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Published on Web 02/11/2009

Cationic Boranes for the Complexation of Fluoride Ions in Water below the 4 ppm Maximum Contaminant Level

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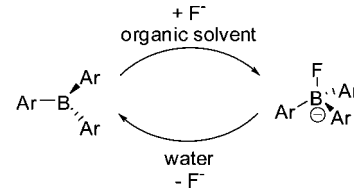
Abstract: In search of a molecular receptor that could bind fluoride ions in water below the maximum contaminant level of 4 ppm set by the Environmental Protection Agency (EPA), we have investigated the water stability and fluoride binding properties of a series of phosphonium boranes of general formula [*p*-(Mes_2B)C_6H_4(PPh_2R)]$^+$ with R = Me ([**1**]$^+$), Et ([**2**]$^+$), *n*-Pr ([**3**]$^+$), and Ph ([**4**]$^+$). These phosphonium boranes are water stable and react reversibly with water to form the corresponding zwitterionic hydroxide complexes of general formula *p*-(Mes_2(HO)B)C_6H_4(PPh_2R). They also react with fluoride ions to form the corresponding zwitterionic fluoride complexes of general formula *p*-(Mes_2(F)B)C_6H_4(PPh_2R). Spectrophotometric acid−base titrations carried out in H_2O/MeOH (9:1 vol.) afford pK_{R+} values of 7.3(±0.07) for [**1**]$^+$, 6.92(±0.1) for [**2**]$^+$, 6.59(±0.08) for [**3**]$^+$, and 6.08(±0.09) for [**4**]$^+$, thereby indicating that the Lewis acidity of the cationic boranes increases in following order: [**1**]$^+$ < [**2**]$^+$ < [**3**]$^+$ < [**4**]$^+$. In agreement with this observation, fluoride titration experiments in H_2O/MeOH (9:1 vol.) show that the fluoride binding constants (K = 840(±50) M^{-1} for [**1**]$^+$, 2500(±200) M^{-1} for [**2**]$^+$, 4000(±300) M^{-1} for [**3**]$^+$, and 10 500(±1000) M^{-1} for [**4**]$^+$) increase in the same order. These results show that the Lewis acidity of the cationic boranes increases with their hydrophobicity. The resulting Lewis acidity increase is substantial and exceeds 1 order of magnitude on going from [**1**]$^+$ to [**4**]$^+$. In turn, [**4**]$^+$ is sufficiently fluorophilic to bind fluoride ions below the EPA contaminant level in pure water. These results indicate that phosphonium boranes related to [**4**]$^+$ could be used as molecular recognition units in chemosensors for drinking water analysis.

Introduction

Water fluoridation or addition of fluoride to toothpaste has become a widespread practice because of the beneficial effects of this anion in dental health. High doses of this anion are, however, dangerous and can lead to dental or skeletal fluorosis.[1] In order to minimize the potential heath risks caused by excessive intake of this anion, the maximum contaminant level for drinking water has been set at 4 ppm (210 μmol) by the Environmental Protection Agency. The same agency, however, recommends that a concentration of 2 ppm (referred to a secondary standard) not be exceeded in drinking water.[2]

Designing water compatible receptors that are competent in this concentration range is complicated by the high hydration enthalpy ($\Delta H° = -504$ kJ/mol) of the fluoride ion. Original efforts focused on receptors that interact with the anionic guest via hydrogen bonds.[3] Unfortunately, such receptors only function in organic solvents and are usually not compatible with water.[4] Faced with these limitations, several groups have considered Lewis acidic receptors which covalently interact with the fluoride anion.[5−8] Triarylboranes, for example, complex fluoride anions in organic solvent with binding constants typically in the 10^5-10^6 M^{-1} range (Scheme 1).[7,8] Unfortunately, the resulting anionic complexes dissociate in the presence of water, a process driven by the high hydration enthalpy of the small fluoride anion (Scheme 1).

Scheme 1[a]



[a] Ar = aryl group.

In order to overcome these limitations, several groups have investigated cationic boron compounds whose anion affinity is

(1) (a) Holland, M. A.; Kozlowski, L. M. *Clin. Pharm.* **1986**, *5*, 737. (b) Carton, R. J. *Fluoride* **2006**, *39*, 163.

(2) EPA National Primary Drinking Water Standards 2003, see http://www.epa.gov/safewater/contaminants/index.html for more information.

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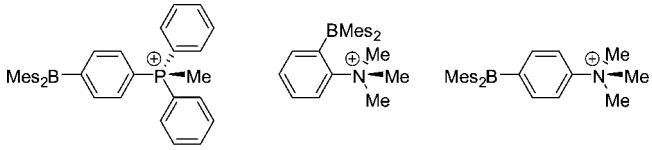
(4) (a) Boiocchi, M.; Del Boca, L.; Gomez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *J. Am. Chem. Soc.* **2004**, *126*, 16507. (b) Lin, Z.-H.; Ou, S.-J.; Duan, C.-Y.; Zhang, B.-G.; Bai, Z.-P. *Chem. Commun.* **2006**, 624.

increased by Coulombic effects.[6,9] As part of our contribution to this effort, we introduced the cationic boranes $[\mathbf{1}]^+$ and $[\mathbf{II}]^+$ and showed that these derivatives complex fluoride in aqueous media with binding constants in the 500−900 M^{-1} range.[10−12] Although these results demonstrate that cationic boranes can overcome the hydration enthalpy of fluoride, the binding constants remain too low for measurements of fluoride concentrations near the permissible level. Motivated by this challenge, we are now searching for strategies to enhance the anion affinity of such cationic boranes.[13] Considering the fact that $[\mathbf{1}]^+$ captures fluoride in water[11] while the more hydrophilic borane $[\mathbf{III}]^+$ does not,[12] we postulated that the increased hydrophobicity of $[\mathbf{1}]^+$ may actually be at the origin of this dichotomy. We further hypothesized that an increase in the hydrophobic character of such cationic boranes may serve to increase their anion affinity. Hoping to validate this new paradigm, we have now synthesized a series of phosphonium boranes of varying hydrophobicity and investigated their fluoride ion affinity.



