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# Synthesis and Characterization of Bis(2,4,6-tris(trifluoromethyl)phenyl) Derivatives of Arsenic and Antimony: X-ray Crystal Structures of $\text{As}(\text{R}_\text{F})_2\text{Cl}$ , $\text{Sb}(\text{R}_\text{F})_2\text{Cl}$ , and $\text{Sb}(\text{R}_\text{F})_2\text{OSO}_2\text{CF}_3$

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Bis(2,4,6-tris(trifluoromethyl)phenyl)chloropnictines,  $\text{Pn}(\text{R}_\text{F})_2\text{Cl}$  ( $\text{Pn} = \text{As}, \text{Sb}$ ) have been synthesized by the reaction of 2 equiv of  $\text{R}_\text{F}\text{Li}$  with  $\text{PnCl}_3$  to provide a homologous series. The crystal structures, elemental analyses, and spectral data confirm the introduction of two  $\text{R}_\text{F}$  substituents onto the pnictogen center.  $\text{Sb}(\text{R}_\text{F})_2\text{Cl}$  reacts quantitatively with silver triflate or trimethylsilyl triflate to give  $\text{Sb}(\text{R}_\text{F})_2\text{OSO}_2\text{CF}_3$ , while  $\text{As}(\text{R}_\text{F})_2\text{Cl}$  does not react with either triflate reagent. The solid-state structure of  $\text{Sb}(\text{R}_\text{F})_2\text{OSO}_2\text{CF}_3$  reveals a covalent  $\text{Sb}-\text{O}$  interaction, indicating that, in contrast to the observations for dicoordinate group 14 element derivatives, the fluoromethyl substituents of  $\text{R}_\text{F}$  are not sufficiently basic to preclude coordination of the weakly basic anion at the cationic stibonium center.

## Introduction

The structure, stability, and reactivity of a molecule are governed, in part, by the size and shape of peripheral substituents. Large bulky hydrocarbon substituents have a dramatic effect on the relative thermodynamic stability of a system<sup>1</sup> and may also render a site unreactive by virtue of the imposed steric shield. Smaller fluorinated substituents impart thermodynamic stability without inhibiting reactivity.<sup>2</sup> In particular, the estimated steric bulk of the 2,4,6-tris(trifluoromethyl)phenyl substituent ( $\text{R}_\text{F}$ )<sup>3</sup> is between those of "mesityl" (2,4,6-trimethylphenyl (mes)) and 2,4,6-tris(isopropyl)phenyl (tip), but the electron-withdrawing effect of  $\text{R}_\text{F}$  and coordinative interactions by the ortho  $\text{CF}_3$  moieties allow for the isolation of structural arrangements that are unstable with the larger substituents tip and "super mesityl" (2,4,6-tris(*tert*-butyl)phenyl (mes\*)).<sup>4</sup> Notable examples include air- and moisture-stable monomeric triarylgallium<sup>5</sup> and -indium<sup>6</sup> compounds, a rare diindane,<sup>6</sup> and compounds containing dicoordinate indium,<sup>7</sup> thallium,<sup>8</sup> germanium,<sup>9,10</sup> tin,<sup>11</sup> and lead.<sup>12</sup>

These observations prompted us to examine the application of  $\text{R}_\text{F}$  substitution to the stabilization of coordi-

