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The coordination chemistry of boryl and borate substituted cyclopentadienyl ligands

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Contents

Abstract

In this article a summary is given of developments in the synthetic, structural and reaction chemistry of complexes containing boryl- and borate-substituted cyclopentadienyl ligands $[(\eta^5\text{-}C_5R_4BX_2)^-$ and $(\eta^5\text{-}C_5R_4BX_3)^{2-}]$.

Keywords: Boryl; Borate; Boron; Metallocene; Cyclopentadienyl; Lewis acid

1. Introduction and scope

Sandwich and half-sandwich compounds containing pendant boryl ($-BX_2$) functions have received a great deal of attention in recent years. Although initial reports of the synthesis of such compounds are now over 40 years old [1], the ever widening range of structural types and of chemical applications continue to excite much interest. Thus, for example, compounds of this type have found application as single component or *ansa*-bridged Group 4 olefin polymerisation catalysts [2–4], as precursors to organometallic polymers or oligomers with unusual electronic properties [5–8], as sensors of anions and neutral molecules [9], and in Boron Neutron Capture Therapy (BNCT) cancer treatment [10]. Compounds of this type have also proved to be fertile ground

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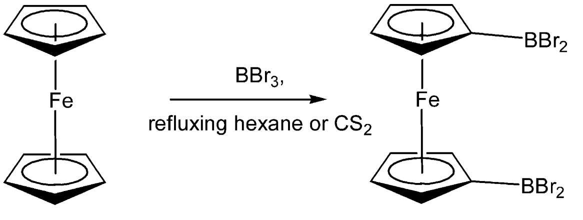
for the exploration of a number of fundamental structure/bonding and reactivity issues such as the extent of electronic communication via three-coordinate boron [11], the evaluation of sites of nucleophilicity in metallocene alkyl and hydride derivatives [12,13] and the change in electronic structure on bending of metallocene frameworks [14]. The vast majority of complexes containing these ligands belong to Groups 4 and 8, and some aspects of their chemistry have previously been reviewed [15–17].

This review is concerned with the chemistry of cyclopentadienyl metal complexes which feature pendant boryl ($-BX_2$) or borate ($-BX_3^-$) functions. Although much research effort has been expounded on compounds which contain these functional groups separated from the cyclopentadienyl unit by an alkyl or heteroatom spacer, this article is confined to those containing directly linked boryl or borate groups i.e. those that contain $(\eta^5\text{-}C_5R_4BX_2)^-$ or $(\eta^5\text{-}C_5R_4BX_3)^{2-}$ ligands. After a brief outline of the routes devised for the synthesis of borylcyclopentadienyl complexes, the review examines the chemistry and applications of such derivatives on a group by group basis.

2. Methods of synthesis

Synthetic routes to metal complexes bearing borylcyclopentadienyl ligands can be divided into two broad, but complementary approaches: (i) modification of the cyclopentadienyl ligand of an existing metal complex; and (ii) reaction of a boryl-containing ligand precursor with an appropriate transition metal halide, alkyl or amide. The former approach may involve direct borylation with an electrophilic borane halide (Schemes 1 and 2) [12,18], or reaction of a suitably metallated cyclopentadienyl ligand (typically containing a lithium, silicon or tin moiety) with a similar boron reagent (Schemes 3 and 4) [5,19]. In many cases, the resulting complex features a dihaloboryl unit which can be further derivatized by boron centred substitution chemistry. The use of metallocenophane precursors (Scheme 4) has been found to bring about borylation under significantly milder conditions than required for less strained metallocene precursors [19].



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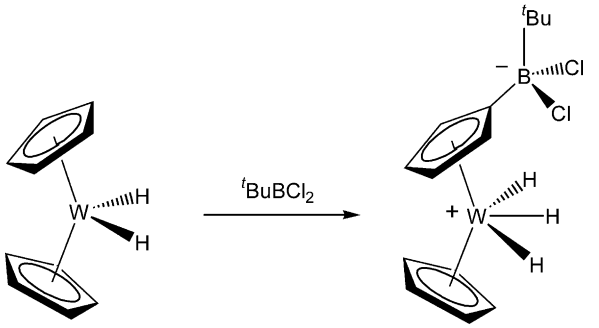
Scheme 1.



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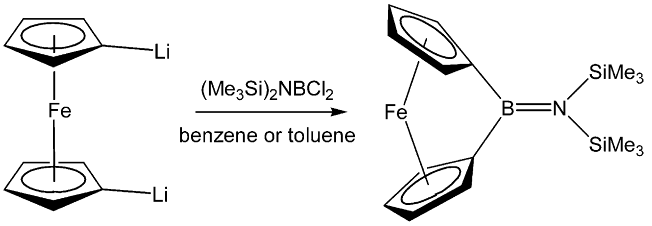
Scheme 2.



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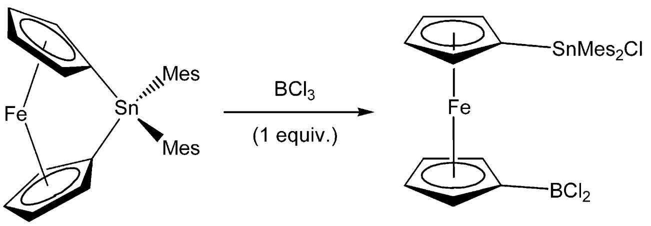
Scheme 3.



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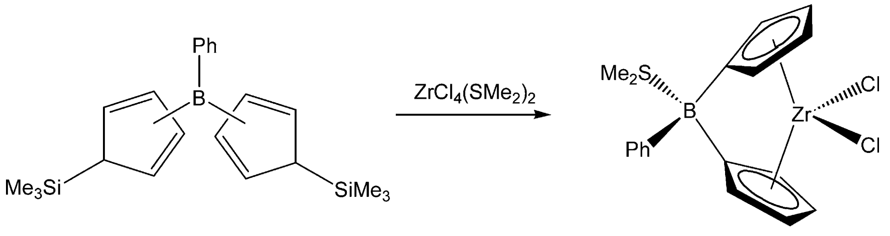
Scheme 4.

The alternative synthetic approach requires ready assembled borylcyclopentadienyl precursors of the type $C_5R_4HBX_2$, $C_5R_4(SiMe_3)BX_2$ or $(C_5R_4BX_2)^-$ [for metal complexes containing the $(\eta^5\text{-}C_5R_4BX_2)^-$ ligand] or $(C_5R_4HBX_3)^-$, $[C_5R_4(SiMe_3)BX_3]^-$ or $(C_5R_4BX_3)^{2-}$ [for metal complexes containing the borate functionalised $(\eta^5\text{-}C_5R_4BX_3)^{2-}$ ligand]. Neutral cyclopentadienyl species containing η^1-bound boryl and silyl substituents have been known for some time [20], and the use of such precursors in the synthesis of borylcyclopentadienyl metal complexes has been reported in a number of cases (Scheme 5) [21–23]. An alternative synthesis involves reaction of the alkali metal salt of a mono-anionic borylcyclopentadienide $M(C_5R_4BX_2)$ (M = Li, Na) [24–26] with the appropriate transition metal halide (Scheme 6) [27,28].

With certain exceptions [29], synthesis of the corresponding borate-functionalized complexes [containing



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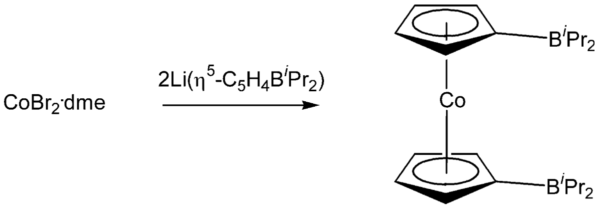
Scheme 5.



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Scheme 6.

the $(\eta^5\text{-}C_5R_4BX_3)^{2-}$ ligand] can be achieved from similar precursors. Thus, for example, reaction of $[Et_4N][C_5H_5B(C_6F_5)_3]$ with an appropriately basic Group 4 metal precursor such as $Zr(NMe_2)_4$ generates $\{[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Zr(NMe_2)_3\}^-$ (**7**) [30], and reaction of $NaLi[C_5H_4B(C_6F_5)_3]$ with $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ generates the zwitterionic complex $(\eta^5\text{-}C_5H_5)_2[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Zr$ (**8**) [31].

Although both synthetic approaches have found application for a wide range of metal complexes, borylation of existing cyclopentadienyl ligands has been most extensively applied to the stable 18 electron sandwich compounds of Group 8. This route, although synthetically convenient, is less generally applicable to cyclopentadienyl derivatives of other metals, and the use of pre-assembled borylcyclopentadienyl precursors has therefore found application, particularly for the single component and *ansa*-bridged catalysts of Group 4.

3. Derivatives containing Group 4 metals

Group 4 metal complexes containing boryl functionalised cyclopentadienyl ligands have received a great deal of recent attention owing to their exploitation in olefin polymerisation catalysis. These types of complex typically include derivatives containing pendant $-BX_2$ or $-BX_3^-$ moieties, as well as systems featuring a boron centre as part of an *ansa*-bridged ligand [16,17].

3.1. Species containing pendant BX_2 and BX_3^- units

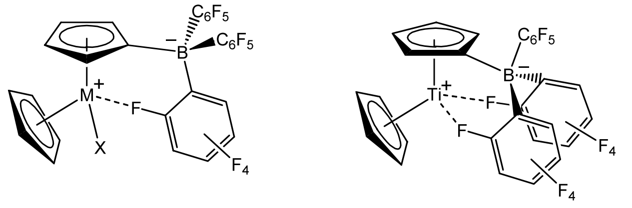
Although Group 4 complexes containing a borylcyclopentadienyl ligand have been known for some time [21], recent developments in the field have owed much to their potential to act as single component olefin polymerisation catalysts. The use of pendant boryl functionalities offers the potential for catalyst systems which obviate the need for external Lewis acid activation [32]. Within this field a number of systems have also been reported containing pendant boryl functions separated from the cyclopentadienyl ring by an alkyl or heteroatom spacer [33–37]. Within the scope of this review only directly linked boryl or borate functions are considered. The majority of complexes reported have been synthesised from pre-formed boron containing ligand precursors, although electrophilic attack at an existing cyclopentadienyl ligand has also been observed.

Initial work by both Reetz [2] and Bochmann [3] reported in 1995 revealed that Group 4 cyclopentadienyl complexes possessing pendant three- or four-coordinate boron functions could act as highly efficient olefin polymerisation catalysts in the presence of a suitable co-catalyst (triethylaluminium or methylalumoxane, MAO). Zirconium and hafnium complexes containing pendant four-coordinate borate functions were synthesised by the reaction of the appropriate metal halide with pre-formed $[C_5H_4B(C_6F_5)_3]^{2-}$ ligands [3]. A similar approach, making use of the mixed Na^+, Li^+ salt of $[C_5H_4B(C_6F_5)_3]^{2-}$ has been used by Erker in the synthesis of the zwitterionic analogue of the tris(cyclopentadienyl)zirconium cation, $(\eta^5\text{-}C_5H_5)_2[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Zr$ (**8**). The crystal structure of this interesting compound features a pronounced Zr–F–aryl interaction perpendicular to the near trigonal planar Zr-(ring centroid)$_3$ unit [31]. By contrast, the reaction of the mono-anionic precursors $Li[C_5H_4RB(C_6F_5)_3]$ (R = H, $SiMe_3$) with zirconium alkyls does not yield products containing the $[\eta^5\text{-}C_5H_3RB(C_6F_5)_3]^{2-}$ ligand, but rather leads to the elimination of the borate function and the synthesis of trimethylsilyl- or methylcyclopentadienyl complexes [29]. Interestingly, however, the $[Et_4N]^+$ salt of $[C_5H_5B(C_6F_5)_3]^-$ *does* react cleanly with $Zr(NMe_2)_4$, to generate $\{[\eta^5\text{-}C_5H_4B(C_6F_5)_3]\text{-}$

$Zr(NMe_2)_3\}^-$ (**7**), from which further halide and benzyl derivatives can readily be prepared [30].

