of the initial modifications envisioned was to include a further reactive site in the diphosphine chelate used to form the cyclic boronium salt. The dppe analogue $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}$, in which one phenyl ring is substituted with a hydrogen, was treated with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ in anticipation of ring-closure (*cf.* dmpe, dcpe, dppe). However, whilst the reaction of dppe with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ readily proceeds at room temperature, the same conditions were found to yield an approximately equal mixture of $\text{Ph}_2\text{P}(\text{BH}_2\text{Br})(\text{CH}_2)_2\text{P}(\text{BH}_2\text{Br})\text{HPh}$ and the intended ring-closed boronium salt. Extraction/washing with toluene or chloroform proved ineffective in resolving the mixture due to the similar solubility of the two species.

The desired boronium salt was observed at δ_{B} -38.0, whilst the resonance at δ_{B} -26.6 was assigned to the disubstituted phosphine adduct. The appearance of only one ^{11}B resonance for the adduct species was thought to reflect overlap of the broad, unresolved signals, or possibly (but less likely), the rapid exchange of the BH_2Br groups. The reaction was repeated with more forcing conditions by heating to reflux in toluene, but the crude reaction product was found to contain none of the desired product at -38.0 ppm in the ^{11}B NMR spectrum, but instead was found to contain a

major ^{11}B NMR peak at -10.7 ppm (amongst other minor peaks), which could not be assigned and was not observed previously when the reaction was performed at room temperature.

4.15. Dihaloboronium Salts

Schmidbaur *et al.* has reported the use of $\text{BHBr}_2\cdot\text{SMe}_2$ to synthesise boronium salts bearing a BHB group by reaction with two equivalents of PMe_3 or PEt_3 , *via* the same process of bromide ionisation.⁷ A BHB group was seen as a more versatile functionality than a BH_2 substituent, offering the possibility of nucleophilic substitution.

The reaction of $\text{BHBr}_2\cdot\text{SMe}_2$ and dppe had already been reported to yield the disubstituted phosphine stabilised adduct $\text{dppe}\cdot(\text{BHBr}_2)_2$, rather than the ring-closed BHB boronium salt.⁷ In the present work, however, the reaction of equimolar amounts of $\text{BHBr}_2\cdot\text{SMe}_2$ with dmpe (benzene, ambient temperature) was found to yield a mixture of boron-containing species with B-P bonding based on ^{11}B and ^{31}P NMR spectroscopy, though as was found for $[\text{H}_2\text{B}(\text{dmpe})]\text{Br}$ (*vide supra*), the characterisation was hindered by similarly poor solubility in common (NMR) solvents.

Despite the reported failure of dppe with $\text{BHBr}_2\cdot\text{SMe}_2$ to form $[\text{BrHB}(\text{dppe})]\text{Br}$, the analogous reaction of the far more basic dcpe with $\text{BHBr}_2\cdot\text{SMe}_2$ was explored and found to provide the desired BHB boronium salt $[\text{BrHB}(\text{dcpe})]\text{Br}$ (Figure 25). The salt eluded isolation in bulk purity due to the difficulties in separating it from the acyclic adduct $\text{dcpe}\cdot(\text{BHBr}_2)_2$ (Figure 26) by any other method than manual crystal picking.

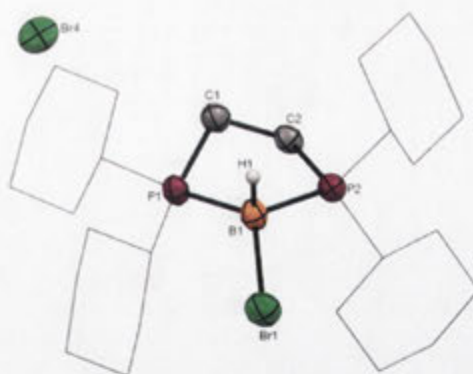


Figure 25: The molecular structure of $[\text{BrHB}(\text{dcpe})]\text{Br}$. (Solvate molecules and alkyl hydrogen atoms omitted for clarity, cyclohexyl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): B1-Br1 2.013(4); B1-P1 1.955(4); B1-P2 1.960(4); Br1-B1-P1 121.8(2); Br1-B1-P2 114.8(2); P1-B1-P2 101.0(2).

The presence of $\text{dcpe} \cdot (\text{BHBBr}_2)_2$ recalls the analogous dppe reaction, though the recovery of $[\text{BrHB}(\text{dcpe})]\text{Br}$ illustrated that the difference in electronic properties between the two diphosphines, dppe and dcpe , appears to be the determining factor with respect to ring-closure. The steric differences between dppe and dcpe are pronounced and Thorpe-Ingold (phosphorus gem-dialkyl type) effects notwithstanding, the steric clutter associated with the PCy_2 termini would be expected to discourage ring-closure, recalling the failure of PCy_3 to provide $[\text{H}_2\text{B}(\text{PCy}_3)_2]\text{Br}$ (Section 4.4).

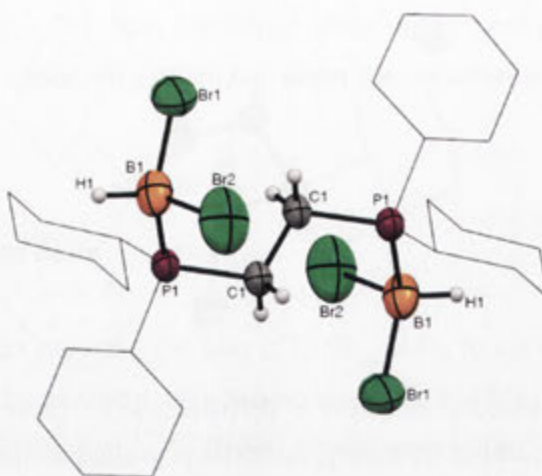


Figure 26: The molecular structure of $\text{dcpe} \cdot (\text{BHBr}_2)_2$. (Alkyl hydrogen atoms omitted for clarity, cyclohexyl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): B1-Br1 1.99(1); B1-Br2 2.01(1); B1-P1 1.96(1); P1-C1 1.817(7); C1-C1' 1.54(1); Br1-B1-Br2 111.6(5); Br1-B1-P1 110.2(5); Br2-B1-P1 105.7(5); B1-P1-C1 111.5(4); P1-C1-C1' 114.4(6).

When the reaction was carried out at room temperature in benzene, the two products were found to form in near equal amounts, as determined by ^{31}P NMR integration. The salt $[\text{BrHB}(\text{dcpe})]\text{Br}$ was observed at δ_{B} -26.8 and δ_{P} 20.9, whilst the adduct $\text{dcpe} \cdot (\text{BHBr}_2)_2$ was apparent at δ_{B} -17.6 and δ_{P} 0.1, along with some unreacted dcpe that was removed upon work-up. The two products, though not separately isolated in bulk quantities, were formulated based on solid-state crystal structure determinations and the trends observed for previously synthesised analogous compounds. Despite bromine being a potential hydrogen bond acceptor, examination of the solid-state structure of $[\text{BrHB}(\text{dcpe})]\text{Br}$ revealed no obvious intermolecular interactions of note between the boron-coordinated bromine and anything else, as might have been expected due to the steric hindrance caused by the surrounding cyclohexyl substituents.

Interestingly, manually picked crystals of $\text{dcpe} \cdot (\text{BHBr}_2)_2$, the identity of which was confirmed crystallographically, were found upon dissolution to have equimolar amounts of $[\text{BrHB}(\text{dcpe})]\text{Br}$ also present in the ^{11}B and ^{31}P NMR spectra. This observation did not change over time, suggesting that the two species existed in equilibrium with one another in DCM, and was supported by the consistency with which the two products were always observed together spectroscopically.

The successful synthesis of $[\text{BrHB}(\text{dcpe})]\text{Br}$ confirmed that strongly σ -basic phosphines would favour the formation of *B*-bromo boronium salts and accordingly, basic monodentate phosphines were next considered. In contrast to *dcpe*, however, the reaction of $\text{BHBr}_2 \cdot \text{SMe}_2$ with two equivalents of PHCy_2 was found to provide the phosphine-stabilised adduct $\text{Cy}_2\text{HP} \cdot \text{BHBr}_2$ (δ_{B} -18.7; δ_{P} 0.6), but not the boronium salt $[\text{BrHB}(\text{PHCy}_2)_2]\text{Br}$. A very minor second product was observed in the ^{11}B NMR spectrum at -45.2 ppm, attributable to $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$, arising from disproportionation of the $\text{BHBr}_2 \cdot \text{SMe}_2$ starting material. Attempted isolation of $\text{Cy}_2\text{HP} \cdot \text{BHBr}_2$ resulted in its decomposition to the phosphonium salt $[\text{PH}_2\text{Cy}_2]\text{Br}$ (Figure 27), the cation of which had been previously observed for the $\text{Cy}_2\text{HP} \cdot \text{BHCl}_2$ adduct as it similarly decomposed to $[\text{PH}_2\text{Cy}_2][\text{HCl}_2]$ (Figure 27). The bichloride anion, $[\text{HCl}_2]^-$, was an unusual counter-ion and one that has relatively few prior solid-state examples.³⁰⁻³² The metrical parameters of $[\text{HCl}_2]^-$ are indistinguishable from those previously reported for other salts containing this anion and therefore no further comment will be made. The recovery of phosphonium salts from reactions of Lewis bases with $\text{BH}_2\text{Br} \cdot \text{SMe}_2$, $\text{BHBr}_2 \cdot \text{SMe}_2$ or BBr_3 was a recurrent feature observed in this chemistry.

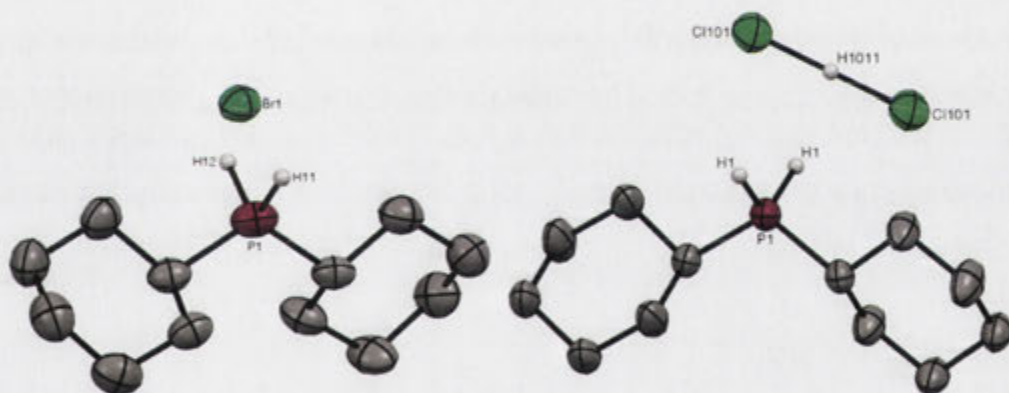


Figure 27: The molecular structures of $[\text{PH}_2\text{Cy}_2]\text{Br}$ (left) and $[\text{PH}_2\text{Cy}_2][\text{HCl}_2]$ (right). (Alkyl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected intermolecular hydrogen bonds (Å) for $[\text{PH}_2\text{Cy}_2]\text{Br}$: P1-H11 $\cdots$ Br1 2.6064(4). Selected bond lengths (Å), angles ($^\circ$) and intermolecular hydrogen bonds (Å) for $[\text{PH}_2\text{Cy}_2][\text{HCl}_2]$: Cl101-H1011 1.5553(2); Cl101-H1011-Cl101 i 180.00; P1-H1 $\cdots$ Cl101 2.7122(2); P1-H1 $\cdots$ Cl101 i 2.9276(1); P1-H1 $\cdots$ H1011 2.3546(1).

As previously discussed, the reaction of two equivalents of PPh_3 with $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ does not progress beyond the initial adduct $\text{Ph}_3\text{P} \cdot \text{BH}_2\text{Br}$, leaving the second equivalent

of PPh_3 unreacted. However, addition of $\text{K}[\text{AsF}_6]$ to facilitate the ionisation of the bromide from the boron (*vide infra*), also found one of the recovered products of the reaction to be $[\text{PPh}_3][\text{AsF}_6]$ (Figure 28).

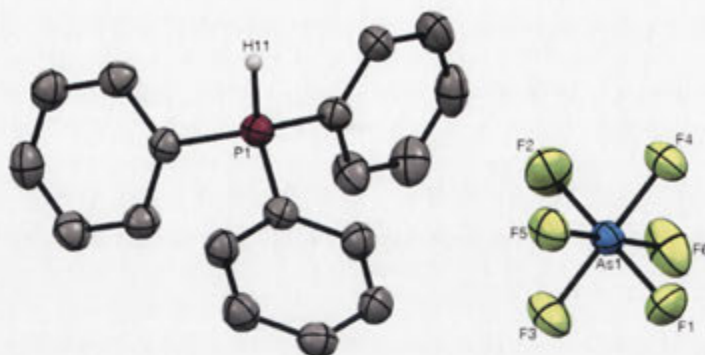


Figure 28: The molecular structure of $[\text{PPh}_3][\text{AsF}_6]$. (Aryl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected intermolecular hydrogen bonds ($\text{\AA}$): $\text{P1-H11} \cdots \text{F4}^{\text{i}}$ 2.45(4); $\text{P1-H11} \cdots \text{F6}^{\text{ii}}$ 2.51(4).

Similarly, the attempt to form a novel boronium salt of 1,10-phenanthroline by reaction with $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ caused not only the analogous iminium salt by double protonation, but proceeded to further reduce another two double bonds to give the product pictured in Figure 29. The method by which this protonation/reduction occurs is open to conjecture, however, it should be noted that the hydrogenation of 1,10-phenanthroline to 1,2,3,4-tetrahydro-1,10-phenanthroline has previously been shown to be catalysed by Raney nickel,³³ or alternatively by employing well-defined homogenous catalysts.³⁴

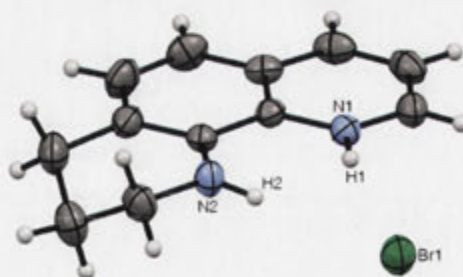


Figure 29: The molecular structure of $[\text{C}_{12}\text{H}_{13}\text{N}_2]\text{Br}$. (Solvate molecules omitted for clarity, 50% displacement ellipsoids). Selected intermolecular hydrogen bonds ($\text{\AA}$): $\text{N1-H1} \cdots \text{Br1}$ 2.3633(3); $\text{N2-H2} \cdots \text{Br1}$ 2.6474(3).

4.16. Dicationic Boronium Salts

An attempt was also made to synthesise a primary phosphine ligated boronium dication of the form of $[\text{HB}(\text{PH}_2\text{Cy})_3]\text{Br}_2$. The analogous PMe_3 boron dication has been previously described,⁷ as well as the $[\text{Tp}^*\text{BR}]^+$ type cages discussed in the previous chapter. The reaction of four equivalents[†] of PH_2Cy with $\text{BHBBr}_2\cdot\text{SMe}_2$ (benzene, ambient temperature) was found to yield a mixture of products which consisted of the phosphine stabilised adduct, $\text{CyH}_2\text{P}\cdot\text{BHBBr}_2$ (δ_{B} -20.5, δ_{P} -35.4), the BHBBr boronium salt $[\text{BrHB}(\text{PH}_2\text{Cy})_2]\text{Br}$ (δ_{B} -29.9;[§] an expected intermediate *en route* to the desired dication), and a small amount of $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$, generated by reaction of PH_2Cy with adventitious $\text{BH}_2\text{Br}\cdot\text{SMe}_2$, arising from $\text{BHBBr}_2\cdot\text{SMe}_2$ disproportionation. Separation of the poorly soluble product mixture into its constituents proved difficult due to extensive decomposition ensuing in any solvents in which it was soluble, precluding isolation.

4.17. Halogenated Boronium Salts from Tertiary Phosphines

Secondary phosphines produced phosphonium salts upon reaction with $\text{BHBBr}_2\cdot\text{SMe}_2$, whilst tertiary phosphines provided simple dibromoborane adducts. This dichotomy might reflect steric or electronic control and accordingly, smaller but strongly σ -basic tertiary phosphines were next investigated given that $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$ has been isolated from the reaction of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ with PMe_2Ph . The reaction of two equivalents of PMe_2Ph with $\text{BHBBr}_2\cdot\text{SMe}_2$ in pentane was found to proceed to the desired boronium salt $[\text{BrHB}(\text{PMe}_2\text{Ph})_2]\text{Br}$ (δ_{B} -21.5, δ_{P} -7.5). The crude product was found to form an oil of reasonable purity, though attempts at further purification led to extensive decomposition. Electrospray MS (+ve ion) analysis further corroborated the identity of the product with an isotopic envelope at $m/z = 367.1$ and 369.1 , confirming bromine inclusion in the cation. Conducting the reaction in DCM was found to only partially proceed to $[\text{BrHB}(\text{PMe}_2\text{Ph})_2]\text{Br}$, with the majority of the crude reaction mixture comprising the adduct $\text{PhMe}_2\text{P}\cdot\text{BHBBr}_2$ (δ_{B} -15.6, δ_{P} -12.1). It would therefore seem that the formation of the boronium salt in pentane is driven by its precipitation, but whilst in

[†] A deliberate excess.

[§] The ^{31}P NMR peak for this compound could not be resolved due to the broadness of being bonded to ^{11}B , but also due to impurities being present.

solution it reverts to the neutral adduct. Conducting the reaction in benzene (another solvent from which salt precipitation might be expected to occur) failed to generate appreciable amounts of the boronium salt, whilst heating (75°C, 3 hours) resulted in formation of the phosphonium salt $[\text{P}(\text{Me}_2)\text{Ph}]\text{Br}$ which precipitated from the benzene solution upon formation (Figure 30).

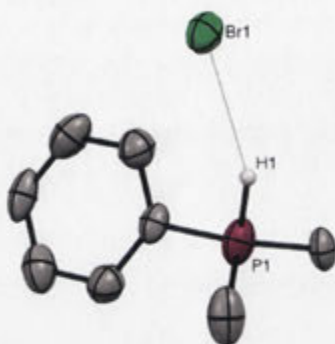


Figure 30: The molecular structure of $[\text{P}(\text{Me}_2)\text{Ph}]\text{Br}$. (Alkyl and aryl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected intermolecular hydrogen bonds (Å): P1-H1 $\cdots$ Br1 2.8300(3).

The most interesting observation was that an equimolar mixture of $\text{B}(\text{HBr}_2) \cdot \text{SMe}_2$ and $\text{P}(\text{Me}_2)\text{Ph}$ in benzene was found to cleanly yield $\text{PhMe}_2\text{P} \cdot \text{B}(\text{HBr}_2)$. While seemingly mundane, in comparison to all of the BH_2Br phosphine adducts, which preferentially form the corresponding BH_2 boronium salts independent of reactant stoichiometry, this was an intriguing observation. The $\text{PhMe}_2\text{P} \cdot \text{B}(\text{HBr}_2)$ adduct was observed (δ_{B} -15.6, δ_{P} -12.1) to persist in solution under an inert atmosphere without any indication of conversion to $[\text{BrHB}(\text{P}(\text{Me}_2)\text{Ph})]\text{Br}$ over a period of 17 hours, and was only observed to decompose when heated.

Thus, the initial non-optimised protocol proved to be the most effective way in which to synthesise essentially pure $[\text{BrHB}(\text{P}(\text{Me}_2)\text{Ph})]\text{Br}$. However, the product being an oil coupled with the observed decomposition when purification was attempted somewhat hindered characterisation and its deployment in further reactivity studies.

4.18. Dihalogenated Boronium Salts

The use of BBr_3 in place of the mixed-bromoboranes $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ and $\text{BHBr}_2\cdot\text{SMe}_2$ might be anticipated to yield $[\text{Br}_2\text{B}(\text{PR}_3)_2]\text{Br}$ boronium salts, however the reaction of BBr_3 with dppe was found to exclusively form the diphosphine bis(tribromoborane) adduct $\text{dppe}\cdot(\text{BBr}_3)_2$, cf. the reaction of $\text{BHBr}_2\cdot\text{SMe}_2$ to yield $\text{dppe}\cdot(\text{BHBr}_2)_2$. The $\text{dppe}\cdot(\text{BBr}_3)_2$ product was observed at δ_{B} -16.7 and δ_{P} -6.7, but was structurally authenticated by single crystal X-ray diffraction (Figure 31).

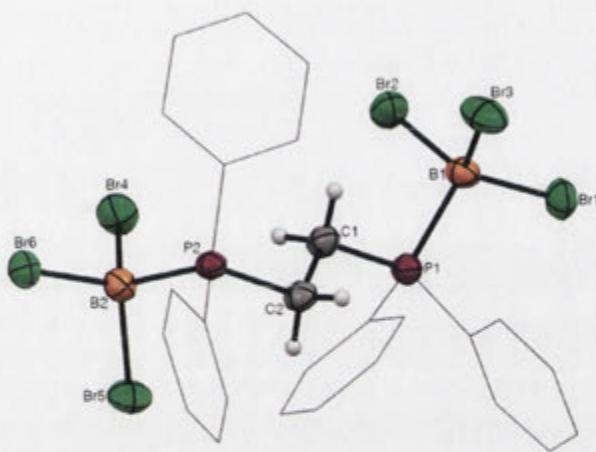


Figure 31: The molecular structure of $\text{dppe}\cdot(\text{BBr}_3)_2$. (Aryl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): B1-Br1 1.983(5); B1-Br2 2.026(5); B1-Br3 2.005(5); B1-P1 1.972(4); B2-Br4 2.012(5); B2-Br5 2.006(5); B2-Br6 2.004(5); B2-P2 1.973(5); Br1-B1-Br2 112.4(2); Br1-B1-Br3 110.9(2); Br1-B1-P1 109.3(2); Br2-B1-Br3 110.2(2); Br2-B1-P1 105.6(2); Br3-B1-P1 108.2(2); Br4-B2-Br5 111.2(2); Br4-B2-Br6 110.5(2); Br4-B2-P2 111.7(2); Br5-B2-Br6 110.2(2); Br5-B2-P2 105.0(2); Br6-B2-P2 108.0(2); B1-P1-C1 107.2(2); B2-P2-C2 110.8(2).

The reaction between BBr_3 and two equivalents of PHCy_2 was also performed with the intention of synthesising $[\text{Br}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$. However, as with $\text{BHBr}_2\cdot\text{SMe}_2$, the only product recovered was the phosphonium salt $[\text{PH}_2\text{Cy}_2]\text{Br}$, as confirmed crystallographically. Minor resonances were observed in the NMR analysis at δ_{B} -18.9

and $\delta_P \sim 54$,²⁶ which were attributed to the phosphine tribromoborane adduct $Cy_2HP \cdot BBr_3$, however this formed in insufficient quantity to cleanly isolate.

Employing the smaller, more basic diphosphine dmpe, the reaction products were found to be insoluble in common deuterated solvents such as $CDCl_3$, which was also observed for the reaction between dmpe and $BHBr \cdot SMe_2$ (*vide supra*). By employing DMSO as the solvent, NMR analysis revealed that none of the desired product was synthesised. Rather, the major product present was identified as $dmpe \cdot (BBr_3)_2$ ($\delta_B -15.1$, $\delta_P -46.6$), in an analogous manner to the formation of $dppe \cdot (BBr_3)_2$.

Thus it would appear that with the phosphines and diphosphines investigated, the formation of $[Br_2B(PR_3)_2]Br$ salts is not a favoured process, though in some cases the initial neutral adduct could be observed.

4.19. Metathesis as a Driving Force for Boronium Salt Formation

The previously discussed stability of boronium salts, along with the success with which the bromide counterions could be exchanged for weakly coordinating anions such as $[AsF_6]^-$, suggested that a salt such as $K[AsF_6]$ might facilitate ionisation of phosphine haloborane adducts allowing coordination of a second equivalent of a phosphine. As discussed previously, PPh_3 was found to be unable to spontaneously form the boronium salt, $[H_2B(PPh_3)_2]Br$, regardless of stoichiometry. Addition of two equivalents of $K[AsF_6]$, to a mixture of uncoordinated PPh_3 and $Ph_3P \cdot BH_2Br$ resulted in the development of a weak, but definitive, ^{11}B NMR resonance observed at -39.3 ppm. The corresponding ^{31}P NMR resonance could not be identified due presumably to the low concentration of the compound and the broadening of the peak from coupling to ^{11}B . The ^{11}B resonance was believed to be the desired salt $[H_2B(PPh_3)_2][AsF_6]$ due to its low frequency shift from the $Ph_3P \cdot BH_2Br$ adduct at $\delta_B -23.2$, combined with its similarity to resonances observed for other boronium salts, *e.g.*, $\delta_B -37.6$ for $[H_2B(PHPh_2)_2]Br$.

Addition of a further six equivalents of $K[AsF_6]$ increased the concentration of the $[H_2B(PPh_3)_2][AsF_6]$ sufficiently so as to be able to discern the broad ^{31}P NMR resonance at -21.5 ppm. Using ten equivalents of $K[AsF_6]$ and heating to approximately

²⁶ The ^{31}P NMR resonance was too broad due to the unresolved B-P coupling for a value to be determined with accuracy.

55°C for 14 hours resulted in the $[\text{H}_2\text{B}(\text{PPh}_3)_2][\text{AsF}_6]$ resonance at δ_{B} -38.8^o being more intense than the peak for $\text{Ph}_3\text{P}\cdot\text{BH}_2\text{Br}$ (δ_{B} -23.2). A new peak of similar intensity emerged at δ_{B} 17.8 and the ^{31}P NMR had two additional broad peaks of similar intensity as those for $\text{Ph}_3\text{P}\cdot\text{BH}_2\text{Br}$ and $[\text{H}_2\text{B}(\text{PPh}_3)_2][\text{AsF}_6]$, though the PPh_3 resonance predominated. Subsequent workup of this crude mixture led to the observation of the phosphonium salt $[\text{PPh}_3][\text{AsF}_6]$ as discussed previously (Figure 28). Thus the desired boronium salt $[\text{H}_2\text{B}(\text{PPh}_3)_2][\text{AsF}_6]$ would appear to be unstable under the forcing conditions required for its predominant formation, although salt elimination (KBr) could be shown to assist its formation, albeit not in usefully separable amounts.

4.20. Acyclic Boronium Salts with Pendant Arsino Groups

In the previous chapter it was shown that $\text{arphos}\cdot\text{BH}_2\text{Br}$ was found to partially disproportionate in solution over a relatively short period of time to the boronium salt $[\text{H}_2\text{B}(\text{arphos})_2]\text{Br}$ (Figure 32). Crystals of this boronium salt could be grown from an undisturbed benzene solution of $\text{arphos}\cdot\text{BH}_2\text{Br}$, a solvent from which the salt preferentially precipitates. Notably, $\text{dppe}\cdot\text{BH}_2\text{Br}$ does not undergo a similar reaction but rather undergoes ring-closure, presumably reflecting the stronger $\text{P}\rightarrow\text{B}$ bonding (*cf.* $\text{As}\rightarrow\text{B}$).

^o The broad nature of the peaks in ^{11}B NMR can cause slight fluctuations in the values recovered between spectra, such as here with a variation of 0.5 ppm between δ_{B} -39.3 and δ_{B} -38.8.

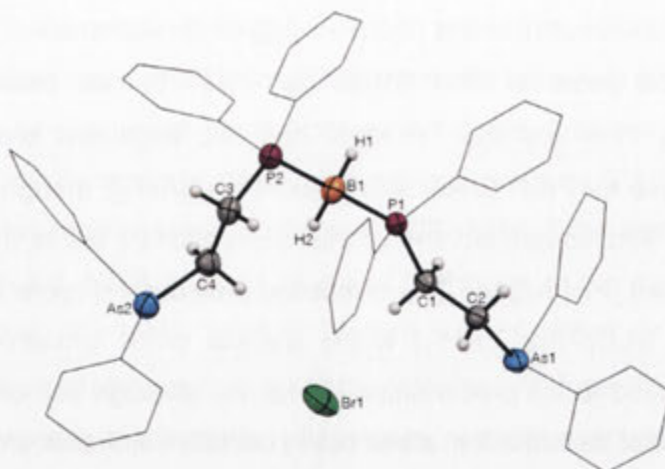


Figure 32: The molecular structure of $[\text{H}_2\text{B}(\text{arphos})_2]\text{Br}$. (Solvate molecules and aryl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): B1-P1 1.929(4); B1-P2 1.927(4); As1-C2 1.985(3); As2-C4 1.980(3); P1-B1-P2 115.0(2); B1-P1-C1 105.0(2); B1-P2-C3 114.4(2).

The ^{11}B and ^{31}P NMR data comprise of resonances at δ_{B} -37.1 and δ_{P} 11.0 (cf. $\text{arphos}\cdot\text{BH}_2\text{Br}$ δ_{B} -24.9; δ_{P} 4.7), with the chemical shifts of both resonances being consistent with those observed for other boronium salts.

The salt $[\text{H}_2\text{B}(\text{arphos})_2]\text{Br}$ presents both a flexible boronium backbone and two free arsine groups suggesting it might serve as a potential chelate in reactions with organometallic precursors. Unfortunately, the spontaneous conversion of $\text{arphos}\cdot\text{BH}_2\text{Br}$ to $[\text{H}_2\text{B}(\text{arphos})_2]\text{Br}$ in the presence of additional arphos does not proceed to completion, even after 2 months at room temperature or upon heating (80°C, 15 hours), during which time additional unidentified resonances (δ_{B} -41.0; δ_{P} -0.3 (br), 55.3 (sharp)) developed.

The addition of $\text{K}[\text{AsF}_6]$ to a 2:1 mixture of arphos and $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ provided the desired salt $[\text{H}_2\text{B}(\text{arphos})_2][\text{AsF}_6]$, the crystal structure of which (Figure 33) revealed structural features comparable to those of $[\text{H}_2\text{B}(\text{arphos})_2]\text{Br}$ and was devoid of any significant inter-ionic interactions. Both C-C bonds adopt *anti* conformations, whilst the two B-P bonds have *anti* and *gauche* conformations. Optimum conversion required two equivalents of $\text{K}[\text{AsF}_6]$ although purification issues somewhat compromised the final isolated yield (44%).

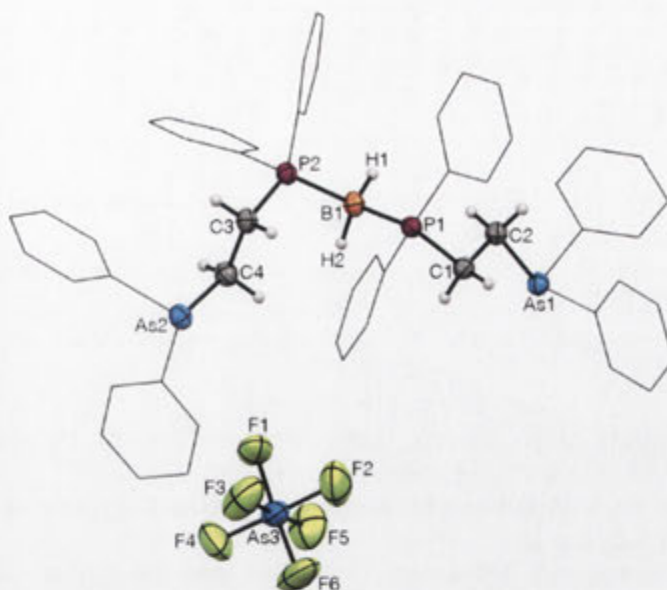


Figure 33: The molecular structure of $[\text{H}_2\text{B}(\text{arphos})_2][\text{AsF}_6]$. (Aryl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): B1-P1 1.926(4); B1-P2 1.927(4); As1-C2 1.984(3); As2-C4 1.986(4); P1-B1-P2 117.1(2); B1-P1-C1 108.6(2), B1-P2-C3 115.1(2).

This method of forcing the loss of bromide from a phosphine monobromoborane adduct was extended in order to incorporate a second, non-phosphine Lewis base to form a boronium salt. The arphos·BH₂Br adduct was seen as an ideal candidate, in that it could form cleanly and no As-B interaction was ever observed by straightforward reaction of arphos and BH₂Br·SMe₂.

The reaction of K[AsF₆] with arphos·BH₂Br was found to proceed, though it required a significant excess of K[AsF₆] (approximately 4 equivalents) to affect even a partial conversion of the arphos·BH₂Br. The reaction was also found to be predominantly split between two products: the desired $[\text{H}_2\text{B}(\text{arphos})][\text{AsF}_6]$ and the previously observed arphos·BH₂Br decomposition borocation $[\text{H}_2\text{B}(\text{arphos})_2]^+$, only this time presumably with a $[\text{AsF}_6]^-$ counterion rather than a bromide. The two compounds displayed similar resonances in the ¹¹B NMR spectrum with $[\text{H}_2\text{B}(\text{arphos})][\text{AsF}_6]$ coming at -41.2 ppm and $[\text{H}_2\text{B}(\text{arphos})_2][\text{AsF}_6]$ at -35.3 ppm, with the higher frequency value of $[\text{H}_2\text{B}(\text{arphos})_2][\text{AsF}_6]$ matching very well to the value of -34.8 ppm found for $[\text{H}_2\text{B}(\text{PMePh}_2)_2]\text{Br}$. The lower frequency value of the $[\text{H}_2\text{B}(\text{arphos})][\text{AsF}_6]$ might be a reflection of the arsine dative bond which, once coordinated to the boron atom, displayed strong coordination much like the phosphine group.

4.21. References

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Chapter 5

Boronium Salts of Heterochelates

5.1. Boronium Salts of Heterochelates

The ability to form As→B bonds as discussed in the previous chapter was of great interest, however, the inclusion of lighter pnictogens was found to provide the most effective heterodentate ligands. Thus whilst *P,P* and *P,As* heterotopic chelates have been shown to form boronium salts, chelates based on a *P,N* donor set have yet to be explored.

The 1,2-phenylene backbone of *N,N*-dimethyl-2-(diphenylphosphino)aniline (amphos) presents amine and phosphine donors in a rigid geometry predisposed towards chelation. The reaction of amphos with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ was found to readily proceed to the boronium salt $[\text{H}_2\text{B}(\text{amphos})]\text{Br}$ in 93% yield (Figure 1). The compound exhibits remarkable stability towards air and moisture both as a solid and in aerobic solutions. Despite the stronger σ -donation of the NMe_2 group in comparison to a PPh_2 group, the ^{11}B NMR resonance observed at -9.3 ppm was found to be significantly higher frequency than that of $[\text{H}_2\text{B}(\text{dppph})]\text{Br}$ (δ_{B} -32.9; dppph = 1,2-bis(diphenylphosphino)benzene).¹ The solid-state structure of $[\text{H}_2\text{B}(\text{amphos})]\text{Br}$ revealed that the BH_2 substituent was displaced out of the P1-C1-C2-N1 plane by 0.49 Å, but interestingly the P-B bond length of 1.947(2) Å was crystallographically indistinguishable from both of those in $[\text{H}_2\text{B}(\text{dppph})]\text{Br}$ (cf. P-B = 1.939(5), 1.941(5) Å), despite the replacement of NMe_2 by PPh_2 .¹

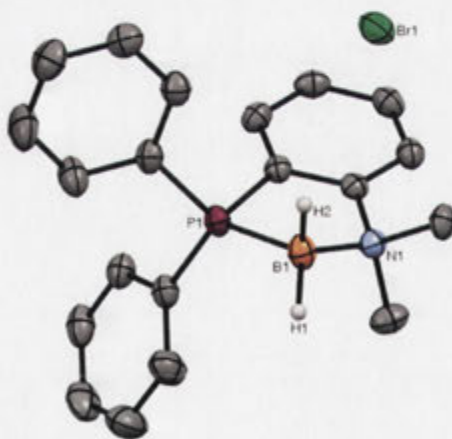


Figure 1: The molecular structure of $[\text{H}_2\text{B}(\text{amphos})]\text{Br}$. (Hydrocarbyl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): B1-N1 1.621(3); B1-P1 1.947(2); N1-B1-P1 101.1(1).

The rigid phenylene backbone coupled with the strong σ -donation of the NMe_2 group in amphos made it a promising candidate for the formation of monobromoboronium salts. The reaction of the strongly σ -donating dcpe ligand to form $[\text{BrHB}(\text{dcpe})]\text{Br}$ had met with limited success due to competition with $\text{dcpe} \cdot (\text{BH}_2\text{Br})_2$ formation, whilst the insolubility of the dmpe analogue $[\text{BrHB}(\text{dmpe})]\text{Br}$ curtailed its detailed study. Similarly, studies on $[\text{BrHB}(\text{PMe}_2\text{Ph})_2]\text{Br}$ were hindered by it being an oil and also by gradual decomposition. Therefore, amphos was envisioned as a bridge between the requirement of sufficiently σ -donating Lewis basic groups, solubilising phenyl and phenylene groups, whilst still being a heterodentate molecule that would gain the benefit of the chelate effect.

The reaction between $\text{BHBr}_2 \cdot \text{SMe}_2$ and amphos proceeded cleanly to the desired boronium product $[\text{BrHB}(\text{amphos})]\text{Br}$ (Figure 2). An NMR analysis of the product revealed resonances at δ_{B} -5.2 and δ_{P} -11.0, along with inequivalent resonances for the diastereotopic methyl groups of the tertiary amine (δ_{H} 3.24, 3.77) adjacent to the chiral boron centre.

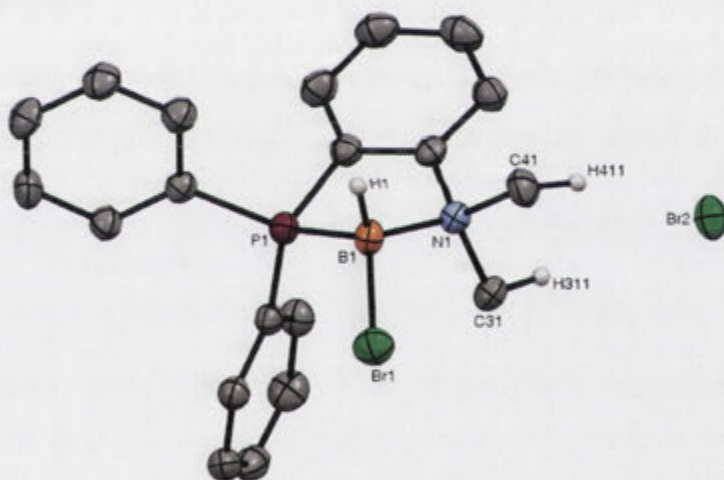


Figure 2: The molecular structure of one enantiomer of $[\text{BrHB}(\text{amphos})]\text{Br}$. (Alternative enantiomer generated by crystallographic $P2_1/a$ symmetry, solvate molecules and alkyl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected bond lengths ($\text{\AA}$), angles ($^\circ$) and intermolecular distances ($\text{\AA}$): B1-Br1 1.980(4); B1-N1 1.621(3); B1-P1 1.947(2); Br1-B1-N1 113.4(2); Br1-B1-P1 116.6(2); N1-B1-P1 101.1(1); C31-H311 $\cdots$ Br2 2.8412(5); C41-H411 $\cdots$ Br2 3.0345(5).

The solid-state structure revealed that the boron atom of [BrHB(amphos)]Br was bent out of the P1-C1-C2-N1 plane significantly more (37.3°) than was found for [H₂B(amphos)]Br (25.8°). This was due to replacement of a hydrogen atom with the sterically more demanding bromine substituent, which assumed an equatorial position with respect to the C₂NPB ring. The centrosymmetric $P2_1/a$ space group adopted by *rac*-[BrHB(amphos)]Br accommodates both enantiomers (Figure 3).

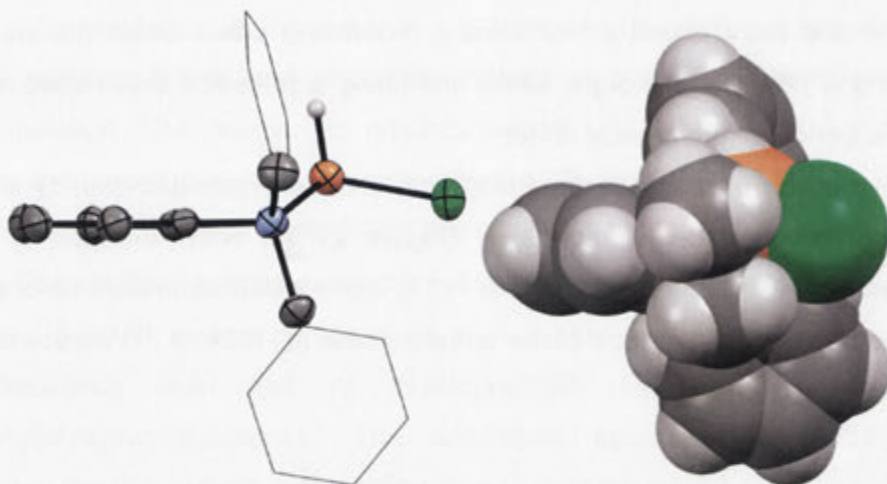


Figure 3: A side-on view of the molecular structure of [BrHB(amphos)]⁺ cation, looking along the amphos N-P plane, which illustrates the equatorial orientation of the bromine atom in both ellipsoid (left) and a spacefill representation (right). (Counterions, solvate molecules and alkyl hydrogen atoms omitted in ellipsoid plot for clarity, phenyl groups simplified, 50% displacement ellipsoids).

The crystallographic packing of [BrHB(amphos)]Br was of interest as it clearly displayed a dimer type arrangement bridged by trifurcated C-H $\cdots$ Br hydrogen bonding between N-CH₃ and Br groups on adjacent cations (Figure 4).

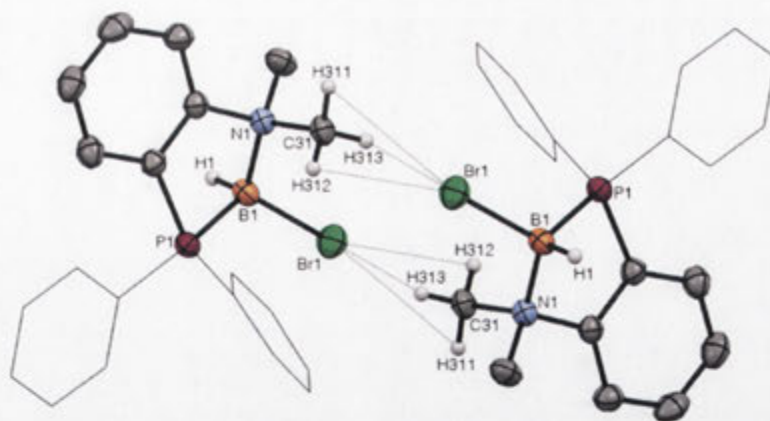


Figure 4: The molecular packing of two $[\text{BrHB}(\text{amphos})]^+$ cations. (Counterions, solvate molecules and some hydrogen atoms omitted for clarity, phenyl groups simplified, 50% displacement ellipsoids). Selected intermolecular hydrogen bonds (Å): C31-H311 $\cdots$ Br1¹ 3.4827(4); C31-H312 $\cdots$ Br1¹ 3.0870(4); C31-H313 $\cdots$ Br1¹ 3.2283(4).

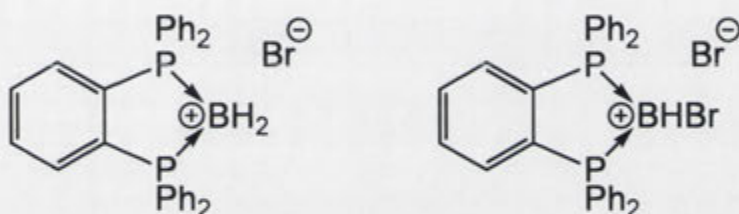


Figure 5: The dppph literature comparison analogues of $[\text{H}_2\text{B}(\text{amphos})]\text{Br}$ and $[\text{BrHB}(\text{amphos})]\text{Br}$: $[\text{H}_2\text{B}(\text{dppph})]\text{Br}$ (left) and $[\text{BrHB}(\text{dppph})]\text{Br}$ (right).¹

When compared to their diphosphine counterparts (Figure 5), $[\text{H}_2\text{B}(\text{amphos})]\text{Br}$ and $[\text{BrHB}(\text{amphos})]\text{Br}$ highlighted some interesting differences. Upon changing one of the hydrogen atoms to a bromine atom, the change in shift of the ^{11}B NMR resonances for the amphos based boronium salts was significantly less than for the diphosphine based boronium salts (

Table 1). As the table shows, the change in the ^{11}B NMR shifts are greater than 10 ppm for both the diphosphine based boronium salts, but for the heterodentate amphos, the difference between the two compounds was only 4.1 ppm.

Table 1: ^{11}B and ^{31}P NMR data (in CDCl_3) for amphos, dppph and dcpe boronium salts.

	BH_2		BHBr	
	δ_{B}	δ_{P}	δ_{B}	δ_{P}
amphos	-9.3	4.5	-5.2	-11.0
dppph	-32.9	23.9	-21.6	6.4
dcpe	-43.7	43.6	-26.8	20.9

However, the trend observed in the ^{31}P NMR spectra was found to be fairly consistent (

Table 1), with the differences in chemical shifts for all three ligands being greater than 15 ppm, though once again the greatest difference being for the dcpe. The small difference between the ^{11}B NMR spectra for the amphos complexes suggested an unusual arrangement for its two respective boronium salts. Despite the boron centre gaining a strongly electronegative bromine atom in $[\text{BrHB}(\text{amphos})]\text{Br}$, the small change in the ^{11}B NMR resonance would indicate that its coordinated Lewis base dative bonds compensated for the lost electron density around the boron atom. However, the ^{31}P NMR spectrum showed the same shift for the single PPh_2 group as found for the diphosphine ligands, which might suggest that it was not the phosphorus atom that moderated electroneutrality, but primarily the more σ -basic NMe_2 group.

