Phase Transfer of Fluoride Ion by Phosphonioborins

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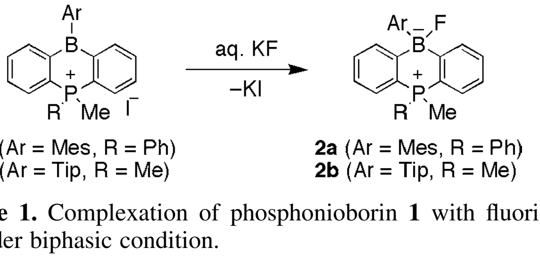
Two cationic triarylboranes based on phosphonioborin frameworks have been investigated. Electron-withdrawing phosphonio groups enhanced the Lewis acidity of these boranes which capture fluoride ion in aqueous media and transport it into organic phase.

It is well known that tricoordinate boranes can form stable complexes with hard Lewis bases, especially fluoride ion. Upon formation of borane–fluoride complexes (fluoroborates), the structure, electronic and optical properties of the boranes change dramatically. For these reasons, optical sensors for fluoride ion based on boranes have been studied extensively.[1,2] Although such molecular sensors can work effectively in organic solvents, detection and capture of fluoride ion in aqueous media remain a difficult task because of the strong hydration to fluoride ion which hampers the formation of the complex. Nevertheless, several triarylboranes with enhanced Lewis acidity have been reported to detect fluoride ion in aqueous media or to promote its transport from aqueous to organic phases.[3]

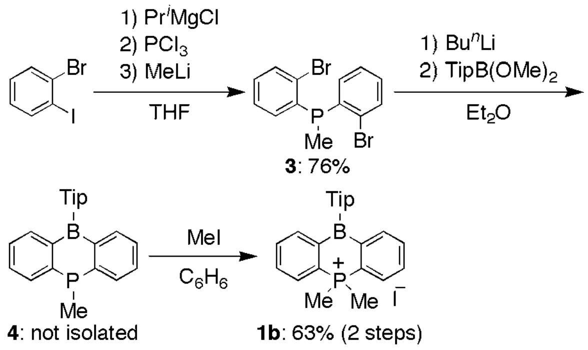
In a previous report, we have described the phase transfer of fluoride ion by phosphonioborin **1a** (Scheme 1). Although **1a** showed a high affinity for the fluoride ion, the low stability of the corresponding fluoroborate **2a** hampered its isolation and structural determination.[4] In this communication, we report the syntheses of new phosphonioborin **1b** and fluoroborate **2b** which are both stable compounds. We also describe the utilization of **1b** for the phase transfer of fluoride ion and comparison with that of **1a**.

The synthesis of *B*-Tip derivative **1b** was performed by an adaptation of the method used previously for **1a** (Scheme 2).[4a] Dibromide **3** was prepared from *o*-bromoiodobenzene by taking advantage of iodine–magnesium exchange reaction using Pr^iMgCl.[5] Phosphaborin **4** was air-sensitive and showed a tendency to oxidation. For this reason, the crude product containing **4** was treated with MeI to give phosphonioborin **1b** as a yellow solid.

Single crystals of **1b** were obtained by recrystallization from $CHCl_3$–EtOH, and the crystal structure was determined by X-ray crystallographic analysis (Figure 1a).[6,7] There were no significant interactions between counter iodide ion and the boron or phosphorus center of **1b**. The boron atom has a trigonal planar structure (Σ_{CBC}: 360°), and the dibenzophosphaborin framework had a butterfly-like structure.



Scheme 1. Complexation of phosphonioborin **1** with fluoride ion under biphasic condition.



Scheme 2. Synthesis of phosphonioborin **1b**.

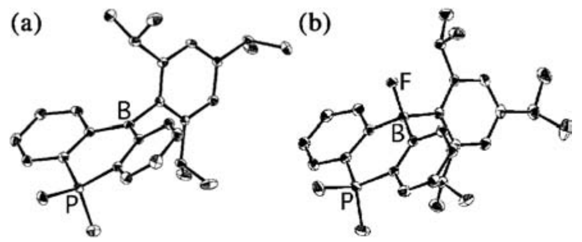


Figure 1. ORTEP drawings of **1b** and **2b** (50% probability). (a) **1b**. Solvent molecules and counter iodide ion were omitted for clarity. (b) **2b**. Solvent molecules were not shown.

Fluoride ion capture by **1** in an organic solvent was investigated. Reactions of **1a** or **1b** with an excess amount of solid KF in $CDCl_3$ were monitored by multinuclear NMR spectroscopy to show quantitative conversion to the corresponding zwitterion **2** after 3 h. However, **2a** could not be obtained as a pure material because it easily decomposed under air by oxidation. On the other hand, **2b** was isolated as a colorless solid in 76% yield and could be obtained as single crystals by recrystallization from $CHCl_3$–EtOH (Figure 1b).[7,8] Due to the tetrahedral geometry around the boron atom in **2b**, rotation around the B–C(Tip) bond was suppressed, and such hindered rotation was confirmed by VT ^1H NMR spectroscopy.[9]

