

Comparative structural and thermodynamic studies of fluoride and cyanide binding by PhBMes₂ and related triarylborane Lewis acids†‡

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Lewis acidic boranes containing the –BMes₂ unit (Mes = 2,4,6-Me₃C₆H₂) have been widely exploited in molecular sensors for the fluoride ion reflecting, at least in part, the stability to air and moisture of derivatives of the type ArBMes₂. In the current study, the fluoride binding capabilities of the simplest such system, PhBMes₂ (**1**), have been investigated by spectroscopic and crystallographic methods, with a view to experimentally determining the fundamental thermodynamic and structural parameters associated with this host/guest interaction. A binding constant, K_F , of $8.9(1.9) \times 10^4 \text{ M}^{-1}$ in dichloromethane solution and a B–F bond length of 1.481(2) Å for the salt $[\text{Bu}_4\text{N}]^+[\text{PhMes}_2\text{BF}]^-$ have thus been elucidated and provide a baseline for the analysis of more complex systems. Competitive binding of the cyanide ion is implied by a similar binding constant, K_{CN} , of $1.9(0.5) \times 10^5 \text{ M}^{-1}$; structurally, similar degrees of pyramidalization of the BC₃ framework are observed on coordination of each anion $\{\Sigma(\text{C}–\text{B}–\text{C}) = 339.8, 340.1^\circ$ for $[\text{Bu}_4\text{N}]^+[\text{PhMes}_2\text{BF}]^-$ and $[\text{K}(18\text{-crown-6})]^+[\text{PhMes}_2\text{BCN}]^-$, respectively}. Linking of two ArBMes₂ units *via* an alkyne spacer results in a 2,2′-bis(dimesitylboryl)tolan system, which is characterized by independent binding of two equivalents of the CN[−] anion, rather than cyanide chelation.

Introduction

The selective detection of CN[−] and F[−] (and of their conjugate acids HCN and HF) constitute significant chemical challenges which have attracted attention not only from a fundamental supramolecular perspective, but also with a view to potential applications in healthcare and environmental monitoring.^{1,2} Thus, for example, the necessity to monitor fluoride concentrations in domestic water supplies has led to considerable research effort being expended on the development of sensors for fluoride, encompassing a range of host/guest strategies to bind the target analyte.^{3–6} Cyanide detection, on the other hand, has received less attention,^{7–11} although the affinity of CN[−] for three-coordinate boranes (even in the presence of water) has been known for almost 50 years.¹² More recently, a number of cyanide receptors have been reported incorporating an array of Lewis acidic centers,^{10a,b} including systems featuring the –BMes₂ (Mes = 2,4,6-Me₃C₆H₂) function,⁷ and in certain cases offering remarkably selective binding in aqueous media.^{7c,g}

Given that boranes of the type ArBMes₂ are typically air- and moisture-stable and that under appropriate conditions a number are known to bind fluoride and/or cyanide,⁷ these compounds are potential components of sensor systems designed to generate a macroscopic reporter response on exposure to these anions. Central to such applications is an in-depth understanding of the anion recognition event; nevertheless comparative experimental data relating to the interaction of F[−]/CN[−] with simple triarylboranes are surprisingly scarce.^{7c} With this in mind, we have sought to address fundamental questions relating to the thermodynamic and geometric consequences of F[−]/CN[−] binding at ArBMes₂ systems, utilizing the simplest possible archetype (*i.e.* PhBMes₂) for these studies. Of particular interest at the outset was a comparison of the relative binding strengths of F[−] vs. CN[−], given their potential for competitive binding at borane Lewis acids, and the fact that their relative basicities are known to be very strongly solvent dependent [HF: p*K*_a 3 (in H₂O), 15 (in DMSO); HCN: p*K*_a 9 (in H₂O), 13 (in DMSO)].¹³

Experimental

(a) General

Manipulations of air-sensitive reagents were carried out under a nitrogen or argon atmosphere using standard Schlenk line or dry box techniques. Non-deuterated solvents were dried using a commercially available Braun Solvent Purification System; [D]chloroform (Goss) was degassed and dried over molecular sieves prior to use. The tetra-*n*-butylammonium salts of fluoride and cyanide were dried to constant weight *in vacuo*, analysed

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for composition (*i.e.* for state of hydration),^{14a} and stored under an atmosphere of dry argon until use. The known compounds phenyldimesitylborane and 2,2'-dibromotolan were prepared by literature protocols.^{14b,c} 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 reference for ¹H and ¹³C NMR spectra; ¹¹B and ¹⁹F NMR spectra were referenced with respect to Et₂O·BF₃ and CFCl₃, respectively. The ¹³C signals of boron-bound Ph, Mes 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: s = singlet, t = triplet, m = multiplet.

