Fluoride ion complexation by a cationic borane in aqueous solution†

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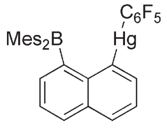
The phosphonium borane $[p\text{-Mes}_2B(C_6H_4)PMePh_2]^+$ complexes fluoride in water containing 10% methanol with a binding constant of $1.0(\pm0.1) \times 10^3$ M^{-1} to afford the zwitterion $p\text{-Mes}_2FB(C_6H_4)PMePh_2$.

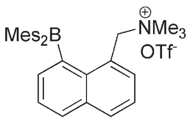
The design of fluoride sensors is an area of active investigations, because of the possible toxicity of this anion which is present in drinking water, toothpaste and osteoporosis drugs. The use of such sensors can also be envisaged for tracking UF_6 and phosphorofluoridate nerve agents which release fluoride upon hydrolysis. A large majority of the molecular sensors reported thus far are unable to overcome the large hydration energy of fluoride (504 kJ mol^{-1}) and cannot operate in water.[1]

Taking into account the strength of the B–F bond, oragnoboranes are receiving increasing attention as alternative fluoride sensors.[2] A majority of the recent research has been focused on neutral monodentate derivatives such as tris(9-anthryl)borane which capture fluoride in THF with association constants in the 10^5–10^6 M^{-1} range.[3–5] Although very selective for fluoride, available data show that such receptors fail to capture this anion in aqueous environments.[6] Because of these difficulties, we and others have explored the use of bidentate boranes such as **I** that chelate fluoride.[7–10] Such systems show an increased fluoride affinity but have remained incompatible with aqueous solutions.

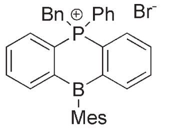
Stimulated by these challenges, we are now exploring the use of cationic boranes whose fluoride affinity should be increased by favorable Coulombic host–guest attractions. Our initial efforts in this area have led us to consider the ammonium borane $[\textbf{II}]^+$,[11] which captures fluoride from water under biphasic conditions. We have also shown that the phosphonium borane $[\textbf{III}]^+$, binds fluoride, chloride and bromide in THF.[12] These recent results have led us to question whether phosphonium boranes can be used for the recognition of fluoride in water.



I



[II][OTf]

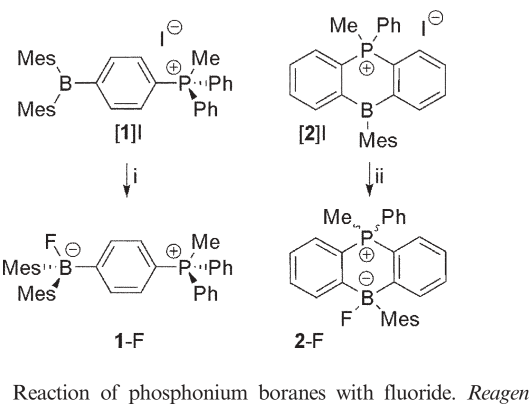


[III][Br]

We have decided to address this question by studying the fluoride binding properties of the phosphonium borane iodide salts [**1**]I and [**2**]I which could be easily obtained from the known 1-dimesitylboryl-4-diphenylphosphinobenzene[13] and *B*-mesityl-*P*-phenylphosphaborin,[14] respectively (Scheme 1).[15]‡ The identity of these salts has been confirmed by multinuclear NMR and elemental analysis. While the ^1H NMR spectra show all the expected resonance, the ^{11}B NMR signal detected at 78.9 pm for [**1**]I and 58.6 ppm for [**2**]I confirms the presence of a base-free trigonal planar boron center. The ^{31}P resonance detected at 21.9 ppm for [**1**]I and 3.1 ppm for [**2**]I is in agreement with the presence of a phosphonium center. Both compounds feature a broad absorption band whose λ_{max} is red shifted when compared to that of Mes_3B (λ_{max} = 347 nm (log ε 3.96) for [**1**]I and 369 nm (log ε = 3.35) for [**2**]I).[9]