$[\mathbf{1}]^+$ $[\mathbf{II}]^+$ $[\mathbf{III}]^+$

Results and Discussion

Synthesis and Characterization. Using a similar synthetic strategy to that employed in the case of $[\mathbf{1}]^+$,[11] we found that the phosphorus atom of the *p*-$(Mes_2B)C_6H_4(PPh_2)$ could be readily alkylated with ethyliodide in acetonitrile and propyliodide in toluene to afford the corresponding salts [*p*-$(Mes_2B)C_6H_4(PPh_2Et)$]I ([**2**]I) and [[*p*-$(Mes_2B)C_6H_4$-(PPh_2nPr)]I ([**3**]I), respectively (Scheme 2). The bromide salt [*p*-$(Mes_2B)C_6H_4(PPh_3)$]Br ([**4**]Br) was synthesized by reaction of (4-bromophenyl)dimesitylborane with PPh_3 in refluxing benzonitrile with $NiBr_2$ as a catalyst (Scheme 2). The new salts have been characterized by multinuclear NMR spectroscopy. In all cases, the ^{11}B NMR resonance measured in $CDCl_3$ is detected in the 70−80 ppm range, which indicates that the boron remains trigonal planar. The presence of a phosphonium center could be easily confirmed by the ^{31}P NMR chemical shifts of 26.3, 23.8, and 22.7 ppm for $[\mathbf{2}]^+$, $[\mathbf{3}]^+$, and $[\mathbf{4}]^+$, respectively. Like $[\mathbf{1}]^+$, these new cationic boranes feature a low energy UV absorption band detected at 325 for $[\mathbf{2}]^+$, 322 for $[\mathbf{3}]^+$, and 325 for $[\mathbf{4}]^+$ in H_2O/MeOH (9:1 vol.). This low absorption band arises from the boron-centered chromophore[7] and serves to confirm that the boron atom is in a trigonal planar geometry. The crystal structure of [**4**]Br has been determined (Table 1 and Figure 1). As indicated by the sum of the $C_{aryl}-B-C_{aryl}$ angles ($\Sigma_{(C-B-C)} = 360°$), the boron center adopts a trigonal planar coordination geometry and does not interact with the bromide counteranion.

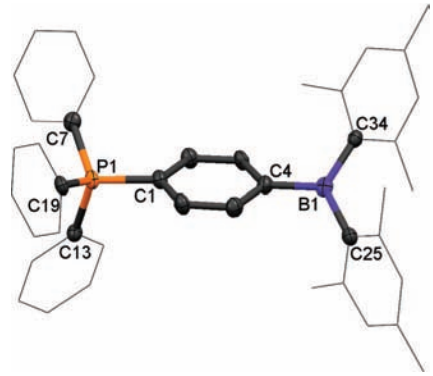


Figure 1. Crystal structure of $[\mathbf{4}]^+$ in [**4**]Br (50% ellipsoid, H-atoms omitted). Selected bond lengths (Å) and angles (deg): C(4)−B(1) 1.579(5), C(25)−B(1) 1.571(5), C(34)−B(1) 1.573(5), P(1)−C(13) 1.789(4), P(1)−C(7) 1.792(4), P(1)−C(19) 1.798(3), P(1)−C(1) 1.803(3); C(25)−B(1)−C(34) 123.3(3),C(25)−B(1)−C(4)118.8(3),C(34)−B(1)−C(4)117.9(3),C(13)−P(1)−C(7) 110.66(16), C(13)−P(1)−C(19) 109.18(16), C(7)−P(1)−C(19) 108.34(16), C(13)−P(1)−C(1) 108.43(16),C(7)−P(1)−C(1) 109.11(17),C(19)−P(1)−C(1) 111.13(16).

Reaction with Hydroxide and pH Stability Range. In order to better understand the properties of these new boranes and

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Scheme 2

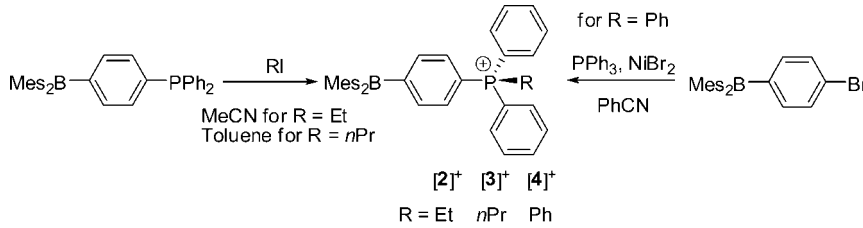

Table 1. Crystal Data, Data Collections, and Structure Refinements

crystal data	[**4**]Br-Et_2O	**1**-OH-$CHCl_3$	**4**-OH-0.5H_2O-0.5CH_2Cl_2	**4**-F-0.5CH_2Cl_2
formula	$C_{46}H_{51}BBrOP$	C_{38} $H_{41}BCl_3OP$	$C_{42.5}H_{44}BClO_{1.5}$ P	$C_{170}H_{168}B_4Cl_4F_4P_4$
M_r	741.56	661.84	656.01	2595.96
crystal size (mm^3)	0.37 × 0.25 × 0.09	0.23 × 0.16 × 0.06	0.35 × 0.12 × 0.06	0.30 × 0.14 × 0.07
crystal system	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	*C*2/*c*	$P\bar{1}$
a (Å)	8.1920(16)	12.262(3)	22.702(4)	18.988(4)
b (Å)	10.305(2)	12.756(3)	14.908(4)	19.806(4)
c (Å)	24.315(5)	12.976(3)	22.802(5)	19.918(4)
α (°)	78.84(3)	73.40(3)	90	99.42(3)
β (°)	85.45(3)	77.77(3)	112.368(4)	104.07(3)
λ (°)	86.33(3)	62.25(3)	90	99.53(3)
V ($Å^3$)	2005.0(7)	1713.8(6)	7137(3)	7001(2)
Z	2	2	8	2
ρ_{calcd} (g cm^{-3})	1.228	1.283	1.221	1.231
μ (mm^{-1})	1.098	0.344	0.186	0.190
F(000)	780	696	2784	2744
data collection				
T (K)	110(2)	110(2)	110(2)	110(2)
scan mode	*ω*	*ω*	*ω*	*ω*
hkl range	−8 → +10, −12 → +12, −30 → +30	−14 → +14, −15 → +7, −15 → +15	−25 → +25, −17 → +17, −26 → +26	−21 → +21, −22 → +22, −22 → +22
measd reflns	11256	8681	30837	62266
unique reflns [R_{int}]	7989 [0.0290]	5926 [0.0490]	5606 [0.0680]	21974 [0.0398]
reflns used for refinement	7989	5926	5606	21974
refinement				
refined parameters	451	397	434	1675
GoF	1.009	1.008	1.007	1.003
R1,[a] wR2[b] all data	0.0830, 0.1354	0.1303, 0.1739	0.0686, 0.1608	0.1001, 0.1669
ρ_{fin} (max/min) (e $Å^{-3}$)	1.156, −0.759	0.607, −0.547	0.604, −0.499	1.125, −0.770