(b) Syntheses

[ⁿBu₄N]⁺[I·F][−]. To a solution of **1** (0.10 g, 0.31 mmol) in chloroform (2 mL) was added [ⁿBu₄N]⁺F[−] (2.0 equiv.) and the reaction mixture stirred at 20 °C for 4 h. Filtration and layering with hexanes at 20 °C led to the formation of single crystals of [ⁿBu₄N]⁺[I·F][−] suitable for X-ray diffraction. Yield 0.13 g, 72%. ¹H NMR ([D]chloroform, 20 °C), δ 1.00 [t, 12H, CH₃ of ⁿBu₄N⁺], 1.38–1.47 [m, 8H, CH₂ of ⁿBu₄N⁺], 1.53–1.62 [m, 8H, CH₂ of ⁿBu₄N⁺], 1.97 [s, 12H, *o*-CH₃ of Mes], 2.18 [s, 6H, *o*-CH₃ of Mes], 3.12–3.22 [m, 8H, CH₂ of ⁿBu₄N⁺], 6.55 [s, 4H, aromatic CH of Mes], 7.02–7.52 [overlapping m, 5H, aromatic CH of Ph]. ¹³C NMR ([D]chloroform, 20 °C), δ 22.7 [*p*-CH₃ of Mes], 24.1 [*o*-CH₃ of Mes], 14.1, 19.7, 31.6, 58.7 [ⁿBu₄N⁺], 127.9, 128.1, 128.2, 136.3, 138.6, 140.8 [aromatic CH of Ph and Mes], boron-bound aromatic quaternary carbons not observed. ¹¹B NMR ([D]chloroform, 20 °C), δ 5. ¹⁹F NMR ([D]chloroform, 20 °C), δ −171.2. MS(ES[−]): 345 (42%) [I·F][−]; exact mass (calc.) *m/z* 344.2232, (meas.) 344.2233. Elemental microanalysis: calc. C 81.70, H 10.81, N 2.38%; meas. C 82.07, H 10.99, N 2.21%. Crystal data: [ⁿBu₄N]⁺[I·F][−], C₄₀H₆₃BFN, monoclinic, *P*2₁/*c*, *a* = 10.3016(2), *b* = 19.4960(3), *c* = 18.7092(4) Å, β = 94.422(1)°, *V* = 3746.37(12) Å³, *Z* = 4, *D_x* = 1.041 Mg m^{−3}, *M_r* = 587.76, *T* = 150(2) K. 48 778 reflections collected, 8185 independent [*R*_{int} = 0.063], 4301 observed [*I* > 2σ(*I*)]. *R*₁ = 0.0407, *wR*₂ = 0.0926 for observed unique reflections [*I* > 2σ(*I*)]; *R*₁ = 0.0590, *wR*₂ = 0.0994 for all unique reflections. Goodness of fit = 1.000. Max. and min. residual electron densities: 0.28 and −0.27 e Å^{−3}. CCDC 765939.

[K(18-crown-6)]⁺[I·CN][−]. To a solution of **1** (0.47 g, 1.43 mmol) in chloroform (5 mL) was added KCN and 18-crown-6 (1.0 equiv. of each) and the reaction mixture stirred at 20 °C for 12 h. Filtration and layering with hexanes at 20 °C led to the formation of single crystals of [K(18-crown-6)]⁺[I·CN][−] suitable for X-ray diffraction. Yield

0.47 g, 50%. ¹H NMR ([D]chloroform, 20 °C), δ 1.98 [s, 12H, *o*-CH₃ of Mes], 2.19 [s, 6H, *o*-CH₃ of Mes], 3.54 [s, 24H, CH₂ of 18-crown-6], 6.61 [s, 4H, aromatic CH of Mes], 6.95–7.04 [m, 2H, *o*-CH of Ph], 7.08–7.15 [m, 2H, *m*-CH of Ph], 8.07–8.14 [m, 1H, *p*-CH of Ph]. ¹³C NMR ([D]chloroform, 20 °C), δ 20.8 [*p*-CH₃ of Mes], 25.3 [*o*-CH₃ of Mes], 69.9 [18-crown-6], 123.1, 125.6, 128.5, 131.9, 135.8, 142.2 [aromatic CH of Ph and Mes], boron-bound aromatic quaternary carbons not observed. ¹¹B NMR ([D]chloroform, 20 °C), δ −13. IR (KBr disk, cm^{−1}), 2165 (νCN). MS(ES[−]): 352 (100%) [I·CN][−]; exact mass (calc. for ¹⁰B isotopomer) *m/z* 351.2278, (meas.) 351.2270. Elemental microanalysis: calc. C 67.74, H 7.84, N 2.14%; meas. C 67.81, H 7.75, N 2.13%. Crystal data: [K(18-crown-6)]⁺[I·CN][−], C₃₇H₅₁BKNO₆, orthorhombic, *Pbca*, *a* = 18.0486(2), *b* = 15.7241(1), *c* = 25.8240(2) Å, *V* = 7328.80(11) Å³, *Z* = 8, *D_x* = 1.189 Mg m^{−3}, *M_r* = 655.72, *T* = 150(2) K. 131 038 reflections collected, 8134 independent [*R*_{int} = 0.099], 5181 observed [*I* > 2σ(*I*)]. *R*₁ = 0.0459, *wR*₂ = 0.0468 for observed unique reflections [*I* > 2σ(*I*)]; *R*₁ = 0.0884, *wR*₂ = 0.0880 for all unique reflections. Goodness of fit = 1.095. Max. and min. residual electron densities: 0.23 and −0.24 e Å^{−3}. CCDC 765940.

