

[Sb(C₆F₅)₄][B(C₆F₅)₄]: An Air Stable, Lewis Acidic Stibonium Salt That Activates Strong Element-Fluorine Bonds

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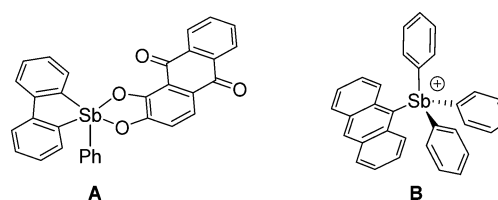
S Supporting Information

ABSTRACT: As part of our ongoing interest in main group Lewis acids for fluoride anion complexation and element-fluorine bond activation, we have synthesized the stibonium borate salt [Sb(C₆F₅)₄][B(C₆F₅)₄] (**3**). The perfluorinated stibonium cation [Sb(C₆F₅)₄]⁺ present in this salt is a potent Lewis acid which abstracts a fluoride anion from [SbF₆]⁻ and [BF(C₆F₅)₃]⁻ indicating that it is a stronger Lewis acid than SbF₅ and B(C₆F₅)₃. The unusual Lewis acidic properties of **3** are further reflected by its ability to polymerize THF or to promote the hydrodefluorination of fluoroalkanes in the presence of Et₃SiH. While highly reactive in solution, **3** is a perfectly air stable salt, making it a convenient Lewis acidic reagent.

Over the past decades, the field of Lewis acid chemistry has witnessed some important developments marked by the advent of electron-deficient molecules such as fluorinated organoboranes.¹ These compounds have become ubiquitous electrophilic activators widely used for applications in catalysis^{1a-c} and small-molecule activation.^{1d-h} Strong Lewis acidity is also observed for silylium derivatives² which have emerged as one of the best platforms for the activation of strong C–F bonds.³ While these advances unambiguously illustrate the Lewis acidity of these tricoordinate group 13 and 14 species, the pioneering work of Olah shows that strong Lewis acidity can also be expressed by group 15 elements, especially antimony.⁴ Early experimental work by Gutmann shows that the chloride ion affinity of SbCl₅ exceeds that of BCl₃, suggesting that the former is a stronger Lewis acid.⁵ A similar conclusion can be derived from a comparison of the computed gas phase fluoride ion affinity of SbF₅ (489 kJ/mol) and BF₃ (338 kJ/mol), with the former exceeding the latter by more than 150 kJ/mol.⁶ However, like BF₃ and BCl₃, the use of these antimony pentahalides is complicated by their highly reactive and corrosive nature. In particular, both SbF₅ and SbCl₅ react violently with water, releasing the corresponding hydrohalic acid. An extension of the lessons learned in the chemistry of fluorinated boranes^{1c} would suggest that the introduction of organic substituents in antimony(V) compounds may afford strong Lewis acids that do not display the inconvenient corrosive properties of the pentahalide derivatives.

In a series of recent papers, we have shown that organostiboranes⁷ such as **A**⁸ and tetraarylstibonium ions⁹ such as **B**¹⁰ are sufficiently Lewis acidic to complex fluoride in aqueous media (Chart 1). Encouraged by these results and inspired by the recent work of Burford on highly Lewis acidic

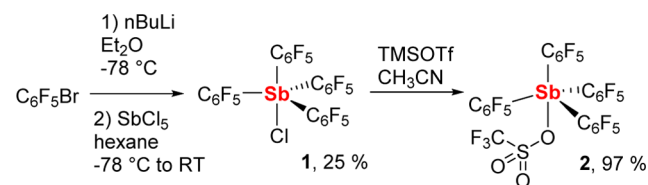
Chart 1



dicationic antimony species,¹¹ we have now decided to investigate the synthesis and properties of pentafluorophenyl-antimony(V) derivatives. In this paper we describe the synthesis and unusual Lewis acidic properties of the tetrakis-(pentafluorophenyl)stibonium cation ([Sb(C₆F₅)₄]⁺), a compound related to highly acidic fluorophosphonium cations¹² such as [FP(C₆F₅)₃]⁺ recently described by Stephan.¹³

The reaction of C₆F₅Li with SbCl₅ in diethyl ether/hexane afforded SbCl(C₆F₅)₄ (**1**) along with the known Sb(C₆F₅)₅ (Scheme 1).¹⁴ Compound **1** can be easily separated from the