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = [[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]]^{1/2}$.

their compatibility with aqueous environments, we have investigated their reaction with hydroxide anions. Interestingly, addition of NaOH to a solution of the cationic boranes in D_2O/MeOH-d_4 (9:1 vol.) for [**1**]$^+$, [**2**]$^+$, and [**3**]$^+$ or pure water for [**4**]$^+$ results in the formation of the corresponding hydroxide adducts as confirmed by multinuclear NMR spectroscopy (Scheme 3). For each of the four cationic boranes, hydroxide binding to the boron center leads to inequivalence of the four hydrogen nuclei of the *p*-phenylene ring. This observation indicates that rotation about the B−C bond connecting the boron atom to the *p*-phenylene moiety is restricted because of steric effects. The ^{11}B NMR signal of these species is detected in the 0−1 ppm range, thus confirming the presence of a coordinatively saturated boron center. In order to further establish the formation of these compounds, **1**-OH and **4**-OH have been isolated as solids and analyzed by single-crystal X-ray analysis (Table 1). The structure of **1**-OH is shown in the Supporting Information and that of **4**-OH in Figure 2. Examination of the structures shows coordination of the hydroxide anion to the boron center via a B−O bond of 1.519(7) Å for **1**-OH and 1.511(4) Å for **4**-OH. These bond distances are comparable to those observed in other triarylborane hydroxide adducts such as 1-$((C_6F_5)_2BOH)$-2-(Ph_2NH)-C_6H_4 (B−O = 1.521(2) Å).[14] The sum of the C_{aryl}−B−C_{aryl} angles ($\Sigma_{(C-B-C)}$ = 336.7° for **1**-OH, 335.8° for **4**-OH) indicates that hydroxide binding induces a substantial pyramidalization of the boron atom that is similar to that observed in **1**-F ($\Sigma_{(C-B-C)}$ = 339.4°).

Having established that these cationic boranes form stable hydroxide adducts, we decided to investigate the pH range within which the boron center remains uncoordinated. Since hydroxide binding to the boron center can be expected to

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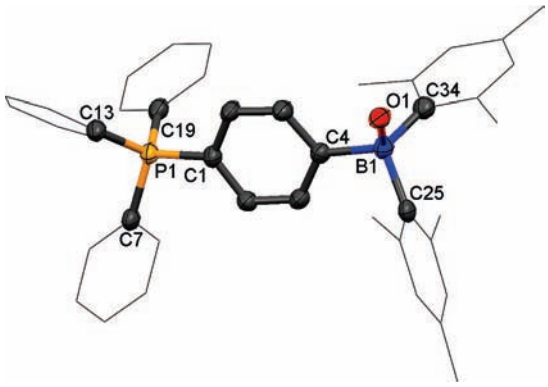
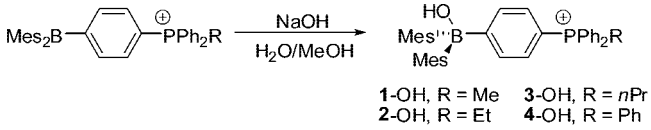


Figure 2. Structure of **4**-OH. Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.780(3), P(1)−C(7) 1.797(3), P(1)−C(13) 1.797(3), P(1)−C(19) 1.798(3), O(1)−B(1) 1.511(4), C(4)−B(1) 1.643(4), C(25)−B(1) 1.667(4), C(34)−B(1) 1.663(4), C(1)−P(1)−C(7) 110.69(12), C(1)−P(1)−C(13) 110.21(13), C(7)−P(1)−C(13) 107.98(13), C(1)−P(1)−C(19) 108.45(13), C(7)−P(1)−C(19) 106.64(13), C(13)−P(1)−C(19) 112.82(13), O(1)−B(1)−C(4) 104.9(2), O(1)−B(1)−C(34) 103.9(2), C(4)−B(1)−C(34) 116.2(2), O(1)−B(1)−C(25) 112.1(2), C(4)−B(1)−C(25) 106.4(2), C(34)−B(1)−C(25) 113.2(2).

Scheme 3



interrupt the π-conjugation mediated by the boron vacant p-orbital,[7] we monitored the absorbance of the boron-centered chromophore as a function of pH (Figure 3). In all cases, the absorption of the boron-centered chromophore is quenched as the pH becomes more basic, in agreement with the formation of the hydroxide adducts. Remarkably, acidification of the solution results in a revival of the absorbance, indicating that hydroxide binding is reversible. Fitting of the titration data to the equilibrium described in eq 1[15] affords $pK_{R+} = 7.3(\pm 0.07)$ for $[\mathbf{1}]^+$, 6.92(±0.1) for $[\mathbf{2}]^+$, 6.59(±0.08) for $[\mathbf{3}]^+$, and 6.08(±0.09) for $[\mathbf{4}]^+$. In turn, these measurements indicate that the Lewis acidity of the boranes increases in the following order: $[\mathbf{1}]^+ < [\mathbf{2}]^+ < [\mathbf{3}]^+ < [\mathbf{4}]^+$. These data firmly demonstrate that increasing the hydrophobicity of the boranes results in an increase of their Lewis acidity. While the exact thermodynamic origins of this effect have not yet been elucidated, we became eager to verify if a similar trend would be observed in the fluoride ion affinity of these new cationic boranes.

