

Anion Recognition by Highly Sterically Encumbered 1,2-Diborylferrocenes[§]

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Summary: The syntheses and structural characterization of sterically encumbered 1,2-diborylferrocenes are reported, together with an investigation of their anion recognition capabilities with respect to fluoride and cyanide. Surprisingly, 1,2-fc($BMes_2$)₂ is found to be highly selective for CN^- , with the uptake of F^- being shown to be not only thermodynamically less favorable but also kinetically much slower.

The selective detection of CN^- and F^- constitute significant chemical challenges both from a supramolecular viewpoint and from the perspective of potential applications in environmental and medical monitoring.^{1–3} The affinity of

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cyanide for three-coordinate boranes has been known for more than 45 years;⁴ recent studies have demonstrated the use of Lewis acid receptors containing the $-BMes_2$ (Mes = 2,4,6-Me₃C₆H₂) function to detect cyanide,⁵ in one case offering selective binding in aqueous media.^{5d} In this respect, a major challenge in sensor design stems from the potential for competitive binding of fluoride at BMes₂-derived receptors.⁶ Recent reports, for example, emphasize the importance not only of electronic factors (i.e., borane Lewis acidity) but also of steric factors in determining the relative binding affinities for cyanide and fluoride.^{5d} In this respect, the use of the proton affinities (or even the pK_as) of F^-/CN^- in a predictive capacity is fraught with difficulty, as reflected by

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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)].⁷ With selective anion binding in mind we have been exploring the interaction of convergent bifunctional Lewis acids with fluoride and cyanide.⁸ Systems based on 1,2-diborylbenzenes (I) or 1,8-diborylnaphthalenes (II) have been known for some time, but despite the additional benefits of the ferrocenediyl unit for electrochemical or colorimetric reporting,⁹ 1,2-diborylferrocenes are essentially unknown.^{10,11} In this communication we report on the synthesis of systems of type III, together with the somewhat surprising selectivity of 1,2-fc(BMes₂)₂ for cyanide (over fluoride), based on both thermodynamic and kinetic factors.

The syntheses of 1,2-bis(diarylboryl)ferrocenes **3**, **3'**, and **3''** can be accomplished in two steps from commercially available 1,1'-dibromoferrocene, **1** (or three steps from ferrocene), according to the methodology outlined in Scheme 1. Synthetically, the key step involves the isomerization of 1,1'-lithio-(bromo)ferrocene in the presence of 2,2,6,6-tetramethylpiperidine (tmp) to the corresponding 1,2-isomer;^{9e,12,13} the intermediate species 1,2-fc(Br)BMes₂ (**2**) and 1,2-fc(Br)BXyl₂ (**2'**) are thus accessible in yields of 50–75%. Subsequent reaction of **2** with "BuLi/tmeda and FBMes₂ gives access to **3** in ca. 38% yield; related chemistry utilizing **2'** and either FBMes₂ or FBXyl₂ gives access to **3'** and **3''**, respectively.¹⁴

3, 3', and 3" have been characterized by standard analytical and spectroscopic techniques, with the ¹¹B NMR shift measured for 3 (δ_B 80 ppm) being typical not only of the three

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(13) Preliminary DFT calculations imply that 1,2-fc(Li)Br is thermodynamically more stable than the corresponding 1,1'-isomer by ca. 15 kJ mol⁻¹ in thf solution.

Scheme 1. Syntheses of Symmetric and Asymmetric 1,2-Bis(diarylboryl)ferrocenes from 1,1'-Dibromoferrocene



compounds but of ferrocenyldiarylboranes in general.5k,15 Moreover, variable-temperature NMR studies, along with the crystallographically determined structure of 3 in the solid state (Figure 1), are consistent with an extremely high degree of steric loading at the Lewis acidic boron centers. This is manifested in considerable distortion of one of the two -BMes₂ units in each of the two 1,2-fc(BMes₂)₂ molecules making up the asymmetric unit. Thus, the $-BMes_2$ groups in question feature boron centers [B(7) and B(76)] that lie ca. 0.5 A out of the plane of the difunctionalized Cp ring [cf. < 0.06 Å for the other boron center in each molecule, B(26) and B(57); the associated BC_2 least-squares plane is canted at an angle of ca. 45° with respect to that of the Cp ring (cf. \sim 5° for the other). In addition, there is a marked difference between the two $B-C_{Cp,ipso}-C_{Cp,ortho}$ angles for both B(7) and B(76) [135.2° (mean) and 114.6 (mean)°], reflecting the need to minimize steric repulsions between mesityl ring systems by "bending back" the -BMes₂ units. Such interactions presumably contribute to the relatively wide

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⁽¹⁴⁾ The monofunctional boranes FcBMes₂ and FcBXyl₂ are invariably encountered as minor side products in the final synthetic step (Scheme 1), resulting from protonation of 1,2-fc(Li)BMes₂ [or 1,2-fc(Li)BXyl₂] in competition with electrophilic quenching by the sterically encumbered electrophile FBMes₂/FBXyl₂; separation is easily achieved by fractional crystallization from hexanes.

