ORGANOMETALLICS

Fluoride Anion Chelation by a Bidentate Stibonium–Borane Lewis Acid

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Supporting Information

ABSTRACT: The stibonium—borane $[o-(Ph_2MeSb)(Mes_2B)C_6H_4]^+$ (4⁺) has been synthesized and isolated as a triflate salt. Competition experiments carried out with $[o-(Ph_2MeP)(Mes_2FB)C_6H_4]$ indicate that 4⁺ exhibits a much higher fluoride affinity than its lighter phosphorus congener. Structural studies show that the higher fluoride affinity of 4⁺ is correlated to the Lewis acidity of the stibonium center, which engages the boron-bound fluoride anion in the formation of a B–F→Sb bridge. These results illustrate that the Lewis acidity of main-group onium ions increases as the group is descended.

 \mathbf{F} ollowing the seminal contribution of Biallas and Shriver, who first showed that bifunctional Lewis acids could be used for anion chelation,¹ the chemistry of boron-based bidentate Lewis acids has been growing at a steady rate,² leading to numerous applications in anion sensing³ and organic/organometallic chemistry.^{4,5} A key aspect of this chemistry lies in the stability of the chelate complex formed between the bidentate host and the anionic guest.⁶ Through a series of recent studies, it has been shown that anion binding at boron could be assisted by an adjacent onium ion via Coulombic effects. $^{5,7-9}$ An in-depth analysis of some of the complexes isolated suggested that these favorable Coulombic effects can also be complemented by donor-acceptor interactions involving nonbonding lone pairs of the anion and low-lying vacant orbitals at the central atom of the onium group. This situation is illustrated by the structure of 1-F, which features a $P \rightarrow F$ bond of 2.66 Å, estimated to contribute 5 kcal mol⁻¹ to the stability of the complex.⁸ Formation of such a donor-acceptor interaction suggested to us that the latent Lewis acidity of onium ions could be exploited in anion sensing. On the basis of this discovery, we have now decided to determine if the anion affinity of bidentate Lewis acids can be enhanced by varying the nature of the onium main-group element.

In a first exploration of this idea, we have recently compared the fluoride anion affinity of the sulfonium and telluronium derivatives 2^+ and 3^+ and found that the telluronium derivative 3^+ has a significantly higher fluoride anion affinity than the sulfonium borane 2^+ .⁹ These results, which can be rationalized by invoking the greater size, electropositivity, and polarizability of the chalcogen in 3^+ , are also in agreement with the stability of halogen-bonded complexes, which increases with the size of the halogen.¹⁰ In an effort to generalize our approach, we are now reporting on the synthesis and fluoride affinity of the antimony analogue of 1^+ .

The reaction of o-(Ph₂Sb)BrC₆H₄¹¹ with 2 equiv of *t*-BuLi in Et₂O at -78 °C, followed by addition of Mes₂BF, afforded o-(Ph₂Sb)(Mes₂B)C₆H₄. Subsequent treatment of this derivative





with MeOTf in Et_2O afforded the triflate salt of 4⁺ in moderate yield as a moisture-sensitive white powder (Scheme 1). The salt 4-OTf is soluble in polar organic solvents such as CHCl₃, CH₂Cl₂, THF, and methanol but not in hydrocarbon solvents such as hexanes and pentane as well as Et₂O. The ¹H NMR spectrum of 4-OTf recorded in CDCl₃ displays a signal at 1.91 ppm assigned to the antimony-bound methyl group. The spectrum also shows a series of broad resonances corresponding to the mesityl aromatic CH and o-CH₃ groups, which suggests steric crowding and hindered rotation of the boron substituents in solution. A broad signal at +80.2 ppm in the ¹¹B NMR spectrum of 4-OTf indicates the existence of a tricoordinate, "base-free" boron atom.⁸ This is supported by the UV-vis absorption spectrum of 4-OTf in CHCl₃, which displays a broad absorption band centered at 334 nm, characteristic of aryldimesitylborane chromophores.^{8,12} This salt quickly reacts with adventitious moisture in CDCl₃ to give rise to an intractable colorless precipitate that has not yet been identified.

Next, we decided to compare the fluoride anion affinity of 4⁺ to that of its phosphonium analogue 1⁺. To this end, we studied the reaction of 4⁺ with an equimolar amount of 1-F in CDCl₃ and observed the quantitative formation of 4-F and 1⁺ using multi-nuclear NMR spectroscopy (Scheme 2). The identity of 4-F was independently confirmed by the reaction of 4-OTf with 1 equiv of $[S(NMe_2)_3][Me_3SiF_2]$ (TASF) in CDCl₃. The ¹¹B NMR spectrum of 4-F displays a single sharp signal at 7.5 ppm, indicative of a tetrahedral boron center.⁸ Similarly, the ¹⁹F NMR

Received: June 9, 2011 Published: August 10, 2011

Scheme 1. Synthesis of Stibonium/Borane 4-OTf



Scheme 2. Competition Reaction between 4⁺ and 1-F



Figure 1. Structure of 4-F. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms have been omitted for clarity, and phenyl and mesityl groups are depicted in wireframe. Selected bond lengths (Å) and angles (deg): Sb(1)-F(1), 2.450(2); F(1)-B(1), 1.521(4); Sb(1)-C(1), 2.093(4); Sb(1)-C(7), 2.107(4); Sb(1)-C(8), 2.092(4); Sb(1)-C(14), 2.135(4); C(8)-Sb(1)-C(1), 115.85(14); C(8)-Sb(1)-C(7), 111.77(16); C(1)-Sb(1)-C(7), 120.50(15); C(14)-Sb(1)-F(1), 173.84(11); C(2)-B(1)-C(20), 118.0(3); C(2)-B(1)-C(29), 108.6(3); C(20)-B(1)-C(29), 116.7(3).

spectrum shows a single resonance at -140.1 ppm, in the expected range for a triarylfluoroborate species. The ¹H NMR resonance of the antimony-bound methyl group is shifted upfield to 1.34 ppm and appears as a doublet ($J_{H-F} = 2.38$ Hz) caused by coupling to the fluorine nucleus. The superior fluoride affinity of 4⁺ was confirmed by the observation that 4-F remained intact when treated with 1 equiv of 1⁺ in CDCl₃.