Scheme 1



mixture by fractional crystallization from Et₂O. This colorless, air stable compound has been fully characterized. Its ¹⁹F NMR spectrum in dichloromethane at –80 °C shows two sets of C₆F₅ resonances whose 1:3 integration ratio suggests that the molecule has trigonal bipyramidal geometry. Upon elevation of the temperature, the two sets of C₆F₅ resonances coalesce, indicating a fluxional behavior by which the equatorial and axial C₆F₅ groups exchange their positions. A line shape analysis indicates an activation energy of 33(±1) kJ/mol for this process, which we propose occurs via a square pyramidal transition state as in the case for Sb(C₆F₅)₅.¹⁴ This value is 9 kJ/mol higher than that reported for Sb(C₆F₅)₅, a factor that we assigned to the decreased steric bulk around antimony in **1** as well as the apicophilicity of the chloride ligand. Solutions of **1** in MeCN are not conductive, indicating the tight coordination of the chloride anion. This is in contrast to

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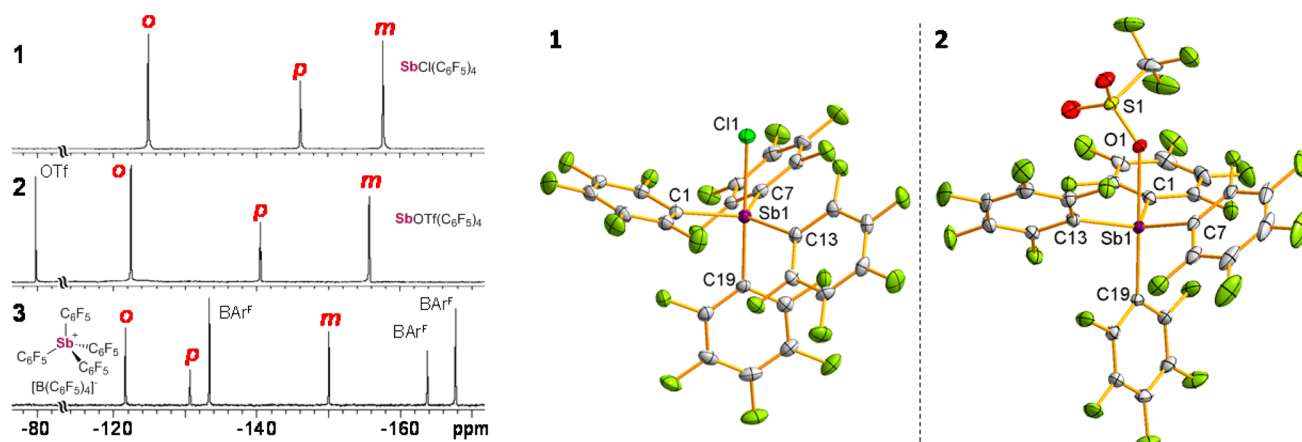
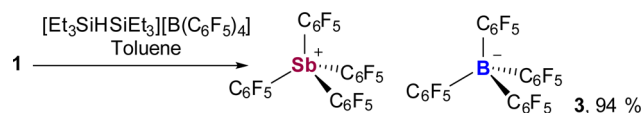


Figure 1. Left: ^{19}F NMR spectra of **1**, **2**, and **3** in CH_2Cl_2 . The ortho, meta, and para resonances of the C_6F_5 groups bound to antimony are identified by the corresponding letters. Right: Solid state structure of **1** and **2**. Ellipsoids are drawn at a 50% probability level. Selected bond lengths (Å) and angles (deg) for **1**: Sb1–Cl1 = 2.4509(11), Sb1–C1 = 2.130(3), Sb1–C7 = 2.144(3) Å, Sb–C13 = 2.143(3), Sb1–C19 2.197(3) Å; C1–Sb1–C13 115.56(12), C1–Sb1–C7 119.49(12), C13–Sb1–C7 124.16(12), C19–Sb1–C1 176.09(8). Selected bond lengths (Å) and angles (deg) for molecule I of **2** with the corresponding metrical parameter for molecule II in brackets: Sb1–C1 2.108(3) [2.090(3)], Sb1–C7 2.100(4) [2.089(3)], Sb1–C13 2.103(3) [2.094(3)], Sb1–C19 2.146(3) [2.145(3)], Sb1–O1 2.377(2) [2.471(2)], C7–Sb1–C13 112.03(14) [113.28(13)], C7–Sb1–C1 117.98(14) [114.01(13)], C13–Sb1–C1 118.76(13) [116.27(13)], C19–Sb1–O1 177.91(11) [174.36(10)].