⁽¹⁵⁾ Data for 3: To a stirred solution of 2 (0.22 g, 0.43 mmol) in Et₂O (15 mL) at -78 °C were added "BuLi and TMEDA (1.0 equiv of each) and (after 1 h) a solution of FBMes2 (1.13 g, 4.21 mmol, 90% purity as received from Sigma Aldrich) in Et₂O (5 mL). After warming to 20 °C over 2 h and stirring for a further 12 h, the reaction mixture was diluted with Et₂O (100 mL) and washed with water (50 mL) and brine (50 mL). Removal of volatiles in vacuo yielded the crude product as a dark red solid. Purification using column chromatography (hexane to 10% ethyl acetate/hexane) yielded 3 as a dark red amorphous solid still contaminated with Mes₂BOBMes₂. Fractional crystallization from hexane (to remove the borinic anhydride) and finally from MeOH/Et2O yielded the product as dark red crystals (0.24 g, 83%). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated solution in diethyl ether. ¹H NMR (300 MHz, [D]chloroform, 20 °C): δ 1.55 (s, 12H, para-CH₃ of Mes), 2.00-2.70 (br overlapping signals, 24H, ortho-CH₃ of Mes), 4.15 (s, 5H, Cp), 4.87 (t, J = 2.5 Hz, 1H, C₅H₃), 5.07 (d, J = 2.5 Hz, 2H, C₅H₃), 6.22 (s, 2H, aromatic CH of Mes), 6.36 (s, 2H, aromatic CH of Mes), 6.74 (s, 2H, aromatic CH of Mes), 6.81 (s, 2H, aromatic CH of Mes). ¹H NMR (300 MHz, [D]toluene, 120 °C): δ 2.07 (s, 12H, para-CH₃ of Mes), 2.25 (s, 24H, ortho-CH₃ of Mes), 3.92 (s, 5H, Cp), 4.52 (m, 1H, C₅H₃), 5.02 (d, J = 2.0 Hz, 2H, C₅H₃), 6.50 (s, 8H, aromatic CH of Mes). ¹H NMR (300 MHz, [D]toluene, $-60 \degree$ C): δ 1.70, 1.77, 2.08, 2.19, 2.25, 2.39, 2.58, 2.97, 3.21 (s, each 3H, ortho-CH₃ of Mes), 2.02 (s, 12H, para-CH₃ of Mes), 3.78 (s, 5H, Cp), 4.26, 4.84, 5.02 (m, each 1H, C_5H_3), 6.02, 6.05, 6.30, 6.58 (2 signals), 6.61 (2 signals), 6.68 (s, each 1H, aromatic CH of Mes). ¹³C NMR (75 MHz, [D]toluene, 120 °C): δ 20.3 (para-CH₃ of Mes), 24.5 (ortho-CH₃ of Mes), 71.2 (Cp), 73.5, 90.1 (C5H3), 128.1 (aromatic CH of Mes), 136.6 (para-quaternary C of Mes), 139.0 (*ortho*-quaternary C of Mes), boron-bound quaternary carbons not observed. ¹¹B NMR (96 MHz, [D]chloroform, 20 °C): δ 80. UV–vis (dichloromethane): $\lambda_{max} = 510$ nm, $\varepsilon = 1903$ mol⁻¹ cm⁻¹ dm³. $E_{1/2}$ (CH₂Cl₂) = +0.177 V (with respect to FcH/FcH+); peak-topeak separation = 65 mV. MS (EI⁺): 682 (100%) M⁺; exact mass (calcd for M⁺, ¹⁰B isotopomer) 680.3677, (meas.) 680.3657. Microanalysis (calcd for C₄₆H₅₂B₂Fe) C 80.91, H 7.68; (measd) C 80.66, H 7.44. Crystallographic data for 3: M_r (82.39, orthorhombic, Pca 21, a = 22.3532(3) Å, b = 11.3185(1) Å, c = 29.4442(4) Å, V = 7447.7(2) Å³, Z = 8, ρ_c = 1.217 Mg m⁻³, T = 150 K, λ = 0.71073 Å; 42 541 reflections collected, 7629 independent [R(int) = 0.000], which were used in all calculations. $R_1 = 0.0459$, $wR_2 = 0.1029$ for observed unique reflections. $[I > 2\sigma(I)]$ and $R_1 = 0.0679$, $wR_2 = 0.1124$ for all unique reflections. Max. and min. residual electron densities 0.45 and $-0.48 \text{ e } \text{Å}^{-1}$ 3. CSD reference: 778112.



