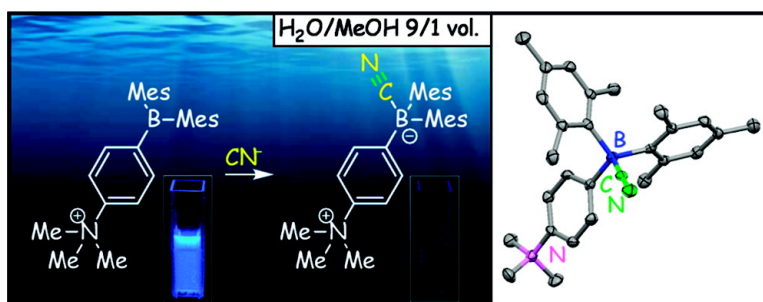


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## Ammonium Boranes for the Selective Complexation of Cyanide or Fluoride Ions in Water

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**Abstract:** With the recognition of aqueous fluoride and cyanide ions as an objective, we have investigated the anion binding properties of two isomeric ammonium boranes, namely [*p*-(Mes<sub>2</sub>B)C<sub>6</sub>H<sub>4</sub>(NMe<sub>3</sub>)]<sup>+</sup> (**[1]**<sup>+</sup>) and [*o*-(Mes<sub>2</sub>B)C<sub>6</sub>H<sub>4</sub>(NMe<sub>3</sub>)]<sup>+</sup> (**[2]**<sup>+</sup>). These cationic boranes, which could be obtained by reaction of the known 4- and 2-dimesitylboryl-*N,N*-dimethylaniline with MeOTf, have been investigated both experimentally and computationally. They both react with fluoride and cyanide ions in organic solvents to afford the corresponding fluoroborate/ or cyanoborate/ammonium zwitterions **1F**, **1CN**, **2F**, and **2CN**. In aqueous solution, however, these cationic boranes behave as remarkably selective receptors. Indeed, **[1]**<sup>+</sup> only complexes cyanide ions while **[2]**<sup>+</sup> only complexes fluoride ions. In H<sub>2</sub>O/DMSO 60:40 vol (HEPES 6 mM, pH 7), the cyanide binding constant of **[1]**<sup>+</sup> and the fluoride binding constant of **[2]**<sup>+</sup> are respectively equal to 3.9 (±0.1) × 10<sup>8</sup> and 910 (±50) M<sup>-1</sup>. Structural and computational studies indicate that both steric and electronic effects contribute to the unusual selectivity displayed by these cationic boranes. Owing to favorable Coulombic effects, the *para*-derivative **[1]**<sup>+</sup> has a very high affinity for cyanide; yet these effects are not sufficiently intense to allow complexation of the more efficiently hydrated and less basic fluoride anion. In the case of the *ortho*-derivative **[2]**<sup>+</sup>, the proximity of the ammonium moiety leads to an increase in the Lewis acidity of the boron center thus making fluoride binding possible. However, steric effects prevent cyanide coordination to the boron center of **[2]**<sup>+</sup>. Finally, cation **[1]**<sup>+</sup> and **[2]**<sup>+</sup> bind their dedicated anions reversibly and show a negligible response in the presence of other common anions including Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, OAc<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and HSO<sub>4</sub><sup>-</sup>.

### Introduction

Cyanide is a toxic anion which binds to and deactivates the cytochrome *c* oxidase enzyme with sometimes fatal consequences.<sup>1</sup> Because cyanide is widely available in both research and industrial settings, its use for harmful purposes or its release in the environment are sources of concern.<sup>2</sup> For these reasons, the development of methods that can sense this anion in water has become a topical objective. Another important nucleophilic anion is the fluoride anion. This anion is often added to drinking water and toothpaste because of its beneficial effects in dental health. It is also administered in the treatment of osteoporosis.<sup>3</sup> As widely documented, however, excessive fluoride intake can be problematic and can lead to the development of dental or skeletal fluorosis.<sup>4</sup> Thus, as for cyanide, the detection of fluoride levels in water is an important task.

To date, the recognition of cyanide and fluoride ions has been successfully implemented in organic solvents using receptors that hydrogen bond with the guest.<sup>5–16</sup> Such receptors are, however, challenged in the presence of water which interferes

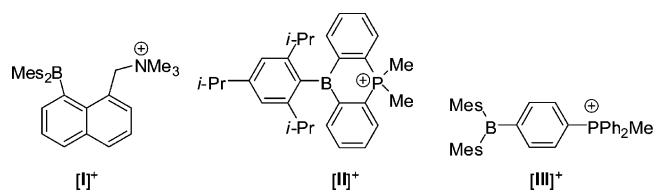
with the host–guest interactions. An added complication exists for the cyanide ion whose competitive protonation (p*K*<sub>a</sub> (HCN) = 9.3) complicates its capture in neutral water. Despite these challenges, recent efforts have afforded a number of receptors<sup>17–23</sup> which sometimes function in water.<sup>18,19,22,24</sup> Most of the cyanide receptors are electrophilic organic reagents which undergo C–C bond forming reactions with cyanide. Some of these reactions necessitate basic pH and their reversibility is not always well documented. Other cyanide receptors or probes with interesting

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properties include boronic acids,<sup>25–29</sup> boron-subphthalocyanines,<sup>24,30</sup> zinc-porphyrins,<sup>31,32</sup> iron-hemes,<sup>33</sup> and transition metal complexes.<sup>34</sup> For fluoride ions, the high hydration enthalpy of  $-504$  kJ/mol is certainly one of the factors making recognition of this anion in aqueous solution especially difficult.<sup>6,7</sup> To circumvent these difficulties, several groups are currently studying receptors in which the fluoride binding site is a Lewis acidic element such as boron,<sup>25,35–55</sup> aluminum,<sup>56</sup> or tin.<sup>57</sup> Recent advances in this area suggest that cationic boranes<sup>58–61</sup> such as **[I]**<sup>+</sup>, **[II]**<sup>+</sup>, and **[III]**<sup>+</sup> may be competent for fluoride capture in water. Indeed, **[I]**<sup>+</sup> and **[II]**<sup>+</sup> promote the transfer of fluoride ions from water into organic or solid phases<sup>59,62</sup> while **[III]**<sup>+</sup> binds fluoride ions in H<sub>2</sub>O/MeOH 90:10 vol with a binding constant of  $1000 (\pm 100) \text{ M}^{-1}$ .<sup>63</sup>

It has long been established that triarylboranes interact with cyanide to form the corresponding cyanoborate complexes. For example, the  $[\text{Ph}_3\text{BCN}]^-$  anion can be used for the precipitation of cesium ions.<sup>64</sup> This simple observation suggests that water-stable triarylboranes could be used for the complexation of



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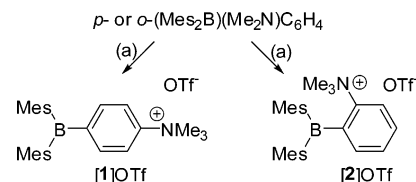
cyanide in water. While this possibility has long gone unnoticed, the group of Jäkle showed recently that polymers containing pendant triarylboranes can serve to probe cyanide in organic solvents.<sup>46</sup> Hoping to achieve the recognition of cyanide in water, we have now turned our attention to cationic boron-based receptors. On the basis of the results that we have obtained on the recognition of fluoride ions,<sup>63</sup> we hypothesized that cationic boranes may be particularly well-adapted for cyanide complexation because of favorable Coulombic receptor-anion attractions.

In this paper, we report the synthesis of the cationic borane  $[p\text{-(Mes}_2\text{B)C}_6\text{H}_4\text{(NMe}_3\text{)}]^+$  (**[I]**<sup>+</sup>) which serves as a selective receptor for cyanide ions in aqueous solutions. We also report the synthesis of its structural isomer  $[o\text{-(Mes}_2\text{B)C}_6\text{H}_4\text{(NMe}_3\text{)}]^+$  (**[2]**<sup>+</sup>) which only complexes fluoride ions in aqueous solutions.

