Inorganic Chemistry

Evaluation of Electronics, Electrostatics and Hydrogen Bond Cooperativity in the Binding of Cyanide and Fluoride by Lewis Acidic Ferrocenylboranes

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Received August 21, 2009

Synthetic approaches based on the direct borylation of ferrocene by BBr₃, followed by boryl substituent modification, or on the lithiation of ferrocene derivatives and subsequent quenching with the electrophile FBMes₂, have given access to a range of ferrocene derivatized Lewis acids with which to conduct a systematic study of fluoride and cyanide binding. In particular, the effects of borane electrophilicity, net charge, and ancillary ligand electronics/cooperativity on the binding affinities for these anions have been probed by a combination of NMR, IR, mass spectrometric, electrochemical, crystallographic, and UV-vis titration measurements. In this respect, modifications made at the para position of the boron-bound aromatic substituents exert a relatively minor influence on the binding constants for both fluoride and cyanide, as do the electronic properties of peripheral substituents at the 1'- position (even for cationic groups). By contrast, the influence of a CH₂NMe₃⁺ substituent in the 2- position is found to be much more pronounced (by >3 orders of magnitude), reflecting, at least in part, the possibility in solution for an additional binding component utilizing the hydrogen bond donor capabilities of the methylene CH₂ group. While none of the systems examined in the current study display any great differentiation between the binding of F⁻ and CN⁻ (and indeed some, such as FcBMes₂, bind both anions with equal affinity within experimental error), much weaker boronic ester Lewis acids will bind fluoride (but give a negative response for cyanide). Thus, by the incorporation of an irreversible redox-matched organic dye, a two-component [BMes₂/B(OR)₂] dosimeter system can be developed capable of colorimetrically signaling the presence of fluoride and cyanide in organic solution by Boolean AND/NOT logic.

Introduction

The selective detection of CN⁻ and F⁻ (and of their conjugate acids HCN and HF) constitute significant chemical challenges both from a fundamental supramolecular perspective and from a more applied viewpoint, for example, in environmental and medical monitoring.^{1,2} While considerable research effort has been expended on the development of sensors for fluoride-containing species, encompassing a range of host/guest strategies to bind the target analyte, cyanide detection has received less attention.^{7–11} Nevertheless, a number of cyanide receptors have been reported in the recent literature incorporating an appropriately positioned

array of Lewis acidic centers, 10a,b and the affinity of cyanide for three-coordinate boranes (even in the presence of water) has been known for more than 45 years.¹² In a similar vein, a number of the studies have recently demonstrated the use of Lewis acid receptors containing the $-BMes_2$ (Mes = 2,4,6-Me₃C₆H₂) function to detect cyanide,⁷ in one case offering remarkable, selective binding in aqueous solution."

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An alternative approach utilizing aryl boronic acids and the ready cleavage of the B–OH function in the presence of aqueous HCN has also been employed for cyanide sensing.⁹

Given the facts that (i) systems of the type ArBMes₂ are known to be air- and moisture-stable, (ii) under appropriate conditions such compounds are known to bind cyanide,⁷ and

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appropriate redox-active organic dye, can be used to produce an amplified colorimetric output,^{4b} we have also targeted systems capable of colorimetric sensing. In this respect, a major sensing challenge stems from the potential for competitive binding of fluoride at strongly Lewis acidic –BMes₂based receptors. Previous work by the group of Gabbaï, for example, has demonstrated the importance not only of electronics (i.e., of borane Lewis acidity) but also of steric factors in determining the relative binding affinities of borane receptors for cyanide and fluoride.^{7c} Moreover, the difficulties in using the relative proton affinities (or even pK_a 's) of cyanide/fluoride in a predictive sense are amply illustrated by the very strong solvent dependence of the relative basicities of F⁻ and CN⁻ [HF: pK_a 3 (in H₂O), 15 (in DMSO); HCN: pK_a 9 (in H₂O), 13 (in DMSO)].¹³ Thus, in order to put the binding of these two important analytes by ferrocenederivatized Lewis acids within a systematic framework, we have undertaken a synthetic study designed to access a range of such systems, offering systematic variation in the nature of the borane substituent, overall charge, and ancillary ligand sterics/electronics. The potential for anion binding by hybrid Lewis acid/hydrogen-bond receptors has also been examined. While these studies targeted a rational, modular approach to understand factors important in sensor design, a more empirical approach is also reported, namely, a two-component sensor system which offers a logical (colorimetric) solution for discriminating between fluoride and cyanide.¹⁴

Experimental Section

i. General Considerations. Manipulations of air-sensitive reagents were carried out under a nitrogen or argon atmosphere using standard Schlenk line or drybox techniques. Nondeuteriated solvents were dried using a commercially available Braun Solvent Purification System. [D₆]Benzene, [D]chloroform, and [D₂]dichloromethane (Goss) were degassed and dried over potassium ([D₆]benzene) or molecular sieves ([D]chloroform, [D₂]dichloromethane) prior to use. Triethylamine (Alfa) was dried over sodium wire before use; the tetra-n-butylammonium salts of fluoride and cyanide were dried to a constant weight in vacuo, analyzed for composition (i.e., for state of hydration),¹⁵ and stored under an atmosphere of dry argon until use. The known compounds FcBBr₂, Fc*BBr₂, MesLi, 1-iodo-2,6-dimethyl-4-fluorobenzene, 1-bromo-2,6-dimethyl-4-methoxybenzene, 1,1'-fcBr₂, FcBO₂C₂H₂Ph₂ (16), and Fc*BO₂C₂- H_2Ph_2 (17) were prepared by literature procedures.^{4p,16} All other reagents were used as received from commercial sources.

NMR spectra were measured on a Varian Mercury VX-300 or Bruker AVII 500 FT-NMR spectrometer. Residual signals of solvent were used as a reference for ¹H and ¹³C NMR; ¹¹B and ¹⁹F NMR spectra were referenced with respect to $Et_2O \cdot BF_3$ and CFCl₃, respectively. The ¹³C signals due to boron-bound C₅H₄ or CN carbon atoms were typically broad or not observed. Infrared spectra were measured for each compound pressed into a disk with an excess of dried KBr or as a solution in an appropriate solvent on a Nicolet 500 FT-IR spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, Swansea University, or by the departmental service. Perfluorotributylamine was used as a standard for high-resolution measurements. Elemental microanalyses were carried out at London Metropolitan University. Abbreviations: b = broad, s = singlet, d = doublet, t = triplet, q = quintet, sept = septet, m = multiplet; Fc = ferrocenyl, (η^{5} - C_5H_5)Fe(η^5 -C₅H₄); Fc* = 1',2',3',4',5'-pentamethyl-ferrocenyl, $(\eta^{5}-C_{5}Me_{5})Fe(\eta^{5}-C_{5}H_{4}); 1,1'-fc = 1,1'-ferrocenedial, (\eta^{5}-C_{5}-C_{5}H_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5})Fe(\eta^{5}-C_{5}$ $H_{4}_{2}Fe; 1,2-fc = 1,2-ferrocenediyl, (\eta^{5}-C_{5}H_{5})Fe(\eta^{5}-C_{5}H_{3}-1,2);$

ii. Syntheses. FcBMes₂ (1) and Fc*BMes₂ (2). Compounds 1 and 2 were prepared by a common method, exemplified for 1. To a solution of FcBBr₂ (2.00 g, 5.62 mmol) in diethyl ether (50 mL) was added dropwise mesityllithium (2.6 equiv) also in diethyl ether (ca. 50 mL) and the reaction mixture stirred for 18 h. At this point, ¹¹B NMR indicated complete conversion to a single product (δ_B 76). After the removal of volatiles in vacuo, extraction into hexanes (ca. 50 mL), and cooling to -30 °C, 1 was obtained as a red powder (yield: 1.52 g, 62%). Single crystals suitable for X-ray diffraction were obtained by the slow evaporation of pentane from a concentrated solution. ¹H NMR $(300 \text{ MHz}, [D_6] \text{benzene}, 20 \,^{\circ}\text{C}): \delta 1.91 (s, 6H, \text{para-CH}_3 \text{ of Mes}),$ 2.21 (s, 12H, ortho-CH₃ of Mes), 3.65 (s, 5H, Cp), 4.09 (m, 2H, C₅H₄), 4.26 (m, 2H, C₅H₄), 6.54 (s, 4H, aromatic CH of Mes). ^{13}C NMR (126 MHz, [D₆]benzene, 20 °C): δ 21.0 (para-CH₃ of Mes), 24.7 (ortho-CH₃ of Mes), 69.6 (Cp), 73.8, 79.6 (C₅H₄), 128.7 (aromatic CH of Mes), 137.9 (para-quaternary of Mes), 139.2 (ortho-quaternary of Mes), boron-bound quaternary carbons not observed. ¹¹B (96 MHz, [D₆]benzene, 20 °C): δ 76. MS(EI): 434 (100%) M⁺; exact mass (calcd for M⁺, ¹⁰B, ⁵⁶Fe isotopomer) = 433.1899, (measd) 433.1899. UV/vis (acetonitrile): $\lambda_{\text{max}} = 510 \text{ nm}, \varepsilon = 1310 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3. E_{1/2} \text{ versus}$ FcH/FcH⁺ (peak-to-peak separation) = +150 (98) mV in dichloromethane; +181 (80) mV in acetonitrile. Elem microanalysis calcd (for 1, C₂₈H₃₁BFe): C, 77.40; H, 7.20. Found: C, 77.37; H, 7.08. Compound 2 was obtained using a similar procedure from Fc*BBr₂ as a purple powder (yield: 0.23 g, 44%). Data for 2 is as follows. ¹H NMR (300 MHz, [D₁]chloroform, 20 °C): δ 1.66 (s, 15H, C₅Me₅), 2.19 (s, 6H, para-CH₃ of Mes), 2.30 (s, 12H, ortho-CH₃ of Mes), 4.05 (m, 2H, C₅H₄), 4.15 (m, 2H, C₅H₄), 6.70 (s, 4H, CH of Mes). ¹³C NMR (126 MHz, [D₆]benzene, 20 °C): δ 11.6 (CH₃ of C₅Me₅), 21.3 (para-CH₃ of Mes), 25.0 (ortho-CH₃ of Mes), 79.9 (quaternary of C₅Me₅), 81.0, 82.1 (C₅H₄), 128.2 (aromatic CH of Mes), 136.9 (para-quaternary of Mes), 139.1 (ortho-quaternary of Mes), boron-bound quaternary carbons not observed. ¹¹B (96 MHz, [D₆]benzene, 20 °C): δ 77. MS(EI): 504 (100%) M⁺; exact mass (calcd for M⁺, ¹⁰B, ⁵⁶Fe isotopomer), 503.2682, Founds: 503.2677. UV/vis (acetonitrile): $\lambda_{max} = 542$ nm, $\varepsilon = 1420 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$. $E_{1/2}$ versus FcH/FcH⁺ (peak-to-peak separation) = -194 (72) mV in dichloromethane; -176 (75) mV in acetonitrile.

FcB(Xyl)₂ (3), FcB(Xyl^F)₂ (4), and FcB(Xyl^{OMe})₂ (5). The three compounds were prepared by a common method, exemplified for 4. To a solution of 1-iodo-2,6-dimethyl-4-fluorobenzene (0.50 g, 2.00 mmol) in diethyl ether (20 mL) was added dropwise *n*-butyllithium (1.0 equiv) at -35 °C and the reaction mixture warmed to room temperature. After stirring for 4 h, a solution of FcBBr₂ (0.41 equiv) also in diethyl ether (ca. 30 mL) was added to the reaction mixture, which was then stirred for a further 18 h. At this point, monitoring by ¹¹B NMR spectroscopy indicated conversion to two products (giving rise to

⁽¹²⁾ Havir, J. Collect. Czech. Chem. Commun. 1961, 26, 1775.

⁽¹³⁾ See, for example: http://www2.lsdiv.harvard.edu/labs/evans/pdf/ evans_pKa_table.pdf (accessed Nov 2009).

⁽¹⁴⁾ A preliminary communication of part of this work has previously been published: Broomsgrove, A. E. J.; Addy, D. A.; Bresner, C.; Fallis, I. A.; Thompson, A. L.; Aldridge, S. *Chem.—Eur. J.* **2008**, *14*, 7525.

⁽¹⁵⁾ The compositions of the tetrabutylammonium fluoride and cyanide hydrates used in anion binding studies (and prepared by prolonged drying in vacuo) were determined to be $["Bu_4N]F\cdot 4H_2O$ and $["Bu_4N]CN\cdot 2H_2O$ by elemental microanalysis.

