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Synthesis and Anion Affinity of a Bidendate Sulfonium Fluorosilane Lewis Acid

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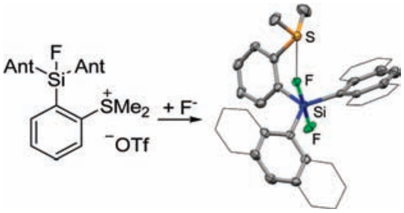
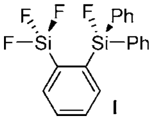
ABSTRACT

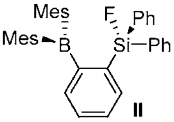


The cationic fluorosilane $[1\text{-}Ant_2FSi\text{-}2\text{-}Me_2S\text{-}(C_6H_4)]^+$ (2^+) readily complexes fluoride ions to afford the corresponding zwitterionic difluorosilicate complex $1\text{-}Ant_2F_2Si\text{-}2\text{-}Me_2S\text{-}(C_6H_4)$ (2-F) with a binding constant in $CHCl_3$ of 7 (±1) × 10^6 M^{-1}. Structural and computational results indicate that the high fluorophilicity of 2^+ arises from both Coulombic and cooperative effects reflected by the formation of a Si−F→S bridge with a F→S distance of 2.741(3) Å.

One of the main themes in the chemistry of polydentate Lewis acids is the discovery of new molecular structures that can support anion chelation. Modulating the structures and varying the elements involved in anion binding provide an effective way to control the affinity of such systems. To date, a great deal of effort has been devoted to the chemistry of boron-based polydentate Lewis acids[1] and their use as sensors for the potentially toxic fluoride anion.[2] By contrast, and despite the widespread use of tetracoordinate halosilanes as Lewis acids in organic synthesis,[3] much less is known about silicon-based polydentate Lewis acids.[4–6] Some of the most notable examples of such compounds include **I**,[5] which displays a high affinity for fluoride anions, and **II**,[6] in which the silicon atom assists fluoride binding at the boron atom.



I



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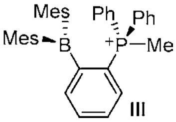

III

In some of our recent exploratory studies, we have demonstrated that the fluoride ion affinity of boranes could be greatly increased by incorporation of proximal third row onium functionality as in **III**.[7] In addition to facilitating anion binding via inductive and Coulombic effects, the phospho-

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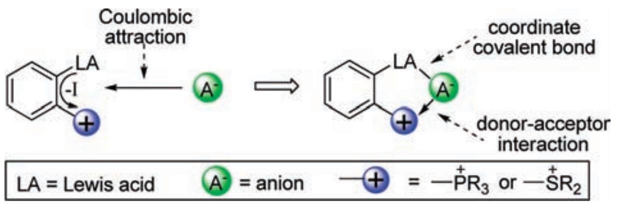
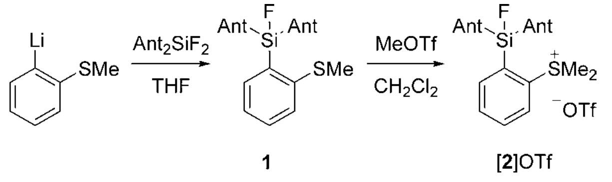


Figure 1. "Onium-based strategy": illustration of the forces and bonding interactions involved in anion binding by a bidentate 3rd row onium/Lewis acid.

nium ion of **III** becomes hypervalent and engages the anion in a donor−acceptor interaction (Figure 1). Similar effects have been observed in the chemistry of sulfonium boranes as cyanide receptors.[8] As part of our ongoing endeavor in the chemistry of polydentate Lewis acids, we have now decided to determine if this "onium-based strategy" (Figure 1) could be extended to silicon Lewis acids.

