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Review

Transition metal boryl and borylene complexes: substitution and abstraction chemistry

Simon Aldridge*, Deborah L. Coombs

Department of Chemistry, Cardiff University, P.O. Box 912, Park Place, Cardiff, Wales CF10 3TB., UK

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Contents

Abstract

In this article, an account is given of recent developments in the chemistry of transition metal complexes of boron. Particular emphasis has been placed on the fundamental reaction chemistry of these systems which leaves the metal–boron bond(s) (M–B) intact. Substitution

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* Corresponding author. Tel.: +44-2920-875495; fax: +44-2920-874030.
E-mail address: aldridges@cardiff.ac.uk (S. Aldridge).

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and abstraction chemistries have been developed in recent years and exploited to give access to a number of novel ligand types. This article summarizes these advances in a previously little investigated area of boryl/borylene chemistry.

Keywords: Boryl; Borylene; Diboran(4)yl; Boron; Transition metal; Substitution; Abstraction; Halide

1. Introduction and scope

Transition metal complexes containing a conventional two-center, two-electron bond to a boron center have received much attention in recent years [1–9]. In part, this reflects a range of powerful and unusual organic transformations in which such complexes have been implicated, notably both stoichiometric and catalytic processes leading to the selective functionalization of alkanes and arenes [10,11], and the hydro- and diboration of carbon–carbon multiple bonds (see, for example [12]). Synthetic efforts have also targeted complexes with novel modes of coordination of the boron ligand, as part of a wider effort to examine in depth the structure and bonding of mixed transition metal/group 13 complexes [13–20].

The breadth of recent studies encompassing synthetic, structural and reaction chemistry of these ligand systems is reflected in the publication of a number of reviews in the period 1998–2003 [3–9]. As such, the scope of this article is not to re-state previously reviewed material, but to focus upon novel aspects of the fundamental chemistry of boryl, borylene and related systems which leads to modification of the ligand while leaving the M–B bond intact. Such chemistry is, in the main, a relatively recent development, and after a brief overview of the field we will concentrate on the boron-centered transformations which have been reported.

2. Overview of transition metal complexes of boron

Since the first crystallographically characterized examples were reported in 1990 [21,22], a number of structural types of transition metal complex featuring a two-center two-electron interaction between a boron atom and a metal center have been reported. These include the borane (type I), boryl (type II), bridging and terminal borylene complexes (types III and IV) shown in Fig. 1, together with the base-stabilized adducts formally derived from boryl and borylene species by coordination of a Lewis base to the two- or three-coordinate boron center.

2.1. Boryl complexes

The first examples of boryl complexes were reported between 1963 and 1970 by Nöth and Schmid, and included compounds such as $(OC)_5MnB(NMe_2)_2$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2BCl_2$ [1]. Much of this work was reviewed in 1970 [1], although none of these compounds were crystallographically characterized and subsequent work has cast doubt on the identity of some of the complexes [23]. Renewed interest was sparked by preliminary reports on metal-catalyzed hydroboration [24], and subsequently the first crystallographically characterized transition metal boryl complexes were reported in 1990 [21,22]. The use of the catecholate (cat, $O_2C_6H_4$-1,2) substituent on boron has greatly facilitated the expansion of this area of study [3]. Bcat-based systems have been employed in more than 50% of structurally authenticated boryl complexes reported in the literature and suitable halide and hydride precursors for the Bcat ligand are commercially available. Recent continued interest in boryl systems is due in no small part to their implication in the functionalization of saturated and unsaturated hydrocarbons [10,11].

The two most commonly used routes for the preparation of transition metal boryl complexes are oxidative addition and salt elimination. The oxidative addition of B–H, B–Cl, B–Br, B–B and even B–Sn bonds to a low-coordinate transition metal center (exemplified by Scheme 1) is the most widely used route to transition metal boryl complexes [2–5,8,25–27]. This route has been exploited for elements of virtually all of the transition metal groups and in the synthesis of mono-, bis- and tris(boryl) derivatives. In general, the transition metal precursor needs to contain ligands that dissociate readily, providing vacant coordination sites that can be utilized in the oxidation step. Rhodium, iridium and platinum complexes are among the most numerous synthesized using this methodology, reflecting at least in part the

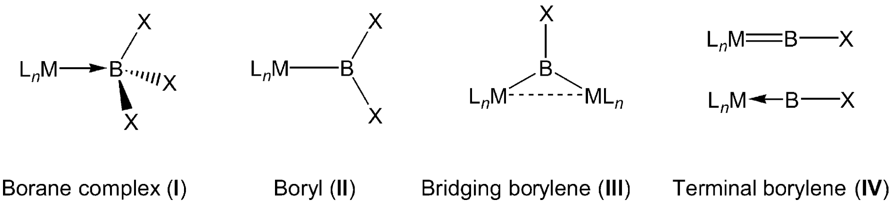
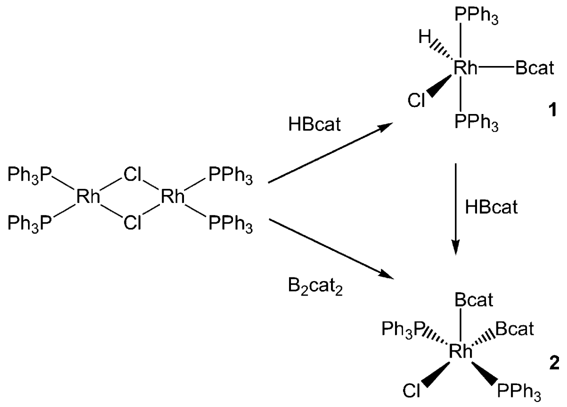


Fig. 1. Structural motifs for transition metal complexes of boron.



Scheme 1.

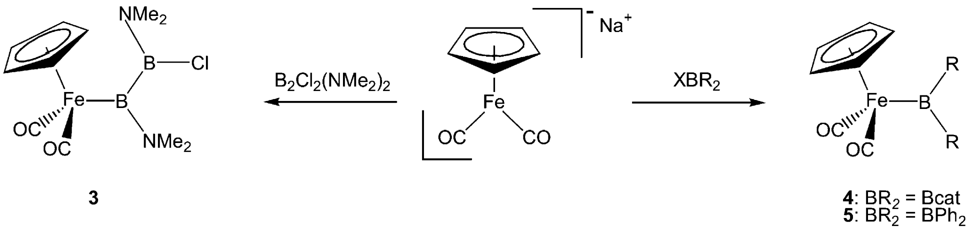
relevance of B–H and B–B oxidative addition processes to Rh(I) and Pt(0) in metal-catalyzed hydro- and diboration reactions [3,12].

The salt elimination reaction between an anionic transition metal fragment and a haloborane precursor is a popular synthetic route to the generation of boryl complexes of the groups 5–8 metals. This approach was successfully used in the preparation of (η^5-C_5H_5)Fe(CO)$_2$Bcat (**4**) and (η^5-C_5H_5)Fe(CO)$_2$BPh$_2$ (**5**) by Hartwig and Huber in 1993 (Scheme 2) [23], and has subsequently been extended to the synthesis of bis(boryl) complexes from dianionic metal fragments [28], and to the synthesis of diboran(4)yl complexes [29–32].

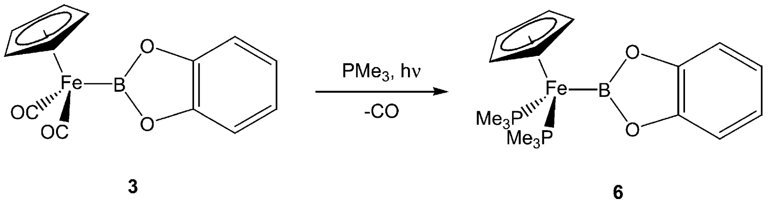
There has been considerable interest in the reactivity of transition metal boryl complexes, in particular due to their implication in a number of catalytic processes leading to the derivatization of hydrocarbons. Thus the scope and mechanism of (i) metal (chiefly rhodium) catalyzed hydroboration of alkenes and related unsaturated species; (ii) platinum catalyzed diboration of alkynes; and (iii) stoichiometric and catalytic selective functionalization of alkanes, alkenes and arenes by boryl complexes of groups 6–9 have been investigated in some depth by a series of studies [10–12]. Such studies have led to a much greater understanding of the fundamental reaction chemistries of boryl complexes which constitute the individual steps making up a catalytic cycle. Hence, these reactions can be conveniently classified as (i) those involving reaction at the metal center; (ii) those involving the M–B bond; and (iii) those involving the boron center [3]. Examples of each type of reactivity are briefly examined below, with reactions at the boron center being examined in depth in Sections 4 and 5.

2.1.1. *Reactions at the metal center*

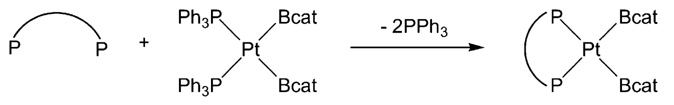
A number of substitution and addition reactions at metal centers bearing boryl ligands have been reported to proceed with retention of the metal–boron (M–B) bond. Replacement of ancillary ligands, for example with phosphines, has been reported in several cases: Hartwig has reported the photolytic substitution of carbonyl ligands in iron and tungsten boryl complexes with PMe$_3$ (Scheme 3) [10b,c] and substitution of the triphenylphosphine ligands in platinum(II) and rhodium(III) bis(boryl) systems has been demonstrated by Norman and co-workers (Scheme 4) [27,33,34]. In addition, five-coordinate ruthenium and osmium Bcat complexes have been shown to bind a variety of Lewis bases *trans* to the boryl ligand thereby yielding coordinatively saturated products (Scheme 5) [3,35]. In the ruthenium systems, substitution is followed by rearrangement of the resulting complex. Furthermore, abstraction of metal-bound ligands by silver salt metathesis has also been shown by Roper and co-workers to be possible without rupture of the metal boron bond. The reaction of Os(Bcat)Cl(CO)(PPh$_3$)$_2$ (**11**) with Ag[SbF$_6$] in the presence of acetonitrile yields the cationic boryl complex [Os(Bcat)(CO)(NCMe)$_2$(PPh$_3$)$_2$]$^+$[SbF$_6$]$^-$ (**14**), which reacts further with CO or *p*-tolylisocyanide



Scheme 2.



Scheme 3.



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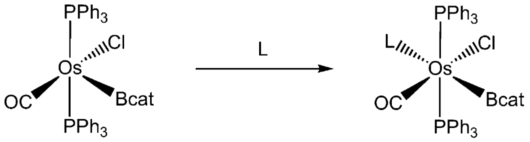
8: P-P = dppe, $Ph_2P(CH_2)_2PPh_2$
9: P-P = dppb, $Ph_2P(CH_2)_4PPh_2$
10: P-P = dcpe, $Cy_2P(CH_2)_2Cy_2$

Scheme 4.



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12: L = CO
13: L = CN-*p*-tolyl

Scheme 5.

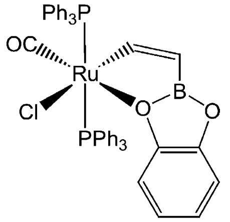

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Fig. 2. Product derived from the insertion of acetylene into the Ru–B bond of $RuCl(CO)(PPh_3)_2Bcat$.

to form $[Os(Bcat)(CO)(NCMe)L(PPh_3)_2]^+[SbF_6]^-$ (**15**: L = CO; **16**: CN-*p*-tolyl) [35].

2.1.2. Reactions at the M–B bond

Although the metal boron bond strength in boryl complexes has been shown in a number of studies to exceed that of M–C bonds in analogous metal alkyl complexes [36], the kinetic lability of the M–B linkage is such that a wide variety of reactions proceed with cleavage of this bond. Reactions with protic reagents HY (Y: OH, OR, NHR, Cl) proceed in the main via M–B breakage with concomitant generation of the borane X_2BY [3]. A number of reactions with non-polar reagents (e.g. H_2, Br_2) have also been shown to lead to rupture of the M–B bond [3].

Insertion reactions of alkenes and alkynes have been investigated in a number of cases, owing to their relevance to hydro- and diboration catalysis. In particular, insertion of an alkyne into the Ru–B bond of $RuCl(CO)(PPh_3)_2Bcat$ to give the structurally characterized complex **17** (Fig. 2) is of clear significance to the mechanism of metal-catalyzed hydro- and diboration reactions [37]. For group 10 systems, a similar compound derived from insertion of an alkyne into a Pd–B bond has been reported, although corresponding platinum species (which are proposed intermediates in Pt-catalyzed alkyne diboration) have yet to be isolated [38]. Intriguingly, the reactions of alkynes with $IrCl(H)(PMe_3)_2Bcat$ result in insertion into the Ir–H rather than the Ir–B bond [21].

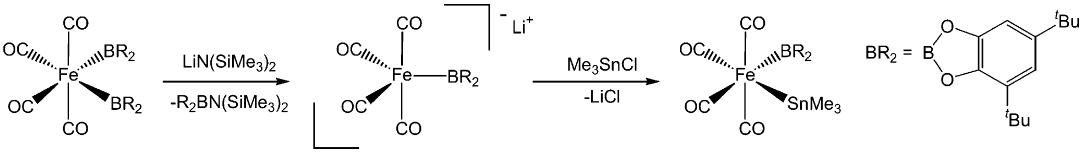
Exchange reactions leading to the overall substitution of a boryl ligand by another electrophilic component have been reported to occur via a number of mechanisms. Thus, abstraction of a boryl fragment from the bis(boryl) complexes $(OC)_4Fe(BR_2)_2$ (**18**—R_2: cat; **19**—R_2: 1,2-O_2-4-^{t}BuC_6H_3; **20**—R_2: 1,2-O_2-3,5-^{t}Bu$_2C_6H_3$) yielded the first examples of anionic boryl complexes $Li^+[(OC)_4Fe(BR_2)]^-$ (Scheme 6). Further reaction of $Li^+[(OC)_4FeB(1,2\text{-}O_2\text{-}3,5\text{-}{}^tBu_2C_6H_3)]$ (**21**) with Me_3SnCl yielded the *cis* stannyl-substituted complex $(OC)_4Fe(SnMe_3)[B(1,2\text{-}O_2\text{-}3,5\text{-}{}^tBu_2C_6H_3)]$ (**22**) [28]. On the other hand, the statistical redistribution of boryl components which occurs in the reaction of $RhCl(PPh_3)_2(Bcat)_2$ (**2**) with tetrakis(aryloxy)diboron(4) reagents, $(RO)_4B_2$, is thought to occur via a σ bond metathesis process [39]. Pairwise exchange of boryl ligands by a combination of oxidative addition and reductive elimination steps has also been observed [26,33].

2.1.3. Reactions at the boron center

Recent review articles have commented on the scarcity of authenticated reactions occurring at the boron center of an existing boryl complex with retention of the metal boron bond [3,8,9]. Such reactivity is the primary subject of this review and is dealt with at length in Sections 4 and 5.

2.2. Borylene complexes

Transition metal complexes featuring the borylene ligand, BX, can adopt one of two possible geometries:



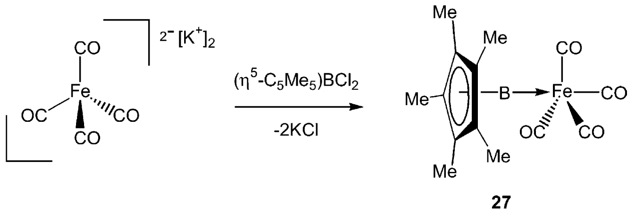
20 **21** **22**

Scheme 6.

(i) terminally bound, with the boron center adopting a coordination number of two (type IV); or (ii) bridging between two metal fragments with a coordination number of three (type III). Base-stabilized variants containing a three- or four-coordinate boron center, respectively, have also been reported [7–9]. In comparison to boryl complexes, borylenes are very rare; both bridging and terminal borylene complexes have only been realized very recently (in 1995 and 1998, respectively) [13,14,40].