To obtain structural insight into the enhanced fluoride affinity of 4^+ , the X-ray crystal structure of 4-F has been determined (Figure 1). Examination of this structure indicates the formation of an unprecedented B-F-Sb chelate motif, demonstrating that 4^+ can be regarded as a bidentate Lewis acid. In agreement with



Figure 2. Plot of the NBO $lp_F \rightarrow \sigma^*_{Sb-C}$ donor-acceptor interactions calculated for 4-F. Density isovalues are set to 0.03, and hydrogen atoms have been omitted for clarity.

the formation of this chelate complex and the bridging location of the fluoride anion,⁹ we note that the B(1)-F(1) bond (1.521(4) Å) is elongated in comparison to terminal B-F bonds found in compounds such as $p-(Ph_2MeP)C_6H_4(BFMes_2)$ (1.476(4) Å).¹³ It is also longer than that observed in the structure of its phosphorus congener 1-F (1.482(3) Å),⁸ suggesting that the antimony atom in 4-F exerts a stronger pull than the phosphorus atom in 1-F. Accordingly, the Sb-F distance in 4-F (2.450(2) Å) is shorter than the P-F distance in 1-F (2.666(2) Å), despite the larger size of the antimony atom. Owing to the bridging location of the fluorine atom, the Sb-F distance in 4-F is elongated in comparison to that in Ph3MeSbF $(2.069(3) \text{ Å})^{14}$ but comparable to that observed in the Sb-F-Sb bridges of polymeric Me₄SbF (2.369(14) and 2.382(12) Å).¹⁵ As a result of the B-F-Sb bridge, the antimony center adopts a distortedtrigonal-bipyramidal geometry defined by $\angle (C(14) - Sb(1) -$ F(1) = 173.8(1)° and $\Sigma \angle (C_{eq} - Sb - C_{eq}) = 348.1°$.

The geometry of 4-F has been optimized using density functional theory (DFT) methods (B3LYP functional with the mixed basis set: aug-cc-pvTz-pp for Sb, 6-31+g(d') for B and F, 6-31g for C and H). The resulting geometry closely matches that determined experimentally and corresponds to a true minimum, as indicated by the absence of imaginary frequencies. Atoms in molecules (AIM) calculations carried out at the optimized geometry located a bond path connecting the antimony and fluorine atoms of 4-F (Figure S3 in Supporting Information). Although bonding orbitals tend to become more diffuse as the size of the atom increases, the value of the electron density at the Sb–F bond critical point (BCP) ($\rho(r) = 4.26 \times 10^{-2}$ e $bohr^{-3}$) is significantly larger than that determined for the P-F bond of 1-F ($\rho(r) = 2.05 \times 10^{-2}$ e bohr⁻³).⁸ The greater BCP electron density observed in 4-F suggests that the Pn-F bond (Pn = P, Sb) in 4-F is stronger than in 1-F. The Sb-Fbond in 4-F has also been investigated using a natural bond orbital (NBO) analysis. This analysis reveals the presence of a $lp_F \rightarrow \sigma^*_{Sb-C}$ donor-acceptor interaction which, as indicated by deletion calculations, contributes $E_{del} = 15.2 \text{ kcal mol}^{-1}$ to the stability of 4-F (Figure 2). This value greatly exceeds that calculated for the P–F bond of 1-F ($E_{del} = 5.0 \text{ kcal mol}^{-1}$), supporting the greater Lewis acidity of the antimony derivative. Finally, we have calculated the enthalpy change for the reaction presented in Scheme 2 by carrying out single-point calculations on 4⁺, 1⁺, 4-F, and 1-F (functional B3LYP, basis sets aug-cc-pvTz-pp for Sb and 6-311+g(2d,p) for all other atoms). These calculations indicate that the reaction is exothermic ($\Delta H =$ -4.9 kcal/mol), thus corroborating the experimental observation as well as the results of the NBO analysis.

In conclusion, the results presented in this communication demonstrate that a net enhancement in the anion affinity of cationic, bidentate boranes can be observed upon introduction of a stibonium ion as a secondary binding site. This enhancement results from the Lewis acidity of the stibonium center, which engages the fluoride anion in a strong donor—acceptor interaction. The strength of the latter can be correlated to the increased size, polarizability, and electropositivity of the heavier pnictogen element.

ASSOCIATED CONTENT

Supporting Information. Text, tables, and figures giving full experimental and computational details and a CIF file giving crystallographic data for 4-F. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This work was supported by the National Science Foundation (No. CHE-0952912), the Welch Foundation (No. A-1423), the Petroleum Research Fund (Grant 44832-AC4), and the U.S. Army Medical Research Institute of Chemical Defense.

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