# ORGANOMETALLICS

## Syntheses and Anion Binding Capabilities of Bis(diarylboryl) **Ferrocenes and Related Systems**

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#### Supporting Information

**ABSTRACT:** Isomeric diborylated ferrocenes featuring 1,1'-, 1,2-, and 1,3-substitution patterns have been targeted via a combination of electrophilic aromatic substitution and directed ortho-lithiation protocols. While none of these systems are competent for the Lewis acid chelation of fluoride, related systems featuring a mixed B/Si acceptor set capture 1 equiv of fluoride via a Si-F-B bridging motif.



### ■ INTRODUCTION

The selective detection of CN<sup>-</sup> and F<sup>-</sup> represent significant chemical challenges with applications, for example, in environmental and medical monitoring/remediation.<sup>1-3</sup> The affinity of cyanide for tricoordinate boranes has been known for more than 50 years,<sup>4</sup> and recent studies have demonstrated the use of Lewis acid receptors containing the related -BMes<sub>2</sub> (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) function to detect cyanide,<sup>5</sup> in one case offering selective binding in aqueous media.<sup>5d</sup> In this respect, a major challenge in sensor design stems from the potential for competitive binding of fluoride at -BMes<sub>2</sub> and related Lewis acid functions.<sup>6,7</sup> Interestingly, recent reports emphasize the importance not only of electronic factors (i.e. borane Lewis acidity) but also of steric factors in determining the relative binding affinities for cyanide and fluoride.5d,n

Lewis acids featuring a ferrocenyl substituent offer the additional possibility for an electrochemical (or even colorimetric) reporter response.<sup>8</sup> Moreover, multifunctional systems of this type offer the potential for the complexation of more than 1 equiv of substrate and an enhanced magnitude of the binding-induced electrochemical shift.<sup>8d</sup> Alternatively, convergent bifunctional systems offer the possibility for the chelation of a single (appropriately shaped) anion, with benefits in terms of enhanced binding affinity and potential selectivity.<sup>9</sup> Disubstituted ferrocenes offer three distinct regiochemistries, and in the current paper we report on synthetic routes to diborylated systems with 1,1'-, 1,2-, and 1,3-dispositions,<sup>10</sup> together with an investigation of their anion binding capabilities with respect to F<sup>-</sup> and CN<sup>-</sup>. One aim was to explore strategies for the binding of fluoride over cyanide via a preorganized chelating motif. While 1,2-diborylated ferrocenes offer superficial promise in this regard, consideration of the size of the anion binding cavity led us also to evaluate Lewis acids featuring larger, second-row elements (e.g. silanes). In the event, among the receptor systems studied, mixed borane/ silane receptors represent the most promising candidates for the Lewis acid chelation of F<sup>-</sup>.

#### RESULTS AND DISCUSSION

Synthetic Chemistry. Synthetically, the 1,1'-ferrocenediyl disubstitution pattern is easiest to achieve, relying on simple electrophilic substitution chemistry to deliver the known 1,1'bis(dibromoboryl) precursor in a single step from ferrocene.<sup>11</sup> Subsequent reaction with excess mesityllithium (although not with the corresponding Grignard reagent)<sup>5k</sup> generates 1,1' $fc(BMes_2)_2$  (1a; fc = ferrocenediyl) as a red microcrystalline material in 60-70% yield (Scheme 1). Particularly diagnostic of

Scheme 1. Syntheses of 1,1'-Bis(diarylboryl)ferrocenes 1a-c in Two Steps from Ferrocene<sup>a</sup>



<sup>a</sup>Key reagents and conditions: (i) BBr<sub>3</sub>, as per ref 11; (ii) ArLi (> 4 equiv), diethyl ether, 18 h, 20 °C, 39-66%.

this transformation is the conversion of the <sup>11</sup>B NMR resonance at  $\delta_B$  50 due to 1,1'-fc(BBr<sub>2</sub>)<sub>2</sub> to a broad peak at  $\delta_B$  76 ppm (cf.  $\delta_B$  76 ppm for FcBMes<sub>2</sub>).<sup>5e</sup> **1a** has been further characterized by standard spectroscopic and analytical methods but has thus far proved impossible to obtain as single crystals suitable for X-ray crystallography, primarily due to its extremely high solubility even in nonpolar organic media. As a consequence, the closely related derivatives 1,1'-fc(BXyl<sup>F</sup><sub>2</sub>)<sub>2</sub> (1b) and  $1,1'-fc(BXyl_2)_2$  (1c) were synthesized by analogous chemistry  $(Xyl^F = 2,6-Me_2-4-F-C_6H_2; Xyl = 2,6-Me_2C_6H_3).$ These compounds were characterized by similar <sup>11</sup>B NMR

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shifts ( $\delta_B$  78 and 77 ppm, respectively), and in the case of 1*c*, suitable single crystals can be obtained by slow evaporation of a solution in diethyl ether.

The molecular structure of **1c** (Figure 1) confirms the expected planar three-coordinate geometry at each borane



**Figure 1.** Molecular structures of 1,1'-fc(BXyl<sub>2</sub>)<sub>2</sub> (**1c**, upper) and 1,3-fc\*(BMes<sub>2</sub>)<sub>2</sub> (**2**, lower) as determined by X-ray crystallography. Hydrogen atoms are omitted and Cp\* methyl groups (for **2**) shown in wireframe format for clarity; thermal ellipsoids are set at the 40% probability level. Key bond lengths (Å) and angles (deg): for **1c**, C(6)-B(7) = 1.546(3), B(7)-C(8) = 1.602(3), B(7)-C(16) = 1.594(3), C(25)-B(29) = 1.552(3), C(6)-B(7)-C(8) = 122.5(2), C(6)-B(7)-C(16) = 119.0(2), C(8)-B(7)-C(16) = 118.3(2); for **2**, C(3)-B(26) = 1.558(3), C(6)-B(7) = 1.549(3), C(6)-B(7)-C(8) = 120.1(2), C(6)-B(7)-C(17) = 119.3(2), C(8)-B(7)-C(17) = 120.4(2).

function (with angles at boron summing to 359.8 and 359.6°); the xylyl substituents are aligned in a propeller-like arrangement, with angles between the least-squares BC<sub>3</sub> plane and the aryl rings of 61.7, 64.0, 64.3, and 71.1°. Additionally, the bending toward the iron center typically observed in ferrocenes featuring a Lewis acidic substituent is not seen in 1c;<sup>12</sup> instead, a contrasting effect is observed whereby the BXyl<sub>2</sub> groups both bend *away* from Fe(1) ( $\angle$ (Cp centroid–C<sub>ipso</sub>–B) = 173.0, 171.4°), presumably on steric grounds.

Electrophilic aromatic substitution chemistry also provides the underpinning synthetic entry point into one class of 1,3disubstituted ferrocene. Thus, the ability to introduce two BBr<sub>2</sub> groups onto a single cyclopentadienyl ring under more forcing conditions can be exploited in the case of pentamethylferrocene to generate 1',2',3',4',5'-pentamethyl-1,3-bis(dibromoboryl)ferrocene, 1,3-fc\*(BBr<sub>2</sub>)<sub>2</sub>;<sup>13</sup> subsequent conversion into the bis(dimesitylboryl) compound 1,3-fc\*(BMes<sub>2</sub>)<sub>2</sub> (**2**; Scheme 2) can be effected by employing the same methodology as used for **1a. 2** has been characterized by standard spectroscopic and analytical techniques and by single-crystal X-ray diffraction (Figure 1).

Both NMR and crystallographic studies are consistent with a very high degree of steric crowding in this system. Thus, the <sup>1</sup>H NMR spectrum of **2** at 20 °C shows a single broad resonance for the ortho methyl groups of the mesityl substituents (and a corresponding broad singlet for the meta aromatic CH

Scheme 2. Synthetic Strategy for the Synthesis of 1,3-Bis(diarylboryl) Systems Featuring a Pentamethylferrocene Skeleton<sup>a</sup>



"Key reagents and conditions: (i)  $BBr_3$  (4.5 equiv), as per ref 13; (ii) MesLi (> 6 equiv), diethyl ether, -78 to +20 °C then 12 h at +20 °C, 43% (as acetone disolvate) after recrystallization from acetone.

protons), reflecting hindered rotation around both the B- $C_{ipso}$  and  $B-C_{Cp}$  bonds. At -50 °C the limiting lowtemperature spectrum is obtained, featuring four ortho and two para methyl signals. Such a spectrum is consistent with the two -BMes<sub>2</sub> groups being related by symmetry, but with slow exchange on the NMR time scale within each -BMes<sub>2</sub> unit. At +50 °C, in contrast, two sharp mesityl methyl signals are observed (in the ratio 2:1) corresponding to all eight ortho and all four para methyl groups, respectively. Interestingly, at -10°C the spectrum shows one signal for the para methyl groups and two signals for the ortho methyls, implying that rotation about the  $B-C_{Cp,ipso}$  linkage is facile (rendering equivalent the two Mes substituents within each -BMes<sub>2</sub> unit) but that rotation about each B-C<sub>Mes,ipso</sub> bond (which would interconvert the ortho methyl groups within each Mes substituent) is not.

Crystallographic studies also provide evidence of the highly strained nature of 2 (Figure 1). Thus the angle  $\alpha$  between the least-squares planes of the Cp and Cp\* rings is 17.9°, a figure which can be put into context by comparison with 0.8° for pentamethylferrocene itself and 16.1° for the single-atom ansabridged system {Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>}Fe.<sup>14</sup> Green has calculated the energetic profile for ferrocene associated with distorting the Cp rings away from coplanarity, and on that basis a penalty of ca. 40–50 kJ mol<sup>-1</sup> can be estimated for the conformation adopted by 2 (in the solid state at least).<sup>15</sup> In addition, as in the case of 1c, the -BAr<sub>2</sub> units in 2 are bent away from the iron center, such that the two  $\angle$ (Cp centroid–C<sub>ipso</sub>–B) angles are 168.9 and 171.1°.

While the "blocking" of one cyclopentadienyl ring to electrophilic attack by permethylation allows a 1,3-disposition of boryl functions to be realized, achieving the same substitution pattern for the parent ferrocene skeleton proves to be more difficult. Perhaps the most promising approach (Scheme 3) utilizes the known intermediate rac-1,2-fc(BMes<sub>2</sub>) Br (3a), itself produced via a convenient isomerization step from readily available 1,1'-fcBr<sub>2</sub>.<sup>10a,c,16</sup> Reaction of 3a with the hindered amide base lithium 2,2,6,6-tetramethylpiperidide, Li(tmp), followed by FBMes<sub>2</sub> leads to the formation of the 2,5-bis(dimesitylboryl)-1-bromo derivative 4 in ca. 50% isolated yield via bromide-directed ortho lithiation. Debromination of 4, however, proves remarkably difficult to drive to completion, presumably due to the highly sterically shielded nature of the Br substituent located between two o-BMes<sub>2</sub> groups. Thus, even in the case of <sup>t</sup>BuLi, the resulting debrominated product 5 could only be obtained in 95% purity, as an intractable mixture with 5% of unreacted 4.

