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# A sandwich complex of trimesitylborane Mes<sub>3</sub>B: synthesis, characterization and anion binding properties of Mes<sub>2</sub>B[( $\eta^6$ -Mes)FeCp]<sup>+</sup><sup>†</sup><sup>‡</sup>

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As part of our continuing interest in the chemistry of Lewis acidic organoboron compounds as anion receptors, we have synthesized the hexafluorophosphate salt of the cationic borane  $Mes_2B[(\eta^6-Mes)FeCp]^+$  ([1]<sup>+</sup>) by reaction of  $[(\eta^6-naphthalene)FeCp][PF_6]$  with  $Mes_3B$ . This compound, which undergoes two quasi-reversible reductions at  $E_{1/2} = -1.56$  V and -2.40 V, reacts with both fluoride and cyanide anions in THF or MeOH to afford the corresponding zwitterionic fluoro- (1-F) and cyano-borate (1-CN) species, respectively. Spectrophotometric titrations carried out in THF indicate that the fluoride and cyanide binding constants of [1]<sup>+</sup> are much larger than those of Mes<sub>3</sub>B. This difference points to the favorable inductive and coulombic effects imparted by the cationic [CpFe]<sup>+</sup> moiety on the Lewis acidity of the boron center.

### Introduction

Owing to their electronic unsaturation and inherent Lewis acidity, organoboranes have found widespread applications for the recognition of nucleophilic anions including the toxic fluoride and cyanide ions.<sup>1–6</sup> These small anions are sufficiently basic to bind to the boron atom of these derivatives leading to the formation of the corresponding borate anions (Chart 1).<sup>7</sup> In an effort to enhance the strength of the anion–boron interaction, a great deal of effort has been devoted to the peripheral decoration of the organoborane by main group onium ions<sup>8–16</sup> such as ammonium,<sup>17–27</sup> phosphonium,<sup>19,22,28–33</sup> sulfonium<sup>19,34–36</sup> and telluronium ions.<sup>36</sup> The presence of these cationic functionalities leads to favorable coulombic effects which stabilize the fluoroborate moiety against dissociation (Chart 1). The success of this approach is illustrated by the ability of such cationic boron derivatives to bind cyanide and fluoride anions in aqueous solutions.<sup>23,28,29</sup>

Cationic organoboranes can also be obtained by positioning the boron moiety in the vicinity of a cationic transition metal moiety<sup>37–41</sup> as in  $[I]^{+42}$  and  $[II]^{+.43}$  In such cases however, dissipation of the cationic charge of the transition metal complex over several ligands may limit its impact on the anion affinity of the boron center. Such limitations may be partly overcome in smaller complexes that more efficiently focus their positive charge close to the boron atom. This possibility is illustrated by the seminal work of Shinkai *et al.* who showed that oxidation of ferrocenyl boronic acid into ferrocenium boronic acid ([**III**]<sup>+</sup>) leads to an increase in the fluoride binding by 3.5 orders of magnitude.<sup>44</sup> This phenomenon has also been shown to impact the anion affinity of a series of other ferrocene boron species<sup>27,38,45,46</sup> including ferrocenyldimesitylborane (**IV**), a complex recently synthesized by the Aldridge group.<sup>47</sup> Inspired by this body of work, we have now decided to determine if similar effects could be observed in borylated [CpFe( $\eta^{6}$ -arene)]<sup>+</sup> cationic sandwich complexes. In this paper, we now report on the synthesis and anion binding properties of Mes<sub>2</sub>B[( $\eta^{6}$ -Mes)FeCp]<sup>+</sup> ([**1**]<sup>+</sup>, Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), a cationic analog of **IV**.



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<sup>†</sup> Dedicated to our friend Didier Astruc, on the occasion of his 65th birthday.

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Chart 1 Anion binding by neutral (left) and cationic (right) organoboranes; X=F, CN; R = organic substituent.



Scheme 1 Synthesis of [1][PF<sub>6</sub>].

