Synthesis, characterization and chemistry of bis-(pentafluorophenyl)boryl ferrocene

Bryon E. Carpenter, Warren E. Piers, Masood Parvez, Glenn P.A. Yap, and Steven J. Rettig

Abstract: Bis-(pentafluorophenyl)boryl ferrocene, **1**, was prepared via borylation of ferrocene with $HB(C_6F_5)_2$ or via a transmetallation reaction involving FcHgCl and $ClB(C_6F_5)_2$ in 87–91% yield. The compound is characterized by a deep maroon colour. A significant intramolecular iron–boron interaction is manifested in the solution spectroscopic ($Fe \rightarrow B$ charge transfer band at ~230 nm, $\varepsilon = 1.33 \times 10^4$) and solid-state crystallographic data (Fe-B = 2.924 Å) This interaction has an impact on the Lewis acidity of the boron center which, unlike the related compound $B(C_6F_5)_3$, does not strongly bind Lewis bases such as acetone, THF, or acetonitrile. However, an adduct between the stronger base PMe_3 and **1** forms readily and this complex (**2**) was fully characterized. The electron withdrawing $-B(C_6F_5)_2$ group causes **1** to be oxidized at +450 mV relative to ferrocene. Oxidation of **1** with $[NO][BF_4]$, $AgOSO_2CF_3$, or AgC_6F_5 leads to the zwitterionic ferrocenium borates **3-F**, **3-OTf**, and **3-C_6F_5**, respectively. Each of these compounds was characterized spectroscopically and via X-ray crystallography. The properties of these compounds relative to **1** suggest that oxidation of the iron center significantly enhances the Lewis acidity of the boron center. Due to the σ-donating ability of the borate substituents, zwitterions **3** are weaker oxidizing agents than unsubstituted ferrocenium salts.

Key words: organoboranes, ferrocene derivatives, Lewis acids.

Résumé : On a préparé le bis-(pentafluorophénylboryl)ferrocène, **1**, par le biais d'une borylation du ferrocène à l'aide de $HB(C_6F_5)_2$ ou par une réaction de transmétallation impliquant le FcHgCl et le $ClB(C_6F_5)_2$; les rendements varient de 87 à 91%. Le composé est caractérisé par une couleur marron foncé. Il se manifeste une interaction intermoléculaire fer–bore significative tant en spectroscopie en solution (un transfert de bande $Fe \rightarrow B$ à environ 230 nm, $\varepsilon = 1{,}33 \times 10^4$) que dans les données cristallographiques à l'état solide (Fe-B = 2,924 Å). Cette interaction a une influence sur l'acidité de Lewis du bore qui, contrairement au composé $B(C_6F_5)_3$ apparenté, ne se lie pas fortement aux bases de Lewis telles que l'acétone, le THF ou l'acétonitrile. Toutefois, il se forme facilement un adduit entre le composé **1** et PMe_3, une base plus forte, et on a fait une caractérisation complète de ce complexe, **2**. La présence du groupe électroaffinitaire $B(C_6F_5)_3$ fait que le composé **1** peut s'oxyder à +450 mV par rapport au ferrocène. L'oxydation du composé **1** par $[NO][BF_4]$, $AgOSO_2CF_3$ ou AgC_6F_5 conduit suivant le cas à la formation des borates de ferrocénium zwitterioniques **3-F**, **3-Otf** et **3-C_6F_5**. Chacun de ces composés a été caractérisé par spectroscopie et par diffraction des rayons X. Les propriétés de ces composés, comparées à celles du composé **1**, suggèrent que l'oxydation du fer augmente de beaucoup l'acidité de Lewis du bore. En raison de la possibilité des substituants borates de donner des électrons σ, les zwitterions **3** sont des agents d'oxydation plus faibles que les sels de ferrocénium non substitués.

Mots clés : organoboranes, dérivés ferrocènes, acides de Lewis.

[Traduit par la Rédaction]

Introduction

Substituted ferrocenyl derivatives play an important role in many different areas of chemistry (1). While much activity has focussed on ferrocenes substituted with Lewis base donors as ligands for various transition metal catalysts, ferrocene derivatives with Lewis acid centers bonded to the cyclopentadienyl (Cp) ring have seen fewer applications. Nonetheless, borylated ferrocenes have been studied in some detail, initially due to the fact that they are isoelectronic to stable ferrocenyl carbocations (2), and are synthons for other substituted ferrocenes. Early examples involve mainly dihaloboryl derivatives, prepared by direct borylation of the metallocene with BX_3 (3). In these reactions, the ferrocene Cp rings can be borylated up to four times. These haloboryl derivatives can be further derivatized and used as precursors

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Dedicated with warmth and deep respect to Professor Brian James on the occasion of his 65th birthday.

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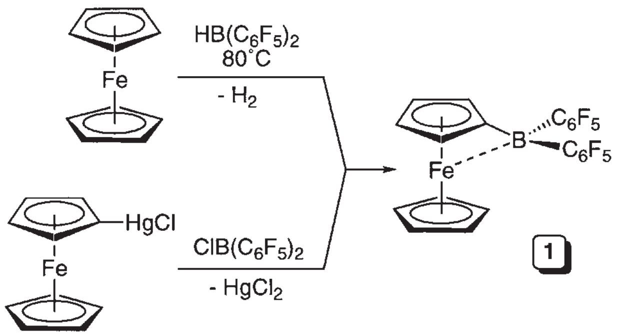
to coordination polymer type materials (4). More recently, a class of *ansa*-ferrocenophanes utilizing a boron atom in the linking bridge have been prepared (5) and subjected to ring-opening polymerization reactions (5*c*).

Our interest in perfluoroaryl substituted boranes (6) led us to develop routes to bis-(pentafluorophenyl)boryl substituted boranes and to explore their properties as Lewis acids. In this paper, we detail the synthesis, properties, and reaction chemistry of the monoborylated ferrocene complex bis-(pentafluorophenyl)boryl ferrocene (**1**).

Results and discussion

Previously, boryl-substituted ferrocenes have been prepared via direct borylation or transmetallation reactions (3). Accordingly, bis-(pentafluorophenyl)borylferrocene (**1**) can be synthesized either via borylation with bis-(pentafluorophenyl)borane, $HB(C_6F_5)_2$, (7) or through reaction of the well-known (chloromercuric)ferrocene, FcHgCl, (8) with bis-(pentafluorophenyl)chloroborane, $ClB(C_6F_5)_2$ (9) (eq. [1]). The former route requires heating for several hours and involves loss of H_2 during the course of the reaction, while the latter reaction occurs at room temperature and produces $HgCl_2$ as the by-product. Both routes are efficient, giving **1** in 87–91% isolated yield.

[1]

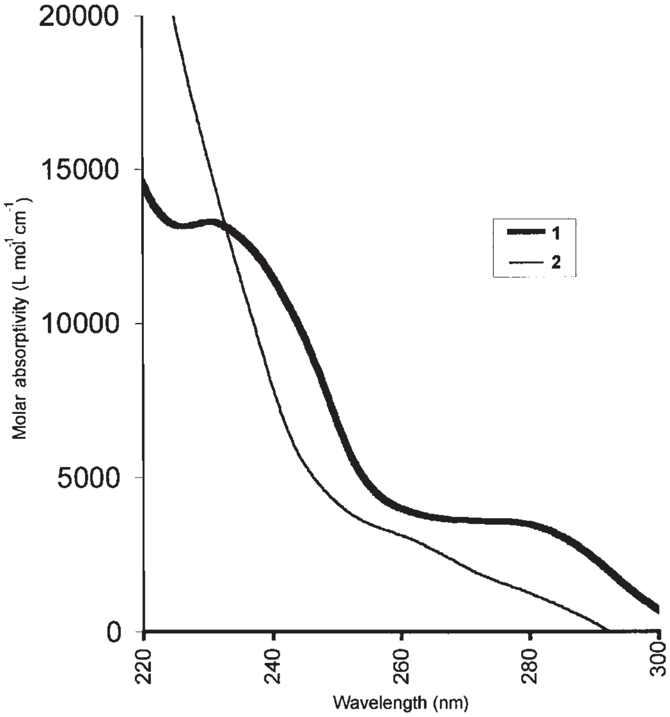


1

Boryl ferrocene **1** is a deeply maroon coloured solid which is highly soluble in common aliphatic and aromatic solvents. The UV–vis spectrum of **1** (Fig. 1) exhibits an intense absorption at ~230 nm ($\varepsilon = 1.33 \times 10^4$) likely assignable to an $\mathrm{Fe}_{dz2/dx2-y2} \rightarrow \mathrm{B_p}$ charge transfer process. Wagner and co-workers (3*j*) have detailed this Fe → B interaction in related dibromoboryl ferrocenes both experimentally and computationally and conclude that the occupied d_{z2} and d_{x2-y2} orbitals on the iron center have appropriate symmetry to interact with the empty *p*-orbital on the boron center, effectively forming a loose intramolecular Lewis acid–Lewis base adduct. A similar phenomenon accounts for the observed stability of ferrocenyl carbocations (2).