Bochmann and co-workers have also reported the synthesis of cyclopentadienyl, indenyl and fluorenyl ligand precursors containing pendant three-coordinate $-B(C_6F_5)_2$ functions and their subsequent conversion to zirconium and titanium borylcyclopentadienyl and indenyl complexes [38]. The synthesis of $[\eta^5\text{-}C_5H_4B(C_6F_5)_2]TiCl_3$ (**9**), for example, from $TiCl_4$ and $C_5H_4(SiMe_3)B(C_6F_5)_2$ makes use of similar chemistry to that previously reported for the homo-bimetallic system $PhB[(\eta^5\text{-}C_5H_4)TiCl_3]_2$ (**10**) [23]. Interestingly Bochmann's complexes display ethylene polymerisation activity under conditions in which the parent $(\eta^5\text{-}C_9H_7)ZrCl_3$ and $(\eta^5\text{-}C_5H_5)TiCl_3$ are inactive. Furthermore, reaction of **9** with lithium cyclopentadienide or indenide results in the formation of the mixed sandwich compounds of the type $(ring)[\eta^5\text{-}C_5H_4B(C_6F_5)_2]TiCl_2$ (ring = $\eta^5\text{-}C_5H_5$ **11**, $\eta^5\text{-}C_9H_7$ **12**) [39]. In contrast to compound **9**, for which a structure of type **I** (Scheme 7) has been determined crystallographically, that of **12** features a $-B(C_6F_5)_2$ moiety acting as an intramolecular Lewis acid by coordinating one of the chloride ligands (type **II**) [38,39]. In solution **12** is fluxional, as the pendant $-B(C_6F_5)_2$ group switches between the two available chloride ligands. This contrast in behaviour is further emphasised by the corresponding amido and hydroxo derivatives $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4B(C_6F_5)_2]Ti(Cl)ER_n$ (ER_n = OH **13**, NH^tBu **14**) which also display intramolecular O or N coordination to the pendant boryl function [39].

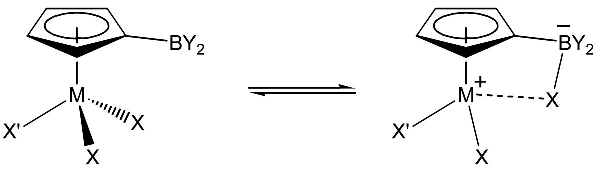
An alternative synthetic approach to using preformed borylcyclopentadienyl ligands is the direct borylation of an existing metallocene or half-sandwich complex. Although this method has been reported not to be widely applicable for earlier transition elements [40], there have been several examples reported for Group 4 derivatives. Erker and co-workers first reported the electrophilic borylation of a bent Group 4 metallocene in 1996 [41]. Initial reaction of the zirconacyclopentadiene $(\eta^5\text{-}C_5H_5)_2Zr(C_8H_{12})$ with tris(pentafluorophenyl)borane generates the zirconocene–betaine system **15a** featuring coordination of an *ortho* fluorine of one of the borate C_6F_5 groups (Fig. 1). Reaction with acetylacetone generates the corresponding acac derivative **15b** with elimination of tetramethylbutadiene [41]. A similar synthetic approach using $(\eta^5\text{-}C_5H_5)_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and tris(pentafluorophenyl)borane has been used to give access to the paramagnetic zwitterionic Ti(III) complex $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti$ (**16**) [42], which has solid state structure featuring two coordinated *ortho* fluorine substituents. Oxidation of this compound generates the dinuclear complex **15c** featuring two Ti(IV) centres linked via a bridging oxo moiety (Fig. 1) [43].



15a: M = Zr, X = $\eta^1\text{-}C_8H_{13}$
15b: M = Zr, X = κ^2-acac
15c: M = Ti, X = μ_2-O

16

Fig. 1. Titanium and Zirconium sandwich complexes featuring coorination of *ortho* fluorines of pendant-$B(C_6F_5)_3^-$ functions.



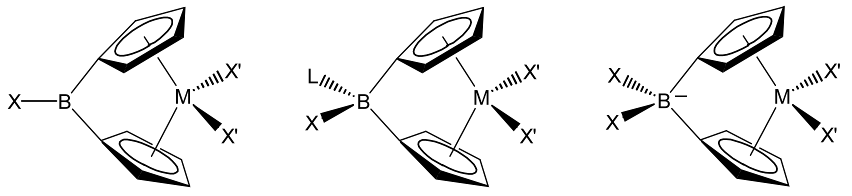
I **II**

Scheme 7.

3.2. *Ansa*-bridged metallocenes

Given that Group 4 metallocenophanes containing a variety of bridging atoms have been shown to be highly selective olefin polymerisation catalysts a natural extension of this approach is the incorporation of a Lewis acidic centre, such as boron in the bridging position. Initial reports describing the synthesis of bora-*ansa*-metallocenes were made by Rufanov et al. [4,44]. However, such complexes were first structurally characterized by Shapiro as late as 1997 [16,22,45], with further examples having been demonstrated recently by Braunschweig [46,47], Ashe [48], Reetz [49] and Bochmann [50]. Generally complexes conform to one of two structural types containing either a three- (**III**) or four-coordinate boron centre (**IV** and **V**) (Fig. 2).

In 1996, Shapiro and co-workers described the synthesis of the ligand precursor $PhB(C_5H_4SiMe_3)_2$ [23] and its reaction with $TiCl_4$ to generate the structurally characterized bimetallic system $PhB[(\eta^5\text{-}C_5H_4)TiCl_3]_2$ (**10**). The corresponding reaction with $ZrCl_4(SMe_2)_2$ generates the type **IV** neutral *ansa*-bridged zirconocene species $[Ph(Me_2S)B(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ (**5**) from which $[Ph(Me_3P)B(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ can then be formed by reaction with PMe_3 [22]. NMR measurements indicate that the lability of the boron-bound Lewis base is reduced by the use of stronger donors (e.g. PMe_3 rather than SMe_2) or more electrophilic boron bridges [e.g. $B(C_6F_5)$ rather than BPh] [16]. Tighter binding of the base in the case of the phosphine adduct is thought to be responsible for improved stability of the boron bridge to nucleophilic attack, thereby permitting alkylation of the zirconium centre and exploitation of



III **IV** **V**

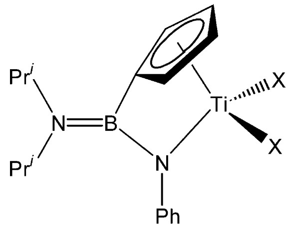
Fig. 2. Types of structurally characterized group 4 ansa-bridged metallocene featuring boron in the bridging position.

the resultant dialkylzirconocene in olefin polymerisation catalysis. Thermodynamically, even in the case of the more weakly bound Me_2S (or ^tBuNC) species, chemical abstraction of the B-coordinated Lewis base has been shown to be difficult, being only partially accomplished through the use of $B(C_6F_5)_3$ [16,45]. Consequently the conversion of base-stabilised type **IV** species into their more electrophilic type **III** counterparts has not been synthetically utilized.

A similar series of *chiral* type **IV** bis(indenyl) derivatives featuring B-coordinated OEt_2, thf or PMe_3 ligands has been reported by Reetz [49]. The nature of the donor function has been found to be vital to the activity of such species as propylene polymerisation catalysts.

Anionic borate-bridged Group 4 metallocenes (**V**) have attracted much interest as potential precursors to zwitterionic catalysts (type **VI**) by alkylation and alkyl anion abstraction (Scheme 8).

Reaction of $[Ph(Me_2S)B(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ (**5**) with Cp^*_2AlMe or [PPN]Cl has been reported by Shapiro to generate the anionic borate-bridged species $\{[Ph(Me)B(\eta^5\text{-}C_5H_4)_2]ZrCl_2\}^-$ (**17**) and $\{[Ph(Cl)B(\eta^5\text{-}C_5H_4)_2]ZrCl_2\}^-$ (**18**), respectively [16]. Complexes of this type have also been reported by Lancaster and Bochmann [50]. The anionic complex $\{[Ph(C_6F_5)B(\eta^5\text{-}C_5H_4)_2]Zr(C_6F_5)_2\}^-$ (**19**) has been formed by the reaction of **5** with three equivalents of LiC_6F_5, and selectively methylated with $AlMe_3$ to give $\{[Ph(C_6F_5)B(\eta^5\text{-}C_5H_4)_2]ZrMe_2\}^-$ (**20**). Similar chemistry gives access to $\{[(C_6F_5)_2B(\eta^5\text{-}C_5H_4)_2]Zr(C_6F_5)_2\}^-$ (**21**) and $\{[(C_6F_5)_2B(\eta^5\text{-}C_5H_4)_2]ZrMe_2\}^-$ (**22**) which can be shown to be useful ethylene polymerisation catalysts in the presence of a suitable activator [50].



25a: X = Cl
25b: X = NMe_2

Fig. 3. Constrained geometry titanium cyclopentadienly/amido complexes featuring a bridging boron atom.

The first structurally characterized examples of type **III** bora-metalloceneophanes containing a three-coordinate bridging boron centre were reported by Braunschweig [46,47,51] and by Ashe [48] in 1999. Sterically bulky and π-electron releasing amido substituents {$X = N(SiMe_3)_2$ [46,47]; $X = N^iPr_2$ [48]} were exploited to yield BX bridged cyclopentadienyl and indenyl derivatives of titanium, zirconium and hafnium. Both $[(^iPr_2N)B(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ (**23**) and $[(^iPr_2N)B(\eta^5\text{-}C_9H_6)_2]ZrCl_2$ (**24**) were reported to be highly active

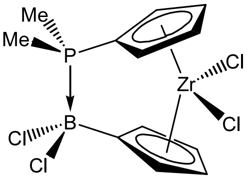


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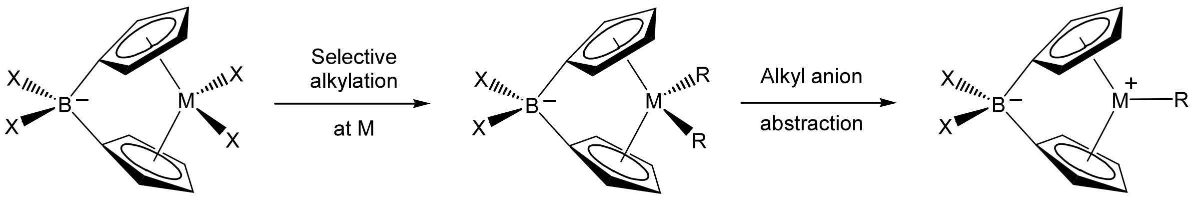
Fig. 4. Structure of a novel ansa-zirconocene featuring a bridging P → B donor/acceptor linkage.



V **VI**

Scheme 8.

olefin polymerisation catalysts in the presence of excess MAO co-catalyst. Of related interest are the 'constrained geometry' titanium complexes **25a** and **25b** (Fig. 3) synthesised via similar methodology, which (in the case of X = Cl) are also shown to be effective ethylene polymerisation catalysts in the presence of MAO [52]. ^{i}Pr$_2$NB-bridged constrained geometry indenyl/carboranyl complexes of lanthanides, containing a similar structural motif have recently been reported by Xie [26].

Ansa-bridged metallocenes featuring boron centres as part of a larger bridging system have also been reported. As part of an extended study, Reetz and co-workers reported the synthesis and structural characterization of the zirconocene derivative $\{O[B(OEt)(\eta^5\text{-}C_5H_4)]_2\}ZrCl_2$ (**26**) [2]. In addition, Starzewski has reported the synthesis, structural characterization and catalytic activity of the novel zirconocene complex **27** featuring a donor/acceptor P → B *ansa*-bridge (Fig. 4). NMR measurements confirmed the retention of the donor/acceptor bond in solution and the compound proved to be an effective and thermally robust olefin polymerisation catalyst [53].