# **Results and discussion**

# Synthesis and characterization of [1][PF<sub>6</sub>]

Sandwich complexes of trimesitylborane (Mes<sub>3</sub>B) have been previously synthesized by the group of Elschenbroich who reported the sequential decoration of the mesityl groups of this derivative by Cr(CO)<sub>3</sub> moieties.<sup>48</sup> Encouraged by these results, we allowed  $[(\eta^6-naphthalene)FeCp][PF_6]^{49}$  to react with trimesitylborane Mes<sub>3</sub>B in 1,3-dichloropropane (Scheme 1). This reaction proceeded via smooth arene exchange to afford  $Mes_2B[(\eta^6-Mes)FeCp]^+$  as an hexafluorophosphate salt ([1][ $PF_6$ ]). This salt, which can be stored in air for extended periods of time, is soluble in solvents of moderate polarity such as CHCl<sub>3</sub>, THF and acetone. It is however poorly soluble in MeOH and CH<sub>3</sub>CN. The <sup>1</sup>H NMR spectrum of the compound in CDCl<sub>3</sub> exhibits one singlet resonance at 4.81 ppm corresponding to the CH groups of the cyclopentadienyl ring. The rest of the spectrum is more challenging to assign. Indeed, since coordination of the [CpFe]<sup>+</sup> moiety to one of the mesityl group will differentiate the two faces of the boron-centered propeller, the six CH<sub>3</sub><sup>Mes</sup> as well as the four aromatic CH<sup>Mes</sup> groups are magnetically unequivalent. Because of accidental overlaps, four resonances are observed in the methyl region. Similarly, four resonances are observed in the 6.2 to 7.0 ppm range for the aromatic CHMes groups. The 19F NMR spectrum exhibits a doublet at -76 ppm which corresponds to the  $PF_6^$ anion. The crystal structure of [1][PF<sub>6</sub>] has been determined (Table 1). The boron atom adopts a trigonal planar geometry as indicated by the sum of the  $C_{aryl}$ -B- $C_{aryl}$  angles ( $\Sigma_{(C-B-C)}$  = 359.8°). One of the mesityl substituents is coordinated to the iron center in an  $\eta^6$ -fashion with a distance of 1.55 Å between the centroid of the coordinated mesityl ring and iron atom. Examination of the Fe–C<sub>Mes</sub> bonds which are within  $\sim 0.1$  Å from one another indicates that the iron atom is essentially centrally located over the mesityl substituent. The increase in steric encumbrance caused by attachment of the [CpFe]<sup>+</sup> group leads to a 0.44 Å displacement of the boron atom above the plane containing the central six-membered ring of the coordinated mesityl substituent (Fig. 1).

The UV-vis absorption spectrum of  $[1][PF_6]$  in THF displays two distinct low-energy bands centered at 335 nm and 290 nm (Fig. 2). To elucidate the origin of these bands, the structure of  $[1]^+$  was optimized using density functional

Crystal data	[1][PF <sub>6</sub> ]	1-F	1-CN
Empirical formula	$C_{32}H_{38}BF_6FeP$	C <sub>32</sub> H <sub>38</sub> BFFe	C <sub>33</sub> H <sub>38</sub> BNFe· CHCl <sub>3</sub>
Formula mass	634.25	508.28	634.67
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$Pna2_1$	$P2_{1}/c$
a/Å	20.827(2)	17.1967(10)	14.5594(7)
b/Å	8.7404(10)	17.6328(10)	13.9523(6)
$c/ m \AA$	16.2270(18)	8.5350(5)	15.6438(7)
$\beta/^{\circ}$	90.00	90.00	96.5310(10)
$V/\text{\AA}^3$	2953.9(5)	2588.0(3)	3157.2(2)
Ζ	4	4	4
$\rho_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.426	1.305	1.335
$\mu/\mathrm{mm}^{-1}$	0.624	0.609	0.756
F(000)	1320	1080	1328
Crystal size/mm	0.20 $\times$ 0.12 $\times$	$0.35 \times 0.09 \times$	0.38 $\times$ 0.12 $\times$
	0.05	0.07	0.05
$\theta_{\min} - \theta_{\max} / ^{\circ}$	2.33-22.19	2.31-24.30	2.33-27.73
T/K	110(2)	110(2)	110(2)
Scan mode	ω, φ	ω, φ	ω, φ
Index range	$-23 \le h \le 23$	$-22 \le h \le 22$	$-19 \le h \le 19$
	$-10 \le k \le 10$	$-23 \le k \le 23$	$-18 \le k \le 18$
	$-18 \leq l \leq 18$	$-11 \leq l \leq 11$	$-20 \leq l \leq 20$
Collected reflections	4636	6449	7834
Unique reflections	4011	4877	6249
Refined parameters	379	326	409
$R_1$ , w $R_2$ (all data)	0.0554, 0.1107	0.0508, 0.0618	0.0544, 0.1077
$\rho_{\rm fin}$ (max., min.)/e·Å <sup>-3</sup>	0.716, -0.417	0.309, -0.355	0.401, -0.517
Flack parameter	0.02(2)	0.676(11)	_



