152 *Organometallics* **2000,** *19,* 152−155

Synthesis and Characterization of Bis(2,4,6-tris(trifluoromethyl)phenyl) Derivatives of Arsenic and Antimony: X-ray Crystal Structures of $As(R_F)_2Cl$, $Sb(R_F)_2Cl$, and $Sb(R_F)_2OSO_2CF_3$

Neil Burford,*,† Charles L. B. Macdonald, Daren J. LeBlanc, and
T. Stanley Cameron*

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

Received September 30, 1999

Bis(2,4,6-tris(trifluoromethyl)phenyl)chloropnictines, $Pn(R_F)_2Cl$ (Pn = As, Sb) have been synthesized by the reaction of 2 equiv of R_FLi with $PnCl_3$ to provide a homologous series. The crystal structures, elemental analyses, and spectral data confirm the introduction of two R_F substituents onto the pnictogen center. $Sb(R_F)_2Cl$ reacts quantitatively with silver triflate or trimethylsilyl triflate to give $Sb(R_F)_2OSO_2CF_3$, while $As(R_F)_2Cl$ does not react with either triflate reagent. The solid-state structure of $Sb(R_F)_2OSO_2CF_3$ reveals a covalent Sb−O interaction, indicating that, in contrast to the observations for dicoordinate group 14 element derivatives, the fluoromethyl substituents of R_F are not sufficiently basic to preclude coordination of the weakly basic anion at the cationic stibenium 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[1] and may also render a site unreactive by virtue of the imposed steric shield. Smaller fluorinated substituents impart thermodynamic stability without inhibiting reactivity.[2] In particular, the estimated steric bulk of the 2,4,6-tris(trifluoromethyl)phenyl substituent (R_F)[3] is between those of "mesityl" (2,4,6-trimethylphenyl (mes)) and 2,4,6-tris(isopropyl)phenyl (tip), but the electron-withdrawing effect of R_F and coordinative interactions by the ortho 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*)).[4] Notable examples include air- and moisture-stable monomeric triarylgallium[5] and -indium[6] compounds, a rare diindane,[6] and compounds containing dicoordinate indium,[7] thallium,[8] germanium,[9,10] tin,[11] and lead.[12]

These observations prompted us to examine the application of R_F substitution to the stabilization of coordinatively unsaturated cations of the pnictogen elements (specifically, pnictenium environments, R_2Pn^+), which are isovalent with the group 14 carbenoids.[9−12] R_F substitution of pnictogen centers has been spectroscopically confirmed for $Pn(R_F)Cl_2$ (Pn = P, As)[13,14] and $P(R_F)_2Cl$,[15] and crystal structures have been reported for R_FNPnR_F (Pn = P,[10] As[14]), R_FPPR_F,[13] $R_FP(Se)PR_F$,[16] $(C_6F_5NPR_F)_2$,[17] and $Bi(R_F)_2Cl$ and $Bi(R_F)_3$[18] (see also $(R_FNPnCl)_2$ (Pn = P, As)[10]). Despite the steric restrictions, the recent synthesis and crystal structure of the phosphide $[Ph_3PMe]^+[P(R_F)_2]^-$ [15] demonstrates that multisubstitution is not restricted to the larger bismuth nucleus.[18] We now report the preparation and characterization of $Pn(R_F)_2Cl$ (Pn = As, Sb), thus completing the $Pn(R_F)_2Cl$ (Pn = P, As, Sb, Bi) homologous series. In addition, we show that the triflate derivative $Sb(R_F)_2OSO_2CF_3$ involves a covalent Sb−O interaction rather than a stibenium cation.

Experimental Section

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

---

† E-mail: burford@is.dal.ca.

[1] Burford, N.; Clyburne, J. A. C.; Chan, M. S. W. *Inorg. Chem.* **1997**, *36*, 3204−3206.

[2] Plenio, H. *Chem. Rev.* **1997**, *97*, 3363−3384.

[3] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

[4] Edelmann, F. T. *Comments Inorg. Chem.* **1992**, *12*, 259−284.

[5] Schluter, R. D.; Isom, H. S.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Oblich, F.; Corbelin, S.; Lagow, R. J. *Organometallics* **1994**, *13*, 4058−4063.

[6] Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070−2071.

[7] Scholz, M.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1383−1384.

