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AND/NOT Sensing of Fluoride and Cyanide Ions by Ferrocene-Derivatised Lewis Acids

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The selective detection of cyanide and fluoride ions, and of their conjugate acids HCN and HF, constitute fundamental chemical challenges with significant potential environmental and health benefits.[1,2] While considerable research effort has been expended on the development of sensors for fluoride and/or HF, encompassing a range of host–guest strategies to bind the target analyte,[3–5] cyanide detection has received less attention.[6–10] Nevertheless, a number of cyanide receptors has recently been reported incorporating, for example, an appropriately spaced array of Lewis acidic centres,[9a,b] and the affinity of cyanide for three-coordinate boranes (even in the presence of water) has been known for more than 45 years.[11] In similar vein, the groups of both Jäkle and Gabbaï have more recently demonstrated the use of Lewis acid receptors containing the -$BMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$) function to detect cyanide,[5k,6c] in one case offering remarkable, selective binding in aqueous solution.[6c]

Given the facts that i) systems of the type $ArBMes_2$ are known to be air- and moisture-stable; ii) under appropriate conditions such compounds can bind cyanide;[5k,6c] and iii) ferrocene-functionalised boranes are known to undergo large electrochemical shifts on anion binding,[4a,k] we have set out to investigate the electrochemical detection of cyanide using ferrocenyl boranes. Moreover, given that an electrochemical response, coupled with an appropriate redox-active organic dye, can be used to produce an amplified colorimetric output,[4b] we have targeted systems capable of colorimetric sensing. Importantly, by exploiting the readily tuneable Lewis acidity of simple ferrocenylboranes, we report a two-component sensor system which offers a logical (colorimetric) solution to the problematic issue of discriminating between fluoride and cyanide.

The air-stable ferrocene-functionalised borane $FcBMes_2$ (**1a**, Fc = (η^5-C_5H_4)Fe(η^5-C_5H_5); Mes = 2,4,6-$Me_3C_6H_2$) is readily synthesised in 60% isolated yield from $FcBBr_2$ and excess mesityllithium, representing an overall conversion of about 50% for the simple two-step synthesis from ferrocene itself (Scheme 1).[12] Compound **1a** was characterised by standard spectroscopic and analytical techniques and its structure in the solid state confirmed by single-crystal X-ray diffraction. Similar chemistry can also be used to give access to the corresponding pentamethylated derivative Fc^*BMes_2 (**1b**, Fc* = (η^5-C_5H_4)Fe(η^5-C_5Me_5)) (see Supporting Information for the characterisation data for **1b** and the structural data for **1a**).

The binding of cyanide (as either KCN/[18]crown-6 or [$n$$Bu_4N$]$^+$[CN]$^-$·2$H_2O$)[13] by **1a** in a range of solvents (chloroform, dichloromethane, acetonitrile) can readily be demonstrated/quantified by a combination of spectroscopic techniques. Thus, the changes in ^{11}B NMR chemical shift (δ_B = 76 to −16 ppm) and IR-detected ν(CN) stretching frequency (2080 to 2162 cm^{-1}) are in line with previous reports of cyanide complexation to boron-based Lewis acids.[6c] In addition, negative-ion ESI-MS sampling of the reaction mixture reveals a 'flag-pole' mass spectrum with an isotopic profile and measured exact mass consistent with the formulation [**1a**·CN]$^-$(see Supporting Information). Moreover, the thermodynamics of cyanide binding by **1a** can readily be assessed by monitoring the intensity of the band at 510 nm (in the UV/Vis spectrum of **1a**) as a function of the concentration of added cyanide. A binding constant of 8.3(2.0)× 10^4 mol^{-1} dm^3 can be determined by fitting the resulting curve of absorbance versus cyanide concentration in dichloromethane solution (see Supporting Information). This value is significantly less than that reported for the cationic receptor [4-$Me_3NC_6H_4BMes_2$]$^+$ (4×10^8 mol^{-1} dm^3 in water/DMSO) or for derivatised 4,4′-bipy$BMes_2$ systems (5× 10^7 mol^{-1} dm^3 in THF).[6c,e] That said, THF has been report-