4. Derivatives containing metals from Groups 5–7

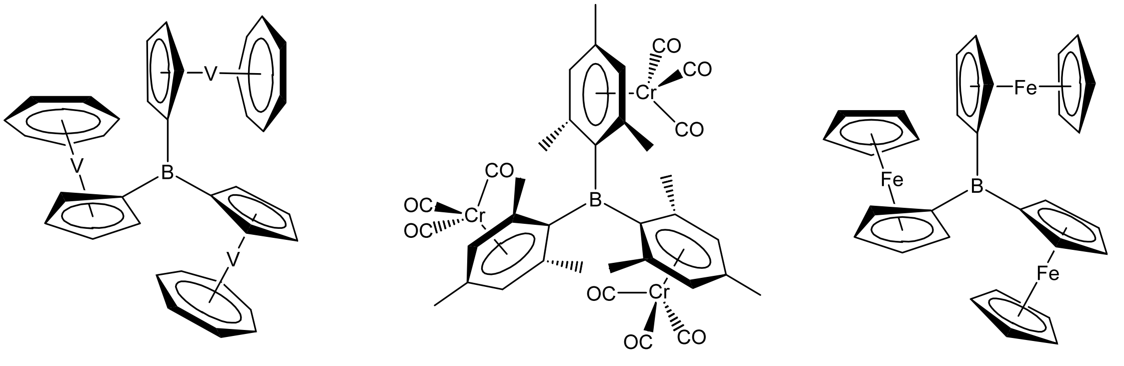
The chemistries of Group 5, 6 and 7 metal complexes containing borylcyclopentadienyl ligands are considerably less developed than those of their Group 4 and Group 8 counterparts, despite initial reports of the borylation of cymantrene, for example, dating from 1976 [18,54]. The work that has been done has provided answers to fundamental questions of structure and bonding. These include investigation of the possibility for electronic communication via three-coordinate boron, and the relative reactivity of sites of nucleophilicity in metallocene hydride and alkyl compounds.

4.1. Group 5

Borylcyclopentadienyl derivatives of the Group 5 metals are few and far between. Those complexes reported have usually been synthesised by the reaction of an existing cyclopentadienyl metal complex with an appropriate electrophilic borane.

One of the principal questions posed by organometallic systems featuring two or more metal arene or cyclopentadienyl fragments linked by a three-coordinate boron centre is the possibility for electronic communication between metal centres via trigonal boron [11,55–59]. This question has been addressed by Elschenbroich and co-workers in a series of papers examining boron-linked chromium arene [58,59] or cyclopentadienyl vanadium fragments (e.g. **28** and **29**, Fig. 5) [11,59]. Reaction of chromium hexacarbonyl with trimesitylborane in the appropriate stoichiometry generates the structurally characterized complexes $[(OC)_3Cr(\eta^6\text{-Mes})]_nB(Mes)_{3-n}$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$; $n = 1$, 2, 3). A combination of EPR, UV/vis and electrochemical studies were undertaken, the latter attesting to a weak electronic interaction between Cr(CO)$_3$ moieties. The sensitive nature of EPR spectroscopy as a probe of electronic communication and the paramagnetic nature of the parent compound trovacene, $(\eta^7\text{-}C_7H_7)V(\eta^5\text{-}C_5H_5)$, led the same group to investigate a series of (5-trovacenyl)boranes $[(\eta^7\text{-}C_7H_7)V(\eta^5\text{-}C_5H_4)]_nBMes_{3-n}$ ($n = 1$, 2, 3). Mono-lithiation of trovacene at the cyclopentadienyl ring followed by addition of the appropriate boron halide Mes$_{3-n}$BF$_n$ ($n = 1, 2, 3$) leads to the isolation of the propeller shaped molecules in reasonable yield [11]. EPR studies for both the ditrovacenyl diradical ($n = 2$) and the tritrovacenyl triradical ($n = 3$) point to an extensive exchange interaction which is significantly diminished on quaternization at boron.

Direct borylation of cyclopentadienyl systems by electrophilic boranes has been demonstrated for niobium. As part of a larger study on the reaction of



28 **29** **30**

Fig. 5. Boron-linked tri-metallocene derivative of vanadium (**28**), chromium (**29**) and iron (**30**).

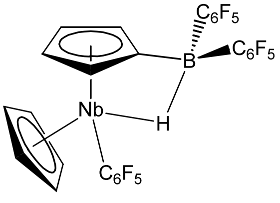


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Fig. 6. Structure of one of the niobocene derivatives reported by Shore from the reaction of niobium organohydroborates with tris(pentafluorophenyl)borane.

metallocene hydrides with electrophilic boranes, Shore and co-workers have reported that the reaction of niobocene cyclic organohydroborates $(\eta^5\text{-}C_5H_5)_2Nb(\mu\text{-}H)_2BR_2$ with tris(pentafluorophenyl)borane is solvent dependent [60]. In the case of toluene or diethyl ether media, attack of the borane at the cyclopentadienyl ligand is observed. In addition, loss of one C_6F_5 moiety from the boron centre occurs, and there is a strong interaction between the resultant pendant $-B(C_6F_5)_2$ group and one of the hydride ligands bound to Nb. The complex isolated from the reaction in ether (**31**) has a structure reminiscent of those reported by Bochmann for similar Ti(IV) sandwich compounds (Fig. 6) [39].

4.2. Group 6

A number of groups have reported the synthesis of Group 6 complexes containing borate-functionalised cyclopentadienyl ligands. In each case these ligands result from attack at an existing cyclopentadienyl ring by a strongly electrophilic borane.

Braunschweig and co-workers instigated the first of several reactivity studies of tungstenocene dihydrides with electrophilic boranes, finding that the principal product is not a donor/acceptor adduct of the type $(\eta^5\text{-}C_5H_5)_2WH_2\cdot BX_3$ as had previously been postulated [61]. Depending on the nature of the borane, the principal products are either zwitterionic species of the type $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4(BX_nR_{3-n})]WH_3$ [BX_nR_{3-n} = ${}^tBuBCl_2$ **2**, ${}^iPrBCl_2$ **32**, $B(C_6F_5)_3$ **33**, or $B(NMe_2)(CF_3)_2$ **34**] resulting from attack at one of the cyclopentadienyl ligands [12,62], or borate salts of the $[(\eta^5\text{-}C_5R_5)_2WH_3]^+$ cation [62,63]. Thus the reaction of $(\eta^5\text{-}C_5H_5)_2WH_2$ with ${}^iPr_2BCl$, BCl_3 or BF_3, or of $(\eta^5\text{-}C_5Me_5)_2WH_2$ with $B(C_6F_5)_3$ or ${}^tBuBCl_2$ leads to the formation of salts of the type $[(\eta^5\text{-}C_5R_5)_2WH_3]^+[\text{borate}]^-$ (R = H, Me) [62,63].

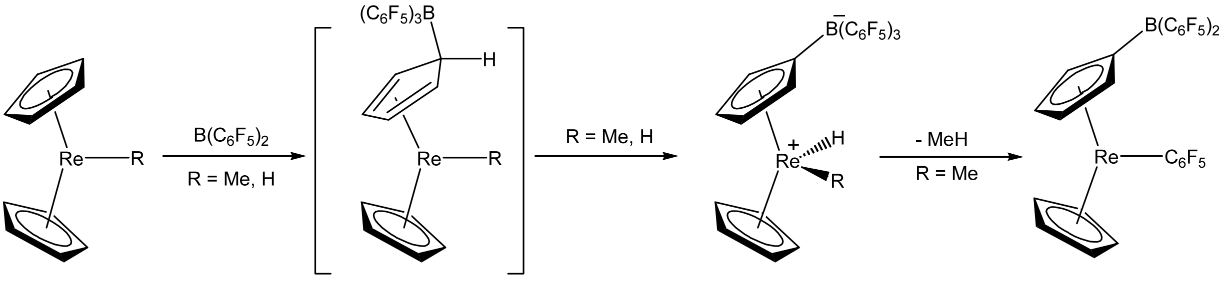
A similar type of reactivity has been postulated by Hartwig to account for the formation of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4BX_2)WH_2$ ($X_2 = Ph_2$ **35**, $1,2\text{-}O_2C_6H_4$ **36**) as the major products from the reactions of $[(\eta^5\text{-}C_5H_5)_2W(H)Li]_4$ and the electrophilic borane Ph_2BCl, and from the reaction of $(\eta^5\text{-}C_5H_5)_2W(H)(BO_2C_6H_4)$ (**37**) with a catalytic quantity of B-chlorocatecholborane [64]. Analogous reactivity in the molybdenum system $[(\eta^5\text{-}C_5H_5)_2Mo(H)Li]_4$ has also been reported by Lappert and co-workers [65].

Green and co-workers have probed mechanistic details of similar chemistry in an extended study of the reactivity of the highly electrophilic boranes $B(C_6F_5)_2X$ (X = C_6F_5, Ph, H, Cl) with hydrido and alkyl derivatives of Group 5–7 metals [13]. The reaction of $(\eta^5\text{-}C_5H_5)_2WH_2$ with $B(C_6F_5)_2X$ is thought to proceed via initial exo-addition of the borane to one of the carbons of the cyclopentadienyl ring to give a 16-electron d^2 intermediate featuring an η^4 bound $C_5H_5B(C_6F_5)_2X$ ligand. Oxidative addition of the endo C–H linkage then yields the 18-electron d^0 zwitterionic complex $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4B(C_6F_5)_2X]WH_3$ (**38**), which has been crystallographically characterized in the case of X = Cl. By contrast, the analogous reactions with $(\eta^5\text{-}C_5H_5)_2MoH_2$ and $(\eta^5\text{-}C_5H_5)_2TaH_3$ yield products resulting from attack at a metal-bound hydride rather than at the cyclopentadienyl ligand. The authors postulate that these differences are due to the decreased tendency for the metal centre to undergo the C–H oxidative addition step implicit in initial attack at the cyclopentadienyl ligand. For molybdenum this reflects greater difficulty in oxidizing a 5d rather than 6d metal, for tantalum the fact that the metal already has a d^0 configuration [13].

Finally, recently reported studies have yielded the first crystallographically characterized borylcyclopentadienyl complexes of chromium [66]. Reaction of the *ansa*-bridged species $[(Me_2C)_2(\eta^5\text{-}C_5H_4)_2]CrCO$ with $[H(OEt_2)_2][B(C_6F_5)_4]$ leads to the formation of the zwitterionic species $\{(Me_2C)_2(\eta^5\text{-}C_5H_4)[\eta^5\text{-}C_5H_4B(C_6F_5)_3]\}Cr(CO)H$ (**39**) containing a pendant $-B(C_6F_5)_3^-$ moiety. On heating this compound to 80 °C two new products are isolated, one of which, $\{(Me_2C)_2(\eta^5\text{-}C_5H_4)[\eta^5\text{-}C_5H_4B(C_6F_5)_3]\}Cr$ (**40**), features coordination of the pendant $-B(C_6F_5)_3^-$ group to the cationic chromium centre through two Cr–F–aryl linkages. This structure is reminiscent of that observed previously for a similar zwitterionic Ti(III) species (**16**, Fig. 1) [42].

4.3. Group 7

Despite the fact that the mono- and di-borylation of cymantrene, $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and methyl-cymantrene, $(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$, by BI_3, BBr_3, $PhBI_2$ and $MeBI_2$ were reported along with that of ferrocene by Siebert and co-workers in 1976 [18,54], the chemistry of Group 7 complexes containing borylcyclopentadienyl ligands remains a little investigated area. Methylation, amination and halide exchange reactions of $(\eta^5\text{-}C_5H_3RBI_2)Mn(CO)_3$ (R = H **41**, Me **42**) were reported in the original papers [18,54], and the conversion of the corresponding dibromoboryl derivatives into cyman-



43: R = H **44**

Scheme 9.

trene functionalised tris(1-pyrazolyl)borates has been reported recently by Wagner [67]. The coordination chemistry of these ligands with respect to Tl(I) has also been investigated, with the crystal structures of the cymantrene and methyl-cymantrene derivatives displaying polymeric and cyclic tetrameric structures, respectively.

The reaction of tris(pentafluorophenyl)borane with (η^5-$C_5H_5)_2$ReH and (η^5-$C_5H_5)_2$ReMe has also been reported by Green and co-workers [13]. In the case of (η^5-$C_5H_5)_2$ReH, electrophilic borylation of the cyclopentadienyl ring yields the zwitterionic product (η^5-C_5H_5)[η^5-$C_5H_4B(C_6F_5)_3$]ReH_2 (**43**). By contrast reaction with (η^5-$C_5H_5)_2$ReMe yields (η^5-C_5H_5)[η^5-$C_5H_4B(C_6F_5)_2$]Re(C_6F_5) (**44**). The initial steps proposed for both reactions are similar (Scheme 9), with the contrasting products presumably reflecting the differing propensities for methane or dihydrogen elimination from Re(V) [13].