The phosphonium borane salt [**1**]I is quantitatively converted into zwitterionic **1**-F when treated with TASF in THF.‡ The ^{11}B NMR signal of the four coordinate boron center of **1**-F appears at 9.8 ppm. The ^{19}F NMR spectrum features a signal at −175.5 ppm which is comparable to the chemical shift observed in other triarylfluoroborate complexes.[5,8,9] Salt [**2**]I reacts with TBAF in $CHCl_3$ to afford **2**-F as a mixture of two isomers which differ by the up or down orientation of the fluorine with respect to the phenyl group bound to phosphorus. Although the ^{11}B (3.6 ppm) and ^{19}F NMR (−161.3 ppm) resonance of these two isomers cannot be resolved, the ^{31}P NMR spectrum features two peaks at 3.3 and −3.1 ppm. Unfortunately, conversion of [**2**]I into **2**-F was accompanied by formation of unidentified decomposition products even under anhydrous and anaerobic conditions. Further decomposition is observed when the reaction is carried out in air or in the presence of water. Because of the chemical instability of $[\textbf{2}]^+$, additional complexation experiments were carried out with $[\textbf{1}]^+$.

The ^1H NMR spectrum of $[\textbf{1}]^+$ in $CDCl_3$ is not affected in the presence of chloride and bromide indicating that the fluoride complexation is selective. This selectivity probably arises from the presence of four *ortho*-methyl substituents which lead to



Scheme 1 Reaction of phosphonium boranes with fluoride. *Reagents and conditions*: (i) $[Me_3SiF_2][S(NMe_2)_3]$, THF, 96%; (ii) TBAF, $CHCl_3$, 25 °C.

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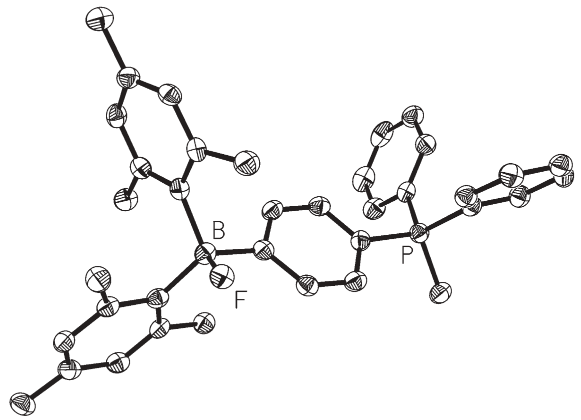

Fig. 1 Crystal structure of **1**-F (50% ellipsoids, H-atoms omitted for clarity, C-atoms not labelled).

substantial steric crowding around the boron center thus preventing approach of larger anions. The presence of two phenyl substituents appended to the phosphonium center may also help to disperse the positive charge thereby lessening its effect on the Lewis acidity of the boron center. Compound **1**-F crystallizes as a $CHCl_3$ solvate in the $P\bar{1}$ space group with no unusually short intermolecular contacts.§ The structure of **1**-F confirms that the fluorine atom is coordinated to the boron center (Fig. 1). The B–F bond length of 1.476(4) Å is comparable to those found in triarylfluoroborate anions (1.47 Å),[5] thus indicating the presence of a usual polar covalent B–F linkage. Accordingly, the sum of the coordination angles at boron ($\sum_{(C\text{–}B\text{–}C)}$ = 339.4°) indicates substantial pyramidalization.

Addition of fluoride to a $CHCl_3$ solution of $[\mathbf{1}]^+$ results in quenching of the absorption band of the borane at 347 nm. This phenomenon[4] reflects conversion of the phosphonium borane into the corresponding phosphonium fluoroborate **1**-F whose stability constant is equal to $6.5(\pm 0.5) \times 10^6$ M^{-1}. Under these conditions, Mes_3B does not form any detectable quantities of $[Mes_3BF]^-$ while the neutral bidentate Lewis acid **I** captures fluoride with an association constant of $2.1(\pm 0.2) \times 10^4$ M^{-1}. These experiments attest to the fluoride affinity displayed by $[\mathbf{1}]^+$ which exceeds that of both monodentate and bidentate neutral boranes by several orders of magnitude. We note in passing that the fluoride binding constants of Mes_3B and **I** in $CHCl_3$ is much lower than those measured in THF ($K = 3.3(\pm 0.4) \times 10^5$ for Mes_3B and $K > 10^8$ M^{-1} for **I**).[9,10] This difference indicates that $CHCl_3$ provides a more competitive medium for fluoride binding.