Since phosphonioborins **1a** and **1b** capture fluoride ion in organic media, we decided to investigate their ability to transport fluoride ion from water into organic phases. $CDCl_3$ solution of **1** and D_2O solution of KF (1 equiv.) were placed in an NMR tube, and the sample was shaken by hand. After shaking for 1 min, the solution color changed from yellow to colorless. The ^1H NMR spectrum of the sample indicated the complete consumption of

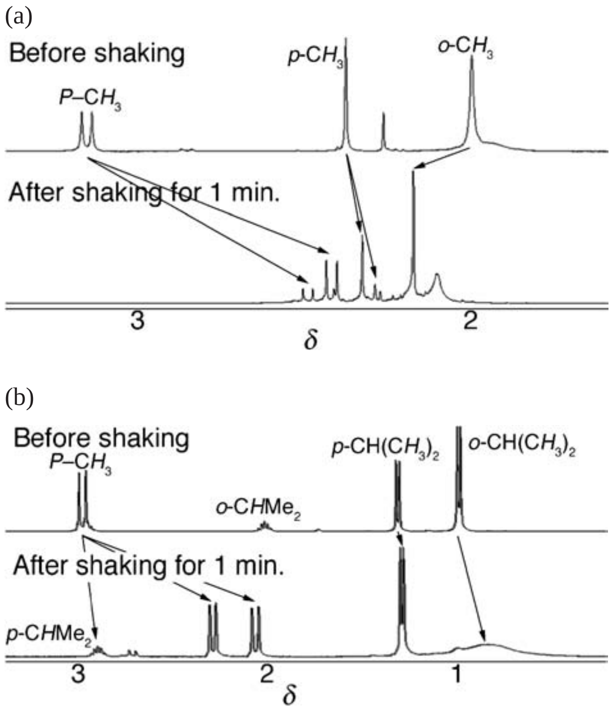


Figure 2. ^{1}H NMR spectral change upon mixing $CDCl_3$ solution of the phosphonioborins with D_2O solution of KF. (a) **1a**. (b) **1b**.

phosphonioborin **1a** or **1b** and the formation of the corresponding zwitterion **2a** or **2b** (Figures 2a and 2b). The yields of **2a** and **2b** were estimated to be close to 95% based on the use of an internal standard.[10]

The fluoride ion transfer was also monitored by UV–vis spectroscopy. The reaction was performed in a quartz cell containing a H_2O solution of KF and a $CHCl_3$ solution of **1a** or **1b** (1.0×10^{-4} M). The absorbance was monitored at 367 nm without stirring. Under these conditions, **1a** completely disappeared after 21 h. On the other hand, the spectral change of **1b** was much slower, and 94% conversion was observed after 36 h. Such decline in the reactivity against aqueous fluoride ion may originate from the steric bulk of Tip group, which decreases the reactivity of the boron center. Another contributing factor may be the increased lipophilicity of **1b** which could decrease its ability to transport fluoride ion from water into organic phases.

Because the phosphonioborins function as phase-transfer reagent against fluoride ion under biphasic conditions, we next tried to scavenge aqueous fluoride ion using **1b** as a solid. A D_2O solution of KF was mixed with solid **1b** (1 equiv.) in an NMR tube. The sample was sonicated and the concentration of fluoride was monitored by ^{19}F NMR spectroscopy. After the sonication for 1 h, the signal corresponding to aqueous fluoride ion had completely disappeared. Moreover, **2b** was not detected in solution indicating that **1b** may serve as an irreversible solid-phase scavenger for fluoride ion. Analogous experiments were carried out with solid $[p\text{-}(Mes_2B)C_6H_4(PMePh_2)]I$.[4a] Despite extended sonication times, fluoride capture was not observed. The increased steric crowding of the dimesitylboryl moiety may be responsible for this observed lack of reactivity.

In conclusion, we have reported the synthesis and structure of a new phosphonioborin as well as the structure of the corresponding zwitterionic fluoroborate. We have used the phosphonioborin for the phase transfer of fluoride ion but observed that the rate of the transfer declines due to the bulk and lipophilicity of the Tip group. These results also show that the phoshonioborin could be used as a solid-phase scavenger for fluoride ion.

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6 Crystal data for $\mathbf{1b}\cdot 2CHCl_3$ (CCDC-643630): triclinic, $P\bar{1}$, $a = 8.429(4)$, $b = 13.259(6)$, $c = 17.080(8)$ Å, $\alpha = 105.475(5)°$, $\beta = 94.91(5)°$, $\gamma = 102.703(5)°$, $V = 1774(1)$ Å^3, $Z = 2$, $R_1 = 0.0241$ $(I > 2\sigma(I))$, $wR_2 = 0.0698$ (all data).

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8 Crystal data for $\mathbf{2b}\cdot 0.5CHCl_3\cdot 0.5EtOH$ (CCDC-643629): monoclinic, $P2_1/c$, $a = 12.223(2)$, $b = 9.611(2)$, $c = 25.351(8)$ Å, $\beta = 101.271(5)°$, $V = 2920.7(1)$ Å^3, $Z = 4$, $R_1 = 0.0472$ $(I > 2\sigma(I))$, $wR_2 = 0.1269$ (all data).

9 See Supporting Information for detail, which is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/.

10 Remaining 5% of the products might be decomposed compounds via oxidation of zwitterion **2a** or **2b**.

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