The flexible electron donation of the NMe_2 group was supported by comparison of the $\text{P}\rightarrow\text{B}$ bond lengths between the amphos and the diphosphine examples, all of which fell in the narrow range 1.939(5) - 1.964(8) Å (*i.e.*, within 6 e.s.d). The $\text{N}\rightarrow\text{B}$ bond lengths were statistically identical for $[\text{H}_2\text{B}(\text{amphos})]\text{Br}$ (1.621(3) Å) and $[\text{BrHB}(\text{amphos})]\text{Br}$ (1.621(5) Å).

The chiral H,Br,P,N donor set of the boronium salt $[\text{BrHB}(\text{amphos})]\text{Br}$ is without precedent (SciFinder[Ⓔ]). The $[\text{H}_2\text{B}(\text{amphos})]\text{Br}$ and $[\text{BrHB}(\text{amphos})]\text{Br}$ boronium salts also have features that differ with their diphosphine counterparts. The higher frequency ^{11}B NMR peaks indicate a more deshielded boron environment, which might be reflected in enhanced reactivity, coupled with far less steric protection provided by the much smaller methyl groups of the amine.

5.2. Boronium Salts Bearing Sulphur Ligands

A brief foray was made into examining $\text{S}\rightarrow\text{B}$ coordination, given the utility of $\text{BH}_n\text{X}_{3-n}\cdot\text{SMe}_2$ ($n = 0-3$, $\text{X} = \text{Cl}, \text{Br}$) reagents. From the results thus far, phosphorus donors are demonstrably more effective coordinators to boron than the simple thioethers. Whilst little variation in coordination preference for other thioethers would be expected, in the corresponding phosphine chemistry chelation was shown to play a significant role. The possibility of exploiting the chelate or macrocyclic effect for thioether coordination was therefore briefly explored with the potentially bi-, tri- and tetradentate ligands di(2-mercapto-1-methylimidazole)methane ($\text{CH}_2(\text{mt})_2$), 1,4,7-

[Ⓔ] SciFinder search - 09/10/14

trithiacyclononane ([9]aneS₃) and 1,4,8,11-tetrathiacyclotetradecane ([14]aneS₄), respectively.

Treating ([14]aneS₄) with two equivalents of BH₂Br·SMe₂ resulted in the precipitation of a material that proved insoluble in most conventional solvents. The material did dissolve in THF, however, this was accompanied by slow effervescence (most likely hydrogen) and the regeneration of the free thioether macrocycle, which was confirmed crystallographically by comparison of unit cell data with those previously published.² Whilst the nature of the material remains open to conjecture, its deposition clearly demonstrates that the macrocycle binds in preference to the monodentate SMe₂. The poor solubility might be accounted for either by the dicationic charge associated with the 1:2 electrolytes (Figure 6), or alternatively by the formation of polymeric species. The polymer formed from a simple 1:1 stoichiometry would be linear, however, the addition of a second equivalent of Me₂S·BH₂Br would be expected to cross-link the polymer. One or all of these possibilities could well be present in the deposited material with little thermodynamic preference operating.

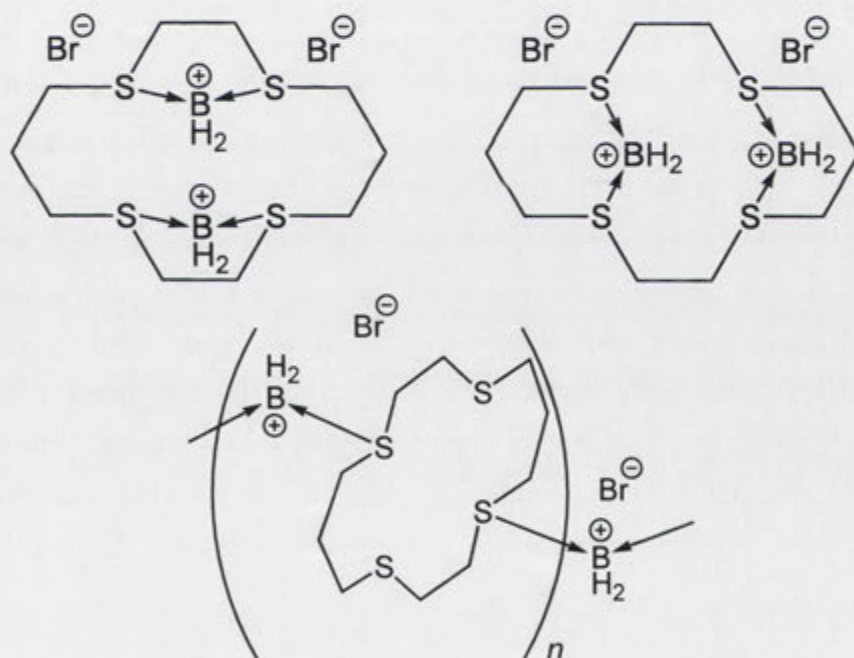


Figure 6: The possible boronium products from the reaction of BH₂Br·SMe₂ and [14]aneS₄: two 5-membered rings (top left), two 6-membered rings (top right) or a polymeric structure (bottom).

It was possible to acquire a ^{11}B NMR spectrum from THF that revealed a mixture of four different boron-containing products. Two higher frequency resonances (δ_{B} 17.0, 26.7) devoid of B-H coupling most likely correspond to decomposition products being in a region typical of B-O bonded species such as $\text{B}(\text{O}^t\text{Bu})_3$ (δ_{B} 18.0) or $\text{B}(\text{OC}_4\text{H}_8\text{Br})_3$, the products of borane induced ring-opening of THF. However, the two lower frequency peaks at δ_{B} -0.7 (d, J 234.3 Hz) and 3.4 (t, J 133.6 Hz) were both found to display B-H coupling, though the splitting of the peak at -0.7 ppm was reflective of a BH rather than a BH_2 group. The lack of $[\text{BH}_2(\text{SR}_2)_2]^+$ type compounds in the literature, with only $[\text{BH}_2(\text{SMe}_2)_2][\text{B}_{12}\text{H}_{12}]$ having being reported in 1964 (with characterisation based solely on microanalytical data),³ meant that the two resonances cannot be commented on other than to state they are shifted toward higher frequency in relation to the $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ starting material, which would be expected at approximately -11 ppm (depending on the deuterated solvent used) in the ^{11}B NMR spectrum. The appearance of a doublet at -0.7 ppm was particularly unusual, given that its coupling was relatively large (>200 Hz), but also because the doublet must have been caused by coupling to another boron atom, given that the spectrum was proton decoupled[†] and ^{13}C only has an abundance of 1%. The identities of these resonances cannot be further elucidated, other than to assume that they might be straightforward sulphur adducts of mixed bromoboranes.

Similarly, the reaction of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ with $\text{CH}_2(\text{mt})_2$ afforded poorly soluble material, requiring the NMR spectrum to be measured using a mixture of CDCl_3 and *protio*-THF. Once again, the higher frequency peaks at 17.0 and 26.7 ppm attributed to THF mediated decomposition were observed in the ^{11}B NMR spectrum.

Finally, $[\text{9}]_{\text{aneS}_3}$ was treated with $\text{BHBr}_2\cdot\text{SMe}_2$ in the hopes of generating a boronium dication by displacement of both bromine atoms (Figure 7), analogous to the compound synthesised by Schmidbaur *et al.* by the use of a tridentate phosphine.⁴

[†] The proton-coupled ^{11}B NMR spectrum revealed a $^1J_{\text{BH}}$ value of 104.3 Hz, which is within the expected range for a coupling of that nature.

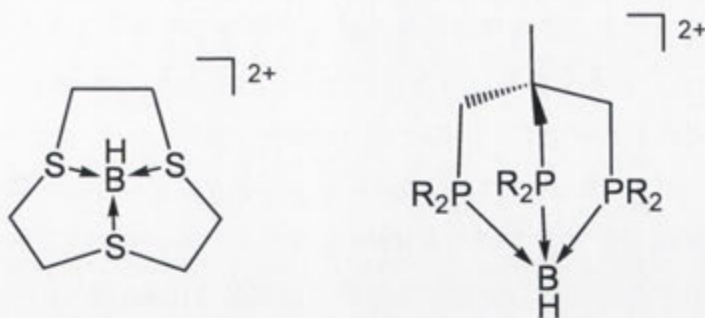


Figure 7: The intended boronium dication product, generated by reaction of $\text{BHBr}_2 \cdot \text{SMe}_2$ with 1,4,7-trithiacyclononane (left) and the dicationic boron cage reported by Schmidbaur *et al.* (right).⁴

After 48 hours of stirring in benzene a precipitate had formed, consistent with the formation of a boronium salt. However, poor solubility in a number of common solvents led to the necessary use of deuterated acetone to conduct the NMR analysis. The ^{11}B NMR spectrum yielded a single strong peak at 20.9 ppm that did not exhibit B-H coupling, but instead was most likely a B-O type compound (*e.g.*, $\text{B}(\text{O}^i\text{Pr})_3$) from acetone hydroboration.

The commonalities of the combined results are: the formation of insoluble materials, which suggest salt formation, in addition to the apparent decomposition when dissolved in THF or acetone. The ring opening of THF by neutral boranes is usually very slow, however, it might be surmised that dissolution of these presumably oligomeric species requires cleavage of one $\text{S} \rightarrow \text{B}$ bond to transiently generate highly electrophilic cationic $\text{R}_2\text{S}-\text{BH}_2^+$ sites that enables donor solvents (THF or acetone) to compete with re-coordination of the pre-ionised bromide.

5.3. Cyclic Boronium Salts with Pendant Arsino Groups

The approach of using heterotopic chelates to selectively bind boron-based groups, whilst leaving other donor groups free for further synthesis, was also applied in the context of boronium salt formation. The exceptional selectivity exhibited in the previously discussed formation of $\kappa^1\text{-P-}a\text{-phos} \cdot \text{BH}_2\text{Br}$ led to the further study of mixed arsino/phosphino donor group ligands.

The potentially tetradentate ligand, *meso*-1,2-bis(phenyl(diphenylarsinoethyl)phosphino)ethane (diphars) (Figure 9), was chosen for

investigation so as to exploit the observations arising from the previous arphos system. The inner diphosphine core would be expected to be analogous to dppe, which reacted cleanly with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ to afford a chelated boronium centre, whilst the outer diphenylarsinoethyl groups would, by analogy with $\kappa^1\text{-P-arphos}\cdot\text{BH}_2\text{Br}$, be unlikely to form enduring $\text{As}\rightarrow\text{B}$ interactions leaving the arsino groups free to be involved in subsequent reactions with softer transition metal substrates. The *meso* form of the diphars was chosen so as to: (i) Simplify potentially complex stereochemical issues, and; (ii) In the event of successful phosphine chelation, this geometry would predispose both arsine donors on the same (*syn*) face of the borocycle so as to facilitate subsequent chelation to a single metal (Figure 8). The *anti* conformation, if presented with a metal capable of coordinating two extraneous ligands, would be expected to form polymeric assemblies.

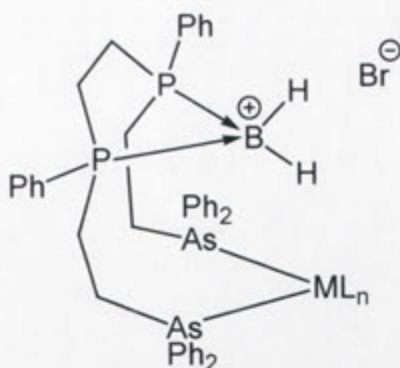


Figure 8: The *syn* addition of BH_2Br to *meso*-diphars to form $[\text{H}_2\text{B}(\kappa^2\text{-P,P'}\text{-diphars})]\text{Br}$, which when coordinated to a metal centre (ML_n) might potentially encourage interaction of the borocation with the metal.

The reaction of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ with diphars proceeded cleanly to the desired boronium salt $[\text{H}_2\text{B}(\kappa^2\text{-P,P'}\text{-diphars})]\text{Br}$ over a period of 18 hours (benzene, ambient temperature, Figure 9), in contrast to the formation of $[\text{H}_2\text{B}(\text{dppe})]\text{Br}$, which was complete in under an hour. The diphars was found to retain its stereochemistry in the product, which meant that the compound was still achiral and in a *meso* form. The *meso* arrangement of the product was confirmed crystallographically, but disorder in the solved structure illustrated that though the model was comprised of two symmetry generated halves, the central five-membered boronium ring was found to be oriented evenly over two possible orientations (Figure 10). However, both orientations possessed a *meso* arrangement of the two phosphorus stereocentres. The $[\text{H}_2\text{B}(\kappa^2\text{-P,P'}\text{-diphars})]\text{Br}$ salt was found to possess the same air and moisture tolerance as the other ring-closed diphosphine-based boronium salts, and could be made purely in a reasonable yield of 73%.

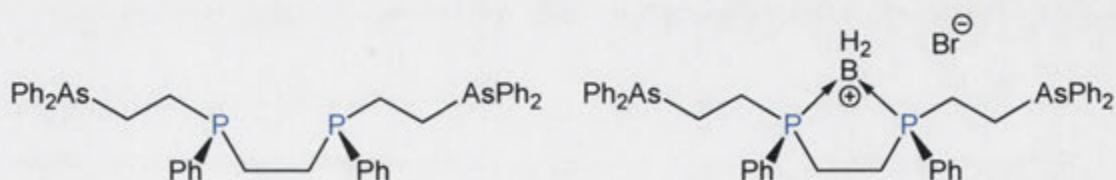


Figure 9: The *meso* form of diphars utilised (left) and the *meso* form of the $[\text{H}_2\text{B}(\kappa^2\text{-P,P'}\text{-diphars})]\text{Br}$ arising from reaction with $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (right). Stereogenic centres highlighted in blue.

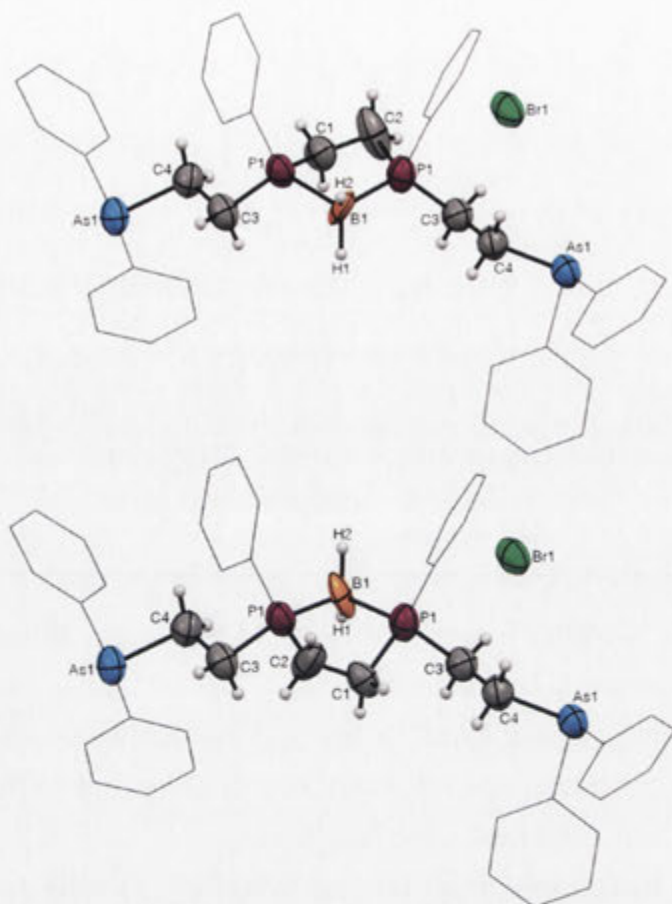


Figure 10: The molecular structure of $[\text{H}_2\text{B}(\kappa^2\text{-}P,P'\text{-diphars})]\text{Br}$ showing the two positionally disordered orientations of the borocycle. (Aryl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles ($^\circ$): B1-P1 1.98(2); B1-P1' 1.87(2); As1-C4 1.991(6); P1-B1-P1' 98(1); B1-P1-C1 97.9(8); B1-P1'-C2 108.4(7).

5.4. Reactions of Cyclic Boronium Salts with Pendant Arsino Groups

An equimolar mixture of the ruthenium complex $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and $[\text{H}_2\text{B}(\kappa^2\text{-}P,P'\text{-diphars})]\text{Br}$ was not found to react in DCM, even after seven days, which was surprising given that this ruthenium complex is known to coordinate to a range of bidentate ligands including diphosphines such as dppe .⁵ The failure of $[\text{H}_2\text{B}(\kappa^2\text{-}P,P'\text{-diphars})]^+$ to replace a PPh_3 ligand in $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, suggested that an organometallic precursor with a more labile ligand might be required. To meet this

criterion, the molybdenum complex $\text{Mo}(\text{C}_7\text{H}_8)(\text{CO})_3$ discussed in previous chapters was chosen as being synthetically equivalent to the 12-electron ' $\text{Mo}(\text{CO})_3$ ' fragment.

An equimolar mixture of $[\text{H}_2\text{B}(\kappa^2\text{-}P,P'\text{-diphars})]\text{Br}$ and $\text{Mo}(\text{C}_7\text{H}_8)(\text{CO})_3$ in benzene was found to precipitate out a brown solid over several minutes. The solid was found to be insufficiently soluble in a battery of solvents, including DMSO, to allow NMR analysis. However, a relatively clean ESI-MS spectrum was obtained with the main isotopic envelopes corresponding to $[\text{Mo}(\text{CO})_4(\text{H}_2\text{B}(\kappa^2\text{-}P,P'\text{-diphars}))]^+$, $[\text{Mo}(\text{CO})_3(\text{H}_2\text{B}(\kappa^2\text{-}P,P'\text{-diphars}))]^+$ and the precursor boronium cation $[\text{H}_2\text{B}(\kappa^2\text{-}P,P'\text{-diphars})]^+$. The MS spectrum was unfortunately unable to give any indication as to whether the boronium centre had interacted with the molybdenum centre. The observation of the molybdenum tetracarbonyl product did suggest that C_7H_8 was completely displaced by the $[\text{H}_2\text{B}(\kappa^2\text{-}P,P'\text{-diphars})]^+$, though the carbonyl scrambling also indicated that it was most likely only interacting with the molybdenum *via* the two arsine groups and not by the boronium centre, as the octahedral centre was already coordinatively saturated.

A very slow reaction ensued between $[\text{H}_2\text{B}(\kappa^2\text{-}P,P'\text{-diphars})]\text{Br}$ and Wilkinson's catalyst, $\text{RhCl}(\text{PPh}_3)_3$, to provide a powder, the low solubility of which compromised the acquisition of informative NMR data. The ^{11}B NMR spectrum comprised a single resonance at 0.7 ppm, shifted significantly to higher frequency from that of $[\text{H}_2\text{B}(\kappa^2\text{-}P,P'\text{-diphars})]\text{Br}$ (δ_{B} -39.1).^o The ^{31}P NMR spectrum comprised of five substantial resonances (δ_{P} 41.3, ~58, 89.8, 93.0, 95.6), which were broadened by interaction with ^{11}B , in addition to the observation of other minor impurities. Satisfactory ^1H NMR spectrum could not be obtained as a complex mixture of compounds crowded the spectrum. This was unfortunate because the spectrum could have indicated if the electron-rich d^8 rhodium centre had oxidatively inserted into the B-H bond of the boronium centre to give a B-Rh-H motif, or alternatively a 3-centre, 2-electron B-H-Rh interaction (Figure 11),⁶⁻⁸ with either outcome resulting in a high field resonance possibly showing coupling to ^{103}Rh (100% natural abundance, $I = 1/2$).

^o ^{11}B NMR spectra were both recorded in CD_2Cl_2 .

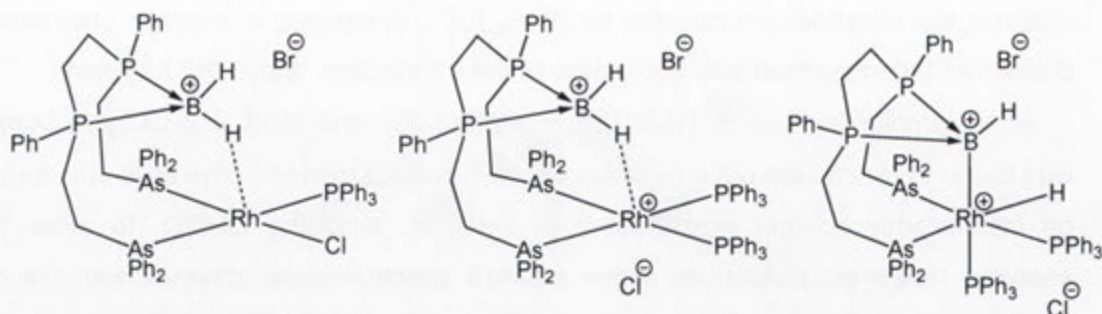


Figure 11: The possible formulations for the adduct of $[\text{H}_2\text{B}(\kappa^2\text{-P,P'-diphars})]^+$ with Wilkinson's complex.

The ESI-MS spectrum suggested that the chloro substituent was no longer present as it contained isotopic envelopes for both $[\text{Rh}(\text{PPh}_3)_2(\text{HB}(\kappa^2\text{-P,P'-diphars}))]^+$ and $[\text{Rh}(\text{PPh}_3)(\text{HB}(\kappa^2\text{-P,P'-diphars}))]^+$, however, some caution must be exercised due to the tendency of halo complexes to dissociate the halide under ESI-MS conditions due to the polar matrix (NCMe or MeOH). Peaks attributable to free $[\text{H}_2\text{B}(\kappa^2\text{-P,P'-diphars})]^+$ were, however, absent under conditions that previously provided a satisfactory spectrum for authentic $[\text{H}_2\text{B}(\kappa^2\text{-P,P'-diphars})]^+$ (*vide supra*), confirming that the $[\text{H}_2\text{B}(\kappa^2\text{-P,P'-diphars})]^+$ had indeed coordinated to the rhodium centre.

The straightforward salt $[\text{Rh}(\text{diphars})]\text{Cl}$ had not been previously reported in the literature, though complexes for Cu, Pd, Ag and Au were known.^{9, 10} Heating $\text{RhCl}(\text{PPh}_3)_3$ with diphars in benzene for 12 hours resulted in the precipitation of a new complex with the ^{31}P NMR spectrum revealing one major peak at 42.2 ppm, which was neither Wilkinson's catalyst nor free diphars. This resonance and two minor (*ca.* 20%) resonances (δ_{P} 41.6, 90.4) were present in the spectrum of the $[\text{H}_2\text{B}(\kappa^2\text{-P,P'-diphars})]^+$ adduct and so it may be concluded that free diphars is liberated during the reaction of $[\text{H}_2\text{B}(\kappa^2\text{-P,P'-diphars})]\text{Br}$ with $\text{RhCl}(\text{PPh}_3)_3$. However, the distinct lack of $^1J_{\text{PRh}}$ coupling for the dominant resonance observed (δ_{P} 42.2) cast doubt as to whether the diphars had complexed to the rhodium. The ESI-MS spectrum was equally inconclusive and only what was believed to be $[\text{RhH}(\text{NCMe})(\text{PPh}_3)_3]^+$ was identified.

5.5. Boronium Salts with Pendant Phosphino Groups

Armed with a better understanding of the nature of phosphine-ligated boronium salts, more complicated species were considered that might facilitate the synthesis of metal-boron bonds. The first was a modification of the previously mentioned dicationic boron cage, $[\text{HB}(\text{triphos}^{\text{Me}})]^{2+}$ ($\text{triphos}^{\text{Me}} = \text{MeC}(\text{CH}_2\text{PMe}_2)_3$), where instead of using $\text{B}(\text{HBr}_2) \cdot \text{SMe}_2$ as reported,⁴ $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ was treated with triphos ($\text{MeC}(\text{CH}_2\text{PPh}_2)_3$). This produced a boronium species within a six-membered heterocycle, to which was appended a pendant phosphine arm that might be available for coordination to metal centres (Figure 12).

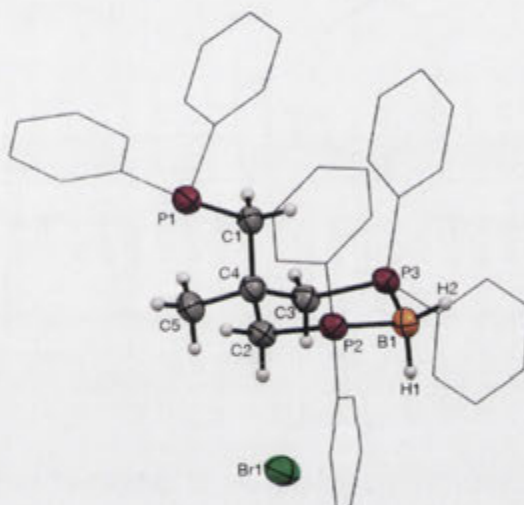


Figure 12: The molecular structure of $[\text{H}_2\text{B}(\text{triphos})]\text{Br}$. (Aryl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): B1-P2 1.921(4); B1-P3 1.932(4); P1-C1 1.852(4); P2-C2 1.825(3); P3-C3 1.816(3); P2-B1-P3 111.2(2); B1-P2-C2 109.5(2); B1-P3-C3 108.9(2); P2-C2-C4 118.2(2); P3-C3-C4 117.6(2); C2-C4-C3 111.2(3).

With the lack of secondary phosphine protons, the bromide counterion was found in the solid state to hydrogen bond to the methylene groups of the borocycle (*cf.* $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$), the acidity of which is inductively enhanced by the boronium centre, relative to the acyclic methylene of the pendant phosphine arm. The solid-state structure also revealed a dimeric assembly for the packing of the $[\text{H}_2\text{B}(\text{triphos})]^+$ cations *via* a rhomboid arrangement of two short and two long dihydrogen bonds

between inversely polarised C-H(δ^+) and B-H(δ^-) bonds, respectively (Figure 13).¹¹⁻¹⁴ Dihydrogen bonding such as C-H $\cdots$ H-B is typically rather weak compared to more conventional hydrogen bond donors N-H and O-H (*cf.* Me₂HN·BH₃).¹⁵

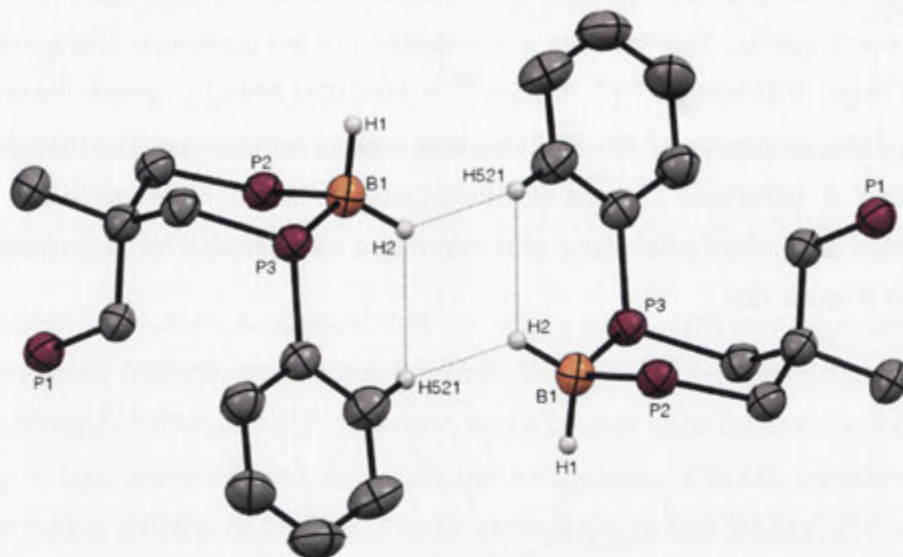


Figure 13: The centrosymmetric molecular packing of two [H₂B(triphos)]⁺ cations illustrating the rhombic dihydrogen bonding. (Selected phenyl rings and alkyl hydrogen atoms omitted for clarity, 50% displacement ellipsoids). Selected intra- and intermolecular hydrogen bonds (Å): B1-H2...H521 2.4781(1); B1-H2...H521' 2.3783(1).

A caveat encountered in the synthesis of [H₂B(triphos)]Br was that the pendant phosphine arm was found on occasion to react with excess BH₂Br·SMe₂ to form a bromoborane adduct (δ_B -23.8, δ_P -4.8) in conjunction to the boronium salt, which had almost identical behaviour towards various solvents as the desired [H₂B(triphos)]Br, making its separation problematic such that particular care must be taken with the stoichiometry of reagents.

For practical purposes, it was found desirable to exchange the bromide counterion of [H₂B(triphos)]Br by metathesis, however, in contrast to the synthesis of [H₂B(PHCy₂)₂][SbF₆] the silver salt Ag[SbF₆] proved problematic in that the pendant phosphine was found to partially coordinate to the silver bromide by-product. Therefore, K[AsF₆] was selected as a replacement allowing the desired product to be isolated in a 67% yield (Figure 14). Interestingly, the solid-state conformation for [H₂B(triphos)][AsF₆] had the pendant phosphine arm in the equatorial position, whilst

for $[\text{H}_2\text{B}(\text{triphos})]\text{Br}$ this was observed in an axial position which is less common for sterically demanding cyclohexane substituents.

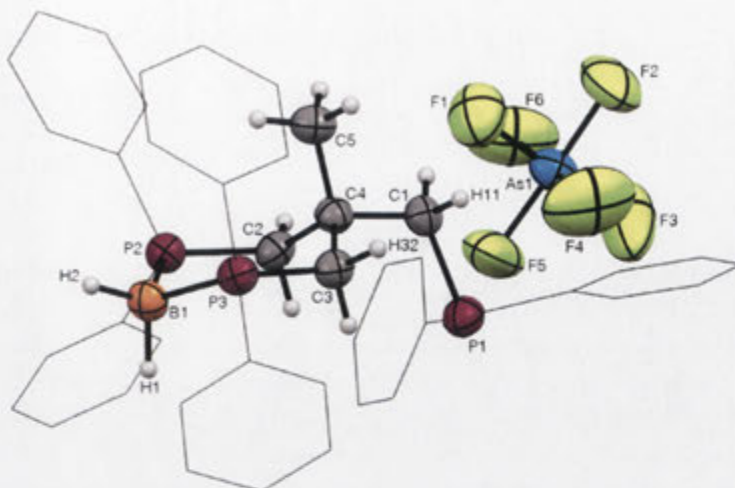


Figure 14: The molecular structure of $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$. (Solvate molecules and aryl hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids).

Selected bond lengths (Å), angles (°) and intermolecular distances (Å): B1-P2 1.918(7); B1-P3 1.927(7); P1-C1 1.866(6); P2-C2 1.818(6); P3-C3 1.814(6); P2-B1-P3 110.7(3); B1-P2-C2 109.7(3); B1-P3-C3 110.6(3); P2-C2-C4 118.5(4); P3-C3-C4 117.0(4); C2-C4-C3 111.1(4); C1-H11...F6 2.588(4); C3-H32...F5 2.559(6).

The solid-state structure of $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$ was similarly (*cf.* $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2][\text{AsF}_6]$) found to coordinate to the $[\text{AsF}_6]^-$ anion *via* the methylene groups of the $[\text{H}_2\text{B}(\text{triphos})]^+$ cation, though in this case through all three of the methylene groups, including the methylene of the pendant phosphine arm. Short hydrogen bond interactions of 2.559(6) and 2.588(4) Å were observed for the borocycle methylene protons and the pendant phosphine arm methylene protons, respectively.

Similar to the acyclic boronium cations such as $[\text{H}_2\text{B}(\text{PHCy}_2)_2]^+$, the effect of anion substitution of the bromide to $[\text{AsF}_6]^-$ was observed to persist in solution. This was found with a shift to lower frequency for the multiplets attributed to the methylene protons in the ^1H NMR spectrum for $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$ (δ_{H} 2.67, 2.72-2.84) in comparison to $[\text{H}_2\text{B}(\text{triphos})]\text{Br}$ (δ_{H} 3.17-3.43, 3.68-3.86).

In contrast to C_{3v} symmetric triphos, the linear triphosphine $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ (triphos-asym; Figure 15) has the potential to form two different boronium salts depending on whether chelation involves both terminal phosphines donors in an eight-

membered ring, or alternatively, a five-membered chelate utilising the internal and (more basic) phosphine donor (Figure 16). As discussed in the previous chapter, once the intended ring size of a potential ring-closing reaction exceeds the formation of a 6-membered ring, the formation of a cyclic boronium salt appears to be disfavoured.

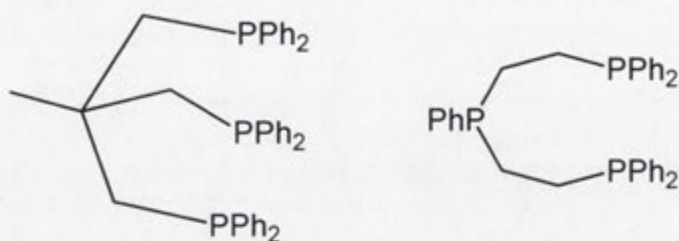


Figure 15: The structures of triphos (left) and triphos-asm (right), both known by the trivial name 'triphos'.

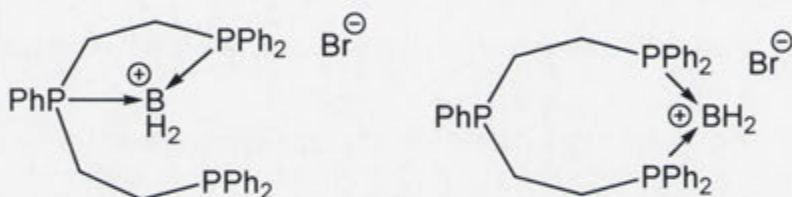


Figure 16: The two potential structures of $[H_2B(\text{triphos-asm})]Br$, where a 5-membered ring boronium salt is formed (left) or an 8-membered ring is formed (right).

The synthesis of $[H_2B(\text{triphos-asm})]Br$ was performed in the same straightforward manner as for $[H_2B(\text{triphos})]Br$, where equimolar amounts of $BH_2Br \cdot SMe_2$ and triphos-asm were heated to reflux in toluene for 18 hours. It was not until the reaction had cooled that the product was observed to precipitate out of the crude reaction mixture and was isolated in a meagre 11% yield. The filtrate was found to also contain the product, but in combination with unreacted triphos-asm starting material. Despite the poor yield and the observation that samples quickly degraded to an insoluble, potentially polymeric material, it was possible to acquire satisfactory 1H , ^{11}B and ^{31}P NMR data before the compound decomposed. The 1H NMR spectrum was as expected, with a range of overlapping multiplets for the methylene groups. However, the ^{11}B NMR spectrum contained a single peak at -37.1 ppm, which very closely resembled the resonances observed for the five-membered ring of $[H_2B(\text{dppe})]Br$ (δ_B -35.7) and the six-membered ring of $[H_2B(\text{triphos})]Br$ (δ_B -39.1). The similarity of the ^{11}B

NMR resonance to both of those species did not definitively determine the triphos-asym coordination mode. However, the ^{31}P NMR data was informative with the spectrum comprising of two broad peaks at δ_{P} -12.0 and δ_{P} 29.8 with approximate relative integrals of 1:2. The high frequency shift of the boron-coordinated peak at δ_{P} 29.8 was very different to the corresponding resonance for $[\text{H}_2\text{B}(\text{triphos})]\text{Br}$ (δ_{P} 0.3), and closer to that for $[\text{H}_2\text{B}(\text{dppe})]\text{Br}$ (δ_{P} 27.8). The five-membered heterocycle formulation would give rise to three phosphorus environments, whilst the eight-membered ring would have a time averaged plane of symmetry so as to only provide two chemical phosphorus environments, therefore the formulation of a five-membered ring may be disregarded. The generally less favourable formation of an eight-membered chelate ring may well explain the instability of the compound with respect to presumed ring-opening polymerisation to afford insoluble material, given that results in earlier sections clearly establish that five- and six-membered chelated boronium salts are stable.

5.6. Reactions of Boronium Salts Bearing Pendant Phosphino Groups

The interaction of $[\text{H}_2\text{B}(\text{triphos})]\text{Br}$ with organometallic precursors was explored, beginning with the molybdenum compound $\text{Mo}(\text{C}_7\text{H}_8)(\text{CO})_3$. A reaction ensued in DCM, however, no new ^{11}B NMR resonances were observed suggesting that the reaction did not involve any direct interaction of the boronium group, *i.e.*, that the ligand possibly coordinated solely through the pendant phosphine arm. Four resonances corresponding to coordination to molybdenum were observed at δ_{P} 11.6, 15.8, 18.5 and 32.6, with approximate relative integrals of 8:2:1:(trace), though the unaltered broad resonance of the boronium substituent (δ_{P} -0.1) from the starting material predominated. The reaction of triphos and $\text{Mo}(\text{C}_7\text{H}_8)(\text{CO})_3$ was investigated in order to establish that the resonance at δ_{P} 18.5 corresponded to $\text{Mo}(\text{triphos})(\text{CO})_3$,^{16, 17} arising from loss of the BH_2Br . The resonance at δ_{P} 32.6 most likely corresponds to $[\text{MoBr}(\text{CO})_3(\text{triphos})]^+$ for which a value of 31.6 has been reported.¹⁸ Thus the high stability of the stable cage complex $\text{Mo}(\text{triphos})(\text{CO})_3$ would appear to dominate the more labile boronium coordination of the phosphine groups.

The bimetallic reagent $[\text{Rh}_2(\mu\text{-Cl})_2(\eta^4\text{-COD})_2]$ readily undergoes halide-bridge splitting reactions with a range of phosphines.¹⁹⁻²¹ The reaction of $[\text{Rh}_2(\mu\text{-Cl})_2(\eta^4\text{-$

COD)₂] with [H₂B(triphos)]Br appeared to proceed after being heated to reflux in toluene with the observation of a deep red colour.[§] However, after all volatiles were removed under high vacuum the remaining solid was a distinct yellow colour. An MS analysis of the crude yellow solid revealed an isotopic envelope for the desired [RhCl(η^4 -COD)(H₂B{triphos})]⁺ cation. Interestingly, the MS analysis also revealed a lesser, but still significant envelope for [RhBr(η^4 -COD)(H₂B{triphos})]⁺, which had presumably been formed *via* halogen exchange of the Rh-Cl with the bromide counterion of [H₂B(triphos)]Br. The crude ³¹P NMR spectrum confirmed the presence of both complexes with the observation of two doublets at 10.2 and 13.9 ppm in an approximate 3:1 ratio with one another. Only one peak was observed for the boronium centre of the [H₂B(triphos)]⁺ cation (δ_P 1.7), as expected if the boronium ring is remote from the site of halogen exchange, though the broad nature of the ¹¹B coupled boronium resonance in the ³¹P NMR spectrum could have possibly eclipsed a smaller second resonance of similar chemical shift.

The main reason for the discussion of this compound was the appearance of two hydride peaks in the ¹H NMR spectrum at -7.78 and -7.02 ppm, which were observed as doublets due to their coupling to the NMR active ¹⁰³Rh nuclei (¹J_{RhH} 70.8 and 76.5 Hz, respectively). However, these resonances were observed in only very minor quantities according to the relative ¹H NMR integrals of the other peaks present in the spectrum.[†] The known complex Rh(H)₂(Bpin)(triphos) has been reported with a ¹H NMR resonance at -8.07 ppm (²J_{PH} 129 Hz, ¹J_{RhH} 23.8 Hz) in *d*₈-THF at -28°C,²² which is very similar in shift to the two hydride peaks observed experimentally. The formation of Rh(H)₂(Bpin)(triphos) also required the reaction to be heated to 50°C, mimicking the necessity of being heated to reflux for the reaction of [Rh₂(μ -Cl)₂(η^4 -COD)₂] with [H₂B(triphos)]Br to proceed. The complex Rh(H)₃(triphos) also has a similar hydride resonance of -8.30 ppm (²J_{PH} 132 Hz, ¹J_{RhH} 20 Hz) in CD₂Cl₂.²³

The source of the hydride peaks was most likely from addition of the boronium group of the [H₂B(triphos)]⁺ ligand that was now tethered to the rhodium centre by coordination of the pendant phosphine group as intended (Figure 17). To facilitate this type of coordination, the COD ligand would have needed to be displaced completely, a

[§] Toluene was used as the reaction solvent due to its solubility with respect to the reagents and not its relatively high boiling point.

[†] The hydride peaks were not very intense, so whilst ²J_{PH} coupling was not observed, its existence cannot be excluded and might have been lost in the signal-to-noise of the spectrum.

speculation supported by the fact that Rh-H bonds often do not persist in the presence of COD as a co-ligand but undergo hydride transfer from the rhodium to the COD.^{24, 25} Unfortunately, pure material could not be obtained by crystallisation or chromatography.

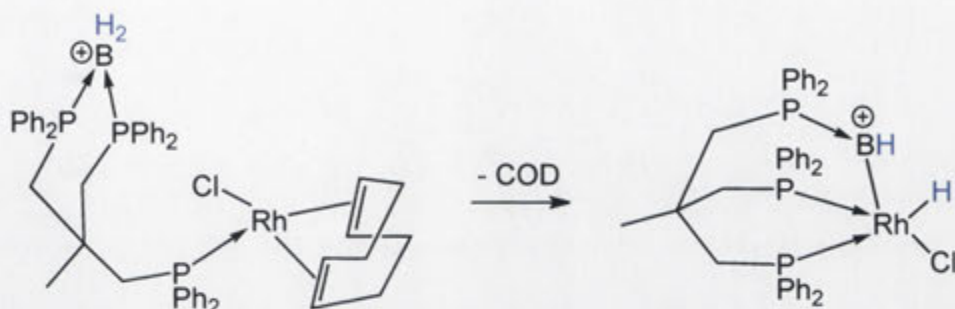


Figure 17: A potential intermediate to account for the hydride resonances observed upon reaction of $\text{Rh}_2(\mu\text{-Cl})_2(\eta^4\text{-COD})_2$ with $[\text{H}_2\text{B}(\text{triphos})]\text{Br}$.

The reaction of $[\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2\text{Cp}^*_2]$ with $[\text{H}_2\text{B}(\text{triphos})][\text{SbF}_6]^\dagger$ was initially intended to facilitate the crystallographic analysis of a simple metal adduct of the $[\text{H}_2\text{B}(\text{triphos})]^+$ ligand and obviate the problem of halogen exchange. The solid-state structure obtained for the product of this reaction definitively revealed the problem of halogen exchange for the first time due to the minor $[\text{H}_2\text{B}(\text{triphos})]\text{Br}$ contamination later found to be present. This was exemplified by the appearance of additional electron density at the two chlorine atom positions which was best modelled by co-location with partially metathesised bromine atoms, in 71:29% and 86:14% ratios of Cl:Br occupancies (Figure 18), to give the overall chemical formula $[\text{RhBr}_{0.43}\text{Cl}_{1.57}\text{Cp}^*(\text{H}_2\text{B}(\text{triphos}))][\text{SbF}_6]$. This result highlighted that the bromide counterion of $[\text{H}_2\text{B}(\text{triphos})]\text{Br}$ was halogen exchanging with both chlorine atoms on the metal centre, and also the difficulty of replacing the bromide counterion completely in the precursor. Whilst confirmation of the presence of a non-coordinating anion such as $[\text{SbF}_6]^-$ could be confirmed by ^{19}F NMR analysis, the absence of the bromide anion could only be checked *via* negative ESI-MS analysis.

[†] The anion exchange of bromide for $[\text{SbF}_6]^-$ was later found to have not gone to completion, which meant that some $[\text{H}_2\text{B}(\text{triphos})]\text{Br}$ was still present in the $[\text{H}_2\text{B}(\text{triphos})][\text{SbF}_6]$ reagent.

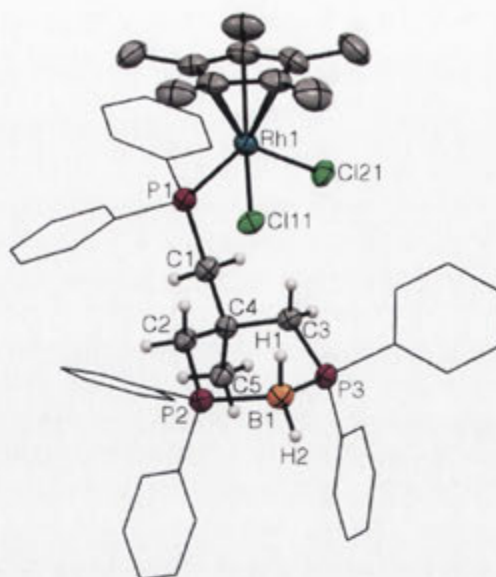


Figure 18: The molecular structure of the cation $[\text{RhBr}_{0.43}\text{Cl}_{1.57}\text{Cp}^*\{\text{H}_2\text{B}(\text{triphos})\}]^+$ showing the major positional disorder isomer with two chlorine atoms for the two rhodium-halide sites.[§] (Solvate molecules and some hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Rh1-Cl11 2.386(9); Rh1-Cl21 2.36(2); Rh1-Br11 2.58(2); Rh1-Br21 2.55(2); Rh1-P1 2.333(2); B1-P2 1.915(5); B1-P3 1.916(5); Cl11-Rh1-C21 97.9(6); Cl11-Rh1-Br21 94.5(6); Cl11-Rh1-P1 89.6(3); Cl21-Rh1-Br11 94.2(7); Cl21-Rh1-P1 87.7(6); Br11-Rh1-Br21 90.8(7); Br11-Rh1-P1 91.2(8); Br21-Rh1-P1 87.4(6); P2-B1-P3 107.3(2); B1-P2-C2 110.0(2); B1-P3-C3 108.9(2).

To combat this deficiency, the methodology employed was changed from this point onwards by using excesses of the reagents such as $\text{K}[\text{AsF}_6]$, and also implementing an iterative process of reacting multiple portions of the metathesis reagents to ensure complete removal of the bromide. Once this issue was identified, $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$ was synthesised as the reagent for subsequent reactions involving organometallic precursors that possessed metal-halide groups. Forearmed by the knowledge of previously observed halogen exchange, a number of reactions of $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$ with organometallic complexes were attempted.