**Fig. 1** Crystal structure of [1][PF<sub>6</sub>] with thermal ellipsoid plots (50% probability). For clarity, the hydrogen, phosphorus and fluorine atoms are omitted and the mesityl substituents are represented by a thin line. Selected bond lengths (Å) and angles (°): Fe(1)–C(6) 2.107(5), Fe(1)–C(7) 2.086(4), Fe(1)–C(8) 2.116(4), Fe(1)–C(9) 2.163(4), Fe(1)–C(10) 2.077(4), Fe(1)–C(11) 2.072(4), B(1)–C(9) 1.593(7), B(1)–C(15) 1.575(6), B(1)–C(24) 1.584(7); C(15)–B(1)–C(24) 122.0(4), C(15)–B(1)–C(9) 113.7(4), C(24)–B(1)–C(9) 124.1(4).



**Fig. 2** Top: experimental UV-vis spectrum of [1][PF<sub>6</sub>] (6.24 ×  $10^{-5}$  mol L<sup>-1</sup>) in THF overlaid with the calculated TD-DFT electronic excitations. The accepting orbitals involved in these electronic excitations are as follows:  $E_{a-d}$ : LUMO;  $E_e$ , LUMO and LUMO + 1,  $E_f$ : LUMO + 1. Bottom: view of the LUMO and LUMO + 1 (isovalue = 0.02) of cation [1]<sup>+</sup>.

theory (DFT) methods (functional: BP86; mixed basis set: Fe: aug-cc-pvTz-pp; B: 6-31 + g(d'); C, H: 6-31g). The optimized structure, which is close to that determined experimentally, was subjected to a time-dependent DFT (TD-DFT) calculation (functional: MPW1PW91; mixed basis set: Fe: aug-ccpvTz-pp; B: 6-31 + g(d'); C, H: 6-31g) using the polarizable continuum model with THF as a solvent. The TD-DFT calculation indicates that the low-energy bands are dominated by transitions from filled orbitals into the LUMO ( $E_a, E_b, E_c$ ,  $E_{\rm d}$ ) for the band observed at 335 nm and the LUMO + 1 ( $E_{\rm f}$ ,  $E_{\alpha}$ ) for that observed at 290 nm (Fig. 2). Inspection of the frontier molecular orbitals shows that the LUMO carries an important contribution from the boron  $p_{\pi}$  orbital, which is typical for triarylboranes, and the LUMO + 1 bears an increased contribution from the iron sandwich moiety with both Fe and Cp/Mes ligand character.

The cyclic voltammogram of [1][PF<sub>6</sub>] in THF shows two quasi-reversible reduction waves at  $E_{1/2} = -1.56$  V and -2.40 V (vs. Fc/Fc<sup>+</sup>) as well as smaller intermediate feature ( $E_{red} = -1.98$  V) which may reflect the appearance of a new species by partial decomposition of [1]<sup>+</sup> under the condition of the electrochemical measurement (Fig. 3). Interestingly, addition of one equivalent of fluoride anion to the electrochemical cell afforded a species that only show one major reduction wave at -2.37 V (vs. Fc/Fc<sup>+</sup>). In a simplistic scenario (Fig. 3), these observations suggest that the wave observed at  $E_{1/2} = -1.56$  V for [1]<sup>+</sup> corresponds to the reduction of the boron center whose electron accepting