natively unsaturated cations of the pnictogen elements (specifically, pnictenium environments,  $\text{R}_2\text{Pn}^+$ ), which are isovalent with the group 14 carbenoids.<sup>9–12</sup>  $\text{R}_\text{F}$  substitution of pnictogen centers has been spectroscopically confirmed for  $\text{Pn}(\text{R}_\text{F})\text{Cl}_2$  ( $\text{Pn} = \text{P}, \text{As}$ )<sup>13,14</sup> and  $\text{P}(\text{R}_\text{F})_2\text{Cl}$ ,<sup>15</sup> and crystal structures have been reported for  $\text{R}_\text{F}\text{NPnR}_\text{F}$  ( $\text{Pn} = \text{P},^{10} \text{As}^{14}$ ),  $\text{R}_\text{F}\text{PPR}_\text{F}$ ,<sup>13</sup>  $\text{R}_\text{F}\text{P}(\text{Se})\text{PR}_\text{F}$ ,<sup>16</sup>  $(\text{C}_6\text{F}_5\text{NPR}_\text{F})_2$ ,<sup>17</sup> and  $\text{Bi}(\text{R}_\text{F})_2\text{Cl}$  and  $\text{Bi}(\text{R}_\text{F})_3$ <sup>18</sup> (see also  $\text{R}_\text{F}\text{NPnCl}_2$  ( $\text{Pn} = \text{P}, \text{As}$ )<sup>10</sup>). Despite the steric restrictions, the recent synthesis and crystal structure of the phosphide  $[\text{Ph}_3\text{PMe}]^+[\text{P}(\text{R}_\text{F})_2]^-$ <sup>15</sup> demonstrates that multi-substitution is not restricted to the larger bismuth nucleus.<sup>18</sup> We now report the preparation and characterization of  $\text{Pn}(\text{R}_\text{F})_2\text{Cl}$  ( $\text{Pn} = \text{As}, \text{Sb}$ ), thus completing the  $\text{Pn}(\text{R}_\text{F})_2\text{Cl}$  ( $\text{Pn} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$ ) homologous series. In addition, we show that the triflate derivative  $\text{Sb}(\text{R}_\text{F})_2\text{OSO}_2\text{CF}_3$  involves a covalent  $\text{Sb}-\text{O}$  interaction rather than a stibonium cation.

## Experimental Section

**General Procedures.** Diethyl ether was obtained from ACP Chemicals Inc., hexane from Van Waters & Rogers,

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arsenic(III) chloride from Kodak Chemicals, and silver triflate from Fisher Scientific. All other chemicals and reagents were obtained from Aldrich Chemical Co. 1,3,5-Tris(trifluoromethyl)benzene and *n*-butyllithium (1.6 M in hexane) were used as received. Phosphorus(III) chloride and arsenic(III) chloride were degassed and distilled in vacuo prior to use. Antimony(III) chloride was sublimed twice in vacuo prior to use. Diethyl ether was dried over sodium with benzophenone, *n*-hexane was dried over CaH<sub>2</sub>, and CD<sub>2</sub>Cl<sub>2</sub> was dried over P<sub>2</sub>O<sub>5</sub> and CaH<sub>2</sub>. All solvents were stored in evacuated bulbs. Solids were handled in nitrogen-filled gloveboxes (Vacuum Atmospheres or Innovative Technologies), and liquids were manipulated in a nitrogen-filled glovebag. Reactions were performed in sealed reactors,<sup>19</sup> which were flame-dried under vacuum before use. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany. Infrared spectra were recorded as Nujol mulls on CsI plates with use of a Nicolet 510P FT-IR spectrometer. Raman spectra were recorded, on neat powdered samples sealed under nitrogen in melting point tubes, using a Bruker RFS 100 spectrometer. NMR spectra were recorded on a Bruker AC-250 Fourier transform spectrometer with spectrometer frequencies of 250.133 MHz for <sup>1</sup>H, 62.896 MHz for <sup>13</sup>C, 101.256 MHz for <sup>31</sup>P, and 235.361 MHz for <sup>19</sup>F. NMR samples were flame-sealed in 5 mm Pyrex tubes. All chemical shifts are reported in ppm relative to an external standard (TMS for <sup>1</sup>H and <sup>13</sup>C, 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P, CFCl<sub>3</sub> for <sup>19</sup>F). Crystalline samples were obtained by distilling solvent in vacuo (static) from the solution compartment by placing the adjoining compartment in a cool stream of water or over liquid nitrogen. Crystals were washed with cool solvent by cold spot back-distillation.

**Vibrational Spectra for P(R<sub>F</sub>)<sub>2</sub>Cl (1).** 1 was prepared by the method of Davidson et al.<sup>15</sup> IR (cm<sup>-1</sup>): 3106 w, 2727 w, 1845 w, 1626 m, 1577 w, 1278 s, 1196 s, 1172 s(sh), 1155 s(sh), 1133 s, 1086 s, 1039 m, 929 w(sh), 915 m, 860 m, 833 m, 754 m, 737 w, 704 m, 700 m, 686 s, 668 m, 564 w, 527 m, 506 w, 478 w, 434 m, 356 w. Raman (cm<sup>-1</sup>; 225 mW (poor scatterer)): 3093 m, 1665 w, 1627 s, 1374 s, 1262 w, 1154 w, 1121 w, 1035 s, 740 s, 527 w, 507 w, 472 w, 437 w, 300 m, 261 m, 212 w, 158 s, 114 m.