The reaction of $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$ with Vaska's complex, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, which was seen as an ideal organometallic precursor due to iridium's history of oxidatively

[§] The dibromo and two mixed chloro/bromo positional disorder isomers were not shown for simplicity, though the bond angles relating to these species are listed in the description of the Figure.

inserting into the B-H bonds of tethered substituents,^{6, 7, 26} was one of the first reactions performed with the anion exchanged $[\text{H}_2\text{B}(\text{triphos})]^+$ complex. Unfortunately, the strongly forcing conditions (refluent toluene) were found to be insufficient to significantly overcome the competition of the labile, but less bulky, PPh_3 groups that were already present on the iridium. This was confirmed by the major stretch in the IR analysis being attributable to unreacted Vaska's complex (ν_{CO} 1964 cm^{-1}), which was also the dominant peak in the ^{31}P NMR spectrum (δ_{P} 29.7). The ESI-MS spectrum (NCMe matrix) also confirmed the presence of an isotopic envelope for the acetonitrile substituted precursor, $[\text{Ir}(\text{NCMe})(\text{CO})(\text{PPh}_3)_2]^+$ (m/z 786). The MS analysis did, however, confirm the presence of small amounts of $[\text{IrCl}(\text{CO})(\text{PPh}_3)(\text{H}_2\text{B}\{\text{triphos}\})]^+$.

The reaction of $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$ with $\text{Ru}(\text{CH}=\text{CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ was also attempted. The ruthenium complex does possess labile PPh_3 groups which would be in competition with the $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$, however, the complex is already coordinatively unsaturated. Unfortunately as with Vaska's complex, though a new compound was observed to form the reaction could not be swayed to yield it as the major product. Instead, the dominant compound present was unreacted $\text{Ru}(\text{CH}=\text{CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (ν_{CO} 1934 cm^{-1}) as observed by IR spectroscopy, with the new compound being observed as a stretch at 1978 cm^{-1} . Being heated to reflux in DCM overnight did not affect the relative ratio of the two IR stretches as had been found prior to heating. This behaviour reflects that already observed for the addition of monodentate phosphines to $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$, where the extraneous phosphine adds *trans* to the σ -phenyl ligand which exerts a potent *trans*-effect such that added phosphine readily dissociates. Only at elevated temperature over a prolonged period does actual phosphine substitution ensue, *e.g.*, with PMe_2Ph and $\text{P}(\text{OMe})_3$, because rearrangement is necessary to place the PPh_3 ligand *trans* to the σ -phenyl ligand prior to ejection.⁵

The installation of the $[\text{H}_2\text{B}(\text{triphos})]^+$ ligand was, however, established when dimeric organometallic halide-bridged precursors of ruthenium and rhodium were employed. The reaction of $\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2(\eta^6\text{-cymene})_2$ with two equivalents of $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$ resulted in the formation of the salt $[\text{RuCl}_2(\eta^6\text{-cymene})(\kappa^1\text{-P-H}_2\text{B}\{\text{triphos}\})][\text{AsF}_6]$. This was confirmed by ^{31}P NMR spectroscopy by replacement of the pendant phosphine resonance (δ_{P} -25.1) with a new peak (δ_{P} 12.2) corresponding to the ruthenium-bound phosphine, though this was to substantially lower frequency than that reported for

$\text{RuCl}_2(\eta^6\text{-cymene})(\text{PPh}_3)$ (δ_{P} 23.1).^{†27} The ESI-MS analysis also confirmed the desired product with an isotopomer envelope observed and confirmed by simulation for the molecular ion. The ^{11}B NMR spectrum revealed that the boronium substituent was not interacting with the ruthenium centre (δ_{B} -40.2). Although crystallographic grade crystals were grown by solvent diffusion of a mixture of CHCl_3 /pentane, the solid-state structure could not be determined due to the rapid loss of solvent from the crystals once removed from their mother liquor.

A similarly successful reaction was achieved for the combination of two equivalents of $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$ with $\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2\text{Cp}^*_2$ to give the desired product $[\text{RhCl}_2\text{Cp}^*(\text{H}_2\text{B}(\text{triphos}))][\text{AsF}_6]$, for which coordination to rhodium was indicated by a resonance in the ^{31}P NMR spectrum (δ_{P} 23.6, $^1J_{\text{PRh}}$ 151.1 Hz), displaying comparable rhodium coupling to that observed for $\text{RhCl}_2\text{Cp}^*(\text{PPh}_3)$ (δ_{P} 31.2, $^1J_{\text{PRh}}$ 143.9 Hz).²⁸ As with the previous complex, the identity was substantiated by ESI-MS that included a well-defined molecular ion isotopomer manifold, whilst ^{11}B NMR spectroscopy confirmed that the boronium substituent does not interact directly with rhodium (δ_{B} -39.8, *cf.* δ_{B} -39.6 for the precursor). The formulation was confirmed by a crystallographic study (Figure 19) which exhibited the expected weak hydrogen bonding of the mildly acidic alkyl protons to the $[\text{AsF}_6]^-$ counterion (C5-H52...F6 2.56(1) Å), in addition to intramolecular hydrogen bonding to one chloro ligand (2.560(3), 3.190(3) Å) causing the rhodium centre to orient itself closer to the boronium substituent.

[†] Both spectra were recorded in CDCl_3 .

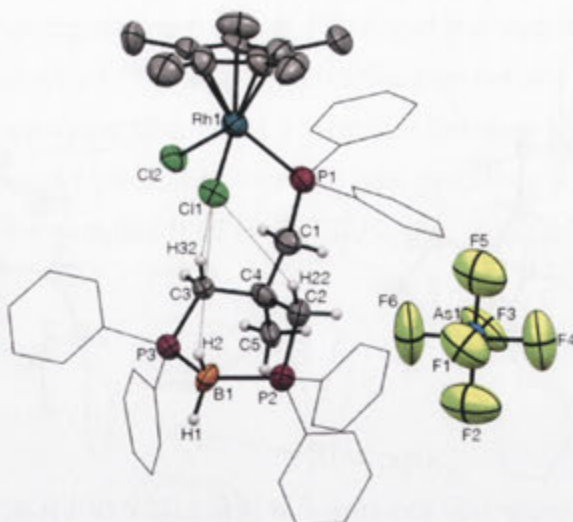


Figure 19: The molecular structure of $[\text{RhCl}_2\text{Cp}^*(\text{H}_2\text{B}\{\text{triphos}\})][\text{AsF}_6]$. (Some hydrogen atoms omitted for clarity, aryl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å), angles ($^\circ$), intramolecular distances (Å) and intermolecular distances (Å):

Rh1-Cl1 2.427(3); Rh1-Cl2 2.427(3); Rh1-P1 2.339(3); B1-P2 1.90(1); B1-P3 1.91(2); Cl1-Rh1-Cl2 93.8(1); Cl1-Rh1-P1 89.1(1); Cl2-Rh1-P1 89.4(1); P2-B1-P3 111.2(9); B1-P2-C2 107.7(6); B1-P3-C3 108.7(6); C2-H22 Cl1 3.190(3); C3-H32 Cl1 2.560(3); C5-H52 F6 2.56(1).

The reaction of two equivalents of $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$ with $\text{Rh}_2(\mu\text{-Cl})_2(\eta^4\text{-COD})_2$ yielded the expected complex $[\text{RhCl}(\eta^4\text{-COD})(\text{H}_2\text{B}\{\text{triphos}\})][\text{AsF}_6]$, the data for which paralleled those for the previous rhodium complex (δ_{B} -39.9, δ_{P} 13.3, $^1J_{\text{PRh}} = 149.9$ Hz; cf. $\text{RhCl}(\eta^4\text{-COD})(\text{PPh}_3)$: δ_{P} 31.3, $^1J_{\text{PRh}} = 150.1$ Hz).²⁹

Interestingly, two solid-state structures were obtained for this complex from different pairs of crystallisation solvents (Figure 20). The solved structures revealed the same intended product $[\text{RhCl}(\eta^4\text{-COD})(\text{H}_2\text{B}\{\text{triphos}\})][\text{AsF}_6]$, with similar, yet distinctly different, unit cells. Both structures contained additional electron density than what was required for $[\text{RhCl}(\eta^4\text{-COD})(\text{H}_2\text{B}\{\text{triphos}\})][\text{AsF}_6]$, which was attributed to disordered solvent molecules. However, in neither structure could the disordered solvates be adequately modelled and they were subsequently accounted for using the 'SQUEEZE' protocol within PLATON. Thus, whilst the final reports for the two structures would seem to indicate they are polymorphs of one another, they are in actual fact not polymorphs but differently solvated forms of the same product.

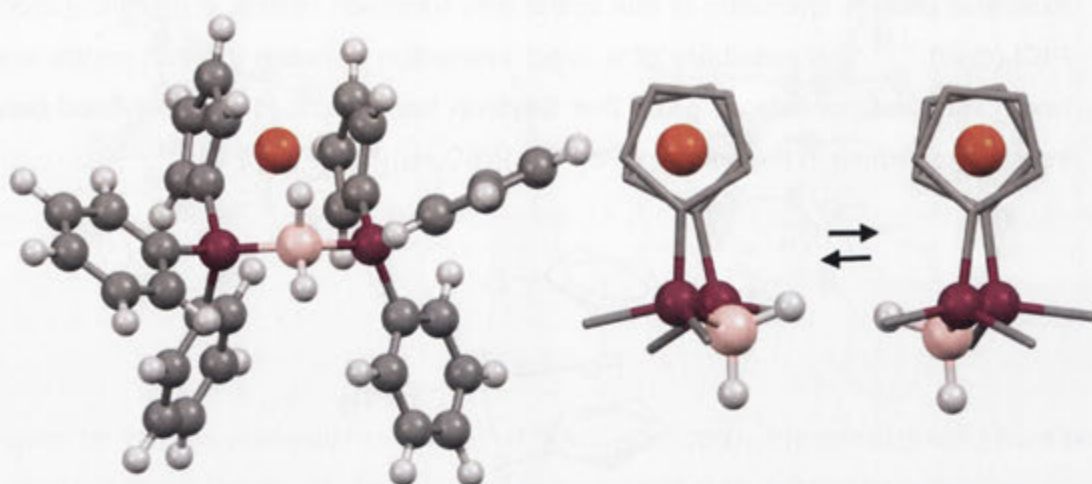


Figure 22: The geometry optimised structure of the ferrocenophane boronium cation $[\text{H}_2\text{B}(\text{dppf})]^+$ and the potential inversion of its geometry.

As would be expected given the polarity of the matrix, the ESI-MS analysis of both the monosubstituted and ferrocenophane revealed an isotopic envelope at m/z 567.1 corresponding to $[\text{H}_2\text{B}(\text{dppf})]^+$. However, in the monosubstituted spectrum, an envelope at m/z 763.3 also established the presence of the disubstituted species plus sodium, $[\text{dppf} \cdot \text{BH}_2\text{Br} + \text{Na}]^+$, most likely due to scrambling of the BH_2Br substituent under the MS conditions, a process not observed for the ferrocenophane salt.

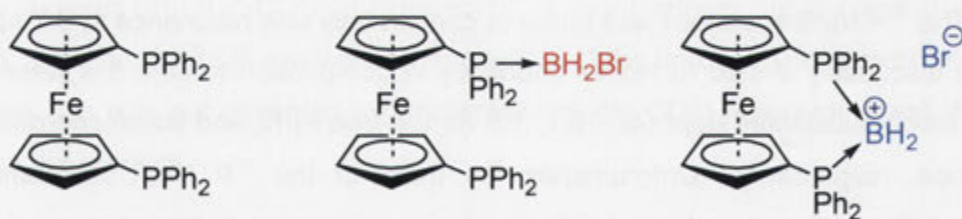


Figure 23: The structures of dppf (left), the monosubstituted $\text{dppf} \cdot \text{BH}_2\text{Br}$ (middle) and the ring-closed boronium salt, $[\text{H}_2\text{B}(\text{dppf})]\text{Br}$ (right).

5.8. Conclusion

At the beginning of chapter 4, ^{11}B NMR data for $[\text{H}_2\text{B}(\text{PH}_2\text{R})_2]\text{Br}$ (where $\text{R} = \text{Cy}$, Mes), $[\text{H}_2\text{B}(\text{PHRR}')_2]\text{Br}$ (where $\text{R} = \text{R}' = \text{Ph}$, Cy and $\text{R} = \text{Et}$, $\text{R}' = \text{Ph}$) and

$[\text{H}_2\text{B}(\text{PRR}'_2)_2]\text{Br}$ (where $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$) were shown to span a narrow range (-35 to -45 ppm) despite considerable differences in the electronic and steric properties of the phosphine substituents. In contrast, the ^{31}P NMR data for these compounds, whilst exhibiting the general trend of shifting to higher frequencies due to increased coordination number, varied considerably, reflecting the differing steric and electronic natures of the phosphine substituents.

Unsurprisingly, the solid-state structures of these boronium compounds also displayed some related trends that were reflected in the NMR analyses (Table 2). Undoubtedly the most interesting property of the collective solid-state data for all the boronium compounds is the very narrow range of P-B bond lengths, often within the limits of statistical significance.[§] The similarity of the P-B bond lengths, despite the greatly varying electronic and steric nature of the substituents on the phosphines, the coordination to BH_2 or BHBr groups, and the cyclic or acyclic nature of these species, is quite remarkable. This indicates that the P-B bond was always of comparable strength and not especially responsive to the environment at either the boron or phosphorus atoms.

The P-B-P bond angles (and P-B-N angles for the two amphos species), however, were more responsive to the steric effects of the phosphine substituents and also reflected the geometrical constraints of chelation for cyclic examples, with the smallest being observed for $[\text{H}_2\text{B}(\text{dppe})]\text{Br}$ ($98.6(2)^\circ$) and other cyclic boronium salts falling in the range $98\text{--}112^\circ$. In contrast, acyclic boronium salts were found to adopt P-B-P angles within the range $110\text{--}117^\circ$, with the largest being found for $[\text{H}_2\text{B}(\text{arphos})_2][\text{AsF}_6]$ ($117.1(2)^\circ$).

A few anomalies were found to be present in the general trends. The acyclic $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$ species, the only solid-state example of a boronium salt with two primary phosphine substituents, had an unusually large value of $117.0(2)^\circ$ despite the bulky cyclohexyl groups in principle being able to avoid one another. The significant differences in P-B-P bond angle between $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ ($112.4(1)^\circ$) and $[\text{H}_2\text{B}(\text{PHCy}_2)_2][\text{SbF}_6]$ ($115.9(3)^\circ$), and between $[\text{H}_2\text{B}(\text{arphos})_2]\text{Br}$ ($115.0(2)^\circ$) and $[\text{H}_2\text{B}(\text{arphos})_2][\text{AsF}_6]$ ($117.1(2)^\circ$), indicates that inter-ionic interactions, *e.g.*, hydrogen bonding, may play a role in determining the angle at boron.

[§] A 6σ tolerance was used to compare crystallographic bonds lengths and angles.

Table 2: Solid-state data of P-B-P angles and average P-B bond lengths for all boronium salts synthesised, sorted by increasing P-B-P angle (angles in degrees, °; bond lengths in angstroms, Å).

	P-B-P (°)	Average P-B (Å)
[H ₂ B(dppe)]Br	98.6(2)	1.944(6)
[BrHB(amphos)]Br	100.3(2)*	1.946(4)
[BrHB(dcpe)]Br	101.0(2)	1.958(6)
[H ₂ B(amphos)]Br	101.1(2)*	1.947(2)
[H ₂ B(dcpe)]Br	101.2(2)	1.944(5)
[RhBr _{0.43} Cl _{1.57} Cp*(H ₂ B{triphos})][SbF ₆]	107.3(2)	1.916(7)
[RhCl(η^4 -COD)(H ₂ B{triphos})][AsF ₆] (1)	107.9(3)	1.94(1)
[RhCl(η^4 -COD)(H ₂ B{triphos})][AsF ₆] (2)	108.7(2)	1.933(6)
[H ₂ B(triphos)][AsF ₆]	110.7(3)	1.92(1)
[H ₂ B(PHPh ₂) ₂]Br	111.0(2)	1.926(3)
[H ₂ B(triphos)]Br	111.2(2)	1.927(6)
[RhCl ₂ Cp*(H ₂ B{triphos})][AsF ₆]	111.2(9)	1.90(2)
[H ₂ B(PHCy ₂) ₂]Br	112.4(1)	1.932(3)
[H ₂ B(arphos) ₂]Br	115.0(2)	1.928(6)
[H ₂ B(PMe ₂ Ph) ₂]Br	115.1(2)	1.921(5)
[H ₂ B(PMe ₂ Ph) ₂][AsF ₆]	115.2(3)	1.923(8)
[H ₂ B(PHCy ₂) ₂][SbF ₆]	115.9(3)	1.923(8)
[H ₂ B(PH ₂ Cy) ₂]Br	117.0(2)	1.918(2)
[H ₂ B(arphos) ₂][AsF ₆]	117.1(2)	1.927(6)

In conclusion, an extensive library of boronium salts has been compiled and structurally characterised. The ease and high purity of boronium salts synthesised from two equivalents of a secondary or primary phosphine and BH₂Br·SMe₂ made them ideal starting materials. Unfortunately these boronium salts were found to possess low reactivity and were therefore deemed unsuitable for further synthesis. This led to a second generation of boronium salts that involved utilising the differing σ -basicity between phosphine and arsine groups to selectively coordinate to the boron

* A P-B-N angle.

substituent *via* the phosphine, leaving the arsine groups free for further synthesis. However, the resulting stabilised mixed haloboranes bearing a pendant arsine group were found to decompose *via* the loss of the boron substituent upon exposure to various metal reagents. A larger analogue bearing two pendant arsine groups and a boronium centre, less reactive than a neutral mixed haloborane adduct, was found to coordinate to organometallic precursors in the desired fashion, but the products of these reactions were found to have very poor solubility and therefore were difficult to characterise.

The increased functionalisation of synthesising boronium salts bearing a bromine atom on the boron offered a potential site at which subsequent manipulations could be envisaged. However, the synthesis of such BHB_r boronium species from BHB_r·SMe₂ presented new difficulties as compared to the straightforward synthesis of the BH₂ boronium species. As a result, only a small number of BHB_r boronium salts could be produced, and only one of them ([BrHB(amphos)]Br) could be adequately isolated and handled.

The use of the triphosphine species 'triphos' in reaction with BHB₂·SMe₂ was found to yield a boronium salt that also possessed a pendant phosphine arm that could act as a tether to metal centres. However, the resulting bromide counterion readily underwent halogen exchange with M-Cl atoms on the organometallic precursors, which complicated the recovered products of these reactions. When the bromide anion was replaced by non-coordinating anions such as [AsF₆]⁻, the halogen exchange process was eliminated and the desired products could be isolated cleanly. This enabled [RhCl₂Cp*(H₂B{triphos})][AsF₆], [RuCl₂(η⁶-cymene)(H₂B{triphos})][AsF₆] and [RhCl(η⁴-COD)(H₂B{triphos})][AsF₆] to be synthesised from [H₂B(triphos)][AsF₆] with the respective transition metal chloro-bridged dimer. While none of these species exhibited a direct metal-boron interaction, they did confirm that metal centres could exist in the presence of the boronium substituent without decomposing. Future investigations of [H₂B(triphos)][AsF₆] with organometallic precursors would most likely focus on substrates that offer more than one vacant coordination site.

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Chapter 6

Experimental

6.1 General Procedures

All manipulations were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk, vacuum-line, and inert-atmosphere drybox (argon) techniques, with dried and degassed solvents which were distilled from either calcium hydride (CH_2Cl_2), magnesium metal (alcohols) or sodium and benzophenone (ethers and paraffins). NMR spectra were obtained at 25°C on an Inova 300 spectrometer (^1H at 299.94 MHz, ^{13}C at 75.42 MHz, ^{11}B at 96.23 MHz, ^{19}F at 282.23 MHz, ^{31}P at 121.42 MHz), a Mercury 400 spectrometer (^1H at 399.87 MHz, ^{13}C at 100.56 MHz, ^{31}P at 161.87 MHz), a Bruker 400 spectrometer (^1H at 400.14 MHz and ^{13}C at 100.63 MHz, ^{11}B at 128.38 MHz, ^{31}P at 161.97 MHz) and an Inova 500 spectrometer (^1H at 500.04 MHz, ^{13}C at 125.75 MHz). Chemical shifts are quoted in ppm relative to external SiMe_4 (^1H , ^{13}C), H_3PO_4 (^{31}P), $\text{BF}_3\cdot\text{Et}_2\text{O}$ (^{11}B) or C_6F_6 (^{19}F) references with n-bond couplings between nuclei A and B, $^nJ_{\text{AB}}$, being quoted in Hz. 't' refers to virtual triplet resonances observed for *trans*-bis(phosphine) complexes with apparent J_{PC} and J_{PH} couplings indicated. It should be noted that due to the 3/2 spin of NMR active ^{11}B , the resulting spectra are naturally broad and B-H coupling is commonly not resolved. ^{11}B - ^1H coupled spectra are only reported here if couplings were reliably resolved. The B-H signals are also rarely observed in ^1H NMR spectra, owing to the ^{11}B coupling that causes the peaks to be especially broad, and as such will not be reported here. Spectra of NMR active ^{31}P nuclei bonded to ^{11}B also experience quadrupolar broadening of their signals, which can often cause imprecise coupling values; in these cases an average value is reported and stated as such. Elemental microanalysis was performed by the microanalytical service of the Australian National University and unless otherwise noted, samples were dried for a prolonged period *in vacuo*. Electrospray (ESI) mass spectrometry was performed by the Research School of Chemistry mass spectrometry service, and unless otherwise stated, the accurate mass data are reported for the most abundant isotopomer. For salts, $[\text{M}]^+$ and $[\text{M}]^-$ refer to the *cationic* and *anionic* component of the salt respectively. Typically a sample was dissolved in dichloromethane and then diluted with methanol or acetonitrile immediately before being analysed. X-ray crystallographic data were collected with a Nonius Kappa CCD diffractometer, an Agilent Xcalibur CCD diffractometer or an Agilent SuperNova CCD diffractometer. Data was extracted using the Denzo (Nonius) or CrysAlis (Agilent) packages, with structure solutions being solved by direct methods (SIR92, Superflip)

using the CRYSTALS program package. The compounds TiTp^* ,¹ $\text{fac-Mo}(\kappa^1\text{-dppm})(\kappa^2\text{-dppm})(\text{CO})_3$,² $[\text{NEt}_4]_2[\text{Fe}_2(\text{CO})_8]$,³ $\text{Mo}(\text{CO})_4(\text{pip})_2$,⁴ $\text{P}(\text{Ph})(\text{CH}_2\text{CH}_2\text{AsPh}_2)_2\text{CH}_2$,⁵ $\text{Mo}(\text{CO})_4(\text{PPh}_2)_2$,⁶ $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$,⁷ $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$,⁸ $\text{Ru}(\text{E-CH=CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$,⁹ $\text{Rh}_2(\mu\text{-Cl})_2(\eta^4\text{-COD})_2$,¹⁰ $\text{Ir}_2(\mu\text{-Cl})_2(\eta^2\text{-COE})_4$,¹¹ $\text{K}[\text{Tp}^*]$,¹² $\text{RhCl}(\text{PPh}_3)_3$,¹³ $\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2\text{Cp}^*_2$,¹⁴ $\text{Ru}(\text{H})\text{Cl}(\text{CO})(\text{PPh}_3)_3$,¹⁵ $\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2(\eta^6\text{-cymene})_2$,¹⁶ $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$,¹⁷ $\text{Ru}(\text{C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2$,¹⁷ $\text{Ru}(\text{H})(\text{S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2$,¹⁸ $\text{Ru}(\text{H})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2$,¹⁸ $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$,^{19, 20} $\text{K}[\text{PhC}\equiv\text{CBF}_3]$,²¹ $\text{K}[\text{Me}_3\text{SiC}\equiv\text{CBF}_3]$,^{21, 22} were synthesised according to reported procedures. The compounds $\text{K}[\text{Tp}]$ and $\text{K}[\text{Tp}^*]$ were prepared by Mr Stephen Lee, and PH_2Mes by Mr Horst Neumann. All other reagents were used as received from commercial sources.

6.2 BMIDA complexes

Synthesis of $\text{Ru}(\text{H})(\text{C}\equiv\text{CBMIDA})(\text{CO})_2(\text{PPh}_3)_2$: A DCM (2 mL) suspension of $\text{Ru}(\text{C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2$ (0.071 g, 0.10 mmol) and ethynyl-BMIDA (0.018 g, 0.1 mmol) was stirred for 15 min, though the yellow solution turned colourless after approximately 3 minutes. All volatiles removed under high vacuum to leave a colourless solid. The solid was extracted with THF (2 mL), followed by extraction with DCM (2 mL), *via* cannula filtration, then all volatiles removed under high vacuum to leave a very pale khaki coloured solid. The compound was recrystallised from a mixture of DCM/pentane at -15°C over 72 h to produce X-ray diffraction quality colourless crystals of two different habits. Yield: 0.086 g (0.1 mmol, 100%). Anal. Found: C, 55.52; H, 4.31; N, 3.54%. Calcd for $\text{C}_{45}\text{H}_{38}\text{BNO}_6\text{P}_2\text{Ru}$: C, 62.66; H, 4.44; N, 1.62%.[§] NMR (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = -5.87$ (t, $^2J_{\text{PH}} 20.0$ Hz, 1H, RuH), 1.80 (s, 3H, NMe), 2.77 (d, $^2J_{\text{HH}} 16.2$ Hz, 2H, CH_2), 3.21 (d, $^2J_{\text{HH}} 15.9$ Hz, 2H, CH_2), 7.35-7.77 (m, 30H, C_6H_5); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = 4.7$; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 45.0$. Acc. Mass: Found: $m/z = 902.0953$. Calcd for $\text{C}_{45}\text{H}_{38}^{11}\text{BKNO}_6\text{P}_2^{102}\text{Ru}$ 902.0948 $[\text{M} + \text{K}]^+$. ESI-MS(+ve ion): $m/z = 886.1$ $[\text{M} + \text{Na}]^+$, 724.3 $[\text{M} + \text{NCMe} - \text{C}\equiv\text{CBMIDA}]^+$. IR (DCM): ν_{CO} 1773, 1988, 2032, 2081 (ν_{CC}) cm^{-1} .[†] *Crystal data*: $\text{C}_{45}\text{H}_{38}\text{BNO}_6\text{P}_2\text{Ru} \cdot 0.3(\text{CH}_2\text{Cl}_2)$, $M_r = 888.11$, $T = 200(2)$ K, triclinic, space

[§] Satisfactory microanalysis could not be obtained, most likely due to the reversible nature of insertion of the ruthenium into the terminal alkyne.

[†] ν_{RuH} was not unequivocally identified due most likely to coupling of the ν_{CO} and ν_{CC} oscillators.

group *P*-1 (No.2), $a = 12.2088(3)$, $b = 19.7555(4)$, $c = 21.8833(5)$ Å, $\alpha = 64.8712(13)$, $\beta = 79.6801(12)$, $\gamma = 89.3128(15)^\circ$, $V = 4689.03(19)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.258$ Mgm⁻³, $\mu(\text{Mo K}\alpha) 0.48$ mm⁻¹, colourless prism, $0.05 \times 0.09 \times 0.32$ mm, 56843 measured reflections with $2\theta_{\text{max}} = 50.0^\circ$, 16497 independent reflections, 16489 absorption-corrected data used in F^2 refinement, 1036 parameters, no restraints, $R_1 = 0.070$, $wR_2 = 0.210$ for 10632 reflections with $I > 2\sigma(I)$. *Crystal data*: C₄₅H₃₈BNO₆P₂Ru, $M_r = 862.63$, $T = 200(2)$ K, triclinic, space group *P*-1 (No.2), $a = 12.2188(4)$, $b = 18.0463(5)$, $c = 21.6354(4)$ Å, $\alpha = 107.8448(17)$, $\beta = 94.2812(15)$, $\gamma = 100.3671(14)^\circ$, $V = 4423.9(2)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.295$ Mgm⁻³, $\mu(\text{Mo K}\alpha) 0.47$ mm⁻¹, colourless block, $0.08 \times 0.12 \times 0.17$ mm, 55677 measured reflections with $2\theta_{\text{max}} = 50.2^\circ$, 15711 independent reflections, 15704 absorption-corrected data used in F^2 refinement, 1233 parameters, 502 restraints, $R_1 = 0.049$, $wR_2 = 0.115$ for 10192 reflections with $I > 2\sigma(I)$.

Alternate Synthesis of Ru(H)(C≡CBMIDA)(CO)₂(PPh₃)₂: A DCM (4 mL) suspension of Ru(CO)₂(PPh₃)₃ (0.094 g, 0.10 mmol) and ethynyl-BMIDA (0.020 g, 0.11 mmol) was stirred for 15 min, though the yellow solution turned very pale yellow after approximately 3 minutes. The product was isolated as described above. Yield: 0.045 g (0.052 mmol, 52%). IR (DCM): ν_{CO} 1773, 1984, 2033 cm⁻¹.

Synthesis of RuCl(C≡CBMIDA)(CO)₂(PPh₃)₂: A CHCl₃ (8 mL, 100 mmol) suspension of Ru(CO)₂(PPh₃)₃ (0.094 g, 0.1 mmol) and ethynyl-BMIDA (0.018 g, 0.1 mmol) was stirred for 2 h. Initially upon partial dissolution a yellow colour developed, but was rapidly lost (for the most part) after ~1 min of stirring. Pet. ether 60-80°C (~10 mL) was added to fully precipitate a beige solid that was collected by filtration, and then washed with pet. ether 60-80°C (~4 mL) and EtOH (~10 mL). The solid was further dried on the sinter for 10 min. The compound was found to be only partially soluble in most common solvents. Yield: 0.030 g (0.033 mmol, 33%). NMR (CDCl₃, 25°C): ¹H: $\delta_{\text{H}} = 3.08$ (d, ⁴ J_{HH} 3.6 Hz, 3H, NMe), 3.73 (dd, ² J_{HH} /⁴ J_{HH} 16.4/3.8 Hz, 2H, CH₂), 3.80 (dd, ² J_{HH} /⁴ J_{HH} 16.4/4.0 Hz, 2H, CH₂), 7.39 (m, 18H, C₆H₅), 7.92 (m, 12H, C₆H₅); ¹¹B{¹H}: $\delta_{\text{B}} = 5.5$; ³¹P{¹H}: $\delta_{\text{P}} = 17.7$. No identifiable peaks were observed by mass spectroscopy. ESI-MS (+ve ion): $m/z = 836.2$ [M - Cl - CO - H]⁺, 807.1, 737.2, 696.1. IR (DCM): ν_{CO} 1775, 1995, 2058, 2080 (ν_{CC}) cm⁻¹; IR (KBr Plate): ν_{CO} 1775, 1992, 2056, 2082 (ν_{CC}) cm⁻¹. A sample partially dissolved in acetone was sonicated for 5 min, then left to stand

as pentane vapour was allowed to diffuse into the mixture at 25°C for 96 h to give X-ray diffraction quality colourless needles of the compounds and $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ (*vide infra*). Crystal data for $\text{HC}\equiv\text{CBMIDA}$: $\text{C}_7\text{H}_8\text{BNO}_4$, $M_r = 180.96$, $T = 200(2)$ K, monoclinic, space group $P2_1/n$, $a = 6.2422(5)$, $b = 11.9040(11)$, $c = 11.5004(9)$ Å, $\beta = 90.726(4)^\circ$, $V = 854.49(12)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.407$ Mgm⁻³, $\mu(\text{Mo K}\alpha) 0.11$ mm⁻¹, colourless prism, $0.05 \times 0.08 \times 0.20$ mm, 7616 measured reflections with $2\theta_{\text{max}} = 50.2^\circ$, 1509 independent reflections, 1504 absorption-corrected data used in F^2 refinement, 119 parameters, 24 restraints, $R_1 = 0.072$, $wR_2 = 0.194$ for 807 reflections with $I > 2\sigma(I)$. Crystal data for $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ (Unit cell determination): $\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{O}_2\text{P}_2\text{Ru}$, $T = 150(2)$ K, monoclinic, space group $P2_1/n$, $a = 10.41$, $b = 25.49$, $c = 12.53$ Å, $\beta = 100.24^\circ$, $V = 3272$ Å³.²³

Synthesis of $[\text{RuCl}(\text{C}\equiv\text{CHBMIDA})(\text{dppe})_2][\text{PF}_6]$: A DCM (4 mL) suspension of $[\text{RuCl}(\text{dppe})_2][\text{PF}_6]$ (0.040 g, 0.04 mmol) and ethynyl-BMIDA (0.007 g, 0.04 mmol) was sonicated for 30 min, then stirred for 3 days during which time the reagents dissolved to afford a dark red solution. All volatiles were removed under high vacuum to leave a light red solid. The solid was recrystallised from a mixture of DCM/pentane to give a pale orange/red coloured solid. Slow recrystallisation of the solid in DCM/pentane over 72 h produced X-ray diffraction quality pale yellow/orange crystals. Yield: 0.033 g (0.026 mmol, 71%). Anal. Found: C, 54.24; H, 4.47; N, 1.23%. Calcd for $\text{C}_{59}\text{H}_{56}\text{BClNO}_4\text{P}_5\text{Ru}\cdot\text{CH}_2\text{Cl}_2$: C, 53.61; H, 4.35; N, 1.04%. The crystallographic structural determination indicated a monosolvate, however, the elemental microanalytical data for the bulk sample dried under high vacuum suggest partial desolvation: Calcd for $\text{C}_{59}\text{H}_{56}\text{BClNO}_4\text{P}_5\text{Ru}\cdot 0.75(\text{CH}_2\text{Cl}_2)$: C, 54.24; H, 4.38; N, 1.06%. NMR (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 2.01$ (s.br, 3H, NMe), 2.74 (m.br, 4H, PCH₂), 2.98 (m.br, 4H, PCH₂), 3.08 (s, 1H, C=CH), 3.33 (m.br, 2H, NCH₂), 3.75 (m.br, 2H, NCH₂), 6.99–7.51 (m, 40H, C₆H₅); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = 6.7$; $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 29.16$ (m, PCH₂), 29.96 (m, PCH₂), 46.27 (NCH₃), 61.60 (NCH₂), 127.98 (C₆H₅), 128.21 (C₆H₅), 128.77 (C₆H₅), 129.12 (C₆H₅), 130.59 (C₆H₅), 131.00 (C₆H₅), 131.59 [d, $^1J_{\text{CP}} 55.7$ Hz, C¹(C₆H₅)], 133.24 (C₆H₅), 134.13 [d, $^1J_{\text{CP}} 61.2$ Hz, C¹(C₆H₅)], 134.16 (C₆H₅), 166.76 [OC(O)], 334.7 [quin, $^2J_{\text{PC}} = 10.2$ Hz, Ru=C]; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -143.8$ (hept, $^1J_{\text{PF}} 711$ Hz, PF₆), 45.5 (dppe). ESI-MS (+ve ion): $m/z = 1119.2$ [M + NMe - Cl - H]⁺, 899.1 [M - Cl - C≡CHBMIDA]⁺. IR (KBr Plate): $\nu_{\text{Ru}=\text{C}} 1636$, $\nu_{\text{CO}} 1774$ cm⁻¹. Crystal data:

[C₅₉H₅₆BCINO₄P₄Ru][PF₆].CH₂Cl₂, $M_r = 1344.22$, $T = 200(2)$ K, triclinic, space group *P*-1 (No.2), $a = 13.1367(8)$, $b = 14.1164(8)$, $c = 16.2360(7)$ Å, $\alpha = 86.068(3)$, $\beta = 73.777(3)$, $\gamma = 87.542(3)^\circ$, $V = 2883.3(3)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.548$ Mgm⁻³, $\mu(\text{Mo K}\alpha) 0.62$ mm⁻¹, pale yellow plate, $0.05 \times 0.10 \times 0.17$ mm, 41835 measured reflections with $2\theta_{\text{max}} = 50.2^\circ$, 10207 independent reflections, 10204 absorption-corrected data used in F^2 refinement, 730 parameters, no restraints, $R_1 = 0.058$, $wR_2 = 0.148$ for 6573 reflections with $I > 2\sigma(I)$.

Synthesis of RuCl(C≡CBMIDA)(dppe)₂: To a DCM (4 mL) solution of [RuCl(=C=CHBMIDA)(dppe)₂][PF₆] (0.033 g, 0.026 mmol) was added a large excess of NEt₃ (~0.1 mL, 0.037 mmol) and stirred for 1 h, after which time the red solution was much paler. Left to settle for 30 min to give a yellow coloured precipitate that was isolated by cannula filtration. The yellow solid was washed with DCM (2 mL) and dried under high vacuum for 30 min. The compound was found to have poor solubility in common solvents which prevented satisfactory ¹H NMR, ¹³C NMR spectra from being obtained. Yield: 0.017 g (0.015 mmol, 59%).[§] Anal. Found: C, 60.41; H, 4.71; N, 1.44%. Calcd for C₅₉H₅₅BCINO₄P₄Ru.0.5([NHET₃][PF₆]): C, 60.20; H, 5.13; N, 1.70%. NMR (CDCl₃, 25°C): ¹B{¹H}: $\delta_B = 5.4$; ³¹P{¹H}: $\delta_P = 47.8$. Acc. Mass: Found: $m/z = 1119.2485$. Calcd for C₆₁H₅₈¹¹BKN₂O₄P₄¹⁰²Ru 1119.2484 [M + NCM_e - Cl]⁺. IR (DCM): ν_{CO} 1745, 1773, 2023 (ν_{CC}) cm⁻¹; IR (KBr Plate): ν_{CO} 1750, 2024 (ν_{CC}) cm⁻¹. In an attempt to remove the presumed ammonium salt contaminant, the yellow solid was washed with dry EtOH (4 mL), followed by dry hexane (4 mL) and dried under high vacuum to leave a yellow solid, which was however found to comprise of an unknown complex, along with a small amount of [RuCl(C≡CBMIDA)(dppe)₂]⁺ due to reprotonation of RuCl(C≡CBMIDA)(dppe)₂ by the alcohol. NMR (CDCl₃, 25°C): ¹B{¹H}: $\delta_B = 9.0$; ³¹P{¹H}: $\delta_P = 37.5, 45.4$ ([RuCl(C≡CBMIDA)(dppe)₂]⁺).

Synthesis of Ru(CH=CHBMIDA)Cl(CO)(PPh₃)₂: Method A: A DCM (10 mL) suspension of Ru(H)Cl(CO)(PPh₃)₃ (0.20 g, 0.21 mmol) and ethynyl-BMIDA (0.040 g, 0.22 mmol) was stirred for 30 min, during which the pale pink suspension changed to a brown solution. The product was precipitated out by the addition of hexane (60 mL) to

[§] Yield calculated including the ammonium salt contaminant suggested by the microanalytical data obtained.

give a mustard coloured solid. The solid was recrystallised from a mixture of DCM/Et₂O, then isolated by cannula filtration, washed with further Et₂O and dried *in vacuo*. Yield: 0.078 g (0.09 mmol, 42%). **Method B:** A DCM (400 mL) suspension of RuHCl(CO)(PPh₃)₃ (8.20 g, 8.61 mmol) and ethynyl-BMIDA (1.56 g, 8.62 mmol) was stirred for 45 min. After several minutes stirring the pale pink suspension changed to a brown solution. The product was precipitated out of solution with the addition of petroleum ether 40-60°C (1.5 L) to give a mustard coloured solid that was left to settle overnight. Precipitate isolated by filtration through a sinter, and then further washed with Et₂O (200 mL). The solid was dissolved in DCM (600 mL) and precipitated out of solution with Et₂O (3.25 L). The precipitate found to be too fine to collect on a sinter or Buchner funnel, therefore it was collected by gravity filtration over 24 h, followed by a further 3 days to air dry on the filter paper. Yield: 0.995 g (1.14 mmol, 13%). Anal. Found: C, 58.75; H, 4.53; N, 1.84%. Calcd for C₄₄H₃₉BClNO₅P₂Ru.0.5(CH₂Cl₂): C, 58.51; H, 4.41; N, 1.53%. NMR (CDCl₃, 25°C): ¹H: δ_H = 2.09 (s, 3H, NMe), 3.09 (d, ²J_{HH} 16.0 Hz, 2H, CH₂), 3.44 (d, ²J_{HH} 16.4 Hz, 2H, CH₂), 5.09 (d, ³J_{HH} 13.6 Hz, 1H, CH=CHBMIDA), 7.36-7.43 (m, 20H, C₆H₅), 7.50-7.52 (m, 10H, C₆H₅), 8.56 (d, ³J_{HH} 13.6 Hz, 1H, CH=CHBMIDA); ¹¹B{¹H}: δ_B = 5.8; ¹³C{¹H}: δ_C = 53.23 (quin, NMe), 61.12 (NCH₂), 128.66 (C₆H₅), 130.51 (C₆H₅), 132.06 (m, C₆H₅), 134.35 (C₆H₅), 167.23 [OC(O)], 177.70 (as determined by 2D HSQC, RuCH); ³¹P{¹H}: δ_P = 32.0. NMR (D₈-THF, 25°C): ¹H: δ_H = 2.16 (s, 3H, NMe), 3.16 (d, ²J_{HH} 16.5 Hz, 2H, CH₂), 3.69 (d, ²J_{HH} 16.5 Hz, 2H, CH₂), 5.10 (d, ³J_{HH} 12.9 Hz, 1H, CH=CHBMIDA), 7.30-7.45 (m, 20H, C₆H₅), 7.54-7.61 (m, 10H, C₆H₅), 8.44 (d, ³J_{HH} 12.9 Hz, 1H, CH=CHBMIDA); ¹¹B{¹H}: δ_B = 5.8; ¹³C{¹H}: δ_C = 54.9 (NMe), 61.61 (NCH₂), 129.01 (C₆H₅), 130.79 (C₆H₅), 133.03 [d, ¹J_{CP} 65.5 Hz, C¹(C₆H₅)], 135.27 (C₆H₅), 168.12 [OC(O)]; ³¹P{¹H}: δ_P = 31.6. The complex was shown to coordinate acetonitrile (*vide infra*), *i.e.*, the matrix employed for ESI-MS. Acc. Mass: Found: *m/z* = 877.1707. Calcd for C₄₆H₄₂¹¹BN₂O₅P₂¹⁰²Ru 877.1706 [M + NCM_e - Cl]⁺. ESI-MS(+ve ion): *m/z* = 836.3 [M - Cl]⁺. IR (DCM): ν_{CO} 1774, 1930 cm⁻¹; IR (KBr Plate): ν_{CO} 1743, 1766, 1921 cm⁻¹. A minor isomer was observed in the crude product mixture which was removed during purification but was not independently isolated. NMR (CDCl₃, 25°C): ¹H: δ_H = 5.57 (d, ³J_{HH} 20.0 Hz, 1H, CH=CHBMIDA), 8.28 (d, ³J_{HH} 19.6 Hz, 1H, CH=CHBMIDA); ³¹P{¹H}: δ_P = 22.6. Attempts to obtain crystallographic grade crystals of the major product by vapour diffusion of pentane into THF (aerobic) over several days instead gave sufficient yellow

co-crystals of $\text{Ru}(\text{O}_2\text{C}-E\text{-CH=CHX})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ($X = \text{Cl}_{0.8}\text{H}_{0.2}$) for diffractometry and mass spectrometry. ESI-MS (+ve ion): $m/z = 857$ $[\text{M} + \text{NCMe} + \text{Na}]^+$. Crystal data: $\text{C}_{40}\text{H}_{32.2}\text{Cl}_{1.8}\text{O}_3\text{P}_2\text{Ru}$, $M_r = 787.73$, $T = 200(2)$ K, monoclinic, space group $C2/c$, $a = 17.0407(5)$, $b = 11.2086(3)$, $c = 19.6906(5)$ Å, $\beta = 103.4013(14)^\circ$, $V = 3658.54(17)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.430$ Mg m⁻³, $\mu(\text{Mo K}\alpha) 0.68$ mm⁻¹, yellow lath, $0.05 \times 0.10 \times 0.45$ mm, 38624 measured reflections with $2\theta_{\text{max}} = 55.0^\circ$, 4212 independent reflections, 4210 absorption-corrected data used in F^2 refinement, 245 parameters, no restraints, $R_1 = 0.047$, $wR_2 = 0.097$ for 2306 reflections with $I > 2\sigma(I)$.

Synthesis of $\text{Ru}(\text{CH=CHBMIDA})\text{Cl}(\text{NCMe})(\text{CO})(\text{PPh}_3)_2$: Dissolution of $\text{Ru}(\text{CH=CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (0.105 g, 0.12 mmol) in NCMe (4 mL) resulted in the formation of a dull grey suspension that was stirred overnight, which was then left to settle. The precipitate was isolated by cannula filtration, then washed with hexane (4 mL) and dried under high vacuum for 2 h. Yield: 0.024 g (0.026 mmol, 22%). The complex is prone to elimination of acetonitrile both as a solid and in solvents other than acetonitrile to regenerate the precursor. Anal. Found: C, 59.66; H, 4.67; N, 4.06%. Calcd for $\text{C}_{48}\text{H}_{45}\text{BClN}_3\text{O}_5\text{P}_2\text{Ru}$: C, 60.48; H, 4.76; N, 4.41%. NMR (CDCl_3 , 25°C): $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 22.4, 25.6, 34.0, 41.3, 51.8$. ESI-MS (+ve ion): $m/z = 877.2$ $[\text{M} - \text{Cl}]^+$, 656.1 $[\text{RuH}(\text{PPh}_3)_2]^+$. IR (KBr Plate): $\nu_{\text{CO}} 1757, 1923$ cm⁻¹.