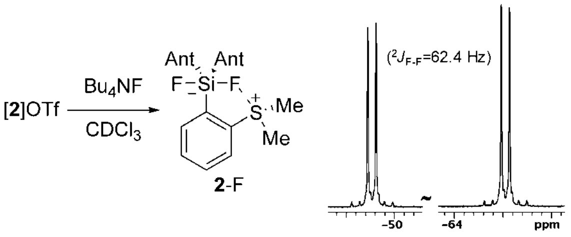
Triarylfluorosilanes bind fluoride anions to form the corresponding triaryldifluorosilicates.[9,10] Careful studies by Tamao and Yamaguchi,[10] who showed that Ant_3SiF (Ant = 9-anthryl) can be used as a fluoride ion sensor in organic solvents, led us to consider such fluorosilanes as a starting point for our studies. To obtain a fluorosilane that could easily be converted into a cationic derivative, we allowed *o*-lithiothioanisole to react with di(9-anthryl)difluorosilane[11] in THF at −78 °C (Scheme 1). The fluorosilane **1** was converted into [**2**]OTf by reaction with MeOTf. Both **1** and [**2**]OTf have been characterized by conventional spectroscopic methods. The ^{29}Si NMR resonances of these new compounds were detected at −2.4 ppm ($^{1}J_{Si-F} = 284.2$ Hz) for **1** and −0.5 ppm ($^{1}J_{Si-F} = 282.0$ Hz) for [**2**]$^{+}$. In the ^{19}F NMR spectra, the slilicon bound fluorine nucleus gives rise to a resonance at −141.0 ppm for **1** and −138.0 ppm for [**2**]$^{+}$ whose chemical shift is close to that of Ant_2PhSiF (δ −143.7).[10] Salt [**2**]OTf is stable in organic solvents but decomposes in the presence of water.

Scheme 1. Synthesis of **1** and [**2**]OTf



With this new cationic silane in hand, we decided to study the responses of [**2**]$^{+}$ to different anions using ^{19}F NMR spectroscopy. Addition of 5.0 equivalents of Cl^{-}, Br^{-} or I^{-} as tetrabutylammonium salts to a $CDCl_3$ solution of [**2**]$^{+}$ resulted in the formation of the neutral silane **1** (δ(^{19}F) −141.0 ppm) indicating demethylation of the aryldimethylsulfonium moiety of [**2**]$^{+}$. By contrast, addition of TBAF to [**2**]$^{+}$ resulted in the formation of **2**-F (Scheme 2). **2**-F could be easily isolated from the reaction of [**2**]OTf with tetrabutylammonium triphenylsilyldifluoride in CH_2Cl_2. Some of its salient NMR spectroscopic features in DMSO-d_6 include: 1) two separate sulfur-bound methyl signals detected at 2.40 and 2.90 ppm in the ^{1}H NMR spectrum; 2) two doublets at −49.5 and −65.1 with $^{2}J_{F-F} = 62.4$ Hz in the ^{19}F NMR spectrum corresponding to the silyl-bound fluorine atoms (Scheme 2); 3) a ^{29}Si NMR resonance at −92.7 ppm (dd, $^{1}J_{Si-F} = 266.7$ Hz, $^{1}J_{Si-F} = 256.5$ Hz) whose chemical shift is comparable to that observed for $[Ant_2PhSiF_2]^{-}$ ($\delta = -97.2$, $J_{Si-F} = 262.9$ Hz).[10] Altogether, these spectroscopic features indicate the presence of two nonequivalent fluorine atoms bound to the silicon center. As indicated by ^{19}F NMR, the chemical shift of one of these two fluorine nuclei is significantly deshielded and exhibits a smaller $^{1}J_{Si-F}$, possibly suggesting the presence of an interaction with the neighboring sulfonium center.[12] The detection of two distinct sulfur-bound methyl group resonances corroborates this possibility. To firmly understand the coordination environment of the silicon and sulfur atoms, the crystal structure of in **2**-F was determined.

Scheme 2. Formation of **2**-F and ^{19}F NMR spectrum



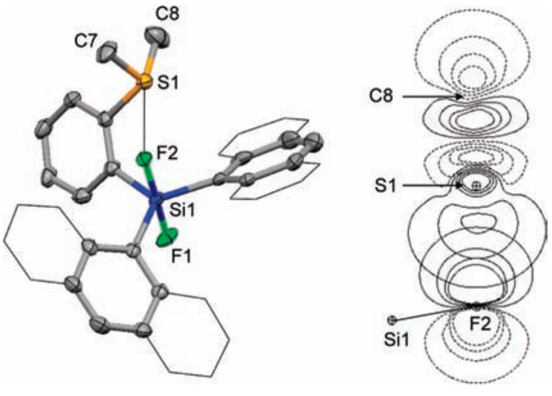


Figure 2. (Left) Structure of **2**-F (50% ellipsoid, H-atoms omitted for clarity). Pertinent metrical parameters are provided in the text. (Right) NBO contour plot showing the lp(F)→σ*(S−C) interaction in **2**-F.