**Preparation and Characterization of Pn(R<sub>F</sub>)<sub>2</sub>Cl (Pn = As (2), Sb (3)).** In a typical reaction, an excess of <sup>n</sup>BuLi (1.6 M in hexane) was slowly added through a septum to a stirred, cooled (0 °C) solution of R<sub>F</sub>H in diethyl ether (50 mL) under nitrogen. After 3–4 h at room temperature, the dark orange solution was added over a period of 15 min to a stirred solution of PnCl<sub>3</sub> in diethyl ether (30 mL), producing a yellow solution and a white precipitate (LiCl). The reaction mixture was frozen, the reactor was evacuated, and the suspension was stirred for 2 days at room temperature. Crystalline material was obtained from the filtered solution as described in the general procedures.

**As(R<sub>F</sub>)<sub>2</sub>Cl (2)** was prepared from R<sub>F</sub>H (4.88 g, 17.3 mmol) and AsCl<sub>3</sub> (1.5 g, 8.3 mmol). The crude yellow solid was sublimed at 75 °C under dynamic vacuum to yield a white solid, which was recrystallized from hexane to give colorless, needle-shaped crystals: yield 0.72 g, 1.1 mmol, 13%; mp 98–100 °C. Anal. Calcd: C, 32.14; H, 0.60; Cl, 5.27. Found: C, 32.20; H, 0.70; Cl, 5.12. IR (cm<sup>-1</sup>): 3377 vw(br), 3100 w, 3087 w(sh), 2727 w, 2671 w(br), 2279 w(br), 1844 w, 1668 w, 1624 m, 1581 w, 1341 m(sh), 1279 s, 1207 s(sh), 1195 s, 1153 s, 1125 s, 1085 s, 1039 m, 930 w(sh), 916 s, 891 w(sh), 857 m, 836 m, 792 w(br), 747 m, 736 w, 695 m, 692 m(sh), 685 s, 671 m, 652 w(sh), 562 w, 435 w, 424 w, 417 w, 408 w, 387 m. Raman (cm<sup>-1</sup>; 225 mW (poor scatterer)): 3089 m, 1665 w, 1625 s, 1588 m, 1022 m, 857 w, 739 s, 461 w, 388 s, 304 m, 260 s, 217 w, 193 w, 158 s, 110 m. NMR (δ; CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H, 8.10 (s); <sup>13</sup>C, 122.6 (q,

<sup>1</sup>J<sub>C-F</sub> = 277.0 Hz, *p*-CF<sub>3</sub>), 123.4 (q, <sup>1</sup>J<sub>C-F</sub> = 276.1 Hz, *o*-CF<sub>3</sub>), 128.7 (s(br), C<sub>m</sub>), 133.3 (q, <sup>2</sup>J<sub>C-F</sub> = 34.8 Hz, C<sub>o</sub>), 136.3 (q, <sup>2</sup>J<sub>C-F</sub> = 34.5 Hz, C<sub>p</sub>), 147.5 (s, C<sub>j</sub>); <sup>19</sup>F, -54.5 (s, 12F), -63.9 (s, 6F).

**Sb(R<sub>F</sub>)<sub>2</sub>Cl (3)** was prepared from R<sub>F</sub>H (1.3 g, 4.7 mmol) and SbCl<sub>3</sub> (0.53 g, 2.3 mmol). Large, hexagon-shaped, pale yellow crystals were obtained: yield 0.69 g, 0.96 mmol, 41%; mp 112–113 °C. Anal. Calcd: C, 30.05; H, 0.56; Cl, 4.93. Found: C, 30.23; H, 0.67; Cl, 4.86. IR (cm<sup>-1</sup>): 3096 w, 3083 w, 1844 w, 1623 s, 1577 m, 1559 w, 1419 w, 1279 s, 1200 s, 1129 s, 1109 s, 1082 s(sh), 1015 w(sh), 930 m, 915 s, 852 s, 837 m, 742 m, 691 s(sh), 684 s, 670 s, 560 w, 432 m, 408 w, 401 w(sh), 366 w, 351 s, 302 w. Raman (cm<sup>-1</sup>; 166 mW (poor scatterer)): 3084 m, 1624 m, 1383 m, 1261 w, 1157 w, 1014 w, 854 w, 738 s, 691 w, 581 w, 451 w, 434 w, 367 w, 349 s, 304 m, 262 s, 211 w, 184 m, 155 s, 126 s, 101 s. NMR (δ; CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H, 8.22 (s); <sup>13</sup>C, 122.8 (q, <sup>1</sup>J<sub>C-F</sub> = 272.8 Hz, *p*-CF<sub>3</sub>), 124.1 (q, <sup>1</sup>J<sub>C-F</sub> = 276.1 Hz, *o*-CF<sub>3</sub>), 128.3 (s(br), C<sub>m</sub>), 133.9 (q, <sup>2</sup>J<sub>C-F</sub> = 34.8 Hz, C<sub>o</sub>), 137.8 (q, <sup>2</sup>J<sub>C-F</sub> = 32.9 Hz, C<sub>p</sub>), 151.9 (s(br), C<sub>j</sub>); <sup>19</sup>F -55.3 (s, 12F), -63.9 (s, 6F).