[8] Roesky, H. W.; Scholz, M.; Noltemeyer, M.; Edelmann, F. T. *Inorg. Chem.* **1989**, *28*, 3829−3830.

[9] Bender, J. E., IV; Banaszak Holl, M. M.; Kampf, J. W. *Organometallics* **1997**, *16*, 2743−2745.

[10] Ahlemann, J. T.; Roesky, H. W.; Murugavel, R.; Parisini, E.; Noltemeyer, M.; Schmidt, H. G.; Müller, O.; Herbst-Irmer, R.; Markovskii, L. N.; Shermolovich, Y. G. *Chem. Ber./Recl.* **1997**, *130*, 1113−1121.

[11] Grützmacher, H.; Pritzkow, H.; Edelmann, F. T. *Organometallics* **1991**, *10*, 23−25.

[12] Brooker, S.; Buijink, J. K.; Edelmann, F. T. *Organometallics* **1991**, *10*, 25−26.

[13] Scholz, M.; Roesky, H. W.; Stalke, D.; Keller, K.; Edelmann, F. T. *J. Organomet. Chem.* **1989**, *366*, 73−85.

[14] Ahlemann, J. T.; Künzel, A.; Roesky, H. W.; Noltemeyer, M.; Markovski, L.; Schmidt, H. G. *Inorg. Chem.* **1996**, *35*, 6644−6645.

[15] Davidson, M. G.; Dillon, K. B.; Howard, J. A. K.; Lamb, S.; Roden, M. D. *J. Organomet. Chem.* **1998**, *550*, 481−484.

[16] Voelker, H.; Pieper, U.; Roesky, H. W.; Sheldrick, G. M. *Z. Naturforsch.* **1994**, *49B*, 255−257.

[17] Lübben, T.; Roesky, H. W.; Gornitzka, H.; Steiner, A.; Stalke, D. *Eur. J. Solid State Inorg. Chem.* **1995**, *32*, 121−130.

[18] Whitmire, K. H.; Labahn, D.; Roesky, H. W.; Noltemeyer, M.; Sheldrick, G. M. *J. Organomet. Chem.* **1991**, *402*, 55−66.

10.1021/om990768w CCC: $19.00

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_2, and CD_2Cl_2 was dried over P_2O_5 and CaH_2. 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,[19] 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 ^{1}H, 62.896 MHz for ^{13}C, 101.256 MHz for ^{31}P, and 235.361 MHz for ^{19}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 ^{1}H and ^{13}C, 85% H_3PO_4 for ^{31}P, $CFCl_3$ for ^{19}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 $P(R_F)_2Cl$ (1). **1** was prepared by the method of Davidson et al.[15] IR (cm^{-1}): 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^{-1}; 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 $Pn(R_F)_2Cl$ (Pn = As (2), Sb (3)). In a typical reaction, an excess of ^{n}BuLi (1.6 M in hexane) was slowly added through a septum to a stirred, cooled (0 °C) solution of R_FH 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 $PnCl_3$ 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.

$As(R_F)_2Cl$ (2) was prepared from R_FH (4.88 g, 17.3 mmol) and $AsCl_3$ (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^{-1}): 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^{-1}; 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_2Cl_2): ^{1}H, 8.10 (s); ^{13}C, 122.6 (q, $^{1}J_{C-F}$ = 277.0 Hz, *p*-CF_3),123.4 (q, $^{1}J_{C-F}$ = 276.1 Hz, o-CF_3), 128.7 (s(br), C_m), 133.3 (q, $^{2}J_{C-F}$ = 34.8 Hz, C_o), 136.3 (q, $^{2}J_{C-F}$ = 34.5 Hz, C_p), 147.5 (s, C_i); ^{19}F, −54.5 (s, 12F), −63.9 (s, 6F).

$Sb(R_F)_2Cl$ (3) was prepared from R_FH (1.3 g, 4.7 mmol) and $SbCl_3$ (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^{-1}): 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^{-1}; 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_2Cl_2): ^{1}H, 8.22 (s); ^{13}C, 122.8 (q, $^{1}J_{C-F}$ = 272.8 Hz, *p*-CF_3), 124.1 (q, $^{1}J_{C-F}$ = 276.1 Hz, *o*-CF_3), 128.3 (s(br), C_m), 133.9 (q, $^{2}J_{C-F}$ = 34.8 Hz, C_o), 137.8 (q, $^{2}J_{C-F}$ = 32.9 Hz, C_p), 151.9 (s(br), C_i); ^{19}F −55.3 (s, 12F), −63.9 (s, 6F).