## Discussion and Results

**Synthesis, Structure, and Properties.** The ammonium borane triflate salts **[1]OTf** and **[2]OTf** could be easily obtained by reaction of the known 4- and 2-dimesitylboryl-*N,N*-dimethylaniline<sup>65–67</sup> with MeOTf in diethyl ether (Scheme 1). These salts dissolve in polar solvents such as acetone, acetonitrile and DMSO but are insoluble in hydrocarbon solvents and diethyl ether. **[1]OTf** and **[2]OTf** are hygroscopic colorless solids which have been characterized by NMR spectroscopy and elemental analysis. The <sup>1</sup>H NMR spectra of **[1]OTf** (CDCl<sub>3</sub>) and **[2]OTf** (acetone-*d*<sub>6</sub>) feature all expected resonances for the aromatic CH groups of the phenylene core. The aryl and methyl proton resonances of the two mesityl groups of **[2]OTf** are split into broad multiple signals thus indicating the existence of a congested structure. The proton resonance of the trimethylammonium group in **[1]OTf** and **[2]OTf** appears at 3.74 ppm (CDCl<sub>3</sub>) and 3.75 ppm (acetone-*d*<sub>6</sub>), respectively. The broad <sup>11</sup>B NMR signals at 74 ppm for **[1]**<sup>+</sup> and 66 ppm for **[2]**<sup>+</sup> (CDCl<sub>3</sub>), respectively, are characteristic of triaryl boranes.

### Scheme 1<sup>a</sup>



<sup>a</sup> Conditions: (a) Et<sub>2</sub>O, MeOTf, 78% for **[1]OTf** and 39% for **[2]OTf**.

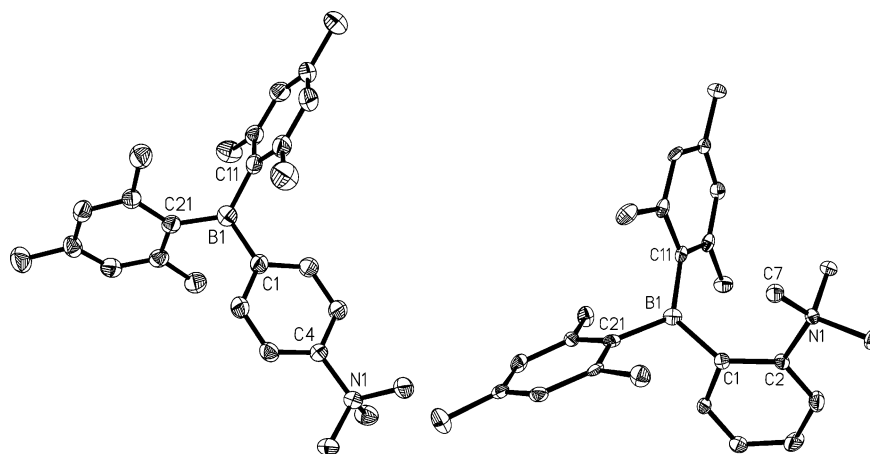
The crystal structures of **[1][OTf]** and **[2][OTf]** have been determined (Table 1, Figure 1). Salt **[1][OTf]** crystallizes in the triclinic space group  $P\bar{1}$  as a toluene solvate with two molecules in the asymmetric unit (Figure 1). Both molecules have very

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**Table 1.** Crystal Data, Data Collection, and Structure Refinement for [1][OTf]-0.5(Toluene), [2][OTf], 1CN-Acetone and 2F

	[1][OTf]-0.5(toluene)	[2][OTf]	1CN-acetone	2F
		Crystal Data		
formula	C <sub>31.50</sub> H <sub>39</sub> BF <sub>3</sub> NO <sub>3</sub> S	C <sub>28</sub> H <sub>35</sub> BF <sub>3</sub> NO <sub>3</sub> S	C <sub>31</sub> H <sub>41</sub> BN <sub>2</sub> O	C <sub>27</sub> H <sub>35</sub> BFN
<i>M<sub>r</sub></i>	579.51	533.44	468.47	403.37
crystal size (mm <sup>3</sup> )	0.23 × 0.20 × 0.20	0.22 × 0.16 × 0.13	0.28 × 0.10 × 0.08	0.29 × 0.21 × 0.20
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub>
<i>a</i> (Å)	8.9107(8)	14.061(4)	9.3438(17)	8.4441(11)
<i>b</i> (Å)	16.1875(15)	12.976(3)	12.777(2)	15.338(2)
<i>c</i> (Å)	23.213(2)	16.329(4)	23.658(4)	8.8250(11)
α (deg)	109.8110(10)			
β (deg)	95.6030(10)	113.423(5)	99.547(2)	95.774(2)
γ (deg)	90.4530(10)			
<i>V</i> (Å <sup>3</sup> )	3132.1(5)	2733.8(12)	2785.4(9)	1137.2(3)
<i>Z</i>	4	4	4	2
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.229	1.296	1.117	1.178
μ (mm <sup>-1</sup> )	0.153	0.169	0.066	0.072
<i>F</i> (000)	1228	1128	1016	436
		Data Collection		
<i>T</i> (K)	110(2)	110(2)	110(2)	110(2)
scan mode	ω	ω	ω	ω
<i>hkl</i> range	-11 → +11 -21 → +21 -30 → +30	-16 → +15 -14 → +14 -12 → +18	-8 → +8 -11 → +11 -20 → +20	-10 → +9 -20 → +19 -11 → +11
measd reflns	29051	11848	12791	8020
unique reflns [ <i>R</i> <sub>int</sub> ]	14466 [0.0394]	4286 [0.0819]	2017 [0.0502]	4989 [0.0710]
reflns used for refinement	14466	4286	2017	4989
		Refinement		
refined parameters	730	335	316	271
GOF on <i>F</i> <sup>2</sup>	1.024	1.024	1.002	1.004
<i>R</i> <sub>1</sub> , <sup>a</sup> <i>wR</i> <sub>2</sub> , <sup>b</sup> all data	0.1094, 0.1172	0.1105, 0.1604	0.0622, 0.1364	0.0668, 0.1485
ρ <sub>fin</sub> (max/min) (e Å <sup>-3</sup> )	0.399, -0.363	0.520, -0.461	0.276, -0.236	0.321, -0.282