Ph_4SbCl which adopts a partially ionic structure in MeCN .¹⁵ This strong coordination of the chloride anion can be explained by the electron-withdrawing properties of the C_6F_5 group. The crystal structure of **1** (Figure 1) supports this interpretation with the Sb–Cl bond distance of **1** (Sb1–Cl1 = 2.451(1) Å) being much shorter than that reported for Ph_4SbCl (2.686(1) Å).¹⁶ The Sb–C bonds in **1** are well differentiated with the axial Sb–C (2.197(3) Å) bond distance being longer than the equatorial ones (av. 2.14 Å).

With compound **1** in hand, we became eager to investigate its conversion into a stibonium cation by abstraction of the chloride ligand. To this end, **1** was allowed to react with trimethylsilyltriflate (TMSOTf) in acetonitrile. This reaction proceeded smoothly to afford the antimony triflate derivative **2** (Scheme 2). The ^{19}F NMR spectrum of this compound

Scheme 2



displays a single set of C_6F_5 resonances. These resonances which show no sign of decoalescence upon cooling are notably more downfield than those of **1** (Figure 1). This downfield shift suggests that the triflate ligand of **2** is more weakly coordinated to antimony than the chloride ligand of **1**, leading to a more electrophilic antimony moiety. Compound **2** crystallizes with two independent molecules (I and II) in the asymmetric unit. Coordination of the triflate ligand is confirmed by the Sb–O bonds of 2.377(2) Å (molecule I) and 2.471(2) Å (molecule II) (Figure 1). Both molecules adopt a distorted trigonal bipyramidal geometry ($\Sigma\angle(\text{C}_{\text{eq}}-\text{Sb}-\text{C}_{\text{eq}}) = 348.7^\circ$ and 343.5° for molecule I and II, respectively) with the triflate acting as an axial ligand. As in **1**, the axial Sb–C bond (av. 2.14 Å) is longer than the equatorial ones (av. 2.10 Å). The observed coordination of the triflate anion prompted us to investigate even less coordinating anions. To this end, compound **1** was treated with $[\text{Et}_3\text{SiHSiEt}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ in

toluene.¹⁷ This reaction proceeded smoothly to afford the stibonium borate salt $[\text{Sb}(\text{C}_6\text{F}_5)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**3**) (Scheme 2). The ^{19}F NMR resonances of the $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ unit are distinctly more downfield than those of **1** and **2**, thus supporting an ionic structure in solution (Figure 1). This salt can be crystallized from CH_2Cl_2 . Salt **3** crystallizes in the tetragonal space group $I\bar{4}$ (Figure 2). The stibonium and the borate units

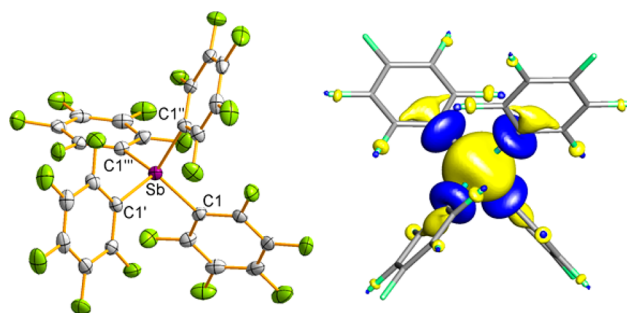


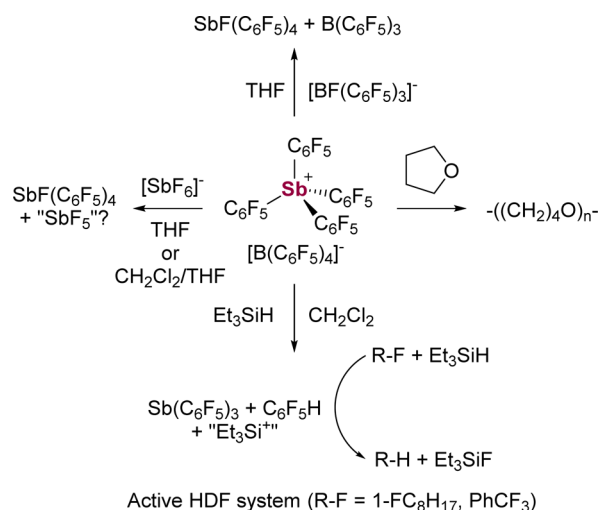
Figure 2. Right: Solid state structure of the $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ cation in **3** as determined by X-ray diffraction. Ellipsoids are drawn at the 30% probability level. Selected bond lengths and angles: Sb–C1 2.095(2); C1'–Sb1–C1'' = C1–Sb1–C1''' = 107.78(13)°, C1–Sb1–C1' = C1–Sb1–C1'' = C1'–Sb1–C1''' = C1''–Sb1–C1''' = C1–Sb1–C1 110.32(7). Left: LUMO $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ overlaid on the optimized geometry (isovalue = 0.05).

