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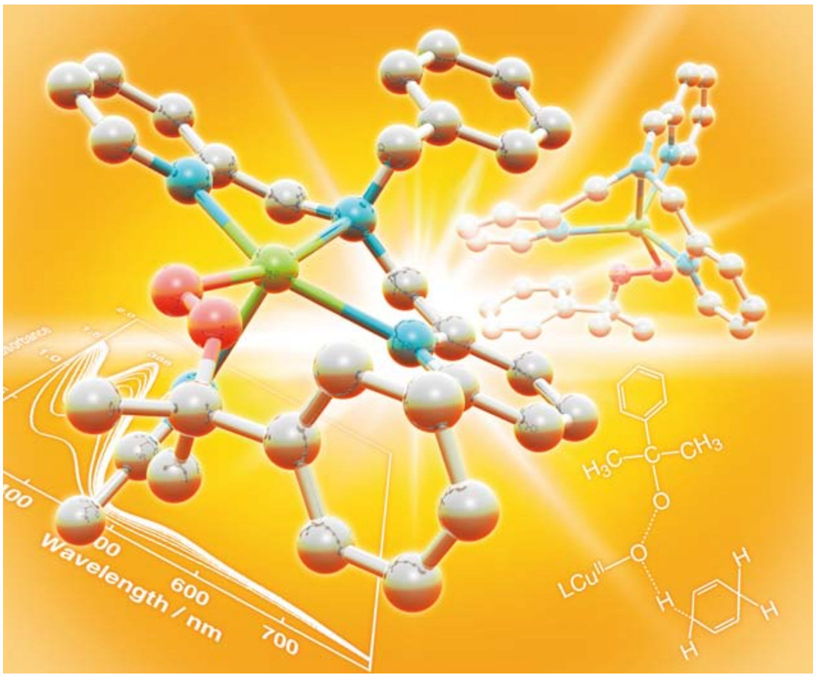

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PAPER

Probing the influence of steric bulk on anion binding by triarylboranes: comparative studies of FcB(*o*-Tol)$_2$, FcB(*o*-Xyl)$_2$ and FcBMes$_2$†

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Steric crowding brought about on pyramidalization at boron has been predicted computationally to be of central importance to the strength and selectivity of anion binding by triarylboranes. The role of steric factors in systems containing a ferrocenyl reporter unit has been systematically probed in the current study by comparison of the F^-/CN^- binding properties of FcB(*o*-Tol)$_2$ (**1**, *o*-Tol = C_6H_4Me-2), FcB(*o*-Xyl)$_2$ (**2**, *o*-Xyl = $C_6H_3Me_2$-2,6) and FcBMes$_2$ (**3**, Mes = $C_6H_2Me_3$-2,4,6)), both in solution and in the solid state. Somewhat surprisingly, the inclusion of an extra *ortho*-methyl aryl substituent (*e.g.* for **2**/**3** *vs.* **1**) is found to have a relatively small effect on the binding affinities of these boranes (*e.g.* $\log_{10}K_{CN}$ = 5.94(0.02), 4.73(0.01), 5.56(0.02), for **1**, **2** and **3** respectively). Consistent with this observation, the degree of pyramidalization at boron determined for the cyanide adducts [**1**·CN]$^-$, [**2**·CN]$^-$ and [**3**·CN]$^-$ in the solid state is also found to be essentially invariant ($\angle C_{aryl}$–B–C_{aryl} = 338, 337, 337°, respectively), as are the B–CN and mean B–C_{aryl} distances. In the solid state at least, it is apparent that the adverse steric effects potentially brought about by increasing *ortho* substitution are mitigated by a greater degree of synchronous rotation of the aryl substituents about the B–C_{aryl} bonds. Thus a mean inter-plane angle of 71° is observed for [**1**·CN]$^-$ while the corresponding values for [**2**·CN]$^-$ and [**3**·CN]$^-$ are 78° and 79°.