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}.$$

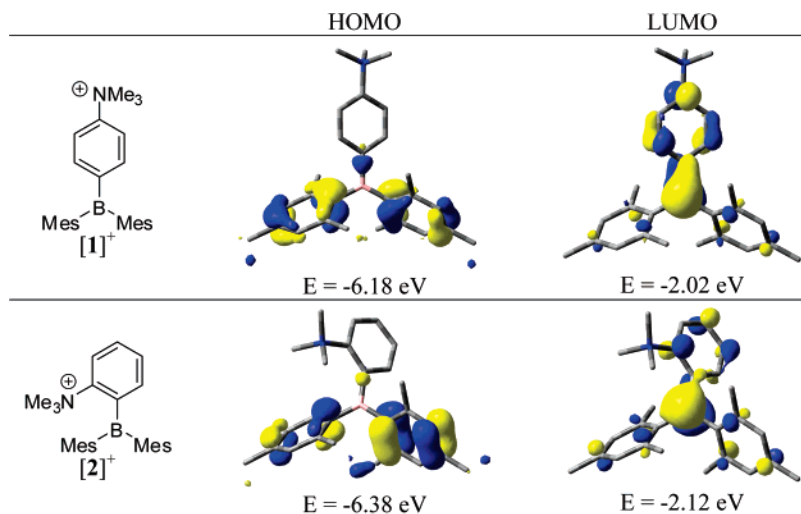


**Figure 1.** Crystal structure of [1]<sup>+</sup> in [1]OTf-0.5(toluene) (left) and [2]<sup>+</sup> in [2]OTf (right) (50% ellipsoid, H-atoms omitted); selected bond lengths (Å) and angles (deg). [1]<sup>+</sup> (the metrical parameters of the second independent molecule are provided in brackets): B(1)–C(11) 1.569(3) [1.577(3)], B(1)–C(21) 1.572(3) [1.578(3)], B(1)–C(1) 1.567(3) [1.559(3)]; C(11)–B(1)–C(21) 125.8(2) [125.6(2)], C(11)–B(1)–C(1) 117.5(2) [116.9(2)], C(21)–B(1)–C(1) 117.0(2) [117.4(2)]. [2]<sup>+</sup>: B(1)–C(21) 1.574(7), B(1)–C(11) 1.578(7), B(1)–C(1) 1.582(7), C(1)–C(2) 1.426(6); C(21)–B(1)–C(11) 121.5(4), C(21)–B(1)–C(1) 116.1(4), C(11)–B(1)–C(1) 122.1(4), C(2)–C(1)–B(1) 135.8(4), C(1)–C(2)–N(1) 121.8(4).

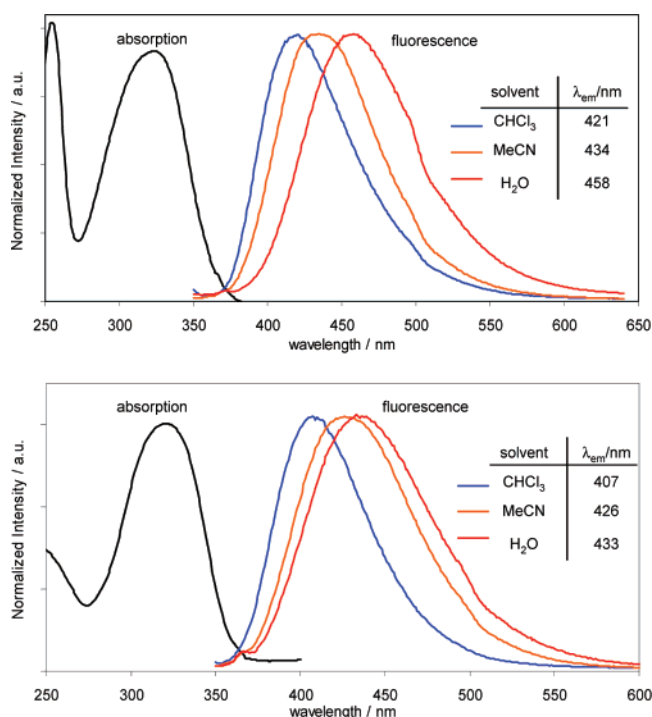
similar structures and do not form unusually short contacts with the triflate anions. Both molecules feature a trigonal planar boron center as indicated by the sum of the C<sub>aryl</sub>–B–C<sub>aryl</sub> angles ( $\sum_{(C-B-C)} = 360^\circ$ ). All carbon–boron bond distances fall in the 1.557(4)–1.580(4) Å range and are comparable to those found in the starting material.<sup>66,67</sup> Salt [2][OTf] crystallizes in the *P*2<sub>1</sub>/*c* space group with one molecule in the asymmetric unit (Figure 1). As for [1]<sup>+</sup>, the boron center is trigonal planar ( $\sum_{(C-B-C)} = 359.7^\circ$ ) and does not interact with the triflate anion. The boron center of the ortho-derivative [2]<sup>+</sup> is separated from the methyl carbon atom C(7) by only 3.175(7) Å. This short

separation indicates that the unsaturated boron center is sterically encumbered. This conclusion is in agreement with (i) the large B(1)–C(1)–C(2) angle (135.8(4)°) which substantially deviates from the value of 126.95° observed in the starting borane 2-dimesitylboryl-*N,N*-dimethylaniline;<sup>65</sup> (ii) the elongated C(1)–C(2) bond of 1.426(6) Å. Despite these distortions, the boron–carbon bonds which are in the 1.574(7)–1.582(7) Å range remain within the norm.<sup>65</sup>

The structures of cations [1]<sup>+</sup> and [2]<sup>+</sup> have been optimized using DFT methods (B3LYP, 6-31g(d) for all aromatic carbon, boron, and nitrogen atoms, 6-31g for all other atoms) and



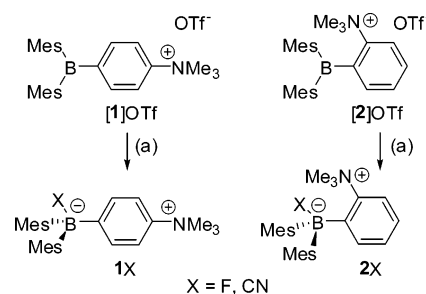
**Figure 2.** HOMO and LUMO of  $[1]^+$  and  $[2]^+$  (isodensity value = 0.05, H-atoms omitted for clarity).



**Figure 3.** Absorption (in H<sub>2</sub>O/DMSO 60:40 vol) and emission spectra of  $[1]^+$  (above) and  $[2]^+$  (below).

subjected to single point energy calculations using the polarizable continuum model<sup>68,69</sup> (PCM) with water as a solvent. Inspection of the frontier orbitals shows that the lowest unoccupied molecular orbital (LUMO) bears an important contribution from the boron-empty p-orbital while the highest occupied molecular orbital (HOMO) is localized on the mesityl rings (Figure 2). The energy of the LUMO in the *ortho*-isomer  $[2]^+$  (−2.12 eV) is lower than in the *para*-isomer  $[1]^+$  (−2.02 eV) which suggests that  $[2]^+$  is a stronger Lewis acid. Since the ammonium moiety is closer to the boron center in  $[2]^+$  than in  $[1]^+$ , the higher Lewis acidity of  $[2]^+$  can also be anticipated on the basis of a simple inductive effect argument. The energies

#### Scheme 2<sup>a</sup>



<sup>a</sup> Conditions: (a) X = F: TBAF in CHCl<sub>3</sub>, 94% for 1-F and 88% for 2-F; X = CN: NaCN, MeOH, 95% for 1-CN and 68% for 2-CN.

of the LUMOs in  $[1]^+$  and  $[2]^+$  are also substantially lower than those calculated for the LUMO of Mes<sub>2</sub>BPh (−1.58 eV) at the same level of theory and with the same solvation model. This last comparison indicates that the positive charge of the cationic boranes substantially increases their Lewis acidity.<sup>58,63,70,71</sup>

In H<sub>2</sub>O/DMSO 60:40 vol, the UV spectra of  $[1]^+$  and  $[2]^+$  feature a broad absorption band at 320 nm ( $\epsilon_{320} = 9104$ ) for  $[1]^+$  and 321 nm ( $\epsilon_{321} = 9200$ ) for  $[2]^+$  (Figure 3). Time-dependent density functional theory calculations carried out using the PCM/water solvation model suggest that the low-energy edge of the absorption spectrum is in fact dominated by the HOMO–LUMO transition. Because of the localization of the frontier orbitals, the HOMO–LUMO transition can be regarded as an intramolecular “ligand-to-element” charge-transfer transition. In agreement with this view, we note that both  $[1]^+$  and  $[2]^+$  give rise to a bright fluorescence whose maximum wavelength depends on the polarity of the solvent (Figure 3). Like other boron based charge-transfer chromophores,<sup>49,72–74</sup> both  $[1]^+$  and  $[2]^+$  show positive fluorosolvatochromism which suggests that the dipole of these molecules is larger in the excited state than in the ground state.<sup>72,75,76</sup>

