6164 *Inorg. Chem.* **1996,** *35,* 6164−6169

Synthesis of Tin Oxide Precursors and Related Germanium and Lead Compounds

Seigi Suh and David M. Hoffman*

Department of Chemistry, University of Houston, Houston, Texas 77204

Received March 14, 1996[⊗]

The goals of this study were to synthesize volatile tin(II) hexafluoroisopropoxide complexes for use as precursors to tin oxide or fluorine-doped tin oxide and to prepare related germanium(II) and lead(II) compounds. $M(N(SiMe_3)_2)_2$ reacts with 2 equiv of R_fOH ($R_f = CH(CF_3)_2$) and 1 equiv of added amine, L, to give $M(OR_f)_2L$ (M = Ge, L = py or H_2NPh; M = Sn, L = $HNMe_2$ or py; M = Pb, L = *p*-$pyNMe_2$) in high yield. Alternatively, $Sn(OR_f)_2(HNMe_2)$ can be prepared by reacting $Sn(NMe_2)_2$ with R_fOH. X-ray crystallographic studies of $Ge(OR_f)_2(H_2NPh)$ and $Sn(OR_f)_2(HNMe_2)$ show they are monomers with trigonal pyramidal geometries. An X-ray structure of the Pb compound shows it is the dimer $[Pb(\mu\text{-}OR_f)(OR_f)(p\text{-}pyNMe_2)]_2$. $Pb(NMe_2)_2$ reacts with 3 equiv of R_fOH to give $[Me_2NH_2][Pb(OR_f)_3]$, which an X-ray structure shows is the dimer $\{[Me_2NH_2][Pb(\mu\text{-}OR_f)(OR_f)_2]\}_2$. Both Pb dimers are held together by weak dative Pb−O interactions. $Sn(N(SiMe_3)_2)_2$ reacts with 2 equiv of R_fOH in the absence of added amine to give amine-free $Sn(OR_f)_2$. By analogy to known tin(II) alkoxide and related compounds, $Sn(OR_f)_2$ is proposed to be a dimer with two bridging alkoxide ligands. The tin compounds are volatile solids, an important criterion for their possible use as conventional tin oxide precursors in chemical vapor deposition processes.

Fluorine-doped tin oxide thin films deposited by the chemical vapor deposition (CVD) technique are used as transparent conductors in various applications.[1−5] A variety of CVD precursors to tin oxide, including $SnCl_4$,[6−8] $SnMe_4$,[2,9,10] *n*-$Bu_2Sn(OAc)_2$,[11,12] Me_2SnCl_2,[13] $Sn(acac)_2$,[14] and $Sn(NMe_2)_4$,[15] have been reported. Fluorine doping can be accomplished by adding a fluorine doping agent (e.g., a fluorocarbon or HF)[2,5] during the deposition process, but the use of a separate doping agent requires the careful control of deposition parameters to obtain reproducible results. To circumvent the need for a separate doping agent, bis(trifluoroacetato)tin(II), which has fluorine incorporated into the ligand, has recently been tested as a precursor to fluorine-doped SnO_2 films.[16]

In this work, our goal was to synthesize thin-film precursors that have the potential to deposit tin oxide or fluorine-doped tin oxide. We chose as a ligand hexafluoroisopropoxide, OR_f, where $R_f = CH(CF_3)_2$, because alkoxide complexes are known to be viable oxide film precursors[17−19] and metal hexafluoroisopropoxide complexes are reported to decompose to metal fluorides under certain conditions.[20] Herein we report the synthesis of potential tin oxide precursors having hexafluoroisopropoxide ligands and the synthesis of related germanium and lead compounds for comparison with the tin compounds.[21]

Expermental Section

General Techniques. All manipulations were carried out in a nitrogen-filled glovebox or by using standard Schlenk techniques. R_fOH was purchased from Aldrich and was degassed before use. Aniline was distilled under argon from CaH_2. Solvents were purified by using standard techniques and stored in the drybox over 4 Å molecular seives until they were needed. $Ge(N(SiMe_3)_2)_2$, $Sn(N(SiMe_3)_2)_2$, $Pb(N(SiMe_3)_2)_2$, $[Sn(NMe_2)_2]_2$, and $[Pb(NMe_2)_2]_2$ were prepared by the literature methods.[22,23] Infrared spectra were obtained using a Mattson Galaxy 5000 FT-IR, and NMR spectra were collected on a GE 300-MHz instrument. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