**Preparation and Characterization of Sb(R<sub>F</sub>)<sub>2</sub>OSO<sub>2</sub>CF<sub>3</sub> (4).** Sb(R<sub>F</sub>)<sub>2</sub>Cl (0.25 g, 0.34 mmol) and AgOSO<sub>2</sub>CF<sub>3</sub> (0.10 g, 0.37 mmol) were combined in hexane (10 mL), and the mixture was stirred for 3 days with exclusion of light. The resultant yellow suspension was filtered through a fine, sintered-glass filter to give a clear yellow solution, from which pale, yellow, diamond-shaped crystals of Sb(R<sub>F</sub>)<sub>2</sub>OSO<sub>2</sub>CF<sub>3</sub> (4) were obtained; yield 0.04 g, 0.05 mmol, 14%; mp 126–127 °C. Anal. Calcd: C, 27.40; H, 0.48. Found: C, 27.36; H, 0.56. IR (cm<sup>-1</sup>): 3105 w, 3087 w, 2726 w, 1625 w, 1578 w, 1377 s, 1280 s, 1268 s(sh), 1238 m(sh), 1220 s(sh), 1198 s, 1171 s, 1183 s(sh), 1152 s(sh), 1140 s, 1084 m, 1077 m, 1013 w, 942 m(sh), 932 s, 916 s, 852 m, 836 w, 767 w, 742 m, 693 m, 685 m, 672 w, 628 m, 603 w, 571 w, 559 w, 537 w, 515 w, 431 w, 408 w, 384 w, 366 w. Raman (cm<sup>-1</sup>; 110 mW (poor scatterer)): 3090 m, 1862 w(br), 1796 w(br), 1626 m, 1384 m, 1264 w, 1238 w, 1085 w, 1042 w(br), 1018 m, 931 w, 856 w, 767 m, 739 w, 693 w, 574 w, 456 w, 434 w, 306 m, 262 s, 212 m, 184 m, 157 s. NMR (δ; CD<sub>2</sub>Cl<sub>2</sub>): <sup>1</sup>H, 8.32 (s); <sup>13</sup>C, 124.1 (q, <sup>1</sup>J<sub>C-F</sub> = 276.1 Hz, *o*-CF<sub>3</sub>) and 128.9 (s(br), C<sub>m</sub>); <sup>19</sup>F, -55.7 (s(br), 33 Hz in CD<sub>2</sub>Cl<sub>2</sub> and 26 Hz in hexane), 12F), -64.0 (s, 6F), -77.3 (s, 3F).

**X-ray Crystallography.** Crystals were obtained as described above, except for **2a**, which was grown from a reaction mixture containing silver triflate. Details of the crystal structure determinations are summarized in Table 1. For each of these structures, there was severe disorder among the para CF<sub>3</sub> groups. Restraints were necessary for the refinement of the disordered CF<sub>3</sub> groups, and their positional and displacement parameters are unreliable.

For **2a**, unit cell determination and data collection were performed, with graphite-monochromated radiation (Mo Kα, λ = 0.710 73 Å) and 1° rotations on Φ scans, on a Nonius KappaCCD diffractometer. Data reduction, including Lorentz, polarization, and absorption corrections, was performed with the DENZO-SMN software package,<sup>20</sup> whereas structure solution and refinement were performed with the SHELX-97<sup>21</sup> and SHELXTL<sup>22</sup> software packages. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms, which were located from a difference map, were refined with a common isotropic displacement parameter. The hydrogen atoms were constrained to ride on their attached carbon atoms, but the coordinates were allowed to vary and the C–H bond distances were restrained to be equal.