Borylene complexes have been the subject of a number of computational studies [41–48]. In particular, it has been shown that complexes with transition metals should have high thermodynamic stability due to the good σ donor and π acceptor properties of the BX ligand. However, low kinetic stability has been predicted for uncoordinated borylene ligands due to high polarity and a small HOMO–LUMO gap. Complexation was found to increase the HOMO–LUMO gap, but an imbalance between σ donation and π acceptance for coordinated borylene fragments leads to a build up of positive charge at boron. Possible strategies for enhancing the stability of borylene complexes therefore include (i) steric shielding, for example using bulky substituents at the boron center [13,17]; (ii) electronic stabilization, for example by complexation to a good π donor binuclear metal fragment (such as $Fe_2(CO)_8$ or $(\eta^5\text{-}C_5H_5)_2Mn_2(CO)_4$) or by incorporation of a strongly π donor X substituent (e.g. NR_2) [14,40]; or (iii) coordination of a Lewis base to the boron center [18,49]. Representative examples are included in Fig. 3.

The synthetic realization of bridging (type III) and terminal borylene complexes (type IV) has been achieved through a number of approaches. Bridged systems [7–9] have been synthesized from dihaloboranes and organometallic anions [50–53], by photochemical borylene transfer from an existing (type IV) complex [16], or from diboranes(4) by B–B bond scission [29,40,54,55]. Terminally bound species were initially reported from the salt elimination reaction between an organometallic dianion and a dihaloborane (Scheme 7) [13,14,17], although subsequent studies have revealed other possible methodologies including photolytic borylene transfer (Scheme 8) [16,19], and modification of an existing boron-containing ligand (Sections 4 and 5) [15,18,20].



Scheme 7.

In contrast to similar boryl systems, the fundamental chemistry of both bridging and terminal borylene systems remains a little investigated area of research. Ligand modification reactions of manganese and osmium borylenes have been reported, and are examined in depth in Section 4. In addition, it has been shown that bulky aminoborylene complexes of tungsten and chromium can act as photolytic transfer agents for the $BN(SiMe_3)_2$ ligand in the generation of novel terminal and bridged borylene complexes (Scheme 8) [16,19].

In general, ligand modification reactions which occur at the boron center of an existing boryl or borylene complex with retention of the metal boron bond remain relatively few in number. Clearly, the kinetic lability of the M–B bond in most cases precludes significant chemical modification at the peripheral boron-bound substituents without rupture of the

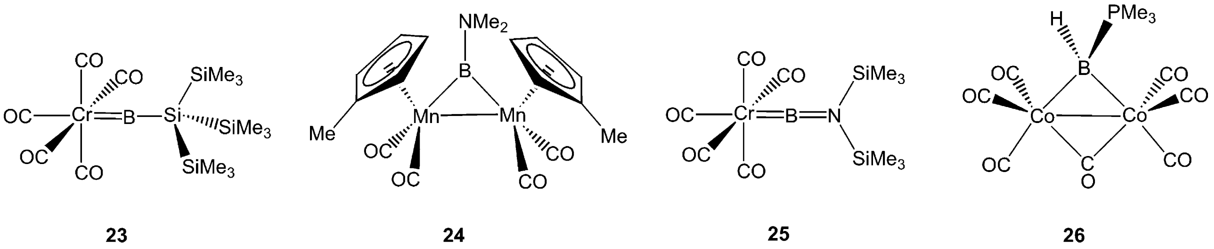
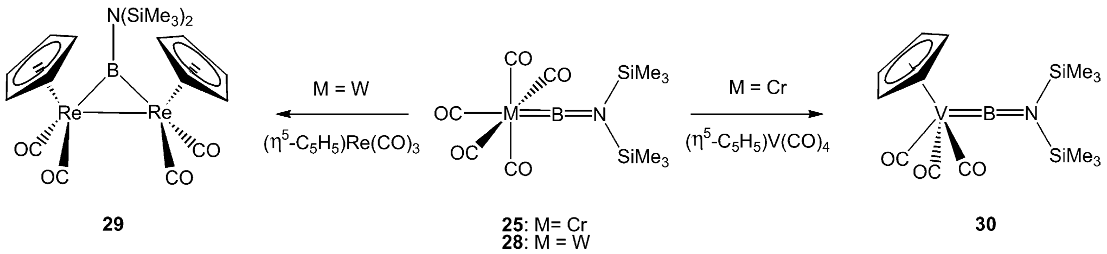


Fig. 3. Representative examples of bridging and terminal borylene complexes.



Scheme 8.

M–B linkage. For such chemistry to be accomplished with retention of this bond requires the use of relatively labile, poorly π donating substituents, X. In the main therefore, such chemistry is confined to haloboryl and borylene complexes (chiefly chlorides and bromides) and a brief summary of their synthetic and structural aspects is given (Section 3) before considering recently reported derivatization chemistry (Sections 4 and 5).

3. Haloboryl, halodiboran(4)yl and haloborylene complexes

3.1. Historical overview

The very lability of boron–halogen linkages which makes haloboryl, diboran(4)yl and borylene complexes attractive substrates for further boron-centered functionalization chemistry is itself a factor in the relatively small number of fully characterized halogenated derivatives reported to date. A number of haloboryl and borylene complexes were reported in the early boryl literature in the 1960s and 1970s, including $(Ph_3P)(OC)_4MnBCl_2$, $[(Ph_3P)(OC)_4Mn]_2BCl$, $(Ph_3P)(OC)_4MnBCl(NMe_2)$, $[(OC)_4FeBBr]_n$, $(dppe)_2CoBCl(Ph)$ (dppe: 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$), L_4CoBCl_2 (L_4: $(CO)_4$, $(CO)_3(PPh_3)$, $(CO)_3(AsPh_3)$), $(dppe)_2Co(BX_2)_2$ (X: Br, I), $(Ph_3P)_3RhBBr_2$, $L_2P^tBr(BBr_2)$ (L_2: $(PPh_3)_2$, dppe) and $(triars)MBBr_2$ (M: Cu, Ag; triars: $MeAs(C_6H_4AsMe_2\text{-}2)_2$) [1,56–58]. However, as has been discussed in a number of recent review articles [2–9], considerable doubt has been cast on the actual nature of many of these complexes (none of which was structurally authenticated) and some caution must be exercised in analysis of their spectroscopic data. Crystallographically characterized monohaloboryl complexes were unknown until 1993 [59] and analogous dihaloboryl derivatives first structurally characterized in 1998 [60].

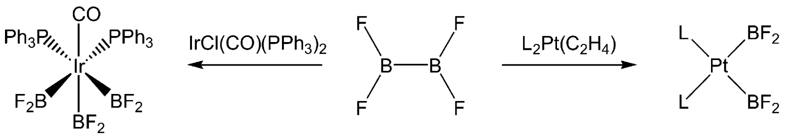
3.2. Synthetic approaches

The main synthetic approaches applied to the generation of boryl [$L_nM\text{–}BX_2$ and $L_nM\text{–}BX(R)$], diboran(4)yl [$L_nM\text{–}B(R)\text{–}BX(R)$] and haloborylene complexes [$(L_nM)_2BX$] bearing halogenated substituents involve either (i) the oxidative addition of B–E bonds (E: B, H, halogen) to low valent mainly late transition metal centers, or (ii) the salt elimination reaction between an appropriately substituted borane halide and an anionic organometallic reagent. In this respect these synthetic routes mirror those applied to boryl complexes in general [3,8]. In the case of halogenated boron ligands, however, an additional synthetic approach has proved successful, namely the modification of an existing boryl or borylene complex (Section 3.2.3). Although more limited in its application, both substitution and addition reactions at the boron center of an existing boryl or borylene have been applied to a number of syntheses.

3.2.1. Oxidative addition

Oxidative addition of B–X bonds (X: H, B, Cl, Br, Sn) to low valent, low-coordinate transition metal fragments, typically created by the loss of a labile ligand, has been applied widely in the synthesis of transition metal boryl systems. Similar methodology has been applied in the synthesis of the only crystallographically characterized dihaloboryl complexes, $(Ph_3P)_2Pt(BF_2)_2$ (**31**), $(dppb)Pt(BF_2)_2$ (**32**) (dppb: 1,4-bis(diphenylphosphino)butane, $Ph_2P(CH_2)_4PPh_2$) and $Ir(CO)(PPh_3)_2(BF_2)_3$ (**33**) [60]. In each case oxidative addition of the B–B bond in B_2F_4 is presumed to be a key step in the reaction, being preceded in the case of platinum complexes **31** and **32** by the loss of the ethylene ligand from $(Ph_3P)_2Pt(C_2H_4)$ (Scheme 9). In the case of iridium tris(boryl) complex **33** subsequent σ bond metathesis or reductive elimination/oxidative addition steps are then proposed to account for the observed reaction stoichiometry. Oxidative addition of B–B bonds can also be used to give access to chloroboryl complexes. Thus, for example, reaction of $(Ph_3P)_2Pt(C_2H_4)$ with $B_2Cl_2(NMe_2)_2$ yields the bis(aminochloroboryl) complex *cis*-$(Ph_3P)_2Pt[BCl(NMe_2)]_2$ (**34**), albeit contaminated with *trans*-$(Ph_3P)_2PtCl[BCl(NMe_2)]$ (**35**), the latter compound being shown to be the product of an undetermined rearrangement reaction of **34** [34].

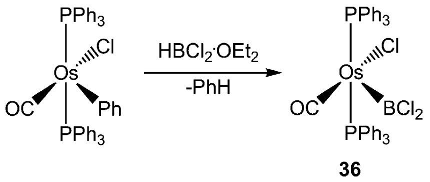
The five-coordinate osmium dichloroboryl complex $OsCl(CO)(PPh_3)_2(BCl_2)$ (**36**) has been synthesized by Roper, Wright and co-workers by the treatment of $Os(Ph)Cl(CO)(PPh_3)_2$ with $HBCl_2{\cdot}OEt_2$ (Scheme 10) [15,61]. Benzene is eliminated in the course of the reaction, and this methodology mirrors that used by the same authors in the synthesis of a range of ruthenium and osmium boryl species containing catecholate and related substituents [3,35,37,61]. Although no structural data has been reported



33

31: L_2 = $(Ph_3P)_2$
32: L_2 = dppb

Scheme 9.



Scheme 10.

for **36**, this compound is unique in being a well characterized dichloroboryl complex with a widely explored boron-centered substitution chemistry. Complex **36** proves to be a versatile source for a variety of osmium boryl and base-stabilized borylene species (see Section 4.3).

Finally, recent work on the synthetic utility of $MesBBr_2$ has demonstrated, that at least in one instance it is possible to synthesize a haloboryl complex by oxidative addition of a boron–halogen bond. Selective reaction of one of the B–Br bonds in $MesBBr_2$ with $(Ph_3P)_2Pt(C_2H_4)$ generates the very moisture sensitive complex *trans*-$(Ph_3P)_2PtBr[BBr(Mes)]$ (**37**) which has been characterized spectroscopically [62].

3.2.2. Salt elimination

A wide range of boryl complexes and a somewhat more limited number of bridging and terminal borylenes have been synthesized by the reaction of an organometallic mono- or dianion with a suitable borane halide (Eqs. (1)–(3)) [1–9].

$$L_nM^- + R_2BX \rightarrow L_nMBR_2 + X^- \quad (1)$$

$$2L_nM^- + RBX_2 \rightarrow (L_nM)_2BR + 2X^- \quad (2)$$

$$L_nM^{2-} + RBX_2 \rightarrow L_nMBR + 2X^- \quad (3)$$

In a number of cases, this methodology has been shown to be appropriate to the synthesis of haloboryl complexes, primarily by the selective replacement of a single halide of a borane trihalide, BX_3, or dihalide, $(R_nE)BX_2$, by an organometallic fragment (Eqs. (4) and (5)). In addition the displacement of two equivalents of halide to give a bridging haloborylene complex (Eq. (6)) has been reported in at least one instance.

$$L_nM^- + BX_3 \rightarrow L_nMBX_2 + X^- \quad (4)$$

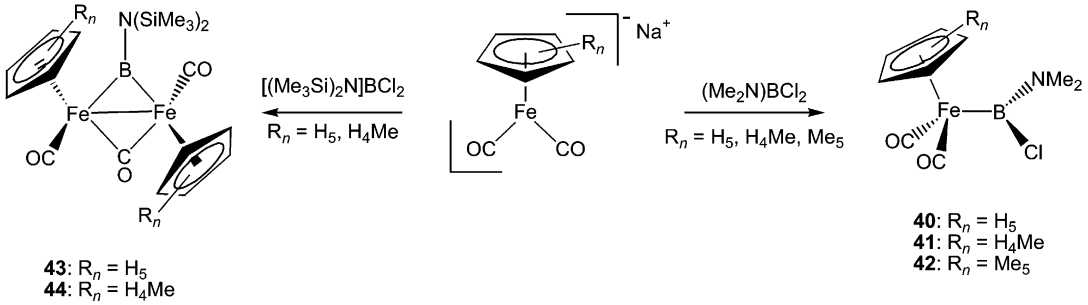
$$L_nM^- + (R_nE)BX_2 \rightarrow L_nMBX(ER_n) + X^- \quad (5)$$

$$2L_nM^- + BX_3 \rightarrow (L_nM)_2BX + 2X^- \quad (6)$$

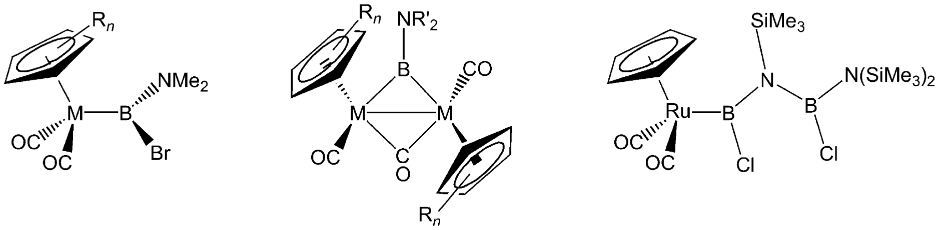
In practice, only a very limited number of dihaloboryl species have been synthesized via reaction (4), and none of these has been structurally characterized. Bergman and co-workers have reported the synthesis of the difluoroboryl complex $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)H(BF_2)$ (**38**) by the reaction of the strongly basic lithium iridiate $Li[(\eta^5\text{-}C_5Me_5)Ir(PMe_3)H]$ with $BF_3{\cdot}OEt_2$ [63]. In addition $(\eta^5\text{-}C_5H_5)Fe(CO)_2BCl_2$ (**39**) has been reported from the reaction of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ with BCl_3, and characterized both spectroscopically and by its reaction with dilithiocatechol to generate the known catecholboryl derivative **4** [23,64]. Reports of the synthesis of asymmetric haloboryl derivatives by salt elimination (reaction (5)) are somewhat more widespread, encompassing a range of amino, silyl and aryl substituents (ER_n: NR_2, SiR_3, aryl). A key point in this synthetic method is establishing, through electronic or steric factors, control of the substitution reaction, such that only one of the two available halides is displaced [50–53,65].

Braunschweig et al. have examined in depth the reaction between cyclopentadienyliron and ruthenium reagents and aminodihaloboranes. In the case of the aminodichloroboranes $(R_2N)BCl_2$ (R: Me or $SiMe_3$), the course of the reaction appears to be driven predominantly by electronic rather than steric factors (Scheme 11) [51]. Hence, with R: Me replacement of one (and only one) of the boron–bound chlorines by cyclopentadienyliron dicarbonyl fragments is possible (yielding **40–42**), with further exchange of the remaining chloride proving impossible. Conversely, the reaction with an aminodichloroborane bearing the more bulky, but poorer π donating $(Me_3Si)_2N$ group results in a single boron containing product with no unreacted B–Cl bonds, irrespective of the ratio of reagents. The aminoborylenes so formed by reaction with cyclopentadienyl- and methylcyclopentadienyliron reagents (**43** and **44**) represented the first bridging borylene complexes of iron [51].