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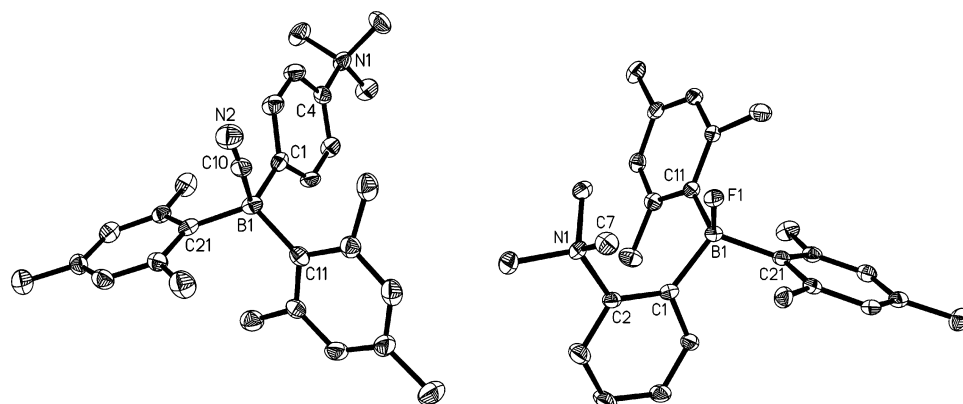
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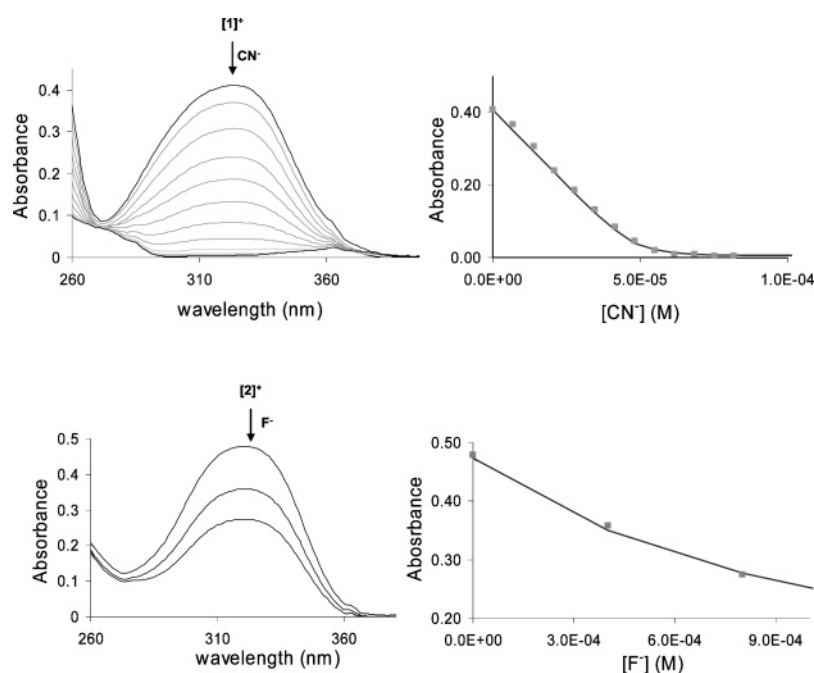
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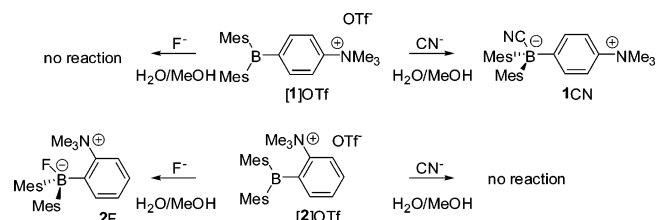
**Figure 4.** Crystal structure of **1CN** (left) and **2F** (right) (50% ellipsoid, H-atoms omitted); selected bond lengths (Å) and angles (deg). **1CN**: B(1)–C(10) 1.618(8), B(1)–C(1) 1.644(7), B(1)–C(21) 1.661(7), B(1)–C(11) 1.662(7), C(10)–B(1)–C(1) 105.0(3), C(10)–B(1)–C(21) 101.7(3); C(1)–B(1)–C(21) 116.8(4), C(10)–B(1)–C(11) 111.0(4), C(1)–B(1)–C(11) 106.6(3), C(21)–B(1)–C(11) 115.1(4). **2F**: B(1)–F(1) 1.465(3), B(1)–C(21) 1.668(4), B(1)–C(11) 1.671(3), B(1)–C(1) 1.684(4), F(1)–C(7) 2.964(3), C(1)–C(2) 1.411(4); F(1)–B(1)–C(21) 105.35(19), F(1)–B(1)–C(11) 105.18(18), C(21)–B(1)–C(11) 116.3(2), F(1)–B(1)–C(1) 108.23(19), C(21)–B(1)–C(1) 108.10(18), C(11)–B(1)–C(1) 113.1(2), C(2)–C(1)–B(1) 132.4(2).



**Figure 5.** Changes in the UV–vis absorption spectra of a solution of (top) **[1]OTf** (3 mL,  $5 \times 10^{-5}$  M in H<sub>2</sub>O/DMSO 60:40 vol; HEPES 6 mM, pH 7) upon addition of a NaCN solution ( $3 \times 10^{-3}$  M in H<sub>2</sub>O); (bottom) **[2]OTf** (3 mL,  $5 \times 10^{-5}$  M in H<sub>2</sub>O/DMSO 60:40 vol; HEPES 6 mM, pH 7) upon addition of a NaF solution (0.3 M in H<sub>2</sub>O).

**Cyanide and Fluoride Ion Complexation in Organic Solvents.** Salts **[1]OTf** and **[2]OTf** are converted into their corresponding cyanide complexes **1CN** and **2CN** upon reaction with NaCN in MeOH (Scheme 2). Analogously, the fluoride complexes **1F** and **2F** form quantitatively when **[1]OTf** and **[2]OTf** are allowed to react with TBAF in CHCl<sub>3</sub> (Scheme 2). These cyanide and fluoride complexes are zwitterions related to compounds such as [*o*-((C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(HO)B)C<sub>6</sub>H<sub>4</sub>(NHPH<sub>2</sub>)]<sup>77</sup> and [*p*-((*n*-Bu)<sub>3</sub>B)C<sub>6</sub>H<sub>4</sub>(NMe<sub>3</sub>)]<sup>78</sup> which have been previously reported. Zwitterions **1CN**, **2CN**, **1F**, and **2F** have been character-

### Scheme 3



ized by NMR spectroscopy and elemental analysis. In all cases, the <sup>11</sup>B NMR signal is in the expected range for a four-coordinate boron center (−12.9 ppm for **1CN**, −14.2 ppm for **2CN**, 5.1 ppm for **1F**, 7.3 ppm for **2F**). For the fluoride complex **1F** and **2F**, the <sup>19</sup>F NMR signal at −170 and −158 ppm, respectively, is close to that observed in compounds featuring triarylfluoroborate moieties.<sup>42,45,55,63</sup> The <sup>1</sup>H NMR spectrum of **1F** and **1CN** features four distinct resonances corresponding to the hydrogen nuclei of the *p*-phenylene ring. The inequivalence