**Fig. 3** Cyclic voltammograms of [1][PF<sub>6</sub>] (top) and *in situ* generated 1-F (bottom) in THF with [[1][PF<sub>6</sub>]] = 1.9 mM, [TBAPF<sub>6</sub>] = 0.1 M (TBA = tetra-*n*-butylammonium) and  $\nu$  = 300 mV s<sup>-1</sup>.

properties are neutralized by coordination of a fluoride anion. The latter implies formation of a stable fluoride adduct, namely 1-F, whose formation has indeed been confirmed (vide infra). The similarity of the potential observed between the second reduction wave of  $[1]^+$  (-2.40 V) and that of 1-F (-2.37 V) suggests that these reduction waves involve addition of a 19th valence electron to the iron sandwich moiety. The formation of 19-electron iron sandwich complexes is a well established phenomenon extensively documented by the contribution of Astruc.<sup>50</sup> The electronic independence of the boron and iron moiety implied in the above discussion is clearly an oversimplification. Indeed, comparison of the first reduction potential of  $[1]^+$  ( $E_{1/2} = -1.56$  V) with that of  $[(\eta^6\text{-mesitylene})\text{FeCp}]^+$  ( $E_{1/2} = -2.01$  vs. Fc/Fc<sup>+</sup>)<sup>50</sup> and  $[4-(Me_3N)-2,6-Me_2-C_6H_2-BMes_2]^+$  ( $E_{1/2} = -2.55$  V vs.  $Fc/Fc^{+})^{21}$  indicates that the two electroactive boron and iron moieties effectively communicate.

Encouraged by this result, we decided to investigate the Lewis acidity of  $[1]^+$  by examination of its reaction with fluoride and cyanide in organic solvents. Reactions of [1][PF<sub>6</sub>] with excess KF or KCN in MeOH resulted in the rapid precipitation of 1-F and 1-CN, which have been isolated

by filtration. When the same reaction was attempted with Mes<sub>3</sub>B, anion coordination to the boron center was not observed thus attesting to the favorable coulombic effects resulting from the decoration of a mesityl ring by a cationic [CpFe]<sup>+</sup> fragment. Compounds 1-F and 1-CN have been isolated and characterized by multinuclear NMR spectroscopy, IR spectroscopy and single crystal X-ray diffraction. The <sup>11</sup>B NMR signals at 5.9 ppm for **1-**F and -14.1 ppm for 1-CN are in the expected range for four coordinate boron species.<sup>23,28,29</sup> The <sup>19</sup>F NMR signal of 1-F appearing at -168.2 ppm indicates the presence of a triarylfluoroborate moiety.<sup>23,29</sup> An absorption band at 2170 cm<sup>-1</sup> in the IR spectrum of 1-CN is typical for triarylcyanoborate species.<sup>23,28</sup> Anion coordination to the boron atom leads to some notable changes in the <sup>1</sup>H NMR spectrum of the complex. While signal overlaps make a clear assignment of the methyl resonances difficult, the number of aromatic CH<sup>Mes</sup> resonances decreases from four in  $[1]^+$  to three resonances of 2:2:2 intensity in both 1-F and 1-CN. One of these three resonances, which appears up-field at 5.56 ppm for 1-F and 5.68 ppm for 1-CN, can be assigned to the aromatic CH<sup>Mes</sup> resonances of the mesityl group coordinated to the iron center.<sup>51</sup> The other two resonances correspond to the aromatic CH<sup>Mes</sup> groups pointing, respectively, above and below the plane of the coordinated mesityl substituent. Altogether, these NMR data