Finally, synthesis of boryl-derivatized rhenium half-sandwich compounds from rhenium halides and mono-anionic ligand precursors has been demonstrated in at least one instance. The 1-borylindenyl complex (η^5-1-BpinC_9H_6)Re$(CO)_3$ (**45**) (pin = $OCMe_2CMe_2O$) has been synthesized from [Re$(CO)_3$(thf)Br]$_2$ and Li(1-BpinC_9H_6) [68].

5. Derivatives containing Group 8 metals

Among the transition elements, borylcyclopentadienyl compounds of the Group 8 metals are by far the most numerous. In part this relates to the ready borylation of Group 8 metallocenes, a reaction which can be carried out selectively to generate mono-, 1,1′-bis, 1,3,1′-tris- and 1,3,1′,3′-tetrakis- borylated derivatives. Typically this reaction generates dibromoboryl complexes, upon which a range of further boron centred functionalization chemistry can be carried out. Hydrolysis and subsequent esterification chemistry gives access to boronic acid and boronic ester derivatives which find widespread application in sensors (Section 5.2). Substitution by nitrogen-containing bases gives rise to a wide range of complexes which themselves find uses as ligands, as novel electronic devices and as metal containing polymers and oligomers (Sections 5.3, 5.4, 5.5 and 5.6). Similar chemistry can also give access to [n]ferrocenophanes ($n \geq 3$), although alternative synthetic routes involving lithioferrocenes are required for the synthesis of the more strained species incorporating only one or two bridging atoms (Section 5.5).

Reflecting the depth of published work in this area, this section has been sub-divided to reflect the diversity of structural types and applications of Group 8 metallocenes containing pendant $-BX_2$ and $-BX_3^-$ groups.

5.1. Haloboryl and related systems

The first reports of the direct borylation of ferrocene date from the 1960s [69–71]. Kotz and Post reported that the reaction of B_2Cl_4 with ferrocene in hexane generated the mono-borylated species (η^5-C_5H_5)(η^5-$C_5H_4BCl_2$)Fe (or FcBCl_2, **46**) which was characterized spectroscopically, along with the trimethylamine adduct (η^5-C_5H_5)(η^5-$C_5H_4BCl_2 \cdot NMe_3$)Fe (**47**) [70]. Further studies by the same authors subsequently probed mechanistic details of the reaction of ferrocene with B_2Cl_4, and also reported that the reaction of (η^5-C_5H_5)(η^5-C_5H_4HgCl)Fe with BCl_3 or of ferrocene itself with BCl_3 or $HBCl_2$ can also be used to give access to **46** [72].

Borylations with BBr_3 and BI_3 are generally more facile than the analogous reactions with BCl_3 and the corresponding syntheses of dibromoborylferrocene (FcBBr_2, **48**) and diiodoborylferrocene (FcBI_2, **49**) from BBr_3 and BI_3, respectively were reported by Siebert and co-workers [54,73]. The conversion of these complexes into fluoro- or chloroboryl derivatives (by reaction with AsX_3, X = F, Cl), into mono- and dialkylboryl species (by reaction with Me_4Sn) or into heteroatom stabilised derivatives (by reaction with diethyl ether, dimethyl disulfide or dialkyl amines) was also reported [54]. Such chemistry gives access to fluoroboryl derivatives of ferrocene, which are otherwise inaccessible by direct borylation, and which consequently remain few in number [74].

Polyborylated derivatives of ferrocene, ruthenocene and osmocene have also been reported [18,75–81]. The synthesis of $(\eta^5\text{-}C_5H_4BBr_2)_2Fe$ [or 1,1′-$Fc(BBr_2)_2$, **1**] was initially reported by Siebert [18]. Furthermore, reaction of ferrocene with an excess of BBr_3 or BI_3 has been reported to yield a mixture of the tri- and tetraborylated species 1,3,1′-$Fc(BX_2)_3$ (X = Br **50**, I **51**) and 1,3,1′,3′-$Fc(BX_2)_4$ (X = Br **52**, I **53**). These reactions proceed via the known intermediates $FcBX_2$ (X = Br **48**, I **49**) and 1,1′-$Fc(BX_2)_2$ (X = Br **1**, I **54**), although evidence for the formation of small quantities of 1,3-$Fc(BX_2)_2$ (X = Br **55**, I **56**) was also presented [75]. Subsequently the clean, high yielding syntheses of 1,3,1′,3′-tetraborylated metallocenes have been reported by Nöth and co-workers using neat BBr_3 [78]. Furthermore, triborylated derivatives are also accessible under similar conditions by using a mono-alkylated ferrocene precursor (thereby generating a 1-alkyl-1′,3,3′-triboryl ferrocene, **57**) [15] (Fig. 7).

In general, these reactions require heating in refluxing solvents such as hexane or CS_2. A milder, room temperature borylation procedure has recently been reported by Manners and co-workers, making use of sila- and stanna-substituted ferrocene precursors (Section 5.6) [19,82,83]. The use of an alternative synthetic route to alkyl-, amido- and halo-boryl substituted ferrocenes, starting from mono- and dilithioferrocene has also been reported [76]. However, only in cases where the borane precursor is part of a mono- or bicyclic system or features a bulky dialkylamido substituents was a clean reaction observed. Finally, although the overwhelming majority of synthetic routes to iron systems feature reaction at an existing cyclopentadienyl ligand, work on related indenyliron systems by Frange and Herberich has demonstrated that both homoleptic and mixed sandwich complexes can be synthesized from ready-assembled borylindenide precursors [68].

As has been alluded to, bromoboryl derivatives of ferrocene have proved to be extremely versatile substrates in the synthesis of further boryl-substituted ferrocenes [18,54,76,84,85]. Hence for example, the use of such compounds in the synthesis of boronic acids, ferrocene functionalised ligand systems, boronium salts, ferrocenophanes and metal containing polymeric and oligomeric species is dealt with in the appropriate section below.

More recent interest in dihaloboryl derivatives of ferrocene, ruthenocene and osmocene has revolved around the prospect of a direct interaction between the metal and boron centres analogous to that found in α-metallocenyl carbocations. Initial studies made use of a comparison of ^{11}B- and ^{13}C-NMR spectroscopic parameters [86–88], but more recent work has exploited a combination of crystallographic and computational approaches [77–79]. Two papers appearing in 1995 reported crystallographic data which pointed towards the existence of a weak metal to boron interaction for dibromoboryl metallocenes [77,78]. The crystal structure of 1,1′-$Fc(BBr_2)_2$ (**1**) features trigonal planar boryl moieties which lie out of the plane of the cyclopentadienyl ligands such that the angle β (Fig. 8) is equal to 10.2° [77]. This angle is smaller than that found in typical α-ferrocenyl carbocations ($\beta = 14–21°$) but is in stark contrast to the corresponding angles found in the bis(diisopropylamino)boryl derivative 1,1′-$Fc[B(N^iPr_2)_2]_2$ (**58**) [77], in triferrocenylborane (**30**) [55] and in 2,4,6-triferrocenyl-1,3,5,2,4,6-triselenatriborinane (**59**) [89], all of which have $\beta \approx 0°$. The authors concluded that a strongly Lewis acidic boron centre is required in order to induce even a relatively weak metal to boron interaction. Similar results have been reported for the tetra-borylated ferrocene 1,3,1′,3′-$Fc(BBr_2)_4$ (**52**)

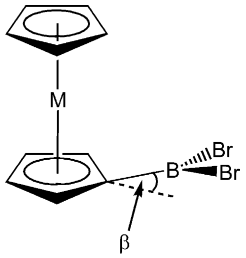
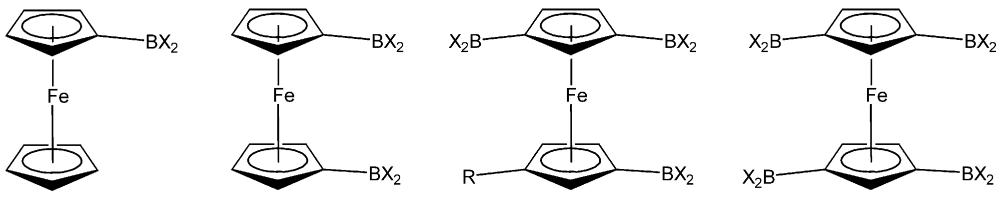


Fig. 8. Definition of the angle, β, reflecting bending of the pendant BBr_2 moiety out of the plane of the cyclopentadienyl ligand.



46: X = Cl
48: X = Br
49: X = I

1: X = Br
54: X = I

50: X = Br, R = H
51: X = I, R = H
57: X = Br, R = Me

52: X = Br
53: X = I

Fig. 7. Dihaloboryl derivatives of ferrocene.

and its ruthenocene (**60**) and osmocene (**61**) analogues [78]. The crystal structures of these molecules reveal two distinct β angles, one associated with each of the BBr_2 groups attached to a given cyclopentadienyl ring. One of the β values remains constant for **52**, **60** and **61** (ca. 7°), whereas the other shows a marked increase on going to the heavier metal (1.5 for **52**, 12.6° for **61**) [78]. More recent structural and computational investigation of $FcBBr_2$ (**48**) has revealed an even more pronounced bending in the mono-borylated compound ($\beta =$ ca. 18°). Furthermore, the electronic origins of this effect were found to lie in a donor/acceptor interaction between filled d-type orbitals at iron and the empty boron centred p orbital [79]. A recent Mössbauer study is in agreement with these findings, suggesting that in both **1** and **48**, electron donation to the boron centre occurs through interaction of the vacant p orbital with the iron-centred e_2 orbital [90].

The chemical significance of this type of interaction has been emphasized in a recent paper by Piers and co-workers [91]. The Fe–B interaction reported for $FcB(C_6F_5)_2$ (**62**) [$\beta = 16°$, d(Fe–B) = 2.924 Å] is sufficiently strong to cause a noticeable reduction in the Lewis acidity of the boron centre. Hence in contrast to $B(C_6F_5)_3$, $FcB(C_6F_5)_2$ does not strongly bind acetone, thf or acetonitrile. Oxidation of the iron centre reduces the extent of the Fe–B interaction such that the putative intermediate $[FcB(C_6F_5)_2]^+$ formed by the reaction of $FcB(C_6F_5)_2$ with [NO][BF_4], abstracts fluoride from BF_4^- to yield the zwitterionic product $[FcB(C_6F_5)_2F]$ (**63**).

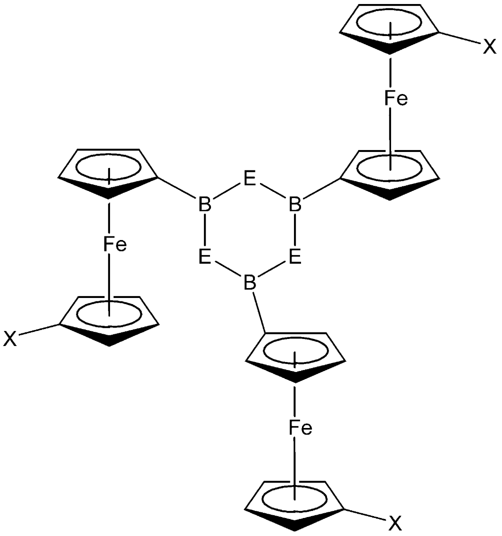
The influence of the strongly electron withdrawing $-B(C_6F_5)_2$ moiety is manifested in an oxidation potential for $FcB(C_6F_5)_2$ which is shifted +450 mV with respect to that of ferrocene. Quaternization of the boron centre by the use of a strongly donating ligand such as PMe_3, however, reverses this effect such that the $-B(C_6F_5)_2 \cdot PMe_3$ unit is a net electron donor ($E_{1/2}$ shifted −100 mV relative to ferrocene). Similar chemistry has been exploited to give access to the analogous bifunctional derivative 1,1′-$Fc[B(C_6F_5)_2]_2$ (**64**) [92,93]. UV/vis data for this compound indicate an Fe–B interaction similar to that found for **62**, although **64** is found to be an appreciably stronger Lewis acid, as manifested by its ability to abstract methide from $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ and to form complexes with weak donors such as acetonitrile.