The NMR data for **1** also supports the notion that an Fe → B interaction is present in the compound. In perfluoroaryl substituted boranes, the chemical shift of the ^{11}B nucleus in the ^{11}B NMR spectrum is reflective of the coordination number and charge associated with the boron center (10). Neutral, three-coordinate boranes generally resonate in the 65–80 ppm range, neutral, four coordinate centers typically fall into the 5–25 ppm range, while anionic borates appear upfield at –10 to –35 ppm. Similarly, the chemical shift difference between the *meta* and *para* fluorines of the C_6F_5 rings is influenced by the amount of electron density at the boron center (11): as the boron proceeds from neutral, three-coordinate through four-coordinate adducts with Lewis bases, to anionic borates, the *para* fluorines become more shielded as the charge on boron increases, and shift upfield closer to the resonance for the *meta* fluorines. ^{11}B chemical shifts and $\Delta_{m,p}$ values for all the new compounds reported here as well as some comparable compounds are collected in Table 1. Inspection of this data shows that, for **1**, the ^{11}B chemical shift (53 ppm) and the $\Delta_{m,p}$ value (9.2 ppm) is intermediate to the numbers observed for purely neutral, three-coordinate examples and neutral, four-coordinate Lewis base adducts. These observations are consistent with the presence of a weak Fe → B interaction in **1**, which is maintained in nondonating solvents.

Fig. 1. UV–vis spectra of compounds **1** and **2** in 1,2-dichloroethane (concentration ~2×10^{-4} M).



This interaction is also manifested in the solid-state structure of **1**, determined by X-ray crystallography. Compound **1** crystallizes in the $P2_12_12_1$ space group with two crystallographically independent molecules in the asymmetric unit. Figure 2 shows the molecular structure of one of these molecules, along with selected metrical parameters; further details on this structure (and the others reported herein) can be found in the *Supplementary information*.[3] Immediately evident from the view shown is that the $B(C_6F_5)_2$ moiety is

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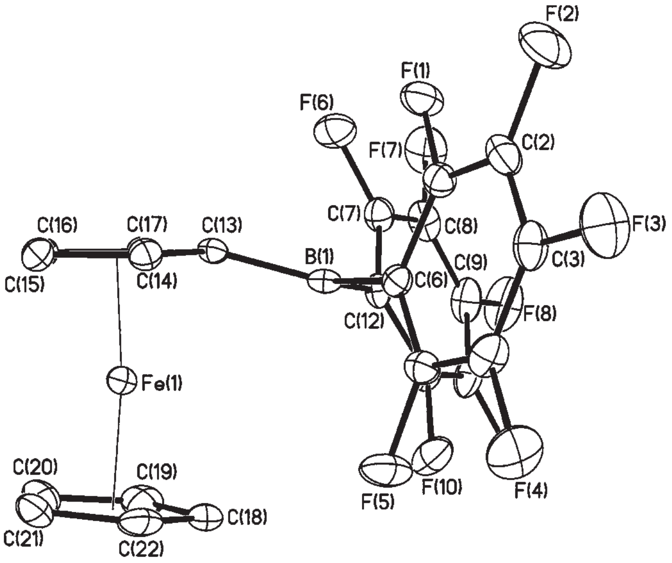
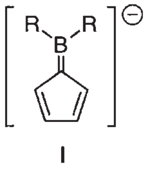
[3] Copies of material on deposit may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). Some of this material has also been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Fig. 2. ORTEP diagram of molecule one of **1**. Selected bond distances (Å): Fe(1)—C(13) 2.043(3), Fe(1)—C(14) 2.027(3), Fe(1)—C(17) 2.036(3), Fe(1)—C(15) 2.060(2), Fe(1)—C(16) 2.062(2), C(13)—C(14) 1.444(3), C(13)—C(17) 1.448(3), C(14)—C(15) 1.414(3), C(16)—C(17) 1.407(4), C(15)—C(16) 1.418(3), B(1)—C(13) 1.501(4), B(1)—C(6) 1.604(4), B(1)—C(12) 1.584(4). Selected nonbonded distance (Å): Fe(1)···B(1), 2.924. Selected bond angles (°): C(6)-B(1)-C(12) 118.4(2), C(6)-B(1)-C(13) 118.0(2), C(12)-B(1)-C(13) 122.5(2).



tilted towards the iron center such that the dip angle of the B(1)-C(13) vector out of the plane defined by the five Cp carbons is ~16°. This compares to the values of 17.7° and 18.9° found for the same parameter in crystallographically independent molecules of the related compound Fc(BBr$_2$) (3*j*). As a consequence of this interaction in **1**, the B(1) center is slightly pyramidalized (the sum of the angles about B(1) is 358.2°) and the Fe(1)—B(1) distance is 2.924 Å. The metrical parameters for the borylated Cp ring suggest a partial contribution from a boratafulvene-like structure (12) akin to **I** is operative for this ligand. Furthermore, the B(1)—C(13) distance of 1.501(4) Å is intermediate between values found for a B(sp^2)-C(sp^2) double bond (e.g., 1.44 Å in LiCH$_2$=B(mes)$_2$ (13)) and that of a B(sp^2)-C(sp^2) single bond (e.g., 1.58 Å in BPh$_3$ (14)). Thus it appears that, in addition to accepting electron density directly from the iron center, the B(C$_6$F$_5$)$_2$ group withdraws π-electron density from the Cp ring as well.



I

The electron-withdrawing capacity of the -B(C$_6$F$_5$)$_2$ group is manifested in the electrochemical behaviour of **1**. Cyclic voltammetric measurements were performed against a silver wire quasireference electrode in ≈100 mM solutions of substrate in α,α,α-trifluorotoluene (TFT) with [NBu$_4$][B(C$_6$F$_5$)$_4$] as the supporting electrolyte (15). Use of the standard [NBu$_4$][BF$_4$] electrolyte led to irreversible oxidations, a result of chemical reactions subsequent to oxidation (vide infra). An internal standard of ferrocene was employed; all $E_{1/2}$ values reported (Table 2) are relative to the Fc/Fc$^+$ couple under these conditions. As can be seen in Fig. 3, **1** exhibits a reversible oxidation wave at +450 mV relative to ferrocene, indicating that it is more difficult to oxidize owing to the electron-withdrawing -B(C$_6$F$_5$)$_2$ substituent.

The flow of electron density into the empty boron *p*-orbital dampens the Lewis acidity of **1** in comparison to other perfluoroaryl substituted boranes. For example, while carbonyl functions, (16) ethers and water, (17) isonitriles and nitriles (18) form strong adducts with B(C$_6$F$_5$)$_3$, when **1** is treated with oxygen nucleophiles such as acetophenone, acetylferrocene, *N*,*N*-di-iso-propylbenzamide or THF, the equilibrium for adduct formation lies far towards the reactants at room temperature. Treatment of **1** with 1 equiv of water leads to rapid formation of FcH and HOB(C$_6$F$_5$)$_2$ (9), indicating that coordination occurs to some extent. Toluene-d_8 solutions of **1** containing a few equiv of acetonitrile, when cooled, change in colour from the deep maroon of **1** to light yellow, indicative of disruption of the Fe → B interaction upon adduct formation. However, the acetonitrile ligand remains labile even at 193 K, as judged by the single resonance for free vs. bound acetonitrile in the sample's ^{1}H NMR spectrum at this temperature. Use of the Childs' method for assessing Lewis acid strength (19) shows that **1** has a Lewis acid strength of 0.37 ± 0.03 relative to BBr$_3$ at 1.00. Comparative values for other Lewis acids, for example,

Table 1. ^{11}B and ^{19}F $\Delta_{m,p}$ values for various pentafluorophenyl-substituted boranes.