Selectivity in these types of reaction has also been shown to be dependent on the nature of the boron–halogen bond and of the incoming organometallic nucleophile. Hence, the corresponding reactions with the more reactive electrophile $(Me_2N)BBr_2$ are less selective. Cyclopentadienyl or methylcyclopentadienyliron regents yield 1:1 mixtures of the bromoboryl complex (**45** or **46**, Fig. 4) and the bridging dimethylaminoborylene (**49** or **50**). Only in the case of the more sterically demanding pentamethylcyclopentadienyl



Scheme 11.



45: M = Fe, R_n = H_5
46: M = Fe, R_n = H_4Me
47: M = Fe, R_n = Me_5
48: M = Ru, R_n = H_5

49: R' = Me, M = Fe, R_n = H_5
50: R' = Me, M = Fe, R_n = H_4Me
51: R' = $SiMe_3$, M = Ru, R_n = H_5

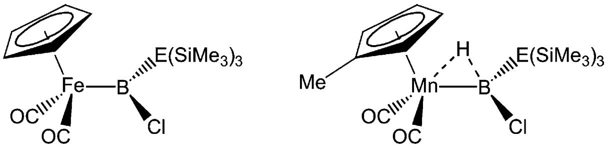
52

Fig. 4. Products isolated from the reactions of iron and ruthenium nucleophiles with aminodihaloboranes.

reagent is the reaction selective for substitution of a single bromide, yielding exclusively the bromoboryl complex **47** [50].

The analogous reactions of $(Me_2N)BX_2$ (X: Cl or Br) with $Na[(\eta^5\text{-}C_5H_5)Ru(CO)_2]$ involve selective replacement of one halide by the organometallic fragment, consistent with the reportedly lower nucleophilicity of the ruthenium reagent compared to its iron counter-part. Bromoboryl complex **48** and its chloro-substituted analogue **53** are the products isolated. Additionally, the reaction of $Na[(\eta^5\text{-}C_5H_5)Ru(CO)_2]$ with $[(Me_3Si)_2N]BCl_2$ has been reported to display selectivity dependent on the stoichiometry employed. An excess of $[(Me_3Si)_2N]BCl_2$ yields the unusual complex **52**, involving condensation of two borane units and elimination of Me_3SiCl; excess of the ruthenium reagent leads to substitution of both B–Cl bonds and the formation of borylene **51** [50].

The sterically encumbered silyl and germylboranes R_nEBCl_2 [ER_n: $Si(SiMe_3)_3$, $Ge(SiMe_3)_3$, $Si(SiMe_2)_2\text{-}Si(SiMe_3)_3$ or $SiPh_3$] prove to be useful substrates for the selective formation of chloroboryl complexes of the type $L_nM\text{–}BCl(ER_n)$ [65]. Hence, reaction of the appropriate borane with $Na[(\eta^5\text{-}C_5R_4R')Fe(CO)_2]$ (R = R′ = H, R = R′ = Me or R: H, R′: Me) or with $K[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2H]$ proceeds via substitution of a single chloride, with a number of the resulting boryl complexes having been structurally characterized (**54**–**56**, Fig. 5). Steric factors are clearly important in the isolation of mono-substituted products from these reactions; indeed in one case, namely the attempted reaction of the extremely bulky $Cl_2BSi(SiMe_2)_2Si(SiMe_3)_3$ with $K[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2H]$, such factors were sufficient as to prevent any reaction at all [65].



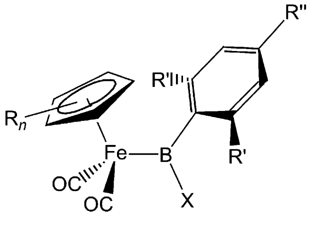
54: E = Si
55: E = Ge

56: E = Si
57: E = Ge

Fig. 5. Iron and manganese complexes containing extremely bulky chloroboryl ligands.

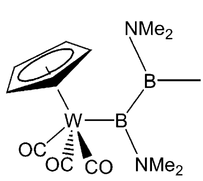
Steric bulk appears also to play a significant role in the selective reactivity observed between nucleophilic organometallic reagents and aryldihaloboranes. Reaction between mesityldibromoborane and a single equivalent of $Na[(\eta^5\text{-}C_5R_4R')Fe(CO)_2]$ (R = R′ = H, R = R′ = Me or R = H, R′ = Me) or $Na[Mn(CO)_5]$ exclusively yields the corresponding mesityl(bromo)boryl complexes. These include iron complexes **58**–**60** (Fig. 6) which represent the only structurally characterized bromoboryl species [52,53]. By employing the sterically demanding pentamethylcyclopentadienyl reagent $Na[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]$ similar selectivity can be observed with phenyldichloroborane, thereby yielding $(\eta^5\text{-}C_5Me_5)Fe(CO)_2BCl(Ph)$ (**62**) [66]. With the exception of the extremely sterically shielded derivative **61** (which is synthesized in an analogous manner) all of these asymmetric aryl(halo)boryl complexes prove to be useful substrates for further substitution chemistry [52,53,66,67]. These tractable but reactive systems offer a series of new routes to novel boron ligand systems (see Sections 4 and 5) [20,52,53].

In addition to haloboryl complexes, it is worth noting that a number of diboran(4)yl complexes containing halide substituents, $L_nM\text{–}B(R)\text{–}BX(R)$, have been synthesized by salt elimination from the corresponding diborane(4), $1,2\text{-}R_2X_2B_2$, and an organometallic nucleophile. These



58: R_n = H_5, R' = R'' = Me, X = Br
59: R_n = H_4Me, R' = R'' = Me, X = Br
60: R_n = Me_5, R' = R'' = Me, X = Br
61: R_n = H_5, R' = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, R'' = H, X = Br
62: R_n = Me_5, R' = R'' = H, X = Cl

Fig. 6. Asymmetric iron aryl(halo)boryl complexes synthesized from the corresponding aryldihaloboranes.



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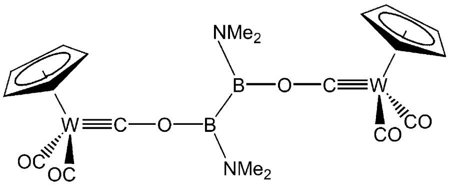

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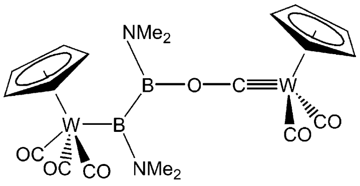

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Fig. 7. Diboran(4)yl and boryloxycarbyne complexes derived from the reaction of K[(η^5-C_5H_5)W(CO)$_3$] with 1,2-(Me_2N)$_2I_2B_2$.

include the chloro-substituted species (η^5-C_5H_5)W(CO)$_3$ B(NMe_2)B(NMe_2)Cl (**63**) and (η^5-C_5H_5)Fe(CO)$_2$B(NR_2) B(NR_2)Cl (**3**—NR_2: NMe_2; **64**—NR_2: NC_4H_8; **65**—NR_2: NC_5H_{10}), and the bromo-substituted complexes (η^5-C_5H_5) Mo(CO)$_3$B(NMe_2)B(NMe_2)Br (**66**) and (η^5-C_5H_5)Ru(CO)$_2$ B(NMe_2)B(NMe_2)Br (**67**) [8,29–31], synthesized in each case by the reaction of 1,2-(R_2N)$_2X_2B_2$ (X: Cl, Br) with a single equivalent of the appropriate organometallic anion. The corresponding reactions with the iodo-diborane(4) reagent 1,2-(Me_2N)$_2I_2B_2$ are illustrative of one of the complications implicit in the salt elimination methodology, namely the existence of alternative sites of nucleophilicity within anionic organometallic reagents. Depending on conditions, the reactions of 1,2-(Me_2N)$_2I_2B_2$ with K[(η^5-C_5H_5)M(CO)$_3$] (M: Mo, W) result in the formation of diboran(4)yl complexes (such as **68**), boryloxycarbyne complexes (such as **69**) or mixed species (such as **70**) (Fig. 7) [32]. Similar oxygen-centered reactivity has also been observed for nickel and triiron anionic nucleophiles [68]; in addition reaction at the cyclopentadienyl ligand has been observed for anionic reagents of both tungsten and iron [69]. Reaction of Na[(η^5-C_5H_4Me)Fe(CO)$_2$] with BCl_3, for example, generates as a minor product the zwitterion [η^5-1,3-C_5H_3Me(BCl_3)]Fe(CO)$_3$ (**71**) [69].

Finally, two further applications of this synthetic methodology are deserving of note. The structurally characterized dimanganese chloroborylene complex [(OC)$_5$Mn]$_2$BCl (**72**) is reported in [4], and although precise details of the synthesis were not given, a salt elimination reaction utilizing Na[Mn(CO)$_5$] (i.e. reaction (6)) is described [4]. Braunschweig has also demonstrated control of the salt elimination reaction in borazine systems by selectively generating the iron complexes [(η^5-C_5H_5)Fe(CO)$_2$]$_n$$B_3N_3H_3Cl_{3-n}$ (**73**–**75**: $n = 1$–3) [70].

3.2.3. Modification of an existing boryl or borylene complex

3.2.3.1. Substitution chemistry. Extensive ligand modification reactions have been reported by Roper and co-workers starting from the dichloroboryl complex OsCl(CO)(PPh_3)$_2$(BCl_2) (**36**) (see also Section 4.3). In a number of cases, this chemistry leads to the synthesis of further haloboryl or haloborylene derivatives [18,71]. The reaction of **36** with 2-hydroxypyridine, for example, leads to substitution of one of the two boron-bound chlorines by the oxygen donor with the pendant pyridyl function completing a five-membered chelate ring through coordination at the osmium center. The compound so formed (**76**) therefore possesses a type V structure (Fig. 8, E: O, $n = 0$) which is sufficiently robust to survive intact substitution reactions at both boron and osmium centers. The corresponding complexes formed by selective replacement of the osmium-bound chloride by iodide (**77**), or of the boron-bound chloride by fluoride (**78**) have also been reported [71].

The analogous reaction of **36** with 2-aminopyridine leads to a mixture of type V and type VI products (E: N, R: H, $n = 1$), and although the chloroborylene (type VI) product (**79**) was not isolated it was trapped by further reaction with ethanol, leading to selective conversion of the B–Cl bond to B-OEt [18]. The chloroboryl (type V) product (**80**) undergoes a variety of further substitution reactions, including selective replacement of the osmium-bound chloride with hydride or bromide yielding crystallographically characterized **81** and **82**, repectively. Interestingly, the corresponding reaction of **36** with 2-(methylamino)pyridine leads exclusively to the type VI product **83** (E: N, R: Me, $n = 1$), from which further derivatives (including the corresponding osmium hydride, **84**) can be formed [18].

Exchange of a boron-bound chloride substituent for fluoride has also been demonstrated as a viable synthetic method for iron complexes in at least one instance, although the generality of this method for half sandwich complexes appears to be limited. Reaction of (η^5-C_5H_5)Fe(CO)$_2$ BCl[Si($SiMe_3$)$_3$] (**54**) with excess thallium(I) fluoride in dichloromethane generates (η^5-C_5H_5)Fe(CO)$_2$ BF[Si($SiMe_3$)$_3$] (**85**) in ca. 50% yield, but the analogous reactions with (η^5-C_5H_5)Fe(CO)$_2$BCl[Ge($SiMe_3$)$_3$] (**55**), (η^5-C_5H_4Me)Mn(CO)$_2$(H)BCl[Si($SiMe_3$)$_3$] (**56**) or

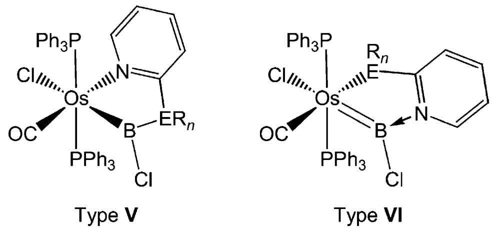


Fig. 8. Types of complex derived from the reaction of OsCl(CO)(PPh_3)$_2BCl_2$ (**36**) with 2-amino- and 2-hydroxy-pyridines.

(η^5-C_5Me_5)$Fe(CO)_2BBr(Mes)$ (**60**), or of **60** with $Ag[BF_4]$ do not yield the corresponding fluoroboryl complexes [62,65].

Boron-centered substitution chemistry has also been demonstrated in the synthesis of bridging haloborylene complexes. Thus the bridged dimanganese dimethylaminoborylene complex **24**, although generally unreactive towards nucleophiles (such as water), is converted in good yield to the corresponding chloroborylene complex **86** by reaction with HCl (Scheme 12). Presumably, given the greater stability of amino-boron linkages over boron-chlorine bonds, the thermodynamic impetus for this reaction is provided by the generation of the salt $[Me_2NH_2]Cl$ [40,54,55]. Compound **86** proves to be a useful substrate for further boron-centered substitution chemistry (see section 4.2) and for the photolytic generation of the novel metallaborane $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2]_2B_2Cl_2$ (**87**), a reaction postulated to proceed via the terminal chloroborylene intermediate $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(BCl)]$ [72].

3.2.3.2. Addition chemistry. Although the reaction chemistry of two-coordinate borylene complexes remains a little investigated area [9], recent computational and synthetic studies have revealed that nucleophilic attack at the boron center is one of the dominant features of such reactivity [41,62]. Thus, for example, addition of halide at the borylene center in $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BMes)]^+[BAr^f_4]^-$ (**88**) gives access to a number of haloboryl derivatives which are inaccessible by more conventional substitution approaches. Hence the attempted substitution reaction of (η^5-C_5Me_5)$Fe(CO)_2BBr(Mes)$ (**60**) with $Ag[BF_4]$ or TlF leads to decomposition rather than the desired fluoroboryl complex (η^5-C_5Me_5)$Fe(CO)_2BF(Mes)$ (**89**). This complex and its chloro and iodo counterparts (**90** and **91**) can, however, be synthesized in good yields by nucleophilic addition to the isolated cationic borylene **88** (Scheme 13) [20,62].

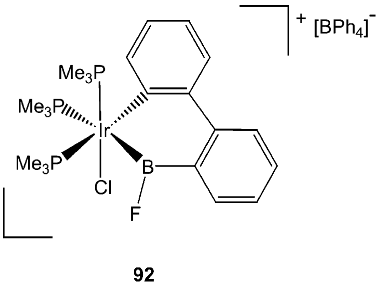


Fig. 9. The unusual Ir(IV) boryl resulting from the reaction of $Ir(PMe_3)_3Cl(C_{12}H_8)$ with $[NO]^+[BF_4]^-$.

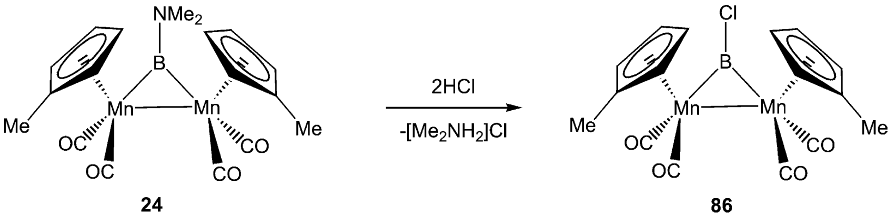
3.2.4. Miscellaneous methods

Crabtree and co-workers have reported the synthesis and structural characterization of the iridium(IV) boryl complex $[Ir(PMe_3)_3Cl(C_{12}H_8BF)]^+[BPh_4]^-$ (**92**, Fig. 9) from the reaction of the biphenyl derivative $Ir(PMe_3)_3Cl(C_{12}H_8)$ with $[NO]^+[BF_4]^-$. The iridium boryl linkage is effectively derived from the insertion of ‘BF’ into one of the Ir–C bonds [59].