2. To a stirred solution of 2,2'-dibromotolan (0.50 g, 1.49 mmol) in diethyl ether (40 mL) at −78 °C was added dropwise *n*-butyllithium (2.0 equiv., 1.86 mL of a 1.6 M solution in hexanes) and the stirred reaction mixture allowed to warm to 20 °C. After 12 h a solution of dimesitylboron fluoride (2.0 equiv., 0.80 g, 2.98 mmol) in diethyl ether (30 mL) was added and stirring continued for a further 6 h at 20 °C. Filtration and removal of volatiles *in vacuo* afforded a yellow solid, which was recrystallized from hexanes (*ca.* 25 mL) at −30 °C as a spectroscopically pure colourless solid in 43% yield. ¹H NMR ([D]chloroform, 20 °C), δ 1.85 [s, 24H, *o*-CH₃ of Mes], 2.18 [s, 12H, *p*-CH₃ of Mes], 6.45–6.55 [m, 2H, aromatic CH of tolan], 6.65 [s, 8H, aromatic CH of Mes], 7.06–7.12 [overlapping m, 6H, aromatic CH of tolan]. ¹³C NMR ([D]chloroform, 20 °C), δ 21.3 [*p*-CH₃ of Mes], 23.2 [*o*-CH₃ of Mes], 93.5 [alkyne quaternary carbon], 127.3 [aromatic quaternary carbon of tolan], 127.4 [aromatic CH of tolan], 128.3 [aromatic CH of Mes], 129.6 [aromatic CH of tolan], 133.2 [aromatic CH of tolan], 133.9 [aromatic CH of tolan], 138.8 [aromatic quaternary of Mes], 140.8 [aromatic quaternary of Mes], 142.9, 149.8 [boron-bound aromatic quaternary carbons]. ¹¹B NMR ([D]chloroform, 20 °C), δ 73. MS(EI): 674 (5%) M⁺; exact mass (calc.) *m/z* 674.4250 (meas.), 674.4252.

[K(18-crown-6)]⁺2[2·(CN)₂]^{2−}. To a slurry of **2** (0.02 g, 0.03 mmol) in acetonitrile (15 mL) was added 18-crown-6 (2.0 equiv., 0.16 g, 0.06 mmol) and potassium cyanide (2.0 equiv., 0.04 g, 0.06 mmol), and the reaction mixture stirred for 12 h at 20 °C. The ¹¹B NMR spectrum of the reaction mixture at this point revealed a single resonance at δ_B −15 ppm characteristic of a triarylborane/cyanide adduct. Concentration of the acetonitrile solution and layering with diethyl ether yielded single crystals of [K(18-crown-6)]⁺2[2·(CN)₂]^{2−} (as the acetonitrile bis-solvate)

suitable for X-ray diffraction. Larger scale preparative reactions (*ca.* 0.1 g) typically yielded $[\text{K}(\text{18-crown-6})]^+ \text{[2-(CN)}_2\text{]}^{2-} \cdot 2\text{CH}_3\text{CN}$ as a spectroscopically pure colourless material in 60–70% isolated yield. ^1H NMR ($[\text{D}]\text{chloroform}$, 20 °C), δ 1.94 [s, 24H, *o*-CH₃ of Mes], 2.10 [s, 12H, *p*-CH₃ of Mes], 3.42 [s, 48H, 18-crown-6], 6.46–6.54 [m, 2H, aromatic CH of tolan], 6.53 [s, 8H, aromatic CH of mesityl], 6.59–6.83 [overlapping m, 6H, aromatic CH of tolan]. ^{13}C NMR ($[\text{D}]\text{chloroform}$, 20 °C), δ 20.9 [*p*-CH₃ of Mes], 25.7 [*o*-CH₃ of mesityl], 70.0 [18-crown-6], 128.4 [aromatic CH of Mes], 128.9, 132.0, 136.4, 143.2 [aromatic CH of tolan], quaternary carbons not observed due to very low solubility. ^{11}B NMR ($[\text{D}]\text{chloroform}$, 20 °C), δ –15. IR (KBr disk, cm^{-1}), 2167 (ν_{CN}). MS(ES⁺): 303 (100%) $[\text{K}(\text{18-crown-6})]^+$; exact mass (calc.) m/z 303.1204, (meas.) 303.1203. MS(ES[–]): 363 (80%) $[\text{2-(CN)}_2]^{2-}$, exact mass (calc.) m/z 363.2164, (meas.) 363.2168. Crystal data: $[\text{K}(\text{18-crown-6})]^+ \text{[2-(CN)}_2\text{]}^{2-} \cdot 2\text{CH}_3\text{CN}$, $\text{C}_{80}\text{H}_{106}\text{B}_2\text{K}_2\text{N}_4\text{O}_{12}$, triclinic, $P\bar{1}$, $a = 12.5667(2)$, $b = 13.3168(3)$, $c = 13.9064(3)$ Å, $\alpha = 102.277(1)^\circ$, $\beta = 110.042(1)^\circ$, $\gamma = 109.954(1)^\circ$, $V = 1906.52(7)$ Å³, $Z = 1$, $D_x = 1.233$ Mg m^{–3}, $M_r = 1415.51$, $T = 293(2)$ K. 28 042 reflections collected, 7775 independent [$R_{\text{int}} = 0.122$], 5459 observed [$I > 2\sigma(I)$], $R_1 = 0.0609$, $wR_2 = 0.1453$ for observed unique reflections [$I > 2\sigma(I)$]; $R_1 = 0.0926$, $wR_2 = 0.1604$ for all unique reflections. Goodness of fit = 1.051. Max. and min. residual electron densities: 0.46 and –0.57 e Å^{–3}. CCDC 765941.