Compound	^{19}F $\Delta_{m,p}$	δ ^{11}B	Reference
HB(C$_6$F$_5$)$_2$	18.3	60.1	7
B(C$_6$F$_5$)$_3$	16.3	80	[a]
C$_6$H$_5$B(C$_6$F$_5$)$_2$	12.6	72.6	[b]
FcBBr$_2$	—	46.7	3*d*
1	9.2	53.0	
2	5.6	–13.5	
3-OTf	6.2	–4.8	
3-C$_6$F$_5$	6.8	–23.7	
4	3.7	–13.2	
LiB(C$_6$F$_5$)$_4$	3.7	–17.3	[b]

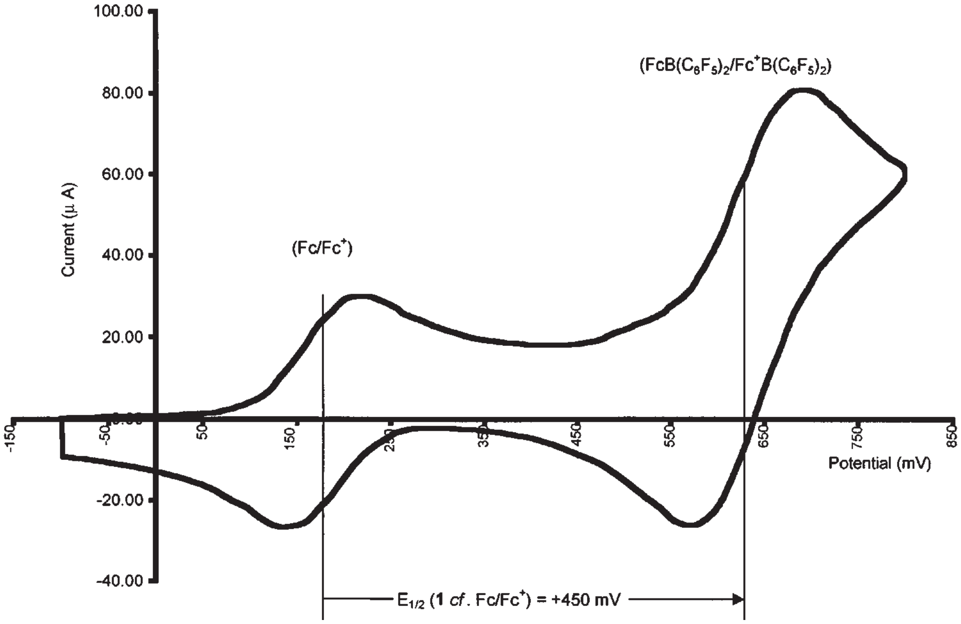
[a] A.G. Massey and A.J. Park. J. Organomet. Chem. **5**, 218 (1966).
[b] P.A. Deck, C.L. Beswick, and T.J. Marks. J. Am. Chem. Soc. **120**, 1771 (1998).

Table 2. Oxidation potentials for ferrocenyl boranes and borates vs. ferrocene$^{+1/0}$.

Compound	Solvent	$E_{1/2}$ (mV)
1	TFT[a]	+450
2	TFT	–100
3-C$_6$F$_5$	TFT	–472
FcC(O)CH$_3$	CH$_2$Cl$_2$	+270[b]

[a] α,α,α-Trifluorotoluene.
[b] Taken from ref. 22.

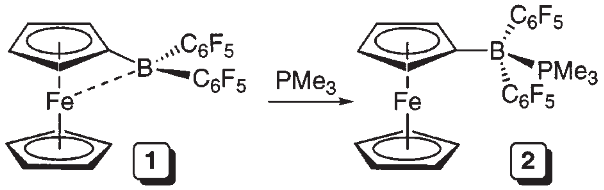
Fig. 3. Representative CV of **1** (1 mM) in α,α,α-trifluorotoluene with $[Bu_4N][B(C_6F_5)_4]$ (100 mM) as supporting electrolyte. Scan rate = 100 mV s^{-1}.



$AlCl_3$ (0.88 ± 0.03), $B(C_6F_5)_3$ (0.77) (20), and $SnCl_4$ (0.56 ± 0.03), show that **1** is a relatively weak Lewis acid by virtue of this Fe → B interaction.

Only strong Lewis bases, such as PMe_3, form adducts irreversibly with **1** (eq. [2]). When maroon solutions of **1** are exposed to PMe_3, an instantaneous colour change to a yellow hue signals formation of adduct **2**. This material was isolated and fully characterized. Notably, the UV–vis spectrum of **2** (Fig. 1) no longer contains a prominent charge transfer band, supporting the assignment of this band for **1** given above. The chemical shift of the ^{11}B nucleus in the NMR spectrum of **2** (–13.5 ppm) is somewhat upfield of the region expected for such four-coordinate adducts but is split into a doublet due to coupling to the ^{31}P nucleus ($J_{B\text{-}P}$ = 46 ± 10 Hz). The $\Delta_{m,p}$ value of 5.6 ppm (Table 1) is consistent with strong coordination of the phosphine to the boron center, although the relatively small value of $J_{B\text{-}P}$ suggests that the phosphine may be labile. The PMe_3 ligated boryl group is now a net electron donator to the Cp ring as judged by the $E_{1/2}$ value of –100 mV (relative to Fc/Fc$^+$, Table 2) in the cyclic voltammagram of **2**. Since the *p*-orbital on boron is plugged with the phosphine lone pair of electrons, the σ-donating ability of the boryl group now dominates the electronic effect of this group on the Fe(II)–Fe(III) redox couple of the iron center.

[2]



The solid-state structure of **2** was determined by X-ray crystallography, and an ORTEP diagram along with selected metrical data is given in Fig. 4. The B(1)—P(1) distance of 1.992(9) Å is comparable to the 2.046(8) Å and 2.015(3) Å values found for the PH_3 and *t*-$BuPH_2$ adducts, respectively, of $B(C_6F_5)_3$ (21). The now four-coordinate boron atom is tilted out of the Cp plane away from the iron center by 6.4°. As expected, the boratafulvene character of **1** is lost and the B(1)—C(1) distance of 1.61(1) Å is characteristic of a B(sp^3)—C(sp^2) bond.

Given the nature of the Fe → B interaction in **1** and related compounds and its dampening effect on the Lewis acidity of the boron center, it seemed logical to presume that oxidation of the iron center should weaken the Fe → B interaction and concommitantly impart stronger Lewis acidity on the borane. Experiments involving chemical oxidation of **1** appear to bear this out. For example, treatment of **1** with $[NO][BF_4]$, a common oxidizing agent for ferrocene derivatives (22), led to oxidation to a ferrocenium complex as indicated by a change in the solution's colour from maroon to dark green, with visible evolution of NO gas. ^{19}F NMR spectroscopy on the crude product showed that the BF_4 anion was no longer present and that one major $B(C_6F_5)_2$ containing product was present as ≈80% of the mixture. Due to the paramagnetism of this compound, ^1H and ^{11}B NMR spectroscopy provided little useful information; however, the C_6F_5 rings are far enough removed to be relatively unaffected by the paramagnetic iron center. While isolable quantities of pure product were not obtained, analysis of crystals isolated from this product mixture by X-ray crystallography, revealed the fluoroborate zwitterion **3-F** to be this major product (Fig. 5). Evidently, the boron center in the putative ferrocenium intermediate **3** (Scheme 1) is Lewis acidic enough to abstract a fluoride ion from the BF_4 counteranion. Fluoride abstraction by other perfluoroaryl boranes, specifi-

Fig. 4. ORTEP diagram of **2**. Selected bond distances (Å): Fe(1)—C(1) 2.098(7), Fe(1)—C(2) 2.044(8), Fe(1)—C(3) 2.012(9), Fe(1)—C(4) 2.037(8), Fe(1)—C(5) 2.022(8), C(1)—C(2) 1.447(9), C(1)—C(5) 1.424(10), C(2)—C(3) 1.400(12), C(4)—C(5) 1.425(10), C(3)—C(4) 1.401(12), B(1)—C(1) 1.609(11), B(1)—C(11) 1.665(10), B(1)—C(17) 1.637(10), B(1)—P(1) 1.992(9). Selected bond angles (°): P(1)-B(1)-C(1) 109.3(5), P(1)-B(1)-C(11) 102.1(5), P(1)-B(1)-C(17) 116.0(6), C(1)-B(1)-C(11) 110.6(6), C(1)-B(1)-C(17) 109.0(6), C(11)-B(1)-C(17) 109.8(6).