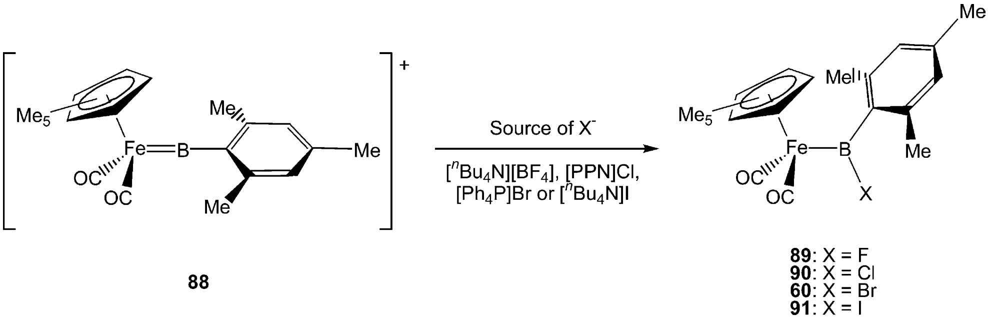
3.3. Spectroscopic and structural features

3.3.1. Bonding in boryl complexes

A simplified bonding model for transition metal complexes bearing three-coordinate boryl ligands (L_nM–BX_2) involves the sp^2 hybridized boron center forming σ bonds with an empty metal-based orbital of σ symmetry and with the boryl substituents X (Fig. 10). In addition to this



Scheme 12.



Scheme 13.

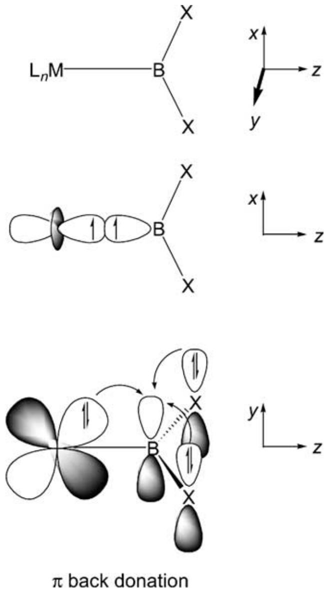


Fig. 10. Basic description of the bonding in transition metal boryl complexes: a ‘competitive π bonding’ model.

there is the possibility of π donation from a metal based frontier orbital of the appropriate symmetry or from a filled non-bonding orbital on the substituents (X) into the empty boron p orbital (Fig. 10). This so-called ‘competitive π-bonding model’ is analogous to that proposed for Fischer carbene complexes [71,73], and the extent of the σ and π contributions to M–B bonding has been the subject of several theoretical studies [45,74,75]. Within this area, dihaloboryl complexes of osmium and iron have been the subject of Density Functional studies [74,75], with an analysis of the σ and π contributions to the Fe–B bond for the complexes $(\eta^5\text{-}C_5H_5)FeL_2BX_2$ (L: CO, PMe_3; X: H, F, Cl), for example, being fully consistent with the competitive π bonding model. Thus the π component of the covalent interaction between the iron and boron centers was found to be minimized by strongly π donating fluoro substituents at boron, although even in the case of weaker π donors such as H or C_6F_5 this component never exceeded 20% [75,76]. Hence, although modification of the boryl substituents X can exert some influence on the extent of metal to boron π bonding, in general the boron-based acceptor orbital is calculated to lie too high in energy with respect to the corresponding filled metal orbital for π back-bonding to be dominant [75].

As has been mentioned above, borylene ligands have also been the subject of a number of computational studies. Among these, several have examined the bonding characteristics of BF as a ligand both to neutral and cationic transition metal centers [41–43,45,46,77,78]. In general BF has been found to be both a superior σ donor and π acceptor to the isoelectronic CO ligand, although the build up of positive charge at boron on coordination implies a marked kinetic lability for such complexes [41–43,45,46].

3.3.2. Spectroscopic features

3.3.2.1. NMR spectroscopy. ^{11}B NMR spectroscopy is a widely used probe for monitoring the formation of metal boryl complexes from borane precursors, there typically being a marked shift to lower field on formation of the metal–boron bond [3,8]. Three-coordinate haloboryl complexes display a wide range of ^{11}B NMR chemical shifts, spanning 23.9 for $(\eta^5\text{-}C_5Me_5)IrH(BF_2)(PMe_3)$ (**38**) [63] to 141.2 for $(\eta^5\text{-}C_5H_5)Fe(CO)_2BCl[Si(SiMe_3)_3]$ (**54**) [65]. In general, for a given metal fragment, the ^{11}B shift reflects the degree of shielding of the boron center afforded by the π donor capabilities of the substituents X [3]. Hence the measured shifts for **54**, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2BCl(Mes)$ (**90**) and $(\eta^5\text{-}C_5Me_5)Fe(CO)_2BCl(NMe_2)$ (**42**) are 141.2, 112.1 and 59.1 ppm, respectively, while the fluoride-substituted analogue of **54** (**85**) displays a signal at 113.2 ppm [51,62,65]. Considering the series of mesityl(halo)boryl complexes $(\eta^5\text{-}C_5Me_5)Fe(CO)_2BX(Mes)$ (X: I, Br, Cl, F) (Table 1) it is clear that the greatest difference in chemical shift is between fluoro-substituted **89** and chloro-substituted **90**, with the three heavier congeners giving rise to complexes with very similar chemical shifts [53,62]. Such behavior is entirely consistent with the known π donor properties of the halide substituents.

Hence the effects of substituents X on the ^{11}B NMR shift of a boryl complex may well be regarded as quantifiable (or even roughly additive) to some degree ($(\eta^5\text{-}C_5H_5)Fe(CO)_2BPh_2$ (**5**) 121.0; $(\eta^5\text{-}C_5Me_5)Fe(CO)_2BCl(Ph)$ (**62**) 111.0; $(\eta^5\text{-}C_5H_5)Fe(CO)_2BCl_2$ (**39**) 90.7) [23,64,66]. The effects of the metal fragment, although pronounced in some cases (e.g. δ_B 23.9 for **38**; 42.3 for $(Ph_3P)_2Pt(BF_2)_2$, **31**), are more difficult to predict [60,63]. For a given system and a given metal fragment some degree of additivity is implied by ^{11}B shifts of 61.6, 111.4 and 158.0 for $MesBBr_2$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2BBr(Mes)$ (**58**) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2BMes$ (**93**) [52], although the use of such shifts in comparing the electronic properties of different metal fragments is fraught with difficulties. Hence $(\eta^5\text{-}C_5H_5)(CO)_2FeBcat$ (**4**) and $(OC)_5MnBcat$ (**94**) give rise to signals at 51.8 and 42.8 ppm, respectively, whereas **58** and its manganese analogue $(OC)_5MnBBr(Mes)$ (**95**) display resonances at 111.4 and 119.4 ppm [10a,23,53]. Comparison between different metal fragments is likely to be strongly influenced by changes in the paramagnetic shielding effect on the directly bonded boron atom [28].

Table 1
Comparison of structural and spectroscopic data for haloboryl complexes of the type $(\eta^5\text{-}C_5Me_5)Fe(CO)_2BX(Mes)$

	91	**60**	**90**	**89**
X in –BX(Mes)	I	Br	Cl	F
ν(CO) (cm^{-1})	2005, 1955	1999, 1942	1996, 1937	1989, 1931
d(Fe–B) (Å)	–	1.972(2)	1.985(2)	2.017(3)
δ_B (ppm)	110.7	113.2	112.1	90.4

In comparison with the corresponding boryl systems, haloborylene complexes typically display even lower field ^{11}B NMR shifts consistent with the existence of two metal boron linkages (e.g. δ_B 163.0 and 133.5 for $[(OC)_5Mn]_2BCl$ (**72**) and $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2]_2BCl$ (**86**), respectively [4,54]).

^{31}P NMR of ancillary phosphine ligands has also been used as a probe of electronic structure in boryl complexes. Of particular value is the magnitude of the $^1J_{Pt–P}$ coupling constants found for a series of *cis*-bis(phosphine)bis(boryl) platinum complexes, $L_2Pt(BX_2)_2$. These are typically of the order of 1500–1600 Hz, and are therefore ca. 200 Hz smaller than those found in analogous *cis*-bis(phosphine)bis(alkyl) complexes and ca. 2000 Hz smaller than that found in $(Ph_3P)_2PtCl_2$ (3675 Hz) [3]. This effect has been ascribed to weakening of the Pt–P bond by the strongly σ donating *trans*-boryl ligands. The coupling constants measured for the bis(difluoroboryl) complexes $(Ph_3P)_2Pt(BF_2)_2$ (**31**) and $(dppb)Pt(BF_2)_2$ (**32**) (1607 and 1526 Hz, respectively) are very similar to those observed for similar catechol and dithiocatechol complexes [33,34,38,60].

3.3.2.2. IR spectroscopy. It is well known that the IR stretching frequencies of CO ligands are very sensitive to the effects of other ligands at the metal center. Hence analysis of the relevant bands in the IR spectra of boryl complexes has been used in a wide range of systems to probe the electronic properties of the BX_2 ligand [3]. Thus, for example, the very similar CO stretching frequencies observed for the iron boryl complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2BPh_2$ (**5**) and $(\eta^5\text{-}C_5H_5)Fe(CO)_2BCl(NMe_2)$ (**40**) and analogous alkyl complexes, and the significantly blue shifted bands observed for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Bcat$ (**4**), have been taken as evidence for no iron to boron back-bonding in **5** and **40** and for a ‘modest’ interaction in **4** [23,51]. However, a number of structural and spectroscopic observations imply that boryl ligands are stronger σ donors than their alkyl or hydride counterparts [3]. Thus a $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ (Fp) complex containing a boryl ligand with no π acceptor properties at all might be expected to show somewhat lower carbonyl stretching frequencies than the analogous alkyl complex. Consistent with this, a number of computational studies have predicted significant polarization of the metal boron bond in the sense $M^{\delta+}\text{-}B^{\delta-}$ for three-coordinate boryl complexes [74]. That most Fp boryl complexes display carbonyl stretching frequencies similar to, or slightly in excess of, those of Fp alkyls attests to an (albeit minor) π acceptor role. Such a role is obviously tempered by the nature of the substituents X. Hence, there is a small increase in stretching frequencies on going from $(\eta^5\text{-}C_5Me_5)Fe(CO)_2BCl(NMe_2)$ (**42**: 1988, 1928 cm^{-1}) to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2BBr(NMe_2)$ (**47**: 1991, 1933 cm^{-1}) and from $(\eta^5\text{-}C_5H_5)Fe(CO)_2BF[Si(SiMe_3)_3]$ (**85**: 2001, 1946 cm^{-1}) to $(\eta^5\text{-}C_5H_5)Fe(CO)_2BCl[Si(SiMe_3)_3]$ (**54**: 2009, 1956 cm^{-1}) [50,51,65]. Similarly the mesityl (halo)boryl complexes $(\eta^5\text{-}C_5Me_5)Fe(CO)_2BX(Mes)$ (X: I, Br, Cl, F) (Table 1) show a steady, stepwise decrease in carbonyl stretching frequencies from values which are similar to those for $(\eta^5\text{-}C_5Me_5)Fe(CO)_2R$ (2005–1999, 1944–1938 cm^{-1} [79]) for X: I (**91**: 2005, 1955 cm^{-1}) to values which are slightly lower for X: F (**89**: 1989, 1931 cm^{-1}) [53,62].

3.3.3. Structural studies

There have been numerous structurally authenticated transition metal boryl complexes reported since 1990 [3]. In general most studies are consistent with a boryl ligand which exerts a strong *trans* influence on account of its very strong σ donor properties, but which is a relatively weak π acceptor. Broadly speaking, boryl complexes of metals to the left and center of the periodic table (e.g. Nb, Ta, W, Mn, Fe) contain M–B bond lengths that are longer than the sum of the covalent radii, whereas those to the right (e.g. Os, Co, Rh, Ir, Pt) generally display a shorter bond consistent with an increased π component to the bond [3]. Modification of the boryl substituents X can exert some influence with on the extent of metal to boron π bonding [74,75], although in general the boron-based acceptor orbital tends to lie too high in energy with respect to the corresponding filled metal orbital for optimal π back-bonding [75].

In comparison to analogous catecholate and related systems, the structural investigation of haloboryl complexes is a relatively underdeveloped area of research. Nevertheless over the past several years some thirty haloboryl, diboran(4)yl and borylene complexes have been reported in the literature, the majority of which feature either iron, ruthenium or osmium. Details of salient structural and spectroscopic parameters for these compounds are included in Table 2.

There are only three examples of crystallographically characterized dihaloboryl complexes, namely the bis(difluoroboryl) complexes $(Ph_3P)_2Pt(BF_2)_2$ (**31**) and $(dppb)Pt(BF_2)_2$ (**32**) and the tris(difluoroboryl) complex $Ir(PPh_3)_2(CO)(BF_2)_3$ (**33**) [60]. Complex **33** contains a fac arrangement of the three BF_2 ligands, consistent with the strong *trans* influence of the BF_2 ligand; a similar geometry is found for all other structurally authenticated tris(boryl) complexes [10f,80,81]. For similar reasons structurally characterized platinum(II) bis(boryl) complexes, $L_2Pt(BX_2)_2$, (L: phosphine donor) display *cis* geometries. Of particular interest in these systems are the relatively acute B–Pt–B (typically 72.9–81.0°) and relatively wide P–Pt–P (100.7 – 107.1°) angles subtended at the platinum center. The origins of this effect are not entirely clear, although steric, rather than electronic factors have been considered to be dominant [3], and the B···B distances for **31** and **32** (2.591(9) and 2.670(8) Å) are consistent with this. In an effort to further probe the origins of these geometric parameters, Norman has compared the structure of **32** to that of the isoelectronic bis(nitrito) complex $(dppb)Pt(NO_2)_2$ (**96**). Compared to **32**, **96** displays shorter Pt–P bond lengths, consistent with NO_2 exerting a weaker *trans* influence than BF_2, and a slightly more obtuse N–Pt–N angle (compared to B–Pt–B). The

Table 2
Structural and spectroscopic properties of crystallographically characterized haloboryl, halodiboran(4)yl and haloborylene complexes

