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Fluoride Ion Capture from Water with a Cationic Borane

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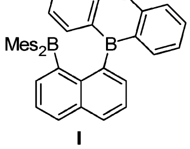
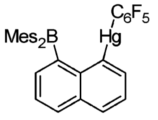
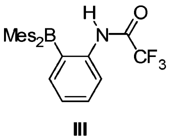
Owing to its small size and high polarizing ability, fluoride has the highest hydration enthalpy of all water stable anions. For this reason, its complexation by molecular receptors in water is extremely challenging. A majority of the current research is focused on the design of receptors which interact with the anionic guest via hydrogen-bonds.[1] Unfortunately, such receptors are not compatible with aqueous environments because water competes with the hydrogen-bond donor groups of the receptors.[2] These limitations, which can sometimes be circumvented by immobilization of the receptors,[3] have led a number of researchers to investigate the use of Lewis acidic triarylborane receptors.[4,5] Such receptors present attractive photophysical properties and capture fluoride with association constants in the 10^5-10^6 M^{-1} range in organic solvents. Like their hydrogen-bond donor counterparts, these boron-based fluoride receptors do not tolerate aqueous environments. To increase the binding constant of borane-based receptors, we and others have explored the use of naphthalene-based bidentate boranes that chelate fluoride.[6−9] Although the fluoride binding constants of such a receptor exceeds that of monofunctional analogues by 3 or 4 orders of magnitude, their use in protic environments remains problematic. For example, chelating diboranes such as **I**[8] will undergo a slow hydrolysis in the presence of water. Compound **II** which captures fluoride in THF/water 90/10 vol,[9] does not capture fluoride from pure water.



I



II

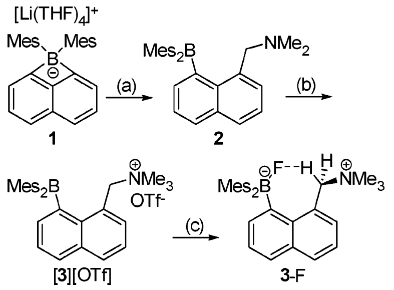


III

In an effort to overcome these challenges, we have recently explored the potential of the hybrid borane/hydrogen-bond donor receptor **III**[10] and are now searching for new paradigms which would improve the water compatibility of boron-based fluoride receptors. Anionic versions of typically neutral Lewis basic ligands are able to stabilize otherwise unstable complexes. The use of anionic phosphine ligands for the stabilization of unusual transition metal complexes[11] illustrates this principle which could a priori be applied to the design of Lewis acidic ligands for anions. In this Communication, we describe the synthesis of a cationic Lewis acidic borane which forms a highly stable zwitterionic ammonium/fluoroborate complex possessing a C−H···F−B hydrogen bond. We also demonstrate how this cationic borane can be used for the extraction of fluoride from water.

The $[Li(THF)_4]^+$ salt of dimesityl-1,8-naphthalenediylborate (**1**)[12] was allowed to react with $[Me_2NCH_2]I$ to afford borane **2** (Scheme 1). This derivative features a free dimethylamino group; it can be methylated with MeOTf (OTf = O_3SCF_3) to afford the cationic borane $[\mathbf{3}]^+$ which has been isolated as a triflate salt. Both **2** and [**3**][OTf] have been fully characterized. The ^1H NMR spectra of both compounds exhibit six distinct resonances that correspond to the aromatic CH groups of the unsymmetrically substituted naphthalene backbone. In addition, six distinct methyl groups are observed for the mesityl substituents indicating that both **2** and $[\mathbf{3}]^+$ have highly congested structures. The methylene hydrogen atoms of **2** and $[\mathbf{3}]^+$ are diastereotopic and give rise to two signals at 3.04 and 3.46 ppm for **2** and 3.69 and 4.81 ppm for $[\mathbf{3}]^+$. Both compounds possess a trigonal planar boron center as confirmed by the ^{11}B NMR signal detected at 69 and 68 ppm for **2** and **3**, respectively. The crystal structure of [**3**][OTf] has been determined. This salt crystallizes in the monoclinic $P\bar{1}$ space group with two independent molecules in the asymmetric unit (Figure 1). Both independent molecules, arbitrarily denoted as molecule **A** and molecule **B**, feature very similar structures. The boron atoms of each molecule adopt a trigonal planar geometry ($\Sigma_{(C-B-C)} = 359.3°$, molecule **A**; $\Sigma_{(C-B-C)} = 359.3°$, molecule **B**) and are separated from the methylene carbon atom by only 3.215(7) (**A**) and 3.189(7) Å (**B**). This short separation indicates that the unsaturated boron centers are sterically encumbered. This conclusion is in agreement with the large B(1)−C(1)−C(9) (125.6(4)° (**A**), 126.2(4)° (**B**)) angle which substantially deviates from the ideal value of 120°.