Figure 1. One of the two independent molecules in the asymmetric unit of 1,2-fc(BMes₂)₂ (**3**). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at the 40% probability level. Key bond lengths (Å) and angles (deg): C(6)-B(7) 1.574(7), C(5)-B(26) 1.569(7), $B(7)\cdots B(26)$ 3.702, C(5)-C(6)-B(7) 135.5(4), C(6)-C(5)-B(26) 133.7(4), C(2)-C(6)-B(7) 114.4(4), C(4)-C(5)-B(26) 120.6(4).



Figure 2. Interconversion of the enantiomeric conformations of 3 by synchronized motion of the $-BMes_2$ units.

B····B separation {3.684 Å (mean) cf. 3.263 Å for 1,2-C₆H₄-[B(C₆F₅)₂]₂ and 3.353 Å for 1,8-C₁₀H₆(BMes₂)(BPh₂)}.^{8g,j}

The influence of steric factors is also apparent in the ¹H NMR spectrum of 3, which features broad signals for both the mesityl ortho-CH₃ and meta-CH protons at 20 °C, characterizing slow rotation about the $B-C_{Cp,ipso}$ bond; a spectrum featuring only one ortho-CH₃ and one meta-CH signal is observed at 120 °C, while eight distinct ortho-CH₃ signals can be identified at -60 °C. In addition, at -60 °C the 2:1 pattern for the protons of the C₅H₃ group is split into three distinct signals (relative intensities: 1:1:1), consistent with slowing of the synchronized "windshield wiper" motion of the two -BMes₂ units (Figure 2). Consideration of the coalescence behavior of the respective signals yields an activation barrier, ΔG^{\ddagger} , of 48 kJ mol⁻¹.¹⁶ A further fluxional process involving completely free rotation about both $B-C_{Cp,ipso}$ and $B-C_{Mes,ipso}$ bonds on the NMR time scale (and thus giving rise to the simple ¹H spectrum observed at +120 °C) can be identified with a coalescence temperature of ca. +45 °C (see Supporting Information for details).

The interaction of **3** with cyanide can readily be monitored by multinuclear NMR (e.g., $\delta_{\rm B}$ 80 to -15 ppm for the CN⁻bound boron center) and IR spectroscopies [ν (CN) shift 2080 to 2162 cm⁻¹] and by cyclic voltammetry (cathodic shift of -430 mV in thf).^{5k} Electrospray mass spectrometry experi-



Figure 3. Molecular structures of (a) $[K(18-crown-6)][3 \cdot CN] \cdot CHCl_3$ and (b) the anionic component of $[K(18-crown-6)][3 \cdot F]$. Hydrogen atoms, solvate molecule [for (a)], and counterion [for (b)] are omitted for clarity, and thermal ellipsoids are set at the 40% probability level. Key bond lengths (Å) and angles (deg): (for $[K(18-crown-6)][3 \cdot CN]$) B(7)-C(8) 1.648(4), C(8)-N(9) 1.146(3), C(6)-B(7) 1.672(4), C(2)-B(28) 1.568(4), $B(7) \cdots B(28)$ 3.887, C(3)-C(2)-B(28) 116.5(2), C(5)-C(6)-B(7) 115.0(2), C(2)-C(6)-B(7) 138.5(2), C(6)-C(2)-B(28) 137.2(2), B(7)-C(8)-N(9) 173.2(3); (for $[K(18-crown-6)][3 \cdot F]$) B(31)-F(50) 1.471(5), $B(12) \cdots B(31)$ 3.602, C(10)-B(31) 1.635(8), C(9)-B(12) 1.548(7), C(8)-C(9)-B(12) 120.9(4), C(11)-C(10)-B(31) 123.2(4), C(10)-C(9)-B(12) 133.0(4), C(9)-C(10)-B(31) 130.6(4).