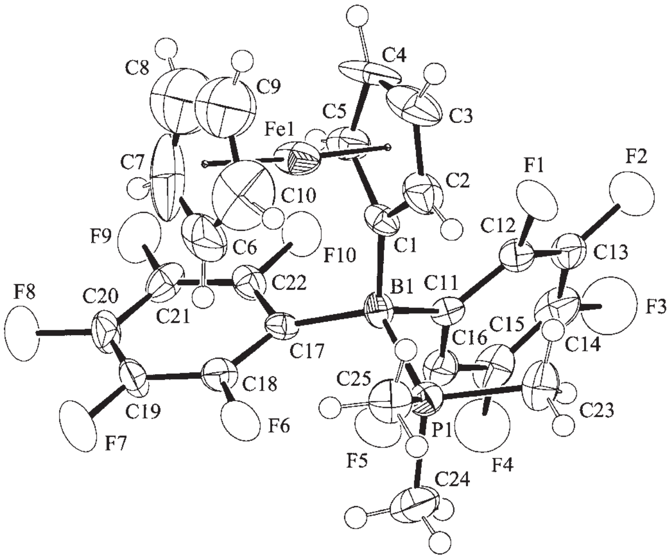
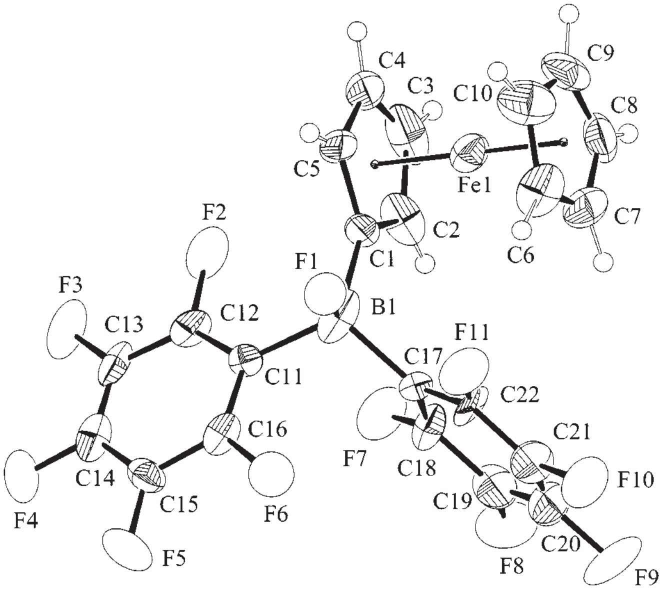
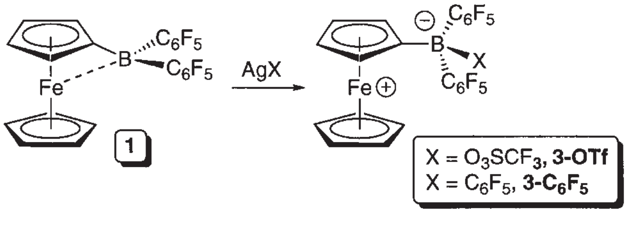


Fig. 5. ORTEP diagram of one molecule of **3-F**. Selected bond distances (Å): C(1)—B(1) 1.626(15), B(1)—F(1) 1.452(12), B(1)—C(11) 1.697(15), B(1)—C(17) 1.651(14). Selected bond angles (°): F(1)-B(1)-C(1) 108.1(11), F(1)-B(1)-C(11) 105.8(9), F(1)-B(1)-C(17) 109.2(8), C(1)-B(1)-C(11) 112.3(8), C(1)-B(1)-C(17) 111.5(10), C(11)-B(1)-C(17) 109.9(10).

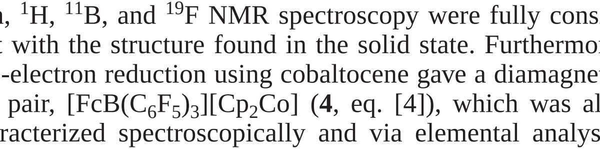


cally $B(C_6F_5)_3$ (23) and the chelating diboryl species 1,2-$C_6F_4[B(C_6F_5)_2]_2$ (24) has also been documented. Significantly, boryl ferrocene **1** does not react with $[NBu_4][BF_4]$, even upon heating. Recall, however, that electrochemical oxidation of **1** in the presence of this electrolyte was irreversible. Taken together, these observations suggest that oxidation of the iron center significantly increases the Lewis acidity of the boron center attached to the Cp ring.

Zwitterion **3-F** crystallizes as two independent molecules with essentially identical metrical parameters, differing only in the orientation of the fluoroborate moiety with respect to the Cp ligand plane. One of the molecules is shown in Fig. 5, along with selected metrical parameters; a picture of the other is given in the deposited material. The borate boron is tetrahedral in geometry and the B(1)—F(1) distance of 1.452(12) Å is typical of these bonding partners.

[3] 

Two other zwitterionic ferrocenium compounds were prepared in high yield and purity by oxidation of **1** with AgOTf and AgC_6F_5 (25) as shown in eq. [3]. Formation of **3-OTf** was essentially immediate upon dissolution of the reactants in dichloromethane, whereas the reaction leading to **3-C$_6$F$_5$** required several hours in toluene solvent. Complex **3-OTf** exhibits a resonance at –89.6 ppm in the ^{19}F NMR spectrum, attributable to the triflate CF_3 group, in addition to those of the C_6F_5 fluorines. The solid-state structure of this compound was determined by X-ray crystallography and an ORTEP diagram and selected metrical data is given in Fig. 6. Again, the quaternized boron center is now directed away (6.0°) from the iron center. The metrical parameters associated with the OTf moiety are similar to other η^1-coordinated trifluoromethanesulfonates (26).

[4] 

Zwitterion **3-C$_6$F$_5$** was also structurally characterized (Fig. 7). Consistent with boron quaternization, the boron atom is 3.59 Å away from the iron center (5.8° tilt). In addition, ^1H, ^{11}B, and ^{19}F NMR spectroscopy were fully consistent with the structure found in the solid state. Furthermore, one-electron reduction using cobaltocene gave a diamagnetic ion pair, $[FcB(C_6F_5)_3][Cp_2Co]$ (**4**, eq. [4]), which was also characterized spectroscopically and via elemental analysis. We were interested in **3-C$_6$F$_5$** as a potential activator for metallocene and related olefin polymerization catalyst precursors, since it is known that ferrocenium salts are capable of oxidizing neutral dialkyl metallocenes to the active cationic alkyl catalysts (27). Unfortunately, **3-C$_6$F$_5$** is not a strong enough oxidizing agent to remove an electron from Cp_2ZrMe_2. In fact, electrochemical measurements on this

Scheme 1.