For **2b**, **3**, and **4**, unit cell determination and data collection were performed, with graphite-monochromated radiation (Mo Kα, λ = 0.710 73 Å for **2b** and **4**, Cu Kα, λ = 1.541 78 Å for **3**) and ω–2θ scans, on a Rigaku AFC5R diffractometer. Data

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**Table 1.** Summary of the Crystal Data, Data Collection, and Refinement Conditions for As(R<sub>F</sub>)<sub>2</sub>Cl (**2a**,**b**), Sb(R<sub>F</sub>)<sub>2</sub>Cl (**3**), and Sb(R<sub>F</sub>)<sub>2</sub>OSO<sub>2</sub>CF<sub>3</sub> (**4**)

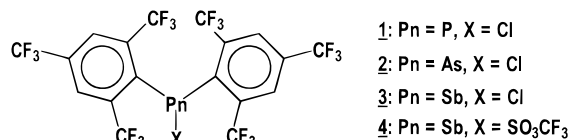
	<b>2a</b>	<b>2b</b>	<b>3</b>	<b>4</b>
empirical formula	C <sub>18</sub> H <sub>4</sub> AsClF <sub>18</sub>	C <sub>18</sub> H <sub>4</sub> AsClF <sub>18</sub>	C <sub>18</sub> H <sub>4</sub> ClF <sub>18</sub> Sb	C <sub>19</sub> H <sub>4</sub> F <sub>21</sub> O <sub>3</sub> SSb
fw	672.58	672.58	719.41	833.03
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	8.6646(2)	8.705(9)	8.296(2)	16.172(4)
<i>b</i> (Å)	9.69650(10)	30.38(1)	30.430(7)	17.758(2)
<i>c</i> (Å)	25.4076(6)	8.167(4)	8.779(3)	9.119(1)
α (deg)	90	90	90	90
β (deg)	90	91.53(6)	94.030(3)	90
γ (deg)	90	90	90	90
<i>V</i> (Å <sup>3</sup> ), <i>Z</i>	2134.65(7), 4	2159(2), 4	2211(1), 4	2618.8(6), 4
<i>D</i> <sub>calcd</sub> (Mg m <sup>-3</sup> )	2.093	2.069	2.161	2.113
λ (Å)	0.710 73	0.710 73	1.541 78	0.710 73
μ (mm <sup>-1</sup> ), <i>F</i> (000)	1.880, 1296	1.859, 1296	12.518, 1368	1.304, 1592
cryst size (mm <sup>3</sup> )	0.30 × 0.25 × 0.15	0.40 × 0.30 × 0.20	0.30 × 0.13 × 0.11	0.50 × 0.40 × 0.40
cryst color, habit	colorless, plate	colorless, prism	light yellow, needle	colorless, block
diffractometer	Nonius KappaCCD	Rigaku AFC5R	Rigaku AFC5R	Rigaku AFC5R
scan type	1° rotations on Φ	ω/2θ	ω/2θ	ω/2θ
temp (K)	130(2)	296(1)	296(1)	296(1)
abs cor	multiscan	ψ-scan	ψ-scan	ψ-scan
transmissn factors	0.766–0.602	1.000–0.615	1.000–0.640	1.000–0.966
no. of data collected	16157	4082	3953	4287
no. of unique data	4353	3825	3874	4287
no. of obsd data, criterion	3925, <i>I</i> > 2σ <i>I</i>	803, <i>I</i> > 3σ <i>I</i>	1022, <i>I</i> > 2σ <i>I</i>	1840, <i>I</i> > 3σ <i>I</i>
<i>R</i> <sub>int</sub> , 2θ <sub>max</sub> (deg)	0.074, 52.74	0.109, 50.2	0.0740, 126.9	–, 60.0
no of refined params	402	206	238	368
refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
<i>R</i> 1, <sup>a</sup> <i>wR</i> 2 (obsd data)	0.0334, 0.0775		0.0550, 0.220	
<i>R</i> 1, <sup>a</sup> <i>wR</i> 2 (all data)	0.0403, 0.0822		–, 0.2793	
<i>R</i> <sub>w</sub> , <sup>b</sup> <i>R</i> <sub>w</sub> (obsd data)		0.067, 0.073		0.043, 0.044
<i>S</i> <sup>c</sup>	1.062	1.73	1.00	1.40
abs structure param	0.002(10)	–		–0.018(4)
final Δρ map (e Å <sup>-3</sup> )	0.451, –0.463	0.53, –0.40	0.630, –0.950	0.72, –0.43