Introduction

In landmark recent studies triarylboranes have been successfully exploited as sensor systems for the environmentally relevant anions fluoride and cyanide.[1–9] In part, such applications rely on the inherent strength of the host/guest interaction (*e.g.* 345 kJ mol^{-1} for the binding of F^- to Ph$_3$B),[10] which offers the basis for overcoming fundamental challenges in supramolecular chemistry, such as the detection of the highly solvated fluoride ion in water.[3s] Thus, borane-based sensors have been reported which capture fluoride from protic media, with a number of these systems even being capable of workable sensing in water itself.[4z] Typically, such receptors are of the form ArBMes$_2$ (Mes = $C_6H_2Me_3$-2,4,6) reflecting not only their high binding affinities for F^-/CN^-, but also their stability to air and moisture.[4,7] Moreover, even simple systems of this type (*i.e.* those lacking in further functionalization) have been shown to display a degree of selectivity in their binding properties, with larger, less basic anions exhibiting very low affinities.[3s] This selectivity is thought to reflect the pyramidalization inherent at boron on formation of the host/guest complex, and the consequent increase in steric repulsion between the aryl substituents. Thus, only small anions (F^-, CN^-, OH^-, N_3^-) which limit the extent to which such interactions can develop, typically bind to ArBMes$_2$ derivatives.[3s]

From the point of view of the receptor itself, the extent to which steric factors can influence binding constants has been predicted computationally, *e.g.* by calculation of the gas-phase fluoride binding enthalpies of Ph$_3$B and PhBMes$_2$ (ΔH = –345 and –269 kJ mol^{-1}, respectively),[10,5x] and the geometric parameters for the adducts [Ph$_3$B·F]$^-$ and [PhBMes$_2$·F]$^-$. If entropic factors are assumed to be comparable, the difference ($\Delta\Delta H$) of –76 kJ mol^{-1} in the fluoride ion affinity for the two compounds points to a difference in $\log_{10}K_F$ of *ca.* 13 orders of magnitude (albeit in the gas phase). Moreover the lower binding affinity of PhBMes$_2$ is also reflected in calculated structural parameters for the F^- adducts which reveal (i) a smaller degree of pyramidalization at the boron centre and (ii) a slightly extended B–F bond in [PhBMes$_2$·F]$^-$ compared to [Ph$_3$B·F]$^-$ [∠C–B–C = 341, 333°, *d*(B–F) = 1.491, 1.465 Å, respectively].[10a,5x]

With sensing applications in mind, related derivatives in which one of the aryl groups is a ferrocenyl function (*e.g.* FcBMes$_2$)[7f,7j] offer additional benefits relating to electrochemical or colorimetric reporting of the anion binding event.[11] As such, we have sought to probe experimentally the influence of steric factors on anion

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† Electronic supplementary information (ESI) available: Details of binding constant determinations for **1**, **2** and **3**. CCDC reference numbers 809729–80973. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10185d

binding by systems of the type $FcBAr_2$. In particular, we have set out to evaluate the consequences of variation in the number of *para*- and more importantly *ortho*- substituents in determining the steric profile of the aryl groups. Thus, in the current manuscript we report comparative studies of fluoride and cyanide binding by $FcB(o\text{-Tol})_2$ (**1**; *o*-Tol = C_6H_4Me-2), $FcB(o\text{-Xyl})_2$ (**2**, *o*-Xyl = $C_6H_3Me_2$-2,6) and $FcBMes_2$ (**3**) in solution and in the solid state. For these systems at least, the effect of increasing *ortho* substitution is shown to be rather smaller, reflecting conformational flexibility about the $B–C_{aryl}$ bonds, and a consequent ability to minimize adverse steric effects.

Experimental

General considerations and physical methods

Manipulations of air-sensitive reagents were carried out in a glove-box, or by means of Schlenk-type techniques involving the use of a dry argon or nitrogen atmosphere. HPLC grade solvents were purified, dried and degassed prior to use by a commercial available Braun Solvent Purification System (SPS 500). The known compounds $FcBBr_2$[12] and *o*-TolLi[13] were prepared according to literature procedures. ^1H and ^{13}C NMR spectra were measured on a Bruker AVII 500 FT-NMR or Varian Mercury VX-300 spectrometer with [D]chloroform as the solvent. ^1H and ^{13}C NMR spectra were calibrated using the residual proton or natural abundance ^{13}C resonances of [D]chloroform (δ_H = 7.26 ppm, δ_C = 77.0 ppm). Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, Swansea University. Elemental microanalysis was carried out at London Metropolitan University.

Synthesis

1: A solution of *o*-TolLi (1.00 g, 10 mmol) in diethyl ether was added to a solution of $FcBBr_2$ (1.45 g, 4 mmol) also in diethyl ether, and the reaction mixture stirred at room temperature for 15 h. Subsequently, volatiles were removed *in vacuo*, the product extracted into hexane, and single crystals of **1** obtained after concentration to near saturation and cooling to −35 °C. Yield 1.17 g (3.1 mmol, 76%).