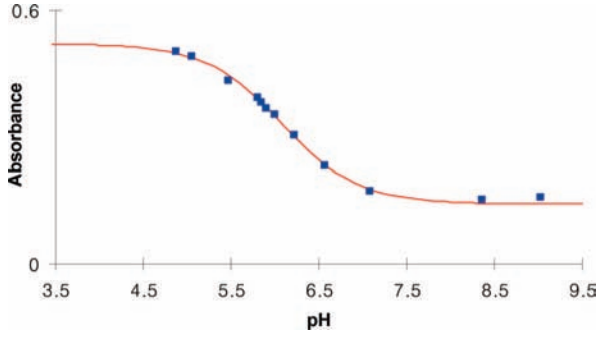


Figure 3. Spectrophotometric titration curve of $[\mathbf{4}]^+$ in H_2O/MeOH (9:1 vol.). Absorbance was measured at 325 nm. The experimental data were fitted to eq 1 using $\varepsilon([\mathbf{4}]^+) = 8400\ M^{-1}\ cm^{-1}$, $\varepsilon(\mathbf{4}\text{-OH}) = 2300\ M^{-1}\ cm^{-1}$, and $pK_{R+} = 6.08(\pm 0.09)$. The spectrophotometric titration curves of $[\mathbf{1}]^+$, $[\mathbf{2}]^+$, and $[\mathbf{3}]^+$ are shown in the Supporting Information.

$$[R_3B]^+ + H_2O \xrightarrow{K_{R+}} R_3B - OH + H^+ \qquad (1)$$

Fluoride Ion Complexation. We first verified that the new cationic boranes $[\mathbf{2}]^+$, $[\mathbf{3}]^+$, and $[\mathbf{4}]^+$ indeed react with fluoride ions. To this end, these cationic boranes were treated with KF in MeOH-d_4 solution to afford the corresponding fluoride complexes **2**-F, **3**-F, and **4**-F (Scheme 4). The presence of a boron-bound fluoride anion is confirmed by the detection of ^{11}B NMR resonances in the 4.3−7.5 range and ^{19}F NMR resonances in the −174 to −171 ppm range. These chemical shifts are close to those measured for **1**-F ($\delta(^{11}B) = 9.8$; $\delta(^{19}F) = -175.5$).[11] The formation of these fluoride adducts was further confirmed by isolation and structural characterization of **4**-F, which crystallizes with four molecules in the asymmetric unit (Table 1 and Figure 4). All four molecules have similar structures which approach that of **4**-OH. The average B(1)−F(1) bond length of 1.46 Å is comparable to those found in other triarylfluoroborate moieties (1.47 Å),[7,11] and the extent of pyramidalization of the boron center (av. $\Sigma_{(C-B-C)} = 338.4°$) is almost identical to that observed in **1**-F ($\Sigma_{(C-B-C)} = 339.4°$). Like $[\mathbf{1}]^+$, these new cationic boranes do not interact with common anions including Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, and HSO_4^-.

Further information on the fluoride affinity of these molecules was gained from titration experiment monitored by UV−vis spectroscopy (Figure 5). In order to maximize the photophysical response of the receptors, these titrations were carried out under buffered conditions at slightly acidic pH values (pH = 4.9 for $[\mathbf{1}]^+$, 4.9 for $[\mathbf{2}]^+$, 4.9 for $[\mathbf{3}]^+$, and 4.6 for $[\mathbf{4}]^+$). The resulting titration data were fitted to a 1:1 binding isotherm which afforded $K = 840(\pm 50)\ M^{-1}$ for $[\mathbf{1}]^+$, $2500(\pm 200)\ M^{-1}$ for $[\mathbf{2}]^+$,

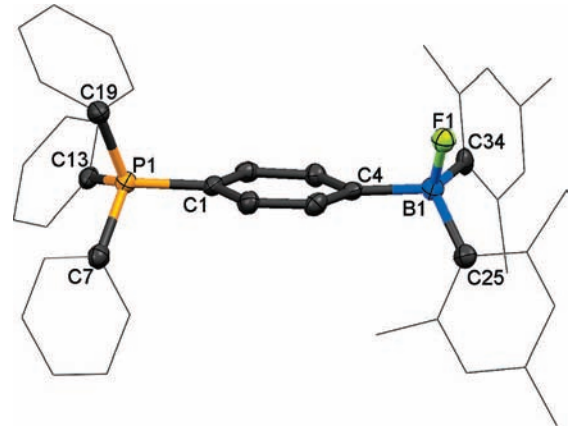
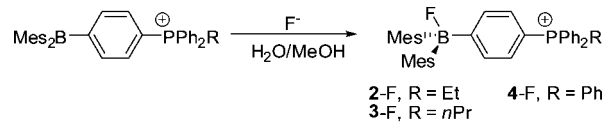


Figure 4. Structure of **4**-F. Only one molecule of the asymmetric unit is shown (50% ellipsoid, H-atoms omitted). Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.786(4), P(1)−C(7) 1.791(4), P(1)−C(13) 1.796(4), P(1)−C(19) 1.799(4), F(1)−B(1) 1.463(5), B(1)−C(34) 1.647(6), B(1)−C(25) 1.652(6), B(1)−C(4) 1.653(6); C(1)−P(1)−C(7) 107.39(18), C(1)−P(1)−C(13) 112.03(18), C(7)−P(1)−C(13) 108.24(18), C(1)−P(1)−C(19) 111.84(18), C(7)−P(1)−C(19) 110.22(19), C(13)−P(1)−C(19) 107.07(18), F(1)−B(1)−C(34) 108.9(3), F(1)−B(1)−C(25) 103.7(3), C(34)−B(1)−C(25) 116.1(3), F(1)−B(1)−C(4) 102.2(3), C(34)−B(1)−C(4) 111.4(3), C(25)−B(1)−C(4) 113.1(3).

Scheme 4



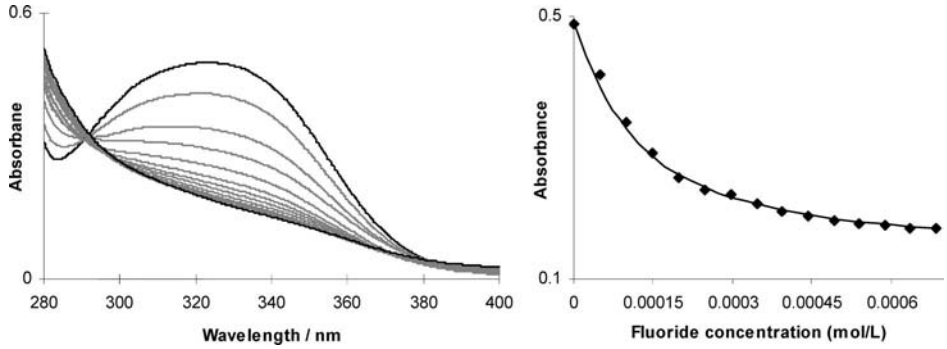


Figure 5. Left: Absorbance change of a solution of $[\mathbf{4}]^+$ after successive additions of fluoride anions in H_2O/MeOH (9/1 vol.; 9 mM pyridine buffer, pH 4.6). Right: The absorbance was measured at 325 nm. Experimental data and calculated 1:1 binding isotherm with $K = 10\,500\ (\pm 1000)\ M^{-1}$ using $\varepsilon([\mathbf{4}]^+) = 8400\ M^{-1}\ cm^{-1}$, $\varepsilon(\mathbf{4}\text{-F}) = 2100\ M^{-1}\ cm^{-1}$.