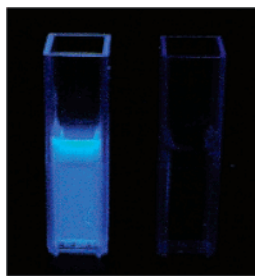
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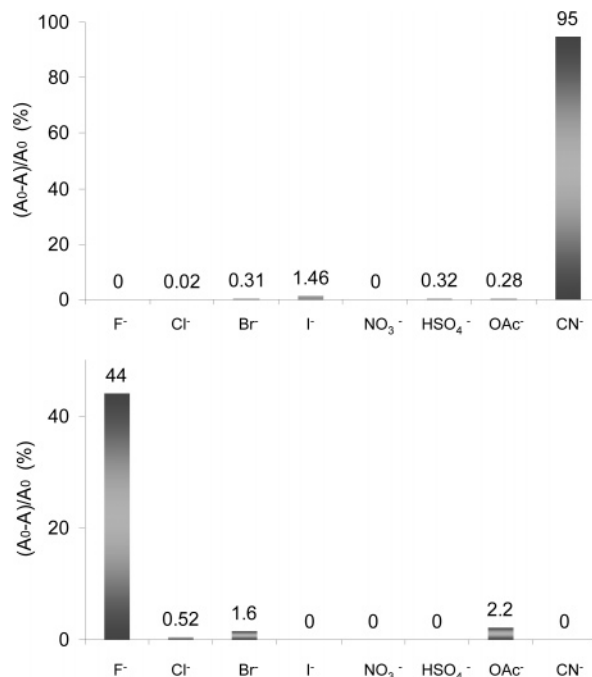


**Figure 6.** Fluorescence of a 5  $\mu\text{M}$  solution of  $[\mathbf{1}]^+$  in  $\text{H}_2\text{O}/\text{MeOH}$  90:10 vol before (left) and after (right) the addition of 1 equiv of cyanide. The cells are illuminated with a hand-held UV lamp.

of these signals indicates that rotation about the B–C bond connecting the boron atom to the *p*-phenylene moiety is restricted because of steric effects. The IR spectra of **1CN** and **2CN** also feature an intense cyanide stretching band at 2162 and 2167  $\text{cm}^{-1}$ , respectively.

The crystal structures of **1CN** and **2F** have been determined (Table 1, Figure 4). These compounds crystallize in the monoclinic space group  $P2_1/n$  for **1CN** and  $P2_1$  for **2F**. In both cases, the sum of the  $\text{C}_{\text{aryl}}\text{--B--C}_{\text{aryl}}$  angles ( $\sum_{(\text{C--B--C})} = 323.5^\circ$  for **1CN**,  $337.5^\circ$  for **2F**) indicates substantial pyramidalization of the boron atom. In **1CN**, the B(1)–C(10) bond connecting the carbon atom of the cyanide anion to the boron center (1.618–(8) Å) is comparable to those typically found in triarylcyano-borate anions such as  $[\text{Ph}_3\text{BCN}]^-$  (1.65 Å).<sup>79</sup> The same type of comment can be made about the B(1)–F(1) bond length of **2F** (1.465(3) (4) Å) which is comparable to those found in triarylfluoroborate anions (1.47 Å).<sup>42,63</sup> The most important feature in the structure of **2F** concerns the B(1)–C(1)–C(2) angle of  $132.4(2)^\circ$  which remains much larger than the ideal value of  $120^\circ$ . This large angle is comparable to that present in  $[\mathbf{2}]^+$  ( $135.8(4)^\circ$ ) thus indicating that the pyramidalization of the boron center does not allow for a great deal of steric relief. The short distance of 2.964(3) Å separating the F(1) fluorine atom from the C(7) methyl carbon atom provides additional evidence for the steric constraints present in this derivative. It can be anticipated that these steric constraints will be even more acute in **2-CN**, whose crystal structure has not been determined.

**Anion Complexation in Aqueous Solution.** The anion binding properties of  $[\mathbf{1}]^+$  and  $[\mathbf{2}]^+$  have been investigated in aqueous solution using UV–vis spectroscopy. This technique is particularly well adapted because binding of a nucleophile to the boron center disrupts the frontier orbitals of the borane leading to drastic changes of their photophysical properties.<sup>42</sup> Remarkably, the UV–vis absorption spectrum of  $[\mathbf{1}]^+$  in  $\text{H}_2\text{O}/\text{DMSO}$  95:5 vol is not affected in the presence of fluoride ions while addition of cyanide induces a rapid quenching of the band at 320 nm followed by precipitation of **1CN** (Scheme 3). In buffered  $\text{H}_2\text{O}/\text{DMSO}$  60:40 vol (HEPES 6 mM, pH 7) precipitation does not occur (Figure 5). Because of the low acidity of HCN, the cyanide binding constant of  $[\mathbf{1}]^+$  can only be determined if one considers the competing protonation of the anion. To this end, we measured the  $\text{p}K_{\text{a}}$  of HCN in  $\text{H}_2\text{O}/\text{DMSO}$  60:40 vol by a potentiometric titration and found it equal to  $9.3 \pm (0.01)$ . On the basis of this value, analysis of the titration



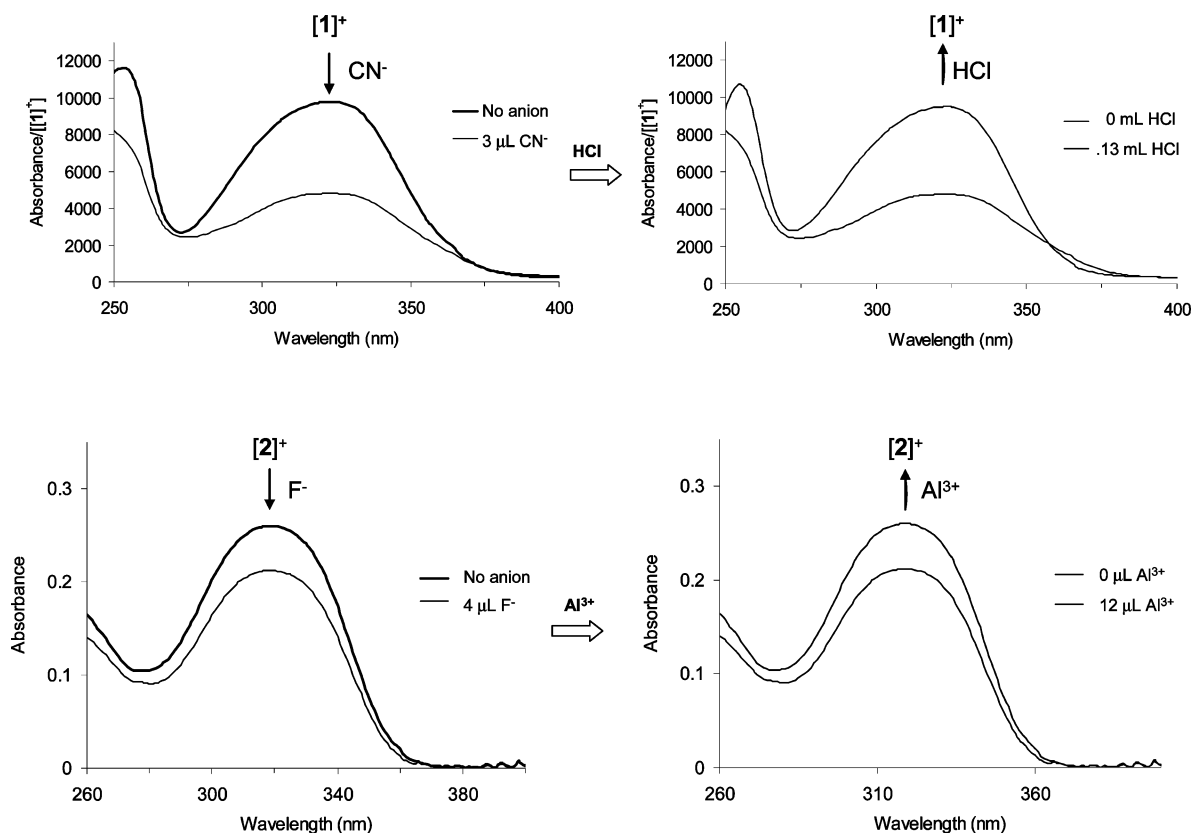
**Figure 7.** Top: Percent decrease of the absorbance of a solution of  $[\mathbf{1}]^+$  ( $5.2 \times 10^{-5}$  M) in  $\text{H}_2\text{O}/\text{DMSO}$  (60:40 vol) at 320 nm in the presence of 80 equiv of various anions. Bottom: Percent decrease of the absorbance of a solution of  $[\mathbf{2}]^+$  ( $4.9 \times 10^{-5}$  M) in  $\text{H}_2\text{O}/\text{DMSO}$  (60:40 vol) at 321 nm in the presence of 80 equiv of various anions. For F<sup>-</sup>, only 20 equiv of the anion was added to avoid precipitation.