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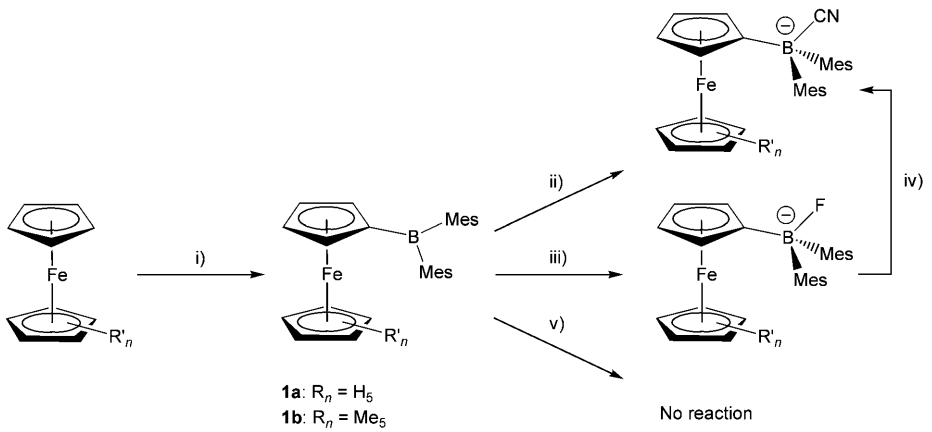

Scheme 1. Syntheses and anion complexation behaviour of ferrocene-functionalised Lewis acids **1a** and **1b**. Key reagents and conditions: i) a) BBr_3, hexanes (as per reference 12), ca. 90%; b) MesLi (2.6 equiv), diethyl ether, 20°C, 18 h, 44-62%; ii) $[nBu_4N]^+[CN]^-\cdot 2H_2O$ or KCN/[18]crown-6; iii) $[nBu_4N]^+F^-\cdot 4H_2O$ or KF/[18]crown-6; iii) excess (>10 equiv) $[nBu_4N]^+[CN]^-\cdot 2H_2O$; iv) sources of other anions for example, $[Ph_3PNPPh_3]^+Cl^-$.

ed to be a less strongly competitive solvent than chlorocarbons,[14] and the effect of net charge is known to strongly influence the thermodynamics of anion complexation; an enhancement of about two orders of magnitude in the cyanide binding constant is observed for cationic derivatives related to **1a**.[14]

Structural authentication of the mode of cyanide binding has been obtained by X-ray crystallography (Figure 1) with the solid-state structure of crystals obtained from a mixed chloroform/hexanes solvent system revealing i) an essentially linear C-bound cyanide complex with metrical parameters for the BCN unit in agreement with previous reports of cyanide/borane complexes (d(B–C) = 1.621(3) Å, ∢B-C-N = 169.8(3)°);[6c,e,15] ii) intermolecular hydrogen bonding between the cyanide nitrogen and a molecule of chloroform solvent (d(N···H) = 2.143 Å; d(N···C) = 3.085(3) Å; ∢C-N···C = 151.5(2)°); and iii) significant elongation of the B–C_{ipso} bond on cyanide binding (d(B–C_{ipso}) = 1.639(4) Å, c.f. 1.546(7) Å for the free receptor **1a**). The latter structural response is consistent with the conversion of a pendant three-coordinate boryl Lewis acid to an anionic four-coordinate borate, and is mirrored by changes in electrochemical behaviour. Thus, a cathodic shift of about −560 mV is measured for **1a** in the presence of cyanide ($E_{1/2}$ = −383 (100) and +181 (80) mV for [**1a**·CN]$^-$and **1a**, respectively),[16] which mirrors the behaviour of related ferrocene-derivatised Lewis acids on coordination of bases such as fluoride or trimethylphosphine (Figure 2).[4a,k,17]