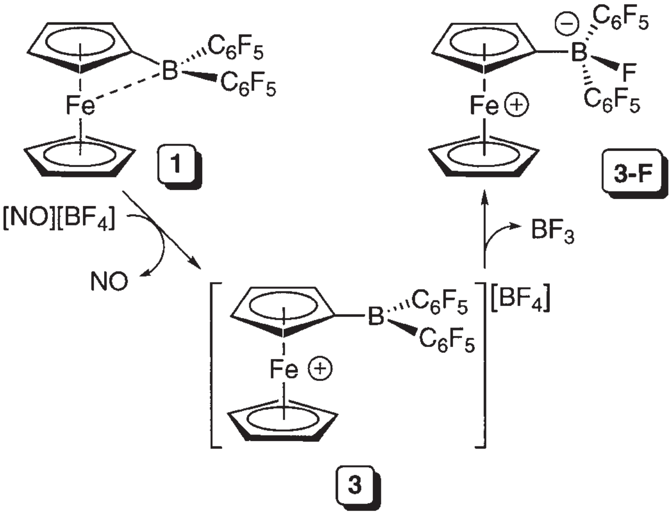
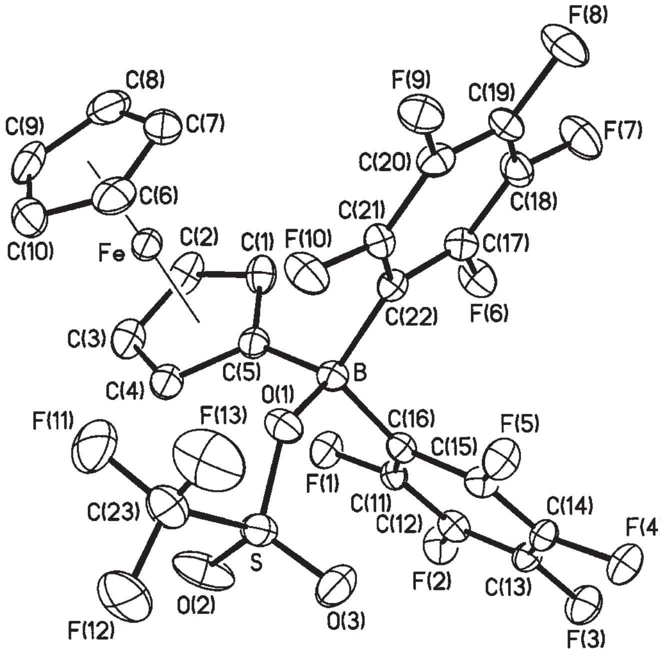
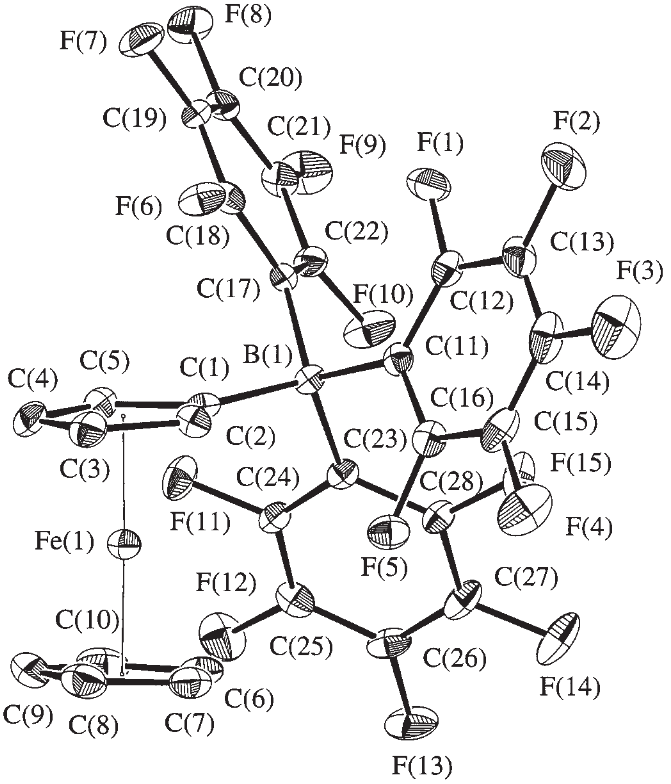


Fig. 6. ORTEP diagram of **3-OTf**. Selected bond distances (Å): B—C(5) 1.601(5), B—C(16) 1.624(5), B—C(22) 1.658(4), B—O(1) 1.575(4), S—O(1) 1.486(2), S—O(2) 1.416(7), S—O(3) 1.392(8), S—C(23) 1.824(6). Selected bond angles (°): O(1)-B-C(5) 107.7(3), O(1)-B-C(16) 109.0(3), O(1)-B-C(22) 104.8(2), C(5)-B-C(16) 112.7(3), C(5)-B-(C(22) 111.7(3), C(16)-B-C(22) 110.5(3).



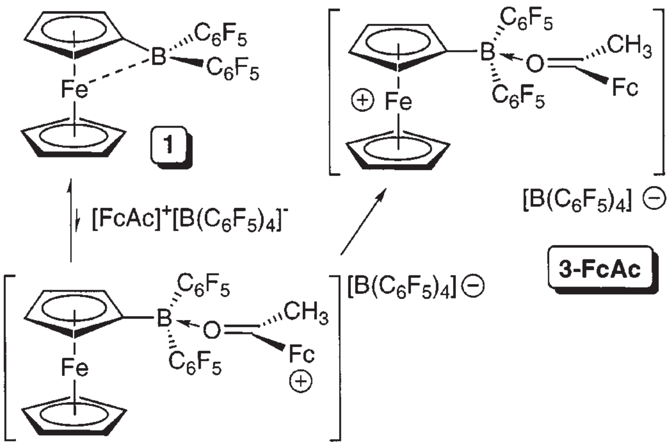
zwitterion show that its oxidation potential is at –472 mV relative to Fc/Fc$^+$, indicating that the -B(C_6F_5)$_3$ borate moiety is a very good σ-donor to the Cp ring, stabilizing the Fe(III) center substantially relative to unsubstituted ferrocene. Structurally, there is nothing unusual about this compound; the borate boron is tetrahedral and the B—C bond lengths are normal. Compound **3-C_6F_5** is related to the zwitterion Fc$^+$B(Fc)$_3$, reported several years ago (28).

Fig. 7. ORTEP diagram of **3-C_6F_5**. Selected bond distances (Å): Fe(1)—C(1) 2.152(2), Fe(1)—C(2) 2.100(2), Fe(1)—C(3) 2.065(2), Fe(1)—C(4) 2.069(2), Fe(1)—C(5) 2.098(2), C(1)—C(2) 1.433(3), C(1)—C(5) 1.434(3), C(2)—C(3) 1.428(3), C(4)—C(5) 1.414(3), C(3)—C(4) 1.409(3), B(1)—C(1) 1.666(3), B(1)—C(11) 1.648(3), B(1)—C(17) 1.657(3), B(1)—C(23) 1.666(3). Selected bond angles (°): C(1)-B(1)-C(11) 106.0(2), C(1)-B(1)-C(17) 105.7(2), C(1)-B(1)-C(23) 112.0(2), C(11)-B(1)-C(17) 113.2(2), C(11)-B(1)-C(23) 110.9(2), C(17)-B(1)-C(23) 108.9(2).



The observations above infer that the boron center of the putative species **3** is more Lewis acidic than that of neutral borane **1**. Unfortunately, attempts to prepare **3** with a weakly coordinating anion, namely [B(C_6F_5)$_4$]$^-$ met with failure, although some of the experiments aimed at preparing **3** with this counteranion support the notion that **3** is a stronger Lewis acid than **1**. For example, **1** may be oxidized using the acetylferrocenium reagent [FcAc]$^+$[B(C_6F_5)$_4$]$^-$. Acetylferrocenium reagents have been used to oxidize other ferrocene derivatives, since its oxidation potential of +270 mV is higher than most substituted ferrocene derivatives (23). Interestingly, it should not be a strong enough oxidizing agent to oxidize **1**, whose potential is at +450 mV relative to ferrocene, and yet when **1** and [FcAc]$^+$[B(C_6F_5)$_4$]$^-$ are mixed together, a rapid redox reaction is observed. Presumably the carbonyl group of the acetyl substituent is able to weakly coordinate the boron center in **1**, converting the electron-withdrawing -B(C_6F_5)$_2$ substituent into an electron-donating (relative to H) -B(L)(C_6F_5)$_2$ group (Scheme 2). Thus, when the acetylferrocenium species coordinates to the boron center in **1**, oxidation is rapid, producing the complex **3-FcAc**. ^{1}H NMR spectroscopy suggests that the neutral

Scheme 2.



acetylferrocene product of the electron transfer reaction remains coordinated to the boron center. All attempts to remove the acetylferrocene failed; clearly, FcAc is bound much more tightly to the Lewis acid center in **3** compared to that in **1**.

In conclusion, we have prepared bis-(pentafluorophenyl)ferrocenylborane and examined its chemical and electrochemical behaviour. The Lewis acidity of the boron center is attenuated due to a significant Fe → B interaction in the Fe(II) species, but oxidation of the iron center to Fe(III) disrupts this interaction, resulting in a more strongly Lewis acidic boron center.