data<sup>80</sup> indicates that the cyanide binding constant of  $[\mathbf{1}]^+$  is equal to  $3.9 (\pm 0.1) \times 10^8 \text{ M}^{-1}$  at pH 7. These experiments show that  $[\mathbf{1}]^+$  has a very high affinity for cyanide which is bound selectively over fluoride in aqueous solution. Since  $\text{Mes}_3\text{B}$  does not complex cyanide under these conditions, the elevated cyanide binding constant of  $[\mathbf{1}]^+$  probably results from favorable Coulombic effects. These effects increase the Lewis acidity of  $[\mathbf{1}]^+$  by contributing electrostatically to the receptor–anion interaction. Interestingly, however, the observed selectivity indicates that these Coulombic effects are not sufficiently intense to permit fluoride binding in aqueous solution. A factor contributing to this selectivity is the high hydration enthalpy and associated low basicity of fluoride ( $\Delta H_{\text{hyd}}^\circ = -504 \text{ kJ/mol}$ ,  $\text{p}K_{\text{a}}(\text{HF}) = 3.18$ ), which this ammonium borane receptor is unable to overcome. Because of its high cyanide binding constant,  $[\mathbf{1}]^+$  can be used for the naked-eye detection of cyanide in the  $\mu\text{M}$  range. For example, the fluorescence of a 5  $\mu\text{M}$  solution of  $[\mathbf{1}]^+$  in  $\text{H}_2\text{O}/\text{MeOH}$  90:10 vol is quenched in the presence of 1 equiv of cyanide as shown in Figure 6.

Interestingly, the behavior of  $[\mathbf{2}]^+$  appears to be the direct opposite of that of  $[\mathbf{1}]^+$ . Indeed, the UV–vis absorption spectrum of  $[\mathbf{2}]^+$  in  $\text{H}_2\text{O}/\text{DMSO}$  95:5 vol is not affected in the presence of cyanide while the addition of fluoride ions induces a rapid quenching of the band at 321 nm followed by precipitation of **2F** (Scheme 3). When the same experiment was repeated in buffered  $\text{H}_2\text{O}/\text{DMSO}$  60:40 vol (HEPES 6 mM, pH 7) precipitation does not occur until after the addition of 20 equiv of fluoride anions. Fitting of the resulting data affords a fluoride binding constant of  $910 (\pm 50) \text{ M}^{-1}$  (Figure 5). This result indicates that  $[\mathbf{2}]^+$  is a selective receptor for fluoride ions

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**Figure 8.** Top: Changes in the UV-vis absorption spectrum of a solution of  $[1][OTf]$  (3 mL,  $5.25 \times 10^{-5}$  M) in  $H_2O/DMSO$  (60:40 vol) after addition of a NaCN solution (left,  $3.0 \times 10^{-2}$  M in  $H_2O$ ) followed by the acidification with HCl to pH 0.5 (right). Bottom: Changes in the UV-vis absorption spectrum of a solution of  $[2][OTf]$  (3 mL,  $3.32 \times 10^{-5}$  M) in  $H_2O/DMSO$  (60:40 vol) after addition of a NaF solution (left,  $3.0 \times 10^{-1}$  M in  $H_2O$ ) followed by additions of an aqueous  $AlCl_3$  solution (right, 0.01 M).

in aqueous solution whose fluoride binding constant is close to that of  $[III]^+$ .<sup>63</sup> In this case, the selectivity most probably arises from a combination of effects: the steric crowding of the boron binding pocket probably hampers binding of the cyanide ion which is larger than the fluoride ion; since cyanide binding to  $[2]^+$  occurs in organic solvents, the observed lack of affinity of  $[2]^+$  for cyanide in aqueous solution must also be the result of the increased solvation and protonation of the anion which makes its complexation thermodynamically unfavorable.

These experiments also allow us to draw some conclusions on the respective anion affinity of  $[1]^+$  and  $[2]^+$ . Since only  $[2]^+$  binds fluoride, it can be concluded that the presence of the trimethylammonium group *ortho* to the boron center leads to an increase in the Lewis acidity of the derivative. This conclusion is in agreement with the computational results which suggest that the LUMO in  $[2]^+$  has a lower energy than in  $[1]^+$ . Thus, for fluoride, the anion affinity seems to be governed by the Lewis acidity of the boron center. A different set of rules seems to apply to the larger cyanide anion. For this anion, steric effects appear to supersede the apparent higher Lewis acidity of  $[2]^+$  and prevent coordination of the cyanide anion to the sterically hindered boron center. Accordingly, the reduced steric congestion of the boron center in  $[1]^+$  makes coordination of the cyanide anion possible. It is also important to note that, unlike  $[1]^+$  or  $[2]^+$ , neutral boranes such as  $Me_3B$  do not complex fluoride or cyanide ions in  $H_2O/DMSO$  95:5 vol or  $H_2O/DMSO$  60:40 vol. This difference in reactivity indicates that the charge of  $[1]^+$  or  $[2]^+$  plays a determining role in increasing the Lewis acidity of these derivatives.

To test the anion binding selectivity of  $[1]^+$  and  $[2]^+$ , their absorption spectrum has been monitored upon the addition of various anions including  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $OAc^-$ ,  $NO_3^-$ , and  $HSO_4^-$ . Despite the addition of an 80-fold excess of anions, the absorbance of the band at 320 nm for  $[1]^+$  and 321 nm for  $[2]^+$  shows no or negligible quenching in the presence of these anions thus confirming the selectivity of these receptors (Figure 7). The absorption spectra of  $[1]^+$  and  $[2]^+$  are also not altered when a neutral phosphate buffer is used indicating that binding of  $H_2PO_4^-$  does not occur. Finally, cyanide binding to  $[1]^+$  is reversible and can be modulated by adjusting the pH. Thus, when the pH of a solution containing 1CN is lowered from 7 to 0.5, the absorption at 320 nm increases, indicating liberation of the cyanide anion and regeneration of free  $[1]^+$  (Figure 8). Finally, addition of an aqueous solution of  $Al^{3+}$  to a solution containing 2-F leads to complete regeneration of  $[2]^+$  showing that fluoride binding is reversible (Figure 8).<sup>63</sup>

## Conclusion

This work demonstrates that cationic boranes such as  $[1]^+$  serve as selective receptors for cyanide in water at neutral pH. While many cyanide receptors are known, few are effective in aqueous solution at neutral pH,<sup>33</sup> conditions under which the cyanide anion exists mostly in a protonated form. The unusual cyanide binding properties of  $[1]^+$  can be assigned to favorable Coulombic effects which increase the Lewis acidity of the boron atom and strengthen the receptor-cyanide interaction. Another important aspect of this work concerns the anion binding selectivity of these cationic boranes which can be tuned using



both steric and electronic effects. Indeed, when the trimethylammonium functionality is positioned *ortho* to the boron center as in **[2]<sup>+</sup>**, the Lewis acidity of the ammonium borane is increased, making fluoride binding possible. However, in this case, the increased steric crowding of the boron center prevents coordination of the larger cyanide anion.