5.2. *Boronic acids, cyclic boronic anhydrides and related systems*

In recent years boronic acids have been used extensively both in synthetic chemistry (typically in C–C bond-forming reactions, [94]) and in analytical applications. In particular, extensive use has been made of boronic acids in the sensing of saccharides [95,96]. The chemical robustness and well-defined electrochemical response of the ferrocene moiety has made the involvement of ferroceneboronic acids in these spheres of chemistry highly desirable. An overview of the synthetic chemistry and applications of such species is therefore outlined below.

Boronic acids of ferrocene have been known for over 40 years [1]. The continued use of such compounds and related derivatives today [and indeed the commercial availability of ferroceneboronic acid, $FcB(OH)_2$, **65**] owes much to their exploitation in molecular and ion sensors and in coupling reactions. Early syntheses of **65** utilized a variety of synthetic approaches [1,56,69,97–100], including the reaction of ferrocenyllithium (FcLi) with trialkylborates, followed by hydrolysis, and direct borylation of ferrocene with BCl_3, again followed by hydrolysis. Yields in either case typically were of the order of 40% [69,97]. At this stage, the quest for boronic acid derivatives of ferrocene owed much to their ready conversion to further ferrocene derivatives (e.g. by reaction with copper(II) halides to yield ferrocenyl halides [1,69,98,101,102]).

Subsequent work by a number of groups suggested alternative synthetic routes involving the reaction of BBr_3 with either FcHgBr, Fc_2Hg or ferrocene itself [103–105]. Although the yields obtained were typically only modest, the direct borylation of ferrocene with BBr_3 (followed by alkaline work up) appeared to avoid problems of contamination with 1,1′-$Fc[B(OH)_2]_2$ (**66**), inherent in lithiation routes [104]. An improved, selective synthesis of **66** has subsequently been reported by



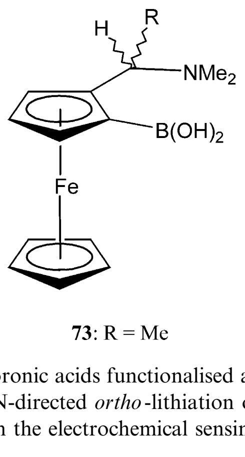
59: E = Se, X = H
69: E = O, X = SPh
70: E = O, X = H
71: E = NH, X = H

Fig. 9. Triferrocenylboroxine and related derivatives containing B_3E_3 rings (E = O, N, Se).

Knapp and Rehahn, using a modifed lithiation route [100].

In addition to the parent boronic acids, early work also examined the corresponding anhydride, triferrocenylboroxine $(FcBO)_3$ (**67**), as well as diferrocenylborinic acid Fc_2BOH (**68**) [56]. Recently the crystal structure of **67** and several related derivatives containing ferrocene-functionalised cyclic B_3E_3 rings have been reported (Fig. 9) [89,106,107]. Reaction of the triethylamine adduct of (dibromoboryl)ferrocene with bis(trimethylsilyl)selenane yields 2,4,6-triferrocenyl-1,3,5,2,4,6-triselenatriborinane (**59**) [89]. The crystal structure of this compound shows it to contain a nearly planar B_3Se_3 ring, and the electronic structure of the related model compound $Ph_3B_3Se_3$ was probed by computational methods. The cyclic boronic anhydride 2,4,6-tris(1′-phenylthio-1-ferrocenyl)boroxin (**69**), on the other hand, is formed by dehydration of the corresponding boronic acid [106]. Hydrolysis of the central B_3O_3 ring by aqueous base regenerates the parent boronic acid required for Suzuki type coupling [108]. The crystal structures of the parent $(FcBO)_3$ (**70**) and the closely related triferrocenylborazine (**71**) were reported by Wagner as late as 2001 [107]. In each case intermolecular C–H···π interactions are observed in the solid state and are enhanced at low temperature.

Synthetic routes to ferroceneboronic acids containing additional functionality attached to either cyclopentadienyl ring have also been reported [108–113]. 1′-substituted 1-ferrocenylboronic acids can be prepared from the corresponding 1,1′-ferrocenyl ditelluride or 1,1′-bis(tributylstannyl)ferrocenes [114,115] by successive lithiation and electrophilic quenching steps [108]. Thus, for example, $(\eta^5\text{-}C_5H_4SPh)[\eta^5\text{-}C_5H_4B(OH)_2]Fe$ (**72**) can be synthesised from $(\eta^5\text{-}C_5H_4Sn^nBu_3)_2Fe$ by lithiation with ^{n}BuLi, quenching with diphenyldisulfide, further lithiation, quenching with trimethylborate and subsequent hydrolytic work up [108]. Ferroceneboronic acids functionalized at the 2 position have also been reported. A number of such species have been made featuring pendant $\text{–CH(R)NR}'_2$ moieties (e.g. **73**, Fig. 10), with the boronic acid function being introduced into the molecule by N-directed ortho lithiation of the corresponding $FcCH(R)NR'_2$ compound [109–113]. In cases where the pendant $\text{–CH(R)NR}'_2$ function is chiral (e.g. R = Me), the regioselectivity of the lithiation step is determined entirely by the configuration at the chiral centre. Hence the use of single enantiomer precursors gives single diastereomer aminoboronic acids, which have been exploited in the electrochemical sensing of sugars [111–113].



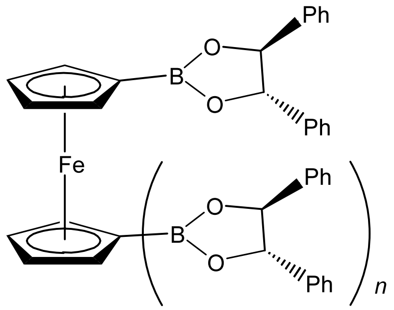
73: R = Me

Fig. 10. Ferrocene boronic acids functionalised at the 2 position have been synthesized by N-directed *ortho*-lithiation of $FcCH(R)NR'_2$ and have been exploited in the electrochemical sensing of sugars.

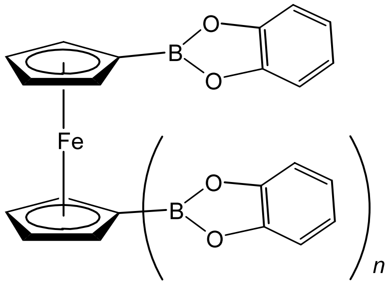
Ferroceneboronic acids have found considerable application as molecular and anion sensors [9,111,113,116–128]. In particular, they have found widespread use in the sensing of fluoride ions or sugars, the former resulting from the considerable affinity of fluoride for the Lewis acidic three-coordinate boron centre, the latter being derived from the propensity of boronic acids to form cyclic boronate esters with diols in aqueous solution [95,96,129]. A number of systems have been developed containing both boronic acid and ferrocenyl moieties which selectively bind saccharides [130,131], however, within the scope of this review only those containing directly linked Fc and $B(OR)_2$ units are considered.

Ferroceneboronic acid itself has been shown to selectively bind fluoride in the presence of other halides and common anions in a mixed methanol/water solvent system [116]. The redox active ferrocene centre provides a versatile electrochemical method of monitoring anion binding, with a binding constant of ca. 10^3 dm^3 mol^{-1} being determined for fluoride binding to $[FcB(OH)_2]^+$ in methanol/water (0.7×10^3 in water). Analogous binding constants for Cl^- and Br^- were ca. three orders of magnitude lower. Coupling of this system with an appropriately chosen dye (methylene blue) at acidic pH facilitates reduction of the dye molecule and generates a method for visual sensing of fluoride [9]. A related 1,1′-disubstituted cyclic boronate ester system (**74**) has been shown to act as a single component orange to green redox-based fluoride ion sensor in CH_2Cl_2 or $CHCl_3$ solution (Fig. 11) [117]. In this case, weak binding of fluoride to both boron centres renders the ferrocene centre easier to oxidize, to the extent that oxidation to ferrocenium can be brought about by atmospheric oxygen. Similar sensor behaviour is observed for the corresponding catechol system (**76**), although no colour change is observed for the analogous monofunctional systems (**75** and **77**) [132].

The binding of sugar molecules to ferroceneboronic acid derivatives through the formation of cyclic boronate esters has been extensively used in recognition and sensing. Although ferroceneboronic acid itself binds saccharides only under strongly alkaline conditions [111,118], the use of a pendant amine donor (e.g. as in **73**) has been shown to facilitate binding at neutral pH. The formation of an intramolecular N→B bond is



74: $n = 1$
75: $n = 0$



76: $n = 1$
77: $n = 0$

Fig. 11. 1,1′-Bis(boronic ester) derivatives of ferrocene investigated for the colorimetric detection of flouride.

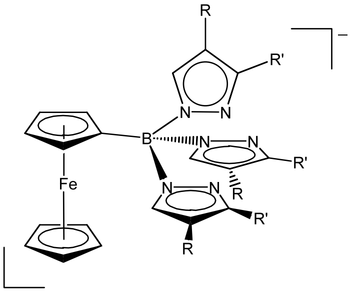
thought to be important in the binding process at neutral pH, since the equilibrium is shifted in the direction of the cyclic boronate when the boron centre is four-coordinate [111,113]. In the case of chiral derivatives, discrimination between certain enantiomeric linear saccharides can be demonstrated electrochemically [111]. In a similar manner to analogous fluoride recognition systems, combination of the ferrocene-based electrochemical response to saccharide binding with an appropriate redox-active dye generates a visual sensor system [9]. Recently the group of Norrild has elucidated further structural information for **73** and the species formed on reaction with sugars. Intriguingly, crystallographic data for **73** have ruled out any significant intramolecular N → B bond in the solid state [113].

Similar chemistry has seen ferroceneboronic acid used extensively in other branches of analytical and separation science [119–128]. In particular its use in binding polyols and providing a simple, easily oxidizable derivatization agent has been well documented. The resulting ferrocenyl boronate esters are readily detected electrochemically [119] and by oxidation to ferrocenium species provide a mild source of cationic derivatives for detection by electrospray mass spectrometry [124–127].

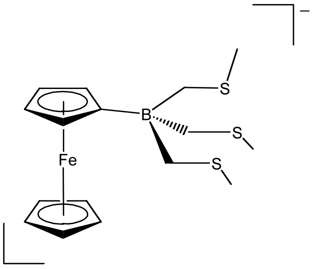
C–C bond formation by the palladium catalysed reaction of boronic acid and aryl halide reagents is an extremely powerful synthetic tool [94]. Despite this, early reports of the application of Suzuki methodology to ferroceneboronic acids revealed unpromising results linked to the loss of the boronic acid functionality [100]. Despite this, Suzuki coupling using ferroceneboronic acids has been applied to a number of synthetic problems requiring the formation of Fc–aryl linkages [100,108,133,134], offering an alternative to the use of haloferrocene precursors [135].

5.3. Ligand systems containing a borylcyclopentadienyl fragment

The coordination chemistry of tripodal ligands based around a central four-coordinate boron atom has been extensively exploited in recent years [136]. Furthermore, the drive towards the development of metal containing polymers with useful magnetic and/or electronic properties has led to advances in a number of areas involving boryl functionalised metallocenes (see Sections 5.4, 5.5 and 5.6). Among these, the development of metallocene functionalised tripodal borate ligands (such as **78** and **91**



78: R = R' = H
83: R = H, R' = Ph
86: R = SiMe$_3$, R' = H
87: R = cyclohexyl, R' = H
88: R = cyclohexylmethyl, R' = H
89: R = Ph, R' = H



91

Fig. 12. Examples of ferrocene-functionalized tripodal borate ligands.

and analogous species functionalised at both cyclopentadienyl rings) offers the possibility for heterobimetallic oligomers and polymers (Fig. 12).