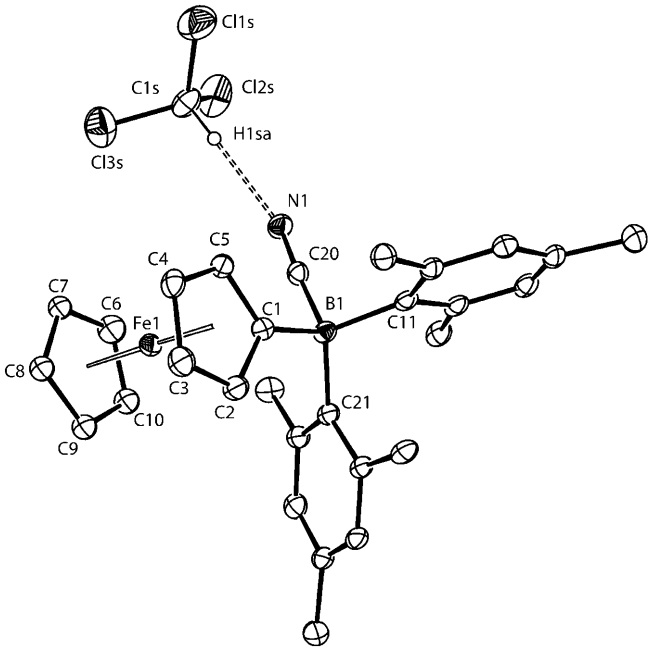

Figure 1. Structure of the anionic component and hydrogen-bonded chloroform solvate of $[nBu_4N]^+$[**1a**·CN]$^-$·$CHCl_3$; cation and hydrogen atoms (except that connected to C1s) omitted from clarity and ORTEP ellipsoids set at the 50% probability level. Relevant bond lengths [Å] and angles [°]: C1–B1 1.639(4), B1–C11 1.672(4), B1–C21 1.661(4), B1–C20 1.621(3), N1–C20 1.150(3), N1–H1sa 2.143, C1sa–H1sa 1.000, N1–C1sa 3.085(3); B1-C20-N1 169.8(3),C20-N1-C1s 151.5(2), C_5H_4 centroid-C1-B1 177.4(2).

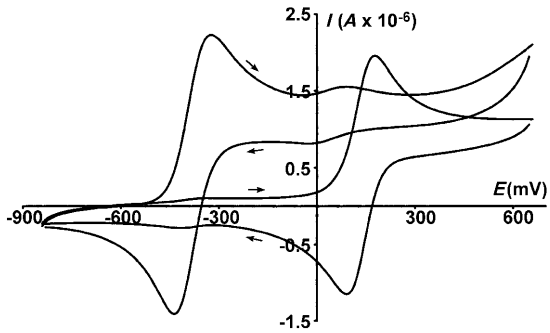

Figure 2. Cyclic voltammograms of acetonitrile solutions of **1a** in the absence (right) and presence (left) of added cyanide.

In terms of the development of a simple colorimetric sensor for cyanide, Lewis acid **1a**—although clearly competent for binding of the target anion—suffers from two practical problems: i) the reporter response is electrochemical but not colorimetric; and ii) a similar reporter response is observed with the potentially competitive analyte fluoride (although not for other anions). These challenges are dealt with in turn.

Simple ferrocene-based colorimetric sensors have been developed (for example, for fluoride) that rely on an electrochemical shift on anion binding which is sufficient to

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render the resulting host–guest complex susceptible to aerobic oxidation. A simple orange to green colour change results from the oxidation of the ferrocene chromophore.[4k] Although the redox potential measured for [**1a**·CN]$^-$ is *not* compatible with oxidation by atmospheric oxygen,[18] the use of the pentamethylated analogue **1b** results in a cathodic shift of about −300 mV in the redox potentials of *both* the free receptor and the cyanide adduct. Thus, **1b** and [**1b**·CN]$^-$are oxidised at −176(75) and −691(95) mV,[16] thereby offering a convenient electrochemical window for choice of a redox-matched oxidant which will oxidise the desired cyanide adduct but not the 'free' receptor.[4b] An attractive class of oxidant in this regard is the tetrazolium dyes, which, in addition to offering a range of compatible redox potentials, offer a vastly enhanced change in extinction coefficient (and hence greater sensitivity). Thus, the results of monitoring the exposure of **1b** to either cyanide or fluoride, in the presence of the compatible redox-active dye tetrazolium violet, both by UV/Vis spectroscopy and colorimetrically are shown in Figure 3a, 3b and 4. As such, **1b** 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 down to 25-40 nmol of analyte.