Preparation and Characterization of $Sb(R_F)_2OSO_2CF_3$ (4). $Sb(R_F)_2Cl$ (0.25 g, 0.34 mmol) and $AgOSO_2CF_3$ (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 $Sb(R_F)_2OSO_2CF_3$ (**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^{-1}): 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^{-1}; 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_2Cl_2): ^{1}H, 8.32 (s); ^{13}C, 124.1 (q, $^{1}J_{C-F}$ = 276.1 Hz, *o*-CF_3) and 128.9 (s(br), C_m); ^{19}F, −55.7 (s(br, 33 Hz in CD_2Cl_2 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_3 groups. Restraints were necessary for the refinement of the disordered CF_3 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,[20] whereas structure solution and refinement were performed with the SHELX-97[21] and SHELXTL[22] 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 $\omega-2\theta$ scans, on a Rigaku AFC5R diffractometer. Data

---

[19] Burford, N.; Müller, J.; Parks, T. M. *J. Chem. Educ.* **1994**, *71*, 807−809.

[20] Nonius, B. V. Denzo-SMN; Delft, Holland, 1997.

[21] Sheldrick, G. M. SHELX-97 (version 97-2); University of Göttingen, Göttingen, Germany, 1997.

[22] Sheldrick, G. M. SHELXTL (version 5.03); Siemens Analytical Xray Instruments Inc., Madison, WI, 1994.

Table 1. Summary of the Crystal Data, Data Collection, and Refinement Conditions for $As(R_F)_2Cl$ (2a,b), $Sb(R_F)_2Cl$ (3), and $Sb(R_F)_2OSO_2CF_3$ (4)

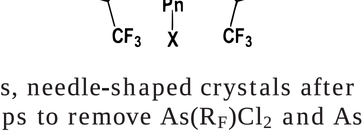
	2a	**2b**	**3**	**4**
empirical formula	$C_{18}H_4AsClF_{18}$	$C_{18}H_4AsClF_{18}$	$C_{18}H_4ClF_{18}Sb$	$C_{19}H_4F_{21}O_3SSb$
fw	672.58	672.58	719.41	833.03
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_1/a$	$P2_1/c$	$P2_12_12_1$
a (Å)	8.6646(2)	8.705(9)	8.296(2)	16.172(4)
b (Å)	9.69650(10)	30.38(1)	30.430(7)	17.758(2)
c (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
V (Å^3), Z	2134.65(7), 4	2159(2), 4	2211(1), 4	2618.8(6), 4
D_{calcd} (Mg m^{-3})	2.093	2.069	2.161	2.113
λ (Å)	0.710 73	0.710 73	1.541 78	0.710 73
μ (mm^{-1}), F(000)	1.880, 1296	1.859, 1296	12.518, 1368	1.304, 1592
cryst size (mm^3)	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	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
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, $I > 2\sigma I$	803, $I > 3\sigma I$	1022, $I > 2\sigma I$	1840, $I > 3\sigma I$
R_{int}, $2\theta_{max}$ (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	F^2	F	F^2	F
R1,[a] wR2 (obsd data)	0.0334, 0.0775		0.0550, 0.220	
R1,[a] wR2 (all data)	0.0403, 0.0822		−, 0.2793	
R,[b] R_w (obsd data)		0.067, 0.073		0.043, 0.044
S[c]	1.062	1.73	1.00	1.40
abs structure param	0.002(10)	-		−0.018(4)
final $\Delta\rho$ map (e Å^{-3})	0.451, −0.463	0.53, −0.40	0.630, −0.950	0.72, −0.43

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [b] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o^2)]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)]^2/(n - p)]^{1/2}$ for **2a** and **3** and $S = [\sum w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$ 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,[23] with the exception of compound **3**, which was refined with SHELXL-97.[21] 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_FLi, prepared in situ, with $PnCl_3$ (Pn = As, Sb) in diethyl ether gives $As(R_F)_2Cl$ (**2**) and $Sb(R_F)_2Cl$ (**3**), respectively, which, together with the previously reported $Pn(R_F)_2Cl$ (Pn = P, Bi)[15,18] compounds, completes the $Pn(R_F)_2Cl$ (Pn = P, As, Sb, Bi) homologous series. Compound **2** was isolated as colorless, needle-shaped crystals after multiple purification steps to remove $As(R_F)Cl_2$ and $As^nBu_xCl_{x-3}$. It crystallizes in both orthorhombic ($P2_12_12_1$; **2a**) and monoclinic ($P2_1/a$; **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 (**2a**, 2.1920(12) Å; **2b**, 2.181(9) Å; cf. $AsPh_2Cl$, 2.26(2) Å,[24] 10-chloro-5,10-dihydrophenarsazine, 2.301(4),[25] 2.270 Å,[26] 10-chlorophenothiarsenin, 2.241(1) Å[27]) and other