Remarkably, $[\mathbf{1}]^+$ is able to capture fluoride from water under biphasic conditions as indicated by NMR spectroscopy. For example, shaking a biphasic mixture consisting of 0.1 mL of a TBAF in solution in D_2O (1.3×10^{-1} M) and 1 mL of a solution of $[\mathbf{1}]^+$ in $CDCl_3$ (1.3×10^{-2} M) results in a 76% conversion of $[\mathbf{1}]^+$ into **1**-F after a few minutes. Such experiments can be carried out in air and without decomposition of $[\mathbf{1}]^+$ or **1**-F. The behavior of $[\mathbf{1}]^+$ parallels that of $[\mathbf{II}]^+$ which also capture fluoride under these conditions. In order to provide additional comparative data, we have carried out the same experiments using **I**[10] and 1-(dimesitylboryl)-8-(10′-bora-9′-thiaanthryl)naphthalene[9] and found that these chelating boranes fail to capture fluoride under these biphasic conditions.

Encouraged by these results, we decided to attempt the use of $[\mathbf{1}]^+$ in water. Although salt [**1**]I is poorly soluble in water, 5×10^{-5} M solution can be readily prepared in H_2O–MeOH (9 : 1 v/v) mixtures. Under these conditions, the UV spectrum of $[\mathbf{1}]^+$, which features a broad band at 321 nm, remains unchanged after several hours thus pointing to the water stability of the phosphonium borane (Fig. 2). The emission spectrum of $[\mathbf{1}]^+$ shows an intense green fluorescence (λ_{max} = 495 nm) which can be easily observed with the naked eye (Fig. 2). This emission is significantly red shifted when compared to that observed in $CHCl_3$ (λ_{max} = 450 nm). This red shift can be correlated to the high polarity of the aqueous medium and suggest that the excited state bears some intramolecular charge transfer character.[16] Remarkably, addition of fluoride quenches both the green fluorescence and low energy absorption band of $[\mathbf{1}]^+$ thus indicating that fluoride complexation also occurs in H_2O–MeOH (9 : 1 v/v) (Fig. 2). The stability constant of **1**-F under these conditions is equal to $1.0(\pm 0.1) \times 10^3$ M^{-1}. The use of a phosphate buffer solution (pH 7, 5×10^{-2} M) does not affect the magnitude of this binding constant confirming that the fluoride and not hydroxide binds to boron. This experiment also indicates that $[H_2PO_4]^-$ does not bind to $[\mathbf{1}]^+$. While addition of KF (80 eq.) to a 5×10^{-5} M of [**1**]I in H_2O–MeOH (9 : 1 v/v) results in a 78% absorbance decrease at 321 nm, addition of KCl, KBr, $NaNO_3$ or $[nBu_4N]I$ (80 eq.) only results in an absorbance decrease of less than 1.5% at the same wavelength. These experiments show that the boron center of $[\mathbf{1}]^+$ has no appreciable affinity for chloride, bromide, iodide and nitrate and is highly selective for fluoride. When evaluated under the same conditions (H_2O–MeOH (9 : 1 v/v)), neutral **I** and cationic $[\mathbf{II}]^+$ do