^{(16) (}a) FcBBr₂: Řenk, T.; Ruff, W.; Siebert, W. J. Organomet. Chem. **1976**, 120, 1. (b) MesLi:Rybinskaya, M. I.; Kreindlin, A. Z.; Fadeeva, S. S.; Petrovskii, P. V. J. Organomet. Chem. **1988**, 345, 341. (c) 1-I-2,6-Me₂-4-F-C₆H₂: Dewar, M. S.; Takeuchi, Y. J. Am. Chem. Soc. **1967**, 89, 390. (d) 1-Br-2,6-Me₂-4-OMe-C₆H₂: Kang, H.; Facchetti, A.; Stern, C. L.; Rheingold, A. L.; Kassel, W. S.; Marks, T. J. Org. Lett. **2005**, 7, 3721. (e) 1,1'-fcBr₂: Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. Organometallics **2000**, 19, 3978.

signals at δ_B 76 and 51). After removal of the volatiles in vacuo, purification by column chromatography (5% Et₂O in hexanes) yielded $FcB(Xyl^F)_2$ (4) as a red powder. Yield: 0.25 g, 70%. Single crystals suitable for X-ray diffraction were obtained by the slow evaporation of solvent from a solution in diethyl ether. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 2.39 (s, 12H, ortho-CH₃ of Xyl^F), 4.15 (s, 5H, Cp), 4.46 (m, 2H, C₅H₄), 4.74 $(m, 2H, C_5H_4), 6.70 (d, J = 9 Hz, 4H, aromatic CH of Xyl^F).$ ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 24.6 (d, ${}^{4}J_{CF} = 2$ Hz, ortho-CH3 of Xyl^F), 69.5 (Cp), 74.0, 79.2 (C5H4), 113.9 (d, ${}^{2}J_{CF} = 19$ Hz, aromatic CH of Xyl^F), 141.6 (d, ${}^{1}J_{CF} = 8$ Hz, ortho-quaternary of Mes^F), 160.7 (d, ${}^{1}J_{CF} = 245$ Hz, CF of Xyl^F). ¹⁹F NMR (282 MHz, [D]chloroform, 20 °C): δ –116.8 (t, J = 9 Hz, para-F of Xyl^F). ¹¹B (96 MHz, [D]chloroform, 20 °C): 77. MS(EI): 442 (100%) M⁺; exact mass (calcd for M⁺, 10 B, 56 Fe isotopomer), 441.1409; found, 441.1413. UV/vis (acetonitrile): $\lambda_{\text{max}} = 509 \text{ nm}, \varepsilon = 1406 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^{3}. E_{1/2} \text{ versus FcH}/$ FcH^+ (peak-to-peak separation) = +184 (60) mV in dichloromethane. Elem microanalysis calcd (for 4, C₂₆H₂₅BF₂Fe): C, 70.58; H, 5.70. Found: C, 70.68; H, 5.66. FcB(Xyl)₂ (3) was prepared from 1-lithio-2,6-dimethylbenzene in an analogous manner. Yield: 0.25 g, 56%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 2.42 (s, 12H, ortho-CH₃ of Xyl), 4.16 (s, 5H, Cp), 4.51 (m, 2H, C₅H₄), 4.71 (m, 2H, C₅H₄), 6.98 (AB mult, 4H, meta-CH of Xyl), 7.12 (AB mult, 2H, para-CH of Xyl). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 24.7 (ortho-CH₃ of Xyl), 69.5 (Cp), 73.7, 79.4 (C₅H₄), 127.2 (meta-CH of Xyl), 127.5 (para-CH of Xyl), 139.0 (ortho-quaternary of Xyl), 145.7 (boron-bound quaternary of Xyl). ¹¹B (96 MHz, [D]chloroform, 20 °C): 74.5. MS(EI): 406.2 (100%) M^+ ; exact mass (calcd for M^+ , ¹⁰B, ⁵⁶Fe isotopomer), 406.1550; found, 406.1551. UV/vis (acetonitrile): $\lambda_{max} = 509 \text{ nm}, \varepsilon = 1280 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$. $E_{1/2}$ versus FcH/FcH⁺ (peak-to-peak separation) = +153 (98) mV in dichloromethane. Elem microanalysis calcd (for 3, $C_{26}H_{27}BFe$): C, 76.84; H, 6.70. Found: C, 76.84; H, 6.74. FcB(Xyl^{OMe})₂ (5) was prepared from 1-lithio-2,6-dimethyl-4methoxybenzene in an analogous manner. Yield: 0.35 g, 67%. Samples prepared using this method are invariably contaminated by ca. 3% of a second ferrocene-containing species, which has been shown by mass spectrometry and NMR studies to be $FcB(Xyl^{OMe})(Ar)$ (where Ar = 1-methoxy-3-methyl-4-bromo-5-methylbenzene). The aryl substituent is derived from a competing deprotonation reaction ortho to the OMe substituent inherent in the reaction of 1-bromo-2,6-dimethyl-4-methoxybenzene with *n*-butyllithium. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 2.39 (s, 12H, ortho-CH₃ of Xyl^{OMe}), 3.78 (s, 6H, OCH₃ of Xyl^{OMe}), 4.14 (s, 5H, Cp), 4.48 (m, 2H, C₅H₄), 4.68 (m, 2H, C₅H₄), 6.53 (s, 4H, aromatic CH of Xyl^{OMe}). ¹³C NMR (126) MHz, [D]chloroform, 20 °C): δ 24.8 (ortho-CH₃ of Xyl^{OMe}), 54.8 (OCH₃ of Xyl^{OMe}), 69.4 (Cp), 73.4, 79.3 (C₅H₄), 112.7 (aromatic CH of Xyl^{OMe}), 141.0 (ortho-quaternary of Xyl^{OMe}), 158.9 (para-quaternary of Xyl^{OMe}). ¹¹B (96 MHz, D]chloroform 20 °C): 75.0 MS(E): 466 (1000) N⁴⁺ [D]chloroform, 20 °C): 75.0. MS(EI): 466 (100%) M⁺; exact mass (calcd for M⁺, ¹⁰B, ⁵⁶Fe isotopomer), 465.1801; found, 465.1797. UV/vis (acetonitrile): $\lambda_{\text{max}} = 502 \text{ nm}, \varepsilon = 1075 \text{ mol}^{-1}$ $\text{cm}^{-1} \text{dm}^{3}$. $E_{1/2}$ versus FcH/FcH⁺ (peak-to-peak separation) = +95 (87) mV in dichloromethane.

1,1'-fc(Br)BMes₂ (6). To a solution of 1,1'-fcBr₂ (0.63 g, 1.84 mmol) in tetrahydrofuran (20 mL) at -78 °C was added, dropwise, *n*-butyllithium (1.15 mL of a 1.6 M solution in hexanes, 1.84 mmol), and the reaction mixture stirred for 30 min at this temperature. To the precipitate so formed was added dimesitylboron fluoride (0.58 g, 1.93 mmol, 90% purity as received from Aldrich) as a solution in tetrahydrofuran (5 mL) and the reaction mixture allowed to warm to room temperature over a period of ca. 4 h. The resulting blood-red solution was diluted with diethyl ether (75 mL) and washed with water (50 mL) and brine (50 mL). The organic fraction was then dried (MgSO₄) and volatiles removed in vacuo to yield a blood-red

solid. Purification of the crude product by column chromatography (hexanes to 5% Et₂O/hexanes) yielded 1,1'-fc(Br)BMes₂ (6) as a blood-red microcrystalline solid. Yield: 0.85 g, 90%. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated solution in diethyl ether. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 2.27 (s, 6H, para CH₃ of Mes), 2.37 (s, 12H, ortho-CH₃ of Mes), 4.16 (AB multiplet, 2H, C₅H₄), 4.35 (AB multiplet, 2H, C₅H₄), 4.57 (AB multiplet, 2H, C₅H₄), 4.87 (AB multiplet, 2H, C₅H₄), 6.80 (s, 4H, CH of Mes). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 21.0 (para-CH₃ of Mes), 24.5 (ortho-CH₃ of Mes), 69.2, 71.0, 78.1, 80.9 (C₅H₄), 128.2 (aromatic CH of Mes), 137.1 (para-quaternary of Mes), 138.9 (ortho-quaternary of Mes), boron-bound quaternary carbons not observed. ¹¹B (96 MHz, [D]chloroform, 20 °C): δ 78. MS(EI⁺): 512 (100%) M⁺; exact mass (calcd for M⁺, ¹⁰B isotopomer), 511.1004; found, 511.1004. UV/vis (acetonitrile): $\lambda_{\text{max}} = 510$ nm, $\varepsilon = 1167$ mol⁻¹ cm⁻¹ dm³. $E_{1/2}$ versus FcH/ FcH^+ (peak-to-peak separation) = +265 (111) mV in dichloromethane. Elem microanalysis calcd (for 6, C₂₈H₃₀BBrFe): C, 65.50; H, 5.89. Found: C, 65.62; H, 5.85.

1,1'-fc(CH₂NMe₂)BMes₂ (7). To a solution of 6 (0.40 g, 0.78 mmol) in tetrahydrofuran (20 mL) at -78 °C was added dropwise t-butyllithium (0.92 mL of a 1.7 M solution in pentane, 1.56 mmol) and the reaction mixture stirred for 30 min at that temperature. Solid N,N-dimethylmethylideneammonium iodide (0.29 g, 1.56 mmol) was then added and the reaction mixture allowed to warm to room temperature overnight. The resulting blood-red solution was diluted with ethyl acetate (ca. 50 mL) and washed with water (25 mL) and brine (25 mL). The organic fractions were then dried (MgSO₄) and volatiles removed in vacuo to yield crude 7, which was purified by column chromatography (hexanes to 5% ethyl acetate/ hexanes, then hexanes to 4% ethyl acetate and 1% NEt₃, and finally hexanes to 49% ethyl acetate and 1% NEt₃) to give 7 as a blood-red solid. Yield: 0.26 g, 69%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 2.01 (s, 6H, NMe₂), 2.20 (s, 6H, para-CH₃ of Mes), 2.34 (s, 12H, ortho-CH₃ of Mes), 2.79 (s, 2H, CH₂ of CH₂NMe₂), 4.06 (AB multiplet, 2H, C₅H₄), 4.09 (AB multiplet, 2H, C₅H₄), 4.32 (AB multiplet, 2H, C₅H₄), 4.55 (AB multiplet, 2H, C_5H_4), 6.74 (s, 4H, CH of Mes). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 20.0 (para-CH₃ of Mes), 23.5 (ortho-CH₃ of Mes), 43.6 (CH₃ of NMe₂), 57.3 (CH2 of CH₂NMe₂), 67.4, 69.0, 70.4, 73.4, 78.9, 82.5 (C₅H₄), 127.2 (aromatic CH of Mes), 135.9 (para-quaternary of Mes), 137.9 (ortho-quaternary of Mes), 141.7 (boron-bound quaternary of Mes). ¹¹B (96 MHz, [D]chloroform, 20 °C): δ 78. MS(ES+): 492 (100%); M + H); exact mass (calcd for M⁺, 10 B, 54 Fe isotopomer), 489.2603; found, 489.2603. UV/vis (acetonitrile): $\lambda_{\text{max}} = 499 \text{ nm}, \varepsilon = 1104 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3. E_{1/2} \text{ versus FcH/} \text{FcH}^+ (\text{peak-to-peak separation}) = +297 (62) \text{ mV in dichlor-}$ omethane.

 $[1,1'-fc(CH_2NMe_3)BMes_2]^+I^-$ (8). To a solution of 7 (0.049 g, 0.10 mmol) in hexanes (5 mL) was added dropwise methyl iodide (0.5 mL, 8.03 mmol) and the reaction mixture stirred for 1 h at room temperature. Volatiles were removed in vacuo, yielding crude 8 as a pale pink powder, which was recrystallized from dichloromethane/hexanes as single crystals suitable for X-ray diffraction. Yield: 0.063 g, 99%). ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 2.22 (s, 6H, para-CH₃ of Mes), 2.38 (s, 12H, ortho-CH₃ of Mes), 2.99 (s, 6H, CH₃ of NMe₃⁺), 3.85 (s, 2H, CH_2 of $CH_2NMe_3^+$), 4.25 (AB multiplet, 2H, C_5H_4), 4.39 (AB multiplet, 2H, C₅H₄), 4.56 (AB multiplet, 2H, C₅H₄), 4.85 (AB multiplet, 2H, C_5H_4), 6.79 (s, 4H, CH of Mes). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 20.0 (para-CH₃ of Mes), 23.6 (ortho-CH₃ of Mes), 51.4 (CH₃ of NMe₃⁺), 65.4 (CH₂ of CH₂NMe₃⁺), 70.9, 71.5, 72.4, 74.6 (C₅H₄), 79.8 (quaternary C of C₅H₄), 127.5 (aromatic CH of Mes), 136.3 (para-quaternary of Mes), 137.9 (ortho-quaternary of Mes), 141.4 (boron-bound quaternary of Mes); boron-bound quaternary C of C₅H₄ not

observed. ¹¹B (96 MHz, [D]chloroform, 20 °C): no signal observed. MS(ES+): 506 (94%) M⁺, 447 (100%) (M – NMe₃)⁺; exact mass (calcd for M⁺, ¹⁰B, ⁵⁴Fe isotopomer), 503.2759; found, 503.2768. UV/vis (acetonitrile): $\lambda_{max} = 487$ nm, $\varepsilon = 898 \text{ mol}^{-1}$ cm⁻¹ dm³. $E_{1/2}$ versus FcH/FcH⁺ (peak-to-peak separation) = +314 (62) mV in dichloromethane. Elem anal. (%) calcd (for **8**·2H₂O): C, 57.39; H, 6.78; N, 2.09. Found: C, 57.19; H, 7.00; N, 2.07.

1,2-fc(CH2NMe2)BMes2 (9). To a solution of (N,N-dimethylaminomethyl)ferrocene (1.50 g, 6.17 mmol) in diethyl ether (ca. 50 mL) at 0 °C was added dropwise n-butyllithium (1.0 equiv) and the reaction mixture stirred at 0 °C for 1 h. After warming to room temperature and stirring for a further 12 h, dimesitylboron fluoride (1.66 g, 6.17 mmol) in diethyl ether (ca. 50 mL) was then added slowly to the reaction mixture at -78 °C. After stirring for a further 1 h, and subsequent warming to room temperature, volatiles were removed in vacuo and the solid extracted into hexanes (ca. 10 mL). Cooling to -30 °C led to the formation of 9 as a purple powder, which was recrystallized from a concentrated pentane solution at -80 °C. Yield: 1.66 g, 55%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 1.71 (s, 6H, para-CH₃ of Mes), 2.17 (s, 6H, NMe₂), 2.25 (s, 12H, ortho-CH₃ of Mes), 3.04 (AB m, 2H, CH₂ of CH₂NMe₂), 4.08 (s, 5H, Cp), 4.25 (m, 1H, CH of C₅H₃), 4.46 (m, 1H, CH of C₅H₃), 4.83 (m, 1H, CH of C₅H₃), 6.65 (s, 4H, aromatic CH of Mes). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 21.1 (para-CH₃ of Mes), 24.7 (ortho-CH₃ of Mes), 44.9 (CH₃ of NMe₂), 57.0 (CH₂ of CH₂NMe₂), 70.2 (Cp), 71.8, 76.8, 77.4, 79.4, 94.3 (C₅H₃), 128.7 (aromatic CH of Mes), 137.2 (para-quaternary of Mes), 139.6 (ortho-quaternary of Mes), 141.1 (boron-bound quaternary of Mes). ¹¹B NMR (96 MHz, [D]chloroform, 20 °C): δ 76 (br). MS(EI): 491 (weak) M⁺, 243 (54%) (M – BMes₂)⁺, 199 (45%) (M – BMes₂NMe₂)⁺, 186 (7%) (M – BMes₂CH₂-NMe₂)⁺; exact mass (calcd for M⁺, ¹⁰B isotopomer), 490.2478; found, 490.2475. UV/vis (dichloromethane): $\lambda_{max} = 510$ nm, $\varepsilon = 1500 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$. Elem anal. (%) calcd (for 9): C, 75.74; H, 7.80; N, 2.85. Found: C, 75.77; H, 7.81; N, 2.85.