## Experimental Section

**General Considerations.** 4-(Dimesitylboryl)-*N,N*-dimethylaniline and 2-(dimesitylboryl)-*N,N*-dimethylaniline were synthesized by published procedures.<sup>65–67</sup> 4-Bromo-*N,N*-dimethylaniline was purchased from Oakwood Products Inc., methyl triflate, dimesitylboryl fluoride, and *N,N*-dimethylaniline were purchased from Aldrich, and *n*-Bu<sub>4</sub>NF·3H<sub>2</sub>O (TBAF) was purchased from Fluka. Et<sub>2</sub>O and THF were dried by reflux over Na/K. Hexane was dried by passing through a column charged with activated alumina. Air-sensitive compounds were handled under a N<sub>2</sub> atmosphere using standard Schlenk and glovebox techniques. UV–vis and fluorescence spectra were recorded on a HP8453 and an Aminco-Bowman 2 luminescence spectrophotometer, respectively. IR spectra were obtained using a Bruker Tensor 37 infrared spectrophotometer. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). NMR spectra were recorded on a Varian Unity Inova 400 FT NMR (399.59 MHz for <sup>1</sup>H, 375.9 MHz for <sup>19</sup>F, 128.19 MHz for <sup>11</sup>B, 100.45 MHz for <sup>13</sup>C) spectrometer at ambient temperature. Chemical shifts  $\delta$  are given in ppm and are referenced against external Me<sub>4</sub>Si (<sup>1</sup>H, <sup>13</sup>C), BF<sub>3</sub>·Et<sub>2</sub>O (<sup>11</sup>B), and CFCl<sub>3</sub> (<sup>19</sup>F). Potentiometric titrations were carried out using a SympHony gel-filled combination electrode from VWR International with a PHM290 pH stat controller from Radiometer Analytical. Melting points were measured on samples in sealed capillaries and are uncorrected.

**Crystallography.** Colorless single crystals of **[1]OTf·0.5(toluene)** could be obtained by slow evaporation of a 1:1 toluene:CH<sub>2</sub>Cl<sub>2</sub> solution. Colorless single crystals could be obtained by vapor diffusion of hexane into a concentrated dichloromethane solution **[2]OTf**. Single crystals of **1CN**–acetone were obtained by crystallization from a concentrated acetone solution. Single crystals of **2F** were obtained by vapor diffusion of hexane into a concentrated acetone solution of **2F**. The crystallographic measurement of **[1]OTf·0.5(toluene)**, **[2]OTf**, **1CN**–acetone, and **2F** was performed using a Siemens SMART-CCD area detector diffractometer, with a graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). A specimen of suitable size and quality was selected and mounted onto glass fiber with apiezon grease. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on *F*<sup>2</sup> using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms.

**Synthesis of [1]OTf.** Methyl triflate (0.53 g, 3.25 mmol) was added to a solution of 4-(dimesitylboryl)-*N,N*-dimethylaniline (1.20 g, 3.25 mmol) in Et<sub>2</sub>O (30 mL) at room temperature. The mixture was stirred overnight which resulted in the formation of a white solid. The solid was collected by filtration, washed with Et<sub>2</sub>O (3  $\times$  10 mL), and dried in under vacuum to afford **[1]OTf** as a white powder (1.35 g, 78% yield). **[1]OTf** is hygroscopic and captures water when exposed to air. Analysis of the crystal structure revealed inclusion of one molecule of toluene in the asymmetric unit: mp 210 °C. <sup>1</sup>H NMR (399.9 MHz, CDCl<sub>3</sub>):  $\delta$  1.93 (s, 12H, Mes-CH<sub>3</sub>), 2.29 (s, 6H, Mes-CH<sub>3</sub>), 3.75 (s, 9H, N-CH<sub>3</sub>), 6.81 (s, 4H, Mes-CH), 7.64–7.72 (m, 4H, phenyl-CH). <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>):  $\delta$  21.22, 23.45 (Mes-CH<sub>3</sub>), 57.32 (N-CH<sub>3</sub>), 118.64 (Mes-*o*-C), 128.53 (Mes-CH), 138.05 (phenyl-CH), 139.75 (Mes-*p*-C), 140.71 (phenyl-CH), 148.89 (B-CMe) B-C<sub>phenyl</sub>, N-C<sub>phenyl</sub>, and CF<sub>3</sub> carbon peaks were not observed. <sup>11</sup>B NMR (128.2 MHz, CDCl<sub>3</sub>):  $\delta$  +74. <sup>19</sup>F NMR (375.9 MHz, CDCl<sub>3</sub>):  $\delta$  –78.3. UV–vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$ /nm (log  $\epsilon$ ) 335 (3.93). Anal. Calcd for C<sub>28</sub>H<sub>38</sub>BNSO<sub>4.5</sub>F<sub>3</sub> (**[1]OTf**·1.5H<sub>2</sub>O): C, 61.71; H, 7.16. Found: C, 61.61; H, 6.72.

**Synthesis of [2]OTf.** Methyl triflate (0.15 mL, 0.948 mmol) was added to a solution of 2-(dimesitylboryl)-*N,N*-dimethylaniline (0.35 g,

0.948 mmol) in Et<sub>2</sub>O (15 mL) at room temperature. The mixture was stirred overnight which resulted in the formation of a white solid. The solid was collected by filtration, washed with Et<sub>2</sub>O (3  $\times$  10 mL), and dried in under vacuum to afford **[2]OTf** as a white powder (0.198 g, 39% yield): mp 219 °C. <sup>1</sup>H NMR (399.9 MHz, CDCl<sub>3</sub>):  $\delta$  1.37 (bs, 3H, Mes-CH<sub>3</sub>), 1.84 (bs, 3H, Mes-CH<sub>3</sub>), 1.95 (bs, 3H, Mes-CH<sub>3</sub>), 2.20 (bs, 3H, Mes-CH<sub>3</sub>), 2.26 (bs, 6H, Mes-CH<sub>3</sub>), 3.55 (s, 9H, N-CH<sub>3</sub>), 6.66–6.88 (bm, 4H, Mes-CH), 7.43 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 4.4 Hz, phenyl-CH), 7.72 (m, 1H, <sup>3</sup>J<sub>H-H</sub> = 4.0 Hz, phenyl-CH), 8.08 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 4.4 Hz, phenyl-CH). <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>):  $\delta$  21.18 (2C, Mes-*p*-CH<sub>3</sub>), 22.55 (1C, Mes-*o*-CH<sub>3</sub>), 23.19 (2C, Mes-*o*-CH<sub>3</sub>), 24.74 (1C, Mes-*o*-CH<sub>3</sub>), 58.25 (N-CH<sub>3</sub>), 120.50 (q, <sup>1</sup>J<sub>C-F</sub> = 319.69 Hz, CF<sub>3</sub>), 122.63 (phenyl-CH), 129.42 (bs, Mes-CMe), 129.66 (bs, Mes-CMe), 129.91 (bs, Mes-CMe), 130.19 (bs, Mes-CMe), 130.49 (phenyl-CH), 133.53 (phenyl-CH), 135.52 (phenyl-CH), 140.01 (bs, B-CMe), 140.65 (bs, N-C<sub>phenyl</sub>), 141.38 (bs, Mes-CMe), 141.71 (Mes-CMe), 141.96 (phenyl-CB), 143.13 (bs, B-CMe), 150.66 (4C, Mes-CH). <sup>11</sup>B NMR (128.2 MHz, CDCl<sub>3</sub>):  $\delta$  +67.6. <sup>19</sup>F NMR (375.9 MHz, CDCl<sub>3</sub>):  $\delta$  –74.4. UV–vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$ /nm (log  $\epsilon$ ) 328 (4.08). Anal. Calcd for C<sub>28</sub>H<sub>35</sub>BNSO<sub>3</sub>F<sub>3</sub>: C, 63.04; H, 6.61. Found: C, 62.82; H, 6.75.