Scheme 1 [a]



[a] (a) $[Me_2NCH_2]I$, THF, 25 °C, 69%. (b) MeOTf, CH_2Cl_2, 25 °C, 88%. (c) $[Me_3SiF_2][S(NMe_2)_3]$, CH_2Cl_2, 25 °C, 64%.

Compound **2** does not show any appreciable affinity for fluoride. For example, the ^1H NMR spectrum of a mixture of **2** and TBAF in $CHCl_3$ only shows resonances corresponding to the free borane. Unlike **2**, $[\mathbf{3}]^+$ is swiftly and quantitatively converted into zwitterionic **3**-F when treated with TBAF or TASF in $CHCl_3$. No changes are observed in the presence of other halides indicating that the complexation is selective. The ^{11}B NMR signal of **3**-F appears at 12.2 ppm as expected for a tetrahedral boron atom. The ^{19}F NMR spectrum features a broad signal at −152 ppm which is comparable to the chemical shift observed in other triarylfluoroborate complexes.[5,7,8] Formation of this fluoride complex noticeably affects the ^1H NMR resonances of the diastereotopic methylene hydrogen atom. In particular, one of the two resonances is shifted downfield and appears at 6.50 ppm. Moreover, this methylene resonance shows coupling to the fluorine nucleus ($^1J_{H-F} = 9.2$ Hz) and appears as a doublet of doublets ($^2J_{H-H} = 12.9$ Hz) (Figure 2). This spectroscopic feature indicates the presence of a C−H···F−B hydrogen bond that persists in solution. Altogether, these results suggest that fluoride binding at boron may in fact be assisted by

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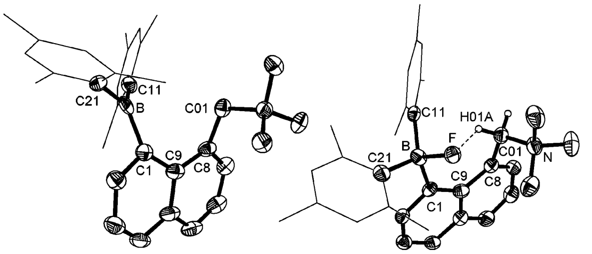

Figure 1. Crystal structure of one of the independent molecules of [**3**]$^+$ in [**3**][OTf] (left) and **3**-F (right) (50% ellipsoid). Pertinent parameters are provided in the text.

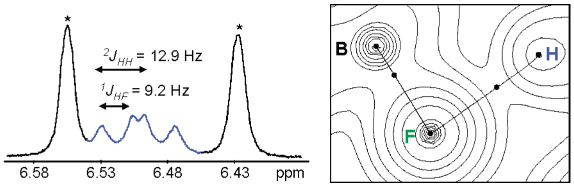

Figure 2. (left) Portion of the NMR showing the resonance of the hydrogen atom hydrogen-bonded to the fluorine atom. The peaks marked by $*$ correspond to mesityl C*H* resonances; (right) contour plot of the electron density of [**3**-F] in the B−F⋯H plane along with bond paths and bond critical points.