 $[1,2-fc(CH_2NMe_3)BMes_2]^+I^-$ (10). To a solution of 9 (0.20 g, 0.41 mmol) in hexanes (ca. 30 mL) was added methyl iodide (0.05 mL, 0.81 mmol) and the reaction mixture stirred at room temperature for 12 h. The pink precipitate of 10 so formed was collected by filtration and dried in vacuo. Single crystals suitable for X-ray diffraction were obtained by recrystallization from dichloromethane/diethyl ether. Yield: 0.19 g, 70%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 2.00 (br s, 6H, ortho-CH₃ of Mes), 2.20 (s, 6H, para-CH₃), 2.78 (s, 9H, CH₃ of [NMe₃]⁺), 4.08 (br s, 1H, CH of CH₂NMe₂), 4.32 (s, 5H, Cp), 4.60 (s, 1H, CH of C₅H₃), 4.81 (s, 1H, CH of C₅H₃), 5.44(s, 1H, CH of C₅H₃), 5.50 (s, 1H, CH of CH₂NMe₂), 6.76 (br s, 4H, aromatic CH of Mes). ¹H NMR (300 MHz, [D₂]dichloromethane, -30 °C): δ 1.77 (s, 3H, ortho-CH₃ of Mes), 2.05 (s, 3H, ortho-CH₃ of Mes), 2.22 (s, 9H, overlapping signals: both para- and one ortho-CH₃ of Mes), 2.58 (s, 9H, CH_3 of NMe_3^+), 3.01 (s, 3H, ortho- CH_3 of Mes), 4.01 (m, 1H, CH of CH₂NMe₃⁺), 4.35 (s, 5H, CH of C₅H₃), 4.57 (s, 1H, CH of C₅H₃), 4.88 (s, 1H, CH of C₅H₃), 5.08 (m, 1H, CH of $CH_2NMe_3^+$), 5.33 (s, 1H, CH of C_5H_3), 6.67 (s, 1H, aromatic CH of Mes), 6.75 (s, 1H, aromatic CH of Mes), 6.83 (s, 1H, aromatic CH of Mes), 7.00 (s, 1H, aromatic CH of Mes). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 20.0 (para-CH₃ of Mes), 23.6 (br, ortho-CH₃ of Mes), 50.9 (CH₃ of NMe₃⁺), 64.5 (CH₂ of CH₂NMe₃⁺), 70.9 (Cp), 73.6, 79.1, 79.5, 81.8, 82.3 (C₅H₃), 127.7 (br, aromatic CH of Mes), 137.3 (br, para-quaternary of Mes), 138.6 (br, ortho-quaternary of Mes), 140.0 (boron-bound quaternary of Mes). ¹¹B NMR (96 MHz, [D]chloroform, 20 °C): δ 80 (br). MS(ES+): 506 (39%) M⁺, 447 (100%; M – NMe₃)⁺, 258 (5%; M – BMes₂)⁺, 199 (17%; M – BMes₂ – NMe₃)⁺; exact mass (calcd for M⁺, ¹⁰B and ⁵⁴Fe isotopomer), 503.2759; found, 503.2754. UV/vis (dichloromethane): $\lambda_{\text{max}} = 502 \text{ nm}, \epsilon = 1300 \text{ mol}^{-1} \text{ cm}^{-1}$

dm³. $E_{1/2}$ versus FcH/FcH⁺ (peak-to-peak separation) = +367 (91) mV in dichloromethane. Elem anal. (%) calcd (for 10 · 1/2CH₂Cl₂): C, 57.73; H, 6.27; N, 2.07. Found: C, 57.55; H, 6.01; N, 2.14.

 $[1,2-fc(CH_2NMe_2H)BMes_2]^+Cl^-$ (11). To a solution of 9 (0.20 g, 0.41 mmol) in diethyl ether (ca. 30 mL) at -30 °C was added a solution of hydrochloric acid in diethyl ether (0.8 mL of a 1 M solution, 0.81 mmol) and the reaction mixture stirred for 30 min at -30 °C. Volatiles were removed in vacuo, and the resulting pink solid recrystallized from dichloromethane/hexanes to yield 11 as a pale red crystalline solid. Yield: 0.12 g, 55%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 1.95 (s, 6H, para-CH₃ of Mes), 2.22 (s, 18H, overlapping signals: CH₃ of NMe₂H⁺ and ortho-CH₃ of Mes), 3.59 (s, 1H, CH of CH₂- NMe_3^+), 4.13 (s, 1H, CH of C_5H_3), 4.20 (s, 5H, Cp), 4.34 (s, 1H, CH of CH₂NMe₃⁺), 4.59 (s, 1H, CH of C₅H₃), 4.74 (s, 1H, CH of C₅H₃), 5.67 (s, 1H, NH), 6.76 (s, 4H, aromatic CH of Mes). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 20.0 (para-CH₃) of Mes), 24.8 (ortho-CH₃ of Mes), 44.3 (CH₃ of NMe₂H⁺), 56.0 (CH₂ of CH₂NMe₃⁺), 70.3 (Cp), 70.5, 71.8, 72.7, 80.3, 82.1 (C₅H₃), 127.5 (aromatic CH of Mes), 137.0 (para-quaternary of Mes), 138.2 (ortho-quaternary of Mes), boron-bound quaternary of Mes not observed. ¹¹B NMR (96 MHz, [D]chloroform, 20 °C): δ 78 (br). MS(EI): 491 (100%; M – H)⁺; exact mass (calcd for $(M - H)^+$, ¹⁰B isotopomer), 490.2478; found, 490.2479. UV/vis (dichloromethane): $\lambda_{\text{max}} = 502 \text{ nm}, \varepsilon = 1120$ $mol^{-1} cm^{-1} dm^3$.

 $[1,2-fc(CH_2NMe_2H)B(Mes)OH]^+[BF_4]^-$ (13). To a solution of 9 (0.20 g, 0.41 mmol) in diethyl ether (ca. 30 mL) was added tetrafluoroboric acid diethyl ether complex (2.0 equiv), and the reaction mixture stirred at room temperature for 12 h. The resulting orange precipitate was collected by filtration and recrystallized from dichloromethane/hexanes as orange crystals of 13 suitable for X-ray diffraction. Yield: 0.01 g, 60%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 2.22 (s, 6H, ortho-CH₃ of Mes), 2.68 (m, 6H, NMe₂H), 2.87 (s, 3H, para-CH₃ of Mes), 4.15 (s, 5H, Cp), 4.22 (s, 1H, CH of C₅H₃), 4.32 (br AB m, 2H, CH₂ of $CH_2NMe_2H^+$), 4.42 (s, 1H, CH of C_5H_3), 4.65 (s, 1H, CH of C₅H₃), 6.55 (s, 1H, OH), 6.75 (s, 2H, aromatic CH of Mes), 7.57 (br s, 1H, NH). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 21.2 (para-CH₃ of Mes), 22.5 (ortho-CH₃ of Mes), 40.6 (CH₃ of NMe_2H^+), 42.2 (CH₃ of NMe₂H⁺), 58.6 (CH₂ CH₂NMe₂H⁺), 69.3 (Cp), 69.8, 69.9, 70.6, 71.0, 72.2 (C5H3), 126.9 (aromatic CH of Mes), 127.6 (para-quaternary of Mes), 137.7 (orthoquaternary of Mes), 138.4 (boron-bound quaternary of Mes). ¹B NMR (96 MHz, [D]chloroform, 20 °C): δ 51. MS(ES+): 390 (22%) M^+ ; exact mass (calcd for M^+ , ¹¹B isotopomer), 390.0715; found, 390.0707.

FcB(**Mes^F**)**F** (14). To a solution of 1,3,5-tris(trifluoromethyl)benzene (0.7 mL, 3.76 mmol) in diethyl ether (ca. 10 mL) was added dropwise *n*-butyllithium (1.0 equiv) at -78 °C, and the reaction mixture warmed to room temperature. After stirring for 18 h, a solution of FcBBr₂ (0.47 equiv) also in diethyl ether (ca. 50 mL) was added to the reaction mixture, which was then stirred for a further 18 h. At this point, monitoring by ¹¹B NMR spectroscopy indicated complete conversion to a single product (δ_B 51). Removal of volatiles in vacuo, extraction into hexanes (ca. 70 mL), and cooling to -30 °C yielded **14** as a red powder. Yield: 0.48 g, 54%. Single crystals suitable for X-ray diffraction were obtained by cooling a concentrated solution in hexanes to -30 °C. ¹H NMR (300 MHz, [D₆]benzene, 20 °C): δ 3.52 (s, 5H, Cp), 3.57 (m, 2H, C₅H₄), 3.68 (m, 2H, C₅H₄), 6.60 (s, 2H, aromatic CH of Mes^F). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): 69.0 (Cp), 73.1 (C₅H₄), 74.8 (d, ³J_{CF} = 4 Hz, C₅H₄), 122.5 (q, ¹J_{CF} = 273 Hz, para-CF₃ of Mes^F), 123.3 (q, ¹J_{CF} = 276 Hz, ortho-CF₃ of Mes^F), 125.9 (sept, ³J_{CF} = 4 Hz, aromatic CH of Mes^F), 132.5 (q, ²J_{CF} = 35 Hz, paraquaternary of Mes^F), 134.4 (q, ²J_{CF} = 34 Hz, ortho-quaternary of Mes^F), 138.6 (br, boron-bound quaternary of Mes^F). ¹¹B (96 MHz, [D₆]benzene, 20 °C): 51. ¹⁹F NMR (282 MHz, [D₆]benzene, 20 °C): δ –49.1 (br s, BF), –57.2 (s, ortho-CF₃ of Mes^F), –63.1 (s, para-CF₃ of Mes^F). MS(EI): 496 (100%) M⁺; exact mass (calcd for M⁺, ¹⁰B isotopomer), 495.0174; found, 495.0173.

FcB(Mes^F)Me (15). To a solution of 14 (0.20 g, 0.40 mmol) in diethyl ether (10 mL) was added dropwise methyllithium (1.0 equiv) at $-78 \,^{\circ}$ C, and the reaction mixture warmed to room temperature. After stirring for 2 h, monitoring by $^{11}\mathrm{B}$ NMR spectroscopy indicated complete conversion to a single product $(\delta_{\rm B} 72)$. After the removal of volatiles in vacuo, extraction into pentane (ca. 20 mL), and cooling to -30 °C, 15 was obtained as a red powder. Yield: 0.12 g, 58%. ¹H NMR (300 MHz, [D₆]benzene, 20 °C): δ 0.57 (sept, ⁶J_{HF} = 2 Hz, 3H, Me), 3.39 (s, 5H, Cp), 3.43 (m, 2H, C₅H₄), 3.61 (m, 2H, C₅H₄), 6.52 (s, 2H, aromatic CH of Mes^F). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): 10.9 (CH₃), 69.0 (Cp), 73.2, 75.4 (C₅H₄), 122.9 (q, ${}^{1}J_{CF} =$ 272 Hz, para-CF₃ of Mes^F), 123.7 (q, J = 275 Hz, ortho-CF₃ of Mes^F), 125.8 (sept, ${}^{3}J_{CF} = 4$ Hz, aromatic CH of Mes^F), 130.6 (q, ${}^{2}J_{CF} = 34$ Hz, para-quaternary of Mes^F), 131.7 (q, ${}^{2}J_{CF} = 33$ Hz, ortho-quaternary of Mes^F), 149.0 (br, boron-bound quaternary of Mes^{F}). ¹¹B (96 MHz, [D₆]benzene, 20 °C): δ 72. ¹⁹F NMR (282 MHz, [D₆]benzene, 20 °C): δ –56.3 (s, ortho-CF₃ of Mes^{F}), -62.9 (s, para-CF₃ of Mes^{F}). MS(EI): 492 (100%) M⁺; exact mass (calcd for M⁺, ¹⁰B isotopomer), 491.0425; found, 491.0423.

 n Bu₄N]⁺[FcBMes₂·CN]⁻ ([n Bu₄N]⁺[1·CN]⁻). A mixture of 1 (0.05 g, 0.12 mmol) and tetra-n-butylammonium cyanide dihydrate (1.05 equiv) in [D]chloroform (5 mL) was stirred for 1 h, at which point the reaction was judged to be complete by ¹¹B NMR spectroscopy (quantitative conversion to a single resonance at $\delta_{\rm B}$ –16). Layering of the reaction mixture with diethyl ether led to the formation of $[^{n}Bu_{4}N]^{+}[1 \cdot CN]^{-}$ as orange crystals suitable for X-ray diffraction. Yield: 0.089 g, 90%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 0.95 (m, 12H, CH₃ of [^{*n*}Bu₄N]⁺), 1.36 $(m, 8H, CH_2 of [^nBu_4N]^+), 1.46 (m, 8H, CH_2 of [^nBu_4N]^+), 2.09$ (s, 18H, ortho- and para-CH₃ of Mes), 2.92 (m, 8H, NCH₂ of [ⁿBu₄N]⁺), 3.90 (s, 5H, Cp), 4.02 (m, 2H, C₅H₄), 4.1 (br m, 2H, C_5H_4), 6.48 (s, 4H, aromatic CH of Mes). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 13.8 (CH₃ of [ⁿBu₄N]⁺), 19.8, 24.1 $(CH_2 \text{ of } [^nBu_4N]^+)$, 20.9 (para-CH₃ of Mes), 25.5 (br, ortho-CH₃) of Mes), 58.6 (NCH₂ of [ⁿBu₄N]⁺), 68.1 (Cp), 67.4, 75.5 (C₅H₄), 128.9 (aromatic CH of Mes), 131.3 (para-quaternary of Mes), 141.7 (ortho-quaternary of Mes), 176.0 (CN⁻), boron-bound quaternary carbons not observed. ¹¹B (96 MHz, [D]chloroform, 20 °C): -16. MS(ES-): 460 (100%) [1 · CN]⁻; exact mass (calcd for [1·CN]⁻, ¹⁰B, ⁵⁴Fe isotopomer), 457.1995; found, 457.1988. UV/vis (chloroform): $\lambda_{max} = 460 \text{ nm}, \varepsilon = 170 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$. IR (CH₂Cl₂): 2162 cm⁻¹ st, ν (CN). $E_{1/2}$ versus FcH/FcH⁺ (peak-to-peak separation) = -383 (100) mV in acetonitrile.Elem microanalysis calcd (for $[^{n}Bu_{4}N]^{+}[1 \cdot CN]^{-} \cdot CHCl_{3}$, C46H68BCl3FeN2): C, 67.21; H, 8.34; N, 3.41. Found: C, 66.83; H, 8.28; N, 3.23.