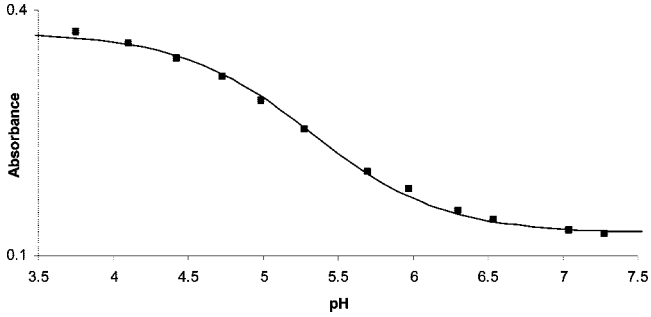


Figure 6. Spectrophotometric titration curve of $[\mathbf{4}]^+$ in H_2O. The absorbance was measured at 322 nm. Experimental data were fitted to eq 1 using $\varepsilon([\mathbf{4}]^+) = 7300\ M^{-1}\ cm^{-1}$, $\varepsilon(\mathbf{4}\text{-OH}) = 2500\ M^{-1}\ cm^{-1}$, and $pK_{R+} = 5.3(\pm 0.08)$.

$4000(\pm 300)\ M^{-1}$ for $[\mathbf{3}]^+$, and $10\,500(\pm 1000)\ M^{-1}$ for $[\mathbf{4}]^+$ as fluoride binding constants. These results show that the fluoride binding constant increases with the hydrophobicity of the borane. These results are therefore in perfect agreement with the acidity scale established on the basis of the pK_{R+} measurements. These results also show that the replacement of the $PMePh_2$ moiety of $[\mathbf{1}]^+$ with a PPh_3 moiety in $[\mathbf{4}]^+$ results in an increase of the fluoride binding constant by more than 1 order of magnitude.

Complexation of Fluoride below the EPA Maximum Contaminant Level in Water. Encouraged by these results, we decided to investigate whether $[\mathbf{4}]^+$ could be used for the detection of fluoride in pure water near or below the EPA maximum contaminant level. With this in mind, we first set out to determine the pK_{R+} of $[\mathbf{4}]^+$ in pure water by monitoring the absorbance as a function of pH. Fitting of the resulting data to eq 1 afforded $pK_{R+} = 5.3(\pm 0.08)$ (Figure 6). This value is substantially lower than the pK_{R+} value of 6.1 measured for $[\mathbf{4}]^+$ in H_2O/MeOH (9:1 vol.). This suggests that the acidity of $[\mathbf{4}]^+$ increases as the polarity of the solution increases. Next, we turned our attention to the case of fluoride and measured the binding constant in pure water at pH 4.9. Working at more acidic pH was not an option because of the competitive protonation of the fluoride anion. However, at this pH, hydroxide binding to the boron center of $[\mathbf{4}]^+$ becomes competitive, a phenomenon that had to be taken into account in order to fit the data (see Supporting Information for equation used). The resulting fluoride binding constant in pure water is equal to $30\,000(\pm 5000)\ M^{-1}$, again indicating that $[\mathbf{4}]^+$ is more Lewis acidic in pure water (Figure 7). This observation further supports that maximizing hydrophobic effects by increasing the water content of the medium leads to an increase of the acidity of the receptor. To finish these studies, we decided to focus on the response that the receptor $[\mathbf{4}]^+$ would give in pure water in the presence of fluoride ions near the secondary standard (2 ppm) set by the EPA. To this end, we measured the extent of absorbance quenching experienced by $[\mathbf{4}]^+$ (3.67×10^{-5} M) in the presence fluoride ions (100 μM or 1.9 ppm) in water. At pH 4.9, an easily detectable 63% quenching of the absorbance is observed, thereby demonstrating that $[\mathbf{4}]^+$ is competent for fluoride sensing in the parts per million range in water (Figure 7). This test can also be carried out at pH 6, where hydroxide binding to $[\mathbf{4}]^+$ occurs. Despite this competitive process, an absorbance quenching of 50% is observed, once again pointing to the performance of $[\mathbf{4}]^+$ as a fluoride binder in pure water (see Supporting Information for experimental data).

Conclusion

The results presented in this paper show that the 1-dimesitylboryl-4-phosphoniobenzenes $[\mathbf{1}]^+$, $[\mathbf{2}]^+$, $[\mathbf{3}]^+$, and $[\mathbf{4}]^+$ are water stable and reversibly form the corresponding hydroxide complexes under basic conditions. More importantly, we also show that the Lewis acidity of these cationic boranes depends on the nature of the phosphorus substituents and readily increases with the hydrophobic character of the phosphonium unit. This trend can be observed both in the pK_{R+} value of the different cationic boranes as well as in their fluoride binding constants. While the exact origin of this effect is still under study, we propose that the decreased solvation of the most hydrophobic cationic boranes facilitates the covalent ion pairing process that occurs upon reaction with fluoride. In the series of compounds studied, the resulting Lewis acidity increase is substantial and exceeds 1 order of magnitude on going from $[\mathbf{1}]^+$ to $[\mathbf{4}]^+$. In turn, $[\mathbf{4}]^+$ is sufficiently fluorophilic to bind fluoride ions below the EPA contaminant level. These results indicate that phosphonium boranes related to $[\mathbf{4}]^+$ could be used as molecular recognition units in chemosensors for drinking water analysis.

Experimental Section

General Considerations. $[\mathbf{1}]I$[11] and (4-bromophenyl)dimesitylborane[16] were prepared by following the known method. Iodoethane, 1-iodidopropane, dimesitylboron fluoride, potassium fluoride, nickel(II) bromide, triphenyl, and potassium bromide were purchased from Aldrich, and methyl iodide was from Acros. Solvents were dried by passing through an alumina column (toluene,

(15) Deno, N. C.; Jaruzelski, J. J.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3044.
(16) Yuan, Z.; Taylor, N. J.; Sun, Y.; Marder, T. B.; Williams, I. D.; Cheng, L.-T. *J. Organomet. Chem.* **1993**, *449*, 27.