Synthesis of $\text{Ru}(\text{CH=CHBMIDA})\text{Cl}(\text{CNMe}_3)(\text{CO})(\text{PPh}_3)_2$: A DCM (2 mL) suspension of $\text{Ru}(\text{CH=CHBMIDA})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (0.052 g, 0.06 mmol) and CNMe₃ (0.009 g, 0.06 mmol) was stirred for 8 h, with a colour change to a dark brown/black solution being observed immediately upon dissolution. The reaction was layered with hexane overnight to give a brown solid that was isolated by cannula filtration and dried *in vacuo*. Yield: 0.049 g (0.048 mmol, 80%). Anal. Found: C, 63.48; H, 4.99; N, 2.89%. Calcd for $\text{C}_{54}\text{H}_{50}\text{BClN}_2\text{O}_5\text{P}_2\text{Ru}$: C, 63.82; H, 4.96; N, 2.76%. NMR (CDCl_3 , 25°C): ^1H : $\delta_{\text{H}} = 1.96$ (s, 6H, $\text{C}_6\text{H}_2\text{Me-2,6}$), 2.09 (s, 3H, NMe), 2.25 (s, 3H, $\text{C}_6\text{H}_2\text{Me-4}$), 3.02 (d, $^2J_{\text{HH}} 16.0$ Hz, 2H, CH_2), 3.37 (d, $^2J_{\text{HH}} 16.0$ Hz, 2H, CH_2), 5.69 (d, $^3J_{\text{HH}} 20.0$ Hz, 1H, CHB), 6.74 (s, 2H, C_6H_2), 7.27 (m, 18H, C_6H_5), 7.59-7.62 (m, 12H, C_6H_5), 8.59 (dt, $^3J_{\text{HH}}/^3J_{\text{PH}} 20.0/2.6$ Hz, 1H, RuCH); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = 10.7$ (br); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 18.45$ $[\text{Me}^{2,6}(\text{C}_6\text{H}_2\text{Me}_3)]$, 21.24 $[\text{Me}^4(\text{C}_6\text{H}_2\text{Me}_3)]$, 45.68 (NMe), 61.27 (NCH₂), 125.33 (CHB), 127.91 [t, $J_{\text{CP}} 4.5$ Hz, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 128.30 [t, $^1J_{\text{CP}} 28.7$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], 129.71 $[\text{C}^4(\text{C}_6\text{H}_5)]$, 131.17 ($\text{C}_6\text{H}_2\text{Me}_3$), 133.62 [t, $J 5.1$ Hz, $\text{C}^1(\text{C}_6\text{H}_2\text{Me}_3)$], 133.93 ($\text{C}_6\text{H}_2\text{Me}_3$), 134.36 [d, $J_{\text{CP}} 4.0$ Hz,

$C^{3.5}(C_6H_5)$], 137.98 [$C^4(C_6H_2Me_3)$], 168.79 [OC(O)], 182.14 [t, $^2J_{CP}$ 13.8 Hz, RuCN], 200.80 (RuCO), α -carbon of vinyl could not be definitively assigned due to overlapping resonances; $^{31}P\{^1H\}$: $\delta_P = 24.9$. Acc. Mass: Found: $m/z = 1022.2598$. Calcd for $C_{56}H_{53}^{11}BKN_3O_5P_2^{102}Ru$ 1022.2597 [M + NCMe - Cl] $^+$. ESI-MS (+ve ion): $m/z = 1271.4$ [M + 2(CNMe) - Cl] $^+$, 1126.3 [M + CNMe - Cl] $^+$, 981.2 [M - Cl] $^+$. IR (DCM): ν_{CO} 1762, 1959, 2118 (ν_{CN}) cm^{-1} ; IR (KBr Plate): ν_{CO} 1762, 1952, 2117 (ν_{CN}) cm^{-1} .

Synthesis of $Ru(CH=CHBMIDA)Cl(CO)_2(PPh_3)_2$: Carbon monoxide was bubbled through a suspension of $Ru(CH=CHBMIDA)Cl(CO)(PPh_3)_2$ (0.052 g, 0.06 mmol) in DCM (4 mL) for approximately 5 min. Upon exposure to CO, the brown suspension changed to a darker brown solution, from which a white precipitate formed over 1 hour. The precipitate was allowed to settle, then separated by cannula filtration and washed with hexane (2 $\times$ 4 mL). The product was found to possess poor solubility in common solvents, which hindered subsequent analyses. Yield: 0.019 g (0.021 mmol, 35%). Anal. Found: C, 59.73; H, 4.39; N, 1.68%. Calcd for $C_{45}H_{39}BCINO_6P_2Ru$: C, 60.12; H, 4.37; N, 1.56%. NMR ($CDCl_3$, 25°C): 1H : $\delta_H = 2.11$ (s, 3H, NMe), 3.04 (d, $^2J_{HH}$ 16.0 Hz, 2H, CH₂), 3.40 (d, $^2J_{HH}$ 16.0 Hz, 2H, CH₂), 5.57 (d, $^3J_{HH}$ 19.6 Hz, 1H, CHB), 7.39 (m, 18H, C₆H₅), 7.74 (m, 12H, C₆H₅), 8.29 (d, $^3J_{HH}$ 19.6 Hz, 1H, RuCH); $^{11}B\{^1H\}$: not observed; $^{31}P\{^1H\}$: $\delta_P = 22.5$. Acc. Mass: Found: $m/z = 905.1643$. Calcd for $C_{47}H_{42}^{11}BKN_2O_6P_2^{102}Ru$ 905.1655 [M + NCMe - Cl] $^+$. ESI-MS(+ve ion): $m/z = 877.2$ [M + NCMe - Cl - CO] $^+$. IR (DCM): ν_{CO} 1763, 1974, 2037 cm^{-1} ; IR (KBr Plate): ν_{CO} 1762, 1966, 2032 cm^{-1} . Crystals, albeit on low quality, suitable for X-ray diffraction analysis were obtained by slow diffusion of head space CO into an undisturbed CH_2Cl_2 solution of $Ru(CH=CHBMIDA)Cl(CO)(PPh_3)_2$ in a narrow sample vial. The best crystal chosen diffracted poorly such that insufficient data were acquired to allow full anisotropic refinement of all atomic positions. The study nevertheless confirmed the geometry. Crystal data: $C_{45}H_{39}BCINO_6P_2Ru$, $M_r = 899.09$, $T = 150(2)$ K, triclinic, space group $P-1$ (No. 2), $a = 10.1224(5)$, $b = 17.350(1)$, $c = 26.591(3)$ Å, $\alpha = 88.449(7)$, $\beta = 89.008(6)$, $\gamma = 83.422(5)^\circ$, $V = 4637.0(6)$ Å³, $Z = 4$, $D_{calcd} = 1.288$ Mg m⁻³, $\mu(Cu K\alpha) 4.279$ mm⁻¹, colourless lath, 0.017 $\times$ 0.050 $\times$ 0.303 mm, 17,677 measured reflections with $2\theta_{max} = 144^\circ$, 17,182 independent absorption-corrected reflections used in F^2 refinement, 457 parameters, no restraints, $R_1 = 0.205$, $wR_2 = 0.419$ for 11,171 reflections with $I > 2\sigma(I)$.

Synthesis of Ru(CH=CHBMIDA)Tp(CO)(PPh₃): Method A: Under ambient conditions, a DCM (20 mL) suspension of Ru(H)Cl(CO)(PPh₃)₃ (0.381 g, 0.40 mmol) and ethynyl-BMIDA (0.080 g, 0.44 mmol) was stirred for 30 min. To the reaction mixture was added K[Tp] (0.121 g, 0.48 mmol), which was stirred for a further 30 min to give a green solution. An intermediate formulated as Ru(CH=CHBMIDA)(κ^2 -Tp)(CO)(PPh₃)₂ could be observed (NMR (CDCl₃, 25°C): ³¹P{¹H}: δ_P = 42.6, 47.0 (d x 2, ²J_{PP} 304 Hz)) but not isolated due to its spontaneous conversion to the desired product. The solution was filtered through a diatomaceous earth plug (~12 cm), followed by the removal of all volatiles under high vacuum to leave a pale green solid. The solid was recrystallised from a mixture of DCM/pet. ether 60-80°C and the off-white precipitate collected by filtration and washed with additional pet. ether 60-80°C. The solid was extracted with benzene and all volatiles removed to leave an off-white solid. Yield: 0.087 g (0.11 mmol, 28%). **Method B:** A DCM (2 mL) suspension of Ru(CH=CHBMIDA)Cl(CO)(PPh₃)₂ (0.052 g, 0.06 mmol) and K[Tp] (0.015 g, 0.06 mmol) was stirred for 15 min, with a colour change to a green/brown solution being observed immediately upon dissolution. Hexane (2 mL) was added to precipitate the KCl and stirred for 15 min, then filtered through a diatomaceous earth plug (~1 cm) to give a pale green solution. All volatiles removed under high vacuum to leave a pale green solid. Yield: 0.040 g (0.04 mmol, 64%). NMR (CDCl₃, 25°C): ¹H: δ_H = 2.61 (s, 3H, NMe), 3.53-3.66 (m, 4H, CH₂), 5.29 (d, ³J_{HH} 6.8 Hz, 1H, Tp), 5.78 (dd, ³J_{HH}/⁴J_{PH} 18.8/6.4 Hz, 1H, CHB), 5.84 (d, ³J_{HH} 4.0 Hz, 1H, Tp), 5.89 (d, ³J_{HH} 4.0 Hz, 1H, Tp), 6.05 (d, ³J_{HH} 3.2 Hz, 1H, Tp), 6.68 (d, ³J_{HH} 5.2 Hz, 1H, Tp), 6.79 (d, ³J_{HH} 4.8 Hz, 1H, Tp), 7.08-7.10 (m, 6H, C₆H₅), 7.24 (m, 6H, C₆H₅), 7.34 (m, 3H, C₆H₅), 7.54-7.67 (m, 3H, Tp), 8.55 (dd, ³J_{HH}/³J_{PH} 18.6/4.6 Hz, 1H, RuCH); ¹¹B{¹H}: δ_B = -3.9 (br, HBN₃), 5.50 (CBNO₂); ³¹P{¹H}: δ_P = 49.7. Acc. Mass: Found: *m/z* = 646.1227. Calcd for C₃₀H₂₈¹¹BN₇OP¹⁰²Ru 646.1230 [M + NMe - CH=CHBMIDA]⁺. ESI-MS(+ve ion): *m/z* = 867.2 [M + PPh₃ - CH=CHBMIDA]⁺, 764.2, 737.1, 696.1. IR (DCM): ν_{CO} 1770, 1939 cm⁻¹. The product

Intermediate product Ru(CH=CHBMIDA)(κ^2 -Tp)(CO)(PPh₃)₂: The complex was found to be present after 30 min of stirring following the addition of K[Tp]. NMR (CDCl₃, 25°C): ³¹P{¹H}: δ_P = 42.6 (d, ²J_{PP} 301.5 Hz), 47.0 (d, ²J_{PP} 306.5 Hz). The product was unstable in solution (benzene, acetone), decomposing entirely within 24 h to HC≡CBMIDA and presumably RuH(CO)(PPh₃)Tp. Data for HC≡CBMIDA: NMR (CDCl₃,

25°C): ^1H : $\delta_{\text{H}} = 2.49$ (s, 1H, C=CH), 3.11 (s, 3H, NMe), 3.79 (s, 4H, CH₂); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = 5.5$. ESI-MS (+ve ion): $m/z = 566.1$ [3(M) + Na]⁺, 385.0 [2(M) + Na]⁺, 220.0 [M + K]⁺, 204.1 [M + Na]⁺, 182.1 [M + H]⁺. IR (DCM): ν_{CO} 1774 cm⁻¹. *Crystal data* (Unit cell determination): HC=CBMIDA, $T = 150(2)$ K, monoclinic, space group $P2_1/n$, $a = 6.25$, $b = 11.89$, $c = 11.49$ Å, $\beta = 90.6^\circ$, $V = 853$ Å³.[§]

Synthesis of Ru(CH=CHBMIDA)(S₂CNEt₂)(CO)(PPh₃)₂: A DCM (2 mL) and MeOH (1 mL) solution of Ru(CH=CHBMIDA)Cl(CO)(PPh₃)₂ (0.052 g, 0.060 mmol) and [NH₂Et₂][S₂CNEt₂] (0.013 g, 0.060 mmol) was stirred for 10 min to give an orange/brown solution. The product was precipitated with hexane to give a light yellow solid that was collected on a sinter and washed with MeOH (50 mL). Vapour diffusion of pentane into an acetone solution afforded yellow X-ray diffraction quality crystals. Yield: 0.026 g (0.026 mmol, 44%). Anal. Found: C, 59.42; H, 5.02; N, 2.96%. Calcd for C₄₉H₄₉BN₂O₅P₂RuS₂: C, 59.82; H, 5.02; N, 2.85%. NMR (CDCl₃, 25°C): ^1H : $\delta_{\text{H}} = 0.57$ (t, $^3J_{\text{HH}}$ 6.8 Hz, 3H, NCH₂CH₃), 0.74 (t, $^3J_{\text{HH}}$ 6.8 Hz, 3H, NCH₂CH₃), 2.03 (s, 3H, NMe), 2.76 (q, $^3J_{\text{HH}}$ 6.8 Hz, 2H, NCH₂CH₃), 2.87 (d, $^2J_{\text{HH}}$ 16.0 Hz, 2H, CH₂), 3.11 (q, $^3J_{\text{HH}}$ 6.8 Hz, 2H, NCH₂CH₃), 3.28 (d, $^2J_{\text{HH}}$ 16.0 Hz, 2H, CH₂), 5.18 (d, $^3J_{\text{HH}}$ 18.0 Hz, 1H, CHB), 7.31 (m, 18H, C₆H₅), 7.53 (m, 12H, C₆H₅), 8.19 (d, $^3J_{\text{HH}}$ 18.0 Hz, 1H, RuCH); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = 7.4$ (br); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 38.4$. NMR (C₆D₆, 25°C): ^1H : $\delta_{\text{H}} = 0.51$ (t, $^3J_{\text{HH}}$ 7.5 Hz, 3H, NCH₂CH₃), 0.56 (t, $^3J_{\text{HH}}$ 7.5 Hz, 3H, NCH₂CH₃), 1.11 (s, 3H, NMe), 2.04 (d, $^2J_{\text{HH}}$ 20.0 Hz, 2H, CH₂), 2.27 (d, $^2J_{\text{HH}}$ 15.0 Hz, 2H, CH₂), 2.67 (q, $^3J_{\text{HH}}$ 8.3 Hz, 2H, NCH₂CH₃), 2.94 (q, $^3J_{\text{HH}}$ 6.7 Hz, 2H, NCH₂CH₃), 5.47 (d, $^3J_{\text{HH}}$ 20.0 Hz, 1H, CHB), 7.01 (t, J 7.5 Hz, 6H, C₆H₅), 7.12 (t, J 7.5 Hz, 12H, C₆H₅), 7.86 (q, J 6.7 Hz, 12H, C₆H₅), 8.57 (d, $^3J_{\text{HH}}$ 20.0 Hz, 1H, RuCH); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 12.00$ (NCH₂CH₃), 12.61 (NCH₂CH₃), 43.63 (NMe), 44.10 (NCH₂), 44.43 (NCH₂CH₃), 60.51 (NCH₂CH₃), 128.35 [C⁴(C₆H₅)], 129.42 (CHB), 134.50 [t^v, J_{CP} 21.4 Hz, C¹(C₆H₅)], 135.18 [t, J_{CP} 5.7 Hz, C^{3,5}(C₆H₅)], 167.29 [OC(O)], 172.53 (RuCH), 205.67 (RuCO), 209.78 (CS₂). Acc. Mass: Found: $m/z = 1007.1435$. Calcd for C₄₉H₄₉¹¹BN₂NaO₅P₂¹⁰²RuS₂ 1007.1592 [M + Na]⁺. ESI-MS(+ve ion): $m/z = 802.1$ [M - CH=CHBMIDA]⁺, 581.0 [M + NCMc - CH=CHMIDA - PPh₃]⁺, 512.0 [Ru(PPh₃)(S₂CNEt₂)]⁺. IR (Benzene): ν_{CO} 1761, 1915 cm⁻¹; IR (DCM): ν_{CO} 1759, 1912 cm⁻¹; IR (KBr Plate): ν_{CO} 1760, 1911 cm⁻¹. *Crystal data*: C₄₉H₄₉BN₂O₅P₂RuS₂·C₃H₆O, $M_r = 1041.98$, $T = 150(2)$ K, monoclinic, space group $P2_1/n$, $a = 12.8444(4)$, $b =$

[§] See synthesis of RuCl(C=CBMIDA)(CO)₂(PPh₃)₂ (6.2).

25.1664(7), $c = 47.1159(13)$ Å, $\beta = 91.700(3)^\circ$, $V = 15223.4(8)$ Å³, $Z = 12$, $D_{\text{calcd}} = 1.364$ Mgm⁻³, $\mu(\text{Cu K}\alpha) = 4.27$ mm⁻¹, yellow plate, $0.02 \times 0.05 \times 0.09$ mm, 43623 measured reflections with $2\theta_{\text{max}} = 144.6^\circ$, 27038 independent reflections, 26923 absorption-corrected data used in F^2 refinement, 1797 parameters, no restraints, $R_1 = 0.084$, $wR_2 = 0.168$ for 16072 reflections with $I > 2\sigma(I)$. A DCM or CHCl₃ solution of Ru(CH=CHBMIDA)(S₂CNEt₂)(CO)(PPh₃)₂ was observed to decompose significantly over 12 h to Ru(S₂CNEt₂)Cl(CO)(PPh₃)₂, and continue to decompose to completion after approximately 6 days. Yellow X-ray quality diffraction crystals were obtained from vapour diffusion of a mixture of chloroform/hexane or chloroform/MeOH and colourless X-ray diffraction quality crystals were obtained from vapour diffusion of benzene/hexane, each solvent system yielding a distinct solvated structure. Yield (Recovered): 0.008 g (0.01 mmol, 8%). Insufficient material was obtained for elemental microanalytical data to be acquired. The complex has, however, been reported previously.²⁴ NMR (CDCl₃, 25°C): ¹H: $\delta_{\text{H}} = 1.15$ (t, ³J_{HH} 7.0 Hz, 6H, CH₃), 2.97 (q, ³J_{HH} 7.0 Hz, 4H, CH₂), 7.19–7.41 (m, 30H, C₆H₅); ³¹P{¹H}: $\delta_{\text{P}} = 36.0$. Acc. Mass: Found: $m/z = 843.1337$. Calcd for C₄₄H₄₃N₂OP₂¹⁰²RuS₂ 843.1336 [M + NCMe - Cl]⁺. ESI-MS(+ve ion): $m/z = 802.1$ [M - Cl]⁺. IR (DCM): $\nu_{\text{CO}} 1947$ cm⁻¹ (cf. lit. $\nu_{\text{CO}} 1940$ cm⁻¹); IR (KBr Plate): $\nu_{\text{CO}} 1935$ cm⁻¹. *Crystal data*: C₄₂H₄₀ClNOP₂RuS₂·2(CHCl₃), $M_r = 1076.14$, $T = 150(2)$ K, triclinic, space group $P-1$ (No.2), $a = 9.90371(17)$, $b = 15.5276(3)$, $c = 18.2972(3)$ Å, $\alpha = 66.3796(16)$, $\beta = 77.3401(15)$, $\gamma = 88.4075(14)^\circ$, $V = 2509.67(8)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.424$ Mgm⁻³, $\mu(\text{Cu K}\alpha) 7.60$ mm⁻¹, yellow block, $0.14 \times 0.23 \times 0.28$ mm, 30901 measured reflections with $2\theta_{\text{max}} = 144.6^\circ$, 9887 independent reflections, 9838 absorption-corrected data used in F^2 refinement, 550 parameters, no restraints, $R_1 = 0.035$, $wR_2 = 0.082$ for 9682 reflections with $I > 2\sigma(I)$. *Crystal data*: C₄₂H₄₀ClNOP₂RuS₂·CH₃OH, $M_r = 869.43$, $T = 150(2)$ K, monoclinic, space group $C2/c$, $a = 14.6330(4)$, $b = 16.6388(3)$, $c = 17.4758(4)$ Å, $\beta = 102.586(2)^\circ$, $V = 4152.68(17)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.391$ Mgm⁻³, $\mu(\text{Mo K}\alpha) 0.66$ mm⁻¹, yellow prism, $0.09 \times 0.12 \times 0.46$ mm, 17610 measured reflections with $2\theta_{\text{max}} = 59.6^\circ$, 5107 independent reflections, 5089 absorption-corrected data used in F^2 refinement, 259 parameters, no restraints, $R_1 = 0.033$, $wR_2 = 0.078$ for 4464 reflections with $I > 2\sigma(I)$. *Crystal data*: C₄₂H₄₀ClNOP₂RuS₂·2.5(C₆H₆), $M_r = 1032.67$, $T = 150(2)$ K, triclinic, space group $P-1$ (No.2), $a = 9.9889(5)$, $b = 14.4392(12)$, $c = 17.9821(13)$ Å, $\alpha = 83.116(6)$, $\beta = 76.954(5)$, $\gamma = 85.934(5)^\circ$, $V = 2505.9(3)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.369$ Mgm⁻³, $\mu(\text{Cu K}\alpha) 4.72$

mm⁻¹, Colourless prism, 0.02 × 0.03 × 0.31 mm, 13864 measured reflections with $2\theta_{\max}$ = 140.2°, 8969 independent reflections, 8915 absorption-corrected data used in F^2 refinement, 586 parameters, 30 restraints, R_1 = 0.118, wR_2 = 0.278 for 6797 reflections with $I > 2\sigma(I)$.

Synthesis of Ru(C≡CBMIDA)(S₂CNMe₂)(CO)(PPh₃)₂: A DCM (16 mL) solution of Ru(H)(S₂CNMe₂)(CO)(PPh₃)₂ (0.194 g, 0.250 mmol) and ethynyl-BMIDA (0.045 g, 0.250 mmol) was heated to reflux overnight. All volatiles were removed under high vacuum and further ethynyl-BMIDA (0.045 g, 0.25 mmol) was added and the combined solids dissolved in THF (16 mL) and again heated to reflux overnight. Hexane (~16 mL) was added and the total solvent volume halved under reduced pressure to give a yellow precipitate that was isolated by filtration. The yellow solid was further washed with hexane (~100 mL) and Et₂O (~200 mL), then the solid was extracted with benzene to leave a white solid (H₂C=CHBMIDA) on the sinter. All volatiles were removed from the benzene extract under reduced pressure and the residue was recrystallised from a mixture of DCM/pentane to give a pale yellow solid. Yellow X-ray diffraction quality crystals were obtained by evaporation of an acetone solution. Yield: 0.056 g (0.059 mmol, 23%).[§] NMR (CDCl₃, 25°C): ¹H: δ_H = 2.27 (s, 3H, BNMe), 2.49 (s, 3H, CNMe), 2.71 (s, 3H, CNMe), 3.20 (d, ²J_{HH} 16.0 Hz, 2H, CH₂), 3.42 (d, ²J_{HH} 16.0 Hz, 2H, CH₂), 7.32 (m, 18H, C₆H₅), 7.84 (m, 12H, C₆H₅); ¹¹B{¹H}: δ_B = 10.1 (br); ¹³C{¹H}: δ_C = 46.58 (BNMe), 61.02 (NCH₂), 61.44 (CNMe), 127.36 [C^{2,6}(C₆H₅)], 129.43 [C⁴(C₆H₅)], 132.12 [d, ¹J_{CP} 60.0 Hz, C¹(C₆H₅)], 135.14 [C^{3,5}(C₆H₅)], 138.38 (C≡CB), 144.94 (RuC), 167.84 [OC(O)];[†] ³¹P{¹H}: δ_P = 39.5. ESI-MS (+ve ion): m/z = 955.2 [M + H]⁺, 815.1 [M + NCMe - CH=CHBMIDA]⁺, 744.1 [M - CH=CHBMIDA]⁺. IR (DCM): ν_{CO} 1765, 1943, 2057 (ν_{CC}) cm⁻¹; IR (KBr Plate): ν_{CO} 1763, 1938, 2060 (ν_{CC}) cm⁻¹. *Crystal data:* C₄₇H₄₃BN₂O₅P₂RuS₂, M_r = 953.83, T = 150(2) K, monoclinic, space group Pc , a = 10.6884(1), b = 10.9013(1), c = 18.7310(1) Å, β = 91.4444(6)°, V = 2181.80(3) Å³, Z = 2, D_{calcd} = 1.452 Mgm⁻³, $\mu(\text{Cu K}\alpha)$ 4.89 mm⁻¹, yellow block, 0.06 × 0.10 × 0.12 mm, 42228 measured reflections with $2\theta_{\max}$ = 144.8°, 7220 independent reflections, 7192

[§] The Ru(H)(S₂CNMe₂)(CO)(PPh₃)₂ was found to be contaminated and therefore the product required additional purification. As a result of this the recovered yield is lower than would be expected.

[†] CS₂ resonance not observed.

absorption-corrected data used in F^2 refinement, 542 parameters, 2 restraints, $R_1 = 0.026$, $wR_2 = 0.070$ for 7088 reflections with $I > 2\sigma(I)$.

Synthesis of $\text{Ru}(\text{C}\equiv\text{CBMIDA})(\text{S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)_2$: A DCM (32 mL) solution of $\text{Ru}(\text{H})(\text{S}_2\text{CNET}_2)(\text{CO})(\text{PPh}_3)_2$ (0.401 g, 0.500 mmol) and ethynyl-BMIDA (0.181 g, 1.00 mmol) was heated to reflux for 36 h to give a yellow solution. All volatiles were removed under reduced pressure and the residue was extracted with benzene (~100 mL) to give a yellow solution and a colourless solid ($\text{H}_2\text{C}=\text{CHBMIDA}$) that, once identified (*vide infra*), was discarded. All volatiles were removed on a rotary evaporator to leave a yellow solid that was recrystallised from a mixture of DCM/pentane by slow concentration to give a yellow precipitate that was isolated by filtration, washed with hexane (~100 mL) and dried *in vacuo*. Yellow X-ray diffraction quality crystals were obtained by solvent diffusion of pentane into a DCM solution of the complex. Yield: 0.310 g (0.316 mmol, 63%). NMR (CDCl_3 , 25°C): ^1H : $\delta_{\text{H}} = 0.56$ (t, $^3J_{\text{HH}}$ 8.0 Hz, 3H, NCH_2CH_3), 0.74 (t, $^3J_{\text{HH}}$ 8.0 Hz, 3H, NCH_2CH_3), 2.24 (s, 3H, NMe), 2.75 (q, $^3J_{\text{HH}}$ 7.2 Hz, 2H, NCH_2CH_3), 2.99 (q, $^3J_{\text{HH}}$ 7.2 Hz, 2H, NCH_2CH_3), 3.17 (d, $^2J_{\text{HH}}$ 16.0 Hz, 2H, CH_2), 3.38 (d, $^2J_{\text{HH}}$ 16.0 Hz, 2H, CH_2), 7.32 (m, 18H, C_6H_5), 7.81 (m, 12H, C_6H_5); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = 10.3$ (br); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 39.5$. Acc. Mass: Found: $m/z = 982.1509$. Calcd for $\text{C}_{49}\text{H}_{47}^{11}\text{BN}_2\text{O}_5\text{P}_2^{102}\text{RuS}_2$ 982.1538 [M] $^+$. ESI-MS(+ve ion): $m/z = 843.1$ [M + NCMe - CH=CHBMIDA] $^+$, 802.1 [M - CH=CHBMIDA] $^+$. IR (DCM): ν_{CO} 1762, 1945, 2062 (ν_{CC}) cm^{-1} ; IR (KBr Plate): ν_{CO} 1759, 1936, 2059 (ν_{CC}) cm^{-1} . *Crystal data*: $2(\text{C}_{49}\text{H}_{47}\text{BN}_2\text{O}_5\text{P}_2\text{RuS}_2) \cdot \text{CH}_2\text{Cl}_2$, $M_r = 2048.70$, $T = 150(2)$ K, triclinic, space group $P-1$ (No.2), $a = 11.89073(17)$, $b = 18.5016(3)$, $c = 23.4234(4)$ Å, $\alpha = 101.8728(15)$, $\beta = 91.4641(13)$, $\gamma = 105.6931(14)^\circ$, $V = 4836.81(14)$ Å 3 , $Z = 2$, $D_{\text{calcd}} = 1.407$ Mg m $^{-3}$, $\mu(\text{Cu K}\alpha)$ 4.95 mm $^{-1}$, yellow plate, 0.05 × 0.14 × 0.19 mm, 28693 measured reflections with $2\theta_{\text{max}} = 144.6^\circ$, 18370 independent reflections, 15813 absorption-corrected data used in F^2 refinement, 1144 parameters, 1 restraints, $R_1 = 0.046$, $wR_2 = 0.111$ for 13765 reflections with $I > 2\sigma(I)$. The complex was observed to decompose completely to $\text{Ru}(\text{S}_2\text{CNET}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ in CHCl_3 solution over approximately 6 days. Anal. Found: C, 60.73; H, 4.98; N, 1.96%. Calcd for $\text{C}_{42}\text{H}_{40}\text{ClINOP}_2\text{RuS}_2$: C, 60.24; H, 4.81; N, 1.67%. IR (DCM): ν_{CO} 1947 cm^{-1} (cf. lit. ν_{CO} 1940 cm^{-1}).²⁴ Yellow X-ray diffraction quality crystals were obtained by solvent diffusion of pentane into a DCM solution of the complex. *Crystal data*: $\text{C}_{42}\text{H}_{40}\text{ClINOP}_2\text{RuS}_2 \cdot \text{CH}_2\text{Cl}_2$, $M_r = 922.32$, $T = 150(2)$ K,

monoclinic, space group $C2/c$, $a = 15.3146(1)$, $b = 15.9984(1)$, $c = 17.1568(1)$ Å, $\beta = 98.9667(5)^\circ$, $V = 4152.20(5)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.475$ Mgm⁻³, $\mu(\text{Cu K}\alpha) = 6.77$ mm⁻¹, yellow prism, $0.13 \times 0.17 \times 0.53$ mm, 22660 measured reflections with $2\theta_{\text{max}} = 144.6^\circ$, 4107 independent reflections, 4089 absorption-corrected data used in F^2 refinement, 257 parameters, 2 restraints, $R_1 = 0.034$, $wR_2 = 0.095$ for 4077 reflections with $I > 2\sigma(I)$.

The white powder that remained on the sinter after the benzene extraction of $\text{Ru}(\text{C}\equiv\text{CBMIDA})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2$ was identified as $\text{H}_2\text{C}=\text{CHBMIDA}$. Colourless X-ray diffraction quality crystals were obtained by solvent diffusion of pentane into a DCM solution of the compound. Yield: 0.065 g (0.36 mmol, 71%). NMR (CDCl_3 , 25°C): ^1H : $\delta_{\text{H}} = 2.67$ (dd, $\text{trans-}^3J_{\text{HH}}/\text{cis-}^3J_{\text{HH}} = 12.0/8.0$ Hz, 1H, CHB), 2.71 (s, 3H, NMe), 3.68 (d, $^2J_{\text{HH}} = 16.4$ Hz, 2H, CH₂), 3.74 (m, 1H, $Z\text{-H}_2\text{C}=\text{CHBMIDA}$), 3.79 (d, $^3J_{\text{HH}} = 13.6$ Hz, 1H, $E\text{-H}_2\text{C}=\text{CHBMIDA}$, geminal $^2J_{\text{HH}}$ not resolved), 3.82 (d, $^2J_{\text{HH}} = 16.0$ Hz, 2H, CH₂); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = 5.3$ (br). Crystal data: $\text{C}_7\text{H}_{10}\text{BNO}_4$, $M_r = 182.97$, $T = 150(2)$ K, monoclinic, space group $P2_1/n$, $a = 6.1164(2)$, $b = 11.9985(4)$, $c = 11.6778(3)$ Å, $\beta = 90.951(3)^\circ$, $V = 856.89(5)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.418$ Mgm⁻³, $\mu(\text{Cu K}\alpha) = 0.97$ mm⁻¹, colourless plate, $0.02 \times 0.18 \times 0.34$ mm, 7522 measured reflections with $2\theta_{\text{max}} = 144.6^\circ$, 1692 independent reflections, 1684 absorption-corrected data used in F^2 refinement, 118 parameters, no restraints, $R_1 = 0.046$, $wR_2 = 0.117$ for 1560 reflections with $I > 2\sigma(I)$.

6.3 Tertiary Phosphine Mixed Haloborane Adducts

Synthesis of triphenylphosphine-dichloroborane, $\text{Ph}_3\text{P}\cdot\text{BHCl}_2$:²⁵ A solution of $\text{BHCl}_2\cdot\text{SMe}_2$ (8.7 molL⁻¹, 0.12 mL, 1.0 mmol) in excess SMe_2 was added drop-wise to a stirred solution of triphenylphosphine (0.26 g, 1.0 mmol) in benzene (10 mL) that was cooled in an ice bath during addition. The mixture was stirred for 1.5 h, and then volatiles were removed under vacuum to leave a white solid. The solid was further dried under high vacuum for several hours. The residue was dissolved in benzene and then diluted with pentane to precipitate a pure product free of unreacted starting materials. Layering a concentrated benzene solution with pentane overnight at 25°C produced diffraction quality colourless needles. Yield 0.22 g (0.64 mmol, 64%). M.p 190°C . Anal. Found: C, 62.55 ; H, 4.63% ; N, 0.00% . Calcd for $\text{C}_{18}\text{H}_{16}\text{BCl}_2\text{P}$: C, 62.66 ; H, 4.67 ; N, 0.00% . NMR (C_6D_6 , 25°C): ^1H : $\delta_{\text{H}} = 6.94\text{--}7.05$ [m, 9 H, $\text{H}^{3-5}(\text{C}_6\text{H}_5)$], 7.61--

7.67 [m, 6 H, $H^{2,6}(C_6H_5)$]; $^{11}B\{^1H\}$: $\delta_B = -4.4$ (d.br, $^1J_{BP}$ 77 Hz); $^{13}C\{^1H\}$: $\delta_C = 123.45$ [d, $^1J_{CP}$ 63.3 Hz, $C^1(C_6H_5)$], 129.19 [d, $^2J_{CP}$ 10.1 Hz, $C^{3,5}(C_6H_5)$], 132.50 [$C^4(C_6H_5)$], 134.15 [d, $^3J_{CP}$ 8.9 Hz, $C^{2,6}(C_6H_5)$]; $^{31}P\{^1H\}$: $\delta_P = -1.3$ (d.br, $^1J_{PB}$ 120 Hz). Acc. Mass: Found: $m/z = 367.0346$. Calcd for $C_{18}H_{16}^{11}B^{35}Cl_2NaP$ 367.0357 [M + Na] $^+$. ESI-MS (+ve ion): $m/z = 263.3$ [$PPh_3 + H$] $^+$. *Crystal data*: $C_{18}H_{16}BCl_2P$, $M_r = 345.02$, $T = 200(2)$ K, monoclinic, space group $P2_1/n$, $a = 12.5148(2)$, $b = 10.6585(2)$, $c = 12.9037(2)$ Å, $\beta = 92.217(1)^\circ$, $V = 1719.92(5)$ Å 3 , $Z = 4$, $D_{calcd} = 1.332$ Mg m $^{-3}$, $\mu(Mo K\alpha) = 0.46$ mm $^{-1}$, colourless plate, $0.10 \times 0.26 \times 0.30$ mm, 32540 measured reflections with $2\theta_{max} = 55.8^\circ$, 3936 independent reflections, 3936 absorption-corrected data used in F^2 refinement, 200 parameters, no restraints, $R_1 = 0.034$, $wR_2 = 0.088$ for 3444 reflections with $I > 2\sigma(I)$.

Synthesis of triphenylphosphine-monobromoborane, $Ph_3P \cdot BH_2Br$:²⁶ A solution of $BH_2Br \cdot SME_2$ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of triphenylphosphine (0.26 g, 1.0 mmol) in benzene (10 mL) that was cooled in an ice bath during addition. The mixture was stirred for 30 min, and then the volume was reduced to approximately 5 mL under high vacuum. Slow addition of pentane resulted in the precipitation of a light orange solid. The solid was dried under high vacuum overnight and then recrystallised from a mixture of DCM/Et $_2$ O to provide colourless X-ray diffraction quality needles. Yield: 0.345 g (0.97 mmol, 97%). M.p 178-180°C. Anal. Found: C, 61.15; H, 4.61; N, 0.00%. Calcd for $C_{18}H_{16}BCl_2P$: C, 60.90; H, 4.83; N, 0.00%. NMR (C_6D_6 , 25°C): 1H : $\delta_H = 6.92$ -7.03 [m, 9 H, $H^{3,5}(C_6H_5)$], 7.59-7.63 [m, 6 H, $H^{2,6}(C_6H_5)$]; $^{11}B\{^1H\}$: $\delta_B = -23.2$ (br); $^{13}C\{^1H\}$: $\delta_C = 125.49$ [d, $^1J_{CP}$ 62.0 Hz, $C^1(C_6H_5)$], 129.08 [d, $^2J_{CP}$ 11.4 Hz, $C^{2,6}(C_6H_5)$], 132.14 [$C^4(C_6H_5)$], 133.68 [d, $^3J_{CP}$ 8.9 Hz, $C^{3,5}(C_6H_5)$]; $^{31}P\{^1H\}$: $\delta_P = 4.8$ (br). Acc. Mass: Found: $m/z = 377.0236$. Calcd for $C_{18}H_{17}^{11}B^{79}BrNaP$ 377.0241 [M + Na] $^+$. ESI-MS (+ve ion): $m/z = 263.3$ [$PPh_3 + H$] $^+$. *Crystal data*: $C_{18}H_{17}BBrP$, $M_r = 355.02$, $T = 200(2)$ K, triclinic, space group $P-1$ (No.2), $a = 9.5192(2)$, $b = 9.6713(2)$, $c = 18.4029(5)$ Å, $\alpha = 94.9989(12)$, $\beta = 91.1311(15)$, $\gamma = 104.6508(17)^\circ$, $V = 1631.37(7)$ Å 3 , $Z = 4$, $D_{calcd} = 1.445$ Mg m $^{-3}$, $\mu(Mo K\alpha) = 2.61$ mm $^{-1}$, colourless block, $0.08 \times 0.09 \times 0.16$ mm, 32394 measured reflections with $2\theta_{max} = 55.2^\circ$, 7286 independent reflections, 7286 absorption-corrected data used in F^2 refinement, 380 parameters, no restraints, $R_1 = 0.039$, $wR_2 = 0.093$ for 5335 reflections with $I > 2\sigma(I)$.

Synthesis of tricyclohexylphosphine-borane, $\text{Cy}_3\text{P}\cdot\text{BH}_3$:²⁷ A solution of $\text{BH}_3\cdot\text{SMe}_2$ (10.5 molL^{-1} , 0.09 mL, 1.0 mmol) in excess SMe_2 was added drop-wise to a stirred solution of tricyclohexylphosphine (0.28 g, 1.0 mmol) in benzene (5 mL) and stirred for 1.5 h. All volatiles were removed under high vacuum to give a white solid that was further dried under high vacuum for 30 min. The solid was recrystallised from a mixture of DCM/diethyl ether to produce colourless X-ray diffraction quality crystals. Yield 0.07 g (0.22 mmol, 22%). The recovered compound was found to be a partial (~25%) DCM solvate, which was observed in both the microanalytical and NMR data, and was accounted for in the yield. Anal. Found: C, 69.66; H, 11.99; N, 0.00%. Calcd for $\text{C}_{18}\text{H}_{35}\text{BBP}\cdot 0.25(\text{CH}_2\text{Cl}_2)$: C, 69.48; H, 11.66; N, 0.00%. NMR (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 1.20\text{--}1.39$ (m, 15H, C_6H_{11}), $1.70\text{--}1.88$ (m, 18H, C_6H_{11}); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -44.3$ (d, $^1J_{\text{BP}} 66\text{ Hz}$); ^{11}B : $\delta_{\text{B}} = -44.3$ (dq, $^1J_{\text{BH}} \approx ^1J_{\text{BP}} 66.0\text{ Hz}/94.3\text{ Hz}$); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 26.62$ [$\text{C}^4(\text{C}_6\text{H}_{11})$], 27.68 [d, $J_{\text{CP}} 10.3\text{ Hz}$, $\text{C}^{3,5}(\text{C}_6\text{H}_{11})$], 28.25 [d, $J_{\text{CP}} 2.3\text{ Hz}$, $\text{C}^{2,6}(\text{C}_6\text{H}_{11})$], 31.26 [d, $^1J_{\text{CP}} 29.9\text{ Hz}$, $\text{C}^1(\text{C}_6\text{H}_{11})$]; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 28.4$ [q.br, $^1J_{\text{BP}} 59\text{ Hz}$ (Average value)]. Acc. Mass: Found: $m/z = 317.2545$. Calcd for $\text{C}_{18}\text{H}_{36}\text{}^{11}\text{B}^{23}\text{NaP}$ 317.2545 [$\text{M} + \text{Na}$] $^+$. ESI-MS (+ve ion): $m/z = 905.8$ [$3\text{M} + \text{Na}$] $^+$, 611.5 [$2\text{M} + \text{Na}$] $^+$. Crystal data: $\text{C}_{18}\text{H}_{36}\text{BP}$, $M_r = 294.26$, $T = 200(2)\text{ K}$, orthorhombic, space group $Pnma$, $a = 10.9430(2)$, $b = 15.7940(3)$, $c = 10.3910(2)\text{ Å}$, $V = 1795.92(6)\text{ Å}^3$, $Z = 4$, $D_{\text{calcd}} = 1.088\text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) 0.14\text{ mm}^{-1}$, colourless block, $0.22 \times 0.25 \times 0.30\text{ mm}$, 21656 measured reflections with $2\theta_{\text{max}} = 55.0^\circ$, 2135 independent reflections, 2129 absorption-corrected data used in F^2 refinement, 101 parameters, 7 restraints, $R_1 = 0.037$, $wR_2 = 0.095$ for 1900 reflections with $I > 2\sigma(I)$.

Synthesis of tricyclohexylphosphine-dichloroborane, $\text{Cy}_3\text{P}\cdot\text{BHCl}_2$: A solution of $\text{BHCl}_2\cdot\text{SMe}_2$ (8.7 molL^{-1} , 0.12 mL, 1.0 mmol) in excess SMe_2 was added drop-wise to a stirred solution of tricyclohexylphosphine (0.28 g, 1.0 mmol) in benzene (10 mL) that was cooled in an ice bath during addition. The mixture was stirred for 2 h, and then volatiles were removed under high vacuum to leave a white solid, which was further dried under high vacuum for 24 h, then dissolved in DCM and cannula filtered away from DCM-insoluble impurities (which were discarded). All volatiles were removed under high vacuum to leave a white powder. The solid was recrystallised from DCM layered with pentane to yield large colourless block crystals of X-ray diffraction quality. Yield 0.12 g (0.33 mmol, 33%). M.p. $170\text{--}172^\circ\text{C}$, with gas evolution from 180°C up to 250°C . Anal. Found: C, 50.60; H, 8.28; N, 0.00%. Calcd for $\text{C}_{18}\text{H}_{34}\text{BCl}_2\text{P}\cdot\text{CH}_2\text{Cl}_2$: C,

50.93; H, 8.10; N, 0.00%. NMR (CD₂Cl₂, 25°C): ¹H: δ_H = 1.29-2.59 (m, 33H, C₆H₁₁); ¹¹B{¹H}: δ_B = -6.2 (d.br, ¹J_{BP} 95 Hz); ¹¹B: δ_B = -6.2 [t.br, ¹J_{BH} = ¹J_{BP} (unresolved)]; ¹³C{¹H}: δ_C = 25.49 [C⁴(C₆H₁₁)], 27.17 [d, J_{CP} 12.7 Hz, C^{3,5}(C₆H₁₁)], 28.33 [m, C^{2,6}(C₆H₁₁)], 31.05 [d, ¹J_{CP} 30.4 Hz, C¹(C₆H₁₁)]; ³¹P{¹H}: δ_P = 27.2 (br). ESI-MS (+ve ion): *m/z* = 281.6 [M + H - BHCl₂]⁺. Crystal data: C₁₈H₃₄BCl₂P, *M_r* = 363.16, *T* = 200(2) K, trigonal, space group *R*3c, *a* = 14.7100(8), *b* = 14.7100(8), *c* = 16.0857(10) Å, γ = 120°, *V* = 3014.4(3) Å³, *Z* = 6, *D*_{calcd} = 1.200 Mg m⁻³, μ(Mo Kα) 0.40 mm⁻¹, colourless prism, 0.16 × 0.17 × 0.39 mm, 7801 measured reflections with 2θ_{max} = 55.7°, 1133 independent reflections, 1131 absorption-corrected data used in *F*² refinement, 91 parameters, 23 restraints, *R*₁ = 0.062, *wR*₂ = 0.169 for 1036 reflections with *I* > 2σ(*I*).

Synthesis of tricyclohexylphosphine-monobromoborane, Cy₃P·BH₂Br:²⁸ A solution of BH₂Br·SMe₂ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of tricyclohexylphosphine (0.28 g, 1.0 mmol) in benzene (10 mL) that was cooled in an ice bath during addition. The solution developed a strong orange colour after stirring for 10 min following addition. The mixture was stirred for 20 min, after which all volatiles were removed under high vacuum to give an orange solid that was further dried under high vacuum for 24 h. The solid was recrystallised from a mixture of DCM/pentane to produce colourless X-ray diffraction quality crystals. Yield 0.12 g (0.32 mmol, 32%). M.p. 156°C. Anal. Found: C, 58.02; H, 9.59; N, 0.00%. Calcd for C₁₈H₃₅BBrP: C, 57.94; H, 9.45; N, 0.00%. NMR (C₆D₆, 25°C): ¹H: δ_H = 0.92-2.02 (m, 33H, C₆H₁₁); ¹¹B{¹H}: δ_B = -26.2 (br); ¹³C{¹H}: δ_C = 26.10 [C⁴(C₆H₁₁)], 27.17 [d, J_{CP} 10.1 Hz, C^{2,6}(C₆H₁₁)], 27.86 [C^{3,5}(C₆H₁₁)], 30.08 [d, J_{CP} 31.6 Hz, C¹(C₆H₁₁)]; ³¹P{¹H}: δ_P = 8.6 (br). ESI-MS (+ve ion): *m/z* = 281.5 [PHCy₃]⁺. Crystal data: C₁₈H₃₅BBrP, *M_r* = 373.16, *T* = 200(2) K, triclinic, space group *P*-1 (No.2), *a* = 10.9360(2), *b* = 12.1555(3), *c* = 15.2312(2) Å, α = 90.4077(12), β = 98.3351(12), γ = 104.3221(11)°, *V* = 1939.12(7) Å³, *Z* = 4, *D*_{calcd} = 1.278 Mg m⁻³, μ(Mo Kα) 2.20 mm⁻¹, colourless block, 0.27 × 0.43 × 0.50 mm, 28777 measured reflections with 2θ_{max} = 55.0°, 8830 independent reflections, 8830 absorption-corrected data used in *F*² refinement, 380 parameters, no restraints, *R*₁ = 0.034, *wR*₂ = 0.088 for 7311 reflections with *I* > 2σ(*I*).