(c) Crystallography

Data for $[\text{Bu}_4\text{N}]^+ [\text{F}]^-$, $[\text{K}(\text{18-crown-6})]^+ [\text{I-CN}]^-$ and $[\text{K}(\text{18-crown-6})]^+ \text{[2-(CN)}_2\text{]}^{2-}$ were collected on a Nonius KappaCCD diffractometer (Mo-K α radiation; $\lambda = 0.71073$ Å) with an Oxford Cryosystems Cryostream N₂ open-flow cooling device.^{15a} Data were processed using the DENZO-SMN package, including inter-frame scaling (which was carried out using Scalepack within DENZO-SMN).^{15b} Structures were solved using SIR92 (for $[\text{Bu}_4\text{N}]^+ [\text{F}]^-$ and $[\text{K}(\text{18-crown-6})]^+ [\text{I-CN}]^-$) or SHELXS (for $[\text{K}(\text{18-crown-6})]^+ \text{[2-(CN)}_2\text{]}^{2-}$).^{15c,d} Refinement was carried out using full-matrix least-squares within the CRYSTALS suite,^{15e} on either F^2 ($[\text{Bu}_4\text{N}]^+ [\text{F}]^-$ and $[\text{K}(\text{18-crown-6})]^+ \text{[2-(CN)}_2\text{]}^{2-}$) or F (for $[\text{K}(\text{18-crown-6})]^+ [\text{I-CN}]^-$). All non-hydrogen atoms were refined with anisotropic displacement parameters. For all three compounds, the majority of hydrogen atoms were visible in the difference map, while the rest were added geometrically; refinement of positions and isotropic displacement parameters using restraints was carried out prior to inclusion into the model with riding constants.†

(d) Binding constant determinations

Binding constants were evaluated for **1** in dichloromethane with fluoride and cyanide using the UV titration method reported by Solé and Gabbai,^{6r} the program LabFit (www.labfit.net) was used to fit the experimentally determined data of A/A_0 vs. anion concentration. Related efforts aimed at the determination of binding constants for **2** were frustrated by precipitation during the titration experiments.

Results and discussion

A report by Yamaguchi *et al.* in 2001 of colorimetric sensors for the fluoride ion based around derivatives of tris(9-anthryl)-borane represented a conceptually simple, but significant advance in the use of triarylboranes in sensing.^{5a} Sterically encumbered systems of this type typically show selectivity for small, highly nucleophilic anions which give rise to strong B–X bonds on coordination (*e.g.* F[–]).^{3s} Moreover, several strategies have subsequently been reported which give rise to enhanced binding constants for the fluoride ion at borane Lewis acids, using, for example, peripheral cationic substituents, chelating binding domains, secondary hydrogen bonding *etc.*^{3s} Such systems offer the potential for binding the highly solvated fluoride ion in more polar media (and ultimately water). In a number of cases, however, the use of such boranes in practical fluoride sensing applications is limited by a competing sensor response for the cyanide ion.^{5gg} With this in mind it is perhaps surprising that comparative *experimental* studies of the fundamental thermodynamic and structural consequences of F[–]/CN[–] binding at simple triarylboranes have yet to be reported.

In seeking to rectify this situation we ruled out the use of the simplest such derivative, Ph₃B, on the grounds of its air- and moisture-sensitivity, and the related compound Mes₃B on the basis that the much increased steric loading renders it incapable of binding F[–] in moderately competitive solvents such as dichloromethane ($\text{AN} = 20.8$).¹⁶ PhBMes₂ (**1**; Chart 1), by contrast, appears to fulfill both criteria, displaying aerobic stability and the ability to bind F[–]/CN[–] in dichloromethane or chloroform. In addition, Gabbai and co-workers have reported quantum chemical studies of fluoride binding by PhBMes₂ in the gas phase,^{6x} thereby offering for illustrative comparisons with solution and/or solid state data. Hence we have examined the interaction of PhBMes₂ with fluoride and cyanide in dichloromethane solution by UV-vis titration methods, and in the solid state by X-ray crystallography. In addition, given the similar binding affinities determined for the two anions (*vide infra*), we report on attempts to link two aryldimesitylborane units *via* an alkyne bridge (as in **2**, Chart 1) to give a bifunctional receptor offering the possibility for size-based selectivity for cyanide (over fluoride).