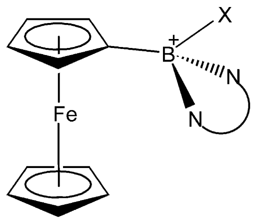
Initial studies of the chemistry of ferrocene functionalized tris(pyrazolyl)borates were reported by Wagner and co-workers in 1996 [6]. The syntheses of the lithium and thallium(I) salts of $\{(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4B(C_3N_2H_3)]Fe\}^-$ {or $[FcB(pz)_3]^-$, **78**} together with that of the parent acid, $FcB(pz)_3H$ (**79**), were reported from (dibromoboryl)ferrocene, pyrazole and trimethylamine. The corresponding hexa-dentate ligand $1,1'\text{-}Fc[B(pz)_3]_2^{2-}$ (**80**) was also reported, although the use of an alternative synthetic route utilizing 1,1′-bis(diaminoboryl)ferrocene precursors was required in order to subvert side reactions leading to N → B *ansa*-bridged species (see Section 5.5). The crystal structure of the thallium complex $[FcB(pz)_3]Tl$ (**81**) was also reported, although in common with analogous cymantrene functionalised systems [67], the ligand binds not as a face-capping tridentate moiety, but bridges two metal centres in κ^1,κ^2 fashion to give a heterobimetallic polymer [6]. Interestingly, suitable steric modification at the pyrazolyl backbone by the introduction of bulky phenyl substituents is sufficient to alter the coordination mode of the (ferrocenyl)pyrazolylborate ligand. Hence the crystal structure of $[FcB(pz^{3Ph})_3]Tl$ (**82**) features a tridentate (κ^3) coordination mode of the $[FcB(pz^{3Ph})_3^-]$ ligand (**83**) and monomeric thallium containing units [137].

The coordination chemistries of $FcB(pz)_3^-$ (**73**) and $1,1'\text{-}Fc[B(pz)_3]_2^{2-}$ (**80**) with a variety of transition metals have been investigated with a view to synthesizing oligomeric bi- and tri-metallic systems. To this end bimetallic molybdenum and zirconium complexes and trimetallic molybdenum and iron systems containing these ligands have been reported [138]. Cyclic voltametry measurements indicate communication between the two molybdenum centres in $1,1'\text{-}Fc[B(pz)_3]_2[Mo(CO)_2(\eta^3\text{-}C_3H_4Me\text{-}2)]_2$ (**84**) and between the two ferrocene centres in $[FcB(pz^{4TMS})_3]_2Fe$ (**85**) {which contains the $[FcB(pz^{4TMS})_3]^-$ ligand, **86**} The introduction of large organic groups in the 4 position of the pyrazolyl backbone has been shown to engender increased solubility of complexes in organic media [139]. A variety of such ligands have been synthesized (**86**–**89**) and their 2:1 complexes $[FcB(pz^{4R})_3]_2M$ (M = Mn, Fe, Co, Ni, Cu, Zn) formed by reaction with the appropriate metal dihalides. Electrochemical studies have revealed that the presence of neutral ferrocenyl substituents in $[FcB(pz^{4R})_3]_2M$ shifts the oxidation potential for the M^{2+}/M^{3+} couple to significantly more cathodic values compared to the corresponding $[HB(pz^{4R})_3]_2M$ species. Conversely, cationic ferrocenium substituents engender an anodic shift of the M^{2+}/M^{3+} transition [139]. Of further interest is the observation of copper mediated electronic communication between the two ferrocene centres in $[FcB(pz^{4R})_3]_2Cu$ (**90**).

Borylferrocene based ligands are not limited to tris(pyrazolyl)borate systems. Riordan and co-workers have reported the synthesis and coordination chemistry of the ferrocenyltris[(methylthio)methyl]borate system (**91**) [140]. The face-capping S_3^- donor set provided by this ligand is analogous to that of the corresponding phenyltris[(methylthio)methyl]borate ligand. The 1:1 complex with Cu(I) and 2:1 complexes with Fe(II), Co(II) and Ni(II) were reported. Cyclic voltametry measurements for the 2:1 complexes show two-electron ligand-centred redox processes occurring at ca. 200 mV negative of the ferrocene/ferrocenium couple and are therefore likely to indicate a lack of communication between ferrocene moieties [140]. In addition, a number of macrobicyclic clathrochelate species have been reported containing borylferrocene moieties as capping units [141,142]. Iron(II) and cobalt(II) compounds containing alkyl, aryl and alicyclic dioxime ligand systems have been reported, via a template synthesis using ferroceneboronic acid as the cross-linking agent [141,142]. In the case of the iron (II) species (**92**) the distorted trigonal prismatic coordination geometry of the encapsulated metal centre was revealed by Mössbauer spectroscopy and X-ray crystallography [141].

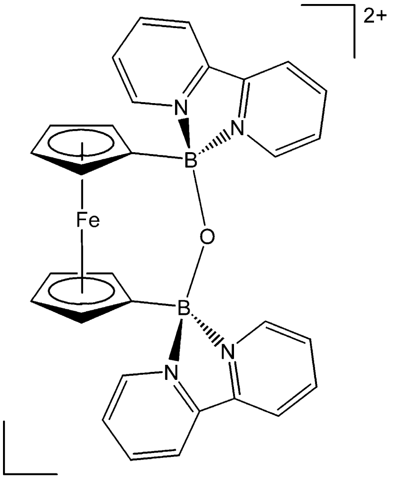
5.4. Ferrocene based boronium salts

The use of ferrocene as the donor component in donor/acceptor compounds having unusual and/or useful electronic properties has long been exploited [143]. Recently there has been a good deal of interest in such systems in which the donor (ferrocene) and acceptor functions are covalently linked [144]. One synthetic approach to the formation of the necessary covalent scaffold has been the use of bipyridylboronium salts as the electron acceptor (e.g. **93**, Fig. 13), since such compounds have been shown to behave as reversible two-step redox systems in DMF [145], and ferrocene derivatives can be synthesized in a single step from the corresponding bromoboryl ferrocene compound $[Fc(BBrX)_n$, $n = 1, 2, 4]$ [146].



93: N⌒N = 2,2′-bipyridyl, X = Me
94: N⌒N = 2,2′-bipyridyl, X = Br
95: N⌒N = 2,2′-bipyridyl, X = OEt
96: N⌒N = 2,2′-bipyridyl, X = NC_4H_8

Fig. 13. Ferrocene-functionalized bipyridyl boronium salts.



100

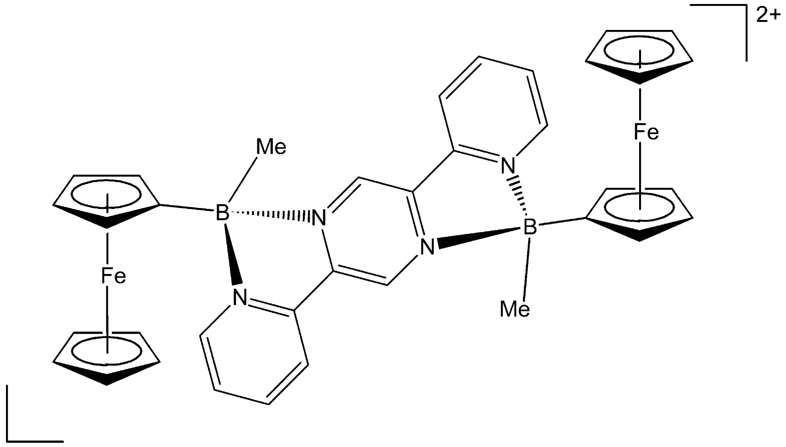
Fig. 14. The redox active ansa-bridged ferrocene derivative resulting from the hydrolysis of **94**.

In 1997 Wagner and co-workers initially reported the synthesis of a series of such bipyridylboronium salts (**93**–**96**), together with their 1,1′-bifunctional and 1,3,1′,3′-tetrasubstituted analogues [146]. Similar salts containing alternative chelating nitrogen bases such as 1,10-phenanthroline and 2,2′-bipyrimidine were also reported. Electrochemical measurements for the methyl substituted system **93** and its 1,1′-bifunctional and 1,3,1′,3′-tetrafunctional analogues **97** and **98**, revealed that these complexes behave as reversible three step redox systems. **93**, **97** and **98** could therefore act, respectively, as sources of three, five or nine electrons. Furthermore, in their cationic state the complexes possess a deep purple colour, assigned to a charge transfer interaction between the electron-rich ferrocene and electron-poor boronium fragments [146]. Hydrolysis of bromo–boronium complexes (e.g. **94**) occurs readily, and in the case of the 1,1′ derivative (**99**) this results in the formation of the novel redox active *ansa*-bridged species **100** (Fig. 14) [147].

Reaction of **94** with the aryl diol hydroquinone, on the other hand, gives access to the dinuclear complex $[FcB(bipy)OC_6H_4OB(bipy)Fc]^{2+}$ (**101**) which contains two ferrocene boronium units linked via an aromatic spacer [148]. This complex can act as a source of six electrons, undergoing two distinct boronium based two-electron processes and a single ferrocene-centred two electron process. Similar chemistry using glycol as the linker, however, does not give access to dinuclear species, but rather to $[FcB(bipy)OCH_2CH_2OH]^+$ (**102**) and to 1,1′-$\{Fc[B(bipy)OCH_2CH_2OH]\}^{2+}$ (**103**) containing pendant hydroxyl functions. The latter compound (**103**) has been suggested as a possible monomer for the generation of redox active polyesters and polyurethanes [148]. The linking of ferrocene boronium units through the use of polypyridine linkers has also been examined. The use of potentially tridentate (pyridyl)pyrazine ligands merely results in the formation of complexes containing a single pendant uncoordinated nitrogen donor. The use of tetradentate bis(pyridyl)pyrazine or quaterpyridine donors, however, results in linked ferrocene units (e.g. **104**) (Fig. 15) [7,149]. The analogous chemistry starting from 1,1′-(bromoboryl)ferrocene precursors leads to the formation of redox active macrocyclic systems [7]. Although these were not structurally characterized, a related macrocyclic structure based on a 2,5-di(pyrazolyl)hydroquinone bridge has recently been elucidated by the same group, based on X-ray powder data [150].

5.5. Ferrocenophanes

Whereas metallocenophanes of the earlier transition elements have found application in the field of homogenous olefin polymerisation catalysis, [*n*]ferrocenophanes have received much attention as precursors to



104

Fig. 15. Coupling of ferrocene boronium salts via tetradentate nitrogen donors.

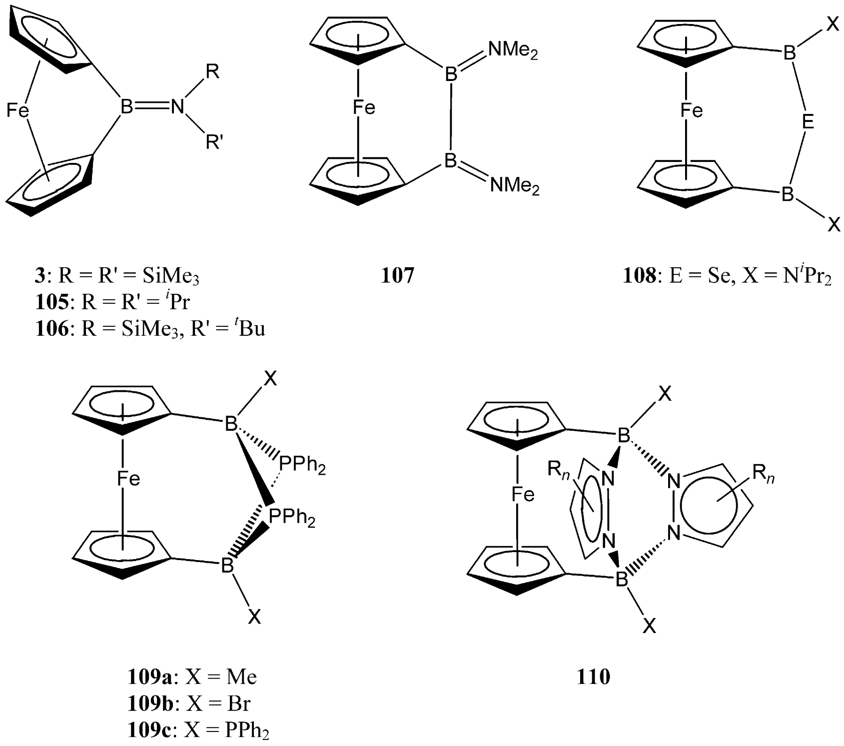
metal containing polymeric materials via ring opening polymerisation (ROP) [151]. Although a wide range of ferrocenophane species are known containing one or more main group atoms in the bridge, boron-containing species are relatively few in number (Fig. 16).