Compound	*d*(M–B) (Å)	δ_B (ppm)	Other spectroscopic and structural properties	Reference
Fluorine containing systems				
(η^5-C$_5$H$_5$)Fe(CO)$_2$BF[Si(SiMe$_3$)$_3$] (**85**)	1.983(9)	113.2	ν(CO): 2001, 1946 cm^{-1}	[65]
(η^5-C$_5$H$_5$)Fe(CO)$_2$BF(Mes)[a] (**89**)	2.017(3)	90.4	ν(CO): 1989, 1931 cm^{-1}	[62]
[Ir(PMe$_3$)$_3$Cl(C$_{12}$H$_8$BF)]$^+$[BPh$_4$]$^-$ (**92**)	2.00(1)	[b]	EPR: g_{xy} 2.15, g_z 1.96	[59]
Ir(PPh$_3$)$_2$(CO)(BF$_2$)$_3$ (**33**)	2.066(10) 2.083(6) 2.088(5)	32.4	ν(CO): 2039 cm^{-1}, *d*(Ir–C): 2.009(8) Å	[60]
(Ph$_3$P)$_2$Pt(BF$_2$)$_2$ (**31**)	2.058(6) 2.052(6)	42.3	$^1J_{\text{Pt–P}}$: 1607 Hz ∠B–Pt–B: 78.2(3)°	[60]
(dppb)Pt(BF$_2$)$_2$[c] (**32**)	2.044(6) 2.047(6)	43.9	$^1J_{\text{Pt–P}}$: 1526 Hz ∠B–Pt–B: 81.5(3)°	[60]
Chlorine containing systems				
(η^5-C$_5$H$_5$)W(CO)$_3$B(NMe$_2$)B(NMe$_2$)Cl (**63**)	2.370(8)	40.3	ν(CO): 1988, 1908, 1892 cm^{-1}	[31]
[(OC)$_5$Mn]$_2$BCl (**72**)	2.169(3)	62.7 BW	*d*(B–B): 1.69(1) Å	[4]
	2.170(3)	163.0	[d]	
[(η^5-C$_5$H$_4$Me)Mn(CO)$_2$]$_2$BCl (**86**)	2.039(11) 1.976(9)	133.5	ν(CO): 1969, 1941, 1912 cm^{-1} *d*(Mn–Mn): 2.824(2) Å	[54,72]
[(η^5-C$_5$H$_4$Me)Mn(CO)$_2$]$_2$B$_2$Cl$_2$ (**87**)	2.077 (mean)	142.2	ν(CO): 2000, 1951 cm^{-1} d(B–B): 1.695(7) Å	[72]
(η^5-C$_5$H$_4$Me)Mn(CO)$_2$(H)BCl[Si(SiMe$_3$)$_3$] (**56**)	2.138(16)	105.8	ν(CO): 1978, 1913 cm^{-1}	[65]
(η^5-C$_5$H$_5$)Fe(CO)$_2$BCl[Si(SiMe$_3$)$_3$] (**54**)	1.964(8)	141.2	ν(CO): 2009, 1956 cm^{-1}	[65]
(η^5-C$_5$H$_5$)Fe(CO)$_2$BCl[Ge(SiMe$_3$)$_3$] (**55**)	1.985(11)	139.0	ν(CO): 2009, 1956 cm^{-1}	[65]
(η^5-C$_5$Me$_5$)Fe(CO)$_2$BCl(NMe$_2$) (**42**)	2.027(5)	59.1	ν(CO): 1988, 1928 cm^{-1}	[51]
(η^5-C$_5$Me$_5$)Fe(CO)$_2$BCl(Mes) (**90**)	1.985(2)	112.1	ν(CO): 1996, 1937 cm^{-1}	[62]
(η^5-C$_5$H$_5$)Fe(CO)$_2$BCl(Ph) (**62**)	2.003(10)[e] 2.006(10)	111.0	ν(CO): 1995, 1929 cm^{-1}	[66]
(η^5-C$_5$H$_5$)Fe(CO)$_2$B(NMe$_2$)B(NMe$_2$)Cl (**3**)	2.090(3)	39.0 69.5 BFe	ν(CO): 1988, 1932 cm^{-1} *d*(B–B): 1.683(3) Å	[31]
(η^5-C$_5$H$_5$)Ru(CO)$_2$B(Cl)N(SiMe$_3$)B(Cl)N(SiMe$_3$) (**52**)	2.115(2)	35.0 60.3 BRu	ν(CO): 2018, 1955 cm^{-1}	[50]
Os[BCl(NHC$_5$H$_4$N)]Br(CO)(PPh$_3$)$_2$ (**81**)	2.047(7)[e]	60.2	ν(CO): 1908 cm^{-1}	[18]
Os[BCl(NHC$_5$H$_4$N)]H(CO)(PPh$_3$)$_2$ (**82**)	2.053(8) 2.104(3)	73.1	ν(CO): 1877 cm^{-1}	[18]
Os[BCl(NC$_5$H$_4$NMe)]H(CO)(PPh$_3$)$_2$ (**84**)	2.078(4)	84.6	ν(CO): 1885 cm^{-1}	[18]
Os[BCl(OC$_5$H$_4$N)]I(CO)(PPh$_3$)$_2$ (**77**)	2.039(4)	62.3	ν(CO): 1919 cm^{-1}	[71]
(Ph$_3$P)$_2$Pt[BCl(NMe$_2$)]$_2$ (**34**)	2.084(3) 2.076(4)	50.8	$^1J_{\text{Pt–P}}$: 1434 Hz ∠B–Pt–B: 75.2(2)°	[34]
(Ph$_3$P)$_2$PtCl[BCl(NMe$_2$)] (**35**)	2.075(10)	36.4	$^1J_{\text{Pt–P}}$: 3188 Hz	[34]
Bromine containing systems				
(η^5-C$_5$H$_5$)Mo(CO)$_3$B(NMe$_2$)B(NMe$_2$)Br (**66**)	2.365(5)	69.5	ν(CO): 1985, 1901, 1887 cm^{-1}	[8,30]
(η^5-C$_5$H$_5$)Fe(CO)$_2$BBr(Mes) (**58**)	1.964(5)	111.4	ν(CO): 2016, 1962 cm^{-1}	[53]
(η^5-C$_5$H$_4$Me)Fe(CO)$_2$BBr(Mes) (**59**)	1.962(4)	111.3	ν(CO): 2009, 1961 cm^{-1}	[52,53]
(η^5-C$_5$Me$_5$)Fe(CO)$_2$BBr(Mes) (**60**)	1.972(2)	113.2	ν(CO): 2006, 1961 cm^{-1}	[53]
(η^5-C$_5$H$_5$)Ru(CO)$_2$B(NMe$_2$)B(NMe$_2$)Br (**67**)	2.173(3)	39.7 63.3 BRu	ν(CO): 2005, 1945 cm^{-1}	[30]

[a] Mes: mesityl, 2,4,6-Me$_3$C$_6$H$_3$.
[b] Paramagnetic.
[c] dppb: 1,4-bis(diphenylphosphino)butane, Ph$_2$P(CH$_2$)$_4$PPh$_2$.
[d] Not given.
[e] Two crystallographically independent molecules in the asymmetric unit.

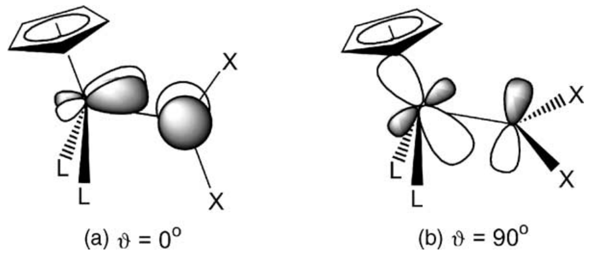


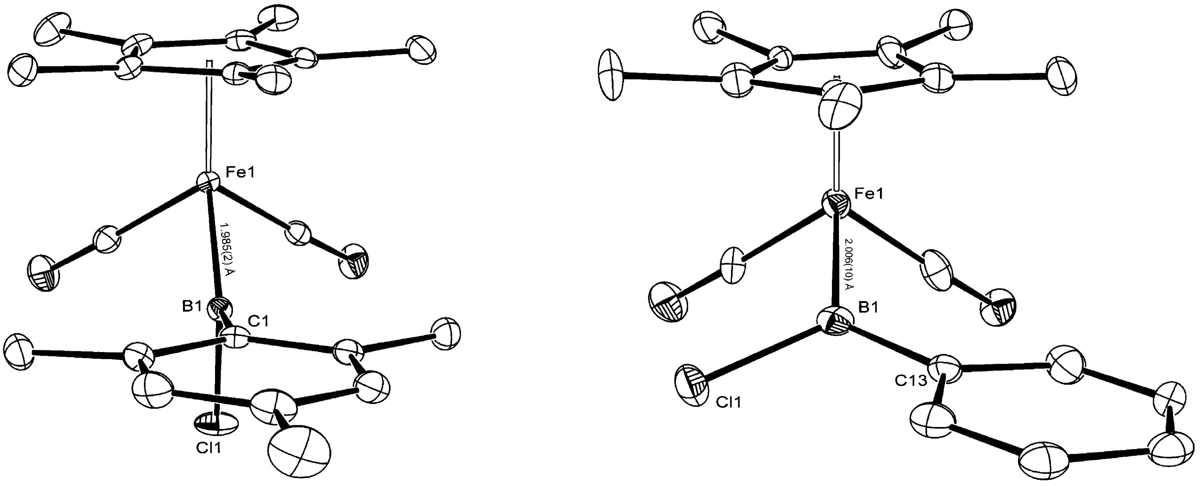
Fig. 11. Possible π bonding interactions in half-sandwich boryl complexes of the (η^5-C_5H_5)FeL_2BX_2: (a) with a centroid–Fe–B–X torsion angle of 0° and (b) with a torsion angle of 90°.

N···N distance (2.837(25) Å) is therefore slightly longer than the B···B separation in **32** [60b]. In each of the difluoroboryl complexes reported and also in the asymmetric species $(Ph_3P)_2Pt[BCl(NMe_2)]_2$ (**34**) the Pt–B bond lengths are reported to fall within the range of distances previously observed for analogous dialkoxoboryls (2.03(2)–2.100(4) Å) and no definitive analysis of the relative π acceptor capacities of these ligands was therefore possible [34,60].

Several half-sandwich haloboryl complexes of manganese and iron have been crystallographically characterized. In addition to metal–boron bond lengths, a number of additional structural features attest to the nature of the M–B interaction in such species. The manganese complex (η^5-C_5H_4Me)$Mn(CO)_2(H)BCl[Si(SiMe_3)_3]$ (**56**) is thought to contain a Mn–H–B bridge, on the basis of a Mn–B distance longer than expected for a straightforward Mn–B single bond, and an ^{11}B NMR resonance shifted upfield from the analogous iron complex **54** [65]. Unfortunately, the poor quality of the diffraction data precluded determination of the exact hydrogen atom position, and hence ruled out any detailed comparison of structure and bonding with the manganese σ borane complexes (η^5-C_5H_4Me)$Mn(CO)_2(HBR_2)$ reported by Hartwig [82].

Among the structurally characterized cyclopentadienyliron haloboryl complexes, there is significant variation not only in the Fe–B distance, but also in the torsion angle ϑ defined as that between the cyclopentadienyl centroid, the iron and boron atoms and the substituent X (Fig. 11). As has been demonstrated both for boryl and isolectronic cationic carbene systems, an angle ϑ of 0° is consistent with optimal π overlap between the a″ HOMO of the metal fragment and the vacant boron-centered p orbital (Fig. 11a) [23,75,83]. For an angle, ϑ of 90° a less favorable π interaction involving the perpendicular a′ symmetry HOMO-2 orbital of the metal fragment is conceivable (Fig. 11b) [83]. The extent of the π interaction between the iron and boron centers is clearly influenced by both steric and electronic factors, as has been argued previously by Hartwig in his analysis of the compounds (η^5-C_5H_5)$Fe(CO)_2BX_2$ (**4**—X_2: cat; **5**—X_2: Ph_2) [23]. Two series of compounds serve to highlight the effects on the Fe–B bond of changes in the electronic properties of the boryl ligand. Hence, examining the groups of compounds (η^5-C_5H_5)$Fe(CO)_2BX[Si(SiMe_3)_3]$ (**54**—X: Cl; **85**—X: F) and (η^5-C_5Me_5)$Fe(CO)_2BX(Mes)$ (**60**—X: Br; **90**—X: Cl; **89**—X: F), sequentially longer Fe–B bond lengths are achieved by replacement of weakly π donor bromo and chloro substituents by the more strongly π donating fluoride (see Table 1) [53,62,65]. This seems to occur irrespective of the relative orientations of the boryl and organometallic fragment. Thus the compounds (η^5-C_5H_5)$Fe(CO)_2BX[Si(SiMe_3)_3]$ are characterized by torsion angles approaching 90° (e.g. $\vartheta = 83.5°$ for X: F, **85**), whereas virtually all complexes of the type (η^5-C_5R_5)$Fe(CO)_2BX(Mes)$ (including halo and alkoxo derivatives) have $\vartheta \approx 0°$ (e.g. 2.3° for **60**) [52,53,62,65–67].

Steric factors can also play a significant structural role, although not always in the manner expected. The structures of the mesityl and phenyl complexes (η^5-C_5Me_5)



90 **62**

Fig. 12. Crystal structures of the complexes (η^5-C_5Me_5)$Fe(CO)_2BCl(Ar)$ (**90**—Ar: Mes; **62**—Ar: Ph) emphasizing the different boryl ligand orientations.

$Fe(CO)_2BCl(Ar)$ (**90**—Ar: Mes; **62**—Ar: Ph), shown in Fig. 12 display markedly different orientations of the boryl ligands [62,66]. These dissimilarities at first inspection appear counter-intuitive, i.e. a significantly shorter Fe–B bond might have been expected for the less sterically demanding phenyl substituent. Examination of the structure of **90** and other mesitylboryl complexes implies that the orientation of the mesityl group is largely determined by steric factors—the near zero torsion angle (ϑ) and near perpendicular arrangement of boryl and aryl planes are essentially fixed by the need to minimize steric repulsions between Mes and (η^5-C_5Me_5) moieties [53,62]. For **62** the smaller size of the phenyl substituent allows for significantly greater conformational freedom. By adopting a conformation with $\vartheta = 78.6(7)^\circ$ and the angle between boryl and aryl planes set to 31.3(9)°, the phenyl ring takes on an orientation within the crystal lattice such that intermolecular π stacking can occur without significant steric repulsion. That the geometry of the boryl complex is markedly influenced by such weak interactions in the solid state further testifies to the relatively small π component of the Fe–B bond [66].

Six-coordinate osmium chloroboryl and borylene complexes also display interesting structural trends determined to large degree by the electronic properties of the boron-bound substituents. Hence the amino-functionalized tethered boryl complex $Os[BCl(NHC_5H_4N)]Br(CO)(PPh_3)$ (**81**) displays a slightly longer Os–B bond length and significantly longer B–Cl bond length than its alkoxo-substituted analogue $Os[BCl(OC_5H_4N)]I(CO)(PPh_3)$ (**77**), consistent with the stronger π donor properties of the nitrogen substituent. Furthermore, replacement of the bromide ligand *trans* to the boryl in **81** with a more strongly σ donating hydride leads to the expected lengthening of the Os–B bond (2.104(3) Å for **82** versus 2.047(7) Å and 2.053(8) Å for **81**). Finally, a comparison of the tethered boryl and borylene complexes **82** and **84** does reveal shorter Os–B and Os–Cl distances for the borylene system, although as discussed with reference to other osmium borylene systems (Section 4.3) the reduction in the bond length is not as great as would have been expected for the formation of an isolated Os=B double bond [15,18,71].

4. Substitution chemistry in boryl and borylene systems

4.1. Historical perspective

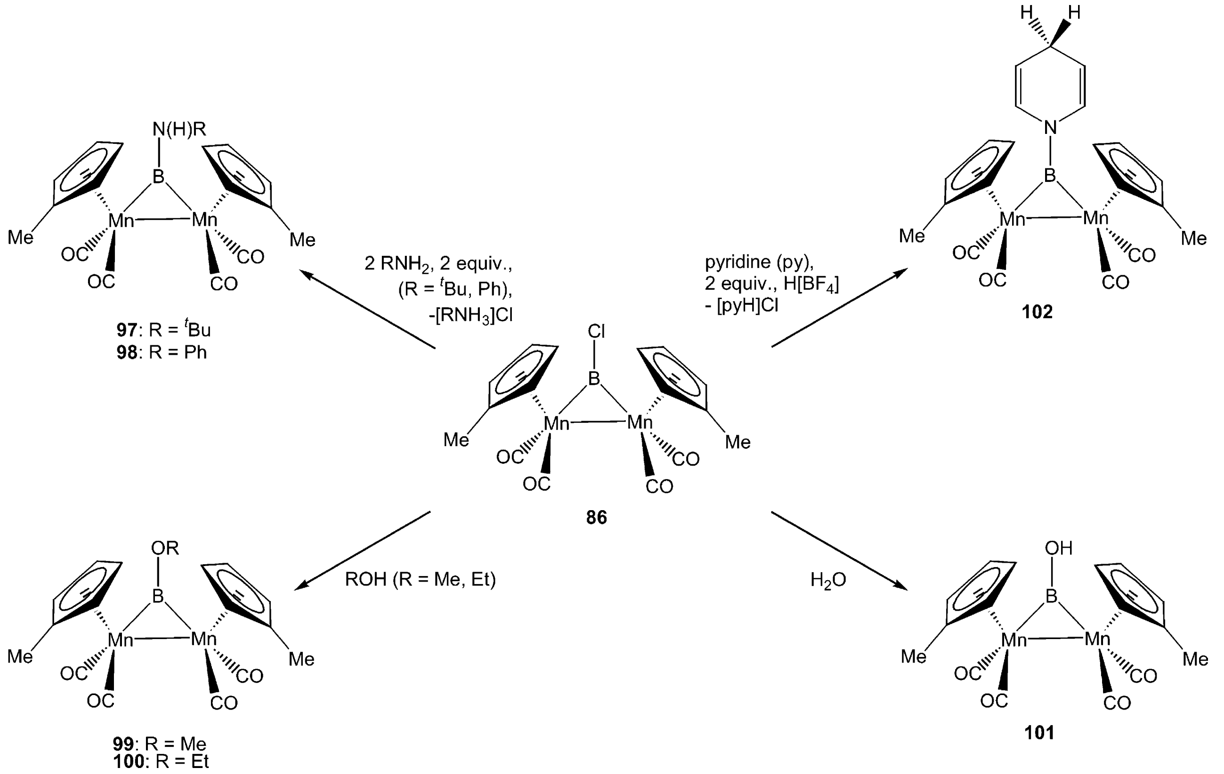
Recent reviews articles published as late as 2001 have highlighted the lack of authenticated boron-centered reactivity which proceeds with retention of the metal–boron bond [3,8]. Reactivity leading to destruction of the M–B bond is relatively more common, but controlled substitution chemistry has been observed only in a limited number of cases. In part this reflects the lability of the M–B linkage and therefore its propensity to undergo cleavage under the conditions required to effect substitution at the boryl substituents. In the interim, however, the synthesis of a range of boryl complexes containing weakly π donor substituents (predominantly halides) has allowed a fuller investigation of functional group transformations at boron and the development of novel boron ligand systems.