Intermediate **3a**, used in conjunction with *alkyl*lithium bases, also provides access to the final (1,2) disubstitution pattern (Scheme 3). Thus, lithiation with "BuLi followed by a FBMes<sub>2</sub>

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Scheme 3. Syntheses of Symmetrical and (Racemic) Unsymmetrical 1,2-Bis(diarylboryl)ferrocenes and of 1,3-Disubstituted Systems through the Intermediacy of rac-1,2- $fc(BMes_2)Br$  (3a)<sup>*a*</sup>



<sup>*a*</sup>Key reagents and conditions: (i) "BuLi (1 equiv), tetramethylpiperidine (1 equiv), thf, -40 °C, 2 h, then FBAr<sub>2</sub> (>3 equiv), thf, -78 to +20 °C then 15 h at +20 °C, 51-76% yield after chromatography and recrystallization; (ii) Li(tmp) (0.94 equiv), thf, -78 °C, 2 h, then FBMes<sub>2</sub> (1.21 equiv), thf, -78 to +20 °C, then 12 h at 20 °C, 52%; (iii) tBuLi (2.2 equiv), thf, -78 °C, 2 h, aqueous workup, then repetition, up to 90–95% purity (remainder 4); (iv) "BuLi (1 equiv), tmeda (1 equiv), diethyl ether, -78 °C, 1 h, then FBAr<sub>2</sub> (> 4 equiv), diethyl ether, -78 to +20 °C then 12 h at +20 °C, 17–83% yield after chromatography and recrystallization.

quench provides access to the 1,2-bis(dimesitylboryl) species 6a, while analogous chemistry utilizing  $rac-1,2-fc(BXyl_2)Br$ (3b) and either FBMes<sub>2</sub> or FBXyl<sub>2</sub> generates  $rac-1, 2-fc(BXyl_2)$ - $(BMes_2)$  (**6b**) and 1,2-fc $(BXyl_2)_2$  (**6c**), respectively (Scheme 3). 6a-c have been characterized by standard spectroscopic and analytical techniques, with the <sup>11</sup>B NMR shift in each case ( $\delta_{\rm B}$  ~80 ppm) again being diagnostic.<sup>5e</sup> Here too, variabletemperature NMR studies, allied to crystallography (Figure 2), reveal very high steric loading at the Lewis acidic boron centers. In this case steric repulsion between the two -BMes<sub>2</sub> units presumably contributes (i) to the wide B--B separation (3.684 Å (mean), cf. 3.263 Å for 1,2- $C_6H_4[B(C_6F_5)_2]_2$  and 3.353 Å for  $1,8-C_{10}H_6(BMes_2)(BPh_2))$ , <sup>9g,j</sup> and (ii) to considerable distortion of one of the two -BMes<sub>2</sub> units. Thus, in each of the two 1,2-fc(BMes<sub>2</sub>)<sub>2</sub> molecules making up the asymmetric unit, one  $-BMes_2$  group features a boron center (i.e. B(7) or B(76)) which lies ca. 0.5 Å out of the plane of the  $C_5H_3$  ring (cf. <0.06 Å for the other boron center in each molecule); the associated BC2 least-squares plane is canted at an angle of ca. 45° with respect to that of the Cp ring (cf.  $\sim 5^{\circ}$  for the other). In addition, there is a marked difference between the two B- $C_{Cp,ipso}$  –  $C_{Cp,ortho}$  angles for both B(7) and B(76) (135.2° (mean) and 114.6° (mean)), reflecting the need to minimize steric repulsions between mesityl ring systems by "bending back" the -BMes<sub>2</sub> units. These geometric factors presumably contribute to a redox potential for 6a (+0.177 V vs FcH/FcH<sup>+</sup> in thf) that while shifted anodically with respect to FcBMes<sub>2</sub> (0.131 V in the same solvent) is less positive than that for the 1,1'-isomer 1a (+0.197 V).

As with complex 2, the influence of steric factors is also apparent in the <sup>1</sup>H NMR spectrum of 6a, which features broad signals for both the mesityl ortho methyl and meta CH protons at 20 °C. A spectrum featuring only one *o*-CH<sub>3</sub> and one *m*-CH



**Figure 2.** Molecular structures of one of the two components of the asymmetric unit of 1,2-fc(BMes<sub>2</sub>)<sub>2</sub> (**6a**, upper) and *rac*-1,2-fc(BMes<sub>2</sub>)-(SiMe<sub>2</sub>OMe) (**9**, lower) as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at the 40% probability level. Key bond lengths (Å) and angles (deg): for **6a**, C(6)-B(7) = 1.574(7), C(5)-B(26) = 1.569(7), B(7)…B(26) = 3.702, C(5)-C(6)-B(7) = 135.5(4), C(6)-C(5)-B(26) = 133.7(4), C(2)-C(6)-B(7) = 114.4(4), C(4)-C(5)-B(26) = 120.6(4); for **9**, C(2)-Si(26) = 1.844(2), C(3)-B(7) = 1.572(3), Si(26)-O(27) = 1.640(2), C(2)-C(3)-B(7) = 132.4(2), C(4)-C(3)-B(7) = 119.4(2), C(3)-C(2)-Si(26) = 127.4(1), C(6)-C(2)-Si(26) = 125.6(2).

signal is observed at 120 °C, while eight distinct *o*-CH<sub>3</sub> signals can be identified at -60 °C. In addition, at -60 °C the 2:1 pattern for the protons of the C<sub>3</sub>H<sub>3</sub> group is split into three distinct signals (with relative intensities 1:1:1), consistent with slowing down of the synchronized "windshield wiper" motion of the two -BMes<sub>2</sub> units. Consideration of the coalescence behavior of the respective signals yields an activation barrier,  $\Delta G^{\ddagger}$ , of 48 kJ mol<sup>-1.10c</sup> A further fluxional process involving completely free rotation about both B-C<sub>Cp,ipso</sub> and B-C<sub>Mes,ipso</sub> bonds on the NMR time scale (and thus giving rise to the simple <sup>1</sup>H spectrum observed at +120 °C) can be identified with a coalescence temperature of +45 °C.<sup>10c</sup>

Finally, in order to explore the broader possibilities for anion chelation by 1,2-disubstituted ferrocenes we have additionally prepared the (racemic) mixed dimesitylboryl/dimethylfluorosilyl species **8**. The synthesis of **8** also relies on the key intermediate **3a**, being accomplished via the corresponding chlorosilyl derivative 7 (Scheme 4).<sup>10a,c,17,18</sup> Characterization was achieved by standard spectroscopic techniques, and although **8** itself proved unsuitable for crystallographic study, the related methoxysilyl derivative **9** could be structurally authenticated (Figure 2). The expected sterically crowded 1,2-disposition of the boryl and silyl functions is thus confirmed. As with the corresponding bis(boryl) system **6a**, comparison of the two  $C_{Cp,ortho}-C_{Cp,ipso}$ –B angles (119.4(2) and 132.4(2)°) is consistent with bending of the boryl function away from the ortho substituent, presumably on steric grounds. Despite the presence of the silyl ether oxygen donor and borane Lewis acid,

Scheme 4. Syntheses of Racemic 1,2-Disubstituted Ferrocenes Featuring Dimesitylboryl and Silyl Substituents<sup>a</sup>



<sup>*a*</sup>Key reagents and conditions: (i) <sup>*n*</sup>BuLi (2.0 equiv), Et<sub>2</sub>O/pentane, -78 °C, 30 min, then Me<sub>2</sub>SiCl<sub>2</sub> (ca. 10 equiv), -78 °C to room temperature, 15 h at room temperature, 91%; (ii) for **8**, CuF<sub>2</sub> (1.0 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 3 h, 93% (of 98% pure material), for **9**, stirring in MeOH, 1 h, room temperature, then MeOH/Et<sub>2</sub>O (1/1), 3 h, room temperature, 82%.

the B···O distance (3.352(3) Å) is comfortably outside the sum of the respective covalent radii.

Fluoride and Cyanide Binding. The reaction of 1a with excess KCN/18-crown-6 in acetonitrile is characterized by a shift in the <sup>11</sup>B NMR spectrum from a broad resonance at  $\delta_{\rm B}$  76 to a sharp peak at  $\delta_{\rm B}$  –16 ppm and is accompanied by a color change from dark red to yellow. Both observations are consistent with the behavior of the parent compound FcBMes<sub>2</sub> in the presence of cyanide.5e With regard to binding stoichiometry, single crystals of the bis(cyanide) adduct  $[K(18 \text{-crown-6})]_2[1a \cdot (CN)_2]$  suitable for crystallography could subsequently be obtained by layering the acetonitrile reaction mixture with diethyl ether. The structure of the dianionic component so determined is centrosymmetric, featuring equivalent binding of cyanide at both receptor sites, which are then oriented so as to be optimally distant from one another. While the quality of the structure solution is not optimal for discussion of the metrical parameters, a very closely related structure has been determined for the corresponding  $Xyl^F$  system  $[K(18\text{-crown-6})]_2[\mathbf{1b}\cdot(CN)_2]$  (Figure 3). In this case the metrics of the B-C-N binding motif are more reliable and are in fact very similar to those determined for the parent complex  $[FcBMes_2 \cdot CN]^-$ : e.g., d(B(1)-C(6)) = 1.630(4) Å and  $\angle (B(1)-C(6)-N(1)) = 171.0(3)^{\circ}$  (cf. 1.621(3) Å and  $169.8(3)^{\circ 5e}$ ). A secondary interaction between the nitrogen atom of the cyanide guest and the potassium center of the  $[K(18\text{-crown-6})]^+$  counterion  $(d(K \cdots N) = 2.780(3) \text{ Å})$  also finds precedent in previously reported cyanide adducts of simple monofunctional ferrocenyl boranes. 5é,k,m

The mode of interaction of cyanide with 1a can be shown to be solvent dependent. Thus, in much more weakly donating chloroform, the reaction of 1a with KCN/18-crown-6 generates the monoanionic monocyanide adduct [K(18-crown-6)] [1a·CN]. The progress of this reaction is difficult to assess unambiguously by <sup>11</sup>B NMR, insofar as the resonance associated with the remaining uncomplexed (three-coordinate) borane is extremely broad and difficult to detect. The fourcoordinate borate center gives rise to a sharp signal at  $\delta_{\rm B}$  -13 ppm, similar to those measured for  $[1a \cdot (CN)_2]^{2-}$  and [FcBMes<sub>2</sub>·CN]<sup>-.5e</sup> Interestingly, the marked color change from deep red to yellow observed on formation of  $[1a \cdot (CN)_2]^{2-}$  from 1a (and indeed on the complexation of CN<sup>-</sup> to the parent system FcBMes<sub>2</sub>) is not observed on formation of  $[1a \cdot CN]^{-}$ , consistent with the idea that the Fe( $\eta^{5}$ - $C_5H_4BMes_2$ ) unit is a key chromophore. The formation of  $[1a \cdot CN]^{-}$  in chloroform solution is supported by the results of negative ion ESI-MS and <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy, the latter