Experimental section

General

All reactions were carried out under an argon atmosphere either on a double manifold high vacuum line or in an Innovative Technology System One dry box. Standard inert atmosphere, Schlenk, vacuum line, and glove box techniques were used throughout, under purified argon. Nuclear magnetic resonance (NMR) spectra were obtained in d_2-methylene chloride (CD_2Cl_2), d_6-benzene, or d_8-toluene on either Bruker AMX400 (^1H NMR, 400.132 MHz, ^{13}C NMR, 100.623 MHz), Bruker AMX300 (^1H NMR, 300.138 MHz, ^{11}B NMR, 96.293 MHz, ^{19}F NMR, 282.371 MHz), Varian XL200 (^{13}C NMR, 50.310 MHz, ^{11}B NMR, 64.184 MHz, ^{31}P NMR, 80.988 MHz) or Bruker ACE-200 (^1H NMR, 200.134 MHz) spectrometers. ^1H and ^{13}C NMR spectra were referenced to tetramethylsilane ($SiMe_4$) via solvent resonances. ^{11}B NMR spectra were externally referenced to borane trifluoride diethyl etherate (δ 0.0 ppm) and ^{19}F NMR spectra were externally referenced to $CFCl_3$ (δ 0.00 ppm) using an external standard of hexafluorobenzene (δ –163.0 ppm) (29). ^{31}P NMR spectra were reference to the external standard H_3PO_4 in deuterium oxide (δ 0.00 ppm). UV–vis spectra were obtained in dry $ClCH_2CH_2Cl$ using a Cary 5E UV–vis and IR spectrometer. The samples were prepared in volumetric flasks (~2.0×10^{-4} M) and transferred to a 1 mm pathlength air-tight cell fused to a Kontes Teflon tap. A background spectrum of the solvent was collected and automatically subtracted from the spectrum collected of the substrate. The molar absorptivity was calculated using Beer's Law. Elemental analyses were performed by Mrs. Dorothy Fox (University of Calgary) on a Control Equipment Corporation 440 elemental analyzer.

Toluene, tetrahydrofuran (THF), and hexanes were purified using the Grubbs purification system (30) and stored in solvent pots over a drying agent. α,α,α-Trifluorotoluene (TFT) was predried over phosphorus pentoxide (P_2O_5) and stored over CaH_2 in a glass bomb. Deuterated solvents were purchased from Cambridge Isotopes Laboratories and dried analogously.

All chemicals were purchased from Aldrich–Sigma unless otherwise stated except tris-(pentafluorophenyl)borane and ferrocene, which were purchased from Boulder Scientific Company. The $B(C_6F_5)_3$ dried as previously described, while ferrocene was purified by sublimation under dynamic vacuum at 55°C. Literature procedures were used to prepare the following reagents: $[n\text{-}Bu_4N]^+[B(C_6F_5)_4]$ (15), ($ClB(C_6F_5)_2$) (9), ($HB(C_6F_5)_2$) (7), ($LiB(C_6F_5)_4 \cdot Et_2O$) (31), ($AgC_6F_5$) (25), (FcHgCl) (8), and $[FcAc]^+[BF_4]^-$ (8).

Preparation of 1

Method A

Ferrocene (1.90 g, 10.2 mmol) and $HB(C_6F_5)_2$ (3.45 g, 9.98 mmol) were dissolved in toluene (60 mL), warmed slowly to 80°C, and stirred for 22.5 h under argon opened to a mercury bubbler. The reaction mixture was cooled and the toluene was removed under vacuum to afford a dark maroon solid. Boryl ferrocene product was extracted from unreacted $HB(C_6F_5)_2$ with hexanes. The hexanes were removed under vacuum to afford a crimson red crystalline solid. Residual ferrocene was removed from the product by sublimation (55°C under full vacuum). Yield of **1**: 4.39 g (8.28 mmol, 91%). X-ray quality crystals were grown from a saturated solution of **1** in dry hexamethyldisiloxane cooled to –35°C. UV (TFT) λ_{max} (nm) (ε): 231 (1.33×10^4). ^1H NMR (C_6D_6): 4.51 (t, 2H, J = 1.8 Hz, H_β), 4.03 (s, 5H, C_5H_5), 3.95 (bs, 2H, H_α). ^{13}C NMR (C_6D_6): 145.9 (d, $^1J_{CF}$ = 242 Hz), 141.9 (d, $^1J_{CF}$ = 242 Hz), 137.7 (d, $^1J_{CF}$ = 251 Hz), 115.0 (bs, WHM = 87 Hz, $C_{ipso}(C_6F_5)$), 79.5 (s, WHM = 7.4 Hz, C_β), 77.7 (s, WHM = 8 Hz, C_α), 70.5 (s, WHM = 7.4 Hz, C_5H_5). ^{11}B NMR (C_6D_6): 53.7 (bs, WHM = 650 Hz). ^{19}F NMR (C_6D_6): –129.3 (dd, 4F, F_o), –152.5 (t, 2F, F_p), –161.7 (dt, 4F, F_m). Anal. calcd. for $C_{22}H_9BF_{10}Fe$: C 49.86, H 1.71; found: C 49.69, H 1.90.

Method B

1-(Chloromercuric)ferrocene (2.403 g, 5.32 mmol) and $ClB(C_6F_5)_2$ (1.987 g, 5.23 mmol) were placed into a 100 mL bomb and hexanes (80 mL) added under vacuum transfer conditions. The mixture was warmed to room temperature and stirred for 22 h. The orange chalky suspension changed to a dark maroon solution with a green–grey precipitate. The suspension was cannula-transferred under argon flow into a 100 mL RBF and filtered to extract **1** from the mercuric chloride by-product. The $HgCl_2$ was washed with hexanes until the washings were colourless. The solvent was removed in vacuo to afford the maroon solid **1**. Yield: 2.461 g (4.64 mmol, 87%). The crude product was subjected to sublimation to remove any residual $ClB(C_6F_5)_2$.

Preparation of 2

Compound **1** (394 mg, 0.743 mmol) was dissolved in toluene and the solution degassed by a freeze–pump–thaw routine. At –196°C, an excess of PMe_3 (>15 cmHg in a 115 cm^3 bulb) was condensed into the flask. The reaction was warmed to –78°C during which time the maroon solution changed colour to light yellow. The solvent was removed in vacuo to afford a yellow powder. Yield: 443 mg (0.731 mmol, 98%). A single crystal was grown from a saturated toluene solution. ^{1}H NMR (d_8-toluene): 4.15 (t, 2H, J = 1.80 Hz, H_β), 3.99 (s, 5H, Fe(C_5H_5)), 3.62 (bs, 2H, H_a), 0.47 (d, 9H, $^2J_{PH}$ = 10.7 Hz, P(CH_3)$_3$). ^{13}C NMR (d_8-toluene): 148.1 (*d*, $^1J_{CF}$ = 234 Hz), 139.7 (*d*, $^1J_{CF}$ = 263 Hz, C_p), 137.7 (*d*, $^1J_{CF}$ = 246 Hz), 120.3 (bs, C_{ipso}(C_6F_5)), 80.2 (bs, C_{ipso}(C_5H_4)), 73.7 (*s*, C_α), 69.9 (*s*, C_β), 68.8 (*s*, Fe(C_5H_5)), 9.5 (*d*, $^1J_{CP}$ = 37 Hz, P(CH_3)$_3$). ^{11}B NMR (d_8-toluene): –13.5 (br d, $^1J_{BP}$ = 46 ± 10 Hz). ^{19}F NMR (d_8-toluene): –127.6 (d, 4F, F_o), –157.6 (t,2F, F_p), –163.2 (dt, 4F, F_m). ^{31}P NMR (d_8-toluene): –12.1 (br m, $^1J_{PB}$ = 46 ± 10 Hz).