Scheme 2. Interaction of Cyanide and Fluoride Ions with 3



ments imply that a single equivalent of cyanide is taken up, and single-crystal X-ray diffraction studies not only confirm this binding stoichiometry but also reveal that the anion is bound in a nonchelating fashion, *exo* to the $B \cdots B$ cavity and (in the solid state at least) to the potassium center of the [K(18-crown-6)]⁺ unit via N(9) (Figure 3a).¹⁷

The thermodynamics of cyanide binding by 3 can be assessed by UV-vis titration experiments (see Supporting Information) and a binding constant, K_{CN} (thf), of 3.7(0.6) × $10^4 \,\mathrm{M^{-1}}$ determined in thf solution (Scheme 2).¹⁸ This can be put into context by the corresponding value for the closely related monofunctional system FcBMes₂, which is indicative of stronger binding of the CN⁻ anion $[8.3(2.0) \times 10^4 \text{ M}^{-1}$ in the more strongly competitive solvent dichloromethane (Gutmann's acceptor number, AN = 20.8, cf. 8 for thf)].^{5k,19} Presumably the presence of a second, highly sterically demanding, -BMes₂ group presents a thermodynamic disincentive for the binding of cyanide, involving as it does an increase in steric bulk on formation of the -BMes₂CN⁻ function. Consistent with this assertion, the B···B separation increases from 3.684 Å (mean) for 3 to 3.883 Å for $[3 \cdot CN]^-$. Interestingly, if crystals of [K(18-crown-6)][3.CN] are redissolved in chloroform-d rapid re-equilibration takes place, leading to loss of cyanide and to the formation of a mixture of $[3 \cdot CN]^-$ and 3. Integration of the respective NMR signals with respect to a tetramethylsilane standard allows an

⁽¹⁶⁾ Coalescence of the two signals is observed at -35 °C; using $\Delta\nu$ determined from the low-temperature limit (0.18 ppm, 54 Hz), k at this temperature can thus be evaluated as 120 Hz. From the Eyring equation, therefore, $\Delta G^{\ddagger} = (24.4)RT = 48 \text{ kJ mol}^{-1}$.

⁽¹⁷⁾ Crystallographic data for [K(18-crown-6)][3·CN]·CHCl₃: M_r 1131.20, monoclinic, $P2_1/c$, a = 16.0148(2) Å, b = 16.4211(2) Å, c = 22.8565(3) Å, $\beta = 106.626(1)^{\circ}$, V = 7447.7(2) Å³, Z = 4, $\rho_c = 1.304$ Mg m⁻³, T = 150 K, $\lambda = 0.71073$ Å; 65 506 reflections collected, 13125 independent [R(int) = 0.050], which were used in all calculations. $R_1 = 0.0547$, $wR_2 = 0.1163$ for observed unique reflections. Max. and min. residual electron densities 1.11 and -0.95 e Å⁻³. CSD reference: 778113.

⁽¹⁸⁾ For a description of the method used for binding constant determination see refs 8s and 9e.

⁽¹⁹⁾ Definition of AN scale: Mayer, U.; Gutmann, V.; Gerger, W. Monatsh. Chem. 1975, 106, 1235.



Figure 4. Plots of (a) $(A - A_{\infty})/(A_0 - A_{\infty})$ vs time and (b) $\ln(A - A_{\infty})$ versus time (both measured at $\lambda = 570$ nm) for the reactions in thf of [^{*n*}Bu₄N]F with 1,2-fc(BMes₂)₂ (\blacklozenge), 1,2-fc(BMes₂)-(BXyl₂) (\blacktriangle), and 1,2-fc(BXyl₂)₂ (\blacksquare). For the logarithmic plot, the solid lines give a least-squares (linear) fit (with $R^2 = 0.998$, 0.996, and 0.993, respectively) from which pseudo-first-order rate constants (k_{obs}) of 1.64 × 10⁻², 2.08 × 10⁻², and 2.79 × 10⁻² s⁻¹ can be derived.

equilibrium constant $K_{CN}(CDCl_3)$ of 1.5 (±0.5) M⁻¹ to be estimated; the significantly weaker binding in this solvent (cf. thf) is consistent with its much more strongly competitive nature (AN = 23.1).¹⁹