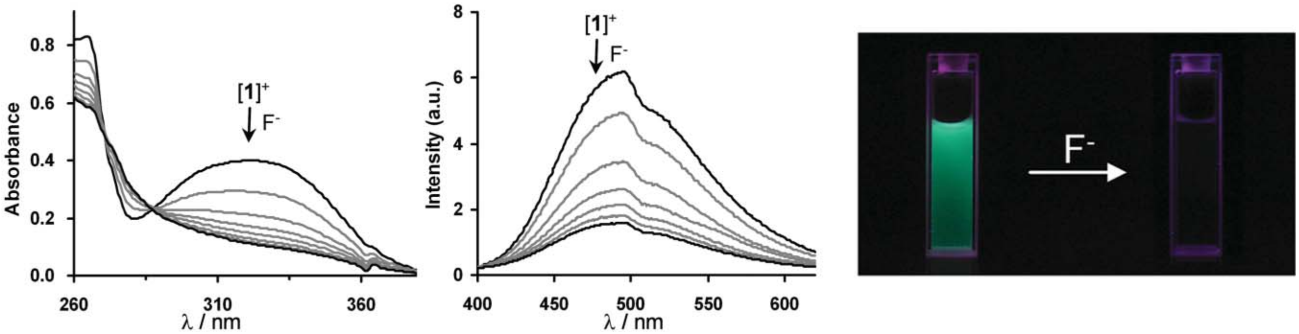

Fig. 2 Spectral changes in UV-vis absorption (left) and emission (middle) of a solution of [**1**]I in H_2O–MeOH (9 : 1 v/v) (5×10^{-5} M) upon addition of KF (3×10^{-1} M in H_2O). The picture on the right shows the emission of the solution before and after fluoride addition under a hand-held UV lamp.

not bind fluoride. Finally, addition of an aqueous solution of Al^{3+} to a solution containing **1**-F leads to complete regeneration of $[\mathbf{1}]^+$ within a few minutes. This result shows that fluoride binding by $[\mathbf{1}]^+$ is readily reversible.

In summary, we report an unprecedented boron-based fluoride receptor ($[\mathbf{1}]^+$) which operates in largely aqueous solutions. This receptor is selective for fluoride and gives rise to a fluorescent ratiometric response in the presence of the analyte. The ability of this cationic receptor to overcome the high hydration enthalpy of fluoride can be correlated to favorable Coulombic effects which enhance the Lewis acidity of the boron center. We are currently investigating the use of such receptors for the binding of cyanide which has been shown to interact with triarylboranes.[3e]

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Notes and references

‡ [**1**]I: MeI (0.15 mL) was added to a solution of 1-dimesitylboryl-4-diphenylphosphinobenzene (400 mg, 0.78 mmol) in Et_2O (20 mL) at room temperature. The mixture was stirred overnight and the solid formed was collected by filtration. After washing with Et_2O (10 mL), drying *in vacuo* afforded [**1**]I as a yellow solid (350 mg, 69% yield) (Found: C, 67.54; H, 6.13. $C_{37}H_{39}BIP$ requires C, 68.12; H, 6.03%).

1-F: [**1**]I (100 mg, 0.15 mmol) and TASF (42 mg, 0.15 mmol) were mixed in THF (20 mL) at room temperature. After stirring for 30 min, the mixture was filtered. The filtrate was exposed to a vacuum to afford a white solid. This solid was washed with Et_2O and dried under vacuum yielding **1**-F (78 mg, 96% crude yield). Colorless single crystals of **1**-F·$CHCl_3$ could be obtained in a 50–60% yield (not optimized) by partial evaporation of a $CHCl_3$ solution of **1**-F (Found: C, 68.56; H, 6.07. $C_{38}H_{40}BCl_3FP$ requires C, 68.75; H, 6.07%.).

§ *Crystal data* for **1**-F: $C_{38}H_{40}BCl_3FP$, M_r = 663.83, triclinic, $P\bar{1}$, a = 12.2069(11), b = 12.6236(12), c = 13.1483(12) Å, α = 71.916(2), β = 76.183(2), γ = 62.797(2)°, V = 1701.7(3) $Å^3$, Z = 2, T = 110(2) K, μ(Mo-Kα) = 0.348 mm^{-1}, 10398 reflections collected, 7517 unique (R_{int} = 0.0697), R_1 = 0.0660 [$I > 2\sigma(I)$], wR_2 = 0.1630 (all data). CCDC 627715. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616814k.

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