Scheme 2 Left: reactions of  $[1][PF_6]$  with potassium fluoride and cyanide ions in methanol. Right: molecular motion-averaged structure of 1-F and 1-CN observed by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

suggest that the molecular motion-averaged solution structure of 1-F and 1-CN is that of a complex of  $C_s$  symmetry as depicted in Scheme 2. The crystal structures of 1-F and 1-CN have been determined (Fig. 4, Table 1). The B-F bond length in 1-F (1.463(3) Å) and B-C<sub>CN</sub> bond length in 1-CN (1.628(3) Å) are comparable to those of other triarylfluoroborate and triarylcyanoborate species, respectively.<sup>18</sup> The boron center of these two compounds is distinctly pyramidalized as indicated by the sum of the Caryl-B-Caryl angles in both structures  $(\Sigma_{(C-B-C)} = 340.7^{\circ} \text{ for } 1\text{-F}, \text{ and } 340.1^{\circ} \text{ for } 1\text{-CN}).$  Interestingly, pyramidalization of the boron center leads to a relief of the steric repulsion occurring between the Mes<sub>2</sub>B and  $[(\eta^6-Mes)FeCp]^+$  moieties of  $[1]^+$ . The decreased steric encumbrance in 1-F and 1-CN when compared to  $[1]^+$  is reflected by the relatively small displacement of the boron atom (0.10 Å in 1-F, 0.19 Å in 1-CN vs. 0.44 Å in [1]<sup>+</sup>) above the plane containing the central six-membered ring of the coordinated mesityl substituent. The separation between the iron atom and the centroid of the coordinated mesityl ring in 1-F (1.54 Å) and 1-CN (1.55 Å) remain virtually identical to that observed in  $[1]^+$  (1.55 Å).

To measure the effect induced by coordination of the  $[CpFe]^+$  moiety to a mesityl ring of Mes<sub>3</sub>B, the anion affinity of [1]<sup>+</sup> has been measured in organic solvents. Addition of TBAF or TBACN (TBA = tetra-*n*-butylammonium) to a THF solution of [1][PF<sub>6</sub>] resulted in a progressive quenching of the low energy band observed in the UV-vis spectrum of [1]<sup>+</sup> (Fig. 5). These changes, which can be rationalized by involvement of the boron  $p_{\pi}$  orbital in the formation of a B–X bond (X=F or CN), indicate that both fluoride and cyanide bind to the boron atom of [1]<sup>+</sup>. Fitting of the resulting data to a 1:1 binding isotherm indicates that the fluoride (*K*(F<sup>-</sup>)) and cyanide binding constants (*K*(CN<sup>-</sup>)) exceed the measurable range and are at least equal to 10<sup>7</sup> M<sup>-1</sup>. Although no accurate number could be obtained, these experiments show that the fluoride and cyanide binding constants of [1]<sup>+</sup> exceed those of



Fig. 4 ORTEP drawings of 1-F (left) and 1-CN (right) with thermal ellipsoid plots (50% probability). For clarity, the hydrogen atoms are omitted and the mesityl substituents are represented by a thin line. Selected bond lengths (Å) and angles (°) for 1-F: Fe(1)–C(6) 2.095(2), Fe(1)–C(7) 2.059(2), Fe(1)–C(8) 2.086(2), Fe(1)–C(9) 2.185(2), Fe(1)–C(10) 2.084(2), Fe(1)–C(11) 2.067(2), B(1)–C(9) 1.684(3), B(1)–C(15) 1.678(3), B(1)–C(24) 1.663(3), F(1)–B(1) 1.463(3); C(24)–B(1)–C(15) 109.9(2), C(24)–B(1)–C(9) 118.6(2), C(15)–B(1)–C(9) 112.2(2), F(1)–B(1)–C(9) 102.1(2). Selected bond lengths (Å) and angles (°) for 1-CN: Fe(1)–C(6) 2.076(2), Fe(1)–C(7) 2.102(2), Fe(1)–C(8) 2.057(2), Fe(1)–C(9) 2.090(2), Fe(1)–C(10) 2.199(2), Fe(1)–C(11) 2.106(2), C(10)–B(1) 1.682(3), C(15)–B(1) 1.684(3), C(24)–B(1) 1.628(3), C(25)–B(1) 1.668(3); C(24)–B(1)–C(10) 104.05(14);C(25)–B(1)–C(10) 118.68(14); C(25)–B(1)–C(15) 107.34(14); C(10)–B(1)–C(15) 114.09(14).