**Figure 3.** Molecular structures of  $[K(18\text{-}crown-6)]_2[\mathbf{1b}\cdot(CN)_2]$ (upper) and  $[K(18\text{-}crown-6)][\mathbf{1a}\cdot CN]$  (lower) as determined by Xray crystallography. Hydrogen atoms and second disorder component (for  $[K(18\text{-}crown-6)][\mathbf{1a}\cdot CN]$ ) are omitted and crown ether molecules shown in wireframe format for clarity; thermal ellipsoids are set at the 40% probability level. Key bond lengths (Å) and angles (deg) for  $[K(18\text{-}crown-6)]_2[\mathbf{1b}\cdot(CN)_2]$ : B(1)-C(6) = 1.630(4), C(6)-N(1) = 1.151(4), N(1)-K(1) = 2.780(3), B(1)-C(1) =1.636(4), B(1)-C(6)-N(1) = 171.0(3), C(6)-N(1)-K(1) =142.3(2).

revealing distinct sets of resonances due to the inequivalent mesityl and  $C_5H_4$  moieties associated with the boryl/borate functionalized Cp rings. The structure of [K(18-crown-6)][1a·CN] in the solid state was also confirmed crystallographically (Figure 3), although here the presence of pernicious disorder rules out an in-depth analysis of metrical data.

UV/vis titrations were carried out in order to estimate the binding affinities of **1a** associated with both the first and second cyanide complexation events; values of log  $K_1 = 8.88(0.20)$  and log  $K_2 = 5.90(0.11)$  were determined in thf solution, the solvent system being chosen to provide compatibility with measurements carried out on 1,2-bifunctional systems (vide infra). The value determined for log  $K_1$  is significantly greater than that for the related monofunctional system FcBMes<sub>2</sub> in thf (log K = 6.55(0.13)), consistent with the (known) electron-withdrawing effects of the additional  $-BMes_2$  group.<sup>5e</sup> The negative cooperativity implied by the value determined for log  $K_2$  reflects obvious electrostatic factors, albeit mitigated somewhat by the conformational flexibility of the ferrocenediyl core.

The parent system FcBMes<sub>2</sub> shows a competing response in the presence of fluoride,<sup>5e</sup> and **1a** was found to be no different in this respect. Reaction with either ["Bu<sub>4</sub>N]F or KF/18-crown-6 in acetonitrile or chloroform results in a shift in the <sup>11</sup>B NMR spectrum from  $\delta_B$  76 to ca. 6 ppm, consistent with previously reported fluoride adducts of ferrocenylboranes.<sup>5e</sup> Moreover, the corresponding <sup>19</sup>F NMR spectrum reveals a broad peak at  $\delta_F$ –181 ppm, also indicative of fluoride complexation. This competing affinity for fluoride can be attributed to the known strength of the B–F bond in such systems;<sup>6</sup> UV/vis titrations were carried out to determine fluoride binding constants in thf solution, which (as with FcBMes<sub>2</sub>) were found to be very similar to the corresponding cyanide affinities (log  $K_1$  = 8.26(0.09), log  $K_2$  = 5.60(0.06)).

Investigation of 1,1'-disubstituted ferrocenes therefore reveals that the two binding sites in these systems act more or less independently of one another. While alternative convergent binding motifs *have* been established for more strongly Lewis acidic 1,1'-diborylated coboltocenium systems,<sup>19</sup> we sought in the current study to encourage chelation by using ferrocene-based frameworks with reduced conformation flexibility. With this in mind, the anion binding capabilities of other diborylated ferrocenes have been investigated, with the ultimate aim of achieving selectivity for anionic guest species based on a chelating mode of interaction.

The 1,3-disubstituted system 1,3-fc\* $(BMes_2)_2$  (2) is clearly not optimized for a chelating mode of anion binding, and (although preliminary experiments are consistent with the binding of only 1 equiv of either fluoride or cyanide) precise structural and thermodynamic data for the respective adducts proved impossible to obtain in our hands due to their unworkable sensitivity toward oxidation.<sup>20</sup> The electronic effects of the Cp\* ligand (estimated to give rise to a cathodic redox shift of ca. -300 mV) render this system markedly more susceptible to electron loss.<sup>8d,21</sup> Superficially, the 1,2-disubstituted systems, although synthetically the most challenging, offer the most favorable degree of preorganization with respect to the chelation of monatomic anions; similar bis(borylated) benzene frameworks, for example, have previously been shown to be capable of the chelation of fluoride (Chart 1).<sup>9z</sup>

Chart 1. Interaction of Fluoride with 1,2-Diborylated Receptors Based on Six (I)- and Five-Membered Carbocyclic Skeletons (II) and Potential Interaction with a Heterotopic Lewis Acid Featuring the Second-Row Lewis Acidic Function  $\text{ER}_n$  (III)



Somewhat surprisingly, however, a number of empirical observations indicate that the binding of fluoride by **6a** is in fact very weak. Thus, no evidence for the formation of  $[\mathbf{6a}\cdot\mathbf{F}]^-$  could be obtained from NMR measurements in either dichloromethane or chloroform solution, and while single crystals of  $[K(18\text{-crown-}6)][\mathbf{6a}\cdot\mathbf{F}]$  could be obtained from thf saturated with fluoride, solutions of the crystalline adduct in thf- $d_8$  rapidly regenerate the free receptor by fluoride loss in the absence of excess anion. Electrochemical studies of **6a** in thf solution are also consistent with a small ( $\ll 100 \text{ mV}$ ) shift even in the presence of excess fluoride. In addition, fluoride binding by **6a** can be shown by simple competition experiments to be weaker than cyanide binding: e.g., by the quantitative formation (by <sup>11</sup>B NMR) of  $[\mathbf{6a}\cdot\mathbf{CN}]^-$  on addition to the free receptor of a solution equimolar in both  $\mathbf{F}^-$  and  $\mathbf{CN}^-$ .

Interestingly, even in the presence of a vast excess of fluoride, the *rate* of formation of the host/guest complex  $[6a \cdot F]^-$  (as appraised by UV–vis spectroscopy; Figure 4) appears to be



**Figure 4.** Plots of (left)  $(A - A_{\infty})/(A_0 - A_{\infty})$  vs time and (right) ln( $A - A_{\infty}$ ) vs time (both measured at  $\lambda$  570 nm) for the reactions in thf of ["Bu<sub>4</sub>N]F with **6a** ( $\blacklozenge$ ), **6b** ( $\blacktriangle$ ), and **6c** ( $\blacksquare$ ). For the logarithmic plot, the solid lines give a least-squares (linear) fit (with  $R^2 = 0.998$ , 0.996, and 0.993, respectively), from which pseudo-first-order rate constants ( $k_{obs}$ ) of 1.64 × 10<sup>-2</sup>, 2.08 × 10<sup>-2</sup>, and 2.79 × 10<sup>-2</sup> s<sup>-1</sup> can be derived.

very slow. Monitoring of the intensity of the band at 570 nm due to the free receptor as a function of time under pseudofirst-order conditions (i.e. in the presence of an 20-fold excess of fluoride) gives a linear plot of  $\ln(A - A_{\infty})$  vs. time, from which a rate constant,  $k_{obs'}$  of 1.64  $\times$  10<sup>-2</sup> s<sup>-1</sup> can be determined. In an attempt to understand the structural origins of the slow fluoride uptake by 6a and the essentially instantaneous binding of cyanide, X-ray diffraction studies were carried out on single crystals of both [K(18-crown-6)][6a·F] and [K(18-crown-6)][6a·CN] (Figure 5). Notably, the F<sup>-</sup> anion interacts with only one of the two boron centers, presumably reflecting the wide B…B separation determined for the free receptor 6a (mean 3.684 Å for the two molecules in the asymmetric unit), in comparison to typical  $B-\mu$ -F bond lengths (e.g. 1.585(5) and 1.633(5) Å for  $[1,8-C_{10}H_8(BMes_2)]$  $(BC_{12}H_8S)(\mu-F)]^{-}$ .<sup>8</sup>s,<sup>22</sup> Nevertheless, the fluoride ion is bound endo to the B"B cavity and features no significant secondary interactions with the  $[K(18-\text{crown-6})]^+$  counterion. In contrast, the structure of  $[K(18-\text{crown-6})][6a \cdot \text{CN}]$ , while revealing that the anion is also bound in a non-chelating fashion, implies that cyanide is situated exo to the B"B cavity (in the solid state at least) and additionally interacts with the potassium center of the  $[K(18 \text{-crown-6})]^+$  unit via N(9).

To determine whether a similar mode of fluoride binding within the B···B binding domain could persist in solution and, given the steric demands of the flanking mesityl substituents, could therefore be implicated in the slow uptake of F<sup>-</sup>, we examined the corresponding rates of reaction for 1,2-fc(BMes<sub>2</sub>)(BXyl<sub>2</sub>) (**6b**) and 1,2-fc(BXyl<sub>2</sub>)<sub>2</sub> (**6c**), which feature successively reduced steric loading on the periphery of the binding cavity. The results of these experiments are shown in Figure 4, from which pseudo-first-order rate constants of 2.08 ×  $10^{-2}$  and 2.79 ×  $10^{-2}$  s<sup>-1</sup> can be determined for **6b**,**c**, respectively. These (reproducible) differences in the rate of fluoride uptake and the more marked difference in the binding kinetics for fluoride and cyanide are consistent with binding of F<sup>-</sup> within the B···B cavity in thf solution.