[^{*n*}Bu₄N]⁺[Fc*BMes₂·CN]⁻ ([^{*n*}Bu₄N]⁺[2·CN]⁻). A mixture of 2 (0.05 g, 0.10 mmol) and tetra-*n*-butylammonium cyanide dihydrate (1.05 equiv) in [D]chloroform (5 mL) was stirred for 1 h, after which time the reaction was deemed complete by ¹¹B NMR spectroscopy (quantitative conversion to a single resonance at δ_B –17). Concentration of the reaction mixture and layering with diethyl ether led to the formation of [^{*n*}Bu₄N]⁺[2·CN]⁻ as an orange microcrystalline solid. Yield: 0.081 g, 91%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 0.96 (m, 12H, CH₃ of [^{*n*}Bu₄N]⁺), 1.34 (m, 8H, CH₂ of [^{*n*}Bu₄N]⁺), 1.47 (m, 8H, CH₂ of [^{*n*}Bu₄N]⁺), 1.75 (s, 15 H, C₅Me₅), 1.95 (s, 6H, para-CH₃ of Mes), 2.06 (s, 12H, ortho-CH₃ of Mes), 2.94 (m, 8H, NCH₂ of [^{*n*}Bu₄N]⁺), 3.52 (s, 2H, C₅H₄), 3.68 (s, 2H, C₅H₄), 6.43 (s, 4H, aromatic CH of Mes). ¹³C NMR (126 MHz, [D₆]benzene, 20 °C): δ 15.5 (CH₃ of C₅Me₅), 17.4 (CH₃ of [^{*n*}Bu₄N]⁺), 23.4, 27.5 (CH₂ of [^{*n*}Bu₄N]⁺), 24.7 (para-CH₃ of Mes), 30.0 (br, ortho-CH₃ of Mes), 61.6 (NCH₂ of ["Bu₄N]⁺), 76.0, 81.2 (C₅H₄), 82.0 (quaternary of C₅Me₅), 133.2 (aromatic CH of Mes), 134.6 (para-quaternary of Mes), 146.0 (orthoquaternary of Mes), 175.6 (CN⁻), boron-bound quaternary carbons not observed. ¹¹B (96 MHz, [D]chloroform, 20 °C): δ -17. MS(ES-): 530 (100%) [2·CN]⁻; exact mass (calcd for [2·CN]⁻, ⁵⁶Fe, ¹⁰B isotopomer), 529.2723; found, 529.2730. UV/vis (acetonitrile): $\lambda_{max} = 481$ nm, $\varepsilon = 295$ mol⁻¹ cm⁻¹ dm³. IR (CHCl₃): 2162 cm⁻¹ st, ν (CN). $E_{1/2}$ versus FcH/FcH⁺ (peak-to-peak separation) = -691 (95) mV in acetonitrile.

 $[K(18-crown-6)]^+[FcB(Xyl)_2 \cdot CN]^- ([K(18-crown-6)]^+[3 \cdot CN]^-).$ The reactions of Lewis acids 3, 4, 5, and 15 with KCN and 18crown-6 were carried out in a similar manner, illustrated here for 3. To a solution of 3 (0.045 g, 0.11 mmol) in chloroform-d (4 mL) was added KCN and 18-crown-6 (1 equiv of each). The reaction mixture was stirred for 1 h at 20 °C, after which it was judged to be complete, by the existence of a single resonance in the ¹¹B NMR spectrum at $\delta_{\rm B}$ ca. -15 ppm. Single crystals suitable for X-ray diffraction were obtained by layering the reaction solution with pentane. Yield: 0.075 g, 81%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 2.20 (br s, 12H, ortho-CH₃ of Xyl), 3.53 (s, 24H, 18crown-6), 3.98 (s, 5H, Cp), 4.12 (br s, 2H, C₅H₄), 4.25 (br s, 2H, C₅H₄), 6.71–6.82 (overlapping m, 6H, ortho- and para-CH of Xyl). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 25.3 (ortho-CH₃ of Xyl), 67.5 (C₅H₄), 68.2 (Cp), 70.1 (18-crown-6), 75.7 (C₅H₄), 123.0 (meta-CH of Xyl), 127.8 (para-CH of Xyl), 141.8 (ortho-quaternary of Xyl), 153.0 (boron-bound quaternary of Xyl). ¹¹B (96 MHz, [D]chloroform, 20 °C): -16. MS(ES-): 432.2 (100%) [3·CN]⁻; exact mass (calcd for [3·CN]⁻, ⁵⁶Fe, ¹⁰B isotopomer), 429.1675; found, 429.1670. UV/vis (dichloromethane): $\lambda_{\text{max}} = 457 \text{ nm}, \varepsilon = 142 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$. IR (CHCl₃): 2164 cm⁻¹ st, ν (CN). $E_{1/2}$ versus FcH/FcH⁺ (peak-to-peak separation) = -327 (90) mV in acetonitrile. Elem microanalysis calcd (for $[K(18-crown-6)]^+[3\cdot CN]^-$, C₃₉H₅₁BFeKNO₆): C, 63.65; H, 6.99; N, 1.90. Found: C, 63.64; H, 7.19; N, 1.80. Data for $[K(18 \text{-crown-6})]^+[FcB(Xyl^F)_2 \cdot CN]^-$, that is, [K(18-crown-6)]⁺[4·CN]⁻. Yield: 0.067 g, 71%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 2.17 (br, s, 12H, ortho-CH₃ of Xyl^F), 3.53 (s, 24H, 18-crown-6), 3.96 (s, 5H, Cp), 4.08 (m, 2H, C₅H₄), 4.14 (m, 2H, C₅H₄), 6.45 (d, ${}^{3}J_{HF} = 9$ Hz, 4H, aromatic CH of Xyl^F). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): 25.4 (s, CH₃ of Xyl^F), 67.5 (C₅H₄), 67.9 (Cp), 70.0 (18-crown-6), 75.4 (C₅H₄), 113.6 (d, ${}^{2}J_{CF} = 16$ Hz, aromatic CH of Xyl^F), 143.7 (d, ${}^{3}J_{CF} = 6$ Hz, ortho-quarternary of Xyl^F), 159.9 (d, ${}^{1}J_{CF} = 238$ Hz, para-CF of Xyl^f). ¹¹B (96 MHz, [D]chloroform, 20 °C): -14. ¹⁹F NMR (282 MHz, [D]chloroform, 20 °C): -124.5 (t, ${}^{3}J_{FH} = 9$ Hz, para-F of WiTE, [D]cholofolini, 20 °C). = 124.5 (i, $J_{\text{FH}} = 9$ HZ, para-P of Xyl^F). MS(ES-): 468 (100%) [4·CN]⁻; exact mass (calcd for [4·CN]⁻, ⁵⁶Fe, ¹⁰B isotopomer), 467.1439; found, 467.1437. UV/ vis (dichloromethane): $\lambda_{\text{max}} = 463$ nm, $\varepsilon = 210$ mol⁻¹ cm⁻¹ dm³. IR (CHCl₃): 2171 cm⁻¹ st, ν (CN). $E_{1/2}$ versus FcH/FcH⁺ (peak-to-peak separation) = -330 (85) mV in acctonitrile. Elem microanalysis calcd (for $[K(18\text{-crown-6})]^+[4 \cdot CN]^-$, $C_{39}H_{49}BF_2$ -FeKNO₆): C, 60.68; H, 6.40; N, 1.82. Found: C, 60.63; H, 6.32; N, 1.75. Data for $[K(18-crown-6)]^+[FcB(Xyl^{OMe})_2 \cdot CN]^-$, that is, $[K(18-crown-6)]^+[5 \cdot CN]^-$. Yield: 0.105 g, 92%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 2.18 (br s, 12H, ortho-CH₃ of Xyl^{OMe}), 3.53 (s, 24H, 18-crown-6), 3.69 (s, 6H, OCH₃ of Xyl^{OMe}), 3.98 (s, 5H, Cp), 4.07 (m, 2H, C₅H₄), 4.16 (br s, C₅H₄) 6.33 (s, 4H, aromatic CH of Xyl^{OMe}). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 25.6 (ortho-CH₃ of Xyl^{OMe}), 54.6 (OCH₃ of Xyl^{OMe}), 67.9 (Cp), 70.0 (18-crown-6), 75.6, 77.1 (C_5H_4), 113.1 (aromatic CH of Xyl^{OMe}), 143.0 (ortho-quaternary of Xyl^{OMe}), 155.4 (para-quaternary of Xyl^{OMe}). ¹¹B (96 MHz, [D]chloroform, 20 °C): -15. MS(ES-): 492.2 (100%) [5 · CN]⁻; exact mass (calcd for [5 · CN]⁻, ⁵⁶Fe, ¹⁰B isotopomer), 489.1886; found, 489.1886. UV/vis (dichloromethane): $\lambda_{\text{max}} = 454 \text{ m}$, $\varepsilon = 162 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$. IR (CHCl₃): 2164 cm⁻¹ st, ν (CN). $E_{1/2}$ versus FcH/FcH⁺ (peak-to-peak separation) = -471(60) mV in acetonitrile. Data for [K(18crown-6)]⁺[FcB(Mes^F)Me·CN]⁻, that is, $[K(18\text{-crown-6})]^+$ -[15·CN]⁻. Yield: 0.089 g, 90%. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 0.46 (s, 3H, CH₃), 3.63 (s, 24H, 18-crown-6), 4.00 (m, 1H, C₅H₄), 4.01 (m, 2H, C₅H₄), 4.12 (s, 5H, Cp), 4.31 (m, 1H, C₅H₄), 7.75 (s, 2H, aromatic CH of Mes). ¹³C NMR (126 MHz, [D]chloroform, 20 °C): δ 8.3 (br, CH₃), 65.8, 67.4 (C₅H₄), 68.4 (Cp), 70.1 (18-crown-6), 123.7 (q, ¹*J*_{CF} = 272 Hz, para-CF₃ of Mes^F), 125.1 (q, *J* = 275 Hz, ortho-CF₃ of Mes^F), 125.6 (br, aromatic CH of Mes^F), 125.8 (q, ²*J*_{CF} = 33 Hz, para-quaternary of Mes^F), 136.9 (q, ²*J*_{CF} = 30 Hz, ortho-quaternary of Mes^F), 145.2 (br, boron-bound quaternary of Mes^F). ¹¹B (96 MHz, [D]chloroform, 20 °C): δ -14. ¹⁹F NMR (300 MHz, [D]chloroform, 20 °C): -50.8 (s, ortho-CF₃ of Mes^F), -62.8 (s, para-CF₃ of Mes^F). MS(ES-): 518 (100%) [**15** · CN]⁻; exact mass (calcd for [**15** · CN]⁻, ¹⁰B, ⁵⁴Fe isotopomer), 515.0514; found, 515.0525.

iii. Crystallographic Method. Data for 1, 4, 6, 8 · CH₂Cl₂, $10 \cdot 1/2 CH_2 Cl_2$, 13, 14, ["Bu₄N]⁺[$1 \cdot CN$]⁻·CHCl₃, [K(18-crown-6)]⁺[$\mathbf{3} \cdot CN$]⁻, [K(18-crown-6)]⁺[$\mathbf{4} \cdot CN$]⁻, [K(18-crown-6)]⁺-[$\mathbf{5} \cdot CN$]⁻, and [K(18-crown-6)]⁺[$\mathbf{15} \cdot CN$]⁻ were collected on a Nonius KappaCCD diffractometer (Mo K α radiation (λ = 0.71073 Å) at 150(2) K with an Oxford Cryosystems Cryostream N₂ open-flow cooling device.^{17a} Data were processed using the DENZO-SMN package, including interframe scaling (which was carried out using Scalepack within DENZO-SMN). ^{7b} The structures were solved using SIR92 (for 4, 6, 8 · CH₂Cl₂, 13, $[K(18 \text{-crown-6})]^+[\mathbf{3} \cdot CN]^-$, $[K(18 \text{-crown-6})]^+[\mathbf{4} \cdot CN]^-$, $[K(18 \text{-crown-6})]^+[\mathbf{5} \cdot CN]^-$, and $[K(18 \text{-crown-6})]^+[\mathbf{15} \cdot CN]^-$, 17c or SHELXS (for 1, $10 \cdot 1/2 CH_2 Cl_2$, 14, and $[^{n}Bu_4N]^{+}[1 \cdot CN]^{-}$. CHCl₃).^{17d} Refinement was carried out using full-matrix least-squares within the CRYSTALS suite, ^{17e} on either F^2 (for 4, 6, $8 \cdot CH_2Cl_2$, 13, 14, $[K(18 \cdot crown - 6)]^+[3 \cdot CN]^-$, $[K(18 \cdot crown - 6)]^+[3 \cdot CN]^-$ 6)]⁺[$4 \cdot CN$]⁻, and [K(18-crown-6)]⁺[$5 \cdot CN$]⁻) or F (for [K(18crown-6)]⁺[15·CN]⁻ only), or with SHELXTL (for 1, 10. $1/2CH_2Cl_2$, and $["Bu_4N]^+[1 \cdot CN]^- \cdot CHCl_3)$.^{17d} In general, all non-hydrogen atoms were refined with anisotropic displacement parameters; however, this was not always possible where there was disorder present (e.g., $[K(18 \text{-crown-6})]^+[4 \cdot CN]^-)$ or the data were of poor quality (e.g., 14). For 4, 6, $8 \cdot CH_2Cl_2$, 13, 14, $[K(18\text{-}crown-6)]^+[3 \cdot CN]^-$, $[K(18\text{-}crown-6)]^+[4 \cdot CN]^-$, $[K(18\text{-}crown-6)]^+[5 \cdot CN]^-$, and $[K(18\text{-}crown-6)]^+[15 \cdot CN]^-$, the majority of hydrogen atoms were visible in the difference map, and the general technique was to refine their positions and isotropic displacement parameters using restraints prior to inclusion into the model with riding constraints. For compounds 1, $10 \cdot 1/2CH_2Cl_2$, and $[^nBu_4N]^+[1 \cdot CN]^- \cdot CHCl_3$, hydrogen atoms were added geometrically and refined using a riding model only.

The data for **14** are very weak and twinned, which together with the pseudosymmetry present meant the refinement was unstable. It was therefore controlled using partial shifts and shift-limiting restraints within CRYSTALS.^{17c} In addition, there was disorder in the nonfunctionalized Cp rings, and the poor quality of the data meant that a partially isotropic refinement was necessary with thermal restraints used for the CF₃ fluoride atoms. Despite the difficulties with this structure, the only real doubt concerning the connectivity is whether there is a fluorine or an OH bound to the boron. Given the similarity in scattering and the quality of the data, it was not possible to tell from the crystallography; however, NMR experiments carried out on the single crystals were conclusive, so fluorine was used in the model. The structure of compound **14** (along with that of **13**) was obtained merely for verification of connectivity, and no discussion of the metrical data is attempted.

In the case of $[K(18\text{-}crown-6)]^+[4\cdot CN]^-$, there was a small amount of disorder present in one crown ether and a phenyl group exhibited some translational disorder, which were modeled with two sites and refined occupancies with isotropic displacement parameters. Similarly, $[K(18\text{-}crown-6)]^+$ - $[15\cdot CN]^-$ exhibited disorder in one of the CF₃ groups, which was modeled with isotropic displacement parameters. On refining $[K(18\text{-}crown-6)]^+[5\cdot CN]^-$, it became evident that there was a large residual electron density peak approximately 1.7 Å from C(25). This was thought to result from a small amount of residual bromine from the previous preparation step, which was modeled as ca. 4% occupied. It is possible that the peak is spurious, due for example to absorption. However, the data are otherwise good, and there is no indication of any other difficulties.