the formation of a hydrogen bond with a neighboring hydrogen-bond donor group. This situation is reminiscent to that encountered in the ammonium fluoroborate $[(\eta^5\text{-}C_5H_5)Fe\{\eta^5\text{-}C_5H_3(BF_3)(CH_2\text{-}NMe_2H)\}]$ which features a N−H⋯F−B hydrogen bond.[13]

Colorless crystals of **3**-F were obtained by evaporation of a Et_2O solution of **3**-F. As indicated by the X-ray crystal structure (Figure 1), the fluorine atom is trapped between the boron atom and the methylene group. The B−F bond length of 1.486(4) Å is not significantly longer than those found in triarylfluoroborate anions (1.47 Å), thus indicating the presence of an usual polar covalent B−F linkage. Accordingly, the sum of the coordination angles at boron ($\Sigma_{(C-B-C)} = 340.71°$) indicates substantial pyramidalization. The distance of 2.826(4) Å separating the fluorine atom and the methylene carbon atom confirms the presence of a C−H⋯F−B hydrogen bond. Hydrogen bonds involving $C(sp^3)$−H groups are rare[14] especially for fluoroborate species.[15] In an effort to better understand this unusual C−H⋯F−B linkage, the structure of **3**-F was optimized using DFT methods (B3LYP, 6-31+g(d′) for the boron and fluorine, 6−31g for all other atoms). The optimized structure is close to that determined experimentally. In particular, the calculated B−F (1.528 Å) and F−C(01) (2.818 Å) distances are within a few hundreds of an angström from that observed in the crystal (1.486 and 2.826 Å, respectively). Analysis of the topology of the electron density using the AIM2000 program[16] shows the presence of a bond path between the hydrogen and fluorine atom of the C−H⋯F−B bridge (Figure 2). Moreover, the value of the electron density ($\rho(r) = 2.5 \times 10^{-2}$ e bohr^{-3}) and the Laplacian value ($-1/4\nabla^2\ \rho(r) = -2.4 \times 10^{-2}$ e bohr^{-5}) at the H⋯F bond critical point fall within the expected range for a moderately strong hydrogen bond.[17] Although moderately strong, this interaction may serve to increase the stability of the fluoroborate motif.[18]

The fluoride binding constant of [**3**]$^+$ in 75/25 (vol) THF/MeOH is equal to 5.0 (±0.5) × 10^6 M^{-1} as indicated by a UV titration experiment carried out by monitoring the absorption of [**3**]$^+$ at λ_{max} = 352 nm (ϵ = 11850). Under these conditions, Mes_3B does not form any detectable quantities of $[Mes_3BF]^-$. Encouraged by these results, we attempted to test the water compatibility of [**3**]$^+$. Although water stable, cation [**3**]$^+$ does not react with fluoride in pure water. Nevertheless, when dissolved in $CHCl_3$, [**3**]$^+$ captures fluoride from water to form **3**-F. For example, shaking a biphasic mixture consisting of TBAF in D_2O (2.7×10^{-1} M, 0.5 mL) and [**3**]OTf in $CDCl_3$ (6.9×10^{-2} M, 0.5 mL) results in a 82% conversion of [**3**]OTf into **3**-F after a few minutes. To our knowledge, such a biphasic fluoride capture is unprecedented for any boron-based fluoride receptors. To provide additional comparative data, we have carried out the same experiments using **I**−**III** and found that these chelating boranes fail to capture fluoride under these biphasic conditions.

The results that we present in this Communication indicate that cationic boranes such as [**3**]$^+$ may be well suited as molecular recognition units for fluoride in water under biphasic conditions. We propose that the high fluoride affinity of [**3**]$^+$ results from favorable Coulombic forces which stabilize the B−F bond against heterolysis. We are currently investigating the use of cationic boranes for the fluorescent sensing of fluoride.

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Note Added in Proof. After submission of this Communication, the complexation of fluoride by a phosphonium borane[19] and by triarylborane-functionalized polystyrenes[20] has been reported.

Supporting Information Available: Experimental details and X-ray crystallographic data for [**3**][OTf] and **3**-F in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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