The competing sensor response of **1a**/**1b** with fluoride can readily be understood in terms of the known (high) B–F bond strength,[19] and quantified by a binding constant for **1a** with fluoride in dichloromethane solution (determined from UV/Vis based titration data) of $7.8(1.2)\times10^4$ mol^{-1} dm^3. This value is similar to those measured previously for the related Lewis acids $BMes_3$ and tris(9-anthryl)borane in tetrahydrofuran ($3.3(0.4)\times10^5$ and $2.8(0.3)\times10^5$ mol^{-1} dm^3, respectively).[5a,e] Although the binding constants for **1a** with fluoride and cyanide cannot be separated within experimental error, stronger binding of cyanide is implied by ^{11}B NMR-monitored competition experiments. While the positive sensor responses demonstrated by dimesitylboryl complexes **1a** and **1b** are characteristic of both fluoride and cyanide, discrimination *can* be achieved by the use of a weaker Lewis acid receptor. Thus, the stilbene diolate boronic ester analogues of **1a** and **1b**, $FcB(OR)_2$ and $Fc^*B(OR)_2$ (**2a**,**b**: $(OR)_2 = R,R$-OC(H)PhC(H)PhO, see Scheme 2) can be shown to undergo an electrochemical shift of about −600 mV on fluoride binding (for example, from −169(80) to −749(95) mV for **2b**).[16] In combination with the same tetrazolium violet redox dye a colorimetric response is therefore generated on exposure of **2b** to fluoride. By contrast, a null response is observed when excess cyanide is added to solutions of **2b** in acetonitrile/methanol under identical conditions (Figure 3c, 3d and 4).[20] Thus, while the stronger Lewis acid **1b** gives positive colorimetric responses to both cyanide AND fluoride, **2b** senses fluoride but NOT cyanide under the same conditions.

In conclusion we have demonstrated that, by appropriate tuning of ferrocene-derivatised Lewis acids, together with the incorporation of a suitable redox-matched organic dye, a two-component sensor system can be developed capable of colorimetrically signalling the presence of fluoride and cyanide ions in organic solution by Boolean AND/NOT logic.

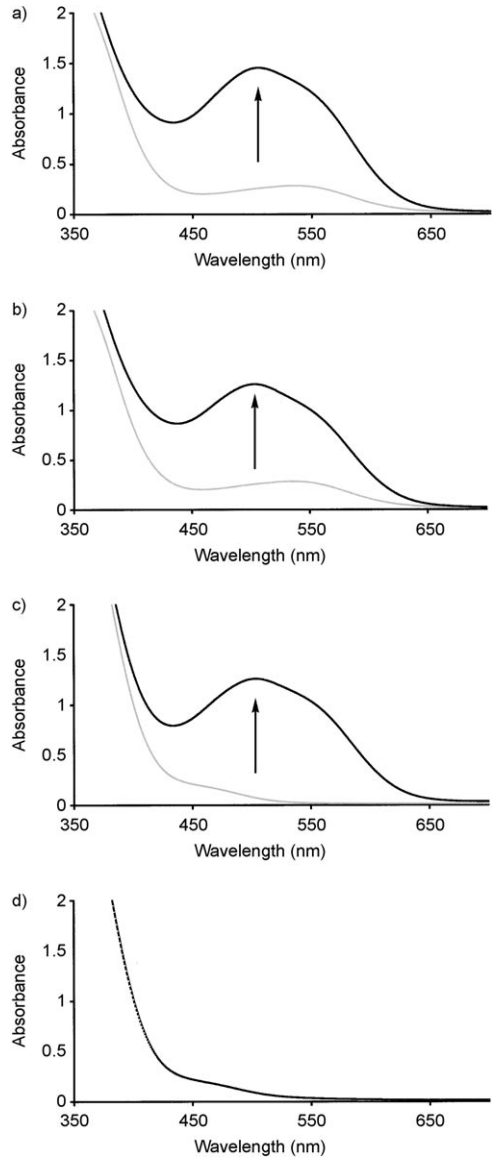

Figure 3. UV/Vis spectra of acetonitrile/methanol (>100:1) solutions containing Lewis acid receptors **1b** or **2b** (0.5 mM) and tetrazolium violet (1.0 mM) in the absence (grey trace) and presence (black trace) of added anion: a) **1b** with F$^-$; b) **1b** with CN$^-$; c) **2b** with F$^-$; d) **2b** with CN$^-$.

Figure 4. Colorimetric responses of receptor molecules **1b** and **2b** to 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.