Selected structural details for the new compounds are included in Table 1, and full crystallographic data for all structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 671665, 671666, and 744798–744807. 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.

iv. Electrochemical Method. Electrochemical analyses were carried out using the following conditions: electrolyte, 0.1 M $[^{n}Bu_{4}N]^{+}[PF_{6}]^{-}$ in dichloromethane or acetonitrile; reference electrode standard, 0.1 M [ⁿBu₄N]⁺[PF₆]⁻, 0.01 M AgNO₃ in acetonitrile. Following degassing of the electrolyte solution with argon, background cyclic voltammetry (CV) scans were measured, and a sample (ca. 2-5 mg) of the ferrocene functionalized Lewis acid was added to the solution. Further degassing served to purge the solution of any additional dissolved oxygen and agitate the solid Lewis acid to dissolve the compound, prior to spectral acquisition. Further CV scans were measured on the addition of aliquots of solid ["Bu₄N]F·4H₂O (or KF/18-crown-6), and on the addition of ferrocene as a reference. Electrochemical data reported in the text are for solutions in acetonitrile or dichloromethane, referenced with respect to the ferrocene/ ferrocenium couple; peak-to-peak separations are listed (in parentheses) in the experimental data.

v. Binding Constant Determinations. Binding constants were evaluated for 1, 3, 4, 5, 6, and 8 in dichloromethane by the method reported by Solé and Gabbaï;^{6r} the program LabFit (www.labfit.net) was used to fit the experimentally determined data of A/A_o versus anion concentration. The binding constants for $[1,2-fc(CH_2NMe_3)BMes_2]^+I^-$ (10) for both fluoride and cyanide, however, were found to be too large to be reliably determined by this method and were therefore determined by a competition experiment between 10 and PhBMes2.^{5w}

Results and Discussion

i. Syntheses. The synthesis of simple ferrocenylboranes of the type $(\eta^5\text{-}C_5R_5)\text{Fe}(\eta^5\text{-}C_5H_4BAr_2)$ (e.g., 1–5, Scheme 1) can readily be accomplished in yields of up to 60% by the reaction of slightly more than 2 equiv of the respective aryllithium reagent with FcBBr₂. This methodology offers a versatile approach to a range of Lewis acids which are both air-stable (provided that each aryl substituent features two *ortho*-methyl groups) and systematically tunable (through the electronic properties of the para substituent). This approach removes the need to the isolate the corresponding (halo)diarylborane, (Hal)BAr₂, as would be a prerequisite, for example, in a synthetic route involving the intermediacy of ferrocenyllithium. Diethyl ether proves to be the optimal reaction medium, with related chemistry carried out in thf, for

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 $\textbf{Table 1. Crystallographic Data for 1, 4, 6, 8 \cdot CH_2Cl_2, 10 \cdot 1/2CH_2Cl_2, 13, 14, ["Bu_4N]^+ [1 \cdot CN]^- \cdot CHCl_3, and [K(18 \cdot crown - 6)]^+ [X \cdot CN]^- (X = 3, 4, 5, 15)$

	1	4	6
empirical formula	C ₂₈ H ₃₁ BFe	$C_{26}H_{25}BF_2Fe$	C ₂₈ H ₃₀ BBrFe
CCDC deposition number	671665	744798	744799
fw (W)	434.19	442.14	513.11
temp (K) wavelength (\mathring{A})	120(2)	150(2)	150(2)
wavelength (A)	0./10/5	0./10/5 orthorhombic	0./10/5
space group	P2, /n	P2,2,2,	P2, /n
unit cell lengths: a, b, c (Å)	10.298(1) 15.728(1) 14.027(1)	7 9136(1) 10 5933(2) 25 2332(5)	10.5687(1), 15.5960(3), 14.8927(2)
α, β, γ (deg)	90, 104.958(3), 90	90, 90, 90	90, 106,9697(8), 90
volume (Å ³), Z	2194.84(16), 4	2115.33(6), 4	2347.87(6)
density (calcd) (Mg/m ³)	1.314	1.388	1.452
abs coeff (mm ^{-1})	0.699	0.740	2.357
F(000)	920	920	1056
cryst size (mm ³)	$0.08 \times 0.06 \times 0.01$	$0.04 \times 0.10 \times 0.24$	$0.08 \times 0.21 \times 0.33$
θ range for data collection (deg)	2.99-25.03	5.153 - 2/.489	5.129 - 2/.488
index ranges (n, κ, l)	-12 10 + 12, -18 10 + 18, -10 10 + 10	$-10\ 10\ +10,\ -13\ 10\ +13,\ -32\ 10\ +32$	-13 10 + 13, -20 10 + 17, -19 10 + 19
no, of indep reflas/ $R_{\rm c}$	3855 (0 1177)	4674 (0.064)	5349 (0.030)
completeness to θ_{max} (%)	99.7	0.989	0.992
absorption correction	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs
max. and min transmission	0.993 and 0.946	0.97 and 0.92	0.83 and 0.67
refinement method	full matrix least sq (F^2)	full matrix least sq (F^2)	full matrix least sq (F^2)
no. of data/restraints/params	3855/0/277	2746/0/272	5348/0/280
goodness-of-fit on F^2	1.094	0.9785	0.9771
final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0658, WR2 = 0.1190	R1 = 0.0349, WR2 = 0.0760	R1 = 0.0357, wR2 = 0.0802
R indices (all data)	R1 = 0.1189, WR2 = 0.1463	R1 = 0.0479, WR2 = 0.0808	R1 = 0.0441, WR2 = 0.0863
largest peak/hole (e A ⁻)	+0.413 and -0.421	+0.43 and -0.39	+0.42 and $= -0.89$
			12
	8.CH2Cl2	$10 \cdot 1/2 CH_2 Cl_2$	13
empirical formula	C ₃₃ H ₄₃ BCl ₂ FeIN	C _{32.50} H ₄₂ BClFeIN	C22H29B2F4FeNO
CCDC deposition number	744800	744801	744802
fw (V)	718.18	675.68	476.94
temp (K)	150(2)	150(2)	150(2)
wavelength (A)	0./10/3	0./10/5 triclinic	0./10/3
space group	$P2_{A/C}$	$\overline{P1}$	P2./c
unit cell lengths: a, b, c (Å)	22.7312(3), 15.5761(2), 9.1112(1)	8.1684(1), 19.1107(2), 20.674(3)	10.5395(1), 8.1667(1), 28.2528(3)
α, β, γ (deg)	90, 101.2240(5), 90	78.271(1), 87.789(1), 89.770(1)	90, 112.0243(4), 90
volume (Å ³), Z	3164.24(7)	3157.5(4)	2254.34(4)
density (calcd) (Mg/m ³)	1.507	1.421	1.405
abs coeff (mm^{-1})	1.644	1.561	0.715
F(000)	1464	1380	992
cryst size (mm ³)	$0.02 \times 0.12 \times 0.50$	$0.02 \times 0.08 \times 0.44$	$0.12 \times 0.17 \times 0.20$
θ range for data collection (deg)	5.185 - 27.488	5.10-27.47	5.159 - 27.484
no of reflue collected	-29 10 +29, -20 10 +20, -11 10 +11	-1010+10, -2410+24, -2410+20	$-13\ 10\ +13,\ -10\ 10\ +10,\ -30\ 10\ +31$
no, of indep reflps/ $R_{\rm c}$	7202 (0.046)	14250 (0.0397)	5152 (0.048)
completeness to θ_{max} (%)	0.992	0.985	0.992
absorption correction	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs
max. and min transmission	0.97-0.81	0.966-0.892	0.92-0.87
refinement method	full matrix least sq (F^2)	full matrix least sq (F^2)	full matrix least sq (F^2)
no. of data/restraints/params	7202/0/352	14250/0/694	5152/0/280
goodness-of-fit on F^2	0.9611	1.204	0.9482
final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0341, WR2 = 0.0676	R1 = 0.0500, wR2 = 0.1037	R1 = 0.0360, WR2 = 0.0770
<i>R</i> indices (all data)	RI = 0.0545, WR2 = 0.0732	RI = 0.0683, WR2 = 0.1098	R1 = 0.0586, WR2 = 0.0832
largest peak/hole (e A)	+1.28 and -0.86	+0.099 and -1.002	+0.50 and -0.58
	14	$[^{n}\mathrm{Bu}_{4}\mathrm{N}]^{+}[1\cdot\mathrm{CN}]^{-}\cdot\mathrm{CHCl}_{3}$	$[K(18\text{-}crown\text{-}6)]^+[3\cdot CN]^-$
empirical formula	$C_{19}H_{11}BF_{10}Fe$	$C_{46}H_{68}BCl_3FeN_2$	C ₃₉ H ₅₁ BFeKNO ₆
CCDC deposition number	744803	671666	744804
fw	495.94	822.03	735.59
temp (K)	150(2)	150(2)	150(2)
wavelength (A)	0./10/3	0./10/3	0./10/3
cryst syst			
space group unit cell lengths: $a = b = a(\mathring{A})$	$F \angle_1/C$ 32 6412(5) 7 5481(1) 23 8131(2)	$F 2_{1/C}$ 11 951(1) 17 294(1) 21 529(1)	$r \ge_{1/n}$ 11.8766(1) 17.6012(2) 18.2248(2)
$\alpha \beta \gamma (deg)$	90 111 3350(7) 90	90 92 344(1) 90	90 91 7759(6) 90
volume $(Å^3)$. Z	5464.98(13)	4445.82(12), 4	3807.93(7)
density (calcd) (Mg/m ³)	1.808	1.228	1.283
abs coeff (mm^{-1})	0.930	0.553	0.551

Table 1. Continued

	14	$[$ ⁿ Bu ₄ N] ⁺ $[1 \cdot CN]^- \cdot CHCl_3$	$[K(18\text{-}crown\text{-}6)]^+[3\cdot CN]^-$
F(000)	2952	1760	1560
cryst size (mm ³)	0.14 imes 0.18 imes 0.18	$0.60 \times 0.20 \times 0.06$	$0.20 \times 0.24 \times 0.26$
θ range for data collection (deg)	5.119-27.479	5.11-27.46	5.146-27.546
index ranges (h, k, l)	-42 to $+42$, -8 to $+9$, -30 to $+30$	-15 to +15, -22 to +20, -25 to +27	-15 to +15, -22 to +22, -23 to +23
no. of reflns collected	82235	38935	47594
no. of indep reflns/ R_{int}	12437 (0.090)	9981 (0.0778)	8689 (0.061)
completeness to θ_{\max} (%)	0.991	98.9	0.987
absorption correction	semiempirical from equivs	integration	semiempirical from equivs
max. and min transmission	0.88 and 0.79	0.935 and 0.680	0.90 and 0.83
refinement method	full matrix least sq (F^2)	full matrix least sq (F^2)	full matrix least sq (F^2)
no. of data/restraints/params	7433/1294/524	9981/45/474	8687/0/442
goodness-of-fit on F^2	1.2015	1.023	0.9467
final R indices $[I > 2\sigma(I)]$	R1 = 0.0540, wR2 = 0.1824	R1 = 0.0528, wR2 = 0.1115	R1 = 0.0433, wR2 = 0.0988
<i>R</i> indices (all data)	R1 = 0.1267, wR2 = 0.3820	R1 = 0.1075, wR2 = 0.1320	R1 = 0.0704, wR2 = 0.1095
Largest peak/hole (e Å ⁻³)	+0.71 and -0.59	+0.511 and -0.457	+0.52 and -0.60
	$[K(18\text{-}crown\text{-}6)]^+[4\cdot CN]^-$	$[K(18\text{-}crown\text{-}6)]^+[5 \cdot CN]^-$	$[K(18\text{-crown-6})]^+[15 \cdot CN]^-$
empirical formula	C ₃₉ H ₄₉ BF ₂ FeKNO ₆	C ₄₁ H _{54.96} BBr _{0.04} FeKNO ₈	C ₃₃ H ₃₈ BF ₉ FeKNO ₆
CCDC deposition number	744805	744806	744807
fw	771.57	798.76	821.41
temp (K)	150(2)	150(2)	150(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	triclinic
space group	$P\overline{1}$	$P2_1/n$	$P\overline{1}$
unit cell dimensions: a, b, c (Å)	12.6363(1), 14.9996(2), 20.2746(2)	12.0544(1), 27.3288(3), 12.4741(2)	11.7599(2), 11.9146(2), 14.1449(3)
α, β, γ (deg)	91.3387(5), 90.2094(5), 97.8732(5)	90, 97.5901(7), 90	102.9276(8), 101.1335(9), 100.6566(9)
volume (Å ³), Z	3805.48(7)	4073.37(9)	1840.60(6)
density (calcd) (Mg/m ³)	1.347	1.302	1.482
abs coeff (mm^{-1})	0.562	0.562	0.612
F(000)	1624	1693.4	844
crystal size (mm ³)	$0.07 \times 0.35 \times 0.40$	0.05 imes 0.21 imes 0.45	$0.04 \times 0.22 \times 0.26$
θ range for data collection (deg)	5.133-27.526	5.104-27.481	5.102-27.464
index ranges (h, k, l)	-16 to +16, -19 to +19, -19 to +26	-15 to $+15$, -32 to $+35$, -16 to $+16$	-15 to +14, -15 to +15, 0 to +18
no. of reflns collected	55708	46021	36759
no. of indep reflns/ R_{int}	17258 (0.036)	9208 (0.047)	8362 (0.046)
completeness to θ_{\max} (%)	0.984	0.986	0.992
absorption correction	semiempirical from equivs	semiempirical from equivs	semiempirical from equivs
max. and min transmission	0.96 and 0.83	0.97 and 0.71	0.98 and 0.86
refinement method	full matrix least sq (F^2)	full matrix least sq (F^2)	full matrix least sq (F)
no. of data/restraints/params	17258/0/884	9208/6/483	5982/12/467
goodness-of-fit on F^2	1.0042	0.9341	1.0838
final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0688, wR2 = 0.1260	R1 = 0.0592, wR2 = 0.1208	R1 = 0.0517, wR2 = 0.0647
R indices (all data)	R1 = 0.0786, wR2 = 0.1349	R1 = 0.0831, wR2 = 0.1315	R1 = 0.0799, wR2 = 0.0849
largest diff. peak/ hole (e $Å^{-3}$)	+1.18 and -0.92	+0.92 and -0.72	+1.22 and -0.83

example, leading to side reactions derived from Lewis acid promoted ring-opening chemistry. Thus, for example, $FcB(Mes)O(CH_2)_4Br$ is the predominant organometallic product obtained from the reaction of $FcBBr_2$ with MesMgBr in thf (see the Supporting Information).