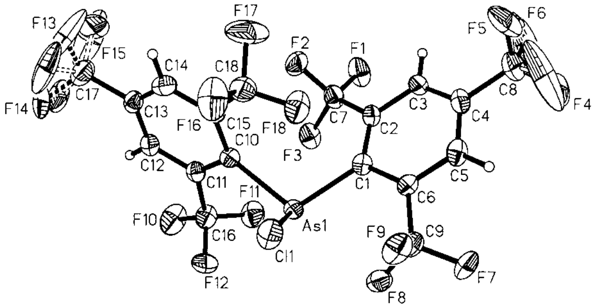


Figure 1. Solid-state structure of $As(R_F)_2Cl$ (**2a**) drawn with 50% probability displacement ellipsoids. Selected bond lengths (Å) and angles (deg) for **2a**: As1−Cl1 = 2.1920(12), As1−C1 = 2.023(4), As1−C10 = 2.016(4); C1−As1−Cl1 = 00.57(12), C10−As1−Cl1 = 92.04(11), C1−As1−C10 = 107.53(16). Selected bond lengths (Å) and angles (deg) for $Sb(R_F)_2Cl$ (**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).

---

[23] teXsan for Windows; Molecular Structure Corp., The Woodlands, TX, 1997.

[24] Trotter, J. *Can. J. Chem.* **1962**, *40*, 1590−1593.

[25] Camerman, A.; Trotter, J. *J. Chem. Soc.* **1965**, 730−738.

[26] Fukuyo, M.; Nakatsu, K.; Shimada, A. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1614−1615.

[27] Pennington, W. T.; Cordes, A. W.; Graham, J. C.; Jung, Y. W. *Acta Crystallogr.* **1983**, *C39*, 712−714.

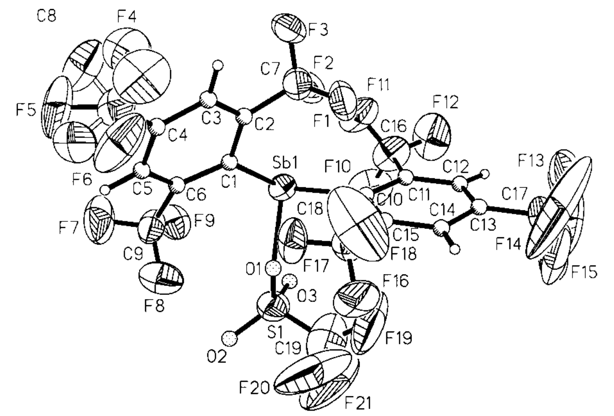


Figure 2. Solid-state structure of $Sb(R_F)_2OSO_2CF_3$ (**4**) drawn with 50% probability displacement ellipsoids for the anisotropically refined atoms. Selected bond lengths (Å) and angles (deg) for **4**: Sb1−O1 = 2.082(8), Sb1−C1 = 2.21(1), Sb1−C10 = 2.23(1), S1−O1 = 1.513(9), S1−O2 = 1.40(1), S1−O3 = 1.41(1), S1−C19 = 1.66(2); O1−Sb1−C1 = 94.8(4), O1−Sb1−C10 = 87.7(4), C1−Sb1−C10 = 105.3(4), O2−S1−O1 = 114.6(6), O3−S1−O1 = 109.9(6), O1−S1−C19 = 100.6(8), O2−S1−O3 = 119.2(7), O2−S1−C19 = 111(1), O3−S1−C19 = 99(1), S1−O1−Sb1 = 124.0(5).