**Synthesis of 1F.** Addition of a solution of TBAF (60 mg, 0.187 mmol) in chloroform (10 mL) to a solution of **[1]OTf** (100 mg, 0.187 mmol) in chloroform (10 mL) resulted in the formation of a precipitate. After stirring for 30 min, the mixture was filtered. This solid was washed with chloroform and dried under vacuum to afford **1F·0.5(CHCl<sub>3</sub>)** as a white powder: 71 mg, 94% yield, mp 260 °C. <sup>1</sup>H NMR (400 MHz, acetonitrile-*d*<sub>3</sub>):  $\delta$  1.85 (s, 12H, Mes-CH<sub>3</sub>), 2.12 (s, 6H, Mes-CH<sub>3</sub>), 3.45 (s, 9H, N-CH<sub>3</sub>), 6.45 (s, 4H, Mes-CH), 7.02–7.48 (bm, 4H, phenyl-CH). <sup>13</sup>C NMR (100.5 MHz, acetonitrile-*d*<sub>3</sub>):  $\delta$  20.85 (Mes-CH<sub>3</sub>), 25.30 (Mes-CH<sub>3</sub>), 57.79 (N-CH<sub>3</sub>), 117.00 (Mes-*o*-CMe), 123.41 (phenyl-CB), 129.11 (Mes-CH), 132.69 (phenyl-CH), 134.21 (B-CMe), 135.66 (Mes-*p*-CMe), 142.10 (phenyl-CH), 144.07 (phenyl-CN). <sup>11</sup>B NMR (128.2 MHz, acetonitrile-*d*<sub>3</sub>):  $\delta$  5.1. <sup>19</sup>F NMR (375.9 MHz, acetonitrile-*d*<sub>3</sub>):  $\delta$  –169.9 (bs). Anal. Calcd for C<sub>27.43</sub>H<sub>35.43</sub>BNFCl<sub>1.29</sub> (**1F**·0.43(CHCl<sub>3</sub>)): C, 72.45; H, 7.85. Found: C, 72.44; H, 7.94.

**Synthesis of 2F.** **2F** was prepared in a 88% yield by following the procedure used for **1F** and was recrystallized from acetonitrile to afford **2F–MeCN**: mp 273 °C. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>):  $\delta$  1.82 (bs, 12H, Mes-CH<sub>3</sub>), 2.11 (s, 6H, Mes-CH<sub>3</sub>), 3.81 (d, 9H, J<sub>F-H</sub> = 2 Hz, N-CH<sub>3</sub>), 6.49 (s, 4H, Mes-CH), 7.02 (t, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz phenyl-CH), 7.12 (t, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz phenyl-CH), 7.62 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz phenyl-CH), 7.67 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz phenyl-CH). <sup>13</sup>C NMR (100.5 MHz, acetone-*d*<sub>6</sub>):  $\delta$  20.88 (Mes-CH<sub>3</sub>), 25.56 (Mes-CH<sub>3</sub>), 57.89 (d, J<sub>F-C</sub> = 12.6 Hz, N-CH<sub>3</sub>), 118.85 (phenyl-CH), 126.69 (phenyl-CH), 128.39 (phenyl-CH), 129.63 (bs, 8C, Mes-*o*-CMe, Mes-CH), 132.96 (phenyl-CH), 142.02 (d, J<sub>F-C</sub> = 6.9 Hz, B-CMe), 153.15 (phenyl-CNMe<sub>3</sub>). Phenyl-CB carbon peak was not observed. <sup>11</sup>B NMR (128.2 MHz, acetone-*d*<sub>6</sub>):  $\delta$  7.3. <sup>19</sup>F NMR (375.9 MHz, acetone-*d*<sub>6</sub>):  $\delta$  –157.9 (bs). Anal. Calcd for C<sub>29</sub>H<sub>38</sub>BN<sub>2</sub>F (**2F**–MeCN): C, 78.37; H, 8.62. Found: C, 78.72; H, 8.52.

**Synthesis of 1CN.** Addition of a solution of NaCN (9.2 mg, 187 mmol) in methanol (10 mL) to a solution of **[1]OTf** (100 mg, 0.187 mmol) in methanol (10 mL) resulted in the formation of a precipitate. After stirring for 30 min, the mixture was filtered. This solid was washed with methanol (3  $\times$  10 mL) and dried under vacuum to afford **1CN–MeOH** as a white powder (99 mg, 95% yield): mp 405 °C (dec). <sup>1</sup>H NMR (399.9 MHz, acetone-*d*<sub>6</sub>):  $\delta$  1.90 (s, 12H, Mes-CH<sub>3</sub>), 2.11 (s, 6H, Mes-CH<sub>3</sub>), 3.29 (s, 3H, MeOH), 3.71 (s, 9H, N-CH<sub>3</sub>), 6.49 (s, 4H, Mes-CH), 7.18 (bs, 1H, phenyl-CH), 7.37 (bs, 1H, phenyl-CH), 7.69 (bs, 1, phenyl-CH), 8.29 (bs, 1H, phenyl-CH). <sup>13</sup>C NMR (100.5 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  20.44 (Mes-*p*-CH<sub>3</sub>), 25.30 (Mes-*o*-CH<sub>3</sub>), 56.26 (N-CH<sub>3</sub>), 79.89 (B-CN), 116.98 (Mes-CH), 128.62 (phenyl-CH), 131.37 (Mes-*o*-CMe), 135.63 (bs, B-CMe), 136.53 (bs, B-Cphenyl), 140.86 (phenyl-CH), 141.02 (N-Cphenyl), 143.69 (Mes-*p*-CMe). <sup>11</sup>B NMR (128.2 MHz, CDCl<sub>3</sub>):  $\delta$  –12.9. IR  $\nu_{\text{CN}}$  =

2162  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{29}\text{H}_{39}\text{BON}_2$  (**1CN**-MeOH): C, 78.72; H, 8.88. Found: C, 78.83; H, 8.47.

**Synthesis of 2CN.** **2CN** was prepared by following the procedure used for **1CN**. **2CN**-MeCN was isolated in a 68% by recrystallization from hot acetonitrile: mp 329 °C (dec).  $^1\text{H}$  NMR (399.9 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  1.77 (bs, 12H, Mes- $\text{CH}_3$ ), 2.11 (s, 6H, Mes- $\text{CH}_3$ ), 3.72 (s, 9H, N- $\text{CH}_3$ ), 6.53 (s, 4H, Mes- $\text{CH}$ ), 6.99 (t, 1H,  $^3J_{\text{H-H}} = 7.2$  Hz phenyl- $\text{CH}$ ), 7.22 (t, 1H,  $^3J_{\text{H-H}} = 8.4$  Hz phenyl- $\text{CH}$ ), 7.46 (d, 1,  $^3J_{\text{H-H}} = 7.6$  Hz phenyl- $\text{CH}$ ), 7.73 (d, 1H,  $^3J_{\text{H-H}} = 8.8$  Hz phenyl- $\text{CH}$ ).  $^{13}\text{C}$  NMR (100.5 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  20.34 (Mes-*p*-CMe), 25.45 (Mes-*o*-CMe), 57.65 (N-CMe), 120.18 (phenyl-CH), 120.40 (B-CN), 126.66 (phenyl-CH), 127.44 (phenyl-CH), 127.78 (phenyl-CH), 129.33 (Mes-CH), 130.06 (phenyl-CB), 132.40 (Mes-*p*-CMe), 137.25 (B-CMes), 140.16 (B-CMes), 141.96 (phenyl-CN), 142.08 (Mes-*o*-CMe), 152.05 (Mes-

*o*-CMe).  $^{11}\text{B}$  NMR (128.2 MHz,  $\text{CDCl}_3$ ):  $\delta$  -14.2. IR  $\nu_{\text{CN}} = 2167$   $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{30}\text{H}_{38}\text{BN}_3$  (**2CN**-MeCN): C, 79.81; H, 8.48. Found: C, 80.42; H, 8.49.

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**Supporting Information Available:** Experimental details and X-ray crystallographic data for [**1**]OTf, [**2**]OTf, **1CN**, and **2F** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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