<sup>a</sup> *R*1 = Σ(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)/Σ|*F*<sub>o</sub>|; *wR*2 = {Σ[*w*(*F*<sub>o</sub><sup>2</sup> – *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[*w*(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]}<sup>1/2</sup>. <sup>b</sup> *R*<sub>w</sub> = Σ(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)/Σ|*F*<sub>o</sub>|; *R*<sub>w</sub> = [Σ*w*(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)<sup>2</sup>/Σ*w*(*F*<sub>o</sub><sup>2</sup>)]<sup>1/2</sup>. <sup>c</sup> *S* = {Σ[*w*(*F*<sub>o</sub><sup>2</sup> – *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>]/(n – p)}<sup>1/2</sup> for **2a** and **3** and *S* = [Σ*w*(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)<sup>2</sup>/(n – p)]<sup>1/2</sup> for **2b** and **4**; n = number of data and p = number of refined parameters.

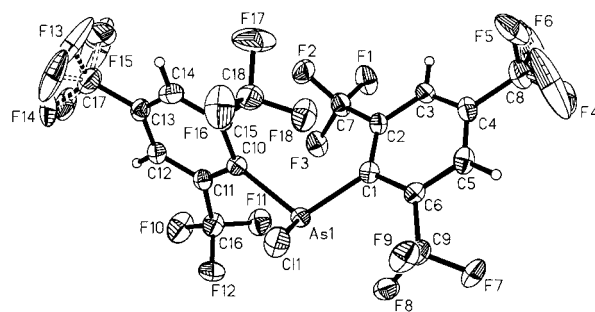
reduction (including Lorentz, polarization, and absorption corrections), structure solution, and refinement were performed with use of the teXsan crystallographic software package,<sup>23</sup> with the exception of compound **3**, which was refined with SHELXL-97.<sup>21</sup> Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included at calculated positions but were not refined.

## Results and Discussion

Reaction of 2 equiv of R<sub>F</sub>Li, prepared in situ, with PnCl<sub>3</sub> (Pn = As, Sb) in diethyl ether gives As(R<sub>F</sub>)<sub>2</sub>Cl (**2**) and Sb(R<sub>F</sub>)<sub>2</sub>Cl (**3**), respectively, which, together with the previously reported Pn(R<sub>F</sub>)<sub>2</sub>Cl (Pn = P, Bi)<sup>15,18</sup> compounds, completes the Pn(R<sub>F</sub>)<sub>2</sub>Cl (Pn = P, As, Sb, Bi) homologous series. Compound **2** was isolated as color-



less, needle-shaped crystals after multiple purification steps to remove As(R<sub>F</sub>)Cl<sub>2</sub> and As<sup>n</sup>Bu<sub>x</sub>Cl<sub>x-3</sub>. It crystallizes in both orthorhombic (*P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>; **2a**) and monoclinic (*P*2<sub>1</sub>/*a*; **2b**) space groups, with essentially identical molecular structures (the structure of **2a** is shown in Figure 1). In both structures, the As–Cl bond length



**Figure 1.** Solid-state structure of As(R<sub>F</sub>)<sub>2</sub>Cl (**2a**) drawn with 50% probability displacement ellipsoids. Selected bond lengths (Å) and angles (deg) for **2a**: As1–Cl1 = 2.1920(12), As1–C1 = 2.023(4), As1–C10 = 2.016(4); C1–As1–Cl1 = 90.57(12), C10–As1–Cl1 = 92.04(11), C1–As1–C10 = 107.53(16). Selected bond lengths (Å) and angles (deg) for Sb(R<sub>F</sub>)<sub>2</sub>Cl (**3**) (structure not shown): Sb1–Cl1 = 2.358(11), Sb1–C1 = 2.22(3), Sb1–C10 = 2.25(3); C1–Sb1–Cl1 = 101.3(9), C10–Sb1–Cl1 = 88.4(9), C1–Sb1–C10 = 107.0(12).