$Sn(OR_f)_2$. A solution of R_fOH (1.98 g, 11.8 mmol) in Et_2O (7 mL) was added dropwise to a cold (−78 °C) yellow solution of $Sn(N(SiMe_3)_2)_2$ (2.59 g, 5.89 mmol) in Et_2O (30 mL). The solution became colorless during the addition. The reaction mixture was warmed slowly to room temperature and then left to stir for an additional 30 min. The volatile components were removed in vacuo to give a cloudy liquid. The crude product appeared to be pure compound according to the NMR spectrum. The crude product was extracted with hexanes

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) Rao, U. V. S.; Kumar, J. S.; Reddy, K. N. *Prog. Cryst. Growth Charact.* **1987**, *15*, 187.

(2) Proscia, J.; Gordon, R. G. *Thin Solid Films* **1992**, *214*, 175.

(3) Gordon, R. G.; Proscia, J.; Ellis Jr., F. B.; Delahoy, A. E. *Solar Energy Mater.* **1989**, *18*, 263.

(4) Bhagavat, G. K.; Sundaram, K. B. *Thin Solid Films* **1979**, *63*, 197.

(5) Mizuhashi, M.; Gotoh, Y.; Adachi, K. *Jpn. J. Appl. Phys.* **1988**, *27*, 2053.

(6) Tan, C.; Xia, Y.; Chen, Y.; Li, S.; Liu, J.; Liu, X.; Xu, B.; Li, J.; Cao, W. *J. Appl. Phys.* **1993**, *73*, 4266.

(7) Kojima, M.; Kato, H.; Imai, A.; Yoshida, A. *J. Appl. Phys.* **1988**, *64*, 1902.

(8) Saxena, A. K.; Thangaraj, R.; Singh, S. P.; Agnihotri O. P. *Thin Solid Films* 1**985**, *131*, 121.

(9) Wan, C. F.; McGrath, R. D.; Keenan, W. F.; Frank, S. N. *J. Electrochem. Soc.* **1989**, *136*, 1459.

(10) Borman, C. G.; Gordon, R. G. *J. Electrochem. Soc.* **1989**, *136*, 3820.

(11) Kane, J.; Schweizer, H.; Kern, W. *J. Electrochem. Soc.* **1975**, *122*, 1144.

(12) Kane, J.; Schweizer, H.; Kern, W. *J. Electrochem. Soc.* **1976**, *123*, 270.

(13) Giunta, C. J.; Strickler, D. A.; Gordon, R. G. *J. Phys. Chem.* **1993**, *97*, 2275.

(14) Maruyama, T.; Ikuta, Y. *Sol. Energy Mater. Sol. Cells* **1992**, *28*, 209.

(15) Atagi, L. M.; Hoffman, D. M.; Liu, J.-R.; Zheng, Z.; Chu, W.-K.; Rubiano, R. R.; Springer, R. W.; Smith, D. C. *Chem. Mater.* **1994**, *6*, 360. Hoffman, D. M.; Atagi, L. M.; Chu, W.-K.; Liu, J.-R.; Zheng, Z.; Rubiano, R. R.; Springer, R. W.; Smith, D. C. *Mat. Res. Soc. Symp. Proc.: Polycryst. Thin Films* **1994**, *343*, 523.

(16) Maruyama, T.; Tabata, K. *J. Appl. Phys.* **1990**, *68*, 4282.

(17) Aboaf, J. A. *J. Electrochem. Soc.* **1967**, *114*, 948.

(18) Adachi, M.; Okuyama, K.; Tohge, N.; Shimada, M.; Sato, J.; Muroyama, M. *Jpn. J. Appl. Phys.* **1993**, *32*, L748.

(19) Battiston, G. A.; Gerbasi, R.; Porchia, M.; Marigo, A. *Thin Solid Films* 1**994**, *239*, 186.

(20) Samuels, J. A.; Chiang, W.-C.; Yu, C.-P.; Apen, E.; Smith, D. C.; Baxter, D. V.; Caulton, K. G. *Chem. Mater.* **1994**, *6*, 1684.

(21) Recent review of divalent Ge, Sn and Pb compounds: Lappert, M. *Main Group Met. Chem.* **1994**, *17*, 183.

(22) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.

(23) Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 413.