The first example of a [1]ferrocenophane containing a boron bridge was reported by Braunschweig and Manners in 1997 [5] and a detailed analysis of the structure, bonding and ROP properties recently added [14]. Reaction of the tetramethylethylenediamine adduct of 1,1′-dilithioferrocene with $(Me_3Si)_2NBCl_2$ in benzene or toluene afforded the highly strained [1]ferrocenophane $[(Me_3Si)_2NB(\eta^5\text{-}C_5H_4)_2]Fe$ (**3**) which was characterized spectroscopically and crystallographically [5]. Similar chemistry gives access to the corresponding diisopropylamino and (trimethylsilyl)-*tert*-butylamino derivatives (**105** and **106**).

The tilt angle α (defined as that between the planes of the two cyclopentadienyl ligands) reported for the bis(trimethylsilyl)amino derivative is, at 34.2°, the largest reported for any [*n*]ferrocenophane, presumably reflecting the small covalent radius of the bridging boron atom. This pronounced ring tilting leads to a marked red shift in the lowest energy UV–vis absorbance (compared to ferrocene itself); the origins of this effect in terms of the size of the HOMO/LUMO gap were probed by DFT methods. As expected for highly strained systems, ring opening and insertion reactions occur readily [5,14,152]. Thus, thermal ROP occurs at 180–200 °C to give insoluble poly(ferrocenylboranes) for **3** and **106** and soluble, lower molecular weight polymer for **105**. Furthermore, reaction with iron or cobalt carbonyl reagents leads to release of strain and coordination of the two cyclopentadienyl rings to distinct metal centres.

[2]Ferrocenophanes containing boron atoms are also extremely rare, with the sole example having been reported by Herberhold and Wrackmeyer in 1997 [153]. Reaction of 1,1′-dilithioferrocene with 1,2-dichloro-bis(dimethylamino)diborane(4) leads to the formation of a 1,2-dibora-[2]ferrocenophane (**107**). This compound has been characterized spectroscopically and the energetic barriers to fluxional processes (rotation about the B–N bonds and interconversion between staggered and eclipsed ring conformations) determined by NMR methods [153].

In addition to the 1,3-dichalcogena-2-bora-[3]ferrocenophanes reported by Habben [154] and by Herberhold [155,156], a number of 1,3-dibora-[3]ferrocenophanes have been reported. Herberhold and Wrackmeyer have reported the synthesis of a range of species featuring –B(X)EB(X)– bridging units by the reaction of the corresponding 1,1′-bis(bromoboryl)ferrocene with either Li_2E (E = O, S, Se, Te) or $(Me_3Si)_2E$ (E = NMe) [157]. Structural characterization in the case of **108** reveals a staggered conformation and slightly tilted arrangement of the cyclopentadienyl rings ($\alpha = 6.4°$). A somewhat different structural motif (**109**) for dibora-[3]ferrocenophanes has been realised by Wagner and co-workers [158,159]. Reaction of either **1** or 1,1′-bis[methyl(bro-



3: R = R' = $SiMe_3$
105: R = R' = ^{i}Pr
106: R = $SiMe_3$, R' = ^{t}Bu

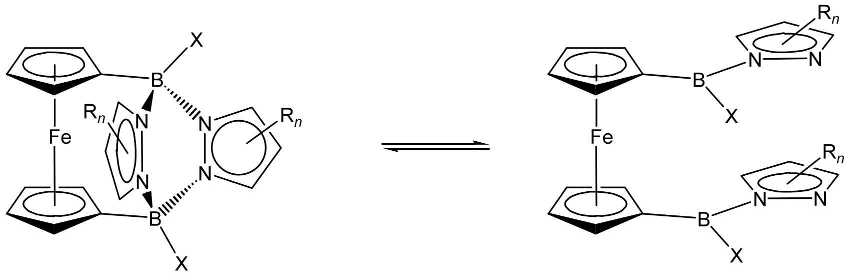
107

108: E = Se, X = N^iPr_2

109a: X = Me
109b: X = Br
109c: X = PPh_2

110

Fig. 16. [n]Ferrocenophanes containing bridging boron atoms.



VII **VIII**

Scheme 10.

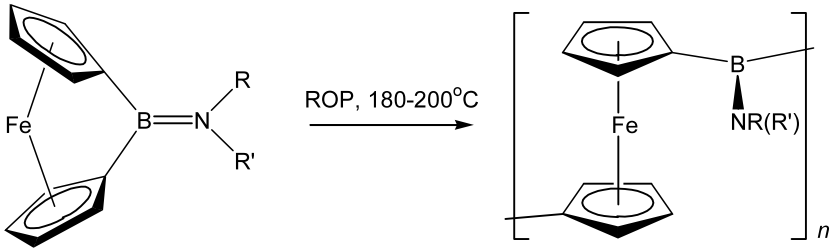
mo)boryl]ferrocene with lithium diphenylphosphide leads to the generation of 1,1′-bis(phoshinoboryl)derivatives which establish a novel *ansa*-bridged structure (**109**) through the formation of two intramolecular P→B donor/acceptor bonds [158,159]. Variable temperature and spin saturation transfer NMR methods have established that rapid breaking and reforming of the P→B linkages occurs with an activation barrier of ca. 70 kJ mol^{-1}. Intriguingly, the analogous complexes in which the phosphine and boryl moieties are separated by an amino group show no intramolecular pairing [158,159]. Reaction of these unusual donor/acceptor bridged species with 4-picoline leads to breakage of the *ansa*-bridge; by contrast reaction with a lithium pyrazolide derivative leads to replacement of one of the B–PPh$_2$–B bridges by a B–(pyrazolide)–B moiety and the formation of an unusual interannular BNNBP heterocyclic bridge [158].

Analogous pyrazole groups have been used extensively by Wagner and co-workers in the synthesis of [4]ferrocenophanes. Intramolecular assembly of N→B donor/acceptor bonds provides an alternative to the isoelectronic C–C coupling in the formation of interannular linkages. Such species (e.g. **110**) have generally been formed by the reaction of a 1,1′-bis(bromoboryl)ferrocene with the requisite pyrazole and have doubly bridged structures in the solid state (Fig. 16) [160–162]. The equilibrium between these interannular N→B bridged species and the corresponding open chain structure has been investigated as a function of the substitution pattern at boron and on the pyrazolyl backbone (Scheme 10). In general the open chain form (**VIII**) is favoured by strongly π electron donating substituents (X) at boron and strongly π electron withdrawing groups on the pyrazole backbone (R) [161,162]. Tethering together pyrazole moieties by the use of rigid spacer groups attached at the 4 position leads to the formation of cyclic oligomers (containing either two or three ferrocene units) which possess a large central cavity [15].

Of related interest are the [4]ferrocenophanes containing –SB(NMe$_2$)B(NMe$_2$)S– bridges (**111**) recently reported by Norman [163] and a lithium binding dianionic macrocycle $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{BMe}_2)]_2^{2-}$ (**112**) recently reported by Wagner [15].

5.6. *Metal containing polymeric and oligomeric species*

Poly(ferrocene) derivatives have received much recent interest as a result of interesting magnetic, electrical and optical properties stemming from electron delocalisation [164,165]. Controlled synthetic routes to such species have become available only relatively recently and have included polycondensation reactions (e.g. ferrocenyl polyesters), polymerisation of pendant functional groups (e.g. vinylferrocene) and ROP of strained ferrocenophanes [151,164,165]. Boryl substituted ferrocene derivatives have been implicated in the formation



3: R = R′ = SiMe$_3$
105: R = R′ = ^{i}Pr
106: R = SiMe$_3$, R′ = ^{t}Bu

Scheme 11.

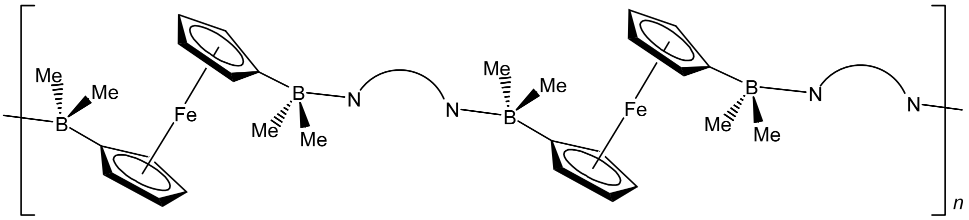
of metal containing polymers by a number of routes. ROP of [1]- and [2]ferrocenophanes has been exploited extensively by Manners and co-workers in the synthesis of organometallic polymers [151,164,165]. In this regard the synthesis and ROP of boron-bridged [1]ferrocenophanes (Scheme 11) is of some note and has been discussed in Section 5.5 [5,14,152]. Other approaches to multimetallic oligomeric and polymeric systems include the use of bifunctional ferrocene based ligands such as $1,1'\text{-Fc}[B(pz)_3]_2^{2-}$ (**80**) (Section 5.3) [139], and the formation of coordination polymers incorporating N → B donor/acceptor linkages.

Manners and co-workers have reported selective ring opening reactions of sila- and stanna-[1]ferrocenophanes with electrophilic borane reagents as a route to poly- and oligomeric species [19]. Reaction of $[Me_2Si(\eta^5\text{-}C_5H_4)_2]Fe$ with BCl_3 under appropriate conditions leads to the selective formation of the borane linked ferrocenes $Cl_{3-n}B[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4SiMe_2Cl)]_n$ ($n = 1$, **113**; 2, **114**), although attempts to form the analogous triferrocenylborane by this method were unsuccessful. A large excess of borane was found to be required in order to selectively form the mono-ferrocenyl borane **113**; by contrast the analogous reaction between the stanna-[1]ferrocenophane $[Mes_2Sn(\eta^5\text{-}C_5H_4)_2]Fe$ and one equivalent of BCl_3, yields only $(\eta^5\text{-}C_5H_4BCl_2)Fe(\eta^5\text{-}C_5H_4SnMes_2Cl)$ (**4**), presumably reflecting the greater steric bulk of the $SnMes_2$ bridge. Ring opening with bifunctional boranes such as **1** leads to the formation of trinuclear species, although the importance of a strongly Lewis acidic sterically unhindered boron centre was emphasized by the lack of similar reactivity towards $1,1'\text{-Fc}[BBr(NMe_2)]_2$ or $1,1'\text{-Fc}[BBr(Mes)]_2$. Furthermore, reduction of chlorosilyl-substituted ferrocenylboranes to the corresponding silane and subsequent $PtCl_2$-catalysed reaction with $[Me_2Si(\eta^5\text{-}C_5H_4)_2]Fe$ allowed the formation of boron-containing poly(ferrocenyl)silane materials [19]. In contrast to the above chemistry reported for [1]ferrocenophanes the analogous reaction of chloroboranes with unstrained 1,1′-distannaferrocenes is reported to yield mixed 1,2-disubstituted stanna-boraferrocenes via an unusual rearrangement reaction [82,83].

Wagner and co-workers have taken a different approach to the formation of poly(ferrocenes), utilizing the formation of N → B donor/acceptor bonds in the formation of coordination polymers and oligomers. In early work these authors exploited the isoelectronic nature of BN and CC linkages to form multimetallic systems under mild conditions. Thus, for example the homo-bimetallic system $FcBBr_2 \cdot NMe_2CH_2Fc$ (**115**) could be formed at room temperature from distinct amino and boryl components and proved to be stable to N → B bond rupture up to 100 °C. Although the N → B donor/acceptor bond in the analogous (benzene)chromium tricarbonyl system $FcBBr_2 \cdot NMe_2(\eta^6\text{-}C_6H_5)Cr(CO)_3$ (**116**) proved to be much less stable, bi- and tri-metallic Fe/Cr systems could be isolated by making use of amido–borane ($R_2N\text{–}BR'_2$) linkages [166].

Adduct formation between pyridine-derived bases and the strongly Lewis acidic borylferrocenes $FcBMe_2$ and $1,1'\text{-Fc}(BMe_2)_2$ has also been exploited in the formation of charge transfer complexes and reversible coordination polymers. Such compounds, typified by the 2:1 adduct **117** formed between $FcBMe_2$ and 4,4′-bipyridyl are highly coloured as a result of charge transfer processes from the electron-rich ferrocene centre to the viologen-like $R_3B\text{–bipy–}BR_3$ acceptor. Such complexes are also highly electrochemically active; the electron donating effect on the ferrocene couple of a single pendant $-BMe_2 \cdot py$ group has been shown by cyclic voltametry to be roughly equal to that of five methyl groups [167]. Extension of this approach to combinations of bifunctional donors and acceptors leads to the formation of coordination polymers (e.g. **118**, Fig. 17), which are stable in the solid state up to several hundred degrees, but which dissociate in solution below 100 °C [8]. The lability of N → B donor/acceptor bonds in solution has been also demonstrated for pyrazine bridged systems (e.g. **119**). Hence, although stable macromolecular species are obtained in the solid state, ^{11}B-NMR data in particular are highly indicative of dissociation into discrete pyrazine and borylferrocene units in solution [168].