Some examples from the early boryl literature detail reactions of BCl_2 complexes with amine and alkoxide reagents leading, for example, to the formation of species containing $B(OMe)_2$, $B(Cl)NMe_2$ or $B[(HN)_2C_6H_4$-1,2] ligands [1,56]. Additionally, the reverse transformation has been reported in the case of $(Ph_3P)(OC)_4MnB(NMe_2)_2$; reaction with four equivalents of HCl was reported to yield $(Ph_3P)(OC)_4MnBCl_2$ [84]. Simple complexation reactions of BCl_2 ligands were also reported leading to the isolation of based stabilized four-coordinate boryl complexes such as (η^5-C_5H_5)$M(CO)_nBCl_2{\cdot}NEt_3$ (M: Mo, W, $n = 3$; M: Fe, $n = 2$) and $(Ph_3P)(OC)_4MnBCl_2{\cdot}NEt_3$ [3,84].

4.2. Cyclopentadienylmanganese and iron species

A number of cyclopentadienylmanganese and iron haloboryl and haloborylene complexes have been shown to be sufficiently robust as to undergo substitution reactions at the boron center with retention of the metal boron bond. One of the first systems to be investigated was the dimanganese chloroborylene complex **86**. In contrast to its dimethylamino-substituted precursor **24**, the more weakly π-stabilized **86** undergoes a number of substitution reactions at the boron center with protic reagents [40,54,55,85]. Hence reactions with primary amines, alcohols and with water generate the corresponding bridged complexes containing BN(H)R, BOR and BOH ligands, respectively (Scheme 14). Such reactivity is indicative of the robustness of the Mn_2B metallacycle, which appears only to be decomposed by powerful halogenating agents such as I_2 or SbF_3. In addition, reaction of **86** with pyridine in the presence of protic reagents such as $H[BF_4]$, H_2S or $H[Co(CO)_4]$ results in the formation of aminoborylene **102** via the formal 1,4-hydroboration of pyridine. The initial step of this interesting reaction has been postulated to be abstraction of the boron-bound chlorine as HCl to give the pyridine-stabilized cationic bridging borylene $\{[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2]_2(Bpy)\}^+$ (py: pyridine) which then abstracts hydride to give **102**. That similar reactivity was observed using $Tl[PF_6]$ adds weight to the suggestion of chloride abstraction as the initial reaction step, although no spectroscopic data could be obtained for the (presumably highly reactive) cationic intermediate [85].

Boron-centered substitution chemistry has also been demonstrated for a number of cyclopentadienyl complexes of group 8 elements. Thus the synthesis of (η^5-C_5H_5)$Fe(CO)_2BF[Si(SiMe_3)_3]$ (**85**) from its chloroboryl analogue has already been described (Section 3.2.3) [65], and the formation of iron and ruthenium borylene complexes of the type $[(\eta^5\text{-}C_5R_5)M(CO)]_2(\mu\text{-}BNR_2)(\mu\text{-}CO)$ (**43**, **44**, **49**–**51**) from aminodihaloboranes and excess metal



Scheme 14.

anion presumably proceeds via substitution of the single remaining halide in the initially formed boryl complex ($(\eta^5\text{-}C_5R_5)M(CO)_2BX(NR_2)$) [50,51]. This chemistry can be demonstrated explicitly for aryl(halo)boryl complexes of the type $(\eta^5\text{-}C_5R_4R')Fe(CO)_2BX(Ar)$ (**58–60, 62**, Fig. 6). In each case synthesis from the corresponding aryldihaloborane can be carried out selectively by replacement of one halide, and a range of further substitution chemistry can then be carried out with main group and organometallic nucleophiles [52,53,62,66,67]. This degree of synthetic control contrasts with that observed in the corresponding aminoboryl systems, i.e. R_2NBCl_2 reacts with cyclopentadienyliron nucleophiles to give the substitutionally inert haloboryl complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2BCl(NR_2)$ (**40**) for R: Me, but exclusively generates $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}BNR_2)(\mu\text{-}CO)$ (**43**) with replacement of both halides for R: $SiMe_3$ [50,51]. Such control, for example, facilitates the synthesis of the first asymmetric bridging borylene complexes (e.g. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2][(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]BMes$, **103**).

Hence reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2BBr(Mes)$ **58** with a range of main group nucleophiles leads to the formation of alkoxo, aryloxo and thiolate derivatives **104–107** in reasonable yields (Scheme 15), including species such as **106** containing pendant pyridyl donors [52,53,67]. Comparisons of spectroscopic and structural parameters for complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2BX(Mes)$ (X: Br (**58**), SPh (**107**), $OC_6H_4{}^t$Bu-4 (**104**) and O^tBu (**105**)) are consistent with the 'competitive π-bonding model' proposed by Roper to account for similar observations in osmium boryl systems (vide infra). Thus the progressively stronger π-donor substituents X (Br, SPh, $OC_6H_4{}^t$Bu, O^tBu) result in longer Fe–B bonds, lower carbonyl stretching frequencies and higher field ^{11}B NMR shifts (Table 3).

For the less sterically encumbered derivatives $(\eta^5\text{-}C_5H_4R)Fe(CO)_2BBr(Mes)$ (R: H (**58**), Me (**59**)) substitution of the remaining halide ligand by organometallic nucleophiles is also possible [52,53,62,66]. Hence the novel unsupported bridging borylenes **93**, **103** and **108** can be synthesized from **58** by addition of a large excess (ca. 4 eq.) of the appropriate organometallic anion (Scheme 16). Additionally, the mixed manganese/iron system $[(\eta^5\text{-}C_5H_5)Fe(CO)_2][(OC)_5Mn]BMes$ (**109**) appears to be accessible from **58** by similar methodology, although in our hands this compound proved to be too thermally fragile to allow complete characterization [53].

Complex **93** and its symmetrical methylcyclopentadienyl analogue $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2BMes$ (**112**) represented the first crystallographically characterized borylene complexes without an accompanying metal-metal bond to appear in the primary literature [52,53].[1] This particular mode of coordination is rare for first row ligands of this type and, in common with analogous gallium and silicon-containing systems [86,87], photolysis induces loss

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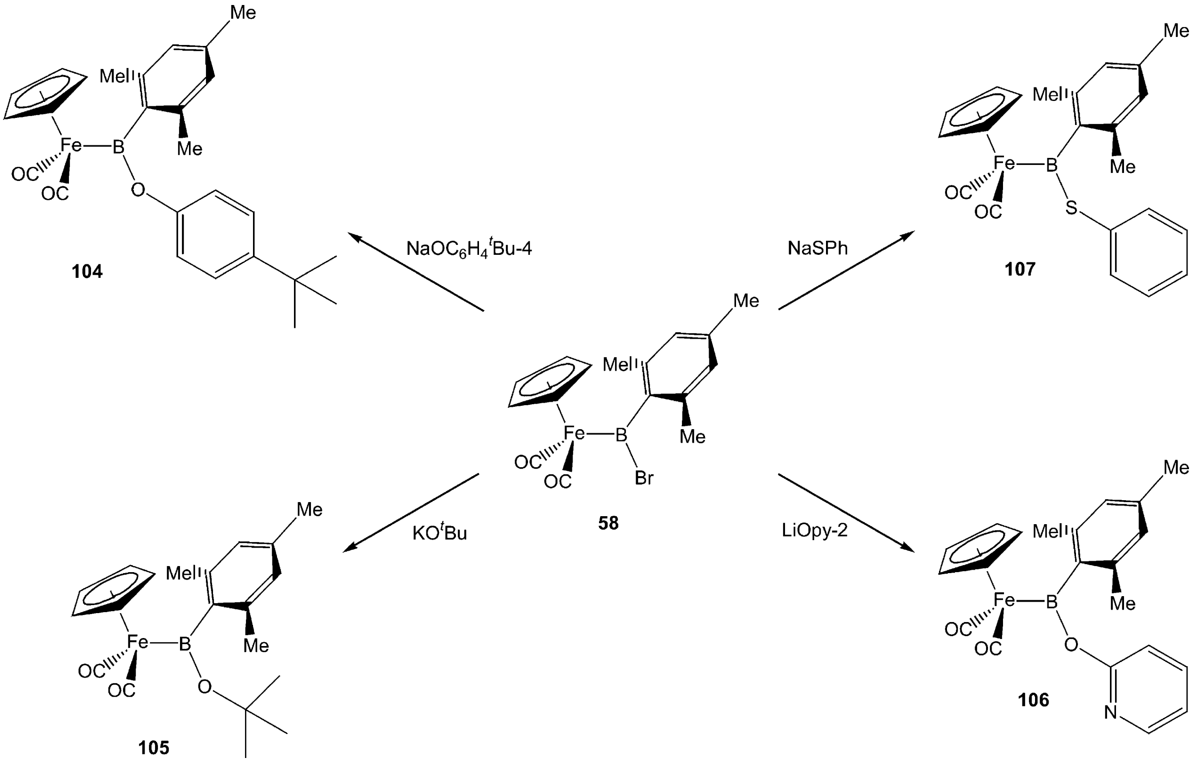
[1] The (as yet unpublished) structures of $[(OC)_5Mn]_2BCl$ and $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2BOMe$ are cited as a personal communication in a single review article [4], with Fe–B bond lengths of 2.068(9) and 2.089(9) Å reported for the latter compound.



Scheme 15.

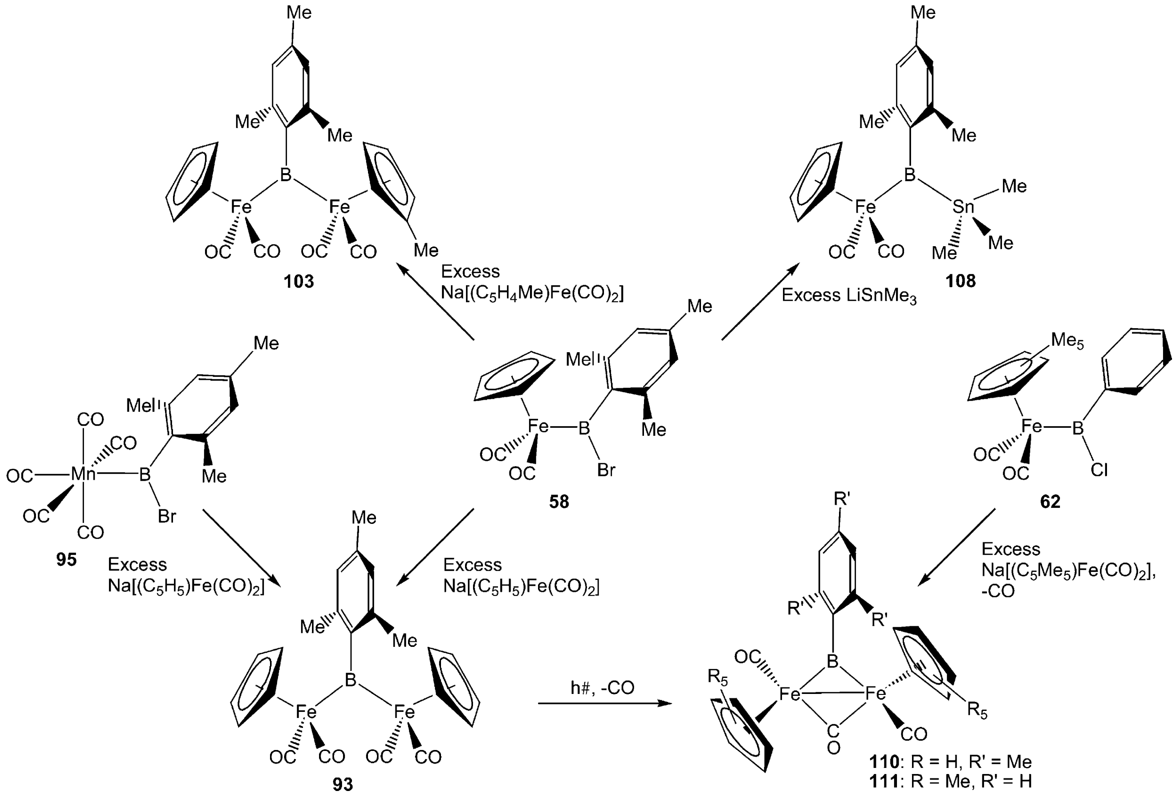
of a single molecule of CO and the formation of the supported mesitylborylene complexes **110** and **113**, respectively [53,86,87]. Both complexes are formed exclusively as the *trans* isomer, a result which contrasts with that observed on photolysis of the analogous gallium containing complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2GaMes$, which yields a mixture of *cis*- and *trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu_2\text{-}CO)(\mu_2\text{-}GaMes)$ (**114**) [86]. Conceivably this difference reflects the differing geometric constraints imposed by bridging borylene and gallylene ligands. The shorter Fe–E bond lengths found for E: B lead to a significantly compressed Fe–Fe distance (2.528(1) Å for **110** versus 2.635(1) Å for *trans*-**114**]. This in turn brings about enhanced steric interactions between the cyclopentadienyl ligands and the mesityl substituent of the bridging borylene ligand. This factor would be expected to be less important for the *trans* isomer, in which rotation about the $B\text{–}C_{ipso}$ bond could place the plane of the mesityl ligand such as to minimize unfavorable inter-ligand contacts. Consistent with this observation, $[(\eta^5\text{-}C_5H_4Me)Fe(CO)]_2(\mu\text{-}CO)[\mu\text{-}BN(SiMe_3)_2]$ (**43**) is also obtained exclusively as the *trans* isomer [51].

There are two major structural differences between the different types of bridging mesitylborylene complex exemplified by **93** and **110** [52,53]. Firstly, the Fe–B–Fe angle is significantly wider in **93** (130.8(5)°) than is typically found in bridging borylenes which form part of a three-membered MBM metallacycle (e.g. 80.3(2)° and 78.9(1)° for **110** and **43**, respectively) [51–53]. The opening out of the M–B–M angle in the absence of a constraining metal-metal bond mirrors the behavior of analogous gallium and indium systems [86]. Secondly, the Fe–B distances in the unsupported complex **93** (2.090(10) and 2.091(10) Å) are significantly longer than those found in similar complexes containing a metal-metal bond (cf. mean values of 1.961(5) and 2.003(3) Å for **110** and **43**, respectively). The much reduced level of steric crowding at boron in the ‘tied-back’ supported bridged systems **110** and **43** almost certainly contributes to the substantial shortening of the Fe–B bonds.