Fluoride binding by 3 can be shown by simple competition experiments to be weaker than cyanide binding, for example, by the quantitative formation (by ¹¹B NMR) of $[3 \cdot CN]^{-1}$ on addition to 3 of a solution equimolar in both F^- and CN^- . Moreover, further experiments reveal that the binding of fluoride is very weak indeed; no evidence for the formation of $[3 \cdot F]^{-}$ could be obtained from NMR measurements in either dichloromethane or chloroform. Single crystals of [K(18crown-6) [3·F] can be grown from thf solutions saturated with fluoride,²⁰ although in the absence of excess anion, solutions in thf- d_8 rapidly regenerate the free receptor by fluoride loss. Interestingly, even in the presence of a vast excess of fluoride, the rate of formation of the host/guest complex (as appraised by UV-vis spectroscopy; Figure 4) appears to be very slow. Monitoring of the intensity of the band at 570 nm due to the free receptor as a function of time under pseudo-first-order conditions (i.e., in the presence of an 20-fold excess of $[^{n}Bu_{4}N]^{+}F^{-}\cdot 4H_{2}O)$,²¹ gives a linear plot of $\ln(A - A_{\infty})$ versus time, from which a rate constant, k_{obs} , of $1.64 \times 10^{-2} \text{ s}^{-1}$ can be determined.

To understand the structural origins of the slow fluoride uptake by 3 (cf. essentially instantaneous binding of cyanide), X-ray diffraction studies were carried out on single crystals of [K(18-crown-6)][3.F] (Figure 3b). Notably, the F⁻ anion interacts with only one of the two boron centers, as might have been expected given the wide $B \cdots B$ separation determined for the free receptor 3 (3.684 Å), compared to typical $B-\mu F$ bond lengths {e.g., 1.585(5) and 1.633(5) Å for $[1,8-C_{10}H_8(BMes_2)(BC_{12}H_8S)(\mu-F)]^{-}$.⁸⁸ Nevertheless, the fluoride ion is bound *endo* to the B···B cavity²² and, in further contrast to [3.CN]-, features no secondary interactions between the anion and the $[K(18-crown-6)]^+$ counterion. In an attempt to determine whether similar binding within the $B \cdots B$ binding domain might be occurring in solution and-given the steric demands of the flanking mesityl substituents-might therefore be implicated in the slow uptake of F⁻, we have examined the corresponding rates of reaction for 1,2-fc(BMes₂)(BXyl₂) (3') and 1,2-fc- $(BXyl_2)_2$ (3"), which feature successively reduced steric loading on the periphery of the binding cavity. The results of these experiments are illustrated in Figure 4, from which pseudo-first-order rate constants of 2.08 \times 10⁻² and 2.79 \times 10^{-2} s⁻¹ were calculated for 3' and 3'', respectively. These (reproducible) differences in the rate of fluoride uptake, together with the more marked difference in the binding kinetics for fluoride and cyanide, are consistent with binding of F^- within the $B \cdots B$ cavity in thf solution.

In summary, bifunctional Lewis acid **3** can discriminate both thermodynamically and kinetically between fluoride and cyanide anions, the latter being attributed to the differential binding modes of cyanide (*exo*) and fluoride (*endo*) within the receptor cavity. Further studies aimed at developing the chemistry of **3** and related derivatives, e.g., for the chelation of chloride, are in progress and will be reported in due course.

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Supporting Information Available: Synthetic and spectroscopic data for 3' and 3''; details of binding constant determinations for 3; synthetic, spectroscopic, and crystallographic data for 2'. This material is available free of charge via the Internet at http://pubs.acs.org.

⁽²⁰⁾ Crystallographic data for [K(18-crown-6)][$3 \cdot F$]: M_r 1039.91, triclinic, PI, a = 10.2123(1) Å, b = 12.6792(2) Å, c = 26.4929(5) Å, $\alpha = 81.506(1)^\circ$, $\beta = 83.000(1)^\circ$, $\gamma = 74.591(1)^\circ$, V = 3258.5(1) Å³, Z = 2, $\rho_c = 1.060$ Mg m⁻³, T = 150 K, $\lambda = 0.71073$ Å; 52.098 reflections collected, 14 705 independent [R(int) = 0.0506], which were used in all calculations. $R_1 = 0.1229$, $wR_2 = 0.2342$ for observed unique reflections. [$I > 2\sigma(I)$] and $R_1 = 0.1496$, $wR_2 = 0.2486$ for all unique reflections. Max. and min. residual electron densities 1.43 and -1.15 e Å⁻³. CSD reference: 778114.

⁽²¹⁾ 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 $[^{n}Bu_{4}N]F\cdot 4H_{2}O$ and $[^{n}Bu_{4}N]CN\cdot 2H_{2}O$ by elemental microanalysis.

⁽²²⁾ For a previous analysis of the factors influencing *endo/exo* coordination of Lewis bases to bifunctional boranes, see ref 8z.