Preparation of 3-F

Borane **1** (306 mg, 0.577 mmol) and nitrosonium tetrafluoroborate ($NOBF_4$) (65 mg, 0.557 mmol) were dissolved in CH_2Cl_2 (20 mL). The reaction vessel was placed into a 60°C oil bath and stirred for 30 min. The solution was cooled, degassed, and taken into the dry box where it was transferred to a flask fitted with a frit assembly. The solution was concentrated and the slurry sonicated; filtration afforded a dark blue solid. Yield: 250 mg (0.405 mmol, 72%). Crystals were grown by layering hexane on a concentrated solution in CH_2Cl_2 at 25°C. ^{1}H NMR: 33.1 (bs, WHM = 1360 Hz, 2H), 28.0 (bs, WHM = 700 Hz, 5H, Fe(C_5H_5)), 30.1 (bs, WHM = 2150 Hz, 2H). ^{19}F NMR: –157.1 (bs, 4F, F_o), –162.4 (t, 2F, F_p), –166.8 (bs, 4F, F_m); the B-F fluorine was not located.

Preparation of 3-Otf

Silver trifluoromethanesulfonate (245 mg, 0.953 mmol) and **1** (505 mg, 0.953 mmol) were placed into a flask fitted with a frit assembly. CH_2Cl_2 (25 mL) was condensed into the vessel under vacuum transfer conditions. The reaction was warmed to room temperature and stirred for 2 h during which time the solution changed from maroon to navy blue. The reaction mixture was filtered with a grey residue remaining on the frit and the solvent was removed under vacuum to afford 585 mg (0.858 mmol, 90%) of a paramagnetic dark blue solid of high purity by ^{19}F NMR. Crystals were grown at 25°C from a minimum amount of CH_2Cl_2 layered with hexane. UV (TFT) λ_{max} (nm) (ε): 256 (1.42 × 10^4). ^{1}H NMR: 42.0 (bs, WHM = 2780 Hz), 33.1 (bs, WHM = 2500 Hz), 30.1 (bs, WHM = 1050 Hz). ^{13}C NMR: 142.9 (d, $^1J_{CF}$ = 245 Hz), 137.7 (d, $^1J_{CF}$ = 257 Hz), 133.0 (d, $^1J_{CF}$ = 241 Hz), 92.1 (bs, C_{ipso}). ^{11}B NMR: –4.75 (bs, WHM = 394 Hz). ^{19}F NMR: –89.6 (s, 3F, CF_3), –155.8 (bs, 4F, F_o), –159.6 (s, 2F, F_p), –165.8 (s, 4F, F_m). Anal. calcd. for $C_{23}H_9BF_{13}FeO_3S$: C 40.68, H 1.34; found: C 40.51, H 1.13.

Preparation of 3-C_6F_5

Pentafluorophenyl silver(I) (AgC_6F_5) (614 mg, 2.23 mmol) and **1** (1.183 g, 2.23 mmol) were placed into a 100 mL bomb to which was added 50 mL of toluene. The vessel was sealed and warmed to 100°C in an oil bath for 23.5 h. The flask was cooled to room temperature and the green solution was cannula-transferred to a two-neck round-bottom flask with a frit assembly under an argon flow. The toluene was removed under vacuum and CH_2Cl_2 was condensed in at –78°C. The green solution was extracted from the silver powder by filtration and washed until the extracts were colourless. The solvent was removed in vacuo to afford a dark green solid. Yield: 1.397 g (2.00 mmol, 90%). Crystals of **3-C_6F_5** were grown at 25°C when dissolved into a minimum amount of dry CH_2Cl_2 layered with hexane. UV (TFT) λ_{max} (nm) (ε): 258 (1.33 × 10^4). ^{1}H NMR (d_8-toluene): 43.8 (bs, WHM = 1150 Hz), 30.2 (bs, WHM = 1400 Hz), 24.2 (bs, WHM = 780 Hz). ^{13}C NMR: 142.7 (d, 4C, $^1J_{CF}$ = 225 Hz), 139.3 (d, 2C, $^1J_{CF}$ = 246 Hz, C_p), 133.6 (d, 4C, $^1J_{CF}$ = 246 Hz). ^{11}B NMR: –23.7 (bs, 55 Hz). ^{19}F NMR: –139.6 (bs, 6F, F_o), –161.0 (s, 3F, F_p), –167.8 (d, 6F, F_m). Anal. calcd. for $C_{28}H_9BF_{15}Fe$: C 48.24, H 1.30; found: C 48.25, H 1.30.

Preparation of [FcB(C_6F_5)$_3$][Cp_2Co] (4)

3-C_6F_5 (420 mg, 0.619 mmol) and cobaltocene (117 mg, 0.619 mmol) were dissolved in dry CH_2Cl_2 (12 mL). The solution was stirred at room temperature for 2 h. The solution was run through a frit and the solvent removed to afford a brown crystalline solid. Yield: 490 mg (0.564 mmol, 91%). ^{1}H NMR: 5.60 (s, 10H, Co(C_5H_5)), 4.00 (t, 2H, J = 1.68 Hz, H_β), 3.94 (bs, 2H, H_α), 3.67 (s, 5H, Fe(C_5H_5)). ^{13}C NMR: 149.3 (d, $^1J_{CF}$ = 246 Hz), 138.4 (d, $^1J_{CF}$ = 245 Hz, C_p), 137.0 (d, $^1J_{CF}$ = 258 Hz), 85.2 (s, Co(C_5H_5)), 75.9 (s, C_α), 68.3 (s, Fe(C_5H_5)), 67.0 (s, C_β). ^{11}B NMR: –13.2 (bs, WHM = 39 Hz). ^{19}F NMR: –128.3 (d, 6F, F_o), –164.5 (dt, 3F, F_p), –168.0 (t, 6F, F_m). Anal. calcd. for $C_{38}H_{19}BCoF_{15}Fe$: C 51.51, H 2.16; found: C 51.30, H 2.34.

Preparation [FcAc]$^+$[B(C_6F_5)$_4$]$^-$

Acetylferrocenium tetrafluoroborate (298 mg, 0.946 mmol) and lithium tetrakis(pentafluorophenyl)borate etherate (843 mg, 0.947 mmol) were dissolved in CH_2Cl_2 and stirred for 12 h. The mixture was filtered and the solid washed with CH_2Cl_2 three times. The solvent was removed from the filtrate to afford a fluffy blue solid. Yield: 794 mg (0.875 mmol, 92%). ^{1}H NMR: 35.8 (bs, WHM = 750 Hz), 30.4 (bs, WHM = 1800 Hz), 0.90 (s, 3H, $COOCH_3$), –12.1 (bs, WHM = 120 Hz). ^{13}C NMR: 147.5 (d, $^1J_{CF}$ = 242 Hz), 138.2 (d, $^1J_{CF}$ = 232 Hz), 135.9 (d, $^1J_{CF}$ = 232 Hz), 126.3 (bs, C_{ipso}(C_6F_5)). ^{11}B NMR: –16.9 (s, WHM = 28 Hz). ^{19}F NMR: –135.6 (s, 8F, F_o), –164.4 (s, 4F, F_p), –169.4 (s, 8H, F_m). Anal. calcd. for $C_{36}H_{12}BF_{20}FeO$: C 47.66, H 1.33; found: C 46.88, H 1.53.

Preparation of 3-FcAc

Borane **1** (262 mg, 0.494 mmol) and [FcAc]$^+$[B(C_6F_5)$_4$]$^-$ (440 mg, 0.485 mmol) were loaded into flask fitted with a frit assembly. CH_2Cl_2 (15 mL) was condensed onto the solids under vacuum transfer conditions. The solution was warmed to room temperature and stirred for 80 min. The solvent was removed in vacuo to afford a violet solid which was triturated with dry hexanes and filtered to collect the solid, which was washed with hexanes three times. Yield: 683 mg (0.475 mmol, 98%). IR (cm^{-1}): 3123, 1644 (C=O), 1516, 1464, 1277, 1089, 979. ^1H NMR: 45.2 (bs, 2H, WHM = 1630 Hz, $H_{\alpha/\beta}$); 31.9 (bs, 5H, WHM = 900 Hz, BCpFe($C_5\mathit{H}_5$)), 22.3 (bs, 2H, WHM = 1900 Hz, $H_{\alpha/\beta}$), 7.21 (s, 2H), 6.85 (s, 5H, AcCpFe($C_5\mathit{H}_5$)), 2.15 (s, 3H, $C\mathit{H}_3$). ^{11}B NMR: –17.0 (s, WHM = 17.4 Hz, $\mathit{B}(C_6F_5)_4$). ^{19}F NMR: –149.8 (s, 1F), –151.2 (s, 2F), –153.4 (s, 1F), –158.9 (s, 1F), 164.8 (s, 1F), –133.2 (s, F_o, 8F), –162.4 (s, F_p, 4F), –167.2 (s, F_m, 8F).