Indeed, the significant steric congestion around the boron center in the unsupported bridged systems **93**, **103** and

Table 3
Comparison of structural and spectroscopic data for complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2BX(Mes)$

	58	**107**	**104**	**105**
X in –BX(Mes)	Br	SPh	$OC_6H_4{}^tBu\text{-}4$	O^tBu
ν(CO) (cm^{-1})	2016, 1962	2000, 1935	1997, 1933	1987, 1918
d(Fe–B) (Å)	1.964(5)	–	2.040(2)	2.056(2)
δ_B (ppm)	111.4	103.5	80.3	72.9



Scheme 16.

112, while almost certainly a factor in the stabilization of these complexes, for example to attack by external nucleophiles, is probably also significant in maintaining the scarcity of this ligand architecture. Thus, for example, increasing the steric bulk of the aryl fragment (as in (η^5-C_5H_5)Fe(CO)$_2$BBr($C_6H_3Trip_2$-2,6) (**61**—Trip: 2,4,6-^{i}Pr$_3$C$_6$H$_2$)) or of the ancilliary cyclopentadienyl ligand (as in (η^5-C_5Me_5)Fe(CO)$_2$BX(Mes), **60**—X: Br; **90**—X: Cl) renders the boryl complex inert to further reaction with organometallic nucleophiles [53,67]. In the case of pentamethylcyclopentadienyl derivatives **60** or **90**, replacing the mesityl substituent with the less bulky phenyl group (to give **62**) does allow substitution of the second halide to occur, although the product isolated in this case is the less congested Fe–Fe bonded system [(η^5-C_5Me_5)Fe(CO)]$_2$(μ-CO)(μ-BPh), **111** [66]. If all elements of steric shielding are removed, as in [(η^5-C_5H_5)Fe(CO)$_2$]$_2$BCl (**115**), then further examples of the unsupported ligand framework can be synthesized, but such compounds (in our hands) have proved to be unworkably fragile [53,62].

Thus, in contrast to the aminoboryl systems discussed in Section 3.2.2, the substitution chemistry of arylhaloboryl complexes appears to be driven principally by steric, rather than electronic factors. One exception to this is the reaction of $(OC)_5$MnBBr(Mes) (**95**) with excess Na[(η^5-C_5H_5)Fe(CO)$_2$] which yields the diiron complex **93**, rather than the mixed Fe/Mn system **109**. Presumably the greater nucleophilicity of the [(η^5-C_5H_5)Fe(CO)$_2$]$^-$ anion and the superior leaving group ability of [Mn(CO)$_5$]$^-$ are responsible for this observation. As previously stated a compound thought to be **109** is isolated from the alternative reaction using (η^5-C_5H_5)Fe(CO)$_2$BBrMes and excess Na[Mn(CO)$_5$] [53].

4.3. Five- and six-coordinate osmium complexes

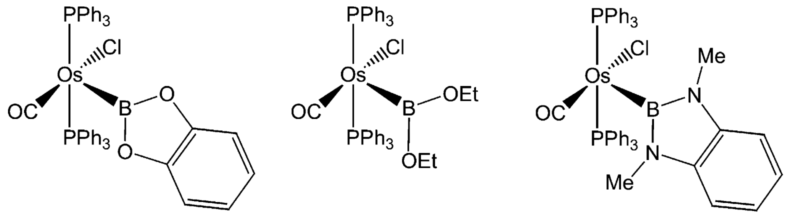
The boron-centered substitution chemistry of five- and six-coordinate osmium complexes containing the BCl_2 ligand is among the most well developed of systems reported to date. In particular OsCl(CO)(PPh$_3$)$_2$(BCl$_2$) (**36**) has proved to be a versatile substrate for the synthesis of a range of novel boryl and base-stabilized borylene complexes [15,18,61,71].

Roper and Wright have observed the controlled hydrolysis of both five- (Eq. (7), R: H) and six-coordinate (Eq. (8), L: CO, CNCH$_2$-*p*-tosyl) osmium boryl complexes containing the BCl_2 ligand [3,61]. Similar reactivity was observed for

$$\mathrm{OsCl(CO)(PPh_3)_2(BCl_2)} \xrightarrow{\mathrm{ROH}} \mathrm{OsCl(CO)(PPh_3)_2[B(OR)_2]} \tag{7}$$

36

116:$(OR)_2 = (OH)_2$
117:$(OR)_2 = (OMe)_2$
118:$(OR)_2 = (OEt)_2$
11:$(OR)_2$ = cat, 1,2-$O_2C_6H_4$



11 **118** **122**

Fig. 13. Alkoxo- and aminoboryl complexes derived by boron-centered substitution chemistry of $\mathrm{OsCl(CO)(PPh_3)_2BCl_2}$ (**36**).

$$\mathrm{OsCl(CO)(PPh_3)_2(BCl_2)} \xrightarrow{\mathrm{L,\ H_2O}} \mathrm{OsCl(L)(CO)(PPh_3)_2[B(OH)_2]} \qquad (8)$$

36

119: L = CO
120: L = $\mathrm{CNCH_2}$-*p*-tosyl

the five-co-ordinate complex **36** in the presence of methanol, ethanol or catechol to generate dialkoxoboryl species **11**, **117** and **118** (Eq. (7)), although no products could be isolated with pinacol, ethylene glycol, 1,2-ethanedithiol or toluenethiol. Interestingly, diethoxyboryl complex **118** is also reported to undergo further substitution chemistry; reaction with 1,2-ethanediol ultimately yields the corresponding complex containing the $\mathrm{BO_2C_2H_4}$ ligand (**121**). This is a very rare example of substitution reaction of a boryl complex where the leaving group is not a halide. Similar substitution of alkoxo substituents at boron has been observed for the ruthenium complex **17**, albeit containing a $\mathrm{B(OR)_2}$ unit linked to the metal center via a –C(H)=C(H)– spacer derived from insertion of ethyne into a Ru–B bond [37].

Mirroring its chemical behavior towards alcohols, reaction of **36** with selected chelating secondary amines leads to the formation of diaminoboryl complexes **122** and **123** (Eq. (9)) [3,61]. The stability of the Os–B bond in these complexes to reagents bearing relatively acidic hydrogens is remarkable. By contrast, the iron haloboryl species $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2B(Br)Mes}$ (**58**) reacts with $4\text{-}{}^t\mathrm{BuC_6H_4OH}$ via Fe–B bond scission, the synthesis of the phenoxoboryl complex $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2}$ $\mathrm{B(OC_6H_4}{}^t\mathrm{Bu\text{-}4)Mes}$ (**104**) requiring the use of the corresponding base $4\text{-}{}^t\mathrm{BuC_6H_4ONa}$ [67].

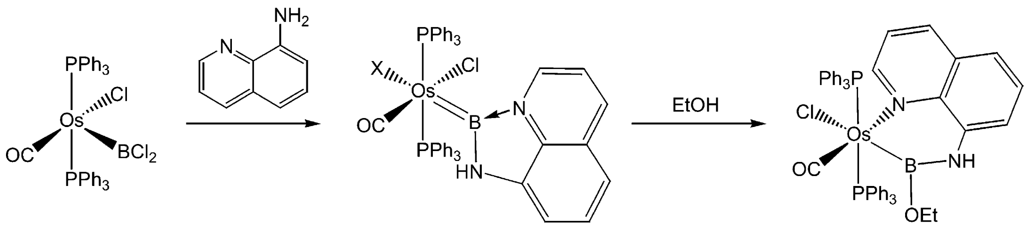
$$\mathrm{OsCl(CO)(PPh_3)_2(BCl_2)} \xrightarrow{\mathrm{R_2NH}} \mathrm{OsCl(CO)(PPh_3)_2[B(NR_2)_2]} \qquad (9)$$

36

122: $\mathrm{(NR_2)_2 = 1,2\text{-}(MeN)_2C_6H_4}$
123: $\mathrm{(NR_2)_2 = MeNCH_2CH_2NMe}$

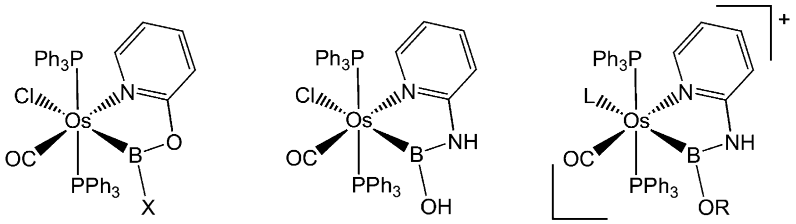
This type of substitution chemistry has allowed for an interesting comparison of structural and spectroscopic properties of boryl complexes as a function of the substituents attached to the boron center. Hence catecolboryl, diethoxyboryl and diaminoboryl complexes **11**, **118** and **122** (Fig. 13) show a concerted increase in the Os–B bond length (2.019(3), 2.076(3) and 2.082(10) Å, respectively) and corresponding decrease in metal carbonyl stretching frequency (1923, 1906 and 1884 $\mathrm{cm^{-1}}$, respectively) as a consequence of the reduced π acceptor properties of the boryl ligand as the π donor properties of the boron substituent become more pronounced [61].

Complex **36** also displays interesting reactivity towards alcohol and amine reagents containing tethered quinoline or pyridine donors, leading to the synthesis of a range of tethered boryl and base-stabilized borylene complexes [15,18,61,71]. The reaction of **36** with 8-aminoquinoline, reported in 2000 (Scheme 17), represented the first synthesis of a base-stabilized terminal borylene complex [15]. The initially synthesized, but sparingly soluble, chloro substituted species **124** was converted into the corresponding iodo complex **125** (by reaction with tetrabutylammonium iodide), which was structurally characterized. The OsB linkage in **125** (2.055(8) Å), although shorter than the corresponding single bonds in six-coordinate osmium boryl species, is perhaps not as short as would be expected for an isolated Os=B double bond. The authors attribute this observation for base-stabilized **125** to significant contributions from valence-bond descriptions featuring formal Os–B single bonds, in a manner analogous to base-stabilized silylene complexes [15]. Interestingly **125** displays the electrophilic character at boron predicted on the basis of theoretical studies [41], reacting with ethanol to produce the ethoxyboryl derivative **126** in which the



36 **124**: X = Cl
125: X = I **126**

Scheme 17.



127: X = NHBu
128: X = OEt
129: X = F

130

131: L = MeCN, R = H
132: L = CO, R = Et

Fig. 14. Boron-centered substitution products derived from tethered chloroboryl complexes.

tethered quinoline donor has shifted from boron to osmium [15].

Finally, the tethered chloroboryl and base-stabilized chloroborylene complexes **76**, **80** and **83** formed by the reaction of 2-hydroxy- or 2-aminopyridines with **36** (Fig. 8), themselves display a range of further substitution chemistry. Thus pyridyl-tethered chloroboryl complex **76** undergoes reaction with protic species HX to give the boron-centered substitution products **127–129** (Fig. 14). Spectroscopic and structural features of these complexes (in particular the ν(CO) stretching frequencies and the Os–B and O–B bond lengths) are consistent with the competitive π-bonding model in which Os, O and X substituents are competitive π donors towards the three-coordinate boron center [71]. Intriguingly, analogous boron-centered substitution chemistry for the amino pyridyl derivative **80** requires activation with a single equivalent of Ag[SbF$_6$] (for neutral substitution products such as **130**) or with two equivalents (for cationic species **131** and **132**). The relative inertness of **80** toward substitution chemistry at boron has been attributed (at least in part) to efficient π donation by both amino and osmium substituents. Similar selectively boron-substituted or doubly (osmium and boron) substituted derivatives are accessible from chloroborylene **83** [18].

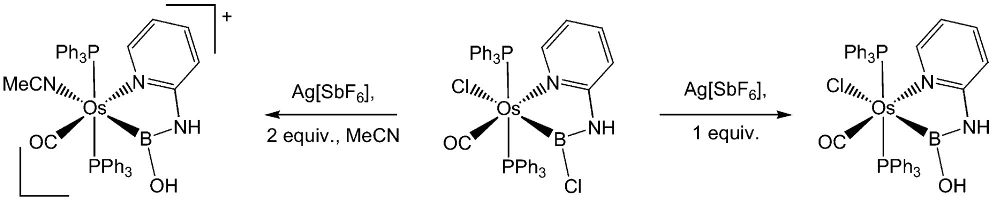
5. Halide abstraction chemistry

5.1. Halide abstraction as a new route to terminal borylene complexes

Substitution chemistry in metal boryl and borylene complexes that proceeds with retention of M–B bonds is therefore an area of the chemistry of these topical systems which has seen considerable growth over the past 5 years. In a number of cases, substitution reactions have been reported which have been postulated to occur via initial abstraction of the boron-bound halide [18,85]. These include the novel 1,4 hydroboration of pyridine by [(η^5-C$_5$H$_4$Me)Mn(CO)$_2$]$_2$(BCl) and the substitution reactions reported for the osmium complex **80** (Scheme 18). In each case the thermodynamic impetus for the halide abstraction is presumably provided by the precipitation of an insoluble (thallium or silver) halide salt.

Inspired by these observations and by Tilley's elegant synthesis of base-free silylenes via halide (or pseudo-halide) abstraction [88], we examined the reaction of the arylhaloboryl complexes **60** and **62** with possible abstraction reagents. In the case of (η^5-C$_5$Me$_5$)Fe(CO)$_2$BCl(Ph) (**62**), reaction with Na[BAr$^f_4$] (Ar^f: C$_6$H$_3$(CF$_3$)$_2$-3,5) leads to complete consumption of the starting material even at low temperatures (−60 °C) over a 30 min period, although no tractable Fe–B containing products could be isolated from the reaction mixture [62]. With the sterically more encumbered mesityl complex (η^5-C$_5$Me$_5$)Fe(CO)$_2$BBr(Mes) (**60**), the analogous reaction with either Na[BAr$^f_4$] or Ag[CB$_{11}$H$_6$Br$_6$] leads to complete conversion of the starting material to a cationic complex with an ^{11}B NMR resonance (δ_B 145) shifted some 30 ppm downfield from that of the starting material. This species, isolated in yields of 50–60% as colorless crystals, has been shown by spectroscopic and crystallographic data to be the cationic terminal borylene complex **88** (Scheme 19) [20].

This compound is the first example of a cationic borylene complex, and its synthesis opens up a new route to a range of related highly unsaturated systems. Of particular interest from a structural viewpoint is the linear Fe–B–C

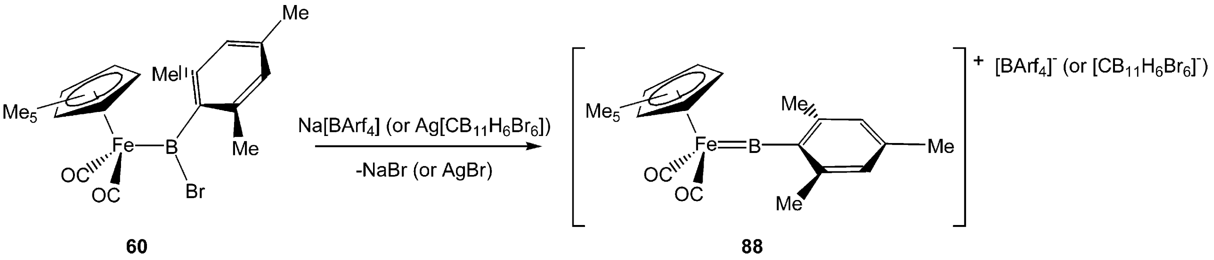


131

80

130

Scheme 18.



Scheme 19.

unit ($\angle$Fe(1)–B(1)–C(1) $= 178.3(6)^\circ$) and the Fe–B distance (1.792(8) Å), which is significantly shorter than any transition metal to boron linkage previously reported. The iron–boron distance in **88** is significantly shorter than similar complexes containing iron–boron single bonds (see Table 4). Additionally the observed shortening (ca. 18% compared to (η^5-C_5Me_4Et)Fe(CO)$_2$BH$_2$·PMe$_3$ (**133**) [89], or 8.5% with respect to (η^5-C_5H_5)Fe(CO)$_2$Bcat (**4**) [23]) is within the range expected on going from a single to a double bond (as demonstrated by comparison with analogous iron/carbon and ruthenium/silicon systems).