Qualitatively, interaction of fluoride with **1** in dichloromethane or chloroform can be demonstrated by ^{11}B NMR, as evidenced by an upfield shift from δ_{B} 78 to 5 ppm and by the presence in the mass spectrum (ES[–]) of a single feature corresponding to the adduct $[\text{1-F}]^-$; similar spectroscopic evidence points to the formation of the corresponding cyanide adduct under analogous conditions. Thus, on cyanide binding, signals are detected at $\delta_{\text{B}} - 13$ (by ^{11}B NMR) and at 2167 cm^{–1}

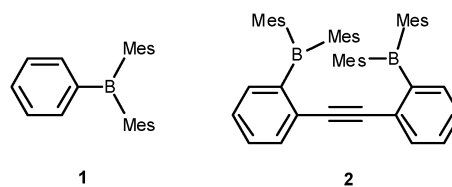


Chart 1

in the IR spectrum, the latter showing the expected shift to higher wavenumber (*cf.* 2080 cm⁻¹ for 'free' cyanide). Quantitative assessment of the host/guest interaction in each case was undertaken by spectroscopic titration methods. In this respect standard ¹H NMR measurements have proved to be ineffective—the binding of cyanide to **1**, for example, being characterized by slow exchange (on the NMR timescale) between the free receptor and the cyanide adduct. Alternative UV-vis titration experiments were therefore carried out; the intensity of the absorption due to **1** at 351 nm was monitored as a function of anion (F⁻ or CN⁻) concentration and the resulting graph of *A/A*₀ fitted using LabFit (Fig. 1).

The binding constants of **1** for F⁻ and CN⁻ are calculated to be 8.9(1.9) × 10⁴ M⁻¹ and 1.9(0.5) × 10⁵ M⁻¹, respectively—values which are not statistically different, given the associated standard deviations. More definitive evidence that the binding of cyanide by **1** is stronger than that of fluoride comes from competition experiments. Thus, addition of excess cyanide to a solution of [1·F]⁻ in dichloromethane can be shown by multinuclear NMR experiments to result in the formation of [1·CN]⁻, while the reverse reaction, *i.e.* the displacement of CN⁻ from [1·CN]⁻ by excess fluoride does not appear to be spontaneous under any of the sets of reaction conditions studied (Scheme 1). The competitive binding of F⁻ and CN⁻ by **1** is perhaps unsurprising given the small steric demands of both anions, and the similar p*K*_as reported for HF/HCN in non-aqueous media (15 and 13, respectively, in dimethyl sulfoxide);¹³ a similar lack of differentiation has also been reported for ferrocenyl derivatized systems.^{5gg}

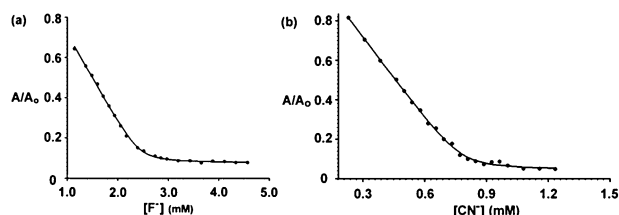
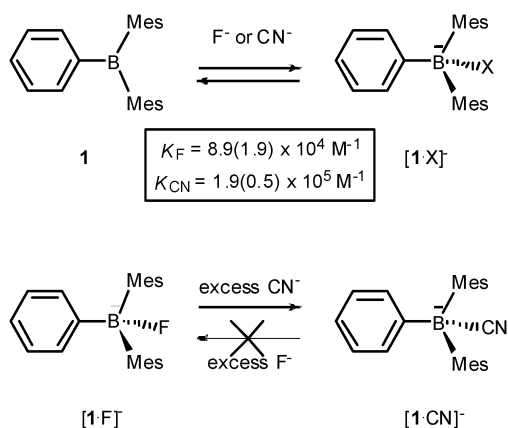


Fig. 1 Calculated fit (line) to experimental data (points) showing the response at 351 nm to the addition of (a) fluoride or (b) cyanide to **1** (*R*² = 0.9991, 0.9987, respectively). The initial concentrations of **1** were 2.28 and 0.79 mM, respectively.



Scheme 1 Comparative binding of fluoride and cyanide by the archetypal triarylborane Lewis acid **1**.