Lewis acids 1–5 have been characterized by standard spectroscopic and analytical techniques and, in the cases of 1 and 4, by single-crystal X-ray diffraction. Particularly diagnostic are the low-field ¹¹B NMR resonances ($\delta_{\rm B}$ ca. 75 ppm) characteristic of triarylboranes, and redox potentials for the Fe(II)/Fe(III) couple which are shifted anodically (by +95 to +184 mV) with respect to the parent ferrocene/ferrocenium system, consistent with the π -electron-withdrawing capabilities of the diarylboryl (-BAr₂) substituents.^{4w,18} For the series of compounds 1, 3, 4, and 5, which differ only in the nature of the *para*-aryl substituent, the trend in the measured values of $E_{1/2}$ is





 a Typical reagents and conditions: (i) ArLi (ca. 2.5 equiv), diethyl ether, 18 h at 20 °C, 40–70%.

consistent with that expected from the respective Hammett parameters ($\sigma_p = +0.06, 0, -0.17, \text{ and } -0.27$ for F, H, Me, and OMe).¹⁹ For the Cp* derivative (2), the electron-donating capabilities of the five methyl groups

⁽¹⁸⁾ See, for example: (a) Carpenter, B. E.; Piers, W. E.; McDonald, R. *Can. J. Chem.* **2001**, *79*, 291. (b) Carpenter, B. E.; Piers, W. E.; Parvez, M. E.; Yap, G. P. A.; Rettig, S. J. *Can. J. Chem.* **2001**, *79*, 857.

⁽¹⁹⁾ Hansch, C.; Leo, A.; Taft, R. W. Chem. Rev. 1991, 91, 165.



Figure 1. Molecular structures of FcBMes₂ (1), FcBXyl^F₂ (4), 1,1'-fc(Br)BMes₂ (6), and the cationic components of $[1,1'-fc(CH_2NMe_3)-BMes_2]^{+}I^{-} \cdot CH_2Cl_2$ (8 · CH_2Cl₂) and $[1,2-fc(CH_2NMe_3)BMes_2]^{+}I^{-} \cdot 1/2CH_2Cl_2$ (10 · 1/2CH₂Cl₂). Hydrogen atoms, solvent molecules, and counterions omitted for clarity; thermal ellipsoids set at the 40% probability level. Key bond lengths (Å) and angles (deg), for 1: B(1)–C(1) 1.546(7), B(1)–C(11) 1.581(7), B(1)–C(20) 1.597(7), C(1)–B(1)–C(11) 119.7(4), C(1)–B(1)–C(20) 122.0(4), C(11)–B(1)–C(20) 118.1(4). For 4: B(7)–C(3) 1.547(4), B(7)–C(8) 1.690(4), B(7)–C(7) 1.588(4), C(3)–B(7)–C(8) 119.8(2), C(3)–B(7)–C(17) 118.0(2), C(8)–B(7)–C(17) 121.9(2). For 6: B(13)–C(9) 1.552(3), B(13)–C(14) 1.589(3), B(13)–C(23) 1.555(3), C(2)–Br(1) 1.879(3), C(9)–B(13)–C(14) 117.6(2), C(9)–B(13)–C(23) 125.1(2), C(14)–B(13)–C(23) 117.3(2). For 8 · CH₂Cl₂: B(8)–C(4) 1.552(4), B(8)–C(9) 1.596(4), B(8)–C(18) 1.598(4), C(4)–B(8)–C(9) 125.2(2), C(4)–B(8)–C(18) 115.7(2), C(9)–B(8)–C(18) 115.8(2), C(5)–C(4)–B(9) 124.5(2). For 10 · 1/2CH₂Cl₂: B(1)–C(101) 1.557(6), B(1)–C(111) 1.595(6), B(1)–C(120) 1.592(6), C(101)–B(1)–C(111) 1.24.7(4), C(101)–B(1)–C(120) 112.6(4), B(1)–C(101)–C(120) 134.4(4).

give rise to a ca. 350 mV cathodic shift in $E_{1/2}$ compared to Cp-substituted 1.²⁰

The molecular structures of 1 and 4 in the solid state are qualitatively very similar (Figure 1 and Table 1), each displaying a propeller-like alignment of the two aryl substituents presumably enforced on steric grounds. The angles between the least-squares BC₃ and aryl ring least-squares planes are 62.1 and 62.2° (for 1) and 59.8 and 63.9° (for 4), and related B-C distances for the two compounds are statistically indistinguishable. Bending of the $-BAr_2$ unit toward the iron center—such that the boron atom lies out of the least-squares plane defined by the Cp substituent—is typically found for strongly Lewis acidic boryl substituents (e.g., FcBBr₂: \angle Cp centroid-C_{ipso}-B = 162°)²¹ but is much less marked in both 1 and 4. Thus, Cp centroid-C_{ipso}-B angles of 172.7 and 177.1° are found for 1 and 4, respectively. This near linearity almost certainly reflects the relatively bulky nature of the BAr_2 (Ar = Mes, Xyl^F) substituents in each case, which constitutes a steric impediment to bending.^{21b}

Attempts to extend this synthetic methodology to systems featuring the bulkier and more strongly

electron-withdrawing 2,4,6-(CF₃)₃C₆H₂ (Mes^F) substituent met with only partial success (Scheme 2). Thus, the reaction of in situ generated Mes^FLi with FcBBr₂ under conditions analogous to those used to synthesize complexes 1-5 does not lead to the isolation of the corresponding diarylboryl derivative FcBMes^F₂ but, rather, the fluoro(aryl)borane $FcB(Mes^F)F$ (14) in ca. 54% vield. Similar chemistry resulting in incomplete substitution of boron-bound halides by Mes^FLi and in B-F bond formation via activation of a CF₃ substituent has been reported by Dillon and co-workers.²² Thus, the reaction of BCl₃ with ca. 0.5 equiv of Mes^FLi in a mixed diethyl ether/hexanes/heptane solvent system has been shown to yield Mes^F₂BF together with Mes^FBCl₂. While **14** can be characterized by standard spectroscopic, analytical, and crystallographic methods (see Supporting Information), its use in fluoride and cyanide binding experiments appears to be limited by the lability of the boron-bound substituents (vide infra). Attempts to introduce a second (different) any group by fluoride substitution proved to be unsuccessful; reaction with MesLi under the relatively forcing conditions required to bring about any conversion of 14 leads to the formation of $FcBMes_2(1)$, resulting from displacement of *both* F and Mes^F substituents. Simple displacement of fluoride *can* be accomplished by the use of the much less bulky *methyl*lithium, to give

^{(20) (}a) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877. (b) Noviandri, I.; Brown, K. N.; Fleming, D. S.; Gulyas, P. T.; Lay, P. A.; Masters, A. F.; Phillips, L. J. Phys. Chem. B **1999**, *103*, 6713.

^{(21) (}a) Appel, A.; Jäkle, F.; Priermeier, T.; Schmid, R.; Wagner, M. *Organometallics* **1996**, *15*, 1188. For a related recent study of a less sterically encumbered diarylborylferrocene with a large tilt angle, see: (b) Kaufmann, L.; Vitze, H.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2008**, *27*, 6215.

⁽²²⁾ Cornet, S.; Dillon, K.; Entwhistle, C. D.; Fox, M. A.; Goeta, A. E.; Goodwin; Marder, T. B.; Thompson, A. L. *Dalton Trans.* **2003**, 4395.

Scheme 2. Syntheses of Mes^F-Substituted Lewis Acids 14 and 15^a



^{*a*} Reagents and conditions: (i) Mes^FLi (2.1 equiv), diethyl ether, 18 h at 20 °C, 54%; (ii) MeLi (1.0 equiv), diethyl ether, -78 to +20 °C then 2 h at 20 °C, 58%.

Scheme 3. Syntheses of 1'-Functionalized Ferrocenyl Dimesitylboranes⁴



^{*a*} Reagents and conditions: (i) ^{*n*}BuLi (1.0 equiv), thf, $-78 \, ^{\circ}$ C, 30 min, then Mes₂BF (0.94 equiv), thf, $-78 \, ^{\circ}$ C, chromatographic purification, 90%; (ii) 'BuLi (2.0 equiv), thf/pentane, $-78 \, ^{\circ}$ C, 30 min, then [Me₂NCH₂]⁺I⁻ (2.0 equiv), $-78 \, ^{\circ}$ C, then 12 h at 20 °C, chromatographic purification, 69%; (iii) MeI (ca. 8 equiv), hexanes, 20 °C, 1 h, 99%.

FcB(Mes^F)Me (15), which is competent for the binding of anions such as fluoride and cyanide, but which—by virtue of the presence of only one ortho-disubstituted aryl substituent—proves to be air- and moisture-sensitive and thus of little practical use in sensing/dosimetry applications.

Syntheses of diarylborylferrocenes bearing additional functionality can readily be accomplished via alternative approaches which make use of lithioferrocene reagents. Thus, systems containing pendant -CH₂NMe₂ and related substituents at either the 1'- or 2- positions can be synthesized by making use of either 1,1'-dibromoferrocene or commercially available (N,N-dimethylaminomethyl)ferrocene as starting materials (Schemes 3 and 4). Sequential lithiation of 1,1'-fcBr₂ and quenching with Mes₂BF and $[Me_2N=CH_2]^+I^-$ leads to the stepwise formation of 1,1'-fc(Br)BMes₂ (6) and 1,1'-fc(CH₂NMe₂)- $BMes_2$ (7); 7 can readily be methylated at nitrogen by methyl iodide to generate the cationic ammonium-functionalized borane $[1,1'-fc(CH_2NMe_3)BMes_2]^+$ (8) as the iodide salt. Spectroscopic data are in line with the proposed formulations for compounds 6-8, with crystallographic confirmation being possible in the cases of 6and 8 (the latter as the dichloromethane solvate; Figure 1). Of note is the considerable anodic shift in the redox potential for 8 (+164 mV with respect to $1/1^+$; +314 mV with respect to ferrocene/ferrocenium), consistent with the presence of an additional pendant cationic fragment. Structurally, the borane fragments within Lewis acids 6 and 8 bear close resemblance to that found in 1. Moreover, there appears to be no contact in the solid state between the tricoordinate boron center and the iodide counterion in 8; the closest contact of I^- to the cationic component of 8 occurs via a $C-H\cdots I$ interaction (2.92 A) involving one of the methyl groups of the NMe_3^+ unit. A similar pattern of intermolecular contacts is observed in the solid-state structure of the isomeric complex 10 (closest C-H····I contact: 3.01 Å, vide infra).²³

Related systems featuring a 1,2 disposition of the -BMes₂ and pendant amine/ammonium functionalities can be accessed from (N,N-dimethylaminomethyl)ferrocene utilizing simple ortho-directed lithiation chemistry.²⁴ Thus, charge-neutral 1,2-fc(CH₂NMe₂)BMes₂ (9) and cationic $[1,2-fc(CH_2NMe_3)BMes_2]^+$ (10, as the iodide salt) can be accessed in 55 and 39% overall yields from FcCH₂NMe₂, as outlined in Scheme 4. Spectroscopic and analytical data for both compounds are consistent with the proposed formulations, with the structure of 10 (as the dichloromethane hemisolvate) in the solid state being confirmed crystallographically (Figure 1). In contrast to the 1,1'-disubstituted system 8, the increase in steric crowding at the BMes₂ unit implicit in functionalization at the 2-position is presumably responsible for a widening of the B(1)-C(101)-C(102) angle $[134.4(4) \text{ cf. } 124.5(2)^{\circ}]$ for 8]. These steric effects are also evident in the ¹H NMR spectrum of 10 in [D]chloroform. Thus, a single broad resonance is observed for the four mesityl ortho-methyl groups at 20 °C, which sharpens on warming, and which can be resolved into four separate signals on cooling to -30 °C, consistent with restricted rotation about the C(Cp)-B bond. As with the isomeric complex 8, the Fe(II)/Fe(III) redox potential for compound 10 experiences a significant anodic shift (+217 mV with respect to $1/1^+$; +367 mV with respect to ferrocene/ferrocenium).

An alternative to methylation of the tertiary amine to introduce a positively charged ammonium function is simple protonation. In terms of anion binding motifs,

⁽²³⁾ These distances fall comfortably within the sum of the Van der Waals radii for hydrogen and iodine (3.35 Å): Emsley, J. *The Elements*; OUP: Oxford, 1995.

⁽²⁴⁾ See, for example: Marr, G.; Moore, R. E.; Rockett, B. W. J. Chem. Soc. C 1968, 24.

Scheme 4. Syntheses of 2-Functionalized Ferrocenyl Dimesitylboranes^a



^{*a*} Reagents and conditions: (i) ^{*n*}BuLi (1.0 equiv), diethyl ether, 0 to 20 °C, then 12 h at 20 °C, then Mes₂BF (1.0 equiv), diethyl ether, -78 to +20 °C, 55%; (ii) MeI (ca. 2 equiv), hexanes, 20 °C, 12 h, 70%; (iii) HCl (as a solution in Et₂O, ca. 2 equiv), diethyl ether, -30 °C, 30 min, 55%; (iv) bench (i.e., wet) chloroform, 144 h, quant. by NMR; (v) tetrafluoroboric acid (2.0 equiv), diethyl ether, 20 °C, 12, 60%.

such reactivity necessarily generates a tertiary ammonium function and hence the potential for stronger host/guest interactions via hydrogen-bond/Lewis acid cooperativity.⁵⁰ In practice, however, the applicability of this mode of anion binding appears to be limited by ready B-C bond cleavage in the presence of a pendant $-CH_2NMe_2H^+$ functionality. Thus, although the reaction of 9 with dry HCl in diethyl ether does lead to the isolation of $[1,2-fc(CH_2NMe_2H)BMes_2]^+Cl^-$ (11) in ca. 55% yield (after recrystallization from dichloromethane/ hexanes), the corresponding reaction with (wet) tetrafluoroboric acid leads instead to the formation of the hydrolysis product $[1,2-fc(CH_2NMe_2H)B(Mes)OH]^+$ - $[BF_4]^-$ (13), which has been characterized by standard spectroscopic/analytical techniques and X-ray crystallography (see the Supporting Information). The presence of a proximal -CH₂NMe₂H⁺ group presumably activates the (otherwise robust) B-Mes linkages to substitution via nucleophilic attack at boron by water. Protonation by the tertiary ammonium salt facilitates a loss of the mesityl group as mesitylene (as demonstrated by ¹H NMR monitoring of the reaction mixture), with the much more rapid kinetics of hydrolysis observed for 11 (versus the corresponding 1,1' isomer) being consistent with such a mechanism. Complete hydrolytic decomposition of 11 is observed in bench (i.e., wet) [D]chloroform over a period of 72 h, while the analogous 1.1' disubstituted compound has a half-life of ca. 10 days under identical conditions. Moreover, monitoring of the reaction of 11 with water over a longer time frame by electrospray mass spectrometry is consistent with the loss of *both* boron-bound mesityl substituents to give $[1,2-fc(CH_2NMe_2H)B(OH)_2]^+$. As such, the ready fragmentation of $-NMe_2H^+$ functionalized receptors under conditions other than those which are strictly nonaqueous led to their abandonment as potential fluoride/cyanide

sensors. As it happens, the C–H bonds of proximal $CH_2NMe_3^+$ groups prove to be a more convenient source of hydrogen-bond donors and exert a marked effect on anion binding affinities, with little detriment to the hydrolytic stability of key B–C linkages (vide infra).

ii. Anion Binding. The propensity of the above range of ferrocene-derivatized Lewis acids to interact with fluoride or cyanide in nonaqueous media has been probed by NMR, IR, mass spectrometric, electrochemical, crystallographic, and UV-vis titration approaches with a view to (i) systematically probing the effects of borane electrophilicity, ancillary functional groups, and net charge on the binding of these anions and (ii) exploiting such systems in the colorimetric sensing of fluoride and cyanide.