Relative Lewis acidity

In the dry box a known amount of Lewis acid was placed into an NMR tube, dissolved in a measured volume of CD_2Cl_2 and capped with a rubber septum. The sample was cooled to –78°C to which dry crotonaldehyde was added via microsyringe to the NMR tube. The tube was quickly shaken to ensure mixing. The ^1H NMR spectrum was collected at –20°C.

Cyclic voltammetry

Cyclic volammetric measurements were made on α,α,α-trifluorotolune (TFT) solutions under argon at 25°C, using a three-electrode cell attached to a Hitek Instruments of England Potentiostat (Type DT2101) and a Waveform Generator PPRI system. The electrolyte employed was $[n\text{-}Bu_4N]^+[B(C_6F_5)_4]^-$ with electrolyte:substrate concentrations of approximately 100:1. The air tight electrochemical cell consisted of a thick-walled glass bulb, Kontes Teflon tap, a set of platinum wire electrodes (working and secondary), and a silver wire quasireference electrode. Each experiment involved collecting the data for the substrate alone, which was then referenced to the Fc/Fc^+ couple in this medium. Samples were prepared in the dry box as follows: a known amount of electrolyte $[nBu_4N]^+[B(C_6F_5)_4]^-$ was dissolved into a minimum amount of dry TFT and added quantitatively to a volumetric flask. This solution was diluted to a known volume with additional TFT. The solution was mixed thoroughly and transferred to the electrochemical cell which contained the substrate and a small stir bar under argon. The Teflon tap was closed and a small amount of ferrocene was placed in a side arm. Outside the dry box, the electrochemical cell was attached to the potentiostat and the data were collected with a scan rate of 0.1 V s^{-1} without stirring. After the data for the substrate were collected the Teflon tap was opened to allow the ferrocene in the side arm to be added and dissolved. The stirring was halted and the CV data for the internal reference were collected along with the substrate. The half-wave potential of the substrate was referenced to that of the Fc/Fc^+ redox couple.

X-Ray crystallography

Suitable crystals were mounted on glass fibers using paraffin oil and cooled to the data collection temperature; details of crystal data, data collection, and structure refinement have been provided in Table 3.

*Structural determination of **1** and **3-Otf***

Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied (32) to **1**. Attempts to correct the data set of **3-OTf** for absorption yielded T_{min}/T_{max} of unity and no correction was applied. Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. Refinement of the Flack parameter for **1** yielded 0.39(1) indicating that the true hand of the data set could not be determined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The triflate ion in **3-OTf** was located disordered in two positions with refined site occupancy of roughly 50/50. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.1 program library (Sheldrick, 1997, WI.).

*Structural determination of **2** and **3-F***

Measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation for **2** and on an Enraf–Nonius CAD-4 diffractometer with graphite monochromated Cu Kα radiation for **3-F**. Cell constants and an orientation matrix for data collection were obtained from 25 reflections. The data were collected at a temperature of 170(2) K (**2**) and 295(2) K (**3-F**) using the ω-2θ scan technique. The intensities of three standard reflections were measured after every 200 reflections and decreased by 1.1% (**2**) and 0.69% (**3-F**). The data were corrected for decay, absorption (33), and for Lorentz and polarization effects. The structure of **2** was solved by direct methods (34) and expanded using Fourier techniques (35). The non-hydrogen atoms were refined anisotropically. The Cp and phenyl rings were constrained as regular pentagons and hexagons, respectively. H-atoms were included at geometrically idealized positions. The structure of **3-F** was solved by direct methods and expanded using Fourier techniques. There were two independent molecules in an asymmetric unit. The non-hydrogen atoms were refined anisotropically. H-atoms were included at geometrically idealized positions. For both structures, the weighting scheme was based on counting statistics and the final difference Fourier map was essentially featureless. Neutral atom scattering factors were taken from Cromer and Waber (36). Anomalous dispersion effects were included in Fcalc (37); the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley (38). The values for the mass attenuation coefficients are those of Creagh and Hubbel (39). All calculations were performed using the teXsan (40) crystallographic software package of Molecular Structure Corporation.

*Structural determination of **3-C_6F_5***

Measurements were made on a Rigaku/ADSC CCD area detector with graphite monochromated Mo Kα radiation. The data were collected at a temperature of –93(1)°C to a max 2θ value of 61.1° in 0.50° oscillations with 14.0 s exposures. A sweep of data was done using ϕ oscillations from 0.0 to 190.0° at χ = –90° and a second sweep was performed

Table 3. Summary of data collection and structure refinement details for **1**, **2**, **3-F**, **3-OTf**, and **3-C_6F_5**.

	1	**2**	**3-F**	**3-OTf**	**3-C_6F_5**
Formula	$C_{22}H_9BF_{10}Fe$	$C_{25}H_{18}BF_{10}PFe$	$C_{22}H_9BF_{11}Fe$	$C_{23}H_9BF_{13}FeO_3S$	$C_{28}H_9BF_{15}Fe$
Fw	529.95	606.02	548.95	679.02	697.01
Temperature (K)	203(2)	170(2)	295(1)	203(2)	180(1)
λ (Å)	0.71073	0.71069	1.54178	0.71073	0.71069
Dimensions (mm^3)	0.4 × 0.2 × 0.1	0.42 × 0.38 × 0.4	0.5 × 0.4 × 0.22	0.1 × 0.1 × 0.2	0.45 × 0.40 × 0.40
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	P	$P2_1/c$	$P2_1/n$
a (Å)	9.758(1)	10.899(3)	12.226(2)	10.909(3)	15.9529(13)
b (Å)	11.994	12.953(2)	13.1790(10)	12.896(4)	10.0171(7)
c (Å)	33.255(4)	17.012(3)	14.123(4)	17.017(5)	16.5882(3)
α (°)			109.40(2)		
β (°)		92.95(2)	108.87(2)	95.177(6)	111.1394(5)
γ (°)			93.150(10)		
V (Å^3)	3892.2(7)	2398.5(8)	1997.1(9)	2384(1)	2472.4(2)
Z	8	4	4	4	4
d_{calc} (mg m^{-3})	1.809	1.678	1.826	1.892	1.872
F(000)	2096	1216	1084	1340	1372
μ (mm^{-1})	0.878	0.786	0.7113	0.850	0.743
Max/min transmission	0.9281/0.5980	0.7334/7541	0.8082–1.000		0.8629–1.000
Scan type		ω-2θ	ω-2θ		
Scan range (°)	1.22–28.65	2.27–27.57	0.80+0.35θ 119.9	1.87–22.50	4.0–66.1
2θ (max) (°)		55.1			66.1
Reflections	29 867	5798	5953	5510	21 247
Unique reflections	9296	5531	5645	3039	6493
No. of variables	614	283	632	443	406
Restraints	0	0	0	38	0
R			0.063		0.035
R_w			0.033		0.032
$R1^a$	0.0373	0.0584		0.0327	
$wR2^a$	0.0616	0.1455		0.0621	
gof	1.008	1.010	2.73	1.082	1.26
Max Δ/σ (final cycle)			0.00		0.0003
Residual density (e Å^{-3})	–0.588–0.585	–0.656–0.744	–0.46–0.58	–0.292–0.295	–0.61–0.59

[a] Final indices $I > 2\theta(I)$.

using ω oscillations between –23.0 and 18.0° at $\chi = -90°$. The crystal-to-detector distance was 38.851(6) mm and the detector swing angle was –10.0°. The data were corrected for decay, absorption (33), and for Lorentz and polarization effects. The structure was solved by direct methods (34) and expanded using Fourier techniques.(35) The non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed in calculated positions with C-H = 0.98 Å. The final cycle of full-matrix least-squares refinement was based on all 6493 unique reflections and 406 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber (36). Anomalous dispersion effects were included in *F*calc (37); the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley (38). The values for the mass attenuation coefficients are those of Creagh and Hubbel (39). All calculations were performed using the teXsan (40) crystallographic software package of Molecular Structure Corporation.

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