Given the extensive use of arylboranes in the sensing of fluoride, and the particularly widespread exploitation of -BMe₂ functionalized systems, the data determined in the current study (*i.e.* *K*_F and *K*_{CN}) provide a convenient baseline against which to judge the effects of peripheral substituents on the strength of anion binding (Table 1). Thus ferrocene-functionalized systems show little divergence in their binding affinities from **1** (except in the case of [1,2-fc(BMe₂)CH₂NMe₃]⁺ which exhibits borane/H-bond cooperativity in its interaction with fluoride), but increased affinities of between three and four orders of magnitude are observed for systems featuring extended aromatic conjugation, cationic substituents and/or peripheral coordination to metal centres.^{3s,5bb,ff,gg,n,r,u,17}

Table 1 BMe₂ substituted arenes: compound **1** as a baseline for comparative fluoride binding data

Compound	<i>K</i> _F ^a /M ⁻¹	References
1	8.9(1.9) × 10 ⁴	This work
	6 × 10 ⁷	3s
	> 10 ⁸ (in chloroform)	5ff
	> 10 ⁸ (<i>K</i> ₁) ~ 10 ⁶ (<i>K</i> ₂)	5r
	> 10 ⁹ (<i>K</i> ₁) ~ 10 ⁶ (<i>K</i> ₂)	5r, 5bb
	2.1(0.3) × 10 ⁴	5n
	5.0(0.2) × 10 ⁵ (in chloroform)	5u
	7.8(1.2) × 10 ⁴	5gg
	9.4(3.6) × 10 ⁵	5gg
	5.6(2.3) × 10 ⁹	5gg

^a In dichloromethane unless otherwise stated (the acceptor numbers as defined by Gutmann *et al.* for dichloromethane and chloroform are 20.4 and 23.1, respectively).¹⁶

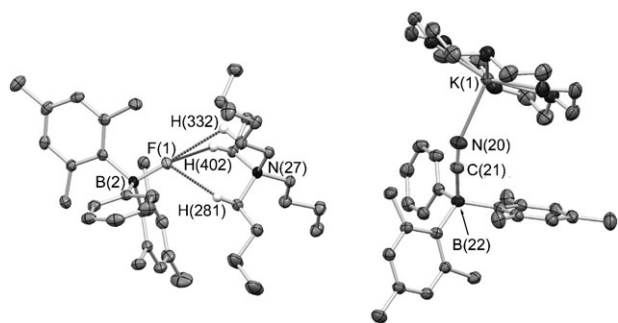


Fig. 2 Crystal structures of $[\text{Bu}_4\text{N}]^+[\text{F}]^-$ (left) and $[\text{K}(\text{18-crown-6})]^+[\text{1-CN}]^-$ (right); hydrogen atoms omitted for clarity and thermal ellipsoids set at the 50% probability level. Key bond lengths (Å) and angles ($^\circ$): (for $[\text{Bu}_4\text{N}]^+[\text{F}]^-$) F(1)–B(2) 1.481(2), C(3)–B(2)–C(12) 115.9(1), C(3)–B(2)–C(21) 117.5(1), C(12)–B(2)–C(21) 106.4(1); (for $[\text{K}(\text{18-crown-6})]^+[\text{1-CN}]^-$) K(1)–N(20) 2.758(2), N(20)–C(21) 1.156(3), C(21)–B(22) 1.631(3), N(20)–C(21)–B(22) 173.4(2), C(23)–B(22)–C(32) 108.1(2), C(23)–B(22)–C(38) 113.7(2), C(32)–B(22)–C(38) 118.4(2).

The structures of $[\text{Bu}_4\text{N}]^+[\text{F}]^-$ and $[\text{K}(\text{18-crown-6})]^+[\text{1-CN}]^-$ have been determined by single crystal X-ray diffraction (Fig. 2). The former is made up of $[\text{Bu}_4\text{N}]^+$ and $[\text{F}]^-$ ions, with the closest secondary contacts consisting of three B–F...H–C hydrogen bonds involving the α -carbon bound hydrogens H(281) and H(402), together with H(332) which is bound to one of the β carbons of the same $[\text{Bu}_4\text{N}]^+$ cation. Similar hydrogen bonds between B–F and C–H linkages (in which the latter is positioned α to a quaternary ammonium function) have been reported recently, with a somewhat shorter C...F distance of 2.826(4) Å having been determined in one case for a related *intramolecular* $\text{ArMes}_2\text{BF}\cdots\text{HC}$ interaction (*cf.* 3.165–3.370 Å for $[\text{Bu}_4\text{N}]^+[\text{F}]^-$).^{5k} Nonetheless, the C...F distances for $[\text{Bu}_4\text{N}]^+[\text{F}]^-$ are comfortably shorter than those reported for an analogous *intermolecular* $\text{BF}\cdots\text{HC}$ system by Gale and co-workers [3.442(4) and 3.447(3) Å].¹⁸