**Fig. 5** Top: changes in the UV-vis absorption spectra of [1][PF<sub>6</sub>] ( $6.24 \times 10^{-5} \text{ mol } L^{-1}$ ) in THF upon addition of TBAF (left); experimental and calculated 1 : 1 fluoride binding isotherms (right). Bottom: changes in the UV-vis absorption spectra of [1][PF<sub>6</sub>] ( $7.70 \times 10^{-5} \text{ mol } L^{-1}$ ) in THF upon addition of TBACN (left); experimental and calculated 1 : 1 cyanide binding isotherms (right).

Mes<sub>3</sub>B by at least two orders of magnitude ( $K(F^-) = 3.3 \times 10^5 \text{ M}^{-1}$ ,  $K(\text{CN}^-) = 4.3 \times 10^4 \text{ M}^{-1}$  for Mes<sub>3</sub>B in THF). To better discriminate between the anion affinity of [1]<sup>+</sup> and Mes<sub>3</sub>B, we also attempted to carry out these titrations in a more competing solvent such as MeOH. In this solvent, NMR experiments showed that Mes<sub>3</sub>B has no measurable affinity for fluoride and cyanide anions ( $K < 0.01 \text{ M}^{-1}$ ). By contrast, we observed the rapid reaction of [1]<sup>+</sup> with both fluoride and cyanide anions, even at 0.05  $\mu$ M concentrations. Although precise titrations could not be completed because of the slow decomposition of [1]<sup>+</sup> in this solvent, the contrasting behavior observed between Mes<sub>3</sub>B and [1]<sup>+</sup> attests to the favorable influence of the [CpFe]<sup>+</sup> moiety on the acidity of the boron center. Finally, [1]<sup>+</sup> quickly decomposes in the presence of water and could not be studied in aqueous solutions.

# Conclusion

In conclusion, we report that Mes<sub>3</sub>B is readily converted into a cationic complex ([1]<sup>+</sup>) by reaction with  $[(\eta^6-naphthalene)-FeCp][PF_6]$ . This new cationic organoboron complex undergoes two quasi-reversible reductions in agreement with the presence of an electroactive boryl and  $[CpFe]^+$  moiety. This complex reacts with fluoride and cyanide anions in MeOH to afford the corresponding zwitterionic fluoroborate and cyanoborate species. Titration experiments carried out in THF indicate that the stability constants of the resulting zwitterionic fluoro-and cyano-borate species are much larger than those of Mes<sub>3</sub>B thus reflecting the favorable inductive and coulombic effects imparted by the  $[CpFe]^+$  moiety on the Lewis acidity of the boron center. While the coordination of cationic

transition metal moieties to aromatic anion receptors has been previously described,<sup>52,53</sup> the results presented in this paper show that this strategy could become applicable to a broad range of Lewis acidic anion receptors that feature aromatic substituents.

# **Experimental section**

# General consideration

[(η<sup>6</sup>-naphthalene)FeCp][PF<sub>6</sub>] was synthesized according to a published procedure.<sup>49</sup> 1,3-Dichloropropane was purchased from TCI America and dried with CaH<sub>2</sub> and distilled under a nitrogen atmosphere. The fluoride and cyanide salts *n*-Bu<sub>4</sub>NF-3H<sub>2</sub>O (TBAF) and *n*-Bu<sub>4</sub>NCN (TBACN) were purchased from Alfa Aesar and Aldrich, respectively. NMR spectra were recorded on a Varian Unity Inova 400 FT NMR (399.6 MHz for <sup>1</sup>H, 375.9 MHz for <sup>19</sup>F, 128.2 MHz for <sup>11</sup>B, 100.5 MHz for <sup>13</sup>C) spectrometer at ambient temperature. Chemical shifts δ are given in parts per million, and are referenced against external Me<sub>4</sub>Si (<sup>1</sup>H, <sup>13</sup>C) and BF<sub>3</sub>·Et<sub>2</sub>O (<sup>11</sup>B, <sup>19</sup>F). Elemental analyses were performed at Atlantic Microlab (Norcross, GA).