^1H NMR (500 MHz, [D]chloroform, 20 °C, ppm) δ_H = 7.75 (dd, 2H, J = 1.3, 7.2 Hz, CH^6), 7.27 (dt, 2H, J = 1.6, 7.4 Hz, CH^4), 7.22 (t, 2H, J = 6.8 Hz, CH^5), 7.13 (d, 2H, J = 7.5 Hz, CH^3), 4.77 (t, 2H, J = 1.9, C_5H_4), 4.36 (t, 2H, J = 1.8, C_5H_4), 4.23 (s, 5H, C_5H_5), 2.18 (s, 6H, CH_3 of Tol). ^{13}C NMR (75 MHz, [D]chloroform, 20 °C, ppm) δ_C = 145.5 (br, C^1 of Tol), 140.0 (C^2 of Tol), 132.4 (C^6 of Tol), 129.6 (C^3 of Tol), 128.3 (C^4 of Tol), 124.2 (C^5 of Tol), 78.0 (C_5H_4), 75.5 (C_5H_4), 69.3 (C_5H_5), 23.1 (CH_3 of Tol). The boron bound carbon atom of C_5H_4 could not be observed. ^{11}B (96 MHz, [D]chloroform, 20 °C, ppm): δ_B = 70. UV/Vis: λ_{max} = 480 nm, ε = 12200 dm^2 mol^{-1}. MS (EI$^-$): M$^+$ mass (calc. for M$^+$, ^{10}B isotopomer) 378.1, (meas.) 378.1 (100%). Elemental microanalysis (%): (calc. for $C_{24}H_{23}BFe$) C 76.24, H 6.13; (meas.) C 76.18 H 6.09.

[K(18-crown-6)][**1**·CN] and [K(18-crown-6)][**1**·F]: The two compounds were prepared by analogous methods from KCN and KF, exemplified here for [K(18-crown-6)][**1**·CN]. To a solution of **1** (0.140 g, 0.37 mmol) in chloroform was added KCN (0.048 g, 0.74 mmol) and 18-crown-6 (0.098 g, 0.37 mmol), and the reaction mixture stirred at room temperature for 15 h. Subsequently the solution was layered with hexane to yield K(18-crown-6)][**1**·CN] as single crystals suitable for X-ray diffraction. Although ^{11}B and ^1H NMR monitoring of the reaction reveals quantitative conversion of **1** to its cyanide adduct, the much lower isolated yield of single crystals reflects its intrinsic solubility. Yield 0.016 g (0.023 mmol, 6%). Spectroscopic data: ^1H NMR (300 MHz, [D]chloroform, 20 °C, ppm) δ_H = 7.64 (d, 2H, J = 7.2 Hz, CH^6 of Tol), 6.92 (m, 6H, CH^3, CH^4 and CH^5 of Tol), 4.16 (s br, 2H, C_5H_4), 4.11 (s, 5H, C_5H_5), 4.05 (s br, 2H, C_5H_4), 3.56 (s, 24H, OCH_2), 2.91 (s, 6H, CH_3 of Tol). ^{13}C NMR (75 MHz, [D]chloroform, 20 °C, ppm) δ_C = 154.2 (br, C^1 of Tol), 141.8 (C^2 of Tol), 135.0 (C^6 of Tol), 128.6, 123.6, 123.4 (CH of Tol), 73.8 (C_5H_4), 69.9 (OCH_2), 67.9 (C_5H_5), 67.2 (C_5H_4), 23.3 (CH_3 of Tol). The boron bound carbon atom of C_5H_4 could not be observed. ^{11}B (96 MHz, [D]chloroform, 20 °C, ppm): δ_B = −14. UV/Vis: λ_{max} = 445 nm, ε = 1500 dm^2 mol^{-1}. MS (ESI$^+$): exact mass (calc. for M$^+$) 303.1204, (meas.) 303.1201 (100%). MS (ESI$^-$): M$^-$ exact mass (calc. for M$^-$, ^{10}B isotopomer) 401.1226, (meas.) 401.1365. Spectroscopic data for [K(18-crown-6)][**1**·F]: ^1H NMR (300 MHz, [D]chloroform, 20 °C, ppm) δ_H = 7.58 (dd, 2H, J = 1.3, 7.2 Hz, CH^6), 6.92 (m, 6H, CH^3, CH^4 and CH^5 of Tol), 4.08 (s br, 2H, C_5H_4), 4.00 (s br, 2H, C_5H_4), 3.90 (s, 5H, C_5H_5), 3.56 (s, 24H, OCH_2), 1.99 (s, 6H, CH_3 of Tol). ^{13}C NMR (75 MHz, [D]chloroform, 20 °C, ppm) δ_C = 158.2 (br., C^1 of Tol), 140.6 (d, J = 1.4 Hz, C^2 of Tol), 133.6 (d, J = 7.3 Hz, C^6), 128.4, 123.4, 123.2 (CH of Tol), 72.5 (d, J = 3.5, C_5H_4), 70.1 (OCH_2), 67.3 (C_5H_5), 66.8 (C_5H_4), 23.3 (CH_3). The boron bound carbon atom of C_5H_4 could not be observed. ^{11}B (96 MHz, [D]chloroform, 20 °C, ppm): δ_B = 5. ^{19}F NMR (282 MHz, [D]chloroform, 20 °C, ppm) δ_F = −185 (br). UV/Vis: λ_{max} = 448 nm, ε = 1000 dm^2 mol^{-1}. MS (ESI$^+$): M$^+$ exact mass (calc. for M$^+$, ^{10}B isotopomer) 303.1204, (meas.) 303.1202 (100%). MS (ESI$^-$): M$^-$ exact mass (calc. for M$^-$, ^{10}B isotopomer) 397.1226, (meas.) 397.1232.