(**2a**, 2.1920(12) Å; **2b**, 2.181(9) Å; cf. AsPh<sub>2</sub>Cl, 2.26(2) Å,<sup>24</sup> 10-chloro-5,10-dihydrophenarsazine, 2.301(4),<sup>25</sup> 2.270 Å,<sup>26</sup> 10-chlorophenothiarsenin, 2.241(1) Å<sup>27</sup>) and other

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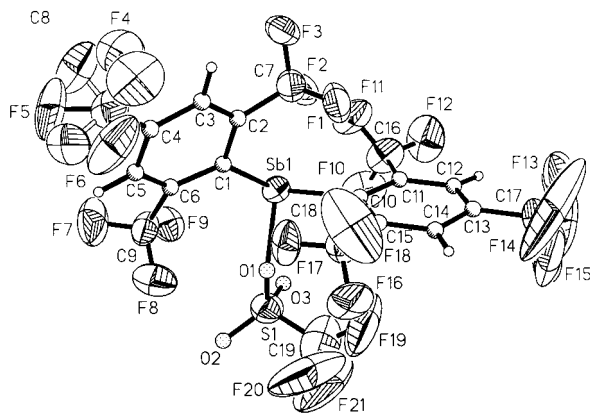
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**Figure 2.** Solid-state structure of  $\text{Sb}(\text{R}_\text{F})_2\text{OSO}_2\text{CF}_3$  (**4**) drawn with 50% probability displacement ellipsoids for the anisotropically refined atoms. Selected bond lengths (Å) and angles (deg) for **4**:  $\text{Sb1}-\text{O1} = 2.082(8)$ ,  $\text{Sb1}-\text{C1} = 2.21(1)$ ,  $\text{Sb1}-\text{C10} = 2.23(1)$ ,  $\text{S1}-\text{O1} = 1.513(9)$ ,  $\text{S1}-\text{O2} = 1.40(1)$ ,  $\text{S1}-\text{O3} = 1.41(1)$ ,  $\text{S1}-\text{C19} = 1.66(2)$ ;  $\text{O1}-\text{Sb1}-\text{C1} = 94.8(4)$ ,  $\text{O1}-\text{Sb1}-\text{C10} = 87.7(4)$ ,  $\text{C1}-\text{Sb1}-\text{C10} = 105.3(4)$ ,  $\text{O2}-\text{S1}-\text{O1} = 114.6(6)$ ,  $\text{O3}-\text{S1}-\text{O1} = 109.9(6)$ ,  $\text{O1}-\text{S1}-\text{C19} = 100.6(8)$ ,  $\text{O2}-\text{S1}-\text{O3} = 119.2(7)$ ,  $\text{O2}-\text{S1}-\text{C19} = 111(1)$ ,  $\text{O3}-\text{S1}-\text{C19} = 99(1)$ ,  $\text{S1}-\text{O1}-\text{Sb1} = 124.0(5)$ .

structural features are normal.  $\text{Sb}(\text{R}_\text{F})_2\text{Cl}$  (**3**) is structurally similar to **2** and also structurally normal ( $\text{Sb}-\text{Cl}$ , 2.358(11) Å; cf. (biphenyl-2,2'-diyl)antimony chloride, 2.423(2) Å;<sup>28</sup> 10-chlorophenothiantimonin, 2.390(2) Å<sup>29</sup>). Noteworthy features of these structures are secondary  $\text{Pn}-\text{F}$  contacts (2.823(2)–3.143(3) Å for **2a**, 2.83(2)–3.14(2) Å for **2b** and 2.80(2)–3.11(2) Å for **3**) beyond the primary tricoordinate pnictogen coordination sphere, typical of  $\text{R}_\text{F}$  compounds. Comparison of FT-IR and FT-Raman spectra of  $\text{Pn}(\text{R}_\text{F})_2\text{Cl}$  derivatives<sup>18</sup> reveal important similarities enabling tentative assignment of the  $\text{Pn}-\text{Cl}$  stretching frequencies, which are distinct in the region of 500–250  $\text{cm}^{-1}$ . IR:  $\text{P}-\text{Cl}$ , 434  $\text{cm}^{-1}$ ;  $\text{As}-\text{Cl}$ , 387  $\text{cm}^{-1}$ ;  $\text{Sb}-\text{Cl}$ , 351  $\text{cm}^{-1}$ ;  $\text{Bi}-\text{Cl}$ , 305  $\text{cm}^{-1}$ . Raman:  $\text{P}-\text{Cl}$ , 437  $\text{cm}^{-1}$ ;  $\text{As}-\text{Cl}$ , 388  $\text{cm}^{-1}$ ;  $\text{Sb}-\text{Cl}$ , 349  $\text{cm}^{-1}$ .