Synthesis of tri(4-fluorophenyl)phosphine-dichloroborane, (C₆H₄F-4)₃P·BHCl₂: A solution of BHCl₂·SMe₂ (8.7 mol L⁻¹, 0.12 mL, 1.0 mmol) in excess SMe₂ was added

drop-wise to a stirred solution of tri(4-fluorophenyl)phosphine (0.32 g, 1.0 mmol) in benzene (3 mL). The mixture was stirred for 2 h, then all volatiles were removed under high vacuum to leave a white solid that was further dried under high vacuum for 1 h. The solid was recrystallised from a mixture of DCM/pentane to produce colourless X-ray diffraction quality crystals. Yield 0.21 g (0.52 mmol, 52%). Sublimed at 136-138°C (1 atm). Anal. Found: C, 54.25; H, 3.54; N, 0.00%. Calcd for $C_{18}H_{13}BCl_2F_3P$: C, 54.19; H, 3.28; N, 0.00%. NMR (CD_2Cl_2 , 25°C): 1H : $\delta_H = 7.27, 7.67$ (AA'BB', 6H $\times$ 2, $^3J_{AB}$ 120.0 Hz C_6H_4F); $^{11}B\{^1H\}$: $\delta_B = -5.3$ (d.br, $^1J_{BP}$ 87.8 Hz); ^{11}B : $\delta_B = -6.00$ (t.br, $^1J_{BH} \approx ^1J_{BP}$ 106 Hz); $^{13}C\{^1H\}$: $\delta_C = 117.4$ (dd, J_{CF}/J_{CP} 22.2/12.0 Hz, C_6H_4F), 119.33 [dd, $^1J_{CP}$ 65.8 Hz, $^4J_{CF}$ 3.8 Hz, $C^1(C_6H_4F)$], 137.01 (dd, $J_{CF} \approx J_{CP}$ 10.1 Hz, C_6H_4F), 165.98 [dd, $^1J_{CF}$ 255.7 Hz, $^4J_{CP}$ 2.6 Hz, $C^4(C_6H_4F)$]; ^{19}F : $\delta_F = -105.4$ (m). $^{31}P\{^1H\}$: $\delta_P = -2.6$ (q.br, $^1J_{BP}$ 54 Hz). ESI-MS (+ve ion): $m/z = 317.08$ [$M + H - BHCl_2$] $^+$. Crystal data: $C_{18}H_{13}BCl_2F_3P$, $M_r = 398.99$, $T = 200(2)$ K, monoclinic, space group Cc , $a = 13.4909(3)$, $b = 18.5705(5)$, $c = 8.0963(2)$ Å, $\beta = 117.4357(14)^\circ$, $V = 1800.25(8)$ Å 3 , $Z = 4$, $D_{calcd} = 1.472$ Mg m $^{-3}$, $\mu(Mo K\alpha)$ 0.48 mm $^{-1}$, colourless block, 0.30 $\times$ 0.34 $\times$ 0.46 mm, 11250 measured reflections with $2\theta_{max} = 55.0^\circ$, 4107 independent reflections, 4107 absorption-corrected data used in F^2 refinement, 227 parameters, 2 restraints, $R_1 = 0.033$, $wR_2 = 0.087$ for 3724 reflections with $I > 2\sigma(I)$.

Synthesis of tri(4-fluorophenyl)phosphine-monobromoborane, $(C_6H_4F)_3P \cdot BH_2Br$: A solution of $BH_2Br \cdot SMe_2$ (1.0 M, 0.50 mL, 0.5 mmol) in dichloromethane was added drop-wise to a stirred solution of tri(4-fluorophenyl)phosphine (0.16 g, 0.5 mmol) in benzene (2 mL). The mixture was stirred for 16 h, and then all volatiles were removed under high vacuum to leave an orange residue. The residue was dissolved in benzene and layered with pentane to give an orange powder and large colourless needles of X-ray diffraction quality (both orange powder and colourless crystals confirmed to be the clean product by NMR analysis). Yield 0.05 g (0.12 mmol, 25%). Gas evolution occurred from 114°C onwards to leave an orange residue. Anal (orange powder). Found: C, 46.56; H, 3.26; N, 0.00%. Calcd for $C_{18}H_{14}BBrF_3P \cdot CH_2Cl_2$: C, 46.20; H, 3.27; N, 0.00%. NMR (CD_2Cl_2 , 25°C): 1H : $\delta_H = 7.25, 7.65$ (AA'BB', 6H $\times$ 2, $^3J_{AB}$ 120.0 Hz C_6H_4F); $^{11}B\{^1H\}$: $\delta_B = -23.9$ (br); $^{13}C\{^1H\}$: $\delta_C = 117.14$ (dd, J_{CF}/J_{CP} 21.5/11.4 Hz, C_6H_4F), 121.37 [dd, $^1J_{CP}$ 65.8 Hz, $^4J_{CF}$ 2.5 Hz, $C^1(C_6H_4F)$], 136.46 (dd, $J_{CF} \approx J_{CP}$ 10.1 Hz, C_6H_4F), 165.71 [dd, $^1J_{CF}$ 254.4 Hz, $^4J_{CP}$ 2.5 Hz, $C^4(C_6H_4F)$]; ^{19}F : $\delta_F =$

-106.23 (m). $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 3.1$ (br). ESI-MS (+ve ion): $m/z = 355.05$ $[\text{M} + \text{Na} + \text{H} - \text{Br}]^+$, 331.08 $[\text{M} + \text{H} - \text{Br}]^+$. Crystal data: $\text{C}_{18}\text{H}_{14}\text{BBBrF}_3\text{P}$, $M_r = 408.99$, $T = 200(2)$ K, orthorhombic, space group $P2_12_12_1$, $a = 10.1462(2)$, $b = 13.0186(2)$, $c = 13.1207(2)$ Å, $V = 1733.10(5)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.567$ Mg m⁻³, $\mu(\text{Mo K}\alpha) 2.49$ mm⁻¹, colourless block, $0.18 \times 0.27 \times 0.31$ mm, 18593 measured reflections with $2\theta_{\text{max}} = 60.1^\circ$, 5056 independent reflections, 5056 absorption-corrected data used in F^2 refinement, 219 parameters, no restraints, $R_1 = 0.034$, $wR_2 = 0.083$ for 4400 reflections with $I > 2\sigma(I)$.

Synthesis of tri(2-tolyl)phosphine-dichloroborane, $(\text{C}_6\text{H}_4\text{Me-2})_3\text{P}\cdot\text{BHCl}_2$: A solution of $\text{BHCl}_2\cdot\text{SMe}_2$ (8.7 molL⁻¹, 0.06 mL, 0.5 mmol) in excess SMe_2 was added drop-wise to a stirred solution of tri(2-tolyl)phosphine (0.15 g, 0.5 mmol) in benzene (2 mL). The mixture was stirred for 1.5 h, and then all volatiles were removed under high vacuum to leave a colourless solid. Subsequent NMR analysis confirmed the presence of unreacted $\text{BHCl}_2\cdot\text{SMe}_2$ and disproportionation products of the parent dichloroborane. NMR (CD_2Cl_2 , 25°C): $^1\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -14.9$ (br), -7.9 ($\text{BH}_2\text{Cl}\cdot\text{SMe}_2$), -3.6 (br), 1.0 ($\text{BHCl}_2\cdot\text{SMe}_2$), 5.2 , 5.9 ($\text{BCl}_3\cdot\text{SMe}_2$), 6.4 .

Synthesis of tri(2-tolyl)phosphine-monobromoborane, $(\text{C}_6\text{H}_4\text{Me-2})_3\text{P}\cdot\text{BH}_2\text{Br}$: A solution of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (1.0 M, 0.50 mL, 0.5 mmol) in dichloromethane was added drop-wise to a stirred solution of tri(2-tolyl)phosphine (0.15 g, 0.5 mmol) in benzene (2 mL). The mixture was stirred for 1 h, and then all volatiles were removed under high vacuum to leave an orange residue. The residue was further dried under high vacuum for 2 h to give an orange crystalline solid. The solid was recrystallised from a mixture of DCM/pentane to give an orange powder. NMR (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 2.27$ (s, 9H, CH_3), 7.25 - 7.53 (m, 12H, C_6H_4); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -19.9$ (br); ^{11}B : $\delta_{\text{B}} = -19.6$ (br); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 13.7$ (br). Acc. Mass: Found: $m/z = 419.0714$. Calcd for $\text{C}_{21}\text{H}_{23}^{11}\text{B}^{79}\text{BrNaP}$ 419.0712 $[\text{M} + \text{Na}]^+$.

Synthesis of dimethylphenylphosphine-dichloroborane, $\text{PhMe}_2\text{P}\cdot\text{BHCl}_2$: A solution of $\text{BHCl}_2\cdot\text{SMe}_2$ (8.7 molL⁻¹, 0.12 mL, 1.0 mmol) in excess SMe_2 was added drop-wise to a stirred solution of dimethylphenylphosphine ($\rho = 0.97$ g mL⁻¹, 0.14 mL, 1.0 mmol) in pentane (10 mL) at 0°C. The mixture was stirred for 1 h, and then all volatiles were removed under high vacuum to leave a clear oil. The product was further dried under high vacuum for 24 h, but remained an oil. As a DCM solution the product

oil was found to decompose over a period of 4 hours to unidentified compounds. NMR (Crude) (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 1.76$ (d, $^2J_{\text{PH}} 11.6$ Hz, 6H, CH_3), 7.54-7.59 [m, 3H, $\text{H}^{3,5}(\text{C}_6\text{H}_5)$], 7.74-7.79 [m, 2H, $\text{H}^{2,6}(\text{C}_6\text{H}_5)$]; $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -5.8$ (d.br, $^1J_{\text{BP}} 110$ Hz); ^{11}B : $\delta_{\text{B}} = -45.2$ [t (overlapping dd) br, $^1J_{\text{BH}} 125$ Hz]; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -9.4$ [q.br, $^1J_{\text{PB}} 127$ Hz (Average)]. ESI-MS (+ve ion): $m/z = 242.28$ [$\text{M} + \text{Na}$] $^+$.

Synthesis of dimethylphenylphosphine-monobromoborane, $\text{PhMe}_2\text{P}\cdot\text{BH}_2\text{Br}$: A solution of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of dimethylphenylphosphine ($\rho = 0.97$ g mL^{-1} , 0.14 mL, 1.0 mmol) in pentane (10 mL) at 0°C . Upon addition the solution changed to a bright purple colour, but slowly decolourised to an orange colour over a couple of minutes. The mixture was stirred for 10 min, and then all volatiles were removed under high vacuum to leave an orange oil. The cooling due to solvent evaporation caused the solution to again turn purple, a colour change that persisted until the oil was warmed to ambient temperature. Drying the oil under vacuum for 3 days caused no change to its consistency. Colourless X-ray diffraction quality crystals of the decomposition product $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$ (*vide infra*) were found to precipitate out of a benzene solution of the compound. NMR (Crude) (C_6D_6 , 25°C): $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -38.4$ {d, $^1J_{\text{BP}} 55$ Hz, $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$ }, -33.3 (t.br), -23.2 (d.br, $^1J_{\text{BP}} 77$ Hz, $\text{PhMe}_2\text{P}\cdot\text{BH}_2\text{Br}$), -15.5 (d.br, $J 114$ Hz); ^{11}B : $\delta_{\text{B}} = -38.4$ {qd, $^1J_{\text{BH}} \approx ^1J_{\text{BP}} 95/59$ Hz, $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$ }, -33.3 (t.vbr), -23.2 [q, $^1J_{\text{BH}} \approx ^1J_{\text{BP}} 105$ Hz (Average), $\text{PhMe}_2\text{P}\cdot\text{BH}_2\text{Br}$], -15.5 (t, $^1J_{\text{BH}} \approx ^1J_{\text{BP}} 132$ Hz); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -12.0$ (q.br, $^1J_{\text{PB}} 122$ Hz), -8.0 (d.br, $^1J_{\text{PB}} 88$ Hz, $\text{PhMe}_2\text{P}\cdot\text{BH}_2\text{Br}$), -3.3 (d.br, $^1J_{\text{PB}} 114$ Hz), 3.8 (q.br). Crystal data (Unit cell determination): $\text{C}_{16}\text{H}_{24}\text{BBP}_2$, $T = 200(2)$ K, monoclinic, space group Cc , $a = 12.51$, $b = 13.58$, $c = 12.28$ Å, $\beta = 119.59^\circ$, $V = 1815$ Å 3 .[§]

Synthesis of 1-diphenylphosphino-monobromoborane-1'-diphenylphosphinoferrocene, $\text{dppf}\cdot\text{BH}_2\text{Br}$: A solution of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (1.0 M, 0.20 mL, 0.20 mmol) in dichloromethane was added drop-wise to a stirred solution of 1,1'-bis(diphenylphosphino)ferrocene (0.11 g, 0.20 mmol) in DCM (4 mL) at -78°C and stirred overnight, gradually warming to room temperature. All volatiles were removed under vacuum to leave an orange solid. The complex was crystallised from a mixture of

[§] See Section 6.5.

DCM and pentane to give an orange microcrystalline solid that was separated *via* cannula filtration, washed with pentane and dried *in vacuo*. Yield 0.072 g (0.11 mmol, 56%). NMR (CDCl₃, 25°C): ¹H: δ_H = 4.42 (d, *J*_{PH} 1.8 Hz, 4H, Cp), 4.56 (d, *J*_{PH} 1.8 Hz, 4H, Cp), 7.42-7.53 (m, 20H, C₆H₅); ¹¹B{¹H}: δ_B = -24.1 (br); ¹³C{¹H}: δ_C = 68.39 [d, ¹*J*_{CP} 71.3 Hz, C¹(C₅H₄)], 74.63 (d, *J*_{CP} 9.2 Hz, C₅H₄), 74.99 (d, *J*_{CP} 6.9 Hz, C₅H₄), 127.09 [d, ¹*J*_{CP} 64.4 Hz, C¹(C₆H₅)], 128.97 (d, *J*_{CP} 10.3 Hz), 132.07 (d, *J*_{CP} 2.3 Hz), 133.32 (d, *J*_{CP} 8.0 Hz); ³¹P{¹H}: δ_P = -16.7 (br, uncoordinated PPh₂), 1.8 (s.br, P·BH₂Br). Acc. Mass: Found: *m/z* = 567.1249 Calcd for C₃₄H₃₀¹¹B⁵⁶FeP₂ 567.1265 [M - Br]⁺. ESI-MS (+ve ion): *m/z* = 763.3 [M + BH₂Br + Na]⁺, 555.4 [M - BH₂Br]⁺.

Synthesis of dimethylphenylphosphine-dibromoborane, PhMe₂P·BHBr₂:

Dimethylphenylphosphine (*ρ* = 0.97 g mL⁻¹, 0.14 mL, 1.0 mmol) was added dropwise to a solution of BHBr₂·SMe₂ (1.0 M, 1.05 mL, 1.05 mmol) in dichloromethane dissolved in benzene (4 mL). After 15 min of stirring all volatiles were removed under vacuum to leave a colourless oil that resisted attempts at crystallisation from a range of solvents. Elemental microanalytical data were therefore not pursued. Yield 0.263 g (0.85 mmol, 85%). NMR (C₆D₆, 25°C): ¹H: δ_H = 1.62 (s, 6H, CH₃), 6.86-6.91 (m, 3H, C₆H₅), 7.09-7.16 (m, 2H, C₆H₅); ¹¹B{¹H}: δ_B = -15.6 (d.br, ¹*J*_{BP} 114 Hz); ¹¹B: δ_B = -15.6 [t.br, ¹*J*_{BH} = ¹*J*_{BP} 132 Hz (Average value)]; ³¹P{¹H}: δ_P = -12.1 [d.br, ¹*J*_{PB} 112 Hz (Average Value)]. Acc. Mass: Found: *m/z* = 367.0550. Calcd for C₁₆H₂₃¹¹B⁷⁹BrP₂ 367.0551 [M + PMe₂Ph - Br]⁺. ESI-MS (+ve ion): *m/z* = 332.5 [M + Na]⁺, 289.5 [M + PMe₂Ph + H - 2Br]⁺. Attempts to crystallise the product led to the isolation of small amounts of the corresponding phosphonium salt which was crystallographically identified. [PHMe₂Ph]Br: NMR (C₆D₆, 25°C): ³¹P{¹H}: δ_P = 29.1. Crystal data: C₈H₁₂BrP, *M_r* = 219.06, *T* = 200(2) K, monoclinic, space group C2/c, *a* = 6.1527(3), *b* = 22.798(2), *c* = 7.0829(7) Å, β = 103.778(6)°, *V* = 964.91(14) Å³, *Z* = 4, *D*_{calcd} = 1.508 Mg m⁻³, μ(Mo Kα) 4.36 mm⁻¹, colourless plate, 0.08 × 0.15 × 0.25 mm, 3844 measured reflections with 2θ_{max} = 57.2°, 1186 independent reflections, 1080 absorption-corrected data used in *F*² refinement, 61 parameters, 6 restraints, *R*₁ = 0.042, *wR*₂ = 0.097 for 782 reflections with *I* > 2σ(*I*).

Synthesis of *P,P'*-bis(dichloroborane)-1,2-bis(diphenylphosphino)ethane, [dppe·(BHCl₂)₂]: A solution of BHCl₂·SMe₂ (8.7 mol L⁻¹, 0.12 mL, 1.0 mmol) in excess

SMe₂ was added drop-wise to a stirred solution of 1,2-bis(diphenylphosphino)ethane (0.40 g, 1.0 mmol) in benzene (25 mL) that was cooled in an ice bath during addition. The mixture was stirred for 1.5 h, and the resulting white precipitate was allowed to settle. The filtrate was removed by cannula filtration and discarded. The solid was dissolved in DCM and precipitated with pentane. The filtrate was removed by cannula filtration (and discarded) and the solid dried under high vacuum overnight. The solid was recrystallised from a mixture of DCM/pentane overnight at 25°C to produce colourless X-ray diffraction quality needles. Yield 0.16 g (0.28 mmol, 57%). M.p. 149–151°C. Anal. Found: C, 55.20; H, 4.61; N, 0.00%. Calcd for C₂₆H₂₆B₂Cl₄P₂: C, 55.38; H, 4.65; N, 0.00%. NMR (CD₂Cl₂, 25°C): ¹H: δ_H = 2.83 (d, ²J_{PH} 4.8 Hz, 4H, CH₂), 7.53–7.70 (m, 20H, C₆H₅); ¹¹B{¹H}: δ_B = -6.8 (br); ¹³C{¹H}: δ_C = 16.10 (d, J_{CP} 36.7 Hz, CH₂), 121.66 [d, J_{CP} 60.7 Hz, C^{3,5}(C₆H₅)], 129.47 [C⁴(C₆H₅)], 133.02 [C^{2,6}(C₆H₅)], 133.27 [C¹(C₆H₅)]; ³¹P{¹H}: δ_P = -2.2 (br). The species did not survive ESI-MS analysis, with only the parent dppe being observed. Crystal data: C₂₆H₂₆B₂Cl₄P₂, M_r = 563.87, T = 200(2) K, triclinic, space group *P*-1 (No.2), *a* = 6.9470(2), *b* = 9.3716(3), *c* = 11.7449(4) Å, α = 111.7416(18), β = 98.2504(17), γ = 98.943(2)°, V = 684.56(4) Å³, Z = 1, D_{calcd} = 1.368 Mg m⁻³, μ(Mo Kα) 0.56 mm⁻¹, colourless block, 0.12 × 0.21 × 0.31 mm, 13565 measured reflections with 2θ_{max} = 55.2°, 3110 independent reflections, 3103 absorption-corrected data used in F² refinement, 155 parameters, no restraints, R₁ = 0.035, wR₂ = 0.090 for 2839 reflections with I > 2σ(I).

Synthesis of *P,P'*-bis(monobromoborane)-1,2-bis(diphenylphosphino)ethane, (dppe·(BH₂Br)₂): A solution of BH₂Br·SMe₂ (1.0 M, 1.0 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of 1,2-bis(diphenylphosphino)ethane (0.20 g, 0.5 mmol) in benzene (2 mL). The mixture was stirred for 1 h, and then precipitated with pentane and isolated by filtration. The precipitate was dried for 48 h under high vacuum. The solid was recrystallised from a mixture of DCM/pentane overnight at 25°C to produce colourless X-ray diffraction quality needles. When the solid was further dried under high vacuum for microanalysis, the compound was observed (NMR) to decompose to [(dppe)BH₂]Br via the loss of BH₂Br over time. NMR (C₆D₆, 25°C): ¹H: δ_H = 3.07 (d, ²J_{PH} 4.8 Hz, 4H, CH₂), 6.90–6.91 [m, 12H, H³⁻⁵(C₆H₅)], 7.64–7.71 [m, 8H, H^{2,6}(C₆H₅)]; ¹¹B{¹H}: δ_B = -25.4 (br); ³¹P{¹H}: δ_P = -3.7 (br). Acc. Mass: Found: *m/z* = 581.0145. Calcd for C₂₆H₂₇¹¹B₂⁷⁹Br₂P₂ 581.0141 [M -

H]⁺. ESI-MS (+ve ion): $m/z = 491.3$ [M - BH₂Br]⁺. Crystal data: C₂₆H₂₈B₂Br₂P₂, $M_r = 583.89$, $T = 200(2)$ K, triclinic, space group $P-1$ (No.2), $a = 10.9073(3)$, $b = 11.3223(3)$, $c = 12.7952(2)$ Å, $\alpha = 90.9286(15)$, $\beta = 106.3419(15)$, $\gamma = 117.4395(10)^\circ$, $V = 1325.84(6)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.462$ Mg m⁻³, $\mu(\text{Mo K}\alpha) 3.19$ mm⁻¹, colourless block, $0.16 \times 0.28 \times 0.30$ mm, 16687 measured reflections with $2\theta_{\text{max}} = 55.0^\circ$, 6065 independent reflections, 6052 absorption-corrected data used in F^2 refinement, 317 parameters, 24 restraints, $R_1 = 0.045$, $wR_2 = 0.126$ for 4906 reflections with $I > 2\sigma(I)$.

Synthesis of P,P' -bis(tribromoborane)-1,2-bis(diphenylphosphino)ethane, dppe·(BBr₃)₂: A solution of BBr₃ (1.0 M, 0.25 mL, 0.25 mmol) in heptane was added drop-wise to a stirred solution of 1,2-bis(diphenylphosphino)ethane (0.10 g, 0.25 mmol) in benzene (5 mL) that was cooled in an ice bath during addition, which upon addition caused a white precipitate to form. The mixture was stirred for 3.5 h, and then all volatiles were removed under high vacuum to leave a white solid. The solid was recrystallised from a mixture of DCM/pentane, then washed with benzene (2 × 5 mL). A DCM solution of the solid was layered overnight with pentane at 25°C to produce colourless X-ray diffraction quality crystals. Yield 0.52 g (0.06 mmol, 46%). NMR (CD₂Cl₂, 25°C): ¹H: $\delta_H = 3.23$ (d, ²J_{PH} 4.8 Hz, 4H, CH₂), 7.53-7.82 (m, 20H, C₆H₅); ¹¹B{¹H}: $\delta_B = -16.7$ (d.br, ¹J_{BP} 143 Hz); ¹³C{¹H}: $\delta_C = 18.33$ (d, ¹J_{CP} 37.3 Hz, CH₂), 121.18 [d, ¹J_{CP} 67.1 Hz, C¹(C₆H₅)], 129.81 [d, ¹J_{CP} 10.7 Hz, C^{2,6}(C₆H₅)], 134.56 (d, ¹J_{CP} 6.8 Hz, C^{3,5}(C₆H₅)], 135.66 [C⁴(C₆H₅)]; ³¹P{¹H}: $\delta_P = -6.7$ [q.br, ¹J_{BP} 136 Hz (Average value)]. The species did not survive ESI-MS analysis, with only the parent dppe being observed. Crystal data: C₂₆H₂₄B₂Br₆P₂, $M_r = 899.47$, $T = 200(2)$ K, orthorhombic, space group $P2_12_12_1$, $a = 12.4827(3)$, $b = 15.2204(3)$, $c = 16.0672(3)$ Å, $V = 3052.63(11)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.957$ Mg m⁻³, $\mu(\text{Mo K}\alpha) 8.01$ mm⁻¹, colourless plate, $0.07 \times 0.14 \times 0.18$ mm, 38207 measured reflections with $2\theta_{\text{max}} = 54.0^\circ$, 6993 independent reflections, 6993 absorption-corrected data used in F^2 refinement, 325 parameters, no restraints, $R_1 = 0.031$, $wR_2 = 0.064$ for 5709 reflections with $I > 2\sigma(I)$.

Synthesis of P,P' -bis(monobromoborane)-1,1-bis(diphenylphosphino)methane, dppm·(BH₂Br)₂: A solution of BH₂Br·SMe₂ (1.0 M, 0.50 mL, 0.50 mmol) in dichloromethane was added drop-wise to a stirred solution of dppm·C₆H₆ (0.38 g, 0.82 mmol) in DCM (10 mL) at -78°C, which caused a colour

change from colourless to orange briefly, then to a forest-green coloured solution. The reaction mixture was stirred overnight to slowly warm to room temperature, after which the solution was again an orange colour. All volatiles were removed under high vacuum to leave an orange solid. The solid was recrystallised from a mixture of DCM/pentane to give a very pale orange solid that was dried under high vacuum overnight. A DCM solution of the solid was layered overnight with pentane at 25°C to produce orange X-ray diffraction quality crystals. (An older bottle of $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ was used and due to the yield of product recovered it is assumed that it was no longer 1.0 M, but notably higher, leading to an excess being inadvertently used. The percentage yield is therefore based on the amount of $\text{dppm} \cdot \text{C}_6\text{H}_6$ used). Yield 0.267 g (0.44 mmol, 53%). Anal. Found: C, 49.88; H, 4.62; N, 0.00%. Calcd for $\text{C}_{25}\text{H}_{26}\text{B}_2\text{Br}_2\text{P}_2 \cdot 0.5(\text{CH}_2\text{Cl}_2)$: C, 50.02; H, 4.44; N, 0.00%. NMR (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 3.75$ [t, $^2J_{\text{PH}} 12.3$ Hz, 2H, CH_2], 7.30–7.68 (m, 20H, C_6H_5); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -23.8$ (br); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 17.43$ (t, $^1J_{\text{CP}} 32.9$ Hz, CH_2), 124.50 [dd, $^1J_{\text{CP}}/J 63.3$ Hz/2.3 Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], 128.70 [$\text{C}^4(\text{C}_6\text{H}_5)$], 129.43 [d, $J_{\text{CP}} 11.4$ Hz, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 133.81 [d, $J_{\text{CP}} 9.1$ Hz, $\text{C}^{3,5}(\text{C}_6\text{H}_5)$]; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -1.8$ (br). Acc. Mass: Found: $m/z = 590.9960$. Calcd for $\text{C}_{25}\text{H}_{26}^{11}\text{B}_2^{79}\text{Br}_2\text{NaP}_2$ 590.9960 $[\text{M} + \text{Na}]^+$. ESI-MS (+ve ion): $m/z = 489.5$ $[\text{M} - \text{Br}]^+$, 477.4 $[\text{M} - \text{BH}_2\text{Br}]^+$, 397.5 $[\text{M} - \text{BH}_2\text{Br} - \text{Br}]^+$, 385.5 $[\text{M} + \text{H} - 2(\text{BH}_2\text{Br})]^+$. Crystal data: $\text{C}_{25}\text{H}_{26}\text{B}_2\text{Br}_2\text{P}_2$, $M_r = 569.86$, $T = 200(2)$ K, monoclinic, space group $P2_1/n$, $a = 10.6639(2)$, $b = 23.7604(6)$, $c = 10.6766(2)$ Å, $\beta = 94.7958(12)^\circ$, $V = 2695.75(10)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.404$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 3.14$ mm⁻¹, orange prism, $0.14 \times 0.17 \times 0.50$ mm, 41452 measured reflections with $2\theta_{\text{max}} = 60.0^\circ$, 7681 independent reflections, 7662 absorption-corrected data used in F^2 refinement, 280 parameters, no restraints, $R_1 = 0.047$, $wR_2 = 0.119$ for 5034 reflections with $I > 2\sigma(I)$.

Synthesis of P,P' -bis(monobromoborane)-1,4-bis(diphenylphosphino)butane, $\text{dppb} \cdot (\text{BH}_2\text{Br})_2$: A solution of $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ (1.0 M, 0.25 mL, 0.25 mmol) in dichloromethane was added drop-wise to a stirred solution of dppb (0.11 g, 0.25 mmol) in benzene (10 mL) that was cooled in an ice bath during addition. The mixture was warmed to room temperature and stirred for 2 h. The resulting orange solution was precipitated with pentane to give an orange solid, which was separated *via* cannula filtration. The solid was dried under high vacuum for 30 min, then twice recrystallised from a mixture of DCM/pentane to give a white solid. A DCM solution of the solid was layered overnight with pentane at 25°C to produce colourless X-ray diffraction quality

crystals. Yield 0.046 g (0.075 mmol, 35%). M.p. 236-238°C. Anal. Found: C, 54.73; H, 4.98; N, 0.00%. Calcd for $C_{28}H_{32}B_2Br_2P_2$: C, 54.96; H, 5.27; N, 0.00%. NMR (CD_2Cl_2 , 25°C): 1H : $\delta_H = 1.65$ - 1.67 (m, $^3J_{PH}/^3J_{HH}$ 4H, CH_2), 2.38 - 2.43 (m, $^2J_{PH}/^3J_{HH}$ 4H, CH_2), 7.45 - 7.63 (m, 20H, C_6H_5); $^{11}B\{^1H\}$: $\delta_B = -25.5$ (br); $^{13}C\{^1H\}$: $\delta_C = 23.16$ (P- CH_2 - CH_2), 24.28 (d, $^1J_{CP}$ 14.9 Hz, P- CH_2 - CH_2), 125.76 [d, $^1J_{CP}$ 60.3 Hz, $C^1(C_6H_5)$], 130.12 [$C^4(C_6H_5)$], 130.63 [d, J_{CP} 12.7 Hz, $C^{2,6}(C_6H_5)$], 133.01 [d, J_{CP} 8.1 Hz, $C^{3,5}(C_6H_5)$]; $^{31}P\{^1H\}$: $\delta_P = 2.7$ (br). Acc. Mass: Found: $m/z = 439.1915$ Calcd for $C_{28}H_{30}^{11}BP_2$ 439.1916 [$M - BH_2Br - Br$] $^+$. Crystal data: $C_{28}H_{32}B_2Br_2P_2$, $M_r = 611.94$, $T = 200(2)$ K, monoclinic, space group $P2_1/n$, $a = 9.8116(2)$, $b = 10.1524(4)$, $c = 14.6397(5)$ Å, $\beta = 105.061(2)^\circ$, $V = 1408.18(8)$ Å 3 , $Z = 2$, $D_{calcd} = 1.443$ Mg m $^{-3}$, $\mu(Mo K\alpha) 3.01$ mm $^{-1}$, colourless block, $0.08 \times 0.10 \times 0.18$ mm, 28349 measured reflections with $2\theta_{max} = 55.0^\circ$, 3225 independent reflections, 3225 absorption-corrected data used in F^2 refinement, 154 parameters, no restraints, $R_1 = 0.055$, $wR_2 = 0.156$ for 2545 reflections with $I > 2\sigma(I)$.

Synthesis of P,P' -bis(tribromoborane)-1,2-bis(dimethylphosphino)ethane, $dmpe \cdot (BBr_3)_2$: A solution of BBr_3 (1.0 M, 0.50 mL, 0.50 mmol) in heptane was added drop-wise to a stirred solution of 1,2-bis(dimethylphosphino)ethane (0.08 mL, 0.50 mmol) in toluene (10 mL), which upon addition caused a white precipitate to form instantaneously, and then was stirred for 15 min. Supernatant: NMR ($CDCl_3$, 25°C): $^{11}B\{^1H\}$: $\delta_B = -15.1$ [d, $^1J_{BP}$ 158 Hz, $dmpe \cdot (BBr_3)_2$]; $^{31}P\{^1H\}$: $\delta_P = -46.6$ (free $dmpe$). The mixture was heated to reflux for 2 h to give a white precipitate and a colourless solution. The precipitate was isolated by cannula filtration and all volatiles removed under high vacuum to leave a white solid. NMR (D_6 -DMSO, 25°C): $^{11}B\{^1H\}$: $\delta_B = -13.7$ [d, $^1J_{BP}$ 150 Hz, $dmpe \cdot (BBr_3)_2$]; $^{31}P\{^1H\}$: $\delta_P = -76.2$ (d, J 21 Hz), -3.0 [q.br, $^1J_{BP}$ 113 Hz (Average), $dmpe \cdot (BBr_3)_2$], 5.6 (s.br), 26.4 (d, J 46 Hz), 33.5 (d, J 46 Hz), 34.1 (s), 40.7 (d, J 43 Hz), 41 (s), 42 (s.br).[†]

Synthesis of E - P,P' -bis(monobromoborane)-1,2-bis(diphenylphosphino)ethene, E - $C_2H_2(PPh_2)_2 \cdot (BH_2Br)_2$: A solution of $BH_2Br \cdot SMe_2$ (1.0 M, 0.50 mL, 0.50 mmol) in dichloromethane was added drop-wise to a stirred

[†] Oxidised $dmpe$, $Me_2P(O)CH_2CH_2P(O)Me_2$ has been reported at δ_P 60.8 and was not observed.²⁹

solution of *E*-1,2-bis(diphenylphosphino)ethene (0.10 g, 0.25 mmol) in benzene (2 mL) to give an orange suspension. The mixture was stirred for 3 h, and then all volatiles were removed under high vacuum to leave an orange solid. The solid was recrystallised from a mixture of DCM/pentane to give a very pale orange solid that was dried under high vacuum overnight. A DCM solution of the solid was layered overnight with pet. ether 40-60°C at 25°C to produce colourless X-ray diffraction quality crystals. Yield 0.124 g (0.21 mmol, 85%). Anal. Found: C, 53.51; H, 4.37; N, 0.00%. Calcd for $C_{26}H_{26}B_2Br_2P_2$: C, 53.67; H, 4.50; N, 0.00%. NMR (CD_2Cl_2 , 25°C): 1H : $\delta_H = 7.22$ [td, ($^2J_{PH}/^3J_{HH}$)/ $^3J_{PH}$ 17.5 Hz/1.7 Hz, 2H, CH=CH], 7.54-7.77 (m, 20H, C_6H_5); $^{11}B\{^1H\}$: $\delta_B = -25.2$ (br); $^{13}C\{^1H\}$: $\delta_C = 129.53$ (br), 130.16 (br), 131.47 (br), 132.80 (br), 133.27 (br); $^{31}P\{^1H\}$: $\delta_P = -4.0$ (br). Acc. Mass: Found: $m/z = 489.0701$. Calcd for $C_{26}H_{25}^{11}B^{79}BrP_2$ 489.0708 [$M + H - BH_2Br$] $^+$. ESI-MS (+ve ion): $m/z = 605.0$ [$M + Na$] $^+$, 511.1 [$M + Na - BH_2Br$] $^+$, 398.1 [$M + H - 2(BH_2Br)$] $^+$. Crystal data: $C_{26}H_{26}B_2Br_2P_2$, $M_r = 581.87$, $T = 200(2)$ K, monoclinic, space group $C2/c$, $a = 15.0676(3)$, $b = 10.0274(2)$, $c = 18.0705(4)$ Å, $\beta = 102.0033(13)^\circ$, $V = 2670.56(10)$ Å 3 , $Z = 4$, $D_{calcd} = 1.447$ Mg m $^{-3}$, $\mu(Mo K\alpha) 3.17$ mm $^{-1}$, colourless plate, 0.04 × 0.14 × 0.28 mm, 28192 measured reflections with $2\theta_{max} = 55.0^\circ$, 3062 independent reflections, 3061 absorption-corrected data used in F^2 refinement, 155 parameters, no restraints, $R_1 = 0.032$, $wR_2 = 0.084$ for 2510 reflections with $I > 2\sigma(I)$.

Synthesis of *E-P,P'*-bis(dichloroborane)-1,2-bis(diphenylphosphino)ethene, $E-C_2H_2(PPh_2)_2 \cdot (BHCl_2)_2$: A solution of $BHCl_2 \cdot SMe_2$ (8.7 molL $^{-1}$, 0.06 mL, 0.50 mmol) in excess SMe_2 was added drop-wise to a stirred solution of 1,2-bis(diphenylphosphino)ethene (0.10 g, 0.25 mmol) in benzene (2 mL), which produced a white precipitate that slowly redissolved to give a colourless solution. The reaction was stirred for 4.5 h, then all volatiles removed under high vacuum to give a white residue. The white precipitate was dissolved in DCM and layered with pentane overnight. The resulting white solid was isolated by cannula filtration. Yield 0.107 g (0.19 mmol, 63%). NMR (CD_2Cl_2 , 25°C): $^{11}B\{^1H\}$: $\delta_B = -6.0$ (br); $^{31}P\{^1H\}$: $\delta_P = -2.7$ (br).

Decomposition to 1-trichloroborate-1,2-bis(diphenylphosphonyl)ethane dichloroboronium, $[Cl_2B(OPPh_2)_2CH(BCl_3)CH_2]$: The white residue obtained above was dissolved in DCM and layered with pentane overnight, to give a white precipitate and a yellow oil. The yellow oil was separated by cannula filtration and discarded. The

white precipitate was dissolved in DCM and again layered with pentane and stored at -20°C for 2 months to give colourless X-ray diffraction quality crystals.[†] NMR (CD_2Cl_2 , 25°C): $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -19.2$ (br, BO_2Cl_2), -5.6 (br, BCl_3); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -2.54, -2.48$. *Crystal data*: $\text{C}_{26}\text{H}_{23}\text{B}_2\text{Cl}_5\text{O}_2\text{P}_2$, $M_r = 628.30$, $T = 200(2)$ K, monoclinic, space group $P2_1/n$, $a = 10.8664(2)$, $b = 17.3935(4)$, $c = 15.4450(2)$ Å, $\beta = 102.3438(13)^{\circ}$, $V = 2851.69(9)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.463$ Mg m⁻³, $\mu(\text{Mo K}\alpha) 0.65$ mm⁻¹, colourless block, $0.16 \times 0.21 \times 0.33$ mm, 59668 measured reflections with $2\theta_{\text{max}} = 55.0^{\circ}$, 6523 independent reflections, 6506 absorption-corrected data used in F^2 refinement, 353 parameters, 12 restraints, $R_1 = 0.044$, $wR_2 = 0.123$ for 4935 reflections with $I > 2\sigma(I)$.

Synthesis of P,P' -diborane-1,2-bis(diphenylphosphino)ethyne, $(\text{Ph}_2\text{PC}\equiv\text{CPh}_2)\cdot(\text{BH}_3)_2$: A solution of $\text{BH}_3\cdot\text{SMe}_2$ (10.5 molL⁻¹, 0.05 mL, 0.50 mmol) in excess SMe_2 was added drop-wise to a stirred solution of 1,2-bis(diphenylphosphino)ethyne (0.10 g, 0.25 mmol) in benzene (1 mL) and stirred for 3 h. All volatiles were removed under high vacuum to give a white residue that was further dried under vacuum for 2 h, by which time it had fully dried to a solid. The solid was recrystallised from a mixture of DCM/pentane to give a white powder. A DCM solution of the solid was layered overnight with pentane at 25°C to produce colourless X-ray diffraction quality crystals. Yield 0.050 g (0.12 mmol, 47%). Anal. Found: C, 62.96 ; H, 5.73 ; N, 0.00% . Calcd for $\text{C}_{26}\text{H}_{26}\text{B}_2\text{P}_2\cdot 1.1(\text{CH}_2\text{Cl}_2)$:[§] C, 63.14 ; H, 5.51 ; N, 0.00% . NMR (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 0.63$ – 1.80 (vbr, 6H , BH_3), 7.46 – 7.80 (m, 20H , C_6H_5); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -38.2$ (br); ^{11}B : $\delta_{\text{B}} = -38.2$ (q.br, $^1J_{\text{BH}} 55$ Hz); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 129.67$ (d, $J_{\text{CP}} 11.5$ Hz, C_6H_5), 130.15 (C_6H_5), 132.42 (C_6H_5), 133.17 [d, $^1J_{\text{CP}} 20.7$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], $\text{C}\equiv\text{C}$ resonance not observed; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 8.7$ (d.br, $^1J_{\text{BP}} 53$ Hz). Acc. Mass: Found: $m/z = 445.1590$ Calcd for $\text{C}_{26}\text{H}_{26}^{11}\text{B}^{23}\text{NaP}_2$ 445.1594 $[\text{M} + \text{Na}]^+$. ESI-MS (+ve ion): $m/z = 469.2$ $[\text{M} + 2\text{Na}]^+$, 423.2 $[\text{M} + \text{H}]^+$, 411.2 $[\text{M} - \text{B}]^+$. *Crystal data*: $\text{C}_{26}\text{H}_{26}\text{B}_2\text{P}_2$, $M_r = 422.06$, $T = 200(2)$ K, monoclinic, space group $P2_1$, $a = 11.4743(6)$, $b = 9.0044(5)$, $c = 12.5327(8)$ Å, $\beta = 109.222(3)^{\circ}$, $V = 1222.68(12)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.146$ Mg m⁻³, $\mu(\text{Mo K}\alpha) 0.19$ mm⁻¹, colourless plate, $0.05 \times 0.14 \times 0.25$ mm, 15866 measured reflections

[†] The prolonged period of crystallisation was not intentional, but was an oversight on the part of the author.

[§] Less solvated DCM was observed in the ^1H NMR spectrum, with a relative integral of approximately 0.4 .

with $2\theta_{\max} = 50.2^\circ$, 4344 independent reflections, 4340 absorption-corrected data used in F^2 refinement, 273 parameters, 1 restraints, $R_1 = 0.050$, $wR_2 = 0.117$ for 3366 reflections with $I > 2\sigma(I)$.

Synthesis of ~1:1 mixture of P,P' -bis(dichloroborane)-1,2-bis(diphenylphosphino)ethyne, $\text{Ph}_2\text{PC}\equiv\text{CPh}_2\cdot(\text{BHCl}_2)_2$ and other unidentified product: A solution of $\text{BHCl}_2\cdot\text{SMe}_2$ (8.7 mol L^{-1} , 0.06 mL, 0.50 mmol) in excess SMe_2 was added drop-wise to a stirred solution of 1,2-bis(diphenylphosphino)ethyne (0.10 g, 0.25 mmol) in benzene (1 mL) and stirred for 6.5 h. All volatiles removed under high vacuum to give a colourless oil that was further dried under high vacuum overnight (after 30 min some of the oil had dried to a white solid). Sublimation of the crude oil under high vacuum produced colourless X-ray diffraction quality crystals. Crude NMR (CD_2Cl_2 , 25°C): $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -5.1$ (br), -18.2 (br); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -1.0$ (br), -9.4 (br). *Crystal data:* $\text{C}_{26}\text{H}_{22}\text{B}_2\text{Cl}_4\text{P}_2$, $M_r = 559.84$, $T = 200(2) \text{ K}$, monoclinic, space group $P2_1/n$, $a = 9.3982(2)$, $b = 15.8733(2)$, $c = 18.6891(4) \text{ \AA}$, $\beta = 99.6652(11)^\circ$, $V = 2748.47(9) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 1.353 \text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) 0.56 \text{ mm}^{-1}$, colourless block, $0.08 \times 0.15 \times 0.18 \text{ mm}$, 55641 measured reflections with $2\theta_{\max} = 55.0^\circ$, 6302 independent reflections, 6302 absorption-corrected data used in F^2 refinement, 327 parameters, 18 restraints, $R_1 = 0.057$, $wR_2 = 0.171$ for 4373 reflections with $I > 2\sigma(I)$.