show no unusually short contacts. The C–Sb–C angles of $107.78(13)^\circ$ or $110.32(7)^\circ$ as well as the short Sb–C bonds (2.095(2) Å) serve as an additional confirmation that the antimony atom is free of interaction with external donors. It is also interesting to note that, as a result of the similar structure and volume of the $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ cation and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, the cell parameters of **3** are close to those of group 14 tetrakis(pentafluorophenyl) derivatives which also crystallize in tetragonal space groups.¹⁸ The LUMO of $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ calculated for the DFT optimized geometry of the cation can be viewed as the linear combination of the four Sb–C σ^* -orbitals (Figure 2). The largest lobe of this orbital is spherically

distributed about the antimony center making the heavy group 15 atom the most acidic site of the molecule.

Compounds **2** and **3** show no sign of decomposition when stored in air for several days. This stability was not anticipated, especially for compound **3** which contains a base-free $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ unit. Surprised by the stability of these complexes, we decided to carry out additional tests. While sharp ^{19}F NMR resonances are observed for the $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ cation when **3** is dissolved in CH_2Cl_2 , much broader resonances are observed in THF, suggesting the possible dynamic coordination of solvent molecules. On standing, the resulting solution undergoes polymerization, indicating that $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ is a potent activator (Scheme 3). No THF

Scheme 3. Reactivity of 3 with Selected Substrates



polymerization was observed when **2** was dissolved in THF. The higher Lewis acidity of **3** was probed in greater details using the Gutmann–Beckett method.¹⁹ We first studied the formation of the Et_3PO adduct by ESI mass spectrometry which showed the corresponding molecular ion ($[(\text{C}_6\text{F}_5)_4\text{Sb}-\text{OPEt}_3]^+$, $m/z = 922.96$) for CH_2Cl_2 solutions containing **2** or **3** and the phosphine oxide. Next, we measured the ^{31}P chemical shifts of the bound Et_3PO which was detected at 73.0 ppm for **2** and 74.6 ppm for **3**. The value obtained for **3** is lower than that reported for the strong Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ (76.6 ppm).^{19b} When the same measurement was carried out with **1**, the chemical shift of Et_3PO (51 ppm) appeared unperturbed, suggesting that **1** does not display any acidity toward this Lewis base.

Bearing in mind that the Lewis acidity of $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ toward relatively large bases such as Et_3PO may be hampered by steric effects, we decided to investigate the behavior of **2** and **3** toward the small fluoride anion. Both **2** and **3** react with KF (in THF for **2** and $\text{CH}_2\text{Cl}_2/\text{THF}$ for **3**) to afford $\text{SbF}(\text{C}_6\text{F}_5)_4$ (**4**), which has been characterized by NMR spectroscopy and elemental analysis. The antimony bound fluoride anion of **4** in CD_3CN leads to a ^{19}F NMR resonance at -25.0 ppm. The ortho, para, and meta C_6F_5 resonances at -124.6 , -144.6 , and -156.6 ppm, respectively, are almost identical to those of **1** (-124.5 , -144.9 , and -156.6 ppm). Having observed that both **2** and **3** quickly react with labile fluoride sources such as KF, we decided to evaluate the fluoride affinity of these two species via a series of competition experiments. Toward this end, we selected two of the most potent and commonly used Lewis