In contrast to related systems based on a benzene backbone,<sup>9z</sup> the dimensions of the B…B cavity in 1,2diborylated ferrocenes therefore appear to preclude fluoride chelation (Chart 1); the constraints of a five- (vs six-) membered carbocyclic ring force the two borane binding sites to lie too far apart, an effect which is exacerbated for the 1,2bis(dimesitylboryl) system due to steric factors. However, the synthetic chemistry outlined in Scheme 3 offers wide applicability in terms of the range of 1,2-difunctional ferrocenes that are potentially accessible. Lithiation of the intermediate *rac*-fc(BMes<sub>2</sub>)Br followed by an electrophilic quench offers



Figure 5. Molecular structures of (upper) the anionic component of  $[K(18\text{-crown-6})][6a \cdot F]$  and (lower)  $[K(18\text{-crown-6})][6a \cdot CN] \cdot CHCl_3$ as determined by X-ray crystallography. Hydrogen atoms, counterion (for F<sup>-</sup> adduct), and solvate molecule (for CN<sup>-</sup> adduct) are omitted, and the crown ether is shown in wireframe format for clarity; thermal ellipsoids are set at the 40% probability level. Key bond lengths (Å) and angles (deg): for  $[K(18-\text{crown-6})][6a \cdot F]$ , B(31)-F(50) = $1.471(5), B(12)\cdots B(31) = 3.602, C(10)-B(31) = 1.635(8), C(9)-$ B(12) = 1.548(7), C(8)-C(9)-B(12) = 120.9(4), C(11)-C(10)-B(31) = 123.2(4), C(10)-C(9)-B(12) = 133.0(4), C(9)-C(10)-B(31) = 130.6(4); for  $[K(18 - crown - 6)][6a \cdot CN], B(7) - C(8) =$ 1.648(4), C(8)-N(9) = 1.146(3), C(6)-B(7) = 1.672(4), C(2)- $B(28) = 1.568(4), B(7) \cdots B(28) = 3.887, C(3) - C(2) - B(28) =$ 116.5(2), C(5)-C(6)-B(7) = 115.0(2), C(2)-C(6)-B(7) =138.5(2), C(6)-C(2)-B(28) = 137.2(2), B(7)-C(8)-N(9) =173.2(3).

access to a wide variety of systems of the type rac-1,2 $fc(BMes_2)(ER_n)$ . With this in mind, we hypothesized that an alternative Lewis acid group, ER,, centered on a second-row element E (such as silicon) might be consistent with fluoride chelation, on the basis of the expectation of a longer  $E-\mu$ -F bond.<sup>17,18</sup> Consistently, ESI-MS measurements reveal the formation of a 1:1 adduct between fluoride and dimethylfluorosilyl system 8. Moreover, data obtained from multinuclear NMR measurements (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>19</sup>F, and <sup>29</sup>Si) in chloroform-d provide strong evidence for a chelating mode of interaction in solution. Thus, the formation of a B-F bond is consistent with the appearance of a doublet ( ${}^{1}J_{BF} = 85 \text{ Hz}$ ) at  $\delta_{B}$ 9 ppm, which compares well with corresponding shift reported by Kawachi and co-workers for  $[1,2-C_6H_4(BMes_2)(SiMe_2F)(\mu-F)]^- (\delta_B 6.5 \text{ ppm}).^{17a}$  The <sup>19</sup>F NMR spectrum is characterized by a small shift from  $\delta_{\rm F}$  -152 to -153 ppm in the resonance associated with the terminal Si-F linkage and by the appearance of a broad unresolved multiplet at  $\delta_{\rm F}$  –165 ppm for the Si–F–B unit (cf.  $\delta_F$  –154 ppm for Kawachi's Si–F–B system but a higher field signal at  $\delta_{\rm F}$  –181 ppm for the terminally bound fluoride adduct of 1a).<sup>17a</sup> The formation of an additional Si-F linkage on addition of fluoride is also supported by the change in the <sup>29</sup>Si spectrum from a simple doublet ( $\delta_{Si}$  23.4 ppm,  ${}^{I}J_{SiF}$  = 275 Hz) for the free receptor to a

doublet of doublets ( $\delta_{Si}$  25.2 ppm,  ${}^{1}J_{SiF} = 70$ , 190 Hz). Additional evidence for a B–F–Si motif comes from the  ${}^{1}$ H NMR signals associated with the diastereotopic Si–Me groups. Thus, in the free receptor these give rise to two doublets (at  $\delta_{\rm H}$ 0.11 and 0.15 ppm, each with  ${}^{3}J_{\rm HF} =$  ca. 8 Hz), while in the fluoride adduct these resonances are not only shifted apart ( $\delta_{\rm H}$ -0.07 and 0.50 ppm) but also further split in each case by an additional coupling (3–4 Hz) to the bridging fluorine (Figure 6).<sup>23</sup> Precedent for this chelating mode of fluoride capture in ferrocene systems comes from a B– $\mu$ -F–SnMe<sub>2</sub>F motif reported by Jäkle and co-workers.<sup>18d</sup>



Figure 6. Doublet of doublets  ${}^{1}H$  NMR resonances for each of the diastereotopic methyl groups in  $[8 \cdot F]^{-}$ .

#### CONCLUSIONS

Isomeric diborylated ferrocenes featuring all three potential substitution patterns have been synthesized via a combination of electrophilic aromatic substitution and ortho-lithiation protocols. Of these, 1,1'-fc(BMes<sub>2</sub>)<sub>2</sub> displays first binding affinities  $(K_1)$  for both F<sup>-</sup> and CN<sup>-</sup> in excess of those of the parent monofunctional system FcBMes2, consistent with the electron-withdrawing properties of the additional -BMes<sub>2</sub> group. The values of  $K_2$  determined for both anions reflect a negative cooperativity of between 2 and 3 orders of magnitude. By comparison, 1,2-fc(BMes<sub>2</sub>)<sub>2</sub> features a more rigid bifunctional motif and, although only 1 equiv of either fluoride or cyanide is taken up, binding in each case occurs via a single B-X bond. Moreover, the diminished binding constants determined for both  $F^-$  and  $CN^-$  in comparison to  $FcBMes_2$ reflect the unfavorable steric effects of the additional o-BMes<sub>2</sub> group. While the size of the binding cavity (notably a B…B separation on the order of 3.7 Å) precludes the chelation of fluoride, the broad versatility of the synthetic methodology employed allows access to a related B/Si heterotopic Lewis acid which captures 1 equiv of fluoride via a Si-F-B bridging motif.

#### EXPERIMENTAL SECTION

**General Procedures.** Manipulations of air-sensitive reagents were carried out in a glovebox or by means of Schlenk-type techniques involving the use of a dry argon or nitrogen atmosphere. HPLC grade solvents were purified, dried, and degassed prior to use by a commercially available Braun Solvent Purification System (SPS 500). NMR solvents CDCl<sub>3</sub> (molecular sieves) and  $C_6D_6$  and  $C_6D_5CD_3$  (both potassium) were predried before use. The known compounds 1,1'-fc(BBr<sub>2</sub>)<sub>2</sub>, 1,3-fc\*(BBr<sub>2</sub>)<sub>2</sub>, 1,1'-fcBr<sub>2</sub>, MesLi, 1-iodo-2,6-dimethyl-4-fluorobenzene, and FBXyl<sub>2</sub> were prepared according to literature

procedures; *o*-XylLi was prepared by minor modification of the method used for MesLi.<sup>11,13,24–27</sup> The syntheses of compounds **3b** and **6b**,**c** have been reported by us previously in communication format.<sup>6c,10a</sup> FBMes<sub>2</sub> was used as supplied (Sigma Aldrich). <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker AVII 500 FT-NMR or Varian Mercury VX-300 spectrometer; <sup>1</sup>H and <sup>13</sup>C NMR spectra were calibrated using the residual proton or natural-abundance <sup>13</sup>C resonances of the solvent, and <sup>11</sup>B and <sup>19</sup>F spectra were referenced with respect to Et<sub>2</sub>O·BF<sub>3</sub> and CFCl<sub>3</sub>, respectively. Mass spectra were measured by the EPSRC National Mass Spectrometry Service, Swansea University, and elemental microanalyses by London Metropolitan University.

Syntheses of New Compounds.  $1, 1'-fc(BMes_2)_2$  (1a),  $1, 1'-fc(BMes_2)_2$  $fc(BXy|_{2}^{f})_{2}$  (1b), and  $1,1'-fc(BXy|_{2})_{2}$  (1c). To a suspension of mesitylithium (0.65 g, 5.14 mmol) in Et<sub>2</sub>O (50 mL) was added 1,1'-fc(BBr<sub>2</sub>)<sub>2</sub> (0.19 equiv) in Et<sub>2</sub>O (50 mL), and the reaction mixture was stirred for 18 h. After which time the reaction was judged to be complete by <sup>11</sup>B NMR spectroscopy. Removal of volatiles in vacuo, extraction into hexanes, concentration, and cooling to -30 °C led to the isolation of 1a as a red microcrystalline material. Yield: 0.43 g, 66%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 20 °C): δ 2.26 (s, 36H, o- and para-CH<sub>3</sub> of Mes), 4.35 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.72 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 6.74 (s, 8H, aromatic CH of Mes). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$ 21.2 (p-CH<sub>3</sub> of Mes), 24.5 (o-CH<sub>3</sub> of Mes), 75.0, 80.6 (C<sub>5</sub>H<sub>4</sub>), 128.4 (o-quaternary C of Mes), 137.3 (p-quaternary C of Mes), 139.2 (aromatic CH of Mes), 142.6 (B-bound quaternary C of Mes). <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  76. UV/vis (thf):  $\lambda_{max}$  542 nm,  $\varepsilon$  = 1420 mol<sup>-1</sup> cm<sup>-1</sup> dm<sup>3</sup>. MS (EI): 682.3 (100%) M<sup>+</sup>, exact mass (calcd for <sup>11</sup>B, <sup>56</sup>Fe isotopomer) 682.3599, (measd) 682.359.  $E_{1/2}$ (CH<sub>2</sub>Cl<sub>2</sub>) = +0.197 V (with respect to  $FcH/FcH^+$ ). The syntheses of 1b,c were carried out in a manner similar to that for **1a** via the reaction of in situ lithiated 1-iodo-2,6-dimethyl-4-fluorobenzene or o-xylyllithium with 1,1'-fc(BBr<sub>2</sub>)<sub>2</sub> (0.22 equiv) in diethyl ether, with the reaction followed by <sup>11</sup>B NMR spectroscopy. Yield of 1b: 0.39 g, 39%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 20 °C): δ 2.26 (s, 24H, o-CH<sub>3</sub> of Xyl<sup>F</sup>), 4.45 (m, 4H,  $C_5H_4$ ), 4.77 (m, 4H,  $C_5H_4$ ), 6.66 (d,  ${}^3J_{HF}$  = 12 Hz, 8H, aromatic CH of Xyl<sup>F</sup>).  ${}^{13}$ C NMR (126 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  24.4 (*o*-CH<sub>3</sub> of Xyl<sup>F</sup>), 75.3, 80.4 (C<sub>5</sub>H<sub>4</sub>), 114.1 (d,  ${}^{2}J_{CF}$  = 19 Hz, aromatic CH of Xyl<sup>F</sup>), 140.7 (B-bound quarternary of Xyl<sup>F</sup>), 141.6 (d,  ${}^{3}J_{CF} = 8$  Hz, oquaternary C of Xyl<sup>F</sup>), 162.5 (d,  ${}^{1}J_{CF}$  = 247 Hz, CF of Xyl<sup>F</sup>).  ${}^{11}$ B NMR (96 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  78.0.  ${}^{19}$ F NMR (282 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta - 116.3$  (t,  ${}^{3}J_{\text{FH}} = 12$  Hz, *p*-F of Xyl<sup>F</sup>). MS (EI): 698.4 (100%) M<sup>+</sup>, exact mass (calcd for M<sup>+</sup>,  ${}^{10}\text{B}$  isotopomer) 698.2596, (measd) 698.2591. Single crystals of 1c suitable for X-ray crystallography were obtained by slow evaporation of a concentrated diethyl ether solution. Yield: 0.35 g, 59%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 20 °C): δ 2.30 (s, 24H, o-CH<sub>3</sub> of Xyl), 4.44 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.76 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 6.93 (AB m, 8H, m-CH of Xyl), 7.10 (AB m, 4H, p-CH of Xyl). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 20 °C): δ 24.5 (o-CH<sub>3</sub> of Xyl), 75.1, 80.5 (C<sub>5</sub>H<sub>4</sub>), 127.3 (m-CH of Xyl), 127.7 (p-CH of Xyl), 138.9 (o-quaternary C of Xyl), 145.2 (B-bound quarternary of Xyl). <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>, 20 °C): δ 77. MS (EI): 626.2 (100%) M<sup>+</sup>, exact mass (calcd for M<sup>+</sup>,  $^{10}\mathrm{B}$  isotopomer) 626.2973, (measd) 626.2978. Anal. Calcd for C42H44B2Fe: C, 80.49; H, 7.08. Found: C, 80.44; H, 7.00.