The B–F distance determined for the anionic component [1.481(2) Å] agrees well with that derived from quantum chemical calculations (1.491 Å), and is somewhat greater than that calculated for $[\text{Ph}_3\text{BF}]^-$ (1.465 Å) as expected on the basis of the relative steric demands of the aryl substituent manifold. It is also marginally longer than that found in the fluoride adduct of the more strongly Lewis acidic cationic system $[\text{1-Me}_3\text{NC}_6\text{H}_4\text{BMes}_2]^+[\text{1.465(3) Å}]$.^{7c} Consistent with these observations, the extent of pyramidalization of the boron centre on fluoride binding (as manifested by the sum of the three BC_2 angles, 339.8°) is similar to that predicted computationally (340.5°) and smaller than that associated with the less hindered borane Ph_3B [$\Sigma(\text{C}–\text{B}–\text{C}) = 333^\circ$]. A similar degree of pyramidalization at the boron centre is observed on cyanide binding, as manifested by the structure of $[\text{K}(\text{18-crown-6})]^+[\text{1-CN}]^-$ [$\Sigma(\text{C}–\text{B}–\text{C}) = 340.9^\circ$]. In this case, and in common with related cyanide adducts of *ferrocenyl* boranes,^{5gg} the C-bound cyanide ligand features an essentially linear B–C–N framework ($\angle \text{B}–\text{C}–\text{N} = 173.4(2)^\circ$, *cf.* $170.2(2)^\circ$ for $[\text{K}(\text{18-crown-6})]^+[\text{FcB}(\text{2,6-Xyl})_2\text{CN}]^-$). The B–CN bond length [1.631(3) Å] is also similar to those found for related ferrocene-derived systems (*e.g.* 1.624(3)°

for $[\text{K}(\text{18-crown-6})]^+[\text{FcB}(\text{2,6-Xyl})_2\text{CN}]^-$). A secondary interaction between the cyanide nitrogen and the potassium centre of the $[\text{K}(\text{18-crown-6})]^+$ cation augments the coordination geometry at the metal centre, with a K...N separation of 2.758(2) Å having been determined. The potassium centre also interacts with one of the phenyl *m*-CH bonds of an adjacent $[\text{1-CN}]^-$ anion, with this additional contact occurring at the distal face of the $[\text{K}(\text{18-crown-6})]^+$ unit. The K...H and K...C distances associated with this interaction (2.913 and 3.357 Å) fall comfortably within the sums of the respective van der Waals radii (3.51 and 4.16 Å, respectively).¹⁹

Given the lack of discrimination for the binding of F^-/CN^- revealed for **1** by UV-vis titration experiments, we have targeted related derivatives which offer selective binding of either anion, based on potentially chelating Lewis acid receptors tailored to the specific sizes/geometries of the two anions. While systems based on *ortho*-disubstituted benzene or ferrocene backbones offer chelating binding of simple monatomic anions bearing >1 lone pair (*e.g.* halides), and the crystal structure of $[\text{C}_6\text{F}_4\text{-1,2-(BF}_2)_2(\mu\text{-F})]^-$, for example, has been reported by Piers and co-workers (Chart 2),^{6y,20} receptors targeting the bifunctional binding of cyanide require a significantly larger binding cavity. Given that strongly Lewis acidic boranes have previously been shown to be capable of binding to both the C- and N-based lone pairs of the cyanide anion,²¹ and reasoning that a $\text{C}\equiv\text{C}$ triple bond should offer a reasonable templating backbone for cyanide chelation, we have synthesized and examined the binding capabilities of the 2,2'-diborylated tolan system **2**.

The synthesis of **2** is readily accomplished from the known compound 2,2'-dibromotolan (Scheme 2) in isolated yields of 40–50% *via* a single step simple lithiation/electrophilic quench procedure, utilizing the commercially available borane Mes_2BF . **2** has been characterized by standard spectroscopic procedures and is competent for the binding of cyanide, as evidenced by the growth of a signal at $\delta_{\text{B}} -15$ on addition of either $[\text{Bu}_4\text{N}]^+[\text{CN}]^- \cdot 2\text{H}_2\text{O}$ or KCN/18-crown-6 in acetonitrile. That said, no evidence has been found for a bridging mode of interaction of a single cyanide ion between the two borane centres. On the contrary, mass spectrometry and crystallographic studies are consistent with the formation of the bis(cyanide) adduct $[\text{2} \cdot (\text{CN})_2]^{2-}$ both in solution and in the solid state. In the presence of *ca.* one equivalent of cyanide, the reaction mixture contains both uncomplexed $-\text{BMes}_2$ and cyanide bound $-\text{BMes}_2\text{CN}^-$ functionalities (by multinuclear NMR spectroscopy), thus arguing against cyanide chelation. Attempts to isolate a 1 : 1 adduct under such conditions for structural characterization have been frustrated by crystallization of the much less soluble bis(cyanide) adduct $[\text{K}(\text{18-crown-6})]_2[\text{2} \cdot (\text{CN})_2]^{2-}$, despite the fact that it is