Reactions of  $\text{Pn}(\text{R}_\text{F})_2\text{Cl}$  derivatives ( $\text{Pn} = \text{As}, \text{Sb}$ ) with  $\text{AgOSO}_2\text{CF}_3$  or  $\text{Me}_3\text{Si}-\text{OSO}_2\text{CF}_3$  in hydrocarbon solvents were examined by  $^{19}\text{F}$  NMR spectroscopy. No reaction was observed for  $\text{Pn} = \text{As}$ , perhaps due to the steric restrictions imposed by  $\text{R}_\text{F}$  ligands (kinetic) or an increase in ligand strain relative to the chloride (thermodynamic) resulting from metathesis. In contrast, the larger antimony nucleus facilitates the quantitative reaction to give  $\text{Sb}(\text{R}_\text{F})_2\text{OSO}_2\text{CF}_3$  (**4**). The broad  $^{19}\text{F}$  NMR signal assigned to the ortho  $\text{CF}_3$  fluorine atoms of **4** is indicative of the increased crowding at the Sb center, relative to **3**; moreover, the assigned  $\text{Sb}-\text{Cl}$  stretch in the IR spectrum of **3** is absent in the spectrum of **4**. X-ray crystallographic analysis of **4** (Figure 2) reveals an  $\text{Sb}-\text{O}$  bond distance (2.082(8) Å) close to the sum of the covalent radii (2.07 Å),<sup>30</sup> in contrast to the

$\text{Pb}-\text{O}$  bond observed in the isovalent carbenoid complex  $(\text{R}_\text{F}\text{S})_2\text{Pb}-\text{THF}$ <sup>31</sup> ( $\text{Pb}-\text{O}$ , 2.495(10) Å; sum of covalent radii, 2.20 Å) and those calculated for other carbenoid complexes.<sup>32</sup> In addition, the  $\text{S}-\text{O}$  bond length distinction (1.40(1), 1.41(1) Å;  $\text{S}-\text{O}(\text{Sb})$  1.513(9) Å) in the triflate moiety of **4** confirms the covalency of the  $\text{Sb}-\text{O}$  interaction (anionic triflate moieties typically exhibit nearly equal  $\text{S}-\text{O}$  bond lengths of 1.42–1.47 Å). The  $\text{C}-\text{Sb}-\text{C}$  angle in **4** is 1.7° smaller than in the chlorine precursor, implicating slight steric strain imposed by the triflate ligand over that of chlorine; however, a substantial increase in pyramidalization is evident (sums of the bond angles at Sb: **4**, 287.8°; **3**, 296.7°). The geometry of the Sb atom is similar to those observed in  $\text{SbPh}_2\text{OAc}$  (sums of the bond angles at Sb: 270.8 and 268.9°)<sup>33</sup> or  $\text{Ph}_2\text{SbOSbPh}_2$  (sums of the bond angles at Sb: 283.0 and 283.4°).<sup>34</sup> Compound **4** also exhibits five intermolecular  $\text{Sb}-\text{F}$  contacts in the range of 2.733(8)–3.131(7) Å.

## Conclusions

Synthetic procedures and characterization data are provided for the arsenic and antimony derivatives of  $\text{Pn}(\text{R}_\text{F})_2\text{Cl}$  to complete the homologous series ( $\text{Pn} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$ ). In contrast to  $\text{As}(\text{R}_\text{F})_2\text{Cl}$ , the chlorine site of the stibine is accessible for metathesis with silver triflate to give  $\text{Sb}(\text{R}_\text{F})_2\text{OSO}_2\text{CF}_3$ , the solid-state structure of which reveals a covalent  $\text{Sb}-\text{O}$  interaction. Therefore, in contrast to the observations for dicoordinate group 14 element derivatives, the fluoromethyl substituents of  $\text{R}_\text{F}$  are not sufficiently basic to preclude coordination of the weakly basic anion at the cationic stibonium center.  $\text{R}_\text{F}$  may be more effective at stabilizing carbenoid anions such as  $[(\text{R}_\text{F})_2\text{M}]^-$  for  $\text{M} = \text{B}, \text{Al}, \text{Ga}, \text{In},$  and  $\text{Tl}$ , which have been highlighted as interesting synthetic targets on the basis of ab initio studies.<sup>35</sup>

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**Supporting Information Available:** Thermal ellipsoid diagrams of **2b** and **3** and tables of crystallographic data, atomic coordinates, isotropic and anisotropic displacement parameters, and bond lengths and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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