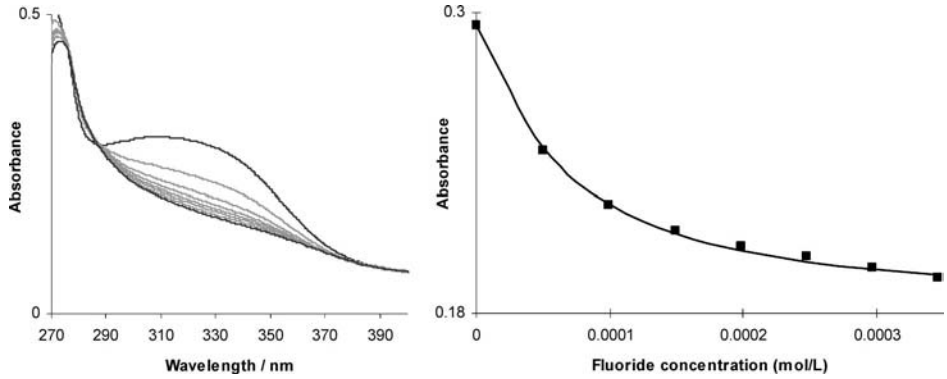


Figure 7. Left: Absorbance change of a solution of $[\mathbf{4}]^+$ after successive additions of fluoride anions in H_2O (10 mM pyridine buffer, pH 4.9). Right: Absorbance was measured at 310 nm. Experimental data and calculated 1:1 binding isotherm with $K = 30\,000(\pm 5000)$ M^{-1} using $\varepsilon([\mathbf{4}]^+) = 7300$ M^{-1} cm^{-1}, $\varepsilon(\mathbf{4}\text{-F}) = 4900$ M^{-1} cm^{-1}, and $\varepsilon(\mathbf{4}\text{-OH}) = 2500$ M^{-1} cm^{-1}. The second experimental point of the titration corresponds to a solution containing 100 μM or 1.9 ppm fluoride ions; a 63% absorbance quenching is observed at this point.

MeCN), by reflux under N_2 over Na/K (Et_2O and THF) or with activated 4 Å molecular sieves (benzonitrile). UV−vis spectra were recorded on an Ocean Optics USB4000 spectrometer with a Ocean Optics ISS light source. Elemental analyses were performed by Atlantic Microlab (Norcross, GA). The pH measurements were carried out with a Radiometer PHM290 pH meter equipped with a VWR SympHony electrode. NMR spectra were recorded on Varian Inova 300 FT NMR (299.96 MHz for ^{1}H, 121.43 MHz for ^{31}P) and Varian Unity Inova 400 FT NMR (399.59 MHz for ^{1}H, 375.99 MHz for ^{19}F, 128.19 MHz for ^{11}B, 161.75 MHz for ^{31}P, 100.45 MHz for ^{13}C) spectrometers at ambient temperature. Chemical shifts δ are given in parts per million and are referenced against external $BF_3 \cdot Et_2O$ (^{11}B), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P).

Crystallography. The crystallographic measurements were performed using a Bruker APEX-II CCD area detector diffractometer (Mo Kα radiation, λ= 0.71069 Å) for **4**-F and **4**-OH and a Siemens SMART-CCD area detector diffractometer (Mo Kα radiation, λ= 0.71069 Å) for **1**-OH and [**4**]Br. In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms.

Synthesis of [2]I. Iodoethane (0.1 mL, 1.25mmol) was added to a solution of 1-dimesitylboryl-4-diphenylphosphinobenzene (50 mg, 0.098 mmol) in MeCN (4 mL) at room temperature. The mixture was refluxed overnight and cooled to room temperature. The solvent was removed in vacuo to yield a residue which was washed with Et_2O (5 mL) and isolated as a pale yellow solid by filtration. Additional washing with Et_2O (5 mL) afforded [**2**]I as a yellow solid (50 mg, 76% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (d, t, 3H, $^3J_{P-H} = 20$ Hz, $^3J_{H-H} = 7.6$ Hz), 1.96 (s, 12H), 2.29 (s, 6H), 3.81 (d, q, 2H, $^2J_{P-H} = 12.6$ Hz, $^3J_{H-H} = 7.2$ Hz), 6.82 (s, 4H), 7.67−7.74 (m, 8H), 7.78−7.83 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.93 (d, $J = 5.5$ Hz), 17.72 (d, $J = 50.9$ Hz), 21.22, 23.52, 117.76 (d, $J = 85.4$ Hz), 120.23 (d, $J = 83.6$ Hz), 128.54, 130.50 (d, $J = 12.5$ Hz), 132.83 (d, $J = 9.5$ Hz), 133.69 (d, $J = 9.5$ Hz), 135.09 (d, $J = 2.7$ Hz), 136.43 (d, $J = 12.2$ Hz), 139.83, 140.49, 140.83, 153.37; ^{11}B NMR (128 MHz, $CDCl_3$) δ +75.0; ^{31}P NMR (161 MHz, $CDCl_3$) δ +26.26. Anal. Calcd for $C_{38}H_{43}BIOP$ ([**2**]I + H_2O): C, 66.68; H, 6.33. Found: C, 66.76; H, 6.19.

Synthesis of [3]I. 1-Iodopropane (0.1 mL, 1.03 mmol) was added to a solution of 1-dimesitylboryl-4-diphenylphosphinobenzene (50 mg, 0.098 mmol) in toluene (4 mL) at room temperature. The mixture was refluxed overnight and cooled to room temperature. The solvent was removed in vacuo to yield a residue which was washed with Et_2O (5 mL) and isolated as a pale yellow solid by filtration. Additional washing with Et_2O (5 mL) afforded [**3**]I as a yellow solid (50 mg, 75% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, 3H, $^3J_{H-H} = 7.6$ Hz), 1.70 (m, 2H), 1.96 (s, 12H), 2.29 (s, 6H), 3.73 (d, t, 2H, $^2J_{P-H} = 12.4$ Hz, $^3J_{H-H} = 8$ Hz), 6.81 (s, 4H), 7.68−7.84 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.37 (d, $J = 17.1$ Hz), 16.60 (d, $J = 4.2$ Hz), 21.21, 23.51, 24.77 (d, $J = 49.3$ Hz), 117.95 (d, $J = 85.4$ Hz), 120.53 (d, $J = 83.5$ Hz), 128.52, 130.48 (d, $J = 12.5$ Hz), 132.80 (d, $J = 9.5$ Hz), 133.67 (d, $J = 9.9$ Hz), 135.05 (d, $J = 3$ Hz), 136.40 (d, $J = 12.1$ Hz), 139.89, 140.68, 140.82, 153.28; ^{11}B NMR (128 MHz, $CDCl_3$) δ +78.0; ^{31}P NMR (161 MHz, $CDCl_3$) δ +23.85. Anal. Calcd for $C_{39}H_{45}BIOP$ ([**3**]I + H_2O): C, 67.06; H, 6.49. Found: C, 67.05; H, 6.35.