Synthesis of 1,2-bis(monobromoborane)-1,2-bis(diphenylphosphino)ethyne, $\text{Ph}_2\text{PC}\equiv\text{CPh}_2\cdot(\text{BH}_2\text{Br})_2$: A solution of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (1.0 M, 0.50 mL, 0.50 mmol) in dichloromethane was added drop-wise to a stirred solution of 1,2-bis(diphenylphosphino)ethyne (0.10 g, 0.25 mmol) in benzene (1 mL) and stirred for 3 h. All volatiles were removed under high vacuum to give an orange solid that was further dried under high vacuum overnight. The orange solid was extracted with benzene, and then all volatiles removed under high vacuum. The solid was twice recrystallised from a mixture of DCM/pentane to give a pale orange solid. A DCM solution of the solid was layered overnight with pentane at -20°C to produce colourless X-ray diffraction quality crystals. Yield 0.050 g (0.086 mmol, 34%). Anal. Found: C, 53.78; H, 4.11; N, 0.00%. Calcd for $\text{C}_{26}\text{H}_{24}\text{B}_2\text{Br}_2\text{P}_2$: C, 53.86; H, 4.17; N, 0.00%. NMR (CD_2Cl_2 , 25°C): 7.52–7.86 (m, 20H, C_6H_5); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -24.1$ (br); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 98.50$ (d, $^1J_{\text{CP}} 98.8 \text{ Hz}$, $\text{C}\equiv\text{C}$), 122.84 [d, $^1J_{\text{CP}} 67.1 \text{ Hz}$, $\text{C}^1(\text{C}_6\text{H}_5)$], 129.54 [$\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 132.72

[d, J_{CP} 11.2 Hz, $\text{C}^{3,5}(\text{C}_6\text{H}_5)$], 133.18 [$\text{C}^4(\text{C}_6\text{H}_5)$]; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -2.0$ (br). ESI-MS (+ve ion): $m/z = 509.4$ [$\text{M} + \text{Na} - \text{BH}_2\text{Br}$] $^+$. *Crystal data*: $\text{C}_{26}\text{H}_{24}\text{B}_2\text{Br}_2\text{P}_2\text{Br}$, $M_r = 579.85$, $T = 200(2)$ K, triclinic, space group $P-1$ (No.2), $a = 9.5477(3)$, $b = 11.7635(4)$, $c = 12.2389(3)$ Å, $\alpha = 86.177(2)$, $\beta = 87.9468(19)$, $\gamma = 71.3735(14)^\circ$, $V = 1299.55(7)$ Å 3 , $Z = 2$, $D_{\text{calcd}} = 1.482$ Mg m $^{-3}$, $\mu(\text{Mo K}\alpha) 3.26$ mm $^{-1}$, colourless prism, $0.13 \times 0.15 \times 0.35$ mm, 26986 measured reflections with $2\theta_{\text{max}} = 55.0^\circ$, 5966 independent reflections, 5966 absorption-corrected data used in F^2 refinement, 290 parameters, no restraints, $R_1 = 0.040$, $wR_2 = 0.098$ for 4538 reflections with $I > 2\sigma(I)$.

Synthesis of *P*-monobromoborane-1-diphenylphosphino-2-diphenylarsino ethane, arphos·BH $_2$ Br: A solution of BH $_2$ Br·SMe $_2$ (1.0 M, 0.10 mL, 0.10 mmol) in dichloromethane was added drop-wise to a stirred solution of arphos (0.044 g, 0.1 mmol) in benzene (2 mL). The reaction was stirred for 30 min, then all volatiles were removed under high vacuum to leave a white residue. The solid was recrystallised from a mixture of DCM/pentane to give a white solid. Yield: 0.044 g (0.082 mmol, 82%). Satisfactory elemental analysis could not be obtained due to compound partially undergoing decomposition to [BH $_2$ (arphos) $_2$]Br. A benzene solution of the solid was layered overnight with pentane at 25°C to produce colourless X-ray diffraction quality crystals. NMR (C $_6$ D $_6$, 25°C): ^1H : $\delta_{\text{H}} = 2.31\text{--}2.37$ (m, 2H, PCH $_2$), 2.49–2.56 (m, 2H, AsCH $_2$), 6.86–7.10 [m, 12 H, $\text{H}^{3,5}(\text{C}_6\text{H}_5)$], 7.29–7.40 [m, 8 H, $\text{H}^{2,6}(\text{C}_6\text{H}_5)$]; $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -24.9$ (br); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 19.42$ (d, $^2J_{\text{CP}}$ 3.8 Hz, AsCH $_2$), 20.06 (d, $^1J_{\text{CP}}$ 36.6 Hz, PCH $_2$), 126.16 [d, J_{CP} 58.2 Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], 129.11 (d, J_{CP} 29.1 Hz, C $_6$ H $_5$), 129.17 (C $_6$ H $_5$), 131.84 (d, 2.5 Hz, C $_6$ H $_5$), 132.96 (d, 7.6 Hz, C $_6$ H $_5$), 133.31 (C $_6$ H $_5$), 133.57 (C $_6$ H $_5$), 139.74 [$\text{C}^1(\text{As-C}_6\text{H}_5)$]; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 4.7$ (br). Acc. Mass: Found: $m/z = 455.1080$. Calcd for $\text{C}_{26}\text{H}_{26}^{75}\text{As}^{11}\text{BP}$ 455.1081 [$\text{M} - \text{Br}$] $^+$. *Crystal data*: $\text{C}_{26}\text{H}_{26}\text{AsBBrP}$, $M_r = 535.10$, $T = 200(2)$ K, triclinic, space group $P-1$ (No.2), $a = 6.6265(1)$, $b = 16.3102(3)$, $c = 23.0216(4)$ Å, $\alpha = 90.4478(7)$, $\beta = 93.5377(10)$, $\gamma = 91.7786(11)^\circ$, $V = 2482.11(7)$ Å 3 , $Z = 4$, $D_{\text{calcd}} = 1.432$ Mg m $^{-3}$, $\mu(\text{Mo K}\alpha) 3.05$ mm $^{-1}$, colourless prism, $0.15 \times 0.15 \times 0.31$ mm, 52754 measured reflections with $2\theta_{\text{max}} = 55.0^\circ$, 11352 independent reflections, 11317 absorption-corrected data used in F^2 refinement, 542 parameters, 18 restraints, $R_1 = 0.067$, $wR_2 = 0.202$ for 8984 reflections with $I > 2\sigma(I)$. Reaction left for two months in CHCl $_3$. NMR (CDCl $_3$, 25°C): $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -41.0$ (s.br), -36.9 (s.br); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -0.3$ (br), 11.0 (br), 55.4.

Decomposition product [BH₂(arphos)]Br: Partial evaporation of a benzene solution of the solid overnight at 25°C produced colourless X-ray diffraction quality crystals. NMR (CDCl₃, 25°C): ¹¹B{¹H}: δ_B = -37.1 (br); ³¹P{¹H}: δ_P = 11.0 (br). Acc. Mass: Found: *m/z* = 897.1913. Calcd for C₅₂H₅₀⁷⁵As₂¹¹BP₂ 897.1913 [M]⁺. *Crystal data:* [C₅₂H₅₀As₂BP₂]Br·C₆H₆, *M_r* = 1055.59, *T* = 200(2) K, triclinic, space group *P*-1 (No.2), *a* = 10.0026(2), *b* = 11.3717(2), *c* = 22.9757(4) Å, α = 87.1774(11), β = 79.5893(9), γ = 82.4700(11)°, *V* = 2547.34(8) Å³, *Z* = 2, *D*_{calcd} = 1.376 Mg m⁻³, μ(Mo Kα) 2.20 mm⁻¹, colourless block, 0.28 × 0.30 × 0.40 mm, 52163 measured reflections with 2θ_{max} = 55.0°, 11641 independent reflections, 11639 absorption-corrected data used in *F*² refinement, 660 parameters, 476 restraints, *R*₁ = 0.047, *wR*₂ = 0.117 for 8918 reflections with *I* > 2σ(*I*).

Reaction of arphos·BH₂Br and Ru(Ph)Cl(CO)(PPh₃)₂: A solution of BH₂Br·SMe₂ (1.0 M, 0.25 mL, 0.25 mmol) in dichloromethane was added drop-wise to a stirred solution of arphos (0.11 g, 0.25 mmol) in benzene (8 mL). The reaction mixture was stirred for 1.5 h and then cannula transferred into a flask containing Ru(Ph)Cl(CO)(PPh₃)₂ (0.19 g, 0.25 mmol) which was stirred for a further 16 h. NMR analysis (CDCl₃) revealed only arphos·BH₂Br (δ_B -25.2, δ_P 4.9), free PPh₃ (δ_P -4.6) and Ru(Ph)Cl(CO)(PPh₃)₂ (δ_P 32.2). The mixture was then heated to reflux overnight to give a yellow/pale orange coloured solution. NMR essay of the crude reaction mixture revealed two resonances in the ¹¹B NMR spectrum and approximately 21 peaks in the ³¹P NMR spectrum. Subsequent recrystallisation of the crude mixture from a mixture of DCM and pentane provided yellow and orange X-ray diffraction quality crystals, but these can not be seen as representative of the bulk sample. Data for bulk mixture: NMR (CDCl₃, 25°C): ¹¹B{¹H}: δ_B = -23.4 (br, Ph₃P·BH₂Br), -17.9 (br); ³¹P{¹H}: δ_P = -4.7 (free PPh₃), 4.7 (br, arphos·BH₂Br), 14.9, 16.7, 17.7, 19.6, 22.1 (dd, *J* 284/20 Hz), 26.0 [t, *J* 105 Hz (Average)], 27.7, 29.4, 41.6, 42.9, 43.4, 44.5, 44.7, 45.9 (d, *J* 96 Hz), 47.3, 50.9, 55.5 (dd, *J* 64/20 Hz), 61.9, 67.5, 70.0. ESI-MS (+ve ion): *m/z* = 1449.0 [Ru(arphos)₃ + Na]⁺, 1168.9 [RuBr₂(arphos)₂ + Na]⁺, 912.0 [RuBr(CO)(arphos)(PPh₃)]⁺, 835.1 [Ru(CO)(arphos)(PPh₃)]⁺.

RuBr₂(arphos)₂: *Crystal data:* C₅₂H₄₈As₂Br₂P₂Ru, *M_r* = 1145.62, *T* = 200(2) K, monoclinic, space group *P*2₁/*c*, *a* = 11.4612(2), *b* = 13.3096(3), *c* = 17.2695(3) Å, β = 97.6623(11)°, *V* = 2610.84(9) Å³, *Z* = 2, *D*_{calcd} = 1.457 Mg m⁻³, μ(Mo Kα) = 3.18 mm⁻¹,

orange block, $0.08 \times 0.14 \times 0.18$ mm, 57038 measured reflections with $2\theta_{\max} = 55.0^\circ$, 6001 independent reflections, 5984 absorption-corrected data used in F^2 refinement, 268 parameters, no restraints, $R_1 = 0.053$, $wR_2 = 0.157$ for 4604 reflections with $I > 2\sigma(I)$.

RuBr₂(CO)(PPh₃)(arphos): Insufficient yield obtained for complete characterisation. Yield: 0.066 g (0.07 mmol, 53%). Anal. Found: C, 50.54; H, 3.98; N, 0.00%. Calcd for C₄₅H₃₉AsBr₂OP₂Ru.1.25(CH₂Cl₂): C, 50.51; H, 3.80; N, 0.00%. IR (DCM): ν_{CO} 1969 cm⁻¹. *Crystal data:* C₄₅H₃₉AsBr₂OP₂Ru.CH₂Cl₂, $M_r = 1078.48$, $T = 200(2)$ K, monoclinic, space group $P2_1/c$, $a = 10.3442(5)$, $b = 16.1262(8)$, $c = 25.8347(11)$ Å, $\beta = 91.910(3)^\circ$, $V = 4307.2(4)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.663$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 3.22$ mm⁻¹, yellow prism, $0.04 \times 0.05 \times 0.22$ mm, 14550 measured reflections with $2\theta_{\max} = 50.0^\circ$, 7545 independent reflections, 7522 absorption-corrected data used in F^2 refinement, 511 parameters, 30 restraints, $R_1 = 0.081$, $wR_2 = 0.186$ for 4179 reflections with $I > 2\sigma(I)$.

Reaction of arphos·BH₂Br and Rh₂(μ-Cl)₂Cl₂Cp*₂: A solution of BH₂Br.SMe₂ (1.0 M, 0.25 mL, 0.25 mmol) in dichloromethane was added drop-wise to a stirred solution of arphos (0.11 g, 0.25 mmol) in benzene (8 mL) and stirred for 1.5 h. The solution was cannula transferred into a flask containing Rh₂(μ-Cl)₂Cl₂Cp*₂ (0.08 g, 0.125 mmol) to give a dark red solution (some precipitate present) that was stirred for 2 h. An ¹¹B NMR spectrum revealed only arphos·BH₂Br was present at $\delta_B -25.31$ (C₆D₆). Reaction was heated to reflux for 16 h (after ~2 h hours the solution was a much darker red). NMR (C₆D₆, 25°C): ¹¹B{¹H}: $\delta_B = 6.3, 7.4$; ¹¹B: $\delta_B = 6.3, 7.4$; ³¹P{¹H}: $\delta_P = 3.7$ (br, arphos·BH₂Br), 30.3, 67.8 (d, J 133 Hz), 76.0 (d, J 133 Hz).

[RhCl_{0.88}Br_{0.12}Cp*(arphos)]Cl_{0.56}Br_{0.44}: All volatiles removed under high vacuum to leave a brown/red solid. The solid was recrystallised from a mixture of DCM/pentane to give red/orange X-ray diffraction quality crystals. Yield: 0.205 g. *Crystal data:* 2[C₃₆H₃₉AsBr_{0.25}Cl_{0.75}PRh]Br_{0.5}Cl_{0.5}, $M_r = 1572.17$, $T = 200(2)$ K, orthorhombic, space group $Pbcn$, $a = 22.8611(2)$, $b = 18.1192(2)$, $c = 32.1647(3)$ Å, $V = 13323.4(2)$ Å³, $Z = 8$, $D_{\text{calcd}} = 1.567$ Mg m⁻³, $\mu(\text{Mo K}\alpha) 2.60$ mm⁻¹, orange block, $0.17 \times 0.21 \times 0.21$ mm, 134378 measured reflections with $2\theta_{\max} = 55.0^\circ$, 15241 independent reflections, 15238 absorption-corrected data used in F^2 refinement, 822 parameters, 36 restraints, $R_1 = 0.050$, $wR_2 = 0.148$ for 10666 reflections with $I > 2\sigma(I)$.

Synthesis of 1-dibromoborane-diphenylphosphino-2-diphenylarsino ethane, $\text{Ph}_2\text{As}(\text{CH}_2)_2\text{PPh}_2\cdot\text{BHBr}_2$: A solution of $\text{BHBr}_2\cdot\text{SMe}_2$ (1.0 M, 0.25 mL, 0.25 mmol) in dichloromethane was added drop-wise to a stirred solution of arphos (0.11 g, 0.25 mmol) in DCM (2 mL). Stirred for 1.5 h, then all volatiles were removed under high vacuum to leave a white solid. Yield: 0.152 g (0.248 mmol, 99%). Anal. Found: C, 42.20; H, 2.72; N, 0.00%. Calcd for $\text{C}_{26}\text{H}_{25}\text{AsBBR}_2\text{P}$: C, 50.86; H, 4.10; N, 0.00%.[†] NMR (CDCl_3 , 25°C): ^1H : $\delta_{\text{H}} = 2.07\text{--}2.15$ (m, 2H, PCH_2), 2.55–2.64 (m, 2H, AsCH_2), 7.32–7.36 (m, 10H, C_6H_5), 7.44–7.62 (m, 10H, C_6H_5). $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -17.0$ (br). $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 18.83$ (br, AsCH_2), 20.30 (d, $^1J_{\text{CP}} 36.7$ Hz, PCH_2), 122.53 [d, $^1J_{\text{CP}} 63.3$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], 128.98 (d, 2.6 Hz, C_6H_5), 129.23 (d, 10.1 Hz, C_6H_5), 132.65 (d, 2.6 Hz, C_6H_5), 133.09 (C_6H_5), 133.76 (d, 7.5 Hz, C_6H_5), 138.95 [d.br, 22.8 Hz, $\text{C}^1(\text{As}-\text{C}_6\text{H}_5)$]. $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -1.5$ (br). Acc. Mass: Found: $m/z = 650.9004$ Calcd for $\text{C}_{26}\text{H}_{25}^{75}\text{As}^{11}\text{B}^{79}\text{Br}_2^{39}\text{KP}$ 650.9007 [$\text{M} + \text{K}$]⁺. ESI-MS (+ve ion): $m/z = 634.9$ [$\text{M} + \text{Na}$]⁺, 615.3 [$\text{M} + \text{H}$]⁺, 535.4 [$\text{M} - \text{Br}$]⁺, 455.5 [$\text{M} + \text{H} - 2\text{Br}$]⁺, 443.5 [$\text{M} + \text{H} - \text{BHBr}_2$]⁺.

Synthesis of 2,2,4,4-tetrabromo-1,1,3,3-tetraphenylcyclo-diphosphinoborane, $[\text{Br}_2\text{B}-\text{PPh}_2]_2$: Synthesised according to reported method with PPh_2 (2.66 mL, 15.3 mmol), BBr_3 (1.0 M, 15 mL, 15.0 mmol) and NEt_3 (2.09 mL, 15.0 mmol) in benzene (58 mL).³⁰ Yield: 1.643 g (2.31 mmol, 31%). Anal. Found: C, 40.67; H, 2.91; N, 0.00%. Calcd for $\text{C}_{24}\text{H}_{20}\text{B}_2\text{Br}_4\text{P}_2$: C, 40.51; H, 2.83; N, 0.00%. NMR (CDCl_3 , 25°C): ^1H : $\delta_{\text{H}} = 7.38\text{--}7.43$ [m, 8H, $\text{H}^{3,5}(\text{C}_6\text{H}_5)$], 7.47–7.51 [m, 4H, $\text{H}^4(\text{C}_6\text{H}_5)$], 7.78–7.84 [m, 8H, $\text{H}^{2,6}(\text{C}_6\text{H}_5)$]; $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -11.5$ (t, $^1J_{\text{BP}} = 97$ Hz); ^{11}B : $\delta_{\text{B}} = -11.5$ [t, $^1J_{\text{BP}} = 97$ Hz (Average)]; $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 126.19$ [t, $^1J_{\text{CP}} = 31.7$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$], 128.83 (t, $J_{\text{CP}} 5.7$ Hz, C_6H_5), 131.68 (C_6H_5), 134.87 (C_6H_5); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -24.1$ [q, $^1J_{\text{BP}} 95$ Hz (Average)]. ESI-MS (+ve ion): $m/z = 735.2$ [$\text{M} + \text{Na}$]⁺, 713.4 [$\text{M} + \text{H}$]⁺. Crystal data: $\text{C}_{24}\text{H}_{20}\text{B}_2\text{Br}_4\text{P}_2$, $M_r = 711.61$, $T = 200(2)$ K, monoclinic, space group $P2_1/n$, $a = 12.0533(1)$, $b = 13.2799(2)$, $c = 17.3094(2)$ Å, $\beta = 109.9501(8)^\circ$, $V = 2604.39(6)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.815$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 6.32$ mm⁻¹, colourless block, 0.17 × 0.25 × 0.35 mm, 68189 measured reflections with $2\theta_{\text{max}} = 60.0^\circ$, 7613 independent reflections, 7613 absorption-corrected data used in F^2 refinement, 290 parameters, no restraints, $R_1 = 0.030$, $wR_2 = 0.068$ for 5914 reflections with $I > 2\sigma(I)$.

[†] Satisfactory microanalysis could not be obtained due to decomposition in the solid state, even under an inert atmosphere.

6.4 Secondary Phosphine Mixed Haloborane Adducts

Synthesis of dicyclohexylphosphine-dichloroborane, $\text{Cy}_2\text{HP}\cdot\text{BHCl}_2$: A solution of $\text{BHCl}_2\cdot\text{SMe}_2$ (8.7 molL^{-1} , 0.12 mL, 1.0 mmol) was added drop-wise to a stirred solution of dicyclohexylphosphine ($\rho = 0.98\text{ g mL}^{-1}$, 0.20 mL, 1.0 mmol) in pentane (10 mL) at 0°C . Upon addition a precipitate formed instantly; the suspension was allowed to warm to room temp. and was stirred for 15 min. All volatiles were removed under high vacuum to leave a white solid that was further dried under high vacuum for 48 h. The ^{31}P NMR spectrum revealed effectively stoichiometric conversion to the desired product: NMR (Crude) (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 1.17\text{--}2.01$ (m, 22H, C_6H_{11}), 4.21 (dd, $^1J_{\text{PH}} 382.7$, $^2J_{\text{PH}} 2.3$ Hz, 1H, PH); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -7.6$ (d.br, $^1J_{\text{BP}} 99$ Hz); ^{11}B : $\delta_{\text{B}} = -7.6$ (dd.br, $^1J_{\text{BP}}/^1J_{\text{BH}} 104/137$ Hz); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 1.7$ [q.br, $^1J_{\text{PB}} 91$ Hz (Average)]; ^{31}P : $\delta_{\text{P}} = 1.7$ [dq.br, $^1J_{\text{PH}}/^1J_{\text{PB}} 375/128$ Hz]. ESI-MS (+ve ion): $m/z = 303.1$ [$\text{M} + \text{Na}$] $^+$, 199.2 [PH_2Cy_2] $^+$. The conversion in solution to $[\text{PH}_2\text{Cy}_2]\text{Cl}$ (*vide infra*) prevented the acquisition of satisfactory elemental microanalytical data.

The solid was dissolved in DCM and cannula filtered away from DCM-insoluble solids (which were discarded). The DCM filtrate was concentrated and layered with pentane to give over a period of 2 hours to give trace amounts of diffraction quality crystals of the phosphonium salt $[\text{PH}_2\text{Cy}_2]\text{Cl}$. **$[\text{PH}_2\text{Cy}_2]\text{Cl}$ decomposition product:** Crystal data: $[\text{C}_{12}\text{H}_{24}\text{P}]\text{Cl}\cdot\text{HCl}$, $M_r = 271.21$, $T = 200(2)$ K, monoclinic, space group C2/c , $a = 20.1535(5)$, $b = 6.8870(3)$, $c = 11.4416(4)$ Å, $\beta = 109.446(2)^\circ$, $V = 1497.47(9)$ Å 3 , $Z = 4$, $D_{\text{calcd}} = 1.203\text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) 0.51\text{ mm}^{-1}$, colourless block, $0.10 \times 0.18 \times 0.20$ mm, 15283 measured reflections with $2\theta_{\text{max}} = 55.2^\circ$, 1722 independent reflections, 1720 absorption-corrected data used in F^2 refinement, 72 parameters, 2 restraints, $R_1 = 0.037$, $wR_2 = 0.091$ for 1332 reflections with $I > 2\sigma(I)$.

Synthesis of dicyclohexylphosphine-monobromoborane, $\text{Cy}_2\text{HP}\cdot\text{BH}_2\text{Br}$: A solution of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of dicyclohexylphosphine ($\rho = 0.98\text{ g mL}^{-1}$, 0.20 mL, 1.0 mmol) in pentane (10 mL) at 0°C . The mixture was stirred for 10 min, then solvents were removed under high vacuum to leave a pale orange solid that was further dried under high vacuum for 17 h. Further attempts at purification by recrystallisation from DCM/pentane caused decomposition to $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ preventing the acquisition of

satisfactory elemental microanalytical data. NMR (Crude, CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 1.22$ – 2.25 (m, 22H, C_6H_{11}), 4.34 (d, $^1J_{\text{PH}} 369$ Hz, 1H, PH); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -27.9$ (br); ^{11}B : $\delta_{\text{B}} = -27.4$ (d.br, $^1J_{\text{BH}} 77$ Hz); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 5.9$ (d.br, $^1J_{\text{PB}} 88$ Hz); ^{31}P : $\delta_{\text{P}} = 5.9$ (dd.br, $^1J_{\text{PH}}/^1J_{\text{PB}} 400/80$ Hz). Acc. Mass: Found: $m/z = 409.3474$. Calcd for $\text{C}_{24}\text{H}_{48}^{11}\text{BP}_2$ 409.3324 $[\text{M} + \text{PHCy}_2 - \text{Br}]^+$.

Attempts to grow crystals resulted in the formation of $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$. **$[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$** : Crystal data (Unit cell determination): $\text{C}_{24}\text{H}_{48}\text{BBP}_2$, $T = 200(2)$ K, triclinic, space group $P-1$ (No.2), $a = 11.11$, $b = 12.02$, $c = 12.60$ Å, $\alpha = 117.03$, $\beta = 109.89$, $\gamma = 96.38^\circ$, $V = 1337$ Å³.[†]

Synthesis of diphenylphosphine-monobromoborane, $\text{Ph}_2\text{HP}\cdot\text{BH}_2\text{Br}$: A solution of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of diphenylphosphine ($\rho = 1.07$ g mL⁻¹, 0.17 mL, 1.0 mmol) in pentane (10 mL) at 0°C . The mixture was stirred for 10 min, by which time an orange oil had separated from the cloudy white solution. All volatiles were removed under high vacuum to leave a pale orange oil that was further dried under high vacuum overnight. In solution, product found to fully decompose to $[\text{H}_2\text{B}(\text{PPh}_2)_2]\text{Br}$ over a period of an hour. Spectroscopic data were rapidly obtained prior to significant decomposition, which precluded the acquisition of elemental microanalytical data. NMR (Crude, CD_2Cl_2 , 25°C): $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -37.4$ {br, $[\text{H}_2\text{B}(\text{PPh}_2)_2]\text{Br}$ }, -25.3 (br, $\text{Ph}_2\text{HP}\cdot\text{BH}_2\text{Br}$), -17.6 (br), -13.5 (br, $\text{BH}_2\text{Br}\cdot\text{SMe}_2$), -7.0 (br, $\text{BHBBr}_2\cdot\text{SMe}_2$); ^{11}B : $\delta_{\text{B}} = -37.7$ {br, $[\text{H}_2\text{B}(\text{PPh}_2)_2]\text{Br}$ }, -25.5 (br, $\text{Ph}_2\text{HP}\cdot\text{BH}_2\text{Br}$), -17.8 (br), -13.5 (t.br, $^1J_{\text{BH}} 172.1$ Hz, $\text{BH}_2\text{Br}\cdot\text{SMe}_2$), -7.0 (d.br, $^1J_{\text{BH}} 172.1$ Hz, $\text{BHBBr}_2\cdot\text{SMe}_2$); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -15.7$ (br, $[\text{H}_2\text{B}(\text{PPh}_2)_2]\text{Br}$), -10.5 (br, $\text{Ph}_2\text{HP}\cdot\text{BH}_2\text{Br}$).

Synthesis of chlorodiphenylphosphine-monobromoborane, $\text{Ph}_2\text{ClP}\cdot\text{BH}_2\text{Br}$: A solution of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of chlorodiphenylphosphine ($\rho = 1.23$ g mL⁻¹, 0.36 mL, 1.0 mmol) in pentane (8 mL) to give a green suspension that was stirred for 1 h. After 15 min stirring the reaction mixture comprised of yellow/orange solution and a yellow/orange oil. All volatiles removed under high vacuum to leave an orange oil. NMR (Crude, C_6D_6 , 25°C): $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -22.4$ (br, $\text{Ph}_2\text{ClP}\cdot\text{BH}_2\text{Br}$), -16.3 (br), -3.4 (br),

[†] See Section 6.5.

7.2, 7.5; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 69.9$ (br, $\text{Ph}_2\text{CIP}\cdot\text{BH}_2\text{Br}$), 73.3 (free PBrPh_2), ^{31}P 82.9 (free PClPh_2) in the relative integral ratio of 2:1:2. ESI-MS (+ve ion): $m/z = 385.5$ [$\text{M} + \text{PPh}_2 - \text{Br} - \text{Cl}$] $^+$, 233.3 [$\text{M} - \text{Br}$] $^+$. Attempts to purify this material were met with rapid decomposition to an insoluble compound for which meaningful analytical data could not be obtained.

Synthesis of dicyclohexylphosphine-dibromoborane, $\text{Cy}_2\text{HP}\cdot\text{BHBr}_2$: A solution of $\text{BHBr}_2\cdot\text{SMe}_2$ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of dicyclohexylphosphine ($\rho = 0.98\text{ g mL}^{-1}$, 0.40 mL, 2.0 mmol) in pentane (4 mL). The mixture was stirred for 24 h, after which all volatiles were removed under high vacuum to leave a colourless oil. Attempts at purification by recrystallisation from a mixture of DCM/pentane caused decomposition to $[\text{PH}_2\text{Cy}_2]\text{Br}$, which was identified crystallographically. NMR (Crude) (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 0.98\text{--}2.17$ (m, 22H, C_6H_{11}), 4.31 (d, $^1J_{\text{PH}} 392.0\text{ Hz}$, 1H, PH); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -45.2$ (br, $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$), -18.7 (br, $\text{Cy}_2\text{HP}\cdot\text{BHBr}_2$); ^{11}B : $\delta_{\text{B}} = -45.2$ (br, $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$), -18.7 (d.br, $^1J_{\text{BH}} 121\text{ Hz}$, $\text{Cy}_2\text{HP}\cdot\text{BHBr}_2$); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -27.3$ (br, free PHCy_2), 0.6 (br, $\text{Cy}_2\text{HP}\cdot\text{BHBr}_2$); ^{31}P : $\delta_{\text{P}} = -27.3$ (d.br, $^1J_{\text{PH}} 143\text{ Hz}$, free PHCy_2), 0.3 (d.br, $^1J_{\text{PH}} 415\text{ Hz}$, $\text{Cy}_2\text{HP}\cdot\text{BHBr}_2$). Acc. Mass: Found: $m/z = 487.2427$. Calcd for $\text{C}_{24}\text{H}_{47}^{11}\text{B}^{79}\text{BrP}_2$ 487.2429 [$\text{M} + \text{PHCy}_2 - \text{Br}$] $^+$. ESI-MS (+ve ion): $m/z = 409.6$ [$\text{M} + \text{PHCy}_2 + \text{H} - 2\text{Br}$] $^+$. Crystal data: $[\text{C}_{12}\text{H}_{24}\text{P}]\text{Br}$, $M_r = 279.20$, $T = 200(2)\text{ K}$, monoclinic, space group $P2_1/c$, $a = 10.9579(3)$, $b = 20.5548(9)$, $c = 12.3344(5)\text{ \AA}$, $\beta = 90.328(2)^\circ$, $V = 2778.12(18)\text{ \AA}^3$, $Z = 8$, $D_{\text{calcd}} = 1.335\text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) = 3.04\text{ mm}^{-1}$, colourless block, $0.06 \times 0.08 \times 0.09\text{ mm}$, 30178 measured reflections with $2\theta_{\text{max}} = 50.2^\circ$, 4915 independent reflections, 4915 absorption-corrected data used in F^2 refinement, 254 parameters, no restraints, $R_1 = 0.044$, $wR_2 = 0.107$ for 2966 reflections with $I > 2\sigma(I)$.

6.5 Acyclic Boronium Salts

Synthesis of bis(dimethylphenylphosphine)boronium bromide, $[\text{H}_2\text{B}(\text{PMe}_2\text{Ph})_2]\text{Br}$: A solution of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of dimethylphenylphosphine ($\rho = 0.97\text{ g mL}^{-1}$, 0.28 mL, 2.0 mmol) in benzene (10 mL). Upon addition the solution changed to a bright purple colour, which faded first to brown and then to orange over 45 min. The mixture was stirred for 2 h, and then all volatiles were removed under high

vacuum to leave an orange oil. The oil was dried under high vacuum for 24 h to produce a white solid. The solid was recrystallised from a mixture of DCM/pentane to give X-ray diffraction quality colourless needles. Yield 0.32 g (0.85 mmol, 85%). Compound melted and resolidified at around 108°C, then remained unchanged up to 250°C. Anal. Found: C, 50.20; H, 6.67; N, 0.00%. Calcd for $C_{16}H_{24}BBrP_2 \cdot 0.25(CH_2Cl_2)$: C, 50.01; H, 6.33; N, 0.00%. The solvated DCM was observed in the 1H and ^{13}C NMR spectra. NMR (CD_2Cl_2 , 25°C): 1H : $\delta_H = 1.84$ (d, $^2J_{PH}$ 9.9 Hz, 12H, CH_3), 7.50-7.60 (m, 10H, C_6H_5); $^{11}B\{^1H\}$: $\delta_B = -33.2$ (t.br, $^1J_{BP}$ 90 Hz); ^{11}B : $\delta_B = -33.2$ (dt.br, $^1J_{BH} \approx ^1J_{BP}$ 96 Hz); $^{13}C\{^1H\}$: $\delta_C = 11.71$ (d, $^1J_{CP}$ 48.1 Hz, CH_3), 126.35 [d, $^1J_{CP}$ 67.1 Hz, $C^1(C_6H_5)$], 130.00 [m, $C^4(C_6H_5)$], 130.90 [m, $C^{2,6}(C_6H_5)$], 132.93 [$C^{3,5}(C_6H_5)$]; $^{31}P\{^1H\}$: $\delta_P = -3.5$ [q.br, $^1J_{PB}$ 88 Hz (Average)]. NMR ($CDCl_3$, 25°C): 1H : $\delta_H = 2.00$ (d, $^2J_{PH}$ 11.2 Hz, 12H, CH_3), 7.50-7.56 (m, 6H, C_6H_5), 7.64-7.67 (m, 4H, C_6H_5); $^{31}P\{^1H\}$: $\delta_P = -3.5$ [q.br, $^1J_{PB}$ 84 Hz (Average)]. Acc. Mass: Found: $m/z = 289.1447$ Calcd for $C_{16}H_{24}^{11}BP_2$ 289.1446 $[M]^+$. ESI-MS (+ve ion): $m/z = 151.2$ $[M - PMe_2Ph]^+$. Crystal data: $C_{16}H_{24}BBrP_2$, $M_r = 369.03$, $T = 200(2)$ K, monoclinic, space group Cc , $a = 12.5325(4)$, $b = 13.6104(5)$, $c = 12.3150(3)$ Å, $\beta = 119.5074(16)^\circ$, $V = 1828.13(10)$ Å³, $Z = 4$, $D_{calcd} = 1.341$ Mg m⁻³, $\mu(Mo K\alpha) 2.41$ mm⁻¹, colourless prism, $0.13 \times 0.16 \times 0.40$ mm, 10394 measured reflections with $2\theta_{max} = 55.0^\circ$, 4040 independent reflections, 4027 absorption-corrected data used in F^2 refinement, 183 parameters, 2 restraints, $R_1 = 0.030$, $wR_2 = 0.060$ for 3496 reflections with $I > 2\sigma(I)$.

Synthesis of bis(dimethylphenylphosphine)boronium hexafluoroarsenate, $[H_2B(PMe_2Ph)_2][AsF_6]$: A solution of $[H_2B(PMe_2Ph)_2]Br$ (0.29 g, 0.79 mmol) in DCM (4 mL) was transferred *via* cannula into a THF (4 mL) solution of $K[AsF_6]$ (0.18 g, 0.79 mmol) to instantaneously form a white precipitate (KBr). The filtrate was separated *via* cannula filtration and all volatiles were removed under high vacuum to leave an orange solid. Vapour diffusion with pet. ether 60-80°C into a concentrated chloroform solution of the compound over two days yielded X-ray diffraction quality colourless crystals. Yield 0.33 g (0.68 mmol, 87%). Anal. Found: C, 39.99; H, 4.94; N, 0.02%. Calcd for $C_{16}H_{24}AsBF_6P_2$: C, 40.20; H, 5.06; N, 0.00%. NMR ($CDCl_3$, 25°C): 1H : $\delta_H = 1.68$ (d, $^2J_{PH}$ 12.0 Hz, 12H, CH_3), 7.50-7.53 (m, 10H, C_6H_5); $^{11}B\{^1H\}$: $\delta_B = -32.0$ (t.br, $^1J_{BP}$ 87 Hz); ^{11}B : $\delta_B = -32.0$ (quintet.br, $^1J_{BH} \approx ^1J_{BP}$ 95 Hz); $^{13}C\{^1H\}$: $\delta_C = 11.10$ (dd, $^1J_{CP}/^3J_{CP}$ 47.3/2.5 Hz, CH_3), 125.58 [d, $^1J_{CP}$ 69.5 Hz, $C^1(C_6H_5)$], 130.08 [m, $C^{3,5}(C_6H_5)$], 130.51 [m,

$C^{2.6}(C_6H_5)]$, 132.9 [$C^4(C_6H_5)]$; $^{31}P\{^1H\}$: $\delta_P = -3.6$ [q.br, $^1J_{PB}$ 79 Hz (Average)]. Acc. Mass: Found: $m/z = 289.1446$ Calcd for $C_{16}H_{24}^{11}BP_2$ 289.1446 [M]⁺. ESI-MS (-ve ion): $m/z = 189.2$ [M]⁻. Crystal data: $[C_{16}H_{24}BP_2][AsF_6]$, $M_r = 478.03$, $T = 200(2)$ K, monoclinic, space group $P2_1/n$, $a = 11.0302(1)$, $b = 16.4541(2)$, $c = 35.0725(5)$ Å, $\beta = 93.3927(5)^\circ$, $V = 6354.22(13)$ Å³, $Z = 12$, $D_{calcd} = 1.499$ Mg m⁻³, $\mu(Mo\ K\alpha) = 1.80$ mm⁻¹, colourless plate, $0.07 \times 0.14 \times 0.42$ mm, 77060 measured reflections with $2\theta_{max} = 55.0^\circ$, 14566 independent reflections, 14557 absorption-corrected data used in F^2 refinement, 703 parameters, 36 restraints, $R_1 = 0.061$, $wR_2 = 0.161$ for 10395 reflections with $I > 2\sigma(I)$.

Observation of diphenylmethylphosphine-monobromoborane $Ph_2MeP\cdot BH_2Br$, bis(diphenylmethylphosphine)boronium bromide, $[H_2B(PMePh_2)_2]Br$: A solution of $BH_2Br\cdot SMe_2$ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of diphenylmethylphosphine ($\rho = 1.08$ g mL⁻¹, 0.19 mL, 1.0 mmol) in benzene (10 mL) that was cooled in an ice bath during addition. Upon addition the solution turned a forest green colour, followed by a change to an orange colour as it was warmed to ambient temperature. The mixture was stirred for 3 h, after which all volatiles were removed under high vacuum to leave a pale yellow residue. The isolation and purification of the individual constituent compounds was hindered by the crude mixture being soluble in both polar and non-polar solvents. NMR (Crude, C_6D_6 , 25°C): $^{11}B\{^1H\}$: $\delta_B = -34.8$ {br, $[H_2B(PMePh_2)_2]Br$ }, -23.3 (d.br, J 38 Hz, $Ph_2MeP\cdot BH_2Br$), -15.6 (d.br, J 81.1 Hz); $^{31}P\{^1H\}$: $\delta_P = -26.2$, -1.7 (br), 3.6 (br), 8.2 (br) in the relative integral ratio of 2:2:1. ESI-MS (+ve ion): $m/z = 413.4$ $[H_2B(PMePh_2)_2]^+$, 337.3 $[H_2B(PMePh_2)(PMePh)]^+$, 213.3 $[H_2B(PMePh_2)]^+$, 201.2 $[PMePh_2]^+$.

Synthesis of bis(dicyclohexylphosphine)boronium bromide, $[H_2B(PHCy_2)_2]Br$: A solution of $BH_2Br\cdot SMe_2$ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of dicyclohexylphosphine ($\rho = 0.98$ g mL⁻¹, 0.40 mL, 2.0 mmol) in pentane (10 mL) at 0°C. Approximately 5 minutes after addition a precipitate formed. The mixture was stirred for 1 h at room temperature, and then all volatiles were removed under high vacuum to leave a pale orange solid. The solid was further dried under high vacuum for 48 h. The solid was recrystallised from a mixture of DCM/pentane to produce colourless X-ray diffraction quality crystals. Yield 0.37 g (0.76 mmol, 76%). M.p 199-201°C. Anal. Found: C, 58.63; H, 10.05; N, 0.00%. Calcd for

$C_{24}H_{48}BBrP_2$: C, 58.91; H, 9.89; N, 0.00%. NMR (CD_2Cl_2 , 25°C): 1H : $\delta_H = 1.25$ -2.27 (m, 44H, C_6H_{11}), 5.78 (d, $^1J_{PH}$ 407.3 Hz, 2H, PH); $^{11}B\{^1H\}$: $\delta_B = -45.2$ (br); ^{11}B : $\delta_B = -45.2$ (d.br, $^1J_{BH}$ 92 Hz); $^{13}C\{^1H\}$: $\delta_C = 25.49$ [$C^{2,6}(C_6H_{11})$], 26.38 [m, $C^4(C_6H_{11})$], 28.26 [d, $^1J_{PC}$ 55.7 Hz, $C^1(C_6H_{11})$], 29.20 [d, $^1J_{PC}$ 40.5 Hz, $C^{3,5}(C_6H_{11})$]; $^{31}P\{^1H\}$: $\delta_P = -0.4$ (d.br, $^1J_{PB}$ 93 Hz); ^{31}P : $\delta_P = -0.5$ (dd.br, $^1J_{PH}/^1J_{PB}$ 399/93 Hz). NMR ($CDCl_3$, 25°C): 1H : $\delta_H = 1.25$ -2.27 (m, 44H, C_6H_{11}), 6.04 (d, $^1J_{PH}$ 408.1 Hz, 2H, PH); $^{31}P\{^1H\}$: $\delta_P = -1.2$ (d.br, $^1J_{PB}$ 79.4 Hz). Acc. Mass: Found: $m/z = 409.3323$. Calcd for $C_{24}H_{48}^{11}BP_2$ 409.3324 $[M]^+$. Crystal data: $C_{24}H_{48}BBrP_2$, $M_r = 489.31$, $T = 200(2)$ K, triclinic, space group $P-1$ (No.2), $a = 11.1026(3)$, $b = 12.0068(3)$, $c = 12.5924(3)$ Å, $\alpha = 117.0693(11)$, $\beta = 109.9315(14)$, $\gamma = 96.4193(13)^\circ$, $V = 1331.87(7)$ Å³, $Z = 2$, $D_{calcd} = 1.220$ Mg m⁻³, $\mu(Mo K\alpha)$ 1.67 mm⁻¹, colourless block, 0.23 × 0.24 × 0.36 mm, 18303 measured reflections with $2\theta_{max} = 56.6^\circ$, 6125 independent reflections, 6108 absorption-corrected data used in F^2 refinement, 254 parameters, no restraints, $R_1 = 0.033$, $wR_2 = 0.076$ for 5022 reflections with $I > 2\sigma(I)$.

Synthesis of bis(dicyclohexylphosphine)boronium hexafluoroantimonate, $[H_2B(PHCy_2)_2][SbF_6]$: A DCM (4 mL) solution of $[H_2B(PHCy_2)_2]Br$ (0.49 g, 1.0 mmol) was added *via* cannula to a THF (4 mL) solution of $Ag[SbF_6]$ (0.34 g, 1.0 mmol) to instantaneously give an off-white coloured precipitate ($AgBr$) and a colourless solution. The filtrate was isolated by cannula filtration and all volatiles were removed under high vacuum to leave a white residue, which was further dried under high vacuum overnight. The residue was dissolved in THF, layered with pentane and stored at -20°C to give mostly beige powder and some colourless crystals of X-ray diffraction quality. The compound was found to decompose over a period of several weeks under an inert atmosphere. Yield 0.603 g (0.94 mmol, 93%). Anal. Found: C, 44.73; H, 7.52; N, 0.00%. Calcd for $C_{24}H_{48}BF_6P_2Sb$: C, 44.68; H, 7.50; N, 0.00%. NMR ($CDCl_3$, 25°C): 1H : $\delta_H = 1.21$ -2.16 (m, 44H, C_6H_{11}), 4.89 (d, $^1J_{PH}$ 400.7 Hz, 2H, PH); $^{11}B\{^1H\}$: $\delta_B = -45.1$ (br); $^{13}C\{^1H\}$: $\delta_C = 25.47$ (C_6H_{11}), 26.43 (C_6H_{11}), 28.81 (C_6H_{11}), 29.31 [d, $^1J_{PC}$ 41.5 Hz, $C^1(C_6H_{11})$]; $^{31}P\{^1H\}$: $\delta_P = -3.3$ (d.br, $^1J_{PB}$ 80 Hz). Acc. Mass: Found: $m/z = 409.3325$. Calcd for $C_{24}H_{48}^{11}BP_2$ 409.3324 $[M]^+$. ESI-MS (-ve ion): $m/z = 235.2$ $[SbF_6]^-$. Crystal data: $[C_{24}H_{48}BP_2][SbF_6]$, $M_r = 643.13$, $T = 200(2)$ K, monoclinic, space group $P2_1/n$, $a = 10.2490(2)$, $b = 19.1746(7)$, $c = 15.1472(5)$ Å, $\beta = 91.516(2)^\circ$, $V = 2975.69(16)$ Å³, $Z = 4$, $D_{calcd} = 1.435$ Mg m⁻³, $\mu(Mo K\alpha)$ 1.08 mm⁻¹, colourless prism, 0.12 × 0.12 × 0.41 mm,

33770 measured reflections with $2\theta_{\max} = 55.0^\circ$, 6792 independent reflections, 6784 absorption-corrected data used in F^2 refinement, 308 parameters, no restraints, $R_1 = 0.056$, $wR_2 = 0.150$ for 4882 reflections with $I > 2\sigma(I)$.

Synthesis of bis(diphenylphosphine)boronium bromide, $[\text{H}_2\text{B}(\text{PPh}_2)_2]\text{Br}$: A solution of $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ (1.0 M, 0.5 mL, 0.5 mmol) in dichloromethane was added drop-wise to a stirred solution of diphenylphosphine ($\rho = 1.07 \text{ g mL}^{-1}$, 0.17 mL, 1.0 mmol) in pentane (4 mL). Upon addition a precipitate was formed instantly, but after 1 minute an orange oil had aggregated at the bottom of the flask and the bulk solution was colourless. The mixture was stirred for 1 h, and then all volatiles were removed under high vacuum to leave a pale orange solid. The solid was further dried under high vacuum for 24 h. The solid was dissolved in DCM and layered with pentane to give white powder, which was isolated by cannula filtration. The solid was recrystallised from a mixture of DCM/pentane to produce colourless X-ray diffraction quality crystals. Yield 0.20 g (0.43 mmol, 87%). Partially melted at around ca. 98°C , then remained unchanged up to 250°C . Anal. Found: C, 61.16; H, 4.95; N, 0.00%. Calcd for $\text{C}_{24}\text{H}_{24}\text{BBrP}_2$: C, 61.98; H, 5.20; N, 0.00%. NMR (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 7.31\text{--}7.39$ (m, 8H, C_6H_5), 7.46–7.51 (m, 4H, C_6H_5), 7.64–7.71 (m, 8H, C_6H_5), 8.95 (d, $^1J_{\text{PH}} 456.4 \text{ Hz}$, 2H, PH); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -37.6$ (br); ^{11}B : $\delta_{\text{B}} = -38.1$ (d.br, $^2J_{\text{BH}} 70 \text{ Hz}$); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 122.22$ [d, $^1J_{\text{PC}} 60.8 \text{ Hz}$, $\text{C}^1(\text{C}_6\text{H}_5)$], 129.76 [m, $\text{C}^{2,6}(\text{C}_6\text{H}_5)$], 132.93 [$\text{C}^4(\text{C}_6\text{H}_5)$], 133.52 [m, $\text{C}^{3,5}(\text{C}_6\text{H}_5)$]; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -16.2$ (d.br, $^1J_{\text{PB}} 86 \text{ Hz}$). ^{31}P : $\delta_{\text{P}} = -16.2$ (dm.br, $^1J_{\text{PH}} 376 \text{ Hz}$). Acc. Mass: Found: $m/z = 385.1446$ Calcd for $\text{C}_{24}\text{H}_{24}^{11}\text{BP}_2$ 385.1446 $[\text{M}]^+$. Crystal data: $\text{C}_{24}\text{H}_{24}\text{BBrP}_2$, $M_r = 465.12$, $T = 200(2) \text{ K}$, monoclinic, space group $P2_1/n$, $a = 8.3066(1)$, $b = 18.0004(3)$, $c = 15.1242(2) \text{ \AA}$, $\beta = 97.2060(9)^\circ$, $V = 2243.54(6) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 1.377 \text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) 1.98 \text{ mm}^{-1}$, colourless block, $0.14 \times 0.20 \times 0.29 \text{ mm}$, 25261 measured reflections with $2\theta_{\max} = 55.0^\circ$, 5139 independent reflections, 5124 absorption-corrected data used in F^2 refinement, 254 parameters, no restraints, $R_1 = 0.030$, $wR_2 = 0.077$ for 4263 reflections with $I > 2\sigma(I)$.