structural features are normal. $Sb(R_F)_2Cl$ (**3**) is structurally similar to **2** and also structurally normal (Sb−Cl, 2.358(11) Å; cf. (biphenyl-2,2′-diyl)antimony chloride, 2.423(2) Å,[28] 10-chlorophenothiantimonin, 2.390(2) Å[29]). Noteworthy features of these structures are secondary Pn−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 R_F compounds. Comparison of FT-IR and FT-Raman spectra of $Pn(R_F)_2Cl$ derivatives[18] reveal important similarities enabling tentative assignment of the Pn−Cl stretching frequencies, which are distinct in the region of 500−250 cm^{-1}. IR: P−Cl, 434 cm^{-1}; As−Cl, 387 cm^{-1}; Sb−Cl, 351 cm^{-1}; Bi−Cl, 305 cm^{-1}. Raman: P−Cl, 437 cm^{-1}; As−Cl, 388 cm^{-1}; Sb−Cl, 349 cm^{-1}.

Reactions of $Pn(R_F)_2Cl$ derivatives (Pn = As, Sb) with $AgOSO_2CF_3$ or $Me_3Si-OSO_2CF_3$ in hydrocarbon solvents were examined by ^{19}F NMR spectroscopy. No reaction was observed for Pn = As, perhaps due to the steric restrictions imposed by R_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 $Sb(R_F)_2OSO_2CF_3$ (**4**). The broad ^{19}F NMR signal assigned to the ortho CF_3 fluorine atoms of **4** is indicative of the increased crowding at the Sb center, relative to **3**; moreover, the assigned Sb−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 Sb−O bond distance (2.082(8) Å) close to the sum of the covalent radii (2.07 Å),[30] in contrast to the Pb−O bond observed in the isovalent carbenoid complex $(R_FS)_2Pb-THF$[31] (Pb−O, 2.495(10) Å; sum of covalent radii, 2.20 Å) and those calculated for other carbenoid complexes.[32] In addition, the S−O bond length distinction (1.40(1), 1.41(1) Å; S−O(Sb) 1.513(9) Å) in the triflate moiety of **4** confirms the covalency of the Sb−O interaction (anionic triflate moieties typically exhibit nearly equal S−O bond lengths of 1.42−1.47 Å). The C−Sb−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 $SbPh_2OAc$ (sums of the bond angles at Sb: 270.8 and 268.9°)[33] or $Ph_2SbOSbPh_2$ (sums of the bond angles at Sb: 283.0 and 283.4°).[34] Compound **4** also exhibits five intermolecular Sb−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 $Pn(R_F)_2Cl$ to complete the homologous series (Pn = P, As, Sb, Bi). In contrast to $As(R_F)_2Cl$, the chlorine site of the stibine is accessible for metathesis with silver triflate to give $Sb(R_F)_2OSO_2CF_3$, the solid-state structure of which reveals a covalent Sb−O interaction. Therefore, in contrast to the observations for dicoordinate group 14 element derivatives, the fluoromethyl substituents of R_F are not sufficiently basic to preclude coordination of the weakly basic anion at the cationic stibenium center. R_F may be more effective at stabilizing carbenoid anions such as $[(R_F)_2M]^-$ for M = B, Al, Ga, In, and Tl, which have been highlighted as interesting synthetic targets on the basis of ab initio studies.[35]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Killam Trust for funding, the Atlantic Regional Magnetic Resonance Centre for the use of instrumentation, and Dr. Alan Lough of the University of Toronto for collecting the X-ray data for **2a**.

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.

OM990768W

---

[28] Millington, P. L.; Sowerby, D. B. *J. Organomet. Chem.* **1994**, *480*, 227−234.

[29] Pennington, W. T.; Cordes, A. W.; Graham, J. C.; Jung, Y. W. *Acta Crystallogr.* **1983**, *C39*, 709−711.

[30] Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 224.

[31] Labahn, D.; Brooker, S.; Sheldrick, G. M.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1992**, *610*, 163−168.

[32] Schoeller, W. W.; Schneider, R. *Chem. Ber./Recl.* **1997**, *130*, 1013−1020.

[33] Bone, S. P.; Sowerby, D. B. *J. Organomet. Chem.* **1980**, *184*, 181−188.

[34] Bordner, J.; Andrews, B. C.; Long, G. G. *Cryst. Struct. Commun.* **1974**, *3*, 53−56.

[35] Cramer, C. J.; Truhlar, D. G.; Falvey, D. E. *J. Am. Chem. Soc.* **1997**, *119*, 12338−12342.