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Examination of the crystal structure of **2**-F confirmed that the silicon atom adopts a trigonal-bipyramidal geometry (F(1)−Si(1)−F(2) = 177.32(15)°, Σ(C−Si−C) = 360°) (Figure 2). Although close to those observed in the $[\mathrm{Ant_3SiF_2}]^-$ anion (1.710−1.716 Å),[10] the silicon−fluorine bond distances in **2**-F (Si(1)−F(1) = 1.706(3) Å; Si(1)−F(2) = 1.732(3) Å) differ by almost 0.03 Å. Further inspection of the structure indicates that the F(2) atom is separated from S(1) by only 2.741(3) Å which is well within the sum of van der Waals radii of two elements (*ca*. 3.27 Å). The resulting F(2)−S(1)−C(8) angle of 166.5(2)° is also close to linearity. Collectively, these metrical parameters suggest the presence of a bonding interaction between the F(2) and S(1) atoms. This view is confirmed by an NBO analysis carried out at the DFT optimized geometry (Figure 2). This analysis reveals a donor−acceptor interaction involving a fluorine lone pair (lp(F)) as a donor and a carbon−sulfur σ^*-orbital (σ^*(S−C)) as the acceptor (Figure 2). A deletion calculation suggest that this interaction stabilizes the molecule by 5.60 kcal/mol. Presumably, existence of this interaction is responsible for the lengthening of the Si(1)−F(2) bond as well as for the somewhat deshielded ^{19}F NMR chemical shift measured for the F(2) nucleus.

Formation of **2**-F can be followed by monitoring the UV−vis absorption spectrum of $[\mathbf{2}]^+$ in chloroform upon incremental addition of TBAF (Figure 3). Analysis of the spectral changes indicate that formation of **2**-F induces a blue shift of the anthryl-based absorption bands. As previously explained for other anthrylfluorosilane species,[10] this response can be assigned to a decrease in intramolecular anthryl−anthryl π-stacking interactions induced by the change in coordination geometry at the silicon center. Fitting of this data to a 1:1 binding isotherm affords a fluoride binding constant $K = 7\ (\pm 1) \times 10^6\ \mathrm{M}^{-1}$. Under these conditions, neutral silane **1** captures fluoride with an association constant $K = 8(\pm 1)\ \mathrm{M}^{-1}$. These experiments demonstrate that the fluoride affinity of $[\mathbf{2}]^+$ exceeds that of neutral silane by at least 5 orders of magnitude. The drastic enhancement observed in the fluoride ion affinity of $[\mathbf{2}]^+$ is assigned to the presence of the sulfonium moiety which: (i) provides a Coulombic and inductive drive for the formation of the difluorosilicate compound and (ii) engages the fluoride anion in a stabilizing lp(F)→σ^*(S−C) interaction. Although triarylfluorosilanes typically display a lower fluoride affinity than triarylboranes,[13] we note that the fluoride binding constant of $[\mathbf{2}]^+$ in chloroform is almost equal to the value of $6.5\ (\pm 0.5) \times 10^6\ \mathrm{M}^{-1}$ measured for the boron-based receptor $[p\text{-}\mathrm{Mes_2B(C_6H_4)PMePh_2}]^+$.[14]

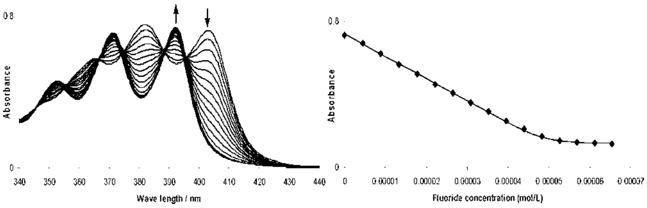

Figure 3. (Left) Absorbance change of a solution of $[\mathbf{2}]^+$ (5.00×10^{-5} M) upon successive additions of fluoride in chloroform. (Right) Binding isotherm measured at 403 nm and fitted with $K = 7 \times 10^6\ \mathrm{M}^{-1}$, $\epsilon([\mathbf{2}]^+) = 14\,600\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ and $\epsilon(\mathbf{2}\text{-F}) = 2600\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$.

The results reported in this communication indicate that proximal third row onium ions can serve to enhance the fluoride affinity of fluorosilanes via cooperative effects. These results also demonstrate the viability of sulfonium ions as Lewis acidic binding sites for fluoride binding.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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