Observation of ethylphenylphosphine-monobromoborane, $\text{PhEtHP} \cdot \text{BH}_2\text{Br}$, and bis(ethylphenylphosphine)boronium bromide, $[\text{H}_2\text{B}(\text{PHEtPh})_2]\text{Br}$: A solution of $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of ethylphenylphosphine ($\rho = 0.98 \text{ g mL}^{-1}$, 0.28 mL, 2.0 mmol) in

pentane (4 mL) and stirred for 2 h. Upon addition, an orange layer separated out below the colourless solvent layer. All volatiles were removed under high vacuum to leave an orange oil that resisted purification attempts. NMR (C_6D_6 , $25^\circ C$): $^{11}B\{^1H\}$: $\delta_B = -41.7$ {d.br, $^1J_{BP}$ 48 Hz, $[H_2B(PHEtPh)_2]Br$ }, -25.7 (d.br, $^1J_{BP}$ 58.6 Hz, $PhEtHP \cdot BH_2Br$), -17.6 (d.br, $^1J_{BP}$ 102.5 Hz), -11.7 ($BH_2Br \cdot SMe_2$), -8.6 (br, $BHBr_2 \cdot SMe_2$); $^{31}P\{^1H\}$: $\delta_P = -8.0$ (d.br, $^1J_{BP}$ 83 Hz, $PhEtHP \cdot BH_2Br$), 1.5 {q.br, $^1J_{BP}$ 60 Hz, $[H_2B(PHEtPh)_2]Br$ }.

Synthesis of bis(cyclohexylphosphine)boronium bromide, $[H_2B(PH_2Cy)_2]Br$: A solution of $BH_2Br \cdot SMe_2$ (1.0 M, 0.50 mL, 0.5 mmol) in dichloromethane was added drop-wise to a stirred solution of cyclohexylphosphine ($\rho = 0.88 \text{ g mL}^{-1}$, 0.13 mL, 1.0 mmol) in pentane (2 mL). The mixture was stirred for 1 h, after which time an orange oil had aggregated at the bottom of the flask and the bulk solution was colourless. All volatiles were removed under high vacuum to leave a pale orange solid. The solid was recrystallised from a mixture of DCM/pentane to give a white powder. The solid was then recrystallised by layering a concentrated DCM solution of the solid with pentane overnight to produce colourless X-ray diffraction quality crystals. Yield 0.07 g (0.20 mmol, 41%). Evolved a gas at $76^\circ C$ to leave a clear residue up to $250^\circ C$. Anal. Found: C, 44.15; H, 8.35; N, 0.00%. Calcd for $C_{12}H_{28}BBP_2$: C, 44.35; H, 8.68; N, 0.00%. NMR (CD_2Cl_2 , $25^\circ C$): 1H : $\delta_H = 1.34$ - 2.22 (m, 22H, C_6H_{11}), 5.60 (d, $^1J_{PH}$ 425.9 Hz, 4H, PH); $^{11}B\{^1H\}$: $\delta_B = -44.5$ (t.br, $^1J_{BP}$ 81 Hz); ^{11}B : $\delta_B = -44.5$ (tt.br, $^1J_{BH} = ^1J_{BP}$ 90 Hz); $^{13}C\{^1H\}$: $\delta_C = 25.69$ [$C^{3,5}(C_6H_{11})$], 26.51 [t, J_{PC} 6.3 Hz, $C^{2,6}(C_6H_{11})$], 28.93 [d, $^1J_{PC}$ 45.5 Hz, $C^1(C_6H_{11})$], 30.12 [$C^4(C_6H_{11})$]; $^{31}P\{^1H\}$: $\delta_P = -38.6$ (q.br, $^1J_{PB}$ 94 Hz); ^{31}P : $\delta_P = -38.7$ [td.br, $^1J_{PH}$ 415 Hz (Average), $^1J_{PB}$ 82 Hz]. Acc. Mass: Found: $m/z = 245.1759$ Calcd for $C_{12}H_{28}^{11}BP_2$ 245.1759 $[M]^+$. Crystal data: $C_{12}H_{28}BBP_2$, $M_r = 325.02$, $T = 200(2)$ K, orthorhombic, space group $Pbcn$, $a = 13.5244(3)$, $b = 12.0969(3)$, $c = 9.8466(2)$ Å, $V = 1610.94(6)$ Å³, $Z = 4$, $D_{calcd} = 1.340 \text{ Mg m}^{-3}$, $\mu(\text{Mo K}\alpha) 2.73 \text{ mm}^{-1}$, colourless block, $0.14 \times 0.26 \times 0.27$ mm, 16490 measured reflections with $2\theta_{max} = 60.1^\circ$, 2352 independent reflections, 2348 absorption-corrected data used in F^2 refinement, 75 parameters, no restraints, $R_1 = 0.026$, $wR_2 = 0.065$ for 1852 reflections with $I > 2\sigma(I)$.

Synthesis of mesitylphosphine-monobromoborane, $MesH_2P \cdot BH_2Br$, and bis(mesitylphosphine)boronium bromide, $[H_2B(PH_2Mes)_2]Br$: A solution of $BH_2Br \cdot SMe_2$ (1.0 M, 0.50 mL, 0.5 mmol) in dichloromethane was added drop-wise to a

stirred solution of mesitylphosphine (0.19 g, 1.25 mmol) in toluene (4 mL) and stirred for 1 h. An aliquot was removed and analysed by NMR spectroscopy: NMR (C_6D_6 , 25°C): $^{11}B\{^1H\}$: $\delta_B = -41.0$ (br, $[H_2B(PH_2Mes)_2]Br$), -26.0 (d.br, $^1J_{BP}$ 44 Hz, $MesH_2P \cdot BH_2Br$), -11.8 ($BH_2Br \cdot SMe_2$); ^{11}B : $\delta_B = -40.8$ {d.br, $^1J_{BH}$ 121 Hz, $[H_2B(PH_2Mes)_2]Br$ }, -26.0 (d.br, $^1J_{BP}$ 48 Hz, $MesH_2P \cdot BH_2Br$), -11.8 [t, $^1J_{BH}$ 130 Hz (Average), $BH_2Br \cdot SMe_2$]; $^{31}P\{^1H\}$: $\delta_P = -155.4$ (PH_2Mes), -72.4 (d, $^1J_{BP}$ 69 Hz, $MesH_2P \cdot BH_2Br$); ^{31}P : $\delta_P = -155.4$ (PH_2Mes), -72.0 [t, $^1J_{PH}$ 394 Hz (Average), $MesH_2P \cdot BH_2Br$]. The remaining reaction mixture was heated to approximately 100°C (bath temperature) overnight. NMR analysis revealed that both PH_2Mes and $BH_2Br \cdot SMe_2$ remained, suggesting the establishment of an equilibrium with the borane adduct and boronium salt: NMR (C_6D_6 , 25°C): $^{11}B\{^1H\}$: $\delta_B = -38.0$ (br, $[H_2B(PH_2Mes)_2]Br$), -25.9 (d.br, $^1J_{BP}$ 44 Hz, $MesH_2P \cdot BH_2Br$), -18.7 (d.br, $^1J_{BP}$ 95 Hz), -13.4 (br), -11.8 ($BH_2Br \cdot SMe_2$), -8.8 (br); $^{31}P\{^1H\}$: $\delta_P = -155.4$ (PH_2Mes), -72.8 (m.br, $MesH_2P \cdot BH_2Br$), -69.6 (br), -58.0 (br). Despite heating the mixture to reflux overnight, unreacted PH_2Mes was still observed to be present: NMR (C_6D_6 , 25°C): $^{11}B\{^1H\}$: $\delta_B = -35.9$ (br), -23.1 (br); $^{31}P\{^1H\}$: $\delta_P = -155.4$ (PH_2Mes), -71.7 (br), -60.5 (br), -52.0 (br).

Observation of dicyclohexylphosphine-diphenylphosphineboronium bromide, $[H_2B(PHCy_2)(PPh_2)]Br$: A solution of $BH_2Br \cdot SMe_2$ (1.0 M, 0.50 mL, 0.5 mmol) in dichloromethane was added drop-wise to a stirred solution of dicyclohexylphosphine ($\rho = 0.98 \text{ g mL}^{-1}$, 0.10 mL, 0.5 mmol) in benzene (10 mL) that was cooled in an ice bath during addition. Stirring was continued for 5 min, after which diphenylphosphine ($\rho = 1.07 \text{ g mL}^{-1}$, 0.09 mL, 0.5 mmol) was added drop-wise. The mixture was stirred for 5 min and then all volatiles were removed under high vacuum to leave an orange oil that was shown by NMR spectroscopy to comprise an approximate 2:1:1 mixture of $[H_2B(PHCy_2)(PPh_2)]Br$, $[H_2B(PHCy_2)_2]Br$ and $[H_2B(PPh_2)_2]Br$. The complete disproportionation to $[H_2B(PHCy_2)_2]Br$ and $[H_2B(PPh_2)_2]Br$ was observed to occur in 30-60 min. NMR (CD_2Cl_2 , 25°C): $^{11}B\{^1H\}$: $\delta_B = -44.6$ {d.br, $^1J_{BP}$ 44 Hz, $[H_2B(PHCy_2)_2]Br$ }, -40.5 {br, $[H_2B(PHCy_2)(PPh_2)]Br$ }, -27.2 (br, $Cy_2HP \cdot BH_2Br$), -18.0 (br); $^{31}P\{^1H\}$: $\delta_P = -40.1$ (free PPh_2), -21.2 {d.br, $^2J_{PP}$ 303 Hz, $[H_2B(PHCy_2)(PPh_2)]Br$ }, -3.2 {d.br, $^2J_{PP}$ 220 Hz, $[H_2B(PHCy_2)(PPh_2)]Br$ }; ^{31}P : $\delta_P = -39.1$ (br, free PPh_2), -20.3 {dd.br, $^1J_{PH}/^2J_{PP}$ 412/240 Hz, $[H_2B(PHCy_2)(PPh_2)]Br$ }, -2.3 {dd.br, $^1J_{PH}/^2J_{PP}$ 463/289 Hz, $[H_2B(PHCy_2)(PPh_2)]Br$ }. $[H_2B(PHCy_2)(PPh_2)]Br$.

Synthesis of cyclohexylphosphine-dicyclohexylphosphineboronium bromide, $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})(\text{PHCy}_2)]\text{Br}$: A solution of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (1.0 M, 0.50 mL, 0.5 mmol) in dichloromethane was added drop-wise to a stirred solution of dicyclohexylphosphine ($\rho = 0.98 \text{ g mL}^{-1}$, 0.10 mL, 0.5 mmol) in DCM (15 mL) at -78°C . The mixture was stirred for 30 min at this temperature, then cyclohexylphosphine ($\rho = 0.88 \text{ g mL}^{-1}$, 0.07 mL, 0.5 mmol) was added drop-wise. Stirred for 1 h, after which all volatiles were removed under high vacuum to leave a yellow/orange oil. The complete disproportionation to $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ and $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$ was observed to occur in <30 min. NMR (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 1.26\text{--}2.22$ (m, 33H, C_6H_{11}), 5.61 (d, $^1J_{\text{PH}} 418.7 \text{ Hz}$, 2H, PH_2Cy), 5.76 (d, $^1J_{\text{PH}} 411.8 \text{ Hz}$, 1H, PHCy_2); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -45.1$ {br, $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})(\text{PHCy}_2)]\text{Br}$ }, -27.3 (br, $\text{Cy}_2\text{HP}\cdot\text{BH}_2\text{Br}$), -20.7 to -18.3 (m); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -110.5$ (free PH_2Cy), -41.6 {d.br, $^2J_{\text{PP}} 73 \text{ Hz}$, $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})(\text{PHCy}_2)]\text{Br}$ }, -6.9 , 0.4 {br, $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})(\text{PHCy}_2)]\text{Br}$ };[†] ^{31}P : $\delta_{\text{P}} = -110.5$ (free PH_2Cy), -41.5 {dt.br, $^1J_{\text{PH}} 375 \text{ Hz}$ (Average), $^1J_{\text{PB}}$ unresolved, $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})(\text{PHCy}_2)]\text{Br}$ }, 0.5 {dd.br, $^1J_{\text{PH}} 401.5 \text{ Hz}$, $^1J_{\text{PB}}$ unresolved, $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})(\text{PHCy}_2)]\text{Br}$ }. Acc. Mass: Found: $m/z = 409.3328$ Calcd for $\text{C}_{24}\text{H}_{48}^{11}\text{BP}_2$ 409.3324 $[\text{M} + \text{PHCy}_2 - \text{PH}_2\text{Cy}]^+$. ESI-MS (+ve ion): $m/z = 327.3$ $[\text{M} + \text{PH}_2\text{Cy} - \text{PHCy}_2]^+$.

Synthesis of bis(1-diphenylphosphino-2-diphenylarsinoethane) boronium hexafluoroarsenate, $[\text{BH}_2(\kappa\text{-P-arphos})_2][\text{AsF}_6]$: A solution of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (1.0 M, 0.1 mL, 0.1 mmol) in dichloromethane was added drop-wise to a stirred solution of arphos (0.088 g, 0.2 mmol) in DCM (2 mL), which was then stirred for 1 h, after which all volatiles were removed under high vacuum to leave a white solid. The solid was redissolved in DCM (4 mL) and cannula transferred into a THF (2 mL) solution of $\text{K}[\text{AsF}_6]$ (0.023 g, 0.1 mmol) to instantaneously form a white precipitate (KBr). The supernatant was separated *via* cannula filtration and freed of volatiles under high vacuum to leave a white solid. This solid was twice more dissolved in DCM (2 mL) and cannula transferred into a THF (2 mL) solution of additional $\text{K}[\text{AsF}_6]$ (0.012 g, 0.05 mmol) to instantaneously form a white precipitate, from which the filtrate was isolated by cannula filtration and all volatiles removed under high vacuum, to give a white solid.

[†] Unlike with $[\text{H}_2\text{B}(\text{PHCy}_2)(\text{PHPh}_2)]\text{Br}$ (*vide supra*), $^2J_{\text{PP}}$ was not observed for $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})(\text{PHCy}_2)]\text{Br}$. However, its identity was clearly established by the difference in the ^{31}P NMR resonances from $[\text{H}_2\text{B}(\text{PH}_2\text{Cy})_2]\text{Br}$ ($\delta_{\text{P}} -38.6$) and $[\text{H}_2\text{B}(\text{PHCy}_2)_2]\text{Br}$ ($\delta_{\text{P}} -0.4$).

Yield: 0.048 g (0.044 mmol, 44%). NMR (CDCl_3 , 25°C): ^1H : $\delta_{\text{H}} = 1.42\text{--}1.50$ (m, 4H, PCH_2), $1.77\text{--}1.83$ (m, 4H, AsCH_2), $6.96\text{--}7.51$ (m, 40H, C_6H_5); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -37.1$ (br); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 18.46$ ($\text{P-CH}_2\text{-CH}_2\text{-As}$), 21.09 (d, $^1J_{\text{CP}} 36.7$ Hz, $\text{P-CH}_2\text{-CH}_2\text{-As}$), 123.07 [d, $^1J_{\text{CP}} 65.8$ Hz, $\text{C}^1(\text{PC}_6\text{H}_5)$], 128.44 (C_6H_5), 129.03 (C_6H_5), 130.08 [d, $^2J_{\text{CP}} 10.1$ Hz, $\text{C}^{2,6}(\text{PC}_6\text{H}_5)$], 132.27 [d, $^3J_{\text{CP}} 8.8$ Hz, $\text{C}^{3,5}(\text{PC}_6\text{H}_5)$], 132.84 (C_6H_5), 133.46 (C_6H_5), 138.59 [$\text{C}^1(\text{AsC}_6\text{H}_5)$]; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 11.0$ (br). ESI-MS (+ve ion): $m/z = 897.1$ $[\text{M}]^+$. Crystal data: $[\text{C}_{52}\text{H}_{50}\text{As}_2\text{BP}_2][\text{AsF}_6]$, $M_r = 1086.48$, $T = 200(2)$ K, monoclinic, space group $P2_1/c$, $a = 13.9473(2)$, $b = 21.2347(4)$, $c = 17.1369(2)$ Å, $\beta = 109.1409(10)^\circ$, $V = 4794.79(13)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.505$ Mg m⁻³, $\mu(\text{Mo K}\alpha) 2.20$ mm⁻¹, colourless plate, $0.04 \times 0.13 \times 0.23$ mm, 68172 measured reflections with $2\theta_{\text{max}} = 52.0^\circ$, 9439 independent reflections, 9438 absorption-corrected data used in F^2 refinement, 778 parameters, 356 restraints, $R_1 = 0.043$, $wR_2 = 0.101$ for 7011 reflections with $I > 2\sigma(I)$.

6.6 Cyclic Boronium Salts

Synthesis of 1,2-bis(dimethylphosphino)ethane boronium bromide, $[\text{BH}_2(\text{dmpe})]\text{Br}$: Neat dmpe (0.17 mL, 1.0 mmol) was added drop-wise to a stirred solution of $\text{BH}_2\text{Br.SMe}_2$ (1.0 M, 1.0 mL, 1.0 mmol) in dichloromethane and benzene (8 mL), to instantaneously produce a white precipitate that did not settle. All volatiles were removed under high vacuum to leave a white powder. The product was found to be insoluble in most common solvents, which hindered complete characterisation. Yield: 0.177 g (0.73 mmol, 73%). Anal. Found: C, 29.28; H, 7.35; N, 0.00%. Calcd for $\text{C}_6\text{H}_{18}\text{BBrP}_2$: C, 29.67; H, 7.47; N, 0.00%. NMR ($\text{D}_6\text{-DMSO}$, 25°C): ^1H : $\delta_{\text{H}} = 1.68$ (d, $^2J_{\text{PH}} 11.7$ Hz, 12H, CH_3), 2.35 (d, $^2J_{\text{PH}} 9.3$ Hz, 4H, CH_2); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -34.5$ (br); ^{11}B : $\delta_{\text{B}} = -34.5$ [t, $^1J_{\text{BH}}$, 78 Hz]; $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 20.3$ (d.br, $^1J_{\text{PB}} 96$ Hz). Acc. Mass: Found: $m/z = 163.0977$. Calcd for $\text{C}_6\text{H}_{18}^{11}\text{BP}_2$ 163.0977 $[\text{M}]^+$.

Synthesis of 1,2-bis(diphenylphosphino)ethane boronium bromide, $[\text{BH}_2(\text{dppe})]\text{Br}$:²⁶ A solution of $\text{BH}_2\text{Br.SMe}_2$ (1.0 M, 1.00 mL, 1.0 mmol) in dichloromethane was added drop-wise to a stirred solution of dppe (0.40 g, 1.0 mmol) in benzene (15 mL) that was cooled in an ice bath during addition. The mixture was allowed to warm to room temperature and stirred for 1.5 h, after which time it was diluted with pentane to give a beige precipitate, which was isolated by filtration. The

solid was dried under high vacuum for 19 h and recrystallised from a mixture of DCM/pentane at 25°C to provide colourless X-ray diffraction quality crystals. Yield: 0.10 g (0.20 mmol, 20%). M.p. 198-200°C. The colourless crystals were ground down and dried for several days *in vacuo* to obtain satisfactory microanalytical data. Anal. Found: C, 63.60; H, 5.39; N, 0.00%. Calcd for $C_{26}H_{26}BBrP_2$: C, 63.58; H, 5.34; N, 0.00%. NMR ($CDCl_3$, 25°C): 1H : $\delta_H = 3.43$ (d, $^2J_{PH}$ 9.6 Hz, 4H, CH_2), 7.48-7.58 [m, 12H, $H^{3,5}(C_6H_5)$], 7.72-7.77 [m, 8H, $H^{2,6}(C_6H_5)$]; $^{11}B\{^1H\}$: $\delta_B = -35.7$ (br); $^{13}C\{^1H\}$: $\delta_C = 24.10$ (t, J_{CP} 24.7 Hz, CH_2), 123.37 [t, J_{CP} 35.4 Hz, $C^1(C_6H_5)$], 129.78 [t, J_{CP} 5.7 Hz, $C^{2,6}(C_6H_5)$], 132.58 [t, J_{CP} 5.1 Hz, $C^{3,5}(C_6H_5)$], 133.20 [$C^4(C_6H_5)$]; $^{31}P\{^1H\}$: $\delta_P = 27.8$ (br). Acc. Mass: Found: $m/z = 411.1604$. Calcd for $C_{26}H_{26}^{11}BP_2$ 411.1603 [M]⁺. Crystal data: [$C_{26}H_{26}BP_2$] $Br \cdot 0.9CH_2Cl_2$, $M_r = 566.96$, $T = 200(2)$ K, monoclinic, space group $P2_1/n$, $a = 12.8454(2)$, $b = 15.8917(3)$, $c = 14.0831(3)$ Å, $\beta = 101.3055(11)^\circ$, $V = 2819.07(9)$ Å³, $Z = 4$, $D_{calcd} = 1.336$ Mgm⁻³, $\mu(Mo K\alpha) 1.75$ mm⁻¹, colourless block, $0.21 \times 0.22 \times 0.37$ mm, 56899 measured reflections with $2\theta_{max} = 55.0^\circ$, 6480 independent reflections, 6465 absorption-corrected data used in F^2 refinement, 308 parameters, 10 restraints, $R_1 = 0.053$, $wR_2 = 0.154$ for 5240 reflections with $I > 2\sigma(I)$.

Synthesis of 1,2-bis(dicyclohexylphosphino)ethane boronium tribromoborate, [$BH_2(dcpe)$][$HBBBr_3$]: A solution of $BH_2Br \cdot SMe_2$ (1.0 M, 0.50 mL, 0.50 mmol) in dichloromethane was added drop-wise to a stirred solution of dcpe (0.21 g, 0.50 mmol) in benzene (10 mL) that was cooled in an ice bath during addition. The mixture was warmed to room temperature and slowly acquired an orange colour whilst being stirred for 5 h. The mixture was freed of all volatiles under high vacuum to give an orange oil, which was recrystallised from a mixture of DCM/pentane at 25°C, then isolated *via* cannula filtration to provide orange X-ray diffraction quality crystals. X-ray crystallographic analysis confirmed the presence of the [$HBBBr_3$]⁻ counterion, presumably due to the use of an aged sample of $BH_2Br \cdot SMe_2$ that over time had become more concentrated than 1.0 M. Yield (based on dcpe): 0.244 g (0.47 mmol, 95%). Anal. Found: C, 45.15; H, 7.17; N, 0.00%. Calcd for $C_{26}H_{51}B_2Br_3P_2$: C, 45.46; H, 7.48; N, 0.00%. NMR (CD_2Cl_2 , 25°C): 1H : $\delta_H = 1.35$ -2.04 (m, 44H, C_6H_{11}), 2.31 (d, $^2J_{PH}$ 6.0 Hz, 4H, CH_2); $^{11}B\{^1H\}$: $\delta_B = -43.7$ (br, P_2BH_2), -14.0 ([$HBBBr_3$]⁻); ^{11}B : $\delta_B = -43.7$ (br, P_2BH_2), -14.0 (d, $^1J_{BH}$, 172 Hz, [$HBBBr_3$]⁻); $^{13}C\{^1H\}$: $\delta_C = 17.99$ (t, J_{CP} 21.6 Hz, CH_2), 25.83 [$C^{3,5}(C_6H_{11})$], 26.82 [q, J_{CP} 6.3 Hz, $C^4(C_6H_{11})$], 27.55 [d, J_{CP} 16.4 Hz, $C^{2,6}(C_6H_{11})$],

31.62 [quin, J_{CP} 17.2 Hz, $C^1(C_6H_{11})$]; $^{31}P\{^1H\}$: $\delta_P = 43.6$ (d.br, $^1J_{PB}$ 74 Hz). Acc. Mass: Found: $m/z = 435.3482$. Calcd for $C_{26}H_{50}^{11}BP_2$ 435.3481 $[M]^+$. Crystal data: $[C_{26}H_{50}BP_2][HBBBr_3]$, $M_r = 686.97$, $T = 200(2)$ K, monoclinic, space group $P2_1/n$, $a = 11.1381(1)$, $b = 12.5367(2)$, $c = 22.3536(3)$ Å, $\beta = 97.2547(8)^\circ$, $V = 3096.36(7)$ Å³, $Z = 4$, $D_{calcd} = 1.474$ Mgm⁻³, $\mu(Mo\ K\alpha) 4.03$ mm⁻¹, colourless plate, $0.07 \times 0.16 \times 0.44$ mm, 62272 measured reflections with $2\theta_{max} = 55.0^\circ$, 7097 independent reflections, 7079 absorption-corrected data used in F^2 refinement, 451 parameters, 176 restraints, $R_1 = 0.045$, $wR_2 = 0.125$ for 5874 reflections with $I > 2\sigma(I)$.

Synthesis of 1,1'-bis(diphenylphosphino)ferrocene boronium bromide, $[H_2B(dppf)]Br$: A solution of $BH_2Br.SMe_2$ (1.0 M, 0.20 mL, 0.20 mmol) in dichloromethane was added drop-wise to a stirred solution of 1,1'-bis(diphenylphosphino)ferrocene (0.11 g, 0.20 mmol) in toluene (10 mL) and heated to reflux for 16 h, which resulted in a pale orange precipitate and an orange solution [found to contain the mono-adduct $dppf \cdot (BH_2Br)$ (*vide supra*)]. The precipitate was separated by cannula filtration. The solid was dissolved in DCM and precipitated out with pentane to give a pale orange solid that was dried under high vacuum for 2 h. Yield 0.048 g (0.074 mmol, 37%). $^{11}B\{^1H\}$: $\delta_B = -27.4$ (br); $^{13}C\{^1H\}$: $\delta_C = 67.38$ [d, $^1J_{CP}$ 83.5 Hz, $C^1(C_5H_4)$], 83.92 (C_5H_4), 84.59 (C_5H_4), 125.06 [d, $^1J_{CP}$ 70.2 Hz, $C^1(C_6H_5)$], 133.31 (C_6H_5), 134.79 (C_6H_5), 135.54 (C_6H_5); $^{31}P\{^1H\}$: $\delta_P = 9.7$ (br). Acc. Mass: Found: $m/z = 567.1265$ Calcd for $C_{34}H_{30}^{11}B^{56}FeP_2$ 567.1265 $[M - Br]^+$.

Synthesis of 1-dimethylamino-2-diphenylphosphinobenzene boronium bromide, $[H_2B(amphos)]Br$: A solution of $BH_2Br.SMe_2$ (1.0 M, 0.50 mL, 0.50 mmol) in dichloromethane was added drop-wise to a stirred solution of 1-diphenylphosphino-2-dimethylaminobenzene (0.15 g, 0.50 mmol) in DCM (2 mL). The mixture was stirred for 1 h, after which all volatiles were removed under high vacuum to leave a white solid. The solid was dissolved in DCM and precipitated out with pentane to give a white precipitate that was separated *via* cannula filtration. The solid was recrystallised from a mixture of DCM/pentane to produce colourless X-ray diffraction quality crystals. Yield 0.185 g (0.46 mmol, 93%). Anal. Found: C, 53.07; H, 5.00; N, 3.22%. Calcd for $C_{20}H_{22}BBrNP \cdot 0.9(CH_2Cl_2)$: C, 52.90; H, 5.06; N, 2.95%. NMR ($CDCl_3$, 25°C): 1H : $\delta_H = 3.46$ (s, 6H, NMe_2), 7.53-7.71 (m, 12H, C_6H_5), 7.94-8.00 (m, 1H, C_6H_4), 8.90 (dd, J_{PH}/J

8.4 Hz/3.9 Hz, 1H, C₆H₄); ¹¹B{¹H}: δ_B = -9.3 (br); ¹³C{¹H}: δ_C = 57.51 (d, ²J_{BC} 4.6 Hz, NMe₂), 119.85 [d, ¹J_{CP} 62.1 Hz, C¹(C₆H₅)], 121.12 [d, ¹J_{CP} 69.1 Hz, C¹(C₆H₄)], 123.86 (d, J_{CP} 8.0 Hz), 130.29 (d, J_{CP} 11.5 Hz), 131.46 (d, J_{CP} 6.9 Hz), 132.04, 133.12 (d, J_{CP} 10.3 Hz), 133.89 (d, J 2.3 Hz), 137.17, 155.52 [d, ²J_{CP} 49.5 Hz, C²(C₆H₄)]; ³¹P{¹H}: δ_P = 4.5 (br). Acc. Mass: Found: *m/z* = 318.1585 Calcd for C₂₀H₂₂¹¹BNP 318.1583 [M]⁺. Crystal data: C₂₀H₂₂BBrNP, *M_r* = 398.09, *T* = 200(2) K, monoclinic, space group *P*2₁/*n*, *a* = 9.5770(2), *b* = 7.3405(1), *c* = 27.7205(5) Å, β = 98.4547(10)°, *V* = 1927.57(6) Å³, *Z* = 4, *D*_{calcd} = 1.372 Mg m⁻³, μ(Mo Kα) = 2.22 mm⁻¹, colourless plate, 0.04 × 0.17 × 0.24 mm, 31237 measured reflections with 2θ_{max} = 55.0°, 4427 independent reflections, 4425 absorption-corrected data used in *F*² refinement, 305 parameters, no restraints, *R*₁ = 0.033, *wR*₂ = 0.082 for 3637 reflections with *I* > 2σ(*I*).

Synthesis of 1-diphenylphosphino-2-diphenylarsinoethane boronium hexafluoroarsenate, [BH₂(arphos)][AsF₆]: A solution of BH₂Br.SMe₂ (1.0 M, 0.12 mL, 0.12 mmol) in dichloromethane was added drop-wise to a stirred solution of arphos (0.044 g, 0.1 mmol) in DCM (2 mL). The reaction was stirred for 30 min, then all volatiles were removed under high vacuum to leave a white solid, that was further dried under high vacuum for 30 min. The solid was dissolved in DCM (4 mL), then cannula transferred into a THF (2 mL) solution of K[AsF₆] (0.046 g, 0.2 mmol) to instantaneously form a white precipitate (KBr). The reaction was stirred for 16 h to give a beige/orange coloured precipitate. The filtrate was separated *via* cannula filtration and all volatiles were removed under high vacuum to leave an orange solid. NMR (CDCl₃, 25°C): ¹¹B{¹H}: δ_B = -41.2 {br, [BH₂(arphos)][AsF₆]}, -35.3 {br, [BH₂(arphos)₂][AsF₆]}, -25.1 (br, arphos·BH₂Br), 18.0 (br); ³¹P{¹H}: δ_P = 4.9 (br, arphos·BH₂Br), 6.5, 11.1 {br, [BH₂(arphos)₂][AsF₆]}, 19.2 {br, [BH₂(arphos)][AsF₆]}, 32.0 (br) in a relative integral ratio of 12:2:3:1:3. Additional K[AsF₆] (0.046 g, 0.2 mmol) was added, then suspended in benzene (4 mL) and heated to reflux for 8 h. All volatiles were removed under high vacuum to leave an orange solid. The unreacted K[AsF₆] and side product KBr were removed by dissolution of the solid in a 1:1 mixture of DCM and THF (in which KBr and K[AsF₆] are not soluble), followed by cannula filtration of the supernatant and removal of all volatiles under high vacuum. NMR (CDCl₃, 25°C): ¹¹B{¹H}: δ_B = -41.3 {br, [BH₂(arphos)][AsF₆]}, -36.8 {br, [BH₂(arphos)₂][AsF₆]}, -25.0 (br, arphos·BH₂Br), -1.6, 17.6 (br); ³¹P{¹H}: δ_P = 4.9 (br, arphos·BH₂Br), 11.2 {br,

$[\text{BH}_2(\text{arphos})_2][\text{AsF}_6]$, 19.2 {br, $[\text{BH}_2(\text{arphos})][\text{AsF}_6]$ in a relative integral ratio of 30:10:1. Acc. Mass: Found: $m/z = 455.1017$. Calcd for $\text{C}_{26}\text{H}_{25}^{75}\text{As}^{11}\text{BP}$ 455.1081 $[\text{M}]^+$. ESI-MS (+ve ion): $m/z = 454.1$ $[\text{M} - \text{H}]^+$.

Synthesis of 1,2-bis(phenyl(2'-diphenylarsinoethyl)phosphino)ethane boronium bromide, $[\text{H}_2\text{B}(\kappa^2\text{-(P(Ph)(CH}_2\text{CH}_2\text{AsPh}_2)_2\text{CH}_2)_2)]\text{Br}$: A solution of $\text{BH}_2\text{Br} \cdot \text{SMe}_2$ (1.0 M, 0.50 mL, 0.50 mmol) in dichloromethane was added drop-wise to a stirred suspension of 1,2-bis(phenyl(2'-diphenylarsinoethyl)phosphino)ethane (0.38g, 0.50 mmol) in toluene (30 mL) at 0°C. Upon addition the suspension turned a lime green colour, and after 5 min stirring the reaction was warmed to ambient temperature during which time it developed a mustard yellow colour. After 30 min stirring, all material had dissolved. The mixture was stirred for 14 h, and then reduced to a third of the volume under high vacuum and diluted with pentane. The resulting precipitate was isolated by cannula filtration to leave a beige solid that was recrystallised from a mixture of DCM/pentane. The solid was recrystallised from a mixture of DCM/pentane at -15°C over 72 h to produce colourless X-ray diffraction quality crystals. Yield 0.31 g (0.36 mmol, 73%). The appearance changed at 92°C to more opaque solid, followed by gas evolution at 210°C to become a viscous oil which turned brown and solidified at 238°C. Anal. Found: C, 54.78; H, 4.86; N, 0.00%. Calcd for $\text{C}_{42}\text{H}_{44}\text{As}_2\text{BBrP}_2 \cdot \text{CH}_2\text{Cl}_2$: C, 55.16; H, 4.95; N, 0.00%. NMR (CD_2Cl_2 , 25°C): ^1H : $\delta_{\text{H}} = 1.92\text{--}1.98$ (m, 4H, PCH_2), 2.08–2.14 (m, 4H, PCH_2), 2.46–2.48 (m, 4H, AsCH_2), 7.24–7.31 (m, 12H, C_6H_5), 7.43–7.64 (m, 18H, C_6H_5); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -39.1$ (br); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 15.12$ (d, $^2J_{\text{CP}} 36.7$ Hz, PCH_2), 19.23 (d, $^1J_{\text{CP}} 83.5$ Hz, PCH_2), 23.11 (m, AsCH_2), 122.47 [d, $^1J_{\text{PC}} 64.5$ Hz, $\text{C}^1(\text{PC}_6\text{H}_5)$], 129.12 (C_6H_5), 129.21 (C_6H_5), 130.03 (m, C_6H_5), 133.18 (t, $J_{\text{PC}} 5.1$ Hz, PC_6H_5), 133.59 (C_6H_5), 139.33 (AsC_6H_5). Acc. Mass: Found: $m/z = 771.1442$. Calcd for $\text{C}_{42}\text{H}_{44}^{75}\text{As}_2^{11}\text{BP}_2$ 771.1443 $[\text{M}]^+$. *Crystal data*: $\text{C}_{42}\text{H}_{44}\text{As}_2\text{BBrP}_2$, $M_r = 851.32$, $T = 200(2)$ K, monoclinic, space group $C2/c$, $a = 27.9522(14)$, $b = 13.3162(8)$, $c = 10.5732(5)$ Å, $\beta = 91.9500(30)^\circ$, $V = 3933.20(40)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.438$ Mg m⁻³, $\mu(\text{Mo K}\alpha) 2.83$ mm⁻¹, colourless block, 0.06 × 0.11 × 0.21 mm, 52052 measured reflections with $2\theta_{\text{max}} = 50.6^\circ$, 3481 independent reflections, 3481 absorption-corrected data used in F^2 refinement, 232 parameters, no restraints, $R_1 = 0.059$, $wR_2 = 0.128$ for 2768 reflections with $I > 2\sigma(I)$.

Synthesis of $[\text{Mo}(\text{CO})_4(\text{H}_2\text{B}(\text{diphars}))]\text{Br}$: A mixture of $[\text{H}_2\text{B}(\text{diphars})]\text{Br}$ (0.09 g, 0.10 mmol) and $\text{Mo}(\text{C}_7\text{H}_8)(\text{CO})_3$ (0.03 g, 0.10 mmol) was dissolved in benzene (4 mL) to give a red solution which was stirred for 16 h, during which time a brown precipitate was observed to form (after ca. 2 min). The precipitate was separated by cannula filtration and washed with benzene (2 mL), then further dried under high vacuum. The product was found to be insoluble in benzene, DCM, THF, acetonitrile, MeOH, CHCl_3 , acetone and DMSO. ESI-MS (+ve ion): $m/z = 980.7 [\text{M}]^+$, $951.5 [\text{M} - \text{CO}]^+$, $771.5 [\text{M} - \text{Mo}(\text{CO})_4]^+$.

Reaction of $[\text{H}_2\text{B}(\text{diphars})]\text{Br}$ and $\text{RhCl}(\text{PPh}_3)_3$: A mixture of $[\text{H}_2\text{B}(\text{diphars})]\text{Br}$ (0.02 g, 0.025 mmol) and $\text{RhCl}(\text{PPh}_3)_3$ (0.02 g, 0.025 mmol) were weighed out together in an NMR tube, then dissolved in CD_2Cl_2 (1 mL), was manually shaken and left for 3 h. NMR (CD_2Cl_2 , 25°C): $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -39.7$ {br, $[\text{H}_2\text{B}(\text{diphars})]\text{Br}$ }, -22.08 (br, $\text{diphars}\cdot\text{BH}_2\text{Br}$), 19.45 (br); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -4.9$ (free PPh_3), 9.6 (br, $\text{diphars}\cdot\text{BH}_2\text{Br}$), 23.5 (dd, $^1J_{\text{PRh}}/^2J_{\text{PP}} 113/22$ Hz), 28.0 , 30.4 (dd, $^1J_{\text{PRh}}/^2J_{\text{PP}} 141/30$ Hz), 32.8 {br, $[\text{H}_2\text{B}(\text{diphars})]\text{Br}$ }, 41.3 (d.br, $^1J_{\text{PRh}} 127$ Hz), 47.9 (d.br, $^1J_{\text{PRh}} 193$ Hz), 97.7 (d, $^1J_{\text{PRh}} 104$ Hz), 114.7 (d, $^1J_{\text{PRh}} 100$ Hz) in the relative integral ratio of 2:3:0.1:4:2:2:0.3:1:0.1:0.1. Acc. Mass: Found: $m/z = 1172.1189$. Calcd for $\text{C}_{60}\text{H}_{60}^{75}\text{As}_2^{11}\text{B}^{35}\text{ClP}_3^{103}\text{Rh}$ 1172.1176 $[\text{M} + \text{H}]^+$. ESI-MS (+ve ion): $m/z = 1135.3 [\text{M} - \text{Cl}]^+$, $889.7 [\text{Rh}(\text{PPh}_3)_3]^+$, $861.4 [\text{Rh}(\text{diphars})]^+$, $771.3 [\text{M} - \text{RhCl}(\text{PPh}_3)]^+$.

Synthesis of 1,1-bis(diphenylphosphinomethyl)boronium-1-(diphenylphosphinomethyl)ethane bromide, $[\text{H}_2\text{B}\{\kappa^2\text{-(PPh}_2\text{CH}_2)_2\text{CMeCH}_2\text{PPh}_2\}]\text{Br}$: A solution of $\text{BH}_2\text{Br}\cdot\text{SMe}_2$ (1.0 M, 0.80 mL, 0.80 mmol) in dichloromethane was added drop-wise to a stirred solution of 1,1,1-tris(diphenylphosphinomethyl)ethane (0.50 g, 0.80 mmol) in benzene (40 mL). Upon addition a precipitate formed in approximately 1 min, and after 15 min the solution had lost its transient orange colour. The mixture was heated to reflux for 4 h, and then the solid was isolated by filtration to leave an off-white powder that was further dried under high vacuum for several hours. The solid was recrystallised from a mixture of DCM/pentane to produce colourless X-ray diffraction quality crystals. Yield 0.318 g (0.44 mmol, 55%). Partially melted at ca. 175°C to leave a glassy residue that remained unchanged up to 250°C . The DCM solvate was confirmed to be present in the X-ray determination, however, it could not be modelled adequately and was subsequently removed with the PLATON program 'Squeeze'.

Anal. Found: C, 60.76; H, 5.37; N, 0.00%. Calcd for $C_{41}H_{41}BBrP_3 \cdot 1.5(CH_2Cl_2)$: C, 60.42; H, 5.25; N, 0.00%. NMR (CD_2Cl_2 , 25°C): 1H : $\delta_H = 0.64$ (s, 3H, CH_3), 3.17 (m, 2H, CH_2), 3.43 (m, 2H, CH_2), 3.68-3.86 (m, 2H, CH_2), 7.46-8.07 (m, 30H, C_6H_5); $^{11}B\{^1H\}$: $\delta_B = -39.1$ (br); $^{13}C\{^1H\}$: $\delta_C = 29.96$ (d, $^1J_{CP}$ 87.0 Hz, CH_2), 32.87 (dm, $^1J_{CP}$ unresolved, CH_2), 35.77 (Me), 123.99 [d, $^1J_{CP}$ 63.2 Hz, $C^1(C_6H_5)$], 126.52 [d, $^1J_{CP}$ 62.1 Hz, $C^1(C_6H_5)$], 129.42-133.85 (C_6H_5); $^{31}P\{^1H\}$: $\delta_P = -25.2$ (vbr, pendant PPh_2), 0.3 (br, P_2B). Acc. Mass: Found: $m/z = 637.2510$. Calcd for $C_{41}H_{41}^{11}BP_3$ 637.2514 $[M]^+$. Crystal data: $C_{41}H_{41}BBrP_3$, $M_r = 717.41$, $T = 200(2)$ K, triclinic, space group $P-1$ (No.2), $a = 13.7686(6)$, $b = 14.0695(5)$, $c = 14.3983(6)$ Å, $\alpha = 98.0020(20)$, $\beta = 114.3643(19)$, $\gamma = 113.6510(20)^\circ$, $V = 2166.66(18)$ Å³, $Z = 2$, $D_{calcd} = 1.100$ Mg m⁻³, $\mu(Mo K\alpha) 1.08$ mm⁻¹, colourless prism, $0.15 \times 0.17 \times 0.34$ mm, 36206 measured reflections with $2\theta_{max} = 50.7^\circ$, 7713 independent reflections, 7713 absorption-corrected data used in F^2 refinement, 415 parameters, no restraints, $R_1 = 0.048$, $wR_2 = 0.150$ for 6309 reflections with $I > 2\sigma(I)$.

Partial oxidation of the pendant phosphine was noted, though the compound was not isolated. $[H_2B\{\kappa^2-(PPh_2CH_2)_2CMeCH_2P(O)Ph_2\}]Br$: NMR ($CDCl_3$, 25°C): 1H : $\delta_H = 0.72$ (s, 3H, CH_3), 2.95 (m.br, 2H, CH_2), 3.47 (d, $^2J_{PH}$ 7.6 Hz, 1H, CH_2), 3.74 (d, $^2J_{PH}$ 12.4 Hz, 1H, CH_2), 4.16-4.33 (m, 2H, CH_2), 7.48-8.04 (m, 30H, C_6H_5); $^{11}B\{^1H\}$: $\delta_B = -39.4$ (br); $^{31}P\{^1H\}$: $\delta_P = -0.3$ (vbr, P_2B), 29.9 (O= PPh_2).

Synthesis of 1,1-bis(diphenylphosphinomethyl)boronium-1-(diphenylphosphinomethyl)ethane hexafluoroantimonate,
 $[H_2B\{\kappa^2-(PPh_2CH_2)_2CMeCH_2PPh_2\}][SbF_6]$: A DCM (8 mL) solution of $[H_2B(triphos)]Br$ (0.318 g, 0.44 mmol) was added *via* cannula to a THF (2 mL) solution of $Ag[SbF_6]$ (0.15 g, 0.44 mmol) to initially give a white precipitate, that rapidly turned dark brown before the addition was complete. The reaction was stirred for 15 min, then left to settle for 2 h (the initial precipitate was found too fine and easily passed through the cannula filter), then separated by cannula filtration. The solid was precipitated out of the filtrate with pentane to give a white solid that was isolated by cannula filtration. The product was sparingly soluble in chloroform, but had good solubility in acetone. However, the product was found to decompose over several days after it had come into contact with acetone. Yield 0.337 g (0.39 mmol, 88%). NMR ($CDCl_3$, 25°C): 1H : $\delta_H = 0.60$ (s, 3H, CH_3), 2.73 (dd, $^2J_{PH}/^4J_{PH}$ 15.3 Hz/9.3 Hz, 2H, CH_2), 3.18 (d, $^2J_{PH}$ 12.3 Hz, 2H, CH_2),

3.51 (t, $^2J_{\text{PH}}$ 14.1 Hz, 2H, CH₂), 7.41-7.61 (m, 22H, C₆H₅), 7.81-7.88 (m, 8H, C₆H₅); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -40.2$ (br). Acc. Mass: Found: $m/z = 637.2518$. Calcd for C₄₁H₄₁ $^{11}\text{BP}_3$ 637.2514 [M]⁺. ESI-MS (-ve ion): $m/z = 235.2$ [M]⁻.