Synthesis of [4]Br. A mixture of $NiBr_2$ (0.335 g, 1.53 mmol), PPh_3 (0.67 g, 2.55 mmol), and (4-bromophenyl)dimesitylborane (0.67 g, 1.65 mmol) in benzonitrile (30 mL) was heated at 200 °C for 3 h. After cooling to room temperature, the solvent was removed in vacuo. The residue was extracted using CH_2Cl_2 (20 mL) and water (10 mL) containing KBr (10 wt %). The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated in vacuo to a final volume of about 3 mL. This concentrate was further purified by flash chromatography over silica gel using first ethyl acetate (50 mL) and then methanol (50 mL). The methanol fraction was then dried in vacuo to afford [**4**]Br as a pale yellow solid. Further purification was achieved by recrystallization induced by diffusion of Et_2O into a concentrated solution of CH_3CN (0.55 g, 50% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98 (s, 12H), 2.29 (s, 6H), 6.83 (s, 4H), 7.53−7.68 (m, 8H), 7.75−7.85 (m, 8H), 7.90−7.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.13, 23.45, 116.96 (d, $J = 88.8$ Hz), 119.73 (d, $J = 86.9$ Hz), 128.50, 130.79 (d, $J = 11.4$ Hz), 130.86 (d, $J = 12.6$ Hz), 133.43 (d, $J = 9.9$ Hz), 134.22 (d, $J = 10.3$ Hz), 135.89, 136.34 (d, $J = 12.6$ Hz), 139.99, 140.60, 153.97 (br s); ^{11}B NMR (128 MHz, $CDCl_3$) δ +75.0; ^{31}P NMR (121 MHz, $CDCl_3$) δ +22.71 (s). Anal. Calcd for $C_{42}H_{44}BBrO_{1.5}P$ ([**4**]Br + 1.5H_2O): C, 72.64; H, 6.39. Found: C, 72.58; H, 6.31.

Synthesis of 1-OH. [**1**]I (50 mg, 0.077 mmol) was dissolved in H_2O/MeOH (9:1 vol., 3 mL) and treated with an aqueous solution of NaOH (2 mL, 2.5 M). After stirring for 30 min, CH_2Cl_2 (10 mL) was added to the reaction mixture. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was washed with Et_2O (5 mL) to afford **1**-OH as a white solid (30 mg, 72% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 12H), 2.19 (s, 6H), 2.54 (d, 3H, $^2J_{P-H} = 12.8$ Hz), 6.62 (s, 4H), 6.81 (br s, 1H), 6.93 (br s, 1H), 7.48−7.53 (m, 4H), 7.65 (m, 5H), 7.77−7.79 (m, 2H), 8.61 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.15 (d, $J = 59.2$ Hz), 20.72, 25.63, 108.15 (d, $J = 91.9$ Hz), 120.78 (d, $J = 88.5$ Hz), 128.74, 129.73, 130.37 (d, $J = 12.6$ Hz), 131.51, 133.10 (d, $J = 10.2$ Hz), 134.98 (d, $J = 3$ Hz), 136.45, 141.12, 156.95; ^{11}B NMR (128 MHz, $CDCl_3$) δ +0.29; ^{31}P NMR (121 MHz, $CDCl_3$) δ +18.63. Anal. Calcd for

$C_{37.33}H_{40.33}BClOP$ (**1**-OH + 0.33$CHCl_3$): C, 77.01; H, 6.98. Found: C, 77.08; H, 7.11.

Synthesis of 4-OH. [**4**]Br (50 mg, 0.075 mmol) was dissolved in H_2O (3 mL) and treated with an aqueous solution of NaOH (2 mL, 2.5 M). After stirring for 30 min, CH_2Cl_2 (10 mL) was added to the reaction mixture. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was washed with Et_2O (5 mL) to afford **4**-OH as a white solid (35 mg, 77% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 12H), 2.20 (s, 6H), 6.63 (s, 4H), 6.99 (br s, 1H), 7.56−7.67 (m, 14H), 7.80−7.83 (m, 3H), 8.62 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.82, 25.56, 105.60 (d, J = 91.1 Hz), 119.74 (d, J = 88.8 Hz), 128.43, 130.05 (d, J = 12.5 Hz), 131.06, 131.86, 134.24 (d, J = 9.9 Hz), 134.78 (d, J = 2.7 Hz), 136.84 (d, J = 12.6 Hz), 141.47, 156.58; ^{11}B NMR (128 MHz, $CDCl_3$) δ +0.16; ^{31}P NMR (121 MHz, $CDCl_3$) δ +22.44. Anal. Calcd for $C_{42.5}H_{44}BClO_{1.5}P$ (**4**-OH + 0.5CH_2Cl_2 + 0.5H_2O): C, 77.81; H, 6.76. Found: C, 75.97, H, 6.70.

Syntheses of 2-OH and 3-OH. These two compounds, which have not been isolated, were prepared as follows and characterized in situ. A D_2O solution of NaOH (0.9 mL, 2.5 M) was mixed with a MeOH-d_4 solution of the cationic borane salt ([**2**]I or [**3**]I) (0.1 mL, 0.2 M) in an NMR tube. The corresponding hydroxide adduct (**2**-OH or **3**-OH), which precipitated immediately upon mixing, was extracted with $CDCl_3$. The $CDCl_3$ layer, which separated at the bottom of the NMR tube, was analyzed by multinuclear NMR spectroscopy. NMR data for **2**-OH: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (d, t, 3H, $^3J_{P-H}$ = 19.2 Hz, $^3J_{H-H}$ = 7.6 Hz), 1.95 (s, 12H), 2.18 (s, 6H), 2.90 (m, 2H), 6.61 (s, 4H), 7.00 (br s, 1H), 7.52−7.67 (m, 10H), 7.77−8.00 (m, 2H), 8.47 (br s, 1H); ^{11}B NMR (128 MHz, $CDCl_3$) δ +0.36; ^{31}P NMR (161 MHz, $CDCl_3$) δ +23.64. NMR data for **3**-OH: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, 3H, $^3J_{H-H}$ = 7.2 Hz), 1.74 (m, 2H), 1.96 (s, 12H), 2.18 (s, 6H), 2.81 (m, 2H), 6.61 (s, 4H), 7.00 (br s, 1H), 7.51−7.66 (m, 10H), 7.76−7.79 (m, 2H), 8.47 (br s, 1H); ^{11}B NMR (128 MHz, $CDCl_3$) δ +0.25; ^{31}P NMR (161 MHz, $CDCl_3$) δ +21.41.