Crystallographic data†

1: M_r = 378.10, Orthorhombic, $Pna2_1$, a = 15.3409(6) Å, b = 7.4354(3) Å, c = 16.5260(7) Å, V = 1885.05(13) Å^3, Z = 2, ρ_c = 1.322 Mg m^{-3}, T = 150 K, λ = 0.71073 Å, 13079 reflections collected, 2211 independent [R(int) = 0.070]. R_1 = 0.0425, wR_2 = 0.1130 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0488, wR_2 = 0.1183 for all unique reflections. Max. and min. residual electron densities 0.56 and −0.46 e Å^{-3}. CCDC reference: 809729.

[K(18-crown-6)][**1**·CN]: M_r = 707.54, Triclinic, $P\bar{1}$, a = 11.5278(2) Å, b = 13.2927(2) Å, c = 13.7154(2) Å, α = 84.1631(7)°, β = 71.6023(7)°, γ = 65.2619(7)°, V = 1810.13(5) Å^3, Z = 2, ρ_c = 1.298 Mg m^{-3}, T = 150 K, λ = 0.71073 Å, 25142 reflections collected, 8175 independent, [R(int) = 0.032]. R_1 = 0.0369, wR_2 = 0.0820 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0536, wR_2 = 0.0897 for all unique reflections. Max. and min. residual electron densities 0.52 and −0.45 e Å^{-3}. CCDC reference: 809730.

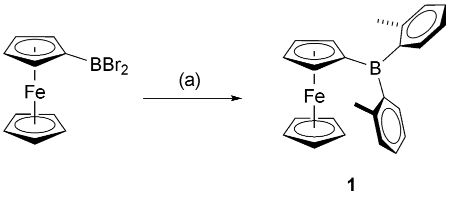
[K(18-crown-6)][**1**·F]: M_r = 819.90, Monoclinic, $P2_1$, a = 8.55170(10) Å, b = 22.6990(3) Å, c = 10.3460(2) Å, β = 101.3943(5)°, V = 1968.73(5) Å^3, Z = 2, ρ_c = 1.383 Mg m^{-3}, T = 150 K, λ = 0.71073 Å, 27162 reflections collected, 8428 independent [R(int) = 0.050]. R_1 = 0.0361, wR_2 = 0.0719 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and R_1 = 0.0492, wR_2 = 0.0780 for all unique reflections. Max. and min. residual electron densities 0.65 and −0.65 e Å^{-3}. CCDC reference: 809731.

Binding constant determination

Typical protocol: 3 mL of a solution of **1** in dichloromethane (typically 0.4–0.6 μM) were placed in the cell and aliquots of $[^nBu_4N]F\cdot4H_2O$ or $[^nBu_4N]CN\cdot2H_2O$ in dichloromethane added (typically 10–20 μL of a 10–15 μM solution). The solution was stirred for 1 min after each addition and the UV-vis spectrum then measured. The program ReactLab Equilibria was subsequently used to determine the binding constants, with data being fitted over the wavelength range 430–530 nm.[14] Full details are available in the ESI.

Results and discussion

The synthesis of **1** can be accomplished in a manner similar to that previously described for **2** and **3**.[7j] Thus, the reaction between $FcBBr_2$ and a slight excess of *o*-tolyl lithium leads to the formation of **1** in reasonable (76%) yield after recrystallisation from hexane (Scheme 1).