The binding of cyanide (as either KCN/18-crown-6 or $[^{n}Bu_{4}N]^{+}[CN]^{-}\cdot 2H_{2}O)^{15}$ by the parent system FcBMes₂ (1) in a range of solvents (chloroform, dichloromethane, acetonitrile) can readily be demonstrated by a combination of spectroscopic techniques. Thus, the changes in ¹¹B NMR chemical shift ($\delta_{\rm B}$ 76 to -16) and IR-detected cyanide stretching frequency (2080 to 2162 cm^{-1}) are in line with previous reports of cyanide complexation to boron-based Lewis acids.⁷ In addition, negative ion ESI-MS sampling of the reaction mixture reveals a "flag-pole" mass spectrum with an isotopic profile and measured exact mass consistent with the formulation $[1 \cdot CN]^{-14}$. The thermodynamics of CN⁻ binding by 1 can readily be assessed by monitoring the intensity of the UV/vis band at 510 nm as a function of cyanide concentration. A binding constant of $8.3(2.0) \times 10^4 \text{ mol}^{-1} \text{ dm}^3$ can be determined by fitting the resulting curve of absorbance versus cyanide concentration in dichloromethane solution (see the Supporting Information). This figure is significantly less than that recently reported for a BMes₂-derivatized BODIPY system $(5 \times 10^7 \text{ mol}^{-1} \text{ dm}^3)$,^{7e} although the

Table 2. Binding Constants of Receptors 1, 3, 4, 5, 6, 8, and 10 for Fluoride and Cyanide^a

receptor	$K_{\rm F}/{ m mol}^{-1}~{ m dm}^3$	$K_{\rm CN}/{ m mol}^{-1}~{ m dm}^3$	$E_{1/2}/\mathrm{mV}^b$
FcBMes ₂ (1)	$7.8(1.2) \times 10^4$	$8.3(2.0) \times 10^4$	+131
$FcB(Xyl)_{2}(3)$	$4.4(0.5) \times 10^5$	$1.4(0.2) \times 10^5$	+153
$FcB(Xyl^F)_2(4)$	$4.3(0.7) \times 10^5$	$7.7(1.8) \times 10^4$	+184
$FcB(Xyl^{OMe})_2$ (5)	$6.6(0.4) \times 10^4$	$1.5(0.2) \times 10^5$	+95
$1, 1'-fc(Br)BMes_2(6)$	$2.8(0.7) \times 10^5$	$6.5(0.8) \times 10^4$	+169
$[1,1'-fc(CH_2NMe_3)BMes_2]^+I^-$ (8)	$9.4(3.6) \times 10^5$	$5.8(1.7) \times 10^5$	+314
$[1,2-fc(CH_2NMe_3)BMes_2]^+I^-$ (10) ^c	$5.6(2.3) \times 10^9$	$5.6(2.4) \times 10^9$	+367

^{*a*} Conditions: dichloromethane, [receptor] = ca. 4×10^{-4} mol dm⁻³. ^{*b*} Measured in dichloromethane and referenced with respect to ferrocene/ferrocenium. ^{*c*} Determined from competition experiments with PhBMes₂.

more competitive nature of the dichloromethane reaction medium (vs thf) together with the differing electronic properties of the BODIPY/Fc substituents are presumably contributory factors.²⁵ Under conditions analogous to those used in the cyanide binding experiments, 1 can also be shown to bind fluoride, a competing affinity which can readily be understood in terms of the known (high) B-F bond strength²⁶ and the comparable basicity reported for F^- (cf. CN^-) in *nonaqueous* media (p K_a 's in DMSO: HF 15, HCN 13).¹³ The binding constant of 1 for fluoride in dichloromethane solution determined from UV/vis titration data $[7.8(1.2) \times 10^4 \text{ mol}^{-1} \text{ dm}^3$; see the Supporting Information] is similar to those measured previously for the related Lewis acids BMes₃ and tris(9anthryl)borane $[3.3(0.4) \times 10^5 \text{ and } 2.8(0.3) \times 10^5 \text{ mol}^{-1}$ dm³, respectively].^{5a,6r} Moreover, although the binding constants for 1 with fluoride and cyanide cannot be separated within experimental error, stronger binding of cyanide is implied by ¹¹B NMR-monitored competition experiments. Thus, cyanide will displace fluoride from $[FcBMes_2 \cdot F]^-$, while $[FcBMes_2 \cdot CN]^-$ is stable in the presence of excess fluoride.²⁷

The use of positively charged peripheral functional groups has been reported to lead to marked enhancement in the anion affinity of borane Lewis acids and to the possibility of binding in protic media.^{7c} With this in mind, we have sought to determine the effect of this and other factors on the binding of fluoride and cyanide by ferrocene-derivatized Lewis acids. The binding constants (for both F^- and CN^-) of 1; the 4-functionalized 2,6-xylyl boranes $FcB(Xyl)_2$ (3), $FcB(Xyl^F)_2$ (4), and FcB- $(Xyl^{OMe})_2$ (5); the 1,1'-difunctionalized ferrocenes fc-(Br)BMes₂ (6) and $[1,1'-fc(CH_2NMe_3)BMes_2]^+I^-$ (8); and the isomeric 1,2-disubstituted cation [1,2-fc- $(CH_2NMe_3)BMes_2]^+I^-$ (10) have been determined by UV-vis titration techniques, and the results are outlined in Table 2 (see the Supporting Information for experimental details). These allow some systematic conclusions to be drawn concerning the effect of net charge, borane substituent, and ancillary ligand electronics/substitution pattern on the strength of F^{-}/CN^{-} binding.

With respect to the binding of fluoride, it is evident that changes made at the para-substituent of the boryl substituent exert a relatively minor influence on $K_{\rm F}$. Thus receptors 1, 3, 4, and 5 featuring para-Me, H, F, and OMe substituents, respectively, give rise to binding constants of 7.8(1.2), 44(5), 43(7), and 6.6(0.4) \times 10⁴ mol⁻¹ dm³. This trend is broadly consistent with the electron withdrawing/ donating properties of the para substituents, as reflected not only by their conventional Hammett parameters $(\sigma_{\rm p} = -0.17, 0, 0.06, \text{ and } -0.27, \text{ respectively})^{19}$ but also in the measured Fe(II)/Fe(III) redox potentials, $E_{1/2}$ (Table 2).²⁸ Thus, **4** is oxidized at a potential of +53mV (with respect to 1), while the corresponding shift for 5 is -36 mV. Interestingly, although the binding constant of 4 for F^- is a factor of ~5 greater than that of 1, the affinity of the two receptors for cyanide is identical within experimental error; indeed, the cyanide binding affinities of receptors 1, 3, 4, and 5 do not appear to differ by more than a factor of 2 across all four systems.

Relatively minor changes in the binding capabilities for fluoride and cyanide are also brought about by the introduction of additional functional groups at the 1' position of the ferrocene core. Thus, the values of $K_{\rm F}$ and $K_{\rm CN}$ determined for 1,1'-fc(Br)BMes₂ (6), and even [1,1' $fc(CH_2NMe_3)BMes_2]^+$ (8, as the iodide salt), are within ca. 1 order of magnitude of those determined for the parent receptor 1. The anion binding capabilities of the isomeric system $[1,2-fc(CH_2NMe_3)BMes_2]^+$ (10, as the iodide salt), however, show a marked enhancement, with values of $K_{\rm F}$ and $K_{\rm CN}$ being determined [5.6(2.3) and 5.6(2.4) × 10⁹ mol⁻¹ dm³], which are (i) > 3 orders of magnitude greater than that for the 1,1' isomer 8, (ii) comparable to the cyanide binding constant measured for $[4-Me_3NC_6H_4BMes_2]^+$ ($K_{CN} = 4 \times 10^8 \text{ mol}^{-1} \text{ dm}^3$ in water/DMSO),^{7c} and (iii) compatible with the observed capability of chloroform solutions of 10 to sequester fluoride from aqueous solution.

While the very similar $E_{1/2}$ potentials for 8 and 10 (+314 and +367 mV, respectively, with respect to ferrocene/ ferrocenium) reflect the additive electron-withdrawing effects of the CH₂NMe₃⁺ and BMes₂ groups on the electron density at the ferrocenediyl core, the marked differences in both fluoride and cyanide binding between 8 and 10 presumably reflect, at least in part, the differing

⁽²⁵⁾ An indication that binding constants for fluoride are typically higher in thf than in chlorocarbon solvents comes from the fact that a value of $K_F = 3.3(0.4) \times 10^5 \text{ mol}^{-1} \text{ dm}^3$ has been determined for BMes₃ in thf, ^{5e} while a null response was observed for the same receptor/analyte combination in chloroform^{5e} or dichloromethane.

⁽²⁶⁾ A gas-phase fluoride affinity of 385 kJ mol⁻¹ has been determined for BF₃:Mallouk, T. E.; Rosenthal, G. L.; Müller, G.; Brusasco, R.; Bartlett, N. *Inorg. Chem.* **1984**, *23*, 3167.

⁽²⁷⁾ The reversibility of fluoride and cyanide binding by ferrocene derivatized boranes could readily be established by the use of AlCl₃ (in the case of fluoride adducts) or HCl (cyanide adducts).

⁽²⁸⁾ Related studies have recently been reported by Gabbaï and by Jäkle and Norton, detailing the effects on the reduction potentials of triarylboranes of systematic replacement of mesityl groups with either C_6F_5 or 2,6- $Me_2C_6H_2NMe_3^+$: (a) Cummings, S. A.; Iimura, M.; Harlan, C. J.; Kwaan, R. J.; Trieu, I. V.; Norton, J. R.; Bridgewater, B. M.; Jäkle, F.; Sundararaman, A.; Tilset, M *J. Am. Chem. Soc.* **2006**, *25*, 1565. (b) Chiu, C.-W.; Kim, Y.; Gabbaï, F. P. J. Am. Chem. Soc. **2008**, *131*, 60.





Figure 2. Proposed $C-H\cdots F$ interaction in 1,2-fc(CH_2NMe_3)BMes₂F.

proximities of the cationic $-NMe_3^+$ function to the -BMes₂ binding site [in the solid state at least, the respective $B \cdots N$ separations are 4.26 and 5.64 Å]. A similar enhancement in Lewis acidity as a function of reduced separation (and increased electrostatic interaction) between a borane receptor site and a pendant cationic group has been used to rationalize the increased fluoride binding affinity of [2-Me₃NC₆H₄BMes₂]⁺, over its 1,4-disubstituted isomer.^{7c} An additional factor in the stronger anion binding by 10 (over 8), which has recent literature precedent, also stems from the close proximity of the $-NMe_3^+$ and $-BMes_2$ groups.^{5k} Chiu and Gabbaï have reported a naphthalenediyl system featuring -BMes₂ and $-CH_2NMe_3^+$ substituents in the 1 and 8 positions which binds fluoride via both a conventional Lewis acid/base interaction (at boron) and a $C-H \cdots F-B$ hydrogen bond utilizing one of the methylene hydrogens of the $CH_2NMe_3^+$ group. The presence of such a cooperative binding motif in the solid state is manifested by a $C \cdots F$ distance of 2.826(4) Å for the fluoride adduct, and by a ${}^{1}J_{\text{HF}}$ coupling constant of 9.2 Hz in chloroform solution. In the case of the fluoride adduct formed on the addition of excess $[(Me_2N)_3S]^+[Me_3SiF_2]^-$ to a solution of **10** in [D]chloroform, the existence of an analogous (borane/hydrogenbond) cooperative binding mode (Figure 2) is signaled by (i) an upfield shift in the ¹¹B NMR signal from $\delta_{\rm B}$ 80 to 5.7 ppm, (ii) a downfield shift in the ¹H NMR resonance for one of the diastereotopic methylene protons from $\delta_{\rm H}$ 5.08 to 5.54 ppm, and (iii) the collapse, on broad-band ¹⁹F decoupling, of the doublet of doublets coupling pattern observed for the latter signal (${}^{1}J_{HF} = 6.6 \text{ Hz}$, ${}^{2}J_{HH} = 12.2 \text{ Hz}$; Figure 2) to a simple doublet. The magnitude of both the coordination-induced shift in the methylene ¹H resonance and the ${}^{1}J_{\rm HF}$ coupling constant itself are indicative of a weaker C-H···F interaction in the case of 1,2fc(CH₂NMe₃)BMes₂F compared to 1,8-(Mes₂FB)- $(Me_3NCH_2)C_{10}H_6$;^{5k} a more similar J_{HF} coupling constant (7.2 Hz) has, however, been determined for a $N-H\cdots F-B$ interaction implicated in the binding of

fluoride by a mixed borane/amide receptor.²⁹ The additional $C-H\cdots F-B$ interaction in 1,2-fc(CH_2NMe_3)-BMes₂F is thus presumably a factor in its enhanced anion binding compared to its 1,1' isomer.

Intriguingly, the cyanide binding constant measured for 10 also appears to be very much enhanced compared to that for 8; the binding constants of 10 for fluoride and cyanide determined by titration methods are essentially identical (Table 2). Moreover, this finding is also consistent with the results of direct competition experiments. Thus, if a dichloromethane solution containing 1 equiv of fluoride and 1 equiv of cyanide (both as the $[^{n}Bu_{4}N]^{+}$ salts) is added to a solution of 10, ¹¹B NMR monitoring reveals the presence of a mixture of the cyanide ($\delta_{\rm B}$ –17 ppm) and fluoride adducts ($\delta_{\rm B} 6$ ppm). Moreover, the fact that addition of excess cyanide to a solution of 1,2fc(CH₂NMe₃)BMes₂F leads to the formation of 1,2-fc-(CH₂NMe₃)BMes₂CN (but the reverse reaction is not spontaneous) implies that, if anything, cyanide binding is a slightly *more* thermodynamically favorable process. This situation contrasts with that observed for $[1,8-(Mes_2B)(Me_3NCH_2)C_{10}H_6]^+$, which binds fluoride (in thf solution) ca. 3 orders of magnitude more strongly than cyanide—a finding attributed to the greater steric bulk of the cyanide anion and the sterically congested binding cavity.^{7d} That no similar steric effect on cyanide binding is apparently observed with 10 presumably reflects a smaller degree of steric crowding at the binding site, which in turn can be related to the geometric consequences of ortho-substitution of the *five-membered* cyclopentadienyl ring.