1,3-fc\*(BMes<sub>2</sub>)<sub>2</sub> (2). To a rapidly stirred solution of 1,3-fc\*(BBr<sub>2</sub>)<sub>2</sub> (0.65 g, 1.09 mmol) in Et<sub>2</sub>O (60 mL) was added mesityllithium (0.83 g, 6.6 mmol) also in  $Et_2O$  (40 mL). The reaction mixture was warmed to 20 °C and stirred for a further 12 h. Volatiles were then removed in vacuo, and the residual solid was extracted into pentane. After concentration and cooling to -35 °C the precipitated solids were removed by filtration, and the solvent was removed from the filtrate in vacuo. Recrystallization of the resulting solid from acetone (25 mL) yielded dark purple crystals of the acetone bis(solvate) 2.2(OCMe<sub>2</sub>) suitable for X-ray crystallography. Yield: 0.35 g, 43%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 20  $^{\circ}$ C):  $\delta$  1.48 (s, 15H, CH<sub>3</sub> of Cp\*), 1.55 (s, CH<sub>3</sub> of acetone), 2.12 (s, 12H, p-CH3 of Mes), 2.54 (br s, 24H, o-CH3 of Mes), 4.88 (s, 2H, C<sub>5</sub>H<sub>3</sub>), 5.08 (s, 1H, C<sub>5</sub>H<sub>3</sub>), 6.79 (br s, 8H, aromatic CH of Mes), acetone solvate not included. <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C): δ 11.6 (CH<sub>3</sub> of Cp\*), 21.5 (p-CH<sub>3</sub> of Mes), 23.6 (o-CH<sub>3</sub> of Mes), 30.4 (CH<sub>3</sub> of acetone), 81.9 (quaternary C of Cp\*), 89.9 (CH

of C<sub>5</sub>H<sub>3</sub>), 95.3 (CH of C<sub>5</sub>H<sub>3</sub>), 129.3 (aromatic CH of Mes), 137.8 (*p*quaternary C of Mes), 139.8 (*o*-quaternary C of Mes), 144.5 (*ipso*quaternary C of Mes); *ipso*-quaternary C of Cp not observed;, acetone solvate not included. <sup>11</sup>B NMR (96 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  79 (br s). UV/vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  313 nm,  $\varepsilon$  = 3940 mol<sup>-1</sup> cm<sup>-1</sup> dm<sup>3</sup>. MS (EI<sup>+</sup>): 753 (100%), M<sup>+</sup>; exact mass (calcd for M<sup>+</sup>, <sup>10</sup>B isotopomer) 750.4428, (measd) 750.4428. Anal. Calcd for C<sub>57</sub>H<sub>74</sub>B<sub>2</sub>FeO<sub>2</sub>: C, 78.76; H, 8.59. Found: C, 79.07; H, 8.57.

rac-1,2-fc(BMes<sub>2</sub>)Br (3a). To a solution of 1,1'-fcBr<sub>2</sub> (1.09 g, 3.16 mmol) in thf (18 mL) at -78 °C was added "BuLi (1.98 mL of a 1.6 M solution in hexanes, 3.16 mmol). After 30 min tetramethylpiperidine (0.53 mL, 3.16 mmol) was added and the resulting mixture warmed to -40 °C. The temperature of the reaction was then carefully maintained between -40 and -30 °C for 2 h. After this time, the reaction mixture was again cooled to -78 °C and FBMes<sub>2</sub> (1.13 g, 4.21 mmol, 90% purity as received from Sigma Aldrich) added as a solution in thf (10 mL); the reaction mixture was slowly warmed to room temperature and stirred for a further 15 h. The resulting red solution was diluted with ether (100 mL) and washed with water (50 mL) and brine (50 mL), before being dried in vacuo, yielding the crude product as a dark red solid. Purification using column chromatography (hexane to 10% ethyl acetate/hexanes) yielded 3a as a dark red amorphous solid. Yield: 1.23 g, 76%. Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a concentrated solution in Et<sub>2</sub>O. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  6.75 (s, 4H, aromatic CH of Mes), 4.98 (m, 1H, C<sub>5</sub>H<sub>3</sub>), 4.51 (virtual t, J = 3 Hz, 1H, C<sub>5</sub>H<sub>3</sub>), 4.38 (m, 1H, C<sub>5</sub>H<sub>3</sub>), 4.25 (s, 5H, Cp), 2.30 (s, 12H, o-CH<sub>3</sub> of Mes), 2.26 (s, 6H, p-CH<sub>3</sub> of Mes). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 20 °C): δ 139.5 (o-quaternary C of Mes), 137.4 (p-quaternary C of Mes), 127.9 (aromatic CH of Mes), 78.7, 77.0 (C<sub>5</sub>H<sub>3</sub>), 71.9 (Cp), 70.5 (C<sub>5</sub>H<sub>3</sub>), 24.3 (*o*-CH<sub>3</sub> of Mes), 21.1 (*p*-CH<sub>3</sub> of Mes); Bbound quaternary carbons not observed. <sup>11</sup>B NMR (96 MHz, [D] chloroform, 20 °C):  $\delta$  78. UV/vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  502 nm,  $\varepsilon$  =  $1028 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ . MS (EI<sup>+</sup>): 512 (100%) M<sup>+</sup>; exact mass (calcd for M<sup>+</sup>, <sup>11</sup>B isotopomer) 512.0973, (measd) 512.0981. Anal. Calcd for C28H30BBrFe: C, 65.54; H, 5.89. Found: C, 65.50; H, 5.92.

1,2,5-fcBr(BMes<sub>2</sub>)<sub>2</sub> (4). A solution of <sup>n</sup>BuLi in pentane (1.31 mL of a 1.6 M solution, 2.1 mmol) was added to a solution of tetramethylpiperidine (0.28 mL, 1.66 mmol) in thf (10 mL) at 0 °C. After it was stirred at 0 °C for 45 min, the reaction mixture was cooled to -78 °C and a solution of 3a (0.92 g, 1.79 mmol) in thf (10 mL) added. After the mixture was stirred for a further 2 h at -78 °C, a solution of FBMes<sub>2</sub> (0.58 g, 2.16 mmol) in thf (10 mL) was added, and the reaction mixture was warmed slowly to room temperature. After this mixture was stirred for 12 h, diluted with Et<sub>2</sub>O (50 mL), and quenched with water, the aqueous layer was extracted with dichloromethane and the combined organic layers were washed with water and brine prior to drying over MgSO<sub>4</sub>. Volatiles were then removed in vacuo, and the crude material was washed with acetone (2  $\times$  10 mL). Yield: 0.71 g, 52%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$ 2.27 (s, 12H, p-CH<sub>3</sub> of Mes), 2.34 (s, 24H, o-CH<sub>3</sub> of Mes), 4.23 (s, 5H, Cp), 4.78 (s, 2H, C<sub>5</sub>H<sub>2</sub>), 6.75 (s, 8H, aromatic CH of Mes). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 20 °C): δ 21.0 (p-CH<sub>3</sub> of Mes), 24.4 (o-CH<sub>3</sub> of Mes), 72.0 (Cp), 80.4 (C<sub>5</sub>H<sub>2</sub>), 85.0 (B-bound quaternary C of C<sub>5</sub>H<sub>2</sub>), 94.0 (Br-bound quaternary C of C<sub>5</sub>H<sub>2</sub>), 128.0 (aromatic CH of Mes), 137.6 (p-quaternary C of Mes), 139.7 (o-quaternary C of Mes), 142.6 (B-bound quaternary C of Mes). <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  89. MS (EI): 760.0 (100%) M<sup>+</sup>, exact mass (calcd for M<sup>+</sup>, <sup>11</sup>B, <sup>56</sup>Fe isotopomer) 760.2710, (measd) 760.2709.

1,3-fc(BMes<sub>2</sub>)<sub>2</sub> (5). To a solution of 4 (0.35 g, 0.45 mmol) in thf at -78 °C was added <sup>t</sup>BuLi (0.63 mL of a 1.6 M solution in hexanes, 1.0 mmol, 2.2 equiv), and the reaction mixture was stirred for 2 h at that temperature. Excess propan-2-ol was then added at -78 °C, the mixture was warmed to room temperature, and water was added. After extraction with Et<sub>2</sub>O and removal of volatiles in vacuo the process was repeated using a further 2.2 equiv of <sup>t</sup>BuLi. Following a second aqueous workup and removal of volatiles in vacuo, analysis by <sup>1</sup>H NMR indicated a crude yield of 5 of 80% contaminated by ca. 20% of unreacted 4. Repeated washing of the crude product with acetone led to the formation of a 95% pure material in low (ca. 5%) overall yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  2.26 (s, 12H, *p*-CH<sub>3</sub> of Mes), 2.40 (s, 24H, *o*-CH<sub>3</sub> of Mes), 4.10 (s, 5H, Cp), 4.65 (s, 1H, C<sub>5</sub>H<sub>3</sub>), 4.95 (s, 1H, C<sub>5</sub>H<sub>3</sub>), 6.79 (s, 8H, aromatic CH of Mes). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  21.0 (*p*-CH<sub>3</sub> of Mes), 24.5 (*o*-CH<sub>3</sub> of Mes), 70.5 (Cp), 82.6, 92.3 (C<sub>5</sub>H<sub>3</sub>), 128.3 (aromatic CH of Mes), 137.2 (*p*quaternary C of Mes), 139.2 (*ortho*-quaternary C of Mes), 142.7 (Bbound quaternary C of Mes). B-bound quaternary C of C<sub>5</sub>H<sub>3</sub> not observed. <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  89.