Synthesis of 4-F. [**4**]Br (200 mg, 0.3 mmol) was dissolved in MeOH (5 mL) and treated with excess of KF, which resulted in the formation of a white solid. After 30 min, the solid was isolated by filtration, washed with MeOH, and dried in vacuo to afford **4**-F as a white solid (100 mg, 55% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (s, 12H), 2.19 (s, 6H), 6.62 (s, 4H), 7.06 (br s, 1H), 7.54−7.70 (m, 14H), 7.78−7.85 (m, 3H), 8.41 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.87, 25.03, 106.61 (d, J = 91.9 Hz), 119.50 (d, J = 89.2 Hz), 128.25, 130.16, 131.39, 132.24, 134.25, 134.89, 136.16, 141.69, 153.08; ^{11}B NMR (128 MHz, $CDCl_3$) δ +5.22; ^{31}P NMR (121 MHz, $CDCl_3$) δ +22.58; ^{19}F NMR (376 MHz, $CDCl_3$) δ −173.83. Anal. Calcd for $C_{42.17}H_{41.33}BCl_{0.33}FP$ (**4**-F + 0.17CH_2Cl_2): C, 81.61; H, 6.71. Found: C, 81.57; H, 6.65.

Syntheses of 2-F and 3-F. These two compounds, which have not been isolated, were prepared by mixing a MeOH-d_4 solution of the cationic borane salt ([**2**]I or [**3**]I) (15 mg) with excess of KF in an NMR tube. The resulting clear solution was analyzed by multinuclear NMR spectroscopy. NMR data for **2**-F: ^{1}H NMR (400 MHz, CD_3OD) δ 1.37 (d, t, 3H, $^3J_{P-H}$ = 19.6 Hz, $^3J_{H-H}$ = 7.2 Hz), 1.90 (s, 12H), 2.16 (s, 6H), 3.30 (m, 2H), 6.54 (s, 4H), 7.30 (br s, 1H), 7.43 (br s, 2H), 7.74−7.81 (m, 8H), 7.85−7.89 (m, 2H), 8.15 (br s, 1H); ^{11}B NMR (128 MHz, CD_3OD) δ +4.35; ^{31}P NMR (121 MHz, CD_3OD) δ +25.31; ^{19}F NMR (376 MHz, CD_3OD) δ −171.31. NMR data for **3**-F: ^{1}H NMR (400 MHz, CD_3OD) δ 1.17 (t, 3H, J = 7.2 Hz), 1.73 (m, 2H), 1.90 (s, 12H), 2.16 (s, 6H), 3.27 (m, 2H), 6.54 (s, 4H), 7.30 (br s, 1H), 7.42 (br s, 2H), 7.72−7.80 (m, 8H), 7.84−7.89 (m, 2H), 8.15 (br s, 1H); ^{11}B NMR (128 MHz, CD_3OD) δ +7.47; ^{31}P NMR (121 MHz, CD_3OD) δ +22.98; ^{19}F NMR (376 MHz, CD_3OD) δ −171.62.

Titration of [1]$^+$, [2]$^+$, [3]$^+$, and [4]$^+$with Fluoride in H_2O/MeOH (9:1 vol.). A solution of [**1**]I (3.0 mL, 6.17 × 10^{-5} M; pyridine buffer 9 mM, pH 4.9), [**2**]I (3.0 mL, 5.43 × 10^{-5} M; pyridine buffer 9 mM, pH 4.9), [**3**]I (3.0 mL, 5.9 × 10^{-5} M; pyridine buffer 9 mM, pH 4.9), and [**4**]Br (3.0 mL, 5.83 × 10^{-5} M; pyridine buffer 9 mM, pH 4.6) was titrated by incremental addition of a solution of KF in water (0.3 M for [**1**]$^+$, [**2**]$^+$ and 0.03 M for [**3**]$^+$, [**4**]$^+$) (see Tables S1−S4 and Figures S1−S4 in the Supporting Information).

Acid−Base Titration of [1]$^+$, [2]$^+$, [3]$^+$, and [4]$^+$ in H_2O/MeOH (9:1 vol.). A solution of [**1**]I (3.0 mL, 3.65 × 10^{-5} M; MES buffer 9 mM), [**2**]I (3.0 mL, 6.0 × 10^{-5} M; MES buffer 9 mM), [**3**]I (3.0 mL, 6.3 × 10^{-5} M; MES buffer 9 mM), and [**4**]Br (3.0 mL, 6.2 × 10^{-5} M; MES buffer 9 mM) was titrated by incremental addition of a solution of NaOH in water (see Figures S5−S8 in the Supporting Information). The resulting data were fitted to the equilibrium shown in eq 1, which yielded the relevant K_{R+}. The solutions were buffered in order to obtain a better control of the pH near the equivalence point.

Acid−Base of [4]$^+$ in Pure Water. A solution of [**4**]Br (3.0 mL, 5.1 × 10^{-5} M; pyridine buffer, 10 mM) was titrated by incremental addition of a solution of NaOH in water (see Figure 6). The resulting data were fitted to the equilibrium shown in eq 1, which yielded the relevant K_{R+}. The solution was buffered in order to obtain a better control of the pH near the equivalence point.

Titration of [4]$^+$with Fluoride in Pure Water. A solution of [**4**]Br (3.0 mL, 3.67 × 10^{-5} M; pyridine buffer, 10 mM, pH 4.9) was titrated by incremental addition of a solution of KF (0.03 M in water) (see Table S5 in the Supporting Information and Figure 7).

Acknowledgment. This work was supported by NSF (CHE-0646916), the Welch Foundation (A-1423), and the U.S. Army Medical Research Institute of Chemical Defense. We thank Paul Cremer and Yi-Qin Gao for useful discussions.

Supporting Information Available: Additional experimental details and X-ray crystallographic data for [**4**]Br-Et_2O, **1**-OH-$CHCl_3$, **4**-OH-0.5H_2O-0.5CH_2Cl_2, and **4**-F-0.5CH_2Cl_2 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JA8091467