Anion binding studies with the closely related *tertiary* ammonium system [1,2-fc(CH₂NMe₂H)BMes₂]⁺Cl⁻ (11) are not straightforward, being complicated by hydrolysis of the mesityl B–C linkages in the presence of water (such as that provided by hydrated sources of fluoride or cyanide). As such, anion binding by these systems was not pursued any further. Lability of the boron-bound substituent(s) under anion complexation conditions also proves to be a feature of the chemistry of FcB(Mes^F)F (14). Thus, NMR monitoring of the reactions of 14 toward fluoride and cyanide sources are consistent

⁽²⁹⁾ Hudnall, T. W.; Bondi, J. F.; Gabbaï, F. P. Main Group Chem. 2006, 5, 319.



Figure 3. Molecular structures of the anionic component of $["Bu_4N]^+[1 \cdot CN]^- \cdot CHCl_3$ and of $[K(18\text{-crown-6})]^+[X \cdot CN]^- (X = 3, 4, 5, 15)$. Hydrogen atoms (except that attached to C(1S)) and $["Bu_4N]^+$ counterion omitted for clarity; thermal ellipsoids set at the 40% probability level. Key bond lengths and angles, for $[1 \cdot CN]^- \cdot CHCl_3$: $B(1) - C(1) \ 1.639(4)$, $B(1) - C(20) \ 1.621(3)$, $N(1) - C(20) \ 1.150(3)$, $N(1) - C(1S) \ 3.085$, $B(1) - C(20) - N(1) \ 169.8(3)$. For $[K(18\text{-crown-6})]^+[3 \cdot CN]^-$: $B(7) - C(2) \ 1.637(3)$, $B(7) - C(16) \ 1.624(3)$, $N(17) - C(16) \ 1.147(3)$, $N(17) - K(31) \ 2.765$, $B(7) - C(16) - N(17) \ 170.2(2)$. For $[K(18\text{-crown-6})]^+[4 \cdot CN]^-$: $B(39) - C(34) \ 1.632(5)$, $B(39) - C(40) \ 1.620(5)$, $N(41) - C(40) \ 1.148(4)$, $N(41) - K(101) \ 2.762$, $B(39) - C(40) - N(41) \ 171.4(3)$. For $[K(18\text{-crown-6})]^+[5 \cdot CN]^-$: $B(12) - C(10) \ 1.633(4)$, $B(12) - C(33) \ 1.621(4)$, $N(34) - C(33) \ 1.148(3)$, $N(34) - K(35) \ 2.755$, $B(12) - C(33) - N(34) \ 171.1(3)$. For $[K(18\text{-crown-6})]^+[15 \cdot CN]^-$: $B(7) - C(2) \ 1.635(4)$, $B(7) - C(26) \ 1.624(5)$, $N(27) - C(26) \ 1.147(4)$, $N(27) - K(34) \ 2.789$, $B(7) - C(26) - N(27) \ 177.8(3)$.

with the formation of $[FcBF_3]^-$ and $[FcB(CN)_3]^-$, respectively.^{1d,30} Substitution of a methyl group for the boronbound fluoride to give $FcB(Mes^F)Me$ (15) appears to prevent such exchange processes—to the extent that $[K(18\text{-crown-6})]^+[15 \cdot CN]^-$ can be isolated from the reaction of 15 with KCN/18-crown-6—but the moisture sensitivity of 15 precludes reliable measurements of binding constants using soluble fluoride/cyanide sources.

Structural authentication of the mode of anion binding in the cases of $[^{n}Bu_{4}N]^{+}[1\cdot CN]^{-}\cdot CHCl_{3}$ and [K(18 $crown-6)]^{+}[X \cdot CN]^{-} (X = 3, 4, 5, 15)$ has been obtained by X-ray crystallography (Figure 3), and a consistent pattern of geometric structure arises from analyses of each of these adducts. Thus, an essentially linear C-bound cyanide adduct is found in each case, with metrical parameters for the BCN unit in agreement with previous reports of cyanide/borane complexes [d(B-C) =1.621(3), 1.624(3), 1.620(5), 1.621(4), 1.624(5) Å, $\angle B-C-N = 169.8(3)$, 170.2(2), 171.4(3), $171.1(3)^{\circ}$, 177.8(3) for $[1 \cdot CN]^{-}$, $[3 \cdot CN]^{-}$, $[4 \cdot CN]^{-}$, $[5 \cdot CN]^{-}$, and $[15 \cdot CN]^{-}$, respectively].^{7c,e,31} No statistically significant trend in either the B-C or C-N distances can be seen for the series of para-substituted systems $[1 \cdot CN]^{-}$, $[3 \cdot CN]^{-}$, $[4 \cdot CN]^{-}$, and $[5 \cdot CN]^{-}$.

Significant elongation of the ferrocenyl B–C_{ipso} bond is observed on cyanide binding $[d(B-C_{ipso}) = 1.639(4),$ 1.632(5) Å for $[1 \cdot CN]^-$ and $[4 \cdot CN]^-$, cf., 1.546(7),1.546(5) Å for the free receptors]. The latter structural

response is consistent with the conversion of a pendant three-coordinate boryl Lewis acid to an anionic fourcoordinate borate and is mirrored by changes in electrochemical behavior. Thus, a cathodic shift of ca. -560 mV is measured for 1 on the addition of cyanide $\{E_{1/2} = -383\}$ and +181 mV for $[1 \cdot \text{CN}]^-$ and 1, respectively, in acetonitrile}, which mirrors the behavior of related ferrocenederivatized Lewis acids on coordination of bases such as fluoride or trimethylphosphine.4a,w,18 For each of the cyanide adducts, further supramolecular interactions can be identified resulting from the residual Lewis basicity of the nitrogen atom of the coordinated cyanide molecule. In the case of $[^{n}Bu_{4}N]^{+}[1 \cdot CN]^{-} \cdot CHCl_{3}$, this takes the form of an intermolecular hydrogen bond between N(1) and the hydrogen atom of the chloroform solvate molecule $[d(N \cdots H) = 2.143 \text{ Å}; d(N \cdots C) =$ 3.085(3) Å; $\angle C - N \cdots C = 151.5(2)^{\circ}$]. In the cases of the $[K(18\text{-crown-6})]^+$ salts, an additional CN⁻ to Lewis acid interaction is observed between the cyanide nitrogen and the potassium counterion {e.g. $d(K \cdots N) =$ 2.762, 2.789 Å for $[4 \cdot CN]^-$ and $[15 \cdot CN]^-$, respectively}. The coordination geometry at the potassium center in $[K(18 \text{-crown-6})]^+ [4 \cdot CN]^-$ is then completed by a secondary $K \cdots O$ interaction $[d(K \cdots O) = 2.812 \text{ Å}]$ involving one of the oxygen atoms from a neighboring $[K(18\text{-crown-6})]^+$ moiety; a reciprocal $K \cdots O$ interaction involving O(65) then links the two adjacent units to give a centro-symmetric supramolecular dimer (Figure 3). In the case of $[K(18\text{-crown-6})]^+[15 \cdot CN]^-$, by contrast, the coordination geometry at each potassium center is completed by weak C-F···K interactions $[d(K \cdot \cdot \cdot F)] =$ 3.033, 3.434 Å] involving two of the fluorine atoms of the *para*-CF₃ group of an adjacent $B(Mes^{F})$ unit. These

⁽³⁰⁾ Yao, H.; Kuhlman, M. L.; Rauchfuss, T. B.; Wilson, S. R. Inorg. Chem. 2005, 44, 6256.

⁽³¹⁾ Kuz²mina, L. G.; Struchkov, Y. T.; Lemenoksky, D. A.; Urazowsky, I. F. J. Organomet. Chem. **1984**, 277, 147.



Figure 4. UV/vis spectra of acetonitrile/methanol (>100:1) solutions containing Lewis acid receptors **2** or **17** (0.5 mM) and tetrazolium violet (1.0 mM) in the absence (gray trace) and presence (black trace) of added anion: (a) **2** with F^- , (b) **2** with CN^- , (c) **17** with F^- , and (d) **17** with CN^- .

interactions fall comfortably within the sum of the van der Waals' radii of potassium and fluorine [4.22 Å],²³ and link adjacent $[K(18\text{-}crown-6)]^+[15 \cdot CN]^-$, units into a loosely bound one-dimensional coordination polymer in the solid state.

iii. Colorimetric Anion Sensing/Dosimetry. Each of the air-stable ferrocene-functionalized receptors 1, 3-6, 8, and 10 has an approximately equal affinity in dichloromethane solution for fluoride to that for for cyanide (Table 2). In the case of the parent system **1**, a larger binding constant for cyanide is implied by ¹¹B NMR monitored competition experiments. However, in terms of developing a workable sensor system, the BMes₂ complexes we have examined do not, in isolation, possess the ability to differentiate between exposure to fluoride and cyanide, although their interaction with other competing anionic analytes is negligible. Discrimination between these two analytes *can* be achieved by the use of a weaker Lewis acid receptor. Thus, boronic ester systems related to 1 and 2 [i.e., FcB(OR)₂ and Fc*B(OR)₂, where, for example $(OR)_2 = OC(H)PhC(H)PhO;$ 16 and 17] have previously been shown to be selective for the binding of fluoride.^{4w} Hence, a two-component system can be envisaged featuring, for example, 1 and 16, which uses AND/NOT Boolean logic to distinguish between fluoride and cyanide in nonaqueous solution.

While the anion binding event can readily be monitored by electrochemical measurements (e.g., by a shift from +181 to -383 mV on going from 1 to $[1 \cdot \text{CN}]^-$ in acetonitrile), an attractive alternative involves the use of a redox-matched dye which will oxidize an electron-rich fluoride/cyanide adduct but not the "free" receptor,

thereby generating a *colorimetric* reporter response.^{4b} Potential candidates as oxidants include the tetrazolium dyes, which in addition to offering a range of compatible redox potentials give rise (on reduction to the corresponding formazan) to very large changes in extinction coefficient at suitable wavelengths in the visible region of the spectrum.³² Moreover, in contrast to previously reported redox indicators,^{4b} the conversion of a tetrazolium to a formazan is a two-electron plus proton reduction (i.e., is effectively hydridic) and under normal conditions is irreversible. Hence, the color changes that characterize fluoride or cyanide binding are rendered irreversible, thereby converting the system from a sensor in the classical sense to an effective dosimeter. By tuning the electrochemical window determined by the receptor and receptor/analyte complex, it has proved possible to select redox-matched tetrazolium dyes which give rise to an appropriate color change. Thus, 2 and $[2 \cdot CN]^{-}$ are oxidized at potentials (-176 and -691 mV, respectively) which are shifted ca. -300 mV cathodically with respect to $1/[1 \cdot CN]^-$ and are thus compatible with the use of tetrazolium violet as the redox indicator (Chart 1).

The results of monitoring the exposure of 2 to either cyanide or fluoride, in the presence of tetrazolium violet, both by UV/vis spectroscopy and colorimetrically, are shown in Figures 4 and 5. Thus, 2 is shown to give a colorimetric response on exposure to both fluoride and cyanide. Such a receptor/dye combination proves to be competent for visual detection

(32) Nineham, A. W. Chem. Rev. 1955, 55, 355.



Figure 5. Colorimetric responses of receptor molecules **2** and **17** to the addition of CN^- (left-hand pair), fluoride (middle pair), and chloride (null response control, right-hand pair) in acetonitrile/methanol (>100:1) in the presence of tetrazolium violet.

Chart 1. Tetrazolium Violet



down to 25–40 nmol of analyte. In a similar fashion, the weaker Lewis acid **17** can be shown to undergo a ca. -580 mV electrochemical shift on fluoride binding [e.g., from -169 to -749 mV in acetonitrile].^{4w} In combination with the same tetrazolium violet redox dye, a colorimetric response is therefore generated on exposure of **17** to fluoride. By contrast, a null response is observed when excess cyanide is added to solutions of **17** in acetonitrile/methanol under identical conditions (Figures 4 and 5).³³ Thus, while the stronger Lewis acid **2** gives positive colorimetric responses to both cyanide AND fluoride, **17** senses fluoride but NOT cyanide under the same conditions.

Conclusions

Synthetic approaches based on the direct borylation of ferrocene by BBr₃, followed by boryl substituent modification, or on the lithiation of ferrocene derivatives and subsequent quenching with the electrophile FBMes₂, have given access to a range of Lewis acids with which to conduct a systematic study of fluoride and cyanide binding. In particular, the effects of borane electrophilicity, net charge, and ancillary ligand electronics/cooperativity have been examined. In this respect, modifications made at the para position of the boron-bound aromatic substituents exert a relatively minor influence on the binding constants for both fluoride and cyanide, as do the electronic properties of peripheral substituents at the ferrocenyl 1'- position (even for cationic substituents). By contrast, the influence of a $CH_2NMe_3^+$ substituent in the 2- position is found to be much more pronounced, reflecting, at least in part, the existence in solution of an additional binding component utilizing the hydrogen-bond donor capabilities of the methylene CH₂ group. While none of the systems examined in the current study display any great differentiation between the binding of fluoride and cyanide (and indeed some, such as 1, bind both anions with equal affinity, within experimental error), much weaker boronic ester Lewis acids will bind fluoride (but give a negative response for cyanide). Thus, by the incorporation of a suitable redox-matched organic dye, a two-component dosimeter system can be developed capable of colorimetrically signaling the presence of fluoride and cyanide in organic solution by Boolean AND/NOT logic.

Acknowledgment. The financial support of the EPSRC and the Joint Grants Scheme is gratefully acknowledged, as are the efforts of the EPSRC National Mass Spectrometry and Crystallography Services. Drs. Nick Rees and Barbara Odell are thanked for assistance with NMR measurements.

Supporting Information Available: Complete details of all crystal structures (CIFs); details of the determination of all binding constants listed in Table 2; spectroscopic data for $FcB(Mes)O(CH_2)_4Br$. This material is available free of charge via the Internet at http://pubs.acs.org.

⁽³³⁾ Although boronic acids are known to bind cyanide in aqueous solution (see ref 9), electrochemical studies of 16 in an acetonitrile solution suggest a significant cyanide binding event only for the oxidized ferrocenium species $[16]^+$.