1,2-fc(BMes<sub>2</sub>)<sub>2</sub> (6a). To a stirred solution of 3a (0.22 g, 0.43 mmol) in Et<sub>2</sub>O (15 mL) at -78 °C were added "BuLi and tmeda (1.0 equiv of each) and (after 1 h) a solution of FBMes<sub>2</sub> (1.13 g, 4.21 mmol, 90% purity as received from Sigma Aldrich) in Et<sub>2</sub>O (5 mL). After it was warmed to room temperature over 2 h and stirred for a further 12 h, the reaction mixture was diluted with Et<sub>2</sub>O (100 mL) and washed with water (50 mL) and brine (50 mL). Removal of volatiles in vacuo yielded the crude product as a dark red solid. Purification using column chromatography (hexanes to 10% ethyl acetate/hexanes) yielded a dark red amorphous solid still contaminated with Mes<sub>2</sub>BOBMes<sub>2</sub>. Fractional crystallization from hexanes (to remove the borinic anhydride) and finally from MeOH/Et2O yielded 6a as dark red crystals. Yield: 0.24 g, 83%. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated solution in Et<sub>2</sub>O. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  1.55 (s, 12H, *p*-CH<sub>3</sub> of Mes), 2.00-2.70 (br overlapping signals, 24H, o-CH<sub>3</sub> of Mes), 4.15 (s, 5H, Cp), 4.87 (t,  ${}^{3}J_{HH} = 3$  Hz, 1H, C<sub>5</sub>H<sub>3</sub>), 5.07 (d,  ${}^{3}J_{HH} = 3$  Hz, 2H,  $C_5H_3$ ), 6.22 (s, 2H, aromatic CH of Mes), 6.36 (s, 2H, aromatic CH of Mes), 6.74 (s, 2H, aromatic CH of Mes), 6.81 (s, 2H, aromatic CH of Mes). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, 120 °C): δ 2.07 (s, 12H, p-CH<sub>3</sub>) of Mes), 2.25 (s, 24H, o-CH3 of Mes), 3.92 (s, 5H, Cp), 4.52 (m, 1H,  $C_5H_3$ ), 5.02 (d,  ${}^{3}J_{HH} = 2$  Hz, 2H,  $C_5H_3$ ), 6.50 (s, 8H, aromatic CH of Mes). <sup>1</sup>H NMR (300 MHz,  $C_6D_5CD_{34}$  -60 °C):  $\delta$  1.70, 1.77, 2.08, 2.19, 2.25, 2.39, 2.58, 2.97, 3.21 (s, each 3H, o-CH3 of Mes), 2.02 (s, 12H, p-CH<sub>3</sub> of Mes), 3.78 (s, 5H, Cp), 4.26, 4.84, 5.02 (m, each 1H, C<sub>5</sub>H<sub>3</sub>), 6.02, 6.06, 6.30, 6.58 (2 signals), 6.61 (2 signals), 6.68 (s, each 1H, aromatic CH of Mes). <sup>13</sup>C NMR (75 MHz,  $C_6D_5CD_3$ , 120 °C):  $\delta$ 20.3 (p-CH<sub>3</sub> of Mes), 24.5 (o-CH<sub>3</sub> of Mes), 71.2 (Cp), 73.5, 90.1 (C<sub>5</sub>H<sub>3</sub>), 128.1 (aromatic CH of Mes), 136.6 (ipso-quaternary C of Mes), 139.0 (o-quaternary C of Mes); B-bound quaternary carbons not observed. <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>, 20 °C): δ 80. UV-vis (dichloromethane):  $\lambda_{max}$  510 nm,  $\varepsilon = 1903 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$ . MS (EI<sup>+</sup>): 682 (100%)  $M^+$ ; exact mass (calcd for  $M^+$ , <sup>10</sup>B isotopomer) 680.3677, (measd) 680.3657. Anal. Calcd for C<sub>46</sub>H<sub>52</sub>B<sub>2</sub>Fe): C, 80.91; H, 7.68. Found: C, 80.66; H, 7.44.  $E_{1/2}(CH_2Cl_2) = +0.177 V$  (with respect to FcH/FcH<sup>+</sup>).

rac-1,2-fc(BMes<sub>2</sub>)(SiMe<sub>2</sub>Cl) (7). To a stirred solution of 3a (0.84 g, 1.64 mmol) in Et<sub>2</sub>O (100 mL) at -78 °C was added dropwise <sup>t</sup>BuLi (1.72 mL of a 1.9 M solution in pentane, 3.27 mmol). After the mixture was stirred at -78 °C for 30 min, Me<sub>2</sub>SiCl<sub>2</sub> (2 mL, 16.6 mmol) was added to the purple solution at -78 °C. The reaction mixture was warmed to room temperature and stirred for 15 h. Volatiles were then removed in vacuo, the residual solid was extracted with pentane  $(3 \times 20 \text{ mL})$ , and the volatiles were removed in vacuo from the combined extracts to afford the target material as an orange solid. Yield: 0.80 g, 91%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 20 °C): δ 0.21 (s, 3H, CH<sub>3</sub> of SiMe<sub>2</sub>Cl), 0.36 (s, 3H, CH<sub>3</sub> of SiMe<sub>2</sub>Cl), 2.12 (br s, 12 H, o-CH<sub>3</sub> of Mes), 2.26 (s, 6H, a-CH<sub>3</sub> of Mes), 4.22 (s, 5H, Cp), 4.58 (m, 1H,  $C_5H_3BSi$ ), 4.73 (m, 1H,  $C_5H_3BSi$ ), 4.83 (m, 1H,  $C_5H_3BSi$ ), 6.74 (s, 4H, aromatic CH of Mes). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  3.6 (CH<sub>3</sub> of SiMe<sub>2</sub>Cl), 4.0 (CH<sub>3</sub> of SiMe<sub>2</sub>Cl), 21.1 (*o*-CH<sub>3</sub> of Mes), 23.6 (p-CH<sub>3</sub> of Mes), 70.7 (Cp), 71.7 (CSi of C<sub>5</sub>H<sub>3</sub>BSi), 73.1 (CH of C<sub>5</sub>H<sub>3</sub>BSi), 80.8 (CH of C<sub>5</sub>H<sub>3</sub>BSi), 87.2 (CH of C<sub>5</sub>H<sub>3</sub>BSi), 94.1 (CB of C5H3BSi), 128.2 (aromatic CH of Mes), 138.0 (pquaternary C of Mes), 139.7 (o-quaternary C of Mes), 142.7 (ipsoquaternary C of Mes). Assignments wree assisted by gCOSY, HSQC, and HMBC NMR (500 MHz (<sup>1</sup>H)/125 MHz (<sup>13</sup>C), CDCl<sub>3</sub>, 20 °C). <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  82. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>, 20 °C): δ 24.5 (SiMe<sub>2</sub>Cl). MS (EI<sup>+</sup>): 526.2 (100%) M<sup>+</sup>; exact mass (calcd for M<sup>+</sup>, <sup>10</sup>B, <sup>35</sup>Cl, <sup>28</sup>Si isotopomer) 523.1795, (measd) 523.1794. Isotopic profile consistent with assignment. Anal. Calcd for C30H36BClFeSi: C, 68.40; H, 6.89. Found: C, 68.42; H, 6.84.

rac-1,2-fc(BMes<sub>2</sub>)(SiMe<sub>2</sub>F) (8) and rac-1,2-fc(BMes<sub>2</sub>)(SiMe<sub>2</sub>OMe) (9). 8 and 9 are most easily prepared from the common precursor 7 by the use of either  $CuF_2$  or MeOH, respectively. For 8: to  $CuF_2$  (0.20 g, 1.00 mmol) was added a solution of 7 (0.50, 1.00 mmol) in dichloromethane (10 mL) at room temperature. After the dark suspension was stirred for 3 h, volatiles were removed in vacuo, the residual solid was extracted with hexanes (3  $\times$  20 mL), and the volatiles were removed in vacuo from the combined extracts to afford the target material as a red tar. Yield: 0.45 g, 93% (98% pure with 2% 7). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  0.11 (d, <sup>3</sup>J<sub>HF</sub> = 8 Hz, 3H, CH<sub>3</sub> of SiMe<sub>2</sub>F), 0.15 (d,  ${}^{3}J_{HF}$  = 8 Hz, 3H, CH<sub>3</sub> of SiMe<sub>2</sub>F), 2.15 (s, 12 H, o-CH<sub>3</sub> of Mes), 2.28 (s, 6H, p-CH<sub>3</sub> of Mes), 4.21 (s, 5H, Cp), 4.61 (m, 1H,  $C_5H_3BSi$ ), 4.77 (m, 1H,  $C_5H_3BSi$ ), 4.78 (m, 1H,  $C_5H_3BSi$ ), 6.76 (s, 4H, aromatic CH of Mes). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  -0.1 (d,  ${}^{2}J_{CF}$  = 16 Hz, CH<sub>3</sub> of SiMe<sub>2</sub>F), 0.2 (d,  ${}^{2}J_{CF}$  = 16 Hz, CH<sub>3</sub> of SiMe<sub>2</sub>F), 21.0 (p-CH<sub>3</sub> of Mes), 23.7 (o-CH<sub>3</sub> of Mes), 69.4 (CSi of C<sub>5</sub>H<sub>4</sub>BSi), 70.4 (Cp), 73.6 (CH of C<sub>5</sub>H<sub>3</sub>BSi), 80.0 (CH of C<sub>5</sub>H<sub>3</sub>BSi), 86.8 (CH of C<sub>5</sub>H<sub>3</sub>BSi), 92.2 (br, CB of C<sub>5</sub>H<sub>3</sub>BSi), 128.0 (aromatic CH of Mes), 137.7 (p-quaternary C of Mes), 139.6 (s, oquaternary C of Mes), 142.8 (br, *ipso*-quaternary C of Mes). <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  83. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  -152.0 (sept with <sup>29</sup>Si satellites, <sup>1</sup>J<sub>FSi</sub> = 275 Hz, <sup>3</sup>J<sub>HF</sub> = 7 Hz). <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  23.4 (d, <sup>1</sup>J<sub>SiF</sub> = 275 Hz). For 9: a suspension of 7 (0.30 g, 0.57 mmol) in methanol (50 mL) was stirred for 1 h, at which point Et<sub>2</sub>O (50 mL) was added and the reaction mixture stirred for a further 3 h. Volatiles were then removed in vacuo, and the residual solid was extracted with hexane  $(3 \times 20 \text{ mL})$ . Volatiles were removed in vacuo from the combined extracts to afford the target material as a red solid. Yield: 0.24 g, 82%. Single crystals suitable for X-ray diffraction were obtained by slow evaporation from hexamethyldisiloxane. <sup>1</sup>H NMR (300 MHz,  $CDCl_2$ , 20 °C):  $\delta$  0.02 (s, 3H, CH<sub>3</sub> of SiMe<sub>2</sub>), 0.03 (s, 3H, CH<sub>3</sub> of SiMe<sub>2</sub>), 2.12 (s, 12 H, o-CH<sub>3</sub> of Mes), 2.25 (s, 6H, p-CH<sub>3</sub> of Mes), 3.31 (s, 3H, CH<sub>3</sub> of SiOMe), 4.15 (s, 5H, Cp), 4.51 (m, 1H, C<sub>5</sub>H<sub>3</sub>BSi), 4.65 (m, 1H, C<sub>5</sub>H<sub>3</sub>BSi), 4.70 (m, 1H, C<sub>5</sub>H<sub>3</sub>BSi), 6.73 (s, 4H, aromatic CH of Mes). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 20 °C): δ –1.2 (SiMe<sub>2</sub>), –1.0 (SiMe<sub>2</sub>), 21.1 (*p*-CH<sub>3</sub> of Mes), 23.6 (o-CH<sub>3</sub> of Mes), 50.2 (SiOMe), 70.1 (Cp), 71.7 (CSi of C<sub>5</sub>H<sub>3</sub>BSi), 72.7 (CH of C<sub>5</sub>H<sub>3</sub>BSi), 80.1 (CH of C<sub>5</sub>H<sub>3</sub>BSi), 85.9 (CH of C<sub>5</sub>H<sub>3</sub>BSi), 128.0 (aromatic CH of Mes), 137.7 (p-quaternary C of Mes), 139.7 (o-quaternary C of Mes), 143.0 (br, ipso-quaternary C of Mes); the signal for the boron bound carbon atom of the C<sub>5</sub>H<sub>3</sub>BSi unit was not observed. Assignments were assisted by gCOSY, HMQC, and HSQC NMR spectra. <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  87 (br). <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  11. MS (EI<sup>+</sup>): 522.2 (100%) M<sup>+</sup>; exact mass (calcd for M<sup>+</sup>,  $^{10}B$ ,  $^{28}Si$  isotopomer) 519.2290. (measd) 519.2288.  $E_{1/2}$ (CH<sub>2</sub>Cl<sub>2</sub>) = +0.047 V (with respect to FcH/  $FcH^+$ )