Scheme 1 Synthesis of **1**; key reagents and conditions: (a) *o*-TolLi (2.5 equiv.), Et_2O, room temperature, 15 h, 76% after recrystallization from hexane.

Characterisation of the product by multinuclear NMR, mass spectrometry, elemental microanalysis and single crystal X-ray diffraction is consistent with its formulation as **1**. The ^{11}B NMR spectrum, for example, shows a broad peak at $\delta_B = 70$ ppm, in the region expected for tri-coordinate boron species featuring two aryl and one ferrocenyl substituents.[7j,7f] In contrast to **2** and **3**, however, **1** is slowly decomposed by moisture in solution, presumably due to the lack of steric protection afforded by a second methyl substituent in the *ortho* position.

The structure of **1** determined by X-ray crystallography is shown in Fig. 1; the aryl groups are aligned in a propeller type arrangement, with the angles between the least squares planes defined by the *o*-tolyl groups and that of the η^5-C_5H_4 substituent being 63° and 62°. The sum of the CBC angles is 359°, consistent with the expected planar tri-coordinate geometry at boron. Notably, there are no significant differences between the solid state structure of **1** and that of **3**; in particular the B–C_{Cp} [1.522(8) and 1.546(7) Å, respectively] and B–C_{aryl} distances [1.577(8), 1.582(9) and 1.581(7), 1.597(7) Å] and the inter-plane torsion angles defining the propeller conformation [63, 62 and 62, 62°] are essentially identical for both receptor compounds.[7j]

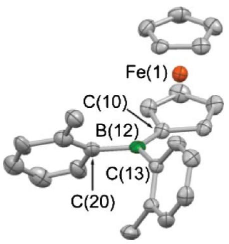


Fig. 1 Molecular structure of **1** with hydrogen atoms omitted for clarity and thermal ellipsoids set at the 40% level. Selected bond length (Å) and angles (°): C(20)–B(12) = 1.582(9), B(12)C(13) = 1.577(8), B(12)–C(10) = 1.522(8), C(20)–B(12)–C(13) = 119.6(5), C(13)–B(12)–C(10) = 122.2(5), C(10)–B(12)–C(20) = 117.7(5).

The response of **1** to the presence of cyanide or fluoride was investigated by a combination of spectroscopic techniques. Exposure to either anion leads to a marked shift of the ^{11}B NMR signal to 5 ppm (fluoride) and −14 ppm (cyanide), respectively. In each case, ^1H NMR spectroscopy reveals complete conversion to the borane/anion host/guest complex in presence of 2 equiv. of the anion and 1 equiv. of 18-crown-6. Additional confirmation of anion binding was obtained in the case of the fluoride adduct through the presence in the ^{13}C NMR spectrum of coupling between the ^{19}F nucleus and the C^6 and C^2 carbon atoms of the *o*-tolyl substituents, as well as by the appearance of a broad signal at $\delta_F = -185$ ppm, which is typical for a fluoride anion bound to a triarylborane moiety.[3s] In addition, the structures of [K(18-crown-6)][**1**·F] and [K(18-crown-6)][**1**·CN] were obtained by X-ray crystallography and are shown in Fig. 2 and 3, respectively.

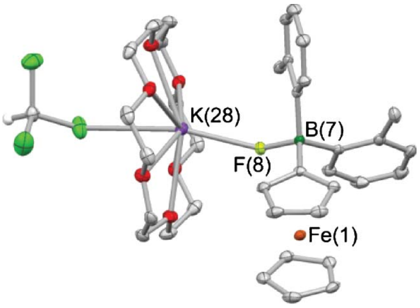


Fig. 2 Molecular structure of [K(18-crown-6)][**1**·F]·$CHCl_3$ with hydrogen atoms (except the chloroform hydrogen) omitted for clarity and thermal ellipsoids set at the 40% level. Selected bond lengths (Å) and angles (°): C(2)–B(7) = 1.622(4), B(7)–C(9) = 1.651(4), B(7)–C(16) = 1.644(3), B(7)–F(8) = 1.481(3), F(8)···K(28) = 2.647(2), C(16)–B(7)–C(9) = 113.6(2), C(9)–B(7)–C(2) = 112.1(2), C(2)–B(7)–C(16) = 110.8(2), K(28)–F(8)–B(7) = 134.0(1).