The bonding between the iron and boron centers in **88** is best described in a similar manner to the Ru=Si double bond in the cationic silylene complex [(η^5-C_5Me_5)Ru(PMe$_3$)$_2$(=SiMe$_2$)]$^+$, which is composed of a Si→Ru donor/acceptor σ component supplemented by Ru→Si π backbonding into the vacant Si-based p orbital [88]. The analogous bonding description for **88** implies a significantly greater Fe → B back-bonding component than is found in (η^5-C_5Me_5)BFe(CO)$_4$ (**24**) [13]. Such an arrangement seems likely given the highly electrophilic nature of the boron center in **88** and the significantly higher DFT-predicted π bonding capability of the BPh ligand compared to B(η^5-C_5H_5) [47,48]. The presence of an appreciable Fe→B backbonding component for **88** is also implied by carbonyl stretching frequencies (2055, 2013 cm^{-1}) in excess of those for pentamethylcyclopentadienyliron Fischer carbene complexes such as {(η^5-C_5Me_5)Fe(CO)$_2$[=CMe(OMe)]}$^+$ (2045, 1999 cm^{-1} [93]). That these values are still short of those reported for [(η^5-C_5Me_5)Fe(CO)$_3$]$^+$ (2105, 2045 cm^{-1} [94]), however, almost certainly reflects the stronger σ donor nature of BR over CO, as predicted by Hoffmann and Baerends [42]. The orientation of the mesityl fragment in **88** (torsion, $\angle$(η^5-C_5Me_5) centroid–Fe(1)–C(1)–C(2) $= 91.3(6)^\circ$) is such that an Fe→B π interaction involving the HOMO of the [(η^5-C_5Me_5)Fe(CO)$_2$]$^+$ fragment [83] could populate one of the two perpendicular vacant p orbitals at boron, with the other being stabilized by π interaction with the mesityl ring. Consistent with this, the distance B(1)–C(1) (1.491(10) Å) is significantly shorter than that found in precursor bromoboryl complex **60** (1.569(3) Å) [53].

Table 4
Comparison of M–E bond lengths for singly- and doubly-bonded boron, carbon and silicon complexes of iron and ruthenium

Compound	d(M–E) (Å)	Reference
[(η^5-C_5Me_5)Fe(CO)$_2$(=BMes)]$^+$ (**88**)	1.792(8), 1.785(8)[a]	[20]
(η^5-C_5Me_5)BFe(CO)$_4$ (**27**)	2.010(3)	[13]
(η^5-C_5Me_4Et)Fe(CO)$_2$BH$_2$·PMe$_3$ (**133**)	2.195(14)	[89]
(η^5-C_5H_5)Fe(CO)$_2$Bcat (**4**)	1.959(6)	[23]
[(η^5-C_5H_5)Fe(CO)$_2$(=CCl$_2$)]$^+$	1.808(12)	[90]
(η^5-C_5H_5)Fe(CO)$_2$(n-C_5H_{11})	2.069(10)	[91]
[(η^5-C_5Me_5)Ru(PMe$_3$)$_2$(=SiMe$_2$)]$^+$	2.238(2)	[88]
[(η^5-C_5Me_5)Ru(PMe$_3$)$_2$(SiMe$_2$CH$_2$PPh$_3$)]$^+$	2.381(2)	[92]

[a] Two crystallographically independent molecules in the asymmetric unit.

Interestingly the orientation of the borylene ligand in **88** is very different from that found in the only other structurally characterized half-sandwich borylene complex, (η^5-C_5H_5)V(CO)$_3$BN(SiMe$_3$)$_2$ (**30**) [19]. The minimum energy structure determined from both crystallographic and DFT studies features a torsion angle ($\angle$(η^5-C_5H_5) centroid–V–N–Si) of ca. 12°. An alternative ligand orientation with a torsion angle of 90° (analogous to that found in **88**) was calculated to be 19 kJ mol^{-1} higher in energy. Clearly however, steric factors play an important role in determining the orientation of the bulky BN(SiMe$_3$)$_2$ ligand; the corresponding complex containing the parent BNH$_2$ ligand has a minimum energy conformation featuring a torsion angle of 90°, with that at 0° being ca. 9 kJ mol^{-1} higher in energy [19]. Consistent with this the minimum energy conformation of the cationic species [(η^5-C_5Me_5)Fe(CO)$_2$BNMe$_2$]$^+$ has been calculated to feature a torsion angle of 84.6° [78].

In order to explore more rigorously the bonding situation in **88** and related complexes, DFT calculations have been carried out for the cations [(η^5-C_5R_5)FeL$_2$(EX)]$^+$ (R: H, Me; L: CO, PMe$_3$; E: B, Al, Ga; X: H, Mes, C$_6$F$_5$, NMe$_2$, OMe, F) at the BLYP/TZP level of theory [20,78]. In the case of **88**, the agreement between (fully optimized) calculated (Fe(1)–B(1) 1.843 Å, B(1)–C(1) 1.495 Å, $\angle$Fe(1)–B(1)–C(1) $= 177.8^\circ$, torsion $= 93.7^\circ$) and measured geometric parameters is generally very good, with a 2–3% over-estimate in the Fe−B bond length mirroring previous studies [75]. Based on a population analysis of the molecular orbitals at the DFT relaxed geometry, the Fe−B bond has a 62:38 σ:π breakdown of the covalent contribution to bonding (cf. 64:36 for [CpFe(CO)$_2$(=CH$_2$)]$^+$ [75]). The occupied MOs (HOMO-3 and HOMO-9, Fig. 15) show,

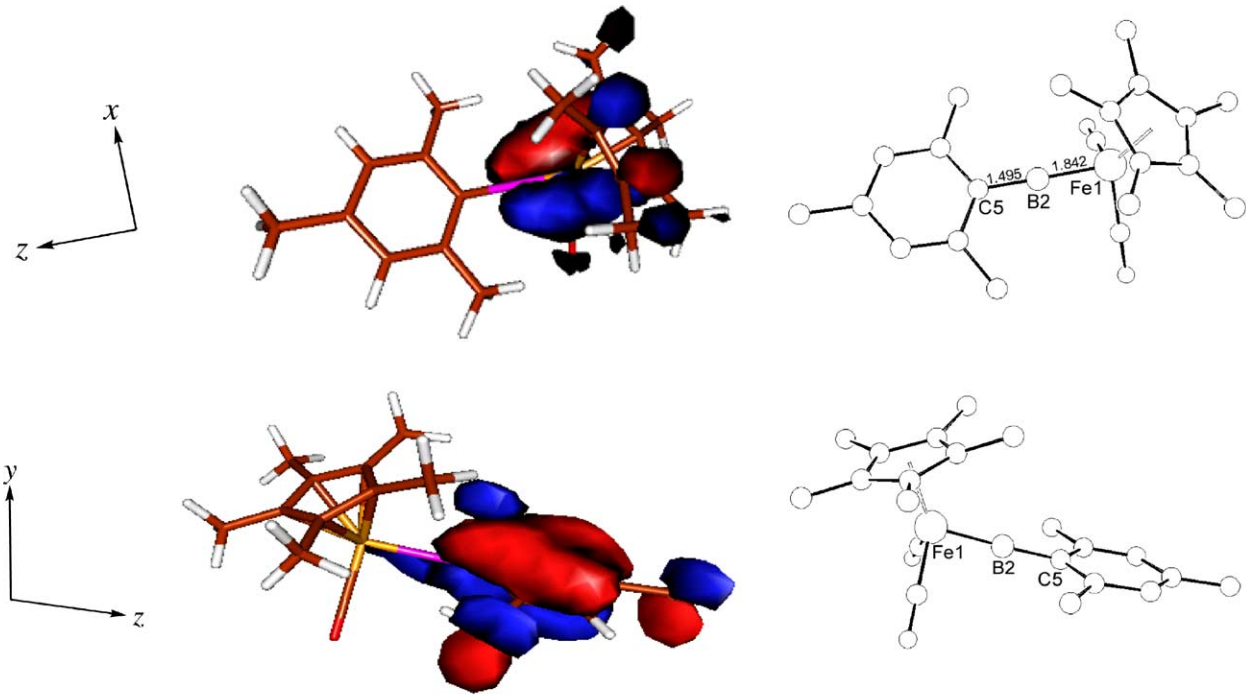


Fig. 15. DFT (BLYP/TZP) calculated HOMO-3 (top) and HOMO-9 (bottom) for $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BMes)]^+$ showing π interactions of the boron with adjacent iron and carbon centers.

respectively, the Fe–B π bond formed by the overlap of B p_x and Fe d_{xz} type orbitals and C–B π bonding utilizing the perpendicular B p_y orbital.

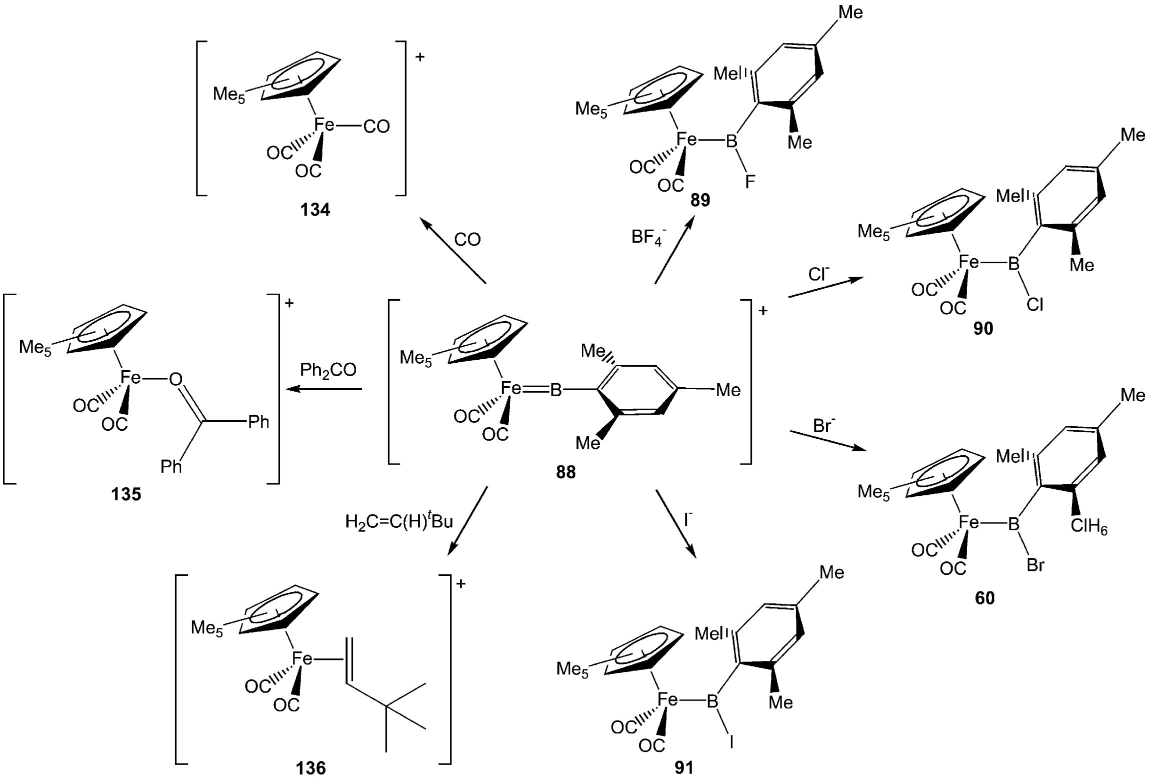
As such, the DFT calculations for **88** support a bonding model in which the interaction of the iron and boron centers consists of a B→Fe donor/acceptor σ component, supplemented by an Fe→B π back-bond (i.e. analogous to Fischer carbenes). In addition there is significant π interaction between the boron atom and the mesityl ring. Furthermore, the idea of π stabilization from both fragments attached to the two-coordinate boron center is corroborated by calculations performed on related derivatives. Thus, comparison of the Fe–B interaction in $[(\eta^5\text{-}C_5H_5)Fe(PMe_3)_2(BMes)]^+$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(BMes)]^+$ reveals a shorter Fe=B bond (1.798 Å versus 1.848 Å), longer B–C bond (1.530 Å versus 1.487 Å) and an enhanced FeB π contribution (45% versus 38%) for the more electron rich phosphine ligated system. In addition, variation in the π donor properties of X in $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BX)]^+$ (X: H, C_6F_5, Mes, NMe_2) results in a steady increase in the Fe=B bond length and accompanying reduction in the FeB π component (1.776, 1.813, 1.843, 1.869 Å and 45, 40, 38, 33%, repectively) [78].

5.2. Reactivity of cationic terminal borylene complexes

Studies of the reactivity of terminal borylene complexes are somewhat limited in number [9,16,18,19,71]. Braunschweig has demonstrated that bulky aminoborylene complexes of tungsten and chromium can act as photolytic transfer agents for the $BN(SiMe_3)_2$ ligand in the generation of novel terminal and bridged borylene complexes (Scheme 8). In addition, Roper and co-workers have shown that base-stabilized terminal borylene complexes maintain electrophilic character at the boron center and can undergo a variety of substitution reactions with nucleophilic reagents (Section 4.3) [16,18,19,71].

A number of computational studies have predicted significant boron-centered reactivity towards nucleophiles for terminal borylene complexes due to the high positive charge and LUMO amplitude at boron [41–43,45,46]. The likelihood of such reactivity for **88** would appear to be increased by the net positive charge on the molecule (and a calculated Mulliken charge at boron of +0.356) and we therefore set out to examine the reactivity of **88** with potential nucleophiles. In addition, given the similarities in electronic structure between **88** and cationic Fischer carbene complexes, and the known reactivity of such carbenes towards unsaturated molecules (see, for example [95]), we have also examined the reactivity of **88** towards multiply bonded substrates. The results of some preliminary studies are outlined in Scheme 20 and indicate that the primary forms of reactivity of this cationic borylene can be divided into two distinct types [62].

Firstly, reactivity towards anionic nucleophiles proceeds, as expected on the basis of computational predictions, via addition at the highly electrophilic boron center. This type of chemistry, exemplified for halide nucleophiles, represents a new synthetic route to asymmetric boryl complexes, and one which gives access to the complete range of halide substituted complexes $(\eta^5\text{-}C_5Me_5)Fe(CO)_2BX(Mes)$ (**60**,



Scheme 20.

89–**91**) which makes for instructive structural comparisons (Section 3.3.3). Reactivity towards unsaturated substrates primarily proceeds via borylene displacement. Thus, for example, reactions with reagents containing CO or CC multiple bonds proceeds via dissociation of the BMes ligand and formation of the corresponding cationic iron complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2\text{L}]^+[\text{BAr}^f_4]^-$ (**134**—L: CO; **135**—L: η^1-OCPh$_2$; **136**—L: η^2-H$_2$C=C(H)^{t}Bu) [62]. Given the strong binding energies predicted for borylene ligands to transition metal centers, the displacement of such a ligand by a ketone or alkene donor is at first sight somewhat surprising. In this case, we believe that the course of the reaction is driven by irreversible removal of the borylene ligand by insertion into the C–H bond of the solvent [62].

6. Conclusions

Although the synthetic and structural chemistry of haloboryl and related complexes has been relatively late to develop, the versatile reaction chemistry of these systems has been exploited in recent years to give access to a variety of novel transition metal complexes of boron. Hence, for example, substitution chemistry of an osmium dichloroboryl has led to the isolation of the first example of a base-stabilized terminal borylene complex, and mesityl(halo)boryl complexes of iron have been shown to be versatile substrates for the formation of three different types of borylene complex via a combination of substitution and abstraction chemistries. Notwithstanding this, functionalization chemistry of this type remains an area ripe for further exploration, and the syntheses of further examples of novel transition metal/group 13 complexes are sure to result.

Acknowledgements

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