[K(18-crown-6)][1a·CN]. To a solution of 1a (0.040 g, 0.06 mmol) in chloroform (5 cm<sup>3</sup>) were added KCN and 18-crown-6 (1.0 equiv of each), and the reaction mixture was stirred for 1 h, at which point the reaction was judged complete by quantitative conversion to a single <sup>11</sup>B NMR resonance at  $\delta_{\rm B}$  –13. Layering of the reaction mixture with diethyl ether led to the isolation of  $[K(18-crown-6)][1a\cdot CN]^-$  as single crystals suitable for X-ray crystallography. Yield: 0.034 g, 81%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 20 °C): δ 2.14 (s, 12H, *o*-CH<sub>3</sub> of Mes), 2.22 (s, 6H, p-CH<sub>3</sub> of Mes), 2.26 (s, 6H, p-CH<sub>3</sub> of Mes) 2.29 (s, 12H, o-CH<sub>3</sub> of Mes), 3.48 (s, 24H, 18-crown-6), 4.04 (br s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.21, 4.26, 4.68 (each br m, 2H, C5H4), 6.52, 6.69 (each s, 4H, aromatic CH of Mes). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 20 °C): δ 20.7, 21.0 (p-CH<sub>3</sub> of Mes), 24.6, 25.2 (o-CH<sub>3</sub> of Mes), 69.9 (18-crown-6), 76.0, 78.9 (C<sub>5</sub>H<sub>4</sub>), 127.8, 128.8 (o-quarternary of Mes), 131.6, 136.0 (p-quaternary C of Mes), 139.1, 141.6 (aromatic CH of Mes), boronbound quaternary carbons not observed. <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>, 20 °C):  $\delta$  –13. MS (EI): 708.3 (100%) M<sup>+</sup>; exact mass (calcd for <sup>56</sup>Fe isotopomer) 706.3687, (measd) 706.3687. Reproducible elemental microanalyses for crystalline samples of [K(18-crown-6)][1a·CN] proved difficult to obtain due to the presence of both chloroform and diethyl ether in the crystal lattice (as shown by X-ray crystallography).

 $[K(18-crown-6)]_2[1a\cdot(CN)_2]$  and  $[K(18-crown-6)]_2[1b\cdot(CN)_2]$ . The two adducts were prepared by a common method exemplified for

 $[K(18-crown-6)]_2[1a(CN)_2]$ . To a solution of 1a (0.040 g, 0.06 mmol) in acetonitrile (5 cm<sup>3</sup>) were added KCN/ and 18-crown-6 (2.0 equiv of each), and the reaction mixture was stirred for 1 h. At this point the reaction was judged to be complete by quantitative conversion to a single <sup>11</sup>B NMR resonance at  $\delta_{\rm B}$  –16 ppm. An accompanying color change from deep red to yellow was observed for the solution together with the precipitation of a yellow-orange solid. Layering of the supernatant solution with Et<sub>2</sub>O led to the formation of  $[K(18\text{-crown-6})]_2[1a\cdot(CN)_2]\cdot OEt_2$  as orange blocks suitable for X-ray crystallography. Yield: 0.023 g, 27%. For [K(18-crown-6)]<sub>2</sub>[1b·(CN)<sub>2</sub>]:  $\delta_{\rm B}$  -15 ppm, yield 0.022 g, 25%. Attempts to fully characterize [K(18-crown-6)]<sub>2</sub>[1a·(CN)<sub>2</sub>] or [K(18-crown- $(6)_{2}$  [1b·(CN)<sub>2</sub>] proved unsuccessful, as crystalline samples of both adduct,s once formed, proved to be resolutely insoluble in compatible solvents. Anal. Calcd for C<sub>76</sub>H<sub>110</sub>B<sub>2</sub>FeK<sub>2</sub>N<sub>2</sub>O<sub>13</sub>: C, 64.46; H, 7.84; N, 1.98. Found: C, 64.33; H, 7.56,; N, 2.18. Calcd for C<sub>66</sub>H<sub>88</sub>B<sub>2</sub>F<sub>4</sub>FeK<sub>2</sub>N<sub>2</sub>O<sub>12</sub>: C, 59.43; H, 6.65; N, 2.10. Found: C, 59.00; H. 6.42: N. 2.38

[K(18-crown-6)][6a·CN]. Potassium cyanide (3.8 mg, 0.059 mmol), 18-crown-6 (1.0 equiv), 6a (1.0 equiv), and thf- $d_8$  (1 mL) were mixed in a J. Young NMR tube, and the resulting mixture was sonicated until the reaction was judged complete by <sup>11</sup>B NMR spectroscopy (quantitative conversion of the signal at  $\delta_{\rm B}$  80 to a signal at -15 ppm). Layering the resulting solution with pentane led to growth of single red crystals of the chloroform solvate suitable for X-ray diffraction. Yield: 0.035 g, 59%. <sup>1</sup>H NMR (500 MHz, thf- $d_8$ , 20 °C):  $\delta$ 1.76, 1.84, 2.04, 2.09, 2.18, 2.22 (each 6H, o- and p-CH<sub>3</sub> of Mes), 3.58 (s, 24H, 18-crown-6), 4.20 (s, 5H, Cp), 4.45, 4.53, 5.56 (s, each 1H, C<sub>5</sub>H<sub>4</sub>), 5.58, 6.08 (s, each 1H, aromatic CH of Mes), 6.30 (overlapping s, 3H, aromatic CH of Mes), 6.51, 6.58, 6.64 (each s, 1H, aromatic CH of Mes). <sup>13</sup>C NMR (126 MHz, thf- $d_8$ , 20 °C):  $\delta$ 13.4, 19.9, 20.0, 20.2, 20.4, 20.5, 22.2, 23.8, 25.5, 27.1, 27.9, 34.1 (oand p- CH3 of Mes), 67.4, 67.5, 68.6 (C5H3), 69.7 (Cp), 70.1 (18crown-6), 126.7, 126.8, 126.9, 127.4, 127.8, 128.2, 128.5, 128.6 (aromatic CH of Mes), 129.0, 129.7, 130.3, 130.8 (p-quaternary C of Mes), 134.8, 135.0, 138.9, 140.4, 140.9, 141.4, 143.0, 143.6 (oquaternary C of Mes); boron-bound quaternary carbons not observed. <sup>11</sup>B NMR (96 MHz,  $d_8$ -THF, 20 °C):  $\delta$  –15, 78 (v br). MS (ES negative ion): 708.3635 (100%) [1,2-fc(BMes<sub>2</sub>)<sub>2</sub>CN]<sup>-</sup>; exact mass (calcd for M<sup>+</sup>, <sup>54</sup>Fe isotopomer) 705.3735, (measd) 705.3724. Anal. Calcd for C<sub>60</sub>H<sub>77</sub>B<sub>2</sub>Cl<sub>3</sub>FeKNO<sub>6</sub>: C, 63.37; H, 6.86; N, 1.24. Found: C, 63.37; H, 6.84; N, 1.22.