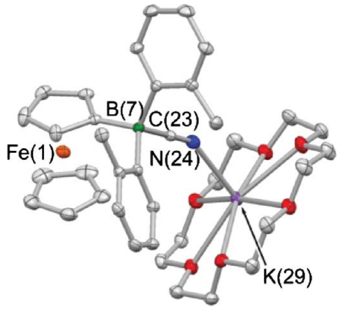


Fig. 3 Molecular structure of [K(18-crown-6)][**1**·CN] with hydrogen atoms omitted for clarity and thermal ellipsoids set at the 40% level. Selected bond length (Å) and angles (°): C(2)–B(7) = 1.627(3), C(15)–B(7) = 1.660(2), C(8)–B(7) = 1.644(2), B(7)–C(22) = 1.622(3), C(22)–N(23) = 1.150(3), N(23)···K(29) = 2.769(2), C(15)–B(7)–C(2) = 111.0(1), C(2)–B(7)–C(8) = 110.5(1), C(8)–B(7)–C(15) = 116.5(1), B(7)–C(22)–N(23) = 179.3(2).

Not unexpectedly, the solid state structure of [K(18-crown-6)][**1**·F] reveals that the coordination sphere around the boron centre has become pyramidalized [$\sum(\angle CBC) = 337°$ for the ferrocenyl and *o*-tolyl substituents] and that the distances between the boron atom and *ipso* carbon atoms of the cyclopentadienyl and *o*-tolyl substituents are elongated compared to **1** [*d*(B–C) = 1.522(8), 1.577(8), 1.582(9) Å for **1** *cf.* d(B–C) = 1.622(4), 1.644(3), 1.651(4) Å for [K(18-crown-6)][**1**·F]]. The B–F distance is similar to that in [^{n}Bu$_4$N][PhBMes$_2$·F] but slightly longer than in [K(2.2.2crypt)][(9-anthryl)$_3$B·F] [*d*(B–F) = 1.481(3), *cf.* 1.481(2) and 1.466(5) Å, respectively].[4ff,4a] In addition, the solid state structure reveals a weak interaction between the fluoride anion and the potassium centre of the [K(18-crown-6]$^+$ counter-ion [*d*(K···F) = 2.647(2) Å, *cf.* 4.22 Å for the sum of the van der Waals' radii of potassium and fluorine].[15] This kind of secondary interaction is unusual for fluoride bound FcBAr$_2$ compounds, but finds precedent in related cyanide adducts,[7j] and in the fluoride adduct of a catecholboryl-functionalized crown ether,[16] as well as in [K(18-crown-6)(thf)][1,2-fc(BMeF)(SnMe$_2$X)·F] (X = Cl or F).[17] In similar fashion, the solid state structure of [K(18-crown-6)][**1**·CN] features a linear boron-bound cyanide unit [$\angle$BCN = 179.3(2)], and an additional secondary interaction between the peripheral nitrogen atom and [K(18-crown-6]$^+$ [*d*(K···N) = 2.769(2) Å, *cf.* 4.30 Å for the sum of the van der Waals' radii of potassium and nitrogen].[15] The boron centre, B(7), is quaternized in a similar manner to that in [K(18-crown-6)][**1**·F] [$\sum(\angle CBC) = 338°$ for the ferrocenyl and *o*-tolyl substituents] and a similar degree of elongation of the aryl B–C bonds is also observed for the two adducts (*d*(B–C) = 1.644(2), 1.627(3), 1.660(2) for [**1**·CN]$^-$, *cf.* 1.644(3), 1.622(4), 1.651(4) for [**1**·F]$^-$).

In order to determine quantitatively the affinity of **1** for fluoride and cyanide, UV-vis titrations were carried out, yielding the binding constants K_F and K_{CN}. The absorption maximum of **1** in dichloromethane is slightly blue shifted and the extinction coefficient slightly lower than the analogous values for **3** (λ_{max} = 480 nm, ε = 12200 dm^2 mol^{-1} for **1**, λ_{max} = 510 nm, ε = 13100 dm^2 mol^{-1} for **3**).[7j] Fig. 4 shows the UV-vis spectra of **1** on exposure to successive aliquots of [^{n}Bu$_4$N]CN·2H$_2$O, and Fig. 5 the corresponding spectra with [^{n}Bu$_4$N]F·4H$_2$O.[18]

These spectra show that **1** is able to act as a colorimetric sensor for fluoride and cyanide anions, with a colour change from deep orange to light yellow effected on addition of either anion. The binding constants were calculated in the wavelength range 430 nm to 530 nm by fitting the absorbance *vs.* anion concentration data (in dichloromethane solution) with ReactLab™ Equilibria.[14] This wavelength range covers the absorption maxima both of **1** and the bound species [**1**·F]$^-$/[**1**·CN]$^-$. As an indication of the fit obtained, the experimental data and the best-fit line at λ = 490 nm are shown in Fig. 4 and 5 (for F$^-$ and CN$^-$, respectively).