S0020-1669(96)00293-5 CCC: $12.00

(4 × 10 mL), and the extracts were combined and then filtered. The filtrate was cooled slowly to −35 °C, producing colorless flakes. Decanting the mother liquor and drying in vacuo gave a white powder (yield 2.43 g, 91%). Anal. Calcd for $C_6H_2O_2F_{12}Sn$: C, 15.92; H, 0.45. Found: C, 15.62; H, 0.26.

^{1}H NMR (CD_3CN): δ 4.95 (septet, 2, $^3J_{HF} = 6.7$ Hz, OCH(CF$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_3CN): 124.7 (q, 2, $^1J_{CF} = 286$ Hz, OCH(CF$_3$)$_2$), 71.8 (septet, 1, $^2J_{CF} = 32$ Hz, OCH(CF$_3$)$_2$). IR (Fluorolube, KBr, cm^{-1}): 2897 br, 1373 sh, 1284 s, 856 s, 689 s.

Sn(OR$_f$)$_2$(HNMe$_2$). Method A. A solution of R$_f$OH (0.96 g, 5.7 mmol) in Et_2O (5 mL) was added dropwise to a cold (−78 °C) yellow solution of [Sn(NMe$_2$)$_2$]$_2$ (0.59 g, 1.4 mmol) in ether (15 mL). The solution became colorless during the addition. The reaction mixture was stirred for 30 min at low temperature and then allowed to warm slowly to room temperature. After being stirred at room temperature for 2 h, the solution was stripped in vacuo to give a white solid. Sublimation from the solid (50−55 °C, 0.1 mmHg) produced colorless blocks on the ice-cooled cold finger (yield 1.2 g, 83%). Anal. Calcd for $C_8H_9NO_2F_{12}Sn$: C, 19.30; H, 1.82; N 2.81. Found: C, 19.28; H, 1.62; N, 2.40.

Method B. A solution of R$_f$OH (2.01 g, 12.0 mmol) in Et_2O (7 mL) was added dropwise to a cold (−78 °C) yellow solution of Sn(N(SiMe$_3$)$_2$)$_2$ (2.63 g, 5.89 mmol) in Et_2O (30 mL). The solution became colorless during the addition. The reaction mixture was stirred at low temperature for 30 min and then allowed to warm to room temperature. The volatile components were removed in vacuo, and Et_2O (20 mL) was added to dissolve the residue. The solution was frozen, and excess HNMe$_2$ (0.67 g, 14.9 mmol) was condensed into the flask via a calibrated vacuum manifold. The mixture was warmed slowly to room temperature and then left to stir for 10 min. The volatile components were removed in vacuo leaving a white powder. The crude product was purified by sublimation as in method A (yield 2.56 g, 86%).

^{1}H NMR (C_6D_6): δ 5.12 (s, 1, HNMe$_2$), 4.22 (septet, 2, $^3J_{HF} = 6.3$ Hz, OCH(CF$_3$)$_2$), 1.63 (s, 6, HNMe_2). ^{13}C{^{1}H} NMR (C_6D_6): 123.7 (q, 4, $^1J_{CF} = 286$ Hz, OCH(CF$_3$)$_2$), 70.9 (septet, 2, $^2J_{CF} = 31$ Hz, OCH(CF$_3$)$_2$), 34.7 (s, 2, HNMe_2). IR (Nujol, KBr, cm^{-1}): 3216 br, 1287 s, 1263 s, 1209 s,1190 s, 1134 s, 1093 s, 1034 w, 891 s, 855 s, 743 s, 687 s, 640 w.

Sn(OR$_f$)$_2$(py). A solution of R$_f$OH (0.31 g, 1.8 mmol) in Et_2O (3 mL) was added dropwise to a cold (−78 °C) yellow solution of Sn(N(SiMe$_3$)$_2$)$_2$ (0.40 g, 0.91 mmol) in Et_2O (10 mL). The solution became colorless during the addition. The reaction mixture was allowed to warm to room temperature slowly where it was left to stir for 2 h. The volatile components were removed in vacuo, leaving a viscous liquid. Diethyl ether (10 mL) was added to the viscous liquid, the resulting solution was cooled to 0 °C, and then pyridine (0.15 g, 1.8 mmol) was added dropwise. The mixture was slowly warmed to room temperature. After being stirred for 20 min at room temperature, the volatile components were removed in vacuo leaving a white solid. The solid was crystallized from a toluene/hexanes (2:1) solution at −35 °C (yield 0.38 g, 79%). The product could be sublimed in vacuo (50−55 °C, 0.1 mmHg). Anal. Calcd for $C_{11}H_7