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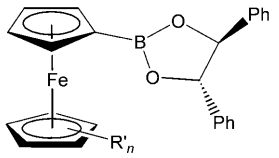

2a: $R_n = H_5$
2b: $R_n = Me_5$

Scheme 2. Stilbene diolate functionalised boronic esters **2a** and **2b**.

Experimental Section

Included here are the synthetic and characterizing data for compounds **1a** and $[n\mathrm{Bu_4N}]^+[\mathbf{1a}\cdot\mathrm{CN}]^-$. Included in the Supporting Information are: crystallographic data for **1a**; binding constant determinations for **1a** with $CN^-$and F^-; and preparative and spectroscopic data for **1b** and $[n\mathrm{Bu_4N}]^+[\mathbf{1b}\cdot\mathrm{CN}]^-$.

$FcBMes_2$ (1a): Mesityllithium (2.6 equiv) in diethyl ether (ca. 50 mL) was added dropwise to a solution of $FcBBr_2$ (2.00 g, 5.62 mmol) in diethyl ether (50 mL) and the reaction mixture stirred for 18 h. At this point ^{11}B NMR spectroscopy indicated complete conversion to a single product ($\delta_B = 75.8$ ppm). After removal of volatiles in vacuo, extraction into hexanes (ca. 50 mL) and cooling to −30 °C, **1a** was obtained as a red powder (yield: 1.52 g, 62 %). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of pentanes from a concentrated solution. ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C): $\delta = 1.91$ (s, 6H, *para*-CH_3 of Mes), 2.21 (s, 12H, *ortho*-CH_3 of Mes), 3.65 (s, 5H, Cp), 4.09 (m, 2H, CH of C_5H_4), 4.26 (m, 2H, CH of C_5H_4), 6.54 ppm (s, 4H, aromatic CH of Mes); ^{13}C NMR (126 MHz, [D$_6$]benzene, 20 °C): $\delta = 21.0$ (*para*-CH_3 of Mes), 24.7 (*ortho*-CH_3 of Mes), 69.6 (Cp), 73.8, 79.6 (C_5H_4), 128.7 (aromatic CH of Mes), 137.9 (*para*-quaternary of Mes), 139.2 ppm (*ortho*-quaternary of Mes), boron-bound quaternary carbons not observed; ^{11}B (96 MHz, [D$_6$]benzene, 20 °C): $\delta = 76$; MS (EI): 434.2 ([M^+], 100 %), exact mass (calcd for ^{10}B isotopomer) 433.1899, (obs.) 433.1896; UV/Vis (CH_3CN): $\lambda_{max} = 510$ nm, $\varepsilon = 1310$ mol^{-1}cm^{-1} dm^3; $E_{1/2}$ versus FcH/FcH$^+$ (peak-to-peak separation) = +181 (80) mV in CH_3CN.