Derivation of these isotherms reveals that $\log_{10}K_{CN}$ for **1** is 5.94(0.02),[19] and $\log_{10}K_F$ = 5.82(0.02).[20] The small difference between these binding constants is consistent with the very similar structural features noted above for [K(18-crown-6)][**1**·F] and [K(18-crown-6)][**1**·CN]. While there is therefore little discrimination between the two analytes, competition experiments are consistent with the stronger binding of CN$^-$.[7j]

In order to put these figures in broader context, the corresponding values of K_{CN} have been re-determined for **2** and **3**,[7j] using a similar wavelength range, 450–550 nm (see Supporting Information; the small shift in λ reflects the slightly shifted absorption maxima for **2**/**3** compared to **1**). These three cyanide adducts offer a basis for probing the underlying structural factors influencing binding affinities, since crystallographic data are also available for [**2**·CN]$^-$ and [**3**·CN]$^-$.[7j] Somewhat surprisingly, the cyanide binding constants determined for **2** and **3** [$\log_{10}K_{CN}$ = 4.73(0.01) and 5.56(0.02), respectively] are actually very similar to that measured for **1**.

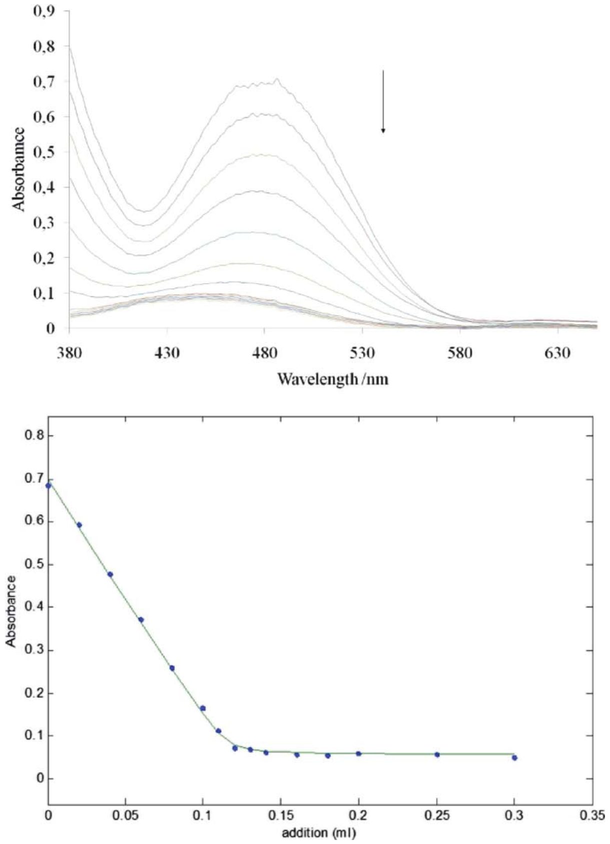


Fig. 4 The response of **1** to exposure to [^{n}Bu$_4$N]CN·2H$_2$O in CH$_2$Cl$_2$ as monitored by UV-vis spectroscopy (top); experimental data (points) obtained at λ = 490 nm as a function of added cyanide, and the best-fit line obtained using ReactLab™ Equilibria (bottom).[14]

Structurally (on the basis of quantum chemical studies carried out on the gas phase [Ph$_3$B·F]$^-$ and [PhMes$_2$B·F]$^-$ ions) a greater degree of pyramidalization of the B(C$_{aryl}$)$_3$ unit might be expected at the boron centre in [**1**·CN]$^-$ compared to [**2**·CN]$^-$ and [**3**·CN]$^-$.[10,5x] Interestingly, however, the sum of the aryl/ferrocenyl CBC angles shows virtually no difference between the three structures ([**1**·CN]$^-$: 338°; [**2**·CN]$^-$: 337°; [**3**·CN]$^-$ 337°). Furthermore, the B–CN bond lengths are also statistically identical (*d*(B–CN) = 1.622(3), 1,624(3), 1.621(3) Å for [**1**·CN]$^-$, [**2**·CN]$^-$ and [**3**·CN]$^-$, respectively), and the same is true for the distances between the boron atoms and the *ipso* carbon atoms of the aryl and cyclopentadienyl substituents.[7j] As such, the steric demands of the additional *ortho* methyl groups do not appear to alter either the degree of pyramidalization at the boron centre or the distance between the anion and the boron atom-findings which are consistent with the similar cyanide binding constants determined for the three receptors.