[K(18-crown-6)][8-F]. A solution of 8 (0.29 g, 0.57 mmol) in toluene (10 mL) was added to KF (0.033 g, 0.57 mmol) and 18crown-6 (0.15 g, 0.57 mmol) and the reaction mixture stirred for 5 h. | Volatiles were removed in vacuo; the residual solid was washed with hexane (10 mL) and then toluene (10 mL) and dried in vacuo to give an orange solid. Yield: 0.25 g, 53%. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 20 °C):  $\delta$  –0.07 (dd,  ${}^{3}J_{HF}$  = 3, 8 Hz, 3H, CH<sub>3</sub> of SiMe<sub>2</sub>F), 0.50 (dd,  ${}^{3}J_{HF}$ = 4, 8 Hz, 3H,  $CH_3$  of  $SiMe_2F$ ), 1.55 (s, 3H, o- $CH_3$  of Mes), 1.79 (s, 3H, o-CH<sub>3</sub> of Mes), 2.05 (m, 6H, o-CH<sub>3</sub> and p-CH<sub>3</sub> of Mes), 2.19 (s, 3H, p-CH<sub>3</sub> of Mes), 2.81 (s, 3H, o-CH<sub>3</sub> of Mes), 3.57 (s, 24H, CH<sub>2</sub> of 18-crown-6), 3.81 (s, 5H, Cp), 3.99 (m, 1H, C<sub>5</sub>H<sub>3</sub>BSi), 4.18 (m, 1H, C<sub>5</sub>H<sub>3</sub>BSi), 4.22 (m, 1H, C<sub>5</sub>H<sub>3</sub>BSi), 6.27 (br s, 1H, aromatic CH of Mes), 6.42 (br s, 1H, aromatic CH of Mes), 6.49 (br s, 1H, aromatic CH of Mes), 6.63 (br s, 1H, aromatic CH of Mes). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN, 20 °C):  $\delta$  1.0 (CH<sub>3</sub> of SiMe<sub>2</sub>F), 2.2 (CH<sub>3</sub> of SiMe<sub>2</sub>F), 19.8 (p-CH<sub>3</sub> of Mes), 20.0 (p-CH<sub>3</sub> of Mes), 23.0 (o-CH<sub>3</sub> of Mes), 24.3 (o-CH<sub>3</sub> of Mes), 25.1 (two o-CH<sub>3</sub> of Mes), 70.1 (CH<sub>2</sub> of 18-crown-6), 68.8 (Cp), 69.9 (CH of C<sub>5</sub>H<sub>3</sub>BSi), 73.3 (CH of C<sub>5</sub>H<sub>3</sub>BSi), 76.5 (CH of C5H3BSi), 127.6 (aromatic CH of Mes), 127.7 (aromatic CH of Mes), 131.4 (aromatic CH of Mes), 131.8 (aromatic CH of Mes). The signals for the quaternary carbons of Mes and the boron- and siliconbound carbon atoms in the  $C_3H_3BSi$  unit were not observed. Assignments were assisted by gCOSY, HSQC, and HMBC spectra. <sup>11</sup>B NMR (96 MHz, CD<sub>3</sub>CN, 20 °C):  $\delta$  5 (d,  ${}^{1}J_{BF}$  = 85 Hz).  ${}^{19}F$  NMR (282 MHz, CD<sub>3</sub>CN, 20 °C): δ -153.3 (br, SiMe<sub>2</sub>F), -164.6 (br, BFSi). <sup>29</sup>Si NMR (60 MHz, CD<sub>3</sub>CN, 20 °C): 25.2 (dd,  ${}^{1}J_{SiF}$  = 70, 190 Hz). MS (ES<sup>-</sup>): 529.2 (M<sup>-</sup>, 100%).

**Determination of Binding Constants: Typical Protocol.** A 3 mL portion of a solution of the receptor in thf (typically  $1.0-2.0 \ \mu$ M) was placed in the cell, and aliquots of ["Bu<sub>4</sub>N]F·3H<sub>2</sub>O or ["Bu<sub>4</sub>N]CN in dichloromethane were added (typically  $10-25 \ \mu$ L of a  $10-15 \ \mu$ M solution). The solution was stirred for 1 min after each addition and the UV–vis spectrum then measured. The program ReactLab Equilibria was subsequently used to determine the binding constants, with data being fitted over the wavelength range 430–530 nm.<sup>28</sup> See the Supporting Information for fuller details.

Crystallography. Included in this paper are the structures of compounds 1c, 2, 9,  $[K(18\text{-crown-6})][1a \cdot CN]$ ,  $[K(18\text{-c$ 6)]<sub>2</sub>[ $\mathbf{1a} \cdot (CN)_2$ ], [K(18-crown-6)]<sub>2</sub>[ $\mathbf{1a} \cdot (CN)_2$ ]·OEt<sub>2</sub>, [K(18-crown-6)]<sub>2</sub>[ $1b\cdot(CN)_2$ ], and ["Bu<sub>4</sub>N][ $8\cdot CN$ ]; those of the hydrolysis products [K(18-crown-6)][rac-1,2-fc(BMes<sub>2</sub>F)(SiMe<sub>2</sub>OH)] and ["Bu<sub>4</sub>N][rac-1,2-fc(BMes<sub>2</sub>CN) (SiMe<sub>2</sub>OH)] have been included in the Supporting Information only (CCDC references 923316 and 924826),<sup>23</sup> and those of 6a, [K(18-crown-6)][6a F], and [K(18crown-6)][6a·CN] have been reported previously by us in communication format (CCDC references: 778111-778113).<sup>10a,c</sup> With the exception of ["Bu<sub>4</sub>N][8·CN], data were collected on a NoniusKappa CCD diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) at 150 K. Data for ["Bu<sub>4</sub>N][8·CN] were collected on an Oxford Diffraction Supernova diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.54184$ Å) at 150 K. Data were processed using the DENZO-SMN package, and structures were solved using SHELXS, Superflip, or SIR92. Refinement was carried out using full-matrix least squares within the CRYSTALS suite or with SHELXTL.<sup>29</sup> Full crystallographic data for all structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC references 923310-923316). Copies of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/ cif.

Crystallographic data for 1c:  $M_r = 626.28$ , monoclinic,  $P2_1/c$ , a = 9.7284(1) Å, b = 30.8099(4) Å, c = 11.1839(2) Å,  $\beta = 96.598(1)^\circ$ , V = 3330.1(1) Å<sup>3</sup>, Z = 4,  $\rho_c = 1.249$  Mg m<sup>-3</sup>, T = 150 K, 27276 reflections collected, 7541 independent (R(int) = 0.048). R1 = 0.0428, wR2 = 0.0927 for observed unique reflections ( $F^2 > 2\sigma(F$  residual electron densities 0.68 and -0.48 e Å<sup>-3</sup>. CSD reference: 923313.

Crystallographic data for **2**:  $M_r = 752.52$ , triclinic,  $P\overline{1}$ , a = 12.8992(2) Å, b = 13.3331(2) Å, c = 15.6365(2) Å,  $\alpha = 96.926(1)^{\circ}$ ,  $\beta = 112.5314(6)^{\circ}$ ,  $\gamma = 90.6447(6)^{\circ}$ , V = 2461.0(1) Å<sup>3</sup>, Z = 2,  $\rho_c = 1.015$  Mg m<sup>-3</sup>, T = 150 K, 11163 reflections collected, 11163 independent (R(int) = 0.026). R1 = 0.0531, wR2 = 0.1537 for observed unique reflections ( $F^2 > 2\sigma(F^2)$ ) and R1 = 0.0706, wR2 = 0.1663 for all unique reflections. Maximum and minimum residual electron densities 0.46 and -0.52 e Å<sup>-3</sup>. CSD reference: 923314.

Crystallographic data for 9:  $M_r = 522.39$ , monoclinic,  $P2_1/c$ , a = 14.9853(2) Å, b = 9.3111(1) Å, c = 20.9000(3) Å,  $\beta = 96.469(1)^\circ$ , V = 2773.1(1) Å<sup>3</sup>, Z = 4,  $\rho_c = 1.251$  Mg m<sup>-3</sup>, T = 150 K, 92997 reflections collected, 6283 independent (R(int) = 0.024). R1 = 0.0434, wR2 = 0.0902 for observed unique reflections ( $F^2 > 2\sigma(F^2)$ ) and R1 = 0.0556, wR2 = 0.0981 for all unique reflections. Maximum and minimum residual electron densities 0.47 and -0.45 e Å<sup>-3</sup>. CSD reference: 923315.

Crystallographic data for [K(18-crown-6)][**1**a-CN]:  $M_r = 1179.52$ , monoclinic,  $P2_1/c$ , a = 21.6605(2) Å, b = 13.7952(1) Å, c = 22.3225(1) Å,  $\beta = 109.212(1)^\circ$ , V = 6299.6(1) Å<sup>3</sup>, Z = 4,  $\rho_c = 1.244$  Mg m<sup>-3</sup>, T = 150 K, 93176 reflections collected, 14307 independent (R(int) = 0.083). R1 = 0.093, wR2 = 0.252 for observed unique reflections ( $F^2 > 2\sigma(F^2)$ ) and R1 = 0.1375, wR2 = 0.2875 for all unique reflections. Maximum and minimum residual electron densities 1.52 and -1.12 e Å<sup>-3</sup>. CSD reference: 923311.

Crystallographic data for [K(18-crown-6)]<sub>2</sub>[1a·(CN)<sub>2</sub>]·OEt<sub>2</sub>:  $M_r$  = 1415.33, monoclinic, C2/*c*, *a* = 23.3200(4) Å, *b* = 16.0340(3) Å, *c* = 22.3901(4) Å,  $\beta$  = 113.478(1)°, *V* = 7678.8(2) Å<sup>3</sup>, *Z* = 4,  $\rho_c$  = 1.224 Mg m<sup>-3</sup>, *T* = 150 K, 16489 reflections collected, 8649 independent (*R*(int) = 0.034). R1 = 0.140, wR2 = 0.3115 for observed unique reflections ( $F^2 > 2\sigma(F^2)$ ) and R1 = 0.1618, wR2 = 0.3200 for all unique reflections. Maximum and minimum residual electron densities 0.54 and -0.72 e Å<sup>-3</sup>. CSD reference: 923310.

Crystallographic data for  $[K(18\text{-crown-6})]_2[\mathbf{1b}\cdot(CN)_2]$ :  $M_r = 1357.07$ , triclinic,  $P\overline{1}$ , a = 11.0600(3) Å, b = 12.3916(2) Å, c = 14.0340(3) Å,  $\alpha = 64.573(1)^\circ$ ,  $\beta = 75.472(1)^\circ$ ,  $\gamma = 79.957(1)^\circ$ , V = 1676.6(1) Å<sup>3</sup>, Z = 1,  $\rho_c = 1.344$  Mg m<sup>-3</sup>, T = 120 K, 30041 reflections collected, 7649 independent (R(int) = 0.053). R1 = 0.0640, wR2 = 0.1554 for observed unique reflections ( $F^2 > 2\sigma(F^2)$ ) and R1 = 0.0816, wR2 = 0.1666 for all unique reflections. Maximum and minimum residual electron densities 1.16 and -0.65 e Å<sup>-3</sup>. CSD reference: 923312.

#### ASSOCIATED CONTENT

#### **Supporting Information**

Text, figures, and CIF files giving details of the crystal structures of products  $[K(18\text{-}crown\text{-}6)][rac\text{-}1,2\text{-}fc(BMes_2F)(SiMe_2OH)]$  and  $[^nBu_4N][rac\text{-}1,2\text{-}fc(BMes_2CN)(SiMe_2OH)]$ , crystallographic data for all structures given in this paper, and fluoride binding isotherms. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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(7) Note the very strong solvent dependence of the relative basicities of F<sup>-</sup> and CN<sup>-</sup>. HF:  $pK_a$  3 (in  $H_2O$ ), 15 (in DMSO). HCN:  $pK_a$  9 (in  $H_2O$ ), 13 (in DMSO). See, for example: http://www2.lsdiv.harvard. edu/labs/evans/pdf/evans\_pKa\_table.pdf.

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