$[n\mathrm{Bu_4N}]^+[\mathrm{FcBMes_2CN}]^-$ that is, $[n\mathrm{Bu_4N}]^+[\mathbf{1a}\cdot\mathrm{CN}]^-$: A mixture of **1a** (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 ^{11}B NMR spectroscopy (quantitative conversion to a single resonance at $\delta_B = -16$ ppm). Layering of the reaction mixture with diethyl ether led to the formation of $[n\mathrm{Bu_4N}]^+[\mathbf{1a}\cdot\mathrm{CN}]^-$as orange crystals suitable for X-ray diffraction (yield: 0.089 g, 90 %). ^{1}H NMR (300 MHz, [D]chloroform, 20 °C): $\delta = 0.95$ (m, 12H, CH_3 of $[n\mathrm{Bu_4N}]^+$), 1.36 (m, 8H, CH_2 of $[n\mathrm{Bu_4N}]^+$), 1.46 (m, 8H, CH_2 of $[n\mathrm{Bu_4N}]^+$), 2.09 (s, 18H, *ortho*- and *para*-CH_3 of Mes), 2.92 (m, 8H, NCH_2 of $[n\mathrm{Bu_4N}]^+$), 3.90 (s, 5H, Cp), 4.02 (m, 2H, CH of C_5H_4), 4.1 (br m, 2H, CH of C_5H_4), 6.48 ppm (s, 4H, aromatic CH of Mes); ^{13}C NMR (126 MHz, [D]chloroform, 20 °C): $\delta = 13.8$ (CH_3 of $[n\mathrm{Bu_4N}]^+$), 19.8, 24.1 (CH_2 of $[n\mathrm{Bu_4N}]^+$), 20.9 (*para*-CH_3 of Mes), 25.5 (br, *ortho*-CH_3 of Mes), 58.6 (NCH_2 of $[n\mathrm{Bu_4N}]^+$), 68.1 (Cp), 67.4, 75.5 (C_5H_4), 128.9 (aromatic CH of Mes), 131.3 (*para*-quaternary of Mes), 141.7 (*ortho*-quaternary of Mes), 176.0 ppm (CN^-), boron-bound quaternary carbons not observed; ^{11}B (96 MHz, [D]chloroform, 20 °C): $\delta = -16.1$ ppm. MS (ES negative-ion mode): 460.2 ([$\mathbf{1a}\cdot\mathrm{CN}]^-$, 100 %), exact mass (calcd for ^{10}B, ^{54}Fe isotopomer) 457.1995, (obs.) 457.1988; elemental analysis (calcd for $C_{46}H_{68}BCl_3FeN_2$ that is, $[n\mathrm{Bu_4N}]^+[\mathbf{1a}\cdot\mathrm{CN}]^-\cdot CHCl_3$): C 67.21, H 8.34, N 3.41; found: C 66.83, H 8.28, N 3.23; UV/Vis ($CHCl_3$): $\lambda_{max} = 460$ nm, $\varepsilon = 170$ mol^{-1}cm^{-1} dm^3; IR (CH_2Cl_2): $\tilde{\nu} = 2162$ cm^{-1} st, ν(CN); $E_{1/2}$ vs. FcH/FcH$^+$ (peak-to-peak separation) = −383 (100) mV in CH_3CN. Crystallographic data (for $[n\mathrm{Bu_4N}]^+[\mathbf{1a}\cdot\mathrm{CN}]^-\cdot CHCl_3$): $C_{46}H_{68}BCl_3FeN_2$, $M_r = 822.03$, monoclinic, $P2_1/c$, $a = 11.9509(2)$, $b = 17.2939(2)$, $c = 21.5289(4)$ Å, $\beta = 92.344(1)°$, $V = 4445.82(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.228$ Mg m^{-3}, $T = 150(2)$ K, $\lambda = 0.71073$ Å. A total of 38935 reflections collected, 9981 independent [R(int) = 0.0778], which were used in all calculations. $R_1 = 0.0528$, $wR_2 = 0.1115$ for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1 = 0.1075$, $wR_2 = 0.1320$ for all unique reflections. Max. and min. residual electron densities 0.51 and −0.46 e Å^{-3}. CCDC 671666 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: boron · boryl compounds · cyanides · ferrocene · fluorides · Lewis acids · sensors

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[14] a) A fluoride binding constant of $3.3(0.4)\times 10^5\,\mathrm{mol}^{-1}\,\mathrm{dm}^3$ has been determined for $BMes_3$ in THF,[5e] while a null response was observed for the same receptor/analyte combination in chloroform[5e] or dichloromethane. b) We have determined a cyanide binding constant of about $10^7\,\mathrm{mol}^{-1}\mathrm{dm}^3$ for $[CpFe\{1,2\text{-}C_5H_3(CH_2NMe_3)BMes_2\}]^+$ in acetonitrile solution by UV/Vis titration methods.

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$E_{1/2} = -1000$ mV versus ferrocenium/ferrocene in DMF, while for $O_2 + H^+ + e^- \rightarrow HO_2$
$E_{1/2} = -280$ mV versus ferrocenium/ferrocene (also in DMF). For the oxidation of cyanide or fluoride adducts of borylated ferrocenes occurring in organic media (e.g. dichloromethane or acetonitrile), the use of $[n\mathrm{Bu}_4\mathrm{N}]\mathrm{X}\cdot x\mathrm{H}_2\mathrm{O}$ (X = CN, F)[13] as the cyanide/fluoride source inevitably introduces a protic component to the reaction mixture, thereby making O_2 a stronger oxidant, than would be anticipated in strictly aprotic media. D. T. Sawyer, J. S. Valentine, *Acc. Chem. Res.* **1981**, *14*, 393–400.

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