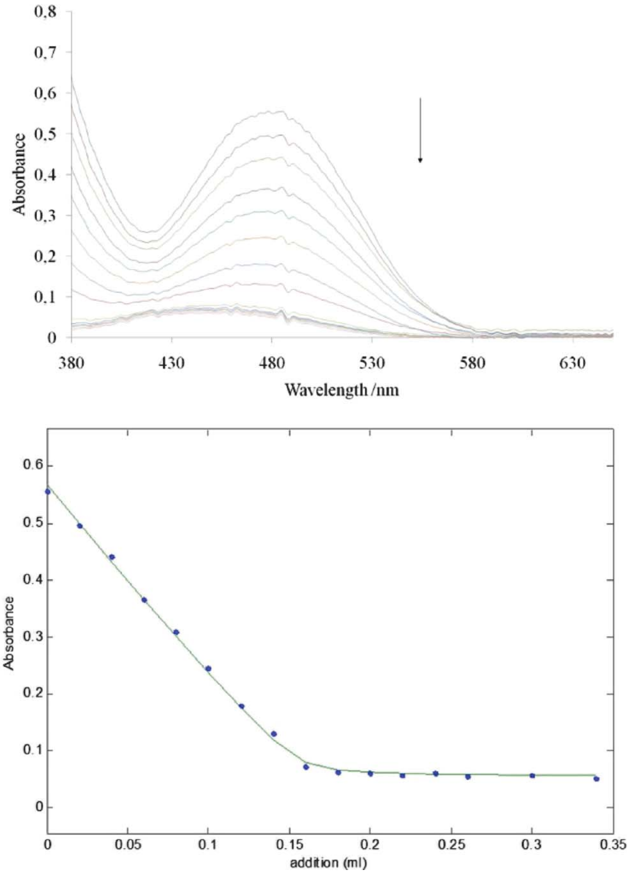


Fig. 5 The response of **1** to exposure to [^{n}Bu$_4$N]F·4H$_2$O in CH$_2$Cl$_2$ as monitored by vis spectroscopy (top); experimental data (points) obtained at λ = 490 nm as a function of added fluoride, and the best-fit line obtained using ReactLab™ Equilibria (bottom).[14]

Further consideration of the conformations adopted by the boron-bound aryl and cyclopentadienyl substituents allows some comment to be made concerning the structural perturbations by which these systems ameliorate the effect of increasing steric bulk. In essence, greater rotation about the B–C$_{ipso}$ bonds is observed for [**2**·CN]$^-$ and [**3**·CN]$^-$, compared to [**1**·CN]$^-$, leading to mean inter-plane angles of 78 and 79° for [**2**·CN]$^-$ and [**3**·CN]$^-$, respectively, compared to 71° for [**1**·CN]$^-$ (Fig. 6). Thus, greater twisting reduces the increase in steric crowding otherwise implicit in greater *ortho* substitution, and presumably is therefore also responsible for smaller variation in anion binding affinities than might have been expected on the basis of related computational studies.

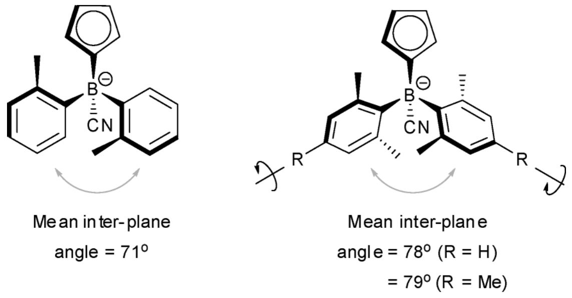


Fig. 6 Orientation of the planes defined by the aryl and cyclopentadienyl substituents in [**1**·CN]$^-$ (left) and [**2**·CN]$^-$/[**3**·CN]$^-$ (right).

Conclusions

The current investigation shows that FcB(*o*-Tol)$_2$ (**1**) is easy accessible *via* the reaction of FcBBr$_2$ with *o*-tolyl lithium and that it acts as a colorimetric anion sensor for cyanide and fluoride anions. Interestingly, the binding affinity of **1** for cyanide is shown to be only slightly enhanced compared to the more sterically encumbered derivatives FcB(*o*-Xyl)$_2$ and FcBMes$_2$, a phenomenon attributed to conformational flexibility about the B–C$_{ipso}$ bonds which mitigates the effects on increasing *ortho* substitution.

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19 Error: ssq = 0.07, $\sigma r = 0.006$.

20 Error: ssq = 0.08, $\sigma r = 0.006$.