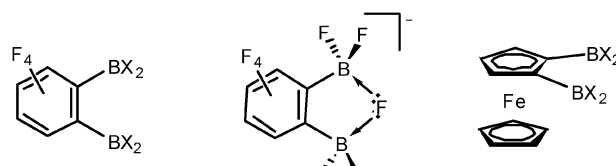
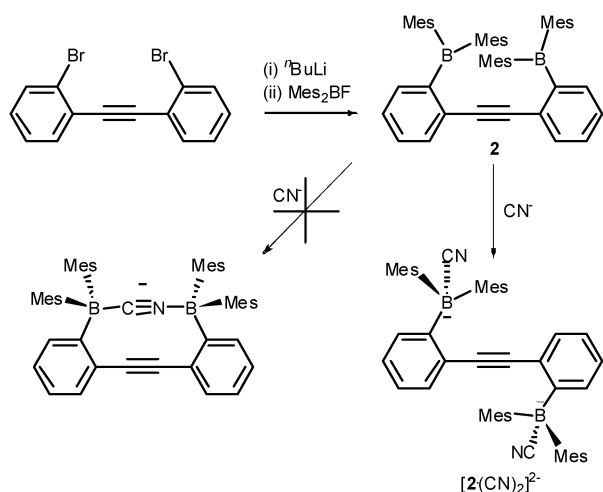


Chart 2



Scheme 2 Synthesis and cyanide binding properties of 2,2'-bis(dimesitylboryl)tolan, **2**.

presumably present in relatively low concentrations at equilibrium.

Evidence for the formation of $[2 \cdot (\text{CN})_2]^{2-}$ in acetonitrile solution comes from *in situ* electrospray mass spectrometry experiments, which give 'flagpole' spectra containing an isotopic envelope centred at $m/z = 363$ (with half-integral spacings) at low cone voltages (*ca.* 20 V). Evidence for the mono(cyanide) adduct $[2 \cdot \text{CN}]^-$ ($m/z = 701$) only becomes apparent at much higher cone voltages, and this species is presumably an artifact of fragmentation during the mass spectrometry experiment. Confirmation of the structure of $[2 \cdot (\text{CN})_2]^{2-}$ in the solid state was obtained from crystallographic studies of $[\text{K}(\text{18-crown-6})]^+_2[2 \cdot (\text{CN})_2]^{2-} \cdot 2\text{MeCN}$ (Fig. 3). The $[\text{K}(\text{18-crown-6})]^+_2[2 \cdot (\text{CN})_2]^{2-}$ unit features two $[\text{ArBMes}_2\text{CN}]^-$ groups related by a centre of inversion, with B–CN and K–NC distances of 1.632(3) and 2.842(2) Å, respectively. The near linear B–C–N and significantly more bent K–N–C angles [177.2(2)° and 143.5(2)°, respectively] are similar to those found for the corresponding unit in $[\text{K}(\text{18-crown-6})]^+[1 \cdot \text{CN}]$ [173.4(2)° and 141.8(2)°]; the degree

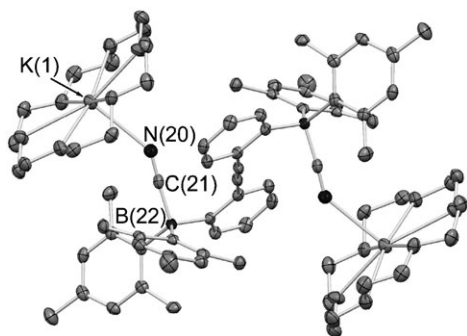


Fig. 3 Crystal structure of $[\text{K}(\text{18-crown-6})]^+_2[2 \cdot (\text{CN})_2]^{2-} \cdot 2\text{MeCN}$; hydrogen atoms and acetonitrile solvent molecules omitted for clarity and thermal ellipsoids set at the 50% probability level. Key bond lengths (Å) and angles (°): K(1)–N(20) 2.842(2), N(20)–C(21) 1.154(3), C(21)–B(22) 1.632(3), N(20)–C(21)–B(22) 177.2(2), K(1)–N(20)–C(21) 143.5(2), C(23)–B(22)–C(32) 109.8(2), C(23)–B(22)–C(41) 111.5(2), C(32)–B(22)–C(41) 119.7(2).

of pyramidalization at B(22) [$\Sigma(\text{C}–\text{B}–\text{C}) = 339.9^\circ$] is also essentially identical to that measured for the corresponding cyanide adduct of **1** (340.9°).

The solid state structure shown in Fig. 3 implies that the $[\text{K}(\text{18-crown-6})]^+$ cation can function as a competing Lewis acid centre for the coordination of the N-based lone pair, in the solid state at least. The identification of $[2 \cdot (\text{CN})_2]^{2-}$ in acetonitrile solution by ESI-MS, however, implies that even in the absence of an intimately bound counter-cation, the use of systems featuring greater conformational rigidity and/or borane Lewis acidity may be required in order to bring about cyanide chelation.

Conclusions

In summary we have shown that in dichloromethane solution fluoride and cyanide bind with very similar affinities to the archetypal triarylborane PhBMes_2 , with similar degrees of pyramidalization at the boron centre also being observed in the solid state for the adducts $[\text{PhBMes}_2\text{X}]^-$. Competition experiments are consistent with marginally stronger binding of CN^- . A related bifunctional system based on a tolan backbone, while similarly competent for the capture of one equivalent of cyanide at each binding domain, does not appear to function as a chelating Lewis acid.

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