### Theoretical calculations

Density functional theory (DFT) calculations (full geometry optimization) were carried out with the Gaussian 03 program using the BP86 functional. Geometry optimization was carried out with the following mixed basis set: Fe: aug-cc-pvTz-pp; B: 6-31 + g(d'); C, H: 6-31g. Frequency calculations, which were carried out on the optimized structure of the compound, confirmed the absence of any imaginary frequencies. TD-DFT calculations were carried out with the Gaussian 03

program using the MPW1PW91 functional and the aforementioned mixed basis set.

**Electrochemistry.** Electrochemical experiments were performed with an electrochemical analyzer from CH Instruments (Model 610A) with a gold working electrode, a platinum auxiliary electrode and a reference silver electrode. The reference electrode solution was built by immersing a silver wire in a vicor-capped glass tube containing a THF solution of TBAPF<sub>6</sub> (0.1 M) and AgNO<sub>3</sub> (0.005 M). All the three electrodes were placed in a THF solution (3 mL) containing TBAPF<sub>6</sub> (0.1 M) and [1][PF<sub>6</sub>] (0.002 M). Ferrocene was used as an internal standard and the potentials are reported relative to the  $E_{1/2}$  of the Fc<sup>+</sup>/Fc redox couple.

Titration of [1]<sup>+</sup> with fluoride and cyanide in THF. A solution of [1][PF<sub>6</sub>] in THF (3 mL) was titrated by addition of incremental amounts of a THF solution of TBAF or TBACN. Concentrations used for the fluoride titrations: [[1][PF<sub>6</sub>]] =  $6.24 \times 10^{-5}$  M and [TBAF] =  $9.50 \times 10^{-3}$  M. Concentrations used for the cyanide titrations: [[1][PF<sub>6</sub>]] =  $7.70 \times 10^{-5}$  M and [TBACN] =  $7.30 \times 10^{-3}$  M.

**Crystallography.** Single crystals of compound [1][PF<sub>6</sub>] were obtained by slow diffusion of hexanes into a solution of the compound in CHCl<sub>3</sub>. Single crystals of 1-F and 1-CN were obtained by slow diffusion of MeOH into CHCl<sub>3</sub> solutions of the compounds. The crystallographic measurement of compounds [1][PF<sub>6</sub>], 1-F and 1-CN were performed using a Bruker APEX-II CCD area detector diffractometer, with a graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). The CIF files have been deposited with the Cambridge structure database and assigned the following numbers: CCDC 817396–817398.

Synthesis of Mes<sub>2</sub>B[( $\eta^6$ -Mes)FeCp][PF<sub>6</sub>] ([1][PF<sub>6</sub>]). [( $\eta^6$ -Naphthalene)FeCp][PF<sub>6</sub>] (0.17 g, 0.43 mmol) was added to a solution of trimesitylborane (0.9 g, 2.4 mmol) in 1,3-dichloropropane (2 mL) under nitrogen. The mixture was heated to reflux for 1.5 h. Following cooling to room temperature, CHCl<sub>3</sub> (2 mL) was added to the reaction mixture which was then filtered. Addition of hexanes (10 mL) to the filtrate resulted in the precipitation of the product  $([1][PF_6])$  as a red solid. The product was recrystallized by slow diffusion of hexanes into the solution of the compound in CHCl<sub>3</sub>, affording [1][PF<sub>6</sub>] (0.09 g, yield: 33%) in a red microcrystalline form. <sup>1</sup>H NMR (399.6 MHz, CDCl<sub>3</sub>):  $\delta$  1.21 (s, 3H, Mes-CH<sub>3</sub>), 2.11 (s, 9H, Mes-CH<sub>3</sub>), 2.20 (s, 3H, Mes-CH<sub>3</sub>), 2.36 (s, 9H, Mes-CH<sub>3</sub>), 2.51 (s, 3H, Mes-CH<sub>3</sub>), 4.81 (s, 5H, Cp-CH), 6.23 (s, 2H, Mes-CH), 6.60 (s, 1H, Mes-CH), 6.72 (s, 1H, Mes-CH), 6.94 (s, 2H, Mes-CH). <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>): δ 20.71 (Mes-CH<sub>3</sub>), 21.46 (Mes-CH<sub>3</sub>), 21.57 (Mes-CH<sub>3</sub>), 21.99 (Mes-CH<sub>3</sub>), 23.15 (Mes-CH<sub>3</sub>), 24.06 (Mes-CH<sub>3</sub>), 24.83 (Mes-CH<sub>3</sub>), 78.31 (Cp-CH), 87.61, 104.81, 111.07, 129.35, 129.73, 130.22, 138.95, 140.66, 140.87, 142.15, 142.24, 142.33, 142.49. <sup>19</sup>F NMR (375.9 MHz, CDCl<sub>3</sub>): -76.06  $(^{2}J_{F-F} = 712.7 \text{ Hz})$ . Anal. Calcd for  $C_{32}H_{38}BF_{6}FeP$ : C, 60.60, H, 6.04%. Found: C, 60.54, H, 6.02%.