Wagner and co-workers have also sought to use benzoquinone linkers to target polymeric charge trans-



118: N⌒N = 4,4'-bipyridyl
119: N⌒N = pyrazine, 1,4-$C_4H_4N_2$

Fig. 17. Ferrocene-containing polymers formed by N → B donor/acceptor linkages between bifunctional Lewis acid and Lewis base components.

fer salts with both ferrocene units and N → B linkages within the backbone [169]. To this end, the synthesis of a number of bimetallic model systems based on borylferrocene moieties linked by benzoquinone units have been reported [169].

Of related interest is the Fe/Co heterobimetallic complex $[Fc(\eta^6\text{-}BC_5H_5)Co(\eta^5\text{-}C_5H_5)]^+$ (**120**) synthesised by Heck and co-workers [170], an NLO chromophore which utilises ferrocene and (η^6-borabenzene)(η^5-cylcopentadienyl)cobalt units as electron donor and acceptor groups, respectively. This compound features a ferrocenyl borabenzene ligand bound to a cobalt centre in η^6 fashion, and is produced by the reaction of $FcBBr_2$ (**48**) with cobaltocene and subsequent oxidation with $FeCl_3$. This compound features a UV–vis absorption at ca. 600 nm, (which is assigned to a donor/acceptor charge transfer transition) and reversible redox couples which are shifted somewhat from the isolated mononuclear parent sandwich compounds [170].

5.7. Miscellaneous examples

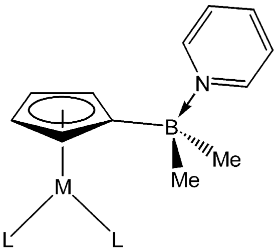
A number of further borylcyclopentadienyl compounds of iron are deserving of mention. The compound triferrocenylborane, $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]_3B$ (or Fc_3B, **30**) has been alluded to in earlier discussion of electronic communication between organometallic fragments via three-coordinate boron (Section 4.1). Its synthesis, spectroscopic characterization and probes of its electronic structure by Mössbauer spectroscopy were reported by Campero and López in 1989 [57]. Subsequently, the crystal structure of **30** was reported by Wrackmeyer and Herberhold in 1995 [55]. For unsubstituted ferrocenes, the steric environment at boron is clearly open enough to allow coordination of further Lewis bases. Thus, for example, the crystal structure of the pyridine adduct $Fc_3B \cdot py$ (**121**) has been reported [171], as has that of the remarkable mixed valence zwitterion (ferricenyl)tris(ferrocenyl)borate (**122**), which features an anionic four-coordinate boron centre linked to three Fe(II) ferrocenyl units and a cationic Fe(III) ferricenyl moiety. Electrochemical data and the presence of a very broad intervalence electronic transition centred at 2200 nm were taken as evidence for a mixed valence formulation for this compound [172].

Much effort has been expended on an evaluation of sites of nucleophilicity in alkyl and hydrido compounds of Groups 6 and 7 (see Sections 4.2 and 4.3) [12,13]. Similar studies have been undertaken with nucleophilic cyclopentadienyl derivatives of iron. Hence, for example, reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ with triphenylborane initially generates the Lewis acid/base adduct $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(BPh_3)]^-$ (**123**) which is thought to have a structure analogous to the corresponding crystallographically characterized aluminium compound [173,174]. In thf solution this species rearranges with migration of the BPh_3 moiety to a cyclopentadienyl ligand generating the structurally characterized diiron complex $[(\eta^5\text{-}C_5H_4BPh_3)Fe(CO)(\mu\text{-}CO)_2Fe(CO)(\eta^5\text{-}C_5H_5)]^-$ **(124)** [173]. Similar chemistry is found in the reaction of $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]^-$ with BCl_3, which in addition to generating the boryl complex $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2BCl_2$ (**125**) also gives rise to the zwitterion $(\eta^5\text{-}1,3\text{-}MeC_5H_3BCl_3)Fe(CO)_3$ (**126**) as a minor product [175,176].

6. Derivatives containing Group 9 metals

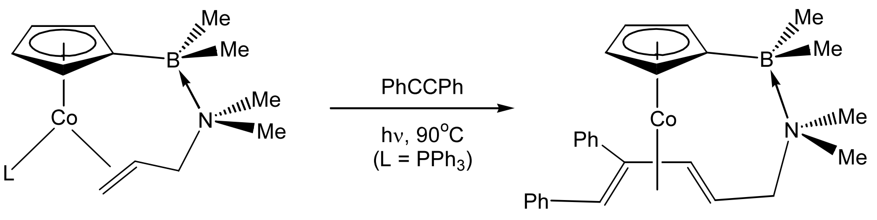
Although borylcyclopentadienyl derivatives of the Group 9 metals have been known for some time [177], their development and application have lagged behind that of the analogous iron systems. Boryl derivatives containing the cationic cobaltocenium moiety, for example, offer significant advantages over the corresponding ferrocene derivatives in the field of anion binding. However, the extra difficulties associated with the synthesis of boryl cobaltocenium species has meant that in contrast to alternative types of anion receptor [178], binding studies by species containing pendant boryl functions has been less well exploited [27,28].

Collum and Klang reported the synthesis of cobalt and rhodium complexes featuring cyclopentadienyl bound $-BMe_2 \cdot py$ (py = pyridine) units as early as 1988 [177]. One of the aims of the study was to investigate the cooperative binding of bifunctional ligands to both boron and metal centres and the subsequent reactivity of bound molecules. Complexes **127** and **128** (Fig. 18) were found to be accessible in moderate yields by the reaction of $C_5H_5BMe_2 \cdot py$ or $Me_3SiC_5H_4BMe_2 \cdot py$ with either $Co_2(CO)_8$ or $[(OC)_2RhCl]_2$. Substitution of carbonyl ligands for phosphines and oxidation of the cobalt centre with iodine were found to occur without competing attack at the pendant boryl function. Exchange of pyridine ligands at boron was found to be rapid on the NMR timescale, and reaction of the cobalt compound $(\eta^5\text{-}C_5H_4BMe_2 \cdot py)Co(CO)_2$ (**127**) with dimethylallylamine



127: M = Co, L = CO
128: M = Rh, L = CO

Fig. 18. Pyridine-stabilized borylcyclopentadienyl complexes of cobalt and rhodium.



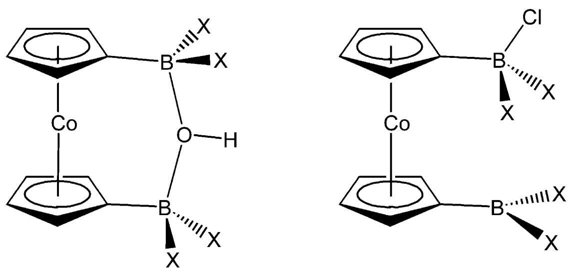
129a: L = CO
129b: L = PPh_3

130

Scheme 12.

under photolytic conditions generated species **129a** featuring cooperative Co/B binding. The phosphine analogue **129b** can also be generated and further reaction in this case with diphenylacetylene generated the *ansa*-bridged cyclopentadienyl/butadiene complex **130** (Scheme 12) [177].

Similar synthetic methodology has been used to generate bis(boryl) cobaltocene and cobaltocenium species from $Li(C_5H_4B^iPr_2)$ [25,27,28]. The paramagnetic cobaltocene derivative $(\eta^5\text{-}C_5H_4B^iPr_2)_2Co$ (**6**) has been prepared in excellent yield from $Li(C_5H_4B^iPr_2)$ and $CoBr_2\cdot dme$ (dme = dimethoxyethane, $MeOCH_2\text{-}CH_2OMe$) and its oxidation chemistry probed [27]. The nature of the product formed is strongly dependent on the oxidizing agent used (Fig. 19). Hence, oxidation with $Fc^+PF_6^-$ yields $[(\eta^5\text{-}C_5H_4B^iPr_2)_2Co]^+PF_6^-$ (**131**) in which there are no specific interactions between the three-coordinate boron centres and the anions, and which is consequently a very strong Lewis acid. Oxidation with $Cu(OH)_2$, on the other hand leads to the formation of an OH^- inverse chelate complex with a cobaltocenophane type structure (**132**, Fig. 19). A third structural variant is observed for the chloride complex **133**; crystallographic data show an asymmetric structure (Fig. 19), although rapid exchange of chloride between boron centres is implied in solution down to −80 °C by NMR measurements. The importance of the Lewis acidity of the boron centre in determining the extent of anion/cation interaction is readily apparent from the observation that the bis(amino)boryl analogue $\{[\eta^5\text{-}C_5H_4B(NMe_2)_2]_2Co\}^+Cl^-$ (**134**) shows no sign of quaternization at boron [28].



132: X = ^{i}Pr
140: X = F

133: X = ^{i}Pr
135: X = Cl

Fig. 19. Binding of anions by bis(boryl) cobaltocenium derivatives: inverse chelate (**132**, **140**) and asymmetric structures (**133**, **135**) observed in the solid state.

Further derivatization at boron, and consequent fuller exploration of the coordination chemistry of bis(boryl) cobaltocenium species, is possible through the synthesis of the highly reactive chloride $(\eta^5\text{-}C_5H_4BCl_2)(\eta^5\text{-}C_5H_4BCl_3)Co$ (**135**) from the reaction of **134** with excess BCl_3. This compound has been shown spectroscopically to have a rapidly fluxional structure analogous to **133** and is a useful precursor for further modification at boron. Hence reaction with pinacol gives $(\eta^5\text{-}C_5H_4Bpin)(\eta^5\text{-}C_5H_4BCl_3)Co$ (**136**) or $[(\eta^5\text{-}C_5H_4Bpin)_2\text{-}1Co]Cl$ (**137**) depending on stoichiometry, and methylation with trimethylaluminium yields salts of the type $[(\eta^5\text{-}C_5H_4BMe_2)_2Co]X$ ($X^- = AlCl_4^-$ **138**, PF_6^- **139**). Furthermore, reaction with commercial (slightly hydrolysed) AsF_3 generates $[(\eta^5\text{-}C_5H_4BF_2)_2Co]OH$ (**140**) which has been shown crystallographically to represent a second example of the inverse chelate structure [28].

Finally, although the vast majority of borylcyclopentadienyl derivatives of Group 9 have been synthesised from preformed boryl-containing ligand precursors, or by further modification at boron once the complex has been made, direct borylation has been reported in at least one case. Reaction of cobaltocene with tris(pentafluorophenyl)borane has been reported to yield a 1:1 mixture of the salt $[(\eta^5\text{-}C_5H_5)_2Co]^+[HB(C_6F_5)_3]^-$ and the zwitterion $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Co$ (**141**), which features a borate-functionalized cyclopentadienyl ligand [179].

7. Conclusions

Cyclopentadienyl complexes containing pendant BX_2 or BX_3^- groups have been synthesized for elements of most transition metal groups, either by modification of existing cyclopentadienyl metal units or by use of a preformed ligand precursor. Such complexes have found widespread application, in part stemming from the existence of metallocene and boryl functions in close proximity. Hence the use of Group 4 systems in olefin polymerisation catalysis, and of ferrocene derivatives in anion sensing, stems from the presence of Lewis acidic boryl ($-BX_2$) functions coupled with catalytically or electrochemically active metal centres. Quaternization at the boron centre (yielding $-BX_3^-$ or $-BX_2 \cdot L$ groups) significantly alters the electronic properties of the ligand system. However, the ease of synthesis of donor/acceptor bonds at boron, together with the well-defined electrochemical properties of the ferrocenyl moiety have led to significant research into the use of such systems as organometallic polymers and novel electronic devices. Given the pre-eminence of the cyclopentadienyl spectator ligand in organometallic chemistry, further applications of boryl functionalized systems in these and related fields are sure to be forthcoming in the future.

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