acids, namely SbF_5 and $\text{B}(\text{C}_6\text{F}_5)_3$ for which fluoride ion affinities of 489 and 444 kJ/mol, respectively, have been calculated.⁶ Compound **2** reacted slowly with $[\text{SbF}_6]^-$ (as a TBA salt) in THF with only a small amount of **4** (<15%) present in the reaction mixture after 30 min. Compound **2** showed no sign of reaction with $[\text{BF}(\text{C}_6\text{F}_5)_3]^-$ (as a TBA salt). Compound **3** showed a drastically different behavior, activating both $[\text{SbF}_6]^-$ and $[\text{BF}(\text{C}_6\text{F}_5)_3]^-$ very rapidly in THF, with both reactions being completed within 5 min, the time necessary to record the NMR spectrum (Scheme 3). While free $\text{B}(\text{C}_6\text{F}_5)_3$ was readily detected in the reaction mixture of **3** and $[\text{BF}(\text{C}_6\text{F}_5)_3]^-$, SbF_5 , the byproduct of $[\text{SbF}_6]^-$ activation, could not be observed in the reaction of **3** and $[\text{SbF}_6]^-$ (Scheme 3). Our inability to observe SbF_5 in THF is certainly concerning. However, we note that no ^{19}F NMR spectrum for SbF_5 in THF is available. Instead, measurements have been carried out for the neat substance or in noninteracting solvents. The SbF_5 resonances are extremely broad, spanning a 70 ppm range,²⁰ and often complicated by aggregation.²¹ Upon standing, the THF solvent used in the reaction of **3** with $[\text{SbF}_6]^-$ polymerized thus complicating analysis of the mixture. We also observed that the use of a donor solvent plays a key role in these reactions. Indeed when **3** was mixed with $[\text{SbF}_6]^-$ (as a TBA salt) in CH_2Cl_2 , a broadening of the $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ and $[\text{SbF}_6]^-$ ^{19}F NMR resonances is observed without any evidence for the formation of **4**. Addition of THF to this solution results in the fast formation of **4** which is detected as the main product of the reaction after 10 min. The synergy observed between THF and $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ in the activation of $[\text{SbF}_6]^-$ is reminiscent of that observed in frustrated Lewis pairs.^{1d–h} It is also reminiscent of the C–F bond activation of CH_3F by SbF_5 , which occurs only in solvents of sufficient donor abilities.²²

To complete this initial survey of the unusual properties of **3**, we decided to test its ability to promote the hydrodefluorination (HDF) of simple fluoroalkanes.^{3,13b} Rapid hydrodefluorination of 1- $\text{C}_8\text{H}_{17}\text{F}$ and PhCF_3 was observed upon combination of these fluoroalkanes with Et_3SiH (2.3 equiv for 1- $\text{C}_8\text{H}_{17}\text{F}$, 9.2 equiv for PhCF_3) and 1 mol % of **3** in CH_2Cl_2 (Scheme 3). The progress of the reaction could be conveniently followed by the disappearance of the fluoroalkane starting material and the appearance of Et_3SiF in the ^{19}F NMR spectrum of the reaction mixture. While we were tempted to propose that $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$ is involved in the C–F bond activation step, we found that **3** does not react with 1- $\text{C}_8\text{H}_{17}\text{F}$ and PhCF_3 . Instead it quickly reacts with Et_3SiH to form $\text{C}_6\text{F}_5\text{H}$ and $\text{Sb}(\text{C}_6\text{F}_5)_3$ as confirmed by ^{19}F NMR spectroscopy. Formation of these two products is consistent with the generation of Et_3Si^+ as the active hydrodefluorination species. The formation of the silylium ion has been confirmed by measuring the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of a concentrated MeCN solution containing **3** and 2 equiv of Et_3SiH . After an overnight data acquisition, the spectrum reveals the presence of solvated Et_3Si^+ at 36.6 ppm^{17a} along with a resonance assigned to the hydrolysis product $(\text{Et}_3\text{Si})_2\text{O}$ (9.0 ppm).²³ The activation of Et_3SiH by **3** is interesting because hydride abstraction from the silicon atom is followed by an irreversible reductive elimination step thereby preventing hydride back-transfer to the silylium center. It also suggests that $\text{Sb}(\text{C}_6\text{F}_5)_3$ is not sufficiently basic to quench the activity of the catalyst.

In summary, we describe the synthesis of $[\text{Sb}(\text{C}_6\text{F}_5)_4]^+$, a new perfluorinated organostibonium ion. This “ SbAr^{F} ” cation is isolated as a $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ salt which presents the advantage of

being air stable. We attribute the air stability of this derivative to the tetrahedral geometry of the stibonium center which prevents an approach by nucleophiles. In solution, however, solvent promoted reorganization processes allow access to the electrophilic antimony center, revealing the unusually high acidity of this derivative. We are currently probing the behavior of this salt toward a broad range of organic and inorganic substrates.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional experimental and computational details. Crystallographic data in cif format. These material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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