Synthesis of 1-F and 1-CN. These adducts were isolated in yields >70% by addition of [1][PF<sub>6</sub>] (80 mg) to a saturated KF

or KCN solution in MeOH (2 mL). Both compounds could be isolated by filtration as light yellow solids. Data for 1-F: <sup>1</sup>H NMR (399.6 MHz, CDCl<sub>3</sub>):  $\delta$  1.53 (s, 9H, Mes-CH<sub>3</sub>), 2.18 (s, 12H, Mes-CH<sub>3</sub>), 2.33 (s, 3H, Mes-CH<sub>3</sub>), 2.52 (s, 3H, Mes-CH<sub>3</sub>), 4.61 (s, 5H, Cp-CH), 5.56 (s, 2H, Mes-CH), 6.45 (s, 2H, Mes-CH), 6.71 (s, 2H, Mes-CH). <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>): 20.84 (Mes-CH<sub>3</sub>), 21.07 (Mes-CH<sub>3</sub>), 24.32 (Mes-CH<sub>3</sub>), 24.37 (Mes-CH<sub>3</sub>), 76.02 (Cp-CH), 88.12, 99.25, 128.57, 128.71, 128.85, 129.72, 133.08. <sup>19</sup>F NMR (375.9 MHz, CDCl<sub>3</sub>): -168.24. <sup>11</sup>B NMR (128.2 MHz, CDCl<sub>3</sub>):  $\delta$  5.86. Anal. Calcd for C<sub>32</sub>H<sub>38</sub>BFFe: C, 75.61, H, 7.54%. Found: C,73.99, H, 7.53% (The deviation between the calculated and observed EA results show that this compound could not be isolated in a pure form. The EA results suggest the presence of inorganic impurities that could not be removed). Data for 1-CN: <sup>1</sup>H NMR (399.6 MHz, CDCl<sub>3</sub>):  $\delta$  1.51 (s, 6H, Mes-CH<sub>3</sub>), 2.17 (s, 12H, Mes-CH<sub>3</sub>), 2.36 (s, 3H, Mes-CH<sub>3</sub>), 2.52 (s, 3H, Mes-CH<sub>3</sub>), 3.06 (s, 3H, Mes-CH<sub>3</sub>), 4.77 (s, 5H, Cp-CH), 5.68 (s, 2H, Mes-CH), 6.45 (s, 2H, Mes-CH), 6.75 (s, 2H, Mes-CH). <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>): 20.78 (Mes-CH<sub>3</sub>), 20.97 (Mes-CH<sub>3</sub>), 25.21 (Mes-CH<sub>3</sub>), 76.82 (Cp-CH), 88.88, 99.44, 128.85, 129.95, 133.66. <sup>11</sup>B NMR (128.2 MHz, CDCl<sub>3</sub>): -15.02. Anal. Calcd for C<sub>33</sub>H<sub>38</sub>BFeN-3/4 (CHCl<sub>3</sub>): C, 67.02, H, 6.46%. Found: C, 67.15, H, 6.47% (The sample used for EA was obtained by recrystallization from CHCl<sub>3</sub>; the EA results indicate partial loss of the interstitial CHCl<sub>3</sub> molecule found in the crystal structure).

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