Synthesis of 1,1-bis(diphenylphosphinomethyl)boronium-1-(diphenylphosphinomethyl)ethane hexafluoroarsenate,

[H₂B{κ²-(PPh₂CH₂)₂CMeCH₂PPh₂}] [AsF₆]: A solution of [H₂B(triphos)]Br (1.763 g, 2.46 mmol) in DCM (8 mL) was added *via* cannula to a THF (4 mL) solution of K[AsF₆] (0.56 g, 2.46 mmol) to initially give a white precipitate and colourless solution. The white precipitate (KBr) was separated by cannula filtration and discarded, whilst the filtrate was added to a second equivalent of K[AsF₆] (0.56 g, 2.46 mmol) to again give a white precipitate. The precipitate (mixture of KBr and unreacted K[AsF₆]) was separated by cannula filtration and again discarded. All volatiles were removed under high vacuum to leave a white solid. The solid was dissolved in acetone (14 mL) and precipitated by dilution with Et₂O, then separated by cannula filtration and washed with benzene (15 mL) and dried *in vacuo*. Yield 1.366 g (1.65 mmol, 67%). A minor contamination of [H₂B(triphos)(BH₂Br)][AsF₆] was found to be present in ~10% yield, but all attempts to remove this contamination failed. The solid was recrystallised from a mixture of DCM/acetone/pentane at -15°C over 48 h to produce colourless X-ray diffraction quality crystals. NMR (CDCl₃, 25°C): ^1H : $\delta_{\text{H}} = 0.72$ (s, 3H, CH₃), 2.67 (s.br, 2H, CH₂), 2.72-2.84 (m, 2H, CH₂), 3.20 (t, $^2J_{\text{PH}}/^2J_{\text{HH}}$ 14.6 Hz (Average), 2H, CH₂), 7.28-7.36 (m, 4H, C₆H₅), 7.40-7.63 (m, 21H, C₆H₅), 7.79-7.90 (m, 5H, C₆H₅); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -39.6$ (br); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 29.74$ (CH₃), 32.62 (CH₂), 33.08 (CH₂), 38.80 (CMe), 123.41 [d, $^1J_{\text{CP}}$ 68.5 Hz, C¹(C₆H₅)], 126.22 [dd, $^1J_{\text{CP}}/J_{\text{CP}}$ 70.1/9.2 Hz, C¹(C₆H₅)], 129.56-133.49 (C₆H₅); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = -25.1$ (br, pendant PPh₂R), -4.8 (br, pendant PPh₂·BH₂Br contaminant), -0.2 [vbr, P₂B]. ESI-MS (+ve ion): $m/z = 637.5$ [M]⁺; ESI-MS (-ve ion): $m/z = 189.2$ [M]⁻. Crystal data: [C₄₁H₄₁BP₃][AsF₆].H₂O, $M_r = 844.43$, $T = 200(2)$ K, monoclinic, space group $P2_1/n$, $a = 13.2239(6)$, $b = 21.5110(9)$, $c = 14.3499(4)$ Å, $\beta = 100.315(2)$, $V = 4016.0(3)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.397$ Mg m⁻³, $\mu(\text{Mo K}\alpha) 1.03$ mm⁻¹, colourless prism, 0.06 × 0.07 × 0.37 mm, 55977 measured reflections with $2\theta_{\text{max}} = 52.2^\circ$, 7922 independent reflections, 7920 absorption-corrected data used in F^2 refinement, 478 parameters, 36 restraints, $R_1 = 0.072$, $wR_2 = 0.193$ for 3988 reflections with $I > 2\sigma(I)$.

[H₂B{ κ^2 -(PPh₂CH₂)₂CMeCH₂P(O)Ph₂}] [AsF₆]: The solid was recrystallised in air from a mixture of acetone/pentane at 25°C over 48 h to produce colourless X-ray diffraction quality crystals of the oxide decomposition product. Crystal data: C₄₁H₄₁AsBF₆O_{0.6}P₃·0.4(H₂O), *M_r* = 843.22, *T* = 200(2) K, monoclinic, space group *P*2₁/*n*, *a* = 13.0162(3), *b* = 21.4161(5), *c* = 14.4005(2) Å, β = 97.8708(13), *V* = 3976.41(14) Å³, *Z* = 4, *D*_{calcd} = 1.408 Mg m⁻³, μ (Mo K α) 1.04 mm⁻¹, colourless prism, 0.09 × 0.15 × 0.45 mm, 17904 measured reflections with $2\theta_{\max}$ = 55.0°, 9120 independent reflections, 9119 absorption-corrected data used in *F*² refinement, 487 parameters, 200 restraints, *R*₁ = 0.056, *wR*₂ = 0.152 for 6292 reflections with *I* > 2 σ (*I*). Crystal data: C₄₁H₄₁AsBF₆OP₃, *M_r* = 842.42, *T* = 200(2) K, monoclinic, space group *P*2₁/*n*, *a* = 12.7639(3), *b* = 21.4218(5), *c* = 14.4115(2) Å, β = 95.4493(13), *V* = 3922.67(14) Å³, *Z* = 4, *D*_{calcd} = 1.426 Mg m⁻³, μ (Mo K α) 1.05 mm⁻¹, colourless prism, 0.08 × 0.13 × 0.28 mm, 58122 measured reflections with $2\theta_{\max}$ = 50.0°, 6921 independent reflections, 6919 absorption-corrected data used in *F*² refinement, 478 parameters, 201 restraints, *R*₁ = 0.052, *wR*₂ = 0.135 for 4974 reflections with *I* > 2 σ (*I*).

Synthesis of bis(2-diphenylphosphinoethyl)phenylphosphine boronium bromide, [H₂B(triphos-*asym*)]Br: A solution of BH₂Br·SMe₂ (1.0 M, 0.40 mL, 0.40 mmol) in dichloromethane was added drop-wise to a stirred solution of bis(2-diphenylphosphinoethyl)phenylphosphine (0.21 g, 0.40 mmol) in toluene (15 mL) and heated to reflux for 16 h. A white precipitate was observed to form whilst the reaction cooled to room temperature. The white precipitate was separated by cannula filtration. The compound was found to decompose after a few hours to a species that was only found to be soluble in MeOH, but the identity of which remains unknown. Yield 0.027 g (0.04 mmol, 11%). NMR (CDCl₃, 25°C): ¹H: δ_{H} = 2.10 (m, 3H, CH₂), 2.35 (m, 1H, CH₂), 3.02 (m, 3H, CH₂), 3.48 (m, 1H, CH₂), 7.07-7.76 (m, 25H, C₆H₅); ¹¹B{¹H}: δ_{B} = -37.1 (br); ³¹P{¹H}: δ_{P} = -12.0 (br), 29.8 (d, ¹*J*_{PB} 140 Hz). Acc. Mass: Found: *m/z* = 547.2049. Calcd for C₃₄H₃₅¹¹BP₃ 547.2045 [*M*]⁺.

Synthesis of 1,1-bis(diphenylphosphinomethyl)boronium-1-(diphenylphosphinomethyl)ethane chloro(cyclooctadiene) rhodium bromide, [H₂B{ κ^2 -(PPh₂CH₂)₂CMeCH₂PPh₂}RhCl(η^4 -COD)]Br: A toluene (8 mL) solution of [H₂B(triphos)]Br (0.287 g, 0.40 mmol) was added *via* cannula to a DCM (3 mL) solution

of $\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2$ (0.10 g, 0.20 mmol) to give a pale orange coloured mixture. The mixture was heated to reflux (toluene) for 16 h, after an hour of which the reaction was a deep red colour. All volatiles were removed under high vacuum to leave a yellow solid. Crude NMR (CDCl_3 , 25°C): ^1H : $\delta_{\text{H}} = -7.78$ (dm, $^1J_{\text{RhH}}$ 70.8 Hz, RhH), -7.02 (dm, $^1J_{\text{RhH}}$ 76.5 Hz, RhH), 0.89 (s, CH_3), $1.62\text{--}1.86$ (m), 2.17 (d.br, J 5.7 Hz), 2.33 (s), 2.63 (s), 3.22 (s), $3.51\text{--}3.56$ (m), $4.33\text{--}4.48$ (m), 5.02 (s.br), $7.09\text{--}7.61$ (m, C_6H_5), $7.77\text{--}7.80$ (m, C_6H_5), $8.04\text{--}8.10$ (m, C_6H_5); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -40.0$ (br); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 1.7$ (br, P_2B), 10.2 (d, $^1J_{\text{PRh}}$ 103.8 Hz, $[\text{RhCl}(\eta^4\text{-COD})\{\text{H}_2\text{B}(\text{triphos})\}]\text{Br}$), 13.9 (d, $^1J_{\text{PRh}}$ 148.8 Hz, $[\text{RhBr}(\eta^4\text{-COD})\{\text{H}_2\text{B}(\text{triphos})\}]\text{Cl}$). ESI-MS (+ve ion): $m/z = 930.2$ $[\text{M} + \text{Br} - \text{Cl}]^+$, 883.3 $[\text{M}]^+$, 777.1 $[\text{M} + \text{H} - \text{C}_8\text{H}_{12}]^+$, 637.3 $[\text{M} - \text{RhCl}(\text{C}_8\text{H}_{12})]^+$.

Synthesis of 1,1-bis(diphenylphosphinomethyl)boronium-1-(diphenylphosphinomethyl)ethane dichloro(η^5 -1,2,3,4,5-pentamethylcyclopentadienyl) rhodium hexafluoroarsenate, $[\text{H}_2\text{B}\{\kappa^2\text{-(PPh}_2\text{CH}_2)_2\text{CMeCH}_2\text{PPh}_2\}\text{RhCl}_2\text{Cp}^*][\text{AsF}_6]$: An acetone (4 mL) solution of $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$ (0.083 g, 0.10 mmol) and $\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2\text{Cp}^*_2$ (0.031 g, 0.05 mmol) was stirred for 16 h to give a strong red/orange coloured solution. All volatiles were removed under high vacuum to leave a red/orange coloured solid. The solid was recrystallised from a mixture of DCM/ Et_2O to give a red/orange coloured powder. Anal. Found: C, 53.01; H, 4.53; N, 0.00%. Calcd for $\text{C}_{51}\text{H}_{56}\text{AsBCl}_2\text{F}_6\text{P}_3\text{Rh}\cdot 0.25(\text{CH}_2\text{Cl}_2)$: C, 53.22; H, 4.92; N, 0.00%. NMR (CDCl_3 , 25°C): ^1H : $\delta_{\text{H}} = 0.51$ (s, 3H, CH_3), 1.29 (s, 9H, Cp^*), 1.62 (s, 6H, Cp^*), 2.38 (s.br, 2H, CH_2), 3.03 (s.br, 2H, CH_2), 3.49 (s.br, 2H, CH_2), $7.36\text{--}7.90$ (m, 30H, C_6H_5); $^{11}\text{B}\{^1\text{H}\}$: $\delta_{\text{B}} = -39.8$ (br); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 1.1$ [br, P_2B], 23.6 (d.br, $^1J_{\text{PRh}}$ 151.1 Hz, RhP). Acc. Mass: Found: $m/z = 945.2137$. Calcd for $\text{C}_{51}\text{H}_{56}^{11}\text{B}^{35}\text{Cl}_2\text{P}_3^{103}\text{Rh}$ 945.2120 $[\text{M}]^+$. ESI-MS (+ve ion): $m/z = 991.2$ $[\text{M} + 2(\text{MeCN}) - \text{Cl}]^+$, 911.3 $[\text{M} - \text{Cl}]^+$, 637.2 $[\text{M} - \text{RhCl}_2\text{Cp}^*]^+$.

Synthesis of 1,1-bis(diphenylphosphinomethyl)boronium-1-(diphenylphosphinomethyl)ethane dichloro(η^6 -cymene) ruthenium hexafluoroarsenate, $[\text{H}_2\text{B}\{\kappa^2\text{-(PPh}_2\text{CH}_2)_2\text{CMeCH}_2\text{PPh}_2\}\text{RuCl}_2(\eta^6\text{-cymene})][\text{AsF}_6]$: An acetone (4 mL) solution of $[\text{H}_2\text{B}(\text{triphos})][\text{AsF}_6]$ (0.083 g, 0.1 mmol) and $\text{Ru}_2(\mu\text{-Cl})_2(\eta^6\text{-cymene})_2$ (0.031 g, 0.05 mmol) was stirred for 18 h to give a strong red coloured solution. All volatiles were removed under high vacuum to leave a red/orange

solid. The solid was recrystallised from a mixture of DCM/Et₂O to give a red/orange coloured powder. Yield 0.065 g (0.057 mmol, 57%). Crude NMR (CDCl₃, 25°C): ¹H: δ_H = 0.55 (s, 3H, CH₃), 1.05 (d, ³J_{HH} 6.8 Hz, 6H, CH₃), 2.17 (s, 3H, CH₃), 2.63-2.69 (m, 2H, CH₂), 2.71-2.74 (m, 1H, CH), 3.02-3.08 (m, 2H, CH₂), 3.20 (s.br, 2H, CH₂), 5.17-5.20 (m, 4H, C₆H₄), 7.30 (m, 4H, C₆H₅), 7.44-7.53 (m, 18H, C₆H₅), 7.73-7.76 (m, 4H, C₆H₅), 7.83-7.88 (m, 4H, C₆H₅); ¹¹B{¹H}: δ_B = -40.2 (br); ³¹P{¹H}: δ_P = 0.6 [br, P₂B], 12.2 (br, RuP). Acc. Mass: Found: *m/z* = 943.2034. Calcd for C₅₁H₅₅¹¹B³⁵Cl₂P₃¹⁰²Ru 943.2030 [M]⁺. ESI-MS (+ve ion): *m/z* = 990.3 [M + 2(MeCN) - Cl]⁺, 637.2 [M - RuCl₂(η⁶-cymene)]⁺.

Synthesis of 1,1-bis(diphenylphosphinomethyl)boronium-1-(diphenylphosphinomethyl)ethane chloro(η⁴-cyclooctadiene) rhodium hexafluoroarsenate, [H₂B{κ²-(PPh₂CH₂)₂CMeCH₂PPh₂}RhCl(η⁴-COD)][AsF₆]: An acetone (4 mL) suspension of [H₂B(triphos)][AsF₆] (0.083 g, 0.10 mmol) and Rh₂(μ-Cl)₂(η⁴-COD)₂ (0.024 g, 0.050 mmol) was stirred for 3 h. After approximately 1 min, the suspension changed from a red/orange colour to yellow. All volatiles were removed under high vacuum to leave a bright yellow solid. The product was insoluble in methanol and ethanol. Yield 0.078 g (0.073 mmol, 73%). Crude NMR (CDCl₃, 25°C): ¹H: δ_H = 0.59 (s, 3H, CH₃), 1.75 [d, ³J_{RhH} 11.1 Hz, 4H, CH₂(COD)], 2.50 [d.br, ³J_{RhH} 10.5 Hz, 4H, CH₂(COD)], 2.72 (dd, ²J_{PH}²J_{HH} 15.0/8.4 Hz, 2H, PCH₂), 3.20 (d, ²J_{PH} 12.9 Hz, 2H, PCH₂), 3.56 [q, ²J_{PH}²J_{HH} 15.6 Hz (Average), 2H, PCH₂], 4.23 [s, 4H, CH(COD)], 7.32-7.59 (m, 22H, C₆H₅), 7.83-7.90 (m, 8H, C₆H₅); ¹¹B{¹H}: δ_B = -39.9 (br); ³¹P{¹H}: δ_P = 1.7 [br, P₂B], 13.3 (d.br, ¹J_{PRh} 149.9 Hz, RhP). Acc. Mass: Found: *m/z* = 883.2183. Calcd for C₄₉H₅₃¹¹B³⁵ClP₃¹⁰³Rh 883.2197 [M]⁺. ESI-MS (+ve ion): *m/z* = 927.2 [M + MeCN + 2H]⁺, 728.2 [M - C₈H₁₂ - Cl - BH]⁺, 636.2 [M - RhCl(C₈H₁₂)]⁺.

6.7 Dihaloboronium Salts

Synthesis of bis(dimethylphenylphosphine)monobromoboronium bromide, [BHBr(PMe₂Ph)₂]Br: A solution of BHBr₂.SMe₂ (1.0 M, 1.00 mL, 1.00 mmol) in dichloromethane was added drop-wise to a stirred solution of dimethylphenylphosphine (ρ = 0.97 g mL⁻¹, 0.28 mL, 2.00 mmol) in pentane (4 mL). The solution went cloudy at the beginning of the addition, but became less opaque as a colourless oil separated

out beneath the solvent layer. After 2 h stirring, all volatiles were removed under high vacuum to leave a colourless oil, which was dried for an additional 2 h *in vacuo*. The compound was observed to decompose over a short period of time (~4 h). Yield 0.42 g (0.94 mmol, 94%). NMR (Crude, CD₂Cl₂, 25°C): ¹¹B{¹H}: δ_B = -21.5 (br); ³¹P{¹H}: δ_P = -7.5 (d.br, ¹J_{PB} 134 Hz). Acc. Mass: Found: *m/z* = 367.0550. Calcd for C₁₆H₂₃¹¹B⁷⁹BrP₂ 367.0551 [M]⁺.

Reaction of dcpe with BHBr₂.SMe₂: Observation of 1,2-bis(dicyclohexylphosphino)ethane monobromoboronium bromide, [BHBr(dcpe)]Br, and isolation of *P,P'*-bis(dibromoborane)-1,2-bis(dicyclohexylphosphino)ethane, (dcpe·(BHBr₂)₂): A solution of BHBr₂.SMe₂ (1.0 M, 0.25 mL, 0.25 mmol) in dichloromethane was added drop-wise to a stirred solution of dcpe (0.11 g, 0.25 mmol) in benzene (5 mL) that was cooled in an ice bath during addition. The mixture was warmed to room temperature and stirred for 6 h, during which time the solution acquired a fine precipitate. All volatiles were removed under high vacuum to leave a white residue. The residue was recrystallised from a mixture of DCM/pentane at -15°C to provide colourless X-ray diffraction quality crystals of [BHBr(dcpe)]Br. The residue was recrystallised from a mixture of DCM/ethanol to provide colourless X-ray diffraction quality crystals of dcpe(BHBr₂)₂. Crude mixture contained approximately a 1:1 stoichiometry of the two products based on NMR integration.

[BHBr(dcpe)]Br: Anal. Found: C, 47.76; H, 7.50; N, 0.00%. Calcd for C₂₆H₂₆BBP₂.CH₂Cl₂: C, 47.75; H, 7.57; N, 0.00%. NMR (CD₂Cl₂, 25°C): ¹¹B{¹H}: δ_B = -26.8 (br); ³¹P{¹H}: δ_P = 20.9 (d.br, ¹J_{PB} 89 Hz). Acc. Mass: Found: *m/z* = 513.2585. Calcd for C₂₆H₄₉¹¹B⁷⁹BrP₂ 513.2586 [M]⁺. ESI-MS (+ve ion): *m/z* = 435.6 [M + H - Br]⁺. *Crystal data:* 2[(C₂₆H₄₉BBP₂)]Br.CH₂Cl₂, *M_r* = 1273.41, *T* = 200(2) K, triclinic, space group *P*-1 (No.2), *a* = 11.8318(3), *b* = 13.6868(3), *c* = 20.5375(4) Å, α = 102.0817(13), β = 99.8011(10), γ = 92.5268(11)°, *V* = 3193.71(13) Å³, *Z* = 2, *D*_{calcd} = 1.324 Mg m⁻³, μ(Mo Kα) 2.74 mm⁻¹, colourless block, 0.16 × 0.17 × 0.28 mm, 66125 measured reflections with 2θ_{max} = 55.0°, 14614 independent reflections, 14574 absorption-corrected data used in *F*² refinement, 586 parameters, 247 restraints, *R*₁ = 0.047, *wR*₂ = 0.132 for 10760 reflections with *I* > 2σ(*I*).

dcpe·(BHBr₂)₂: Anal. Found: C, 40.75; H, 6.64; N, 0.00%. Calcd for C₂₆H₅₀B₂Br₄P₂: C, 40.78; H, 6.58; N, 0.00%. NMR (CD₂Cl₂, 25°C): ¹¹B{¹H}: δ_B = -17.6 (br); ³¹P{¹H}: δ_P = 0.1 (br). Crystal data: C₂₆H₅₀B₂Br₄P₂, *M_r* = 765.87, *T* = 273(2) K (crystals found to crack at 200K), monoclinic, space group *C2/c*, *a* = 18.4285(7), *b* = 8.5936(3), *c* = 20.9657(8) Å, β = 94.666(2)°, *V* = 3309.3(2) Å³, *Z* = 4, *D_{calcd}* = 1.537 Mg m⁻³, μ(Mo Kα) 4.98 mm⁻¹, colourless prism, 0.04 × 0.07 × 0.16 mm, 22553 measured reflections with 2θ_{max} = 50.0°, 2903 independent reflections, 2903 absorption-corrected data used in *F*² refinement, 155 parameters, 119 restraints, *R*₁ = 0.065, *wR*₂ = 0.182 for 2052 reflections with *I* > 2σ(*I*).

Synthesis of 1-diphenylphosphino-2-dimethylaminobenzene monobromoboronium bromide, [BrHB(NMe₂C₆H₄PPh₂-2)Br: A solution of BHBr₂·SMe₂ (1.0 M, 0.50 mL, 0.50 mmol) in dichloromethane was added drop-wise to a stirred solution of 1-diphenylphosphino-2-dimethylaminophenylene (0.15 g, 0.50 mmol) in DCM (2 mL) and stirred for 1.5 h. All volatiles were removed under high vacuum to leave an off-white solid. The solid was recrystallised from a mixture of DCM/pentane overnight to produce colourless X-ray diffraction quality crystals. Yield: 0.201 g (0.42 mmol, 84%). Anal. Found: C, 33.70; H, 2.06; N, 1.69%. Calcd for C₂₀H₂₁BBr₂NP.2(CHCl₃): C, 36.92; H, 3.24; N, 1.96%.[§] NMR (CDCl₃, 25°C): ¹H: δ_H = 3.24 (s, 3H, NMe), 3.77 (d, 1.8 Hz, 3H, NMe), 7.57-7.81 (m, 12H, C₆H₄/C₆H₅), 8.13 [t, 8 Hz, 1H, C₆H₄], 9.14 (dd, *J*_{PH}/*J* 8/5 Hz), 1H, C₆H₄]; ¹¹B{¹H}: δ_B = -5.2 (br); ¹³C{¹H}: δ_C = 53.57 (NMe), 55.45 (NMe), 117.23 [d, ¹*J*_{CP} 65.2 Hz, C¹(C₆H₅)], 118.35 [d, ¹*J*_{CP} 69.4 Hz, C¹(C₆H₄)], 119.18 [d, ¹*J*_{CP} 75.5 Hz, C¹(C₆H₅)], 124.30, 125.05 (d, *J*_{CP} 6.8 Hz), 129.31, 130.05, 130.57 (dd, *J*_{CP}/*J* 11.9 Hz/4.2 Hz), 132.09 (d, *J*_{CP} 7.6 Hz), 132.91, 133.52 (d, *J*_{CP} 10.2 Hz), 133.74 (d, *J*_{CP} 9.3 Hz), 134.58 (d, *J*_{CP} 11.9 Hz), 138.49, 154.44 [d, ²*J*_{CP} 17.0 Hz, C²(C₆H₄)]; ³¹P{¹H}: δ_P = -11.0 (br). Acc. Mass: Found: *m/z* = 396.0686 Calcd for C₂₀H₂₁¹¹B⁷⁹BrNP 396.0688 [*M*]⁺. Crystal data: C₂₀H₂₁BBr₂NP.2(CHCl₃), *M_r* = 715.74, *T* = 200(2) K, monoclinic, space group *P2₁/a*, *a* = 14.6204(2), *b* = 14.0880(3), *c* = 14.7554(3) Å, β = 109.0115(15)°, *V* = 2873.42(10) Å³, *Z* = 4, *D_{calcd}* = 1.654 Mg m⁻³, μ(Mo Kα) = 3.45 mm⁻¹, colourless block, 0.16 × 0.28 × 0.29 mm, 52435 measured reflections with 2θ_{max} = 55.0°, 6590 independent reflections, 6590 absorption-corrected

[§] Satisfactory microanalysis could not be obtained due to decomposition in the solid state, even under an inert atmosphere.

data used in F^2 refinement, 298 parameters, no restraints, $R_1 = 0.043$, $wR_2 = 0.102$ for 4632 reflections with $I > 2\sigma(I)$.

6.8 Miscellaneous

Synthesis of *fac*-Mo(κ^1 -dppm)(κ^2 -dppm)(CO)₃: The compound was prepared according to the literature procedure for *mer*-Mo(κ^1 -dppm)(κ^2 -dppm)(CO)₃.² However, the characterisation matched that reported for *fac*-Mo(κ^1 -dppm)(κ^2 -dppm)(CO)₃. The solid was recrystallised from a mixture of DCM/Et₂O to produce yellow X-ray diffraction quality crystals. Yield: 0.797 g (0.84 mmol, 42%). NMR (CDCl₃, 25°C): ³¹P{¹H}: $\delta_P = -26.6$ (d, 1P, ²J_{PP} 29 Hz, pendant κ^1 -dppm), 2.0 (d, 2P, ²J_{PP} 26 Hz, κ^2 -dppm), 28.8 (dt, 1P, ²J_{PP}/²J_{PP} 31/26 Hz, coordinated κ^1 -dppm). *Crystal data*: C₅₃H₄₄MoFeO₃P₄, $M_r = 948.76$, $T = 200(2)$ K, monoclinic, space group C2/c, $a = 42.4148(3)$, $b = 9.6462(1)$, $c = 23.6826(2)$ Å, $\beta = 111.9876(4)^\circ$, $V = 3225.61(18)$ Å³, $Z = 8$, $D_{\text{calcd}} = 1.403$ Mg m⁻³, $\mu(\text{Mo K}\alpha) 0.48$ mm⁻¹, yellow prism, 0.11 × 0.14 × 0.49 mm, 115124 measured reflections with $2\theta_{\text{max}} = 60.2^\circ$, 13158 independent reflections, 13133 absorption-corrected data used in F^2 refinement, 550 parameters, no restraints, $R_1 = 0.031$, $wR_2 = 0.076$ for 10774 reflections with $I > 2\sigma(I)$.

Synthesis of RuBr₂(κ^2 -arphos)₂: A mixture of arphos (0.088 g, 0.2 mmol) and RuBr₂(PPh₃)₃ (0.104 g, 0.1 mmol) was suspended in benzene (4 mL) to give a dark brown coloured suspension that was heated to reflux for 16 h. The dark brown precipitate was allowed to settle, and the relatively colourless solution removed by cannula filtration. The solid was washed with hexane (2 × 4 mL) and dried under high vacuum to leave a pale brown solid. A recrystallisation in DCM was attempted, but the product was subsequently found to have poor solubility in common solvents, which hindered characterisation. Yield: 0.021 g (0.018 mmol, 18%). Anal. Found: C, 51.88; H, 3.87; N, 0.00%. Calcd for C₅₂H₄₈As₂Br₂P₂Ru·CH₂Cl₂: C, 51.73; H, 4.10; N, 0.00%. NMR (CDCl₃, 25°C): ³¹P{¹H}: $\delta_P = 23.3$. Acc. Mass: Found: $m/z = 1143.9089$ Calcd for C₅₂H₄₈⁷⁵As₂⁷⁹Br₂P₂Ru 1143.9073 [M]⁺. ESI-MS (+ve ion): $m/z = 1108.0$ [M + NCMe - Br]⁺, 1067.0 [M - Br]⁺, 1026.1 [M + NCMe - 2(Br)]⁺.

Synthesis of $\text{RhCl}_2\text{Cp}^*(\kappa^1\text{-P-arphos})$: A mixture of arphos (0.088 g, 0.20 mmol) and $\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2\text{Cp}^*_2$ (0.062 g, 0.10 mmol) was suspended in THF (4 mL) to give a red suspension that was stirred for 18 h. All volatiles were removed under high vacuum to leave an orange/red solid. A DCM solution of the solid was layered with hexane overnight to give an orange precipitate and a red solution. The red solution was isolated by cannula filtration and its volume reduced to approximately half on a rotary evaporator to give a red precipitate, which was isolated by decanting off the effectively colourless solution. Dark red X-ray diffraction quality crystals were found to precipitate out of a saturated solution of the solid in wet acetone after 5 min. The compound was found to convert completely to $[\text{RhClCp}^*(\kappa^2\text{-arphos})]\text{Cl}$ if left in chloroform for two days. Yield: 0.100 g (0.13 mmol, 67%). Anal. Found: C, 57.43; H, 5.17; N, 0.00%. Calcd for $\text{C}_{36}\text{H}_{39}\text{AsCl}_2\text{PRh}$: C, 57.54; H, 5.23; N, 0.00%. NMR (CDCl_3 , 25°C): ^1H : $\delta_{\text{H}} = 1.32$ (d, $^3J_{\text{RhH}}$ 1.6 Hz, 15H, Cp^*), 1.88 (dt, $^2J_{\text{PH}}/^3J_{\text{HH}}$ 10.0/7.2 Hz, 2H, PCH_2), 2.87 (dt, $^3J_{\text{PH}}/^3J_{\text{HH}}$ 8.8/8.6 Hz, 2H, AsCH_2), 7.22 (s, 8H, C_6H_5), 7.39-7.47 (m, 8H, C_6H_5), 7.73-7.78 (m, 4H, C_6H_5); $^{13}\text{C}\{^1\text{H}\}$: $\delta_{\text{C}} = 10.04$ (C_5Me_5), 24.69 (AsCH_2), 29.22 (d, $^1J_{\text{PC}}$ 35.8 Hz, PCH_2), 104.07 (dd, $^1J_{\text{RhC}}/^2J_{\text{PC}}$ 5.6/2.2 Hz, C_5Me_5), 128.93 (d, J_{PC} 10.6 Hz, C_6H_5), 129.71 (d, J_{PC} 23.2 Hz, C_6H_5), 130.13 (d, $^1J_{\text{PC}}$ 36.0 Hz, C_6H_5), 131.83 (d, J_{PC} 5.8 Hz, C_6H_5), 132.04 (C_6H_5), 132.81 (d, J_{PC} 8.8 Hz, C_6H_5), 134.11 (C_6H_5), 134.47 (d, J_{PC} 11.2 Hz, C_6H_5); $^{31}\text{P}\{^1\text{H}\}$: $\delta_{\text{P}} = 32.1$ (d, $^1J_{\text{RhP}}$ 137.7 Hz). Acc. Mass: Found: $m/z = 715.0751$ Calcd for $\text{C}_{36}\text{H}_{39}^{75}\text{As}^{35}\text{ClP}^{103}\text{Rh}$ 715.0749 $[\text{M} - \text{Cl}]^+$. Crystal data: $\text{C}_{36}\text{H}_{39}\text{AsCl}_2\text{PRh}$, $M_r = 751.41$, $T = 150(2)$ K, monoclinic, space group $P2_1/c$, $a = 16.5830(1)$, $b = 9.3185(1)$, $c = 20.9738(1)$ Å, $\beta = 100.7744(5)^\circ$, $V = 3183.92(4)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.567$ Mg m⁻³, $\mu(\text{Cu K}\alpha) = 7.69$ mm⁻¹, red plate, $0.02 \times 0.10 \times 0.13$ mm, 60955 measured reflections with $2\theta_{\text{max}} = 144.8^\circ$, 6296 independent reflections, 6272 absorption-corrected data used in F^2 refinement, 370 parameters, no restraints, $R_1 = 0.020$, $wR_2 = 0.051$ for 6170 reflections with $I > 2\sigma(I)$.

Synthesis of $[\text{RhClCp}^*(\kappa^2\text{-arphos})]\text{Cl}$: A mixture of arphos (0.088 g, 0.20 mmol) and $\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2\text{Cp}^*_2$ (0.062 g, 0.10 mmol) was suspended in THF (4 mL) to give a red suspension that was stirred for 18 h. All volatiles were removed under high vacuum to leave an orange/red solid. A DCM solution of the solid was layered with hexane overnight to give an orange precipitate and a red solution. The orange precipitate was isolated by cannula filtration and was recrystallised from a mixture of DCM/hexane to

give an orange powder. Yield: 0.043 g (0.06 mmol, 30%). Anal. Found: C, 46.33; H, 4.66; N, 0.00%. Calcd for $C_{36}H_{39}AsCl_2PRh \cdot 3(CH_2Cl_2)$: C, 46.55; H, 4.51; N, 0.00%. NMR ($CDCl_3$, 25°C): 1H : $\delta_H = 1.61$ (d, $^3J_{RhH}$ 4.0 Hz, 15H, Cp*), 2.17 (m, 1H, CH_2), 2.75 (m, 1H, CH_2), 2.88 (m, 1H, CH_2), 3.15 (m, 1H, CH_2), 7.34-7.86 (m, 20H, C_6H_5); $^{13}C\{^1H\}$: $\delta_C = 6.51$ ($AsCH_2$), 8.93 (d, $^1J_{PC}$ 17.6 Hz, PCH_2), 10.07 (C_5Me_5), 104.10 (dd, $^1J_{RhC}/^2J_{PC}$ 5.1/1.8 Hz, C_5Me_5), 128.94 (d, J_{PC} 10.6 Hz, C_6H_5), 129.72 (d, J_{PC} 23.6 Hz, C_6H_5), 131.86 (C_6H_5), 132.04 (C_6H_5), 132.82 (d, J_{PC} 6.9 Hz, C_6H_5), 133.66 (C_6H_5), 134.12 (C_6H_5), 134.48 (d, J_{PC} 11.2 Hz, C_6H_5); $^{31}P\{^1H\}$: $\delta_P = 69.7$ (d, $^1J_{RhP}$ 131.2 Hz). Acc. Mass: Found: $m/z = 715.0754$ Calcd for $C_{36}H_{39}^{75}As^{35}ClP^{103}Rh$ 715.0749 [M] $^+$.

Synthesis of $[RhClCp^*(\kappa^2\text{-arphos})][AsF_6]$: A mixture of arphos (0.088 g, 0.20 mmol) and $Rh_2(\mu\text{-Cl})_2Cl_2Cp^*_2$ (0.062 g, 0.10 mmol) was suspended in DCM (4 mL) and stirred for 5 min, and then a solution of $K[AsF_6]$ (0.091 g, 0.40 mmol) in THF (4 mL + 1 mL washing) was added *via* cannula. Upon addition a slight colour change from dark red to orange/red occurred. The reaction was stirred for 96 h and the resulting orange filtrate was isolated by cannula filtration from the beige precipitate (KCl). All volatiles were removed under high vacuum to leave an orange solid. A saturated DCM solution of the solid was layered with hexane overnight to produce orange X-ray diffraction quality crystals. Yield: 0.135 g (0.15 mmol, 75%). NMR ($CDCl_3$, 25°C): 1H : $\delta_H = 1.55$ (d, $^3J_{RhH}$ 4.0 Hz, 15H, Cp*), 2.15 (hept, J 6.0 Hz, 1H, PCH_2), 2.71 (m, 1H, $AsCH_2$), 2.84 (m, 1H, CH_2), 3.12 (m, 1H, CH_2), 6.99 (d, J 8.0 Hz, 2H, C_6H_5), 7.31-7.74 (m, 18H, C_6H_5); $^{13}C\{^1H\}$: $\delta_C = 9.63$ (C_5Me_5), 24.47 ($AsCH_2$), 29.13 (d, $^1J_{PC}$ 36.6 Hz, PCH_2), 104.12 (d, $^1J_{RhC}$ 4.0 Hz, C_5Me_5), 128.87 (d, J_{PC} 10.7 Hz, C_6H_5), 129.64 (d, J_{PC} 21.2 Hz, C_6H_5), 131.76 (d, J_{PC} 5.0 Hz, C_6H_5), 131.99 (C_6H_5), 132.78 (d, J_{PC} 8.8 Hz, C_6H_5), 133.56 (C_6H_5), 134.11 (C_6H_5), 134.41 (d, J_{PC} 11.1 Hz, C_6H_5); $^{31}P\{^1H\}$: $\delta_P = 69.6$ (d, $^1J_{RhP}$ 131.1 Hz). Acc. Mass: Found: $m/z = 715.0855$ Calcd for $C_{36}H_{39}^{75}As^{35}ClP^{103}Rh$ 715.0749 [M] $^+$. Crystal data: $[C_{36}H_{39}AsClPRh][AsF_6]$, $M_r = 904.87$, $T = 150(2)$ K, orthorhombic, space group $P2_12_12_1$, $a = 12.9214(2)$, $b = 13.8109(2)$, $c = 19.7036(2)$ Å, $V = 3516.23(8)$ Å 3 , $Z = 4$, $D_{calcd} = 1.709$ Mg m $^{-3}$, $\mu(\text{Mo K}\alpha) 2.53$ mm $^{-1}$, orange prism, $0.22 \times 0.27 \times 0.71$ mm, 61796 measured reflections with $2\theta_{max} = 59.2^\circ$, 9006 independent reflections, 8964 absorption-corrected data used in F^2 refinement, 444 parameters, no restraints, $R_1 = 0.024$, $wR_2 = 0.041$ for 8413 reflections with $I > 2\sigma(I)$.

Reaction of BCl₂Ph and K[MoTp*(CO)₃]: A mixture of K[Tp*] (0.34 g, 1.0 mmol) and Mo(C₇H₈)(CO)₃ (0.27 g, 1.0 mmol) were weighed out together into the same flask, suspended in benzene (10 mL) and stirred for 2.5 h to give a red suspension. Neat BCl₂Ph (0.13 mL, 1.0 mmol) was added drop-wise to immediately cause a brown precipitate, though the solution remained red, accompanied by a noticeable temperature rise of the solution. The reaction was stirred for 1 h during which time the initial brown precipitate re-dissolved and another formed. The precipitate was left to settle for several hours to give an orange solid that was separated by cannula filtration. NMR (CDCl₃, 25°C): ¹H{¹H}: δ_B = -31.6 (br), -10.5 (br), -3.5 (br), 0.3 (br). The red filtrate was concentrated under high vacuum to give a red residue. NMR (CDCl₃, 25°C): ¹H{¹H}: δ_B = -32.3 (br), 0.4 (br), 27.3 (br).

[Tp*BPh][MoTp*(CO)₃]: The orange precipitate was dissolved in DCM and layered with pentane overnight to give a trace amount of pale red X-ray diffraction quality crystals. *Crystal data:* [C₂₁H₂₇B₂N₆][C₁₈H₂₂BMoN₆O₃], *M_r* = 862.27, *T* = 200(2) K, orthorhombic, space group *Pnma*, *a* = 19.2832(4), *b* = 12.9579(2), *c* = 16.7743(3) Å, *V* = 4191.39(13) Å³, *Z* = 4, *D_{calcd}* = 1.366 Mg m⁻³, μ(Mo Kα) 0.37 mm⁻¹, pale red needle, 0.07 × 0.07 × 0.23 mm, 57457 measured reflections with 2θ_{max} = 55.0°, 5010 independent reflections, 5008 absorption-corrected data used in *F*² refinement, 305 parameters, 18 restraints, *R*₁ = 0.043, *wR*₂ = 0.112 for 3481 reflections with *I* > 2σ(*I*).

Reaction of BCl(catechol) and Ti[Tp*]: A mixture of TiTp* (0.13 g, 0.25 mmol) and BCl(catechol) (0.04 g, 0.25 mmol) in DCM (4 mL) was stirred for 3 h. The colourless supernatant was separated from the resultant white precipitate (TiCl) by cannula filtration. NMR (CDCl₃, 25°C): ¹H: δ_H = 1.95 (s, 6H), 2.03 (s, 18H), 2.15 (s, 18H), 2.28 (s, 6H), 5.78 (s, 2H), 6.04 (s, 6H), 6.78 (s, 8H); ¹B: δ_B = -6.8 (br), 6.3, 13.2.

HB(OC₆H₄OH-2)(μ-pz*)₂B(O₂C₆H₄): NMR (CDCl₃, 25°C): ¹H: δ_H = 1.95 (s, 6H), 2.28 (s, 6H), 5.78 (s, 2H), 6.78 (s, 8H); ¹B: δ_B = -6.8 (br), 6.3. Layering of the crude DCM solution with hexane gave colourless X-ray diffraction quality crystals after 7 days. The crystals were found to decompose in 2-3 h following exposure to air. *Crystal data:* C₂₂H₂₄B₂N₄O₄, *M_r* = 430.08, *T* = 200(2) K, monoclinic, space group *P2₁/n*, *a* = 13.1696(7), *b* = 13.2375(6), *c* = 15.4237(7) Å, β = 115.145(3)°, *V* = 2434.0(2) Å³, *Z* = 4, *D_{calcd}* = 1.174 Mg m⁻³, μ(Mo Kα) = 0.08 mm⁻¹, colourless plate, 0.04 × 0.09 × 0.14 mm, 26878 measured reflections with 2θ_{max} = 50.0°, 4300 independent reflections, 4284

absorption-corrected data used in F^2 refinement, 290 parameters, no restraints, $R_1 = 0.062$, $wR_2 = 0.173$ for 2202 reflections with $I > 2\sigma(I)$.

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Appendices

Appendix 1: N→B bond lengths of all structurally determined BMIDA-functionalised compounds, R-BMIDA (Compounds highlighted in blue were determined for this thesis; multiple N→B bond lengths being reported for a single compound is due to more than one crystallographically distinct molecule existing in the respective asymmetric unit cell).

R	N→B			
2-pyridyl ¹	1.638(2)			
3-bromophenylvinyl ²	1.642(7)	1.647(9)	1.653(8)	1.667(9)
<i>E</i> -2-methyl- <i>E</i> -4-(B{glycol})-buta-1,3-dien-1-yl ³	1.684(3)			
<i>E</i> -2-bromovinyl ⁴	1.644(4)	1.648(4)	1.648(6)	1.654(4)
<i>E</i> -2-B(glycol)vinyl ⁴	1.62(2)	1.64(2)		
2-thiazolyl ⁵	1.649(3)			
2-pyrazinyl ⁵	1.635(2)			
1,2-dioxo-2-phenylethyl ⁶	1.630(2)			
phenyl ⁷	1.661(4)	1.672(3)		
2-(4-bromo-5-oxofuran-2-ylidene)prop-1-enyl ⁸	1.641(7)	1.652(7)		
1-bromoprop-1-en-2-yl ⁸	1.658(3)			
<i>Z</i> -2-bromovinyl ⁹	1.651(2)			
1-phenyl-1-bromo-2-oxoethyl ¹⁰	1.57(2)	1.66(1)		
4-iodo-1-(4-nitrophenyl)-1H-pyrazol-3-yl ¹¹	1.668(5)			
4-methyl-3-pyridyl ¹²	1.640(2)			
4-(hydroxymethyl)phenyl ¹³	1.667(2)			
1-bromovinyl ¹⁴	1.634(5)			
5-(B{glycol})-2-thienyl ¹⁵	1.658(2)			
2-phenyl-1-benzofuran-3-yl ¹⁶	1.669(2)			
2-(trifluoromethyl)cyclopropyl ¹⁷	1.62(1)	1.65(1)	1.65(1)	1.67(1)
ethynyl	1.635(6)			
ethenyl	1.649(2)			
Ru(H)(C≡CBMIDA)(CO) ₂ (PPh ₃) ₂	1.648(7)	1.65(1)	1.655(6)	1.67(1)
[Ru(=C=CHBMIDA)Cl(dppe) ₂][PF ₆]	1.664(8)			
Ru(C≡CBMIDA)(S ₂ CNEt ₂)(CO)(PPh ₃) ₂	1.665(6)	1.665(7)		
Ru(C≡CBMIDA)(S ₂ CNMe ₂)(CO)(PPh ₃) ₂	1.674(4)			
Ru(CH=CHBMIDA)(S ₂ CNEt ₂)(CO)(PPh ₃) ₂	1.65(1)	1.66(1)	1.68(1)	

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Appendix 2: Tolman Cone Angle ($^{\circ}$), Tolman electronic parameter (ν) and % Buried Volume ($\%V_{\text{Bur}}$)[§] of some tertiary, secondary and primary phosphines.^{1, 2}

Phosphine	cone angle ($^{\circ}$)	ν (cm^{-1})	$\%V_{\text{Bur}}$ (2.00 Å)	$\%V_{\text{Bur}}$ (2.28 Å)
PPh ₃	145	2068.9	34.5	29.6
PCy ₃	170	2056.4	37.1	31.8
P(C ₆ H ₄ Me-2) ₃	194	2066.6	46.7	41.4
P(C ₆ F ₅) ₃	184	2090.9	42.6	37.3
P(C ₆ H ₄ F-4) ₃	145	2071.3	-	-
PMe ₂ Ph	122	2065.3	-	-
PMePh ₂	136	2067.0	-	-
PH ₂ Ph	101	2077.0	-	-
PHPh ₂	128	2073.3	-	-

References

1. C. A. Tolman, *Chemical Reviews*, 1977, **77**, 313-348.
2. H. Clavier and S. P. Nolan, *Chemical Communications*, 2010, **46**, 841-861.

[§] Though the percentage buried volume software, 'SambVca', is available online (<http://www.molnac.unisa.it/OMtools/sambvca.php>), meaningful data could not be obtained from the program, despite using both .XYZ files created in Spartan 14, or .cif files (appropriately modified as per instructions) from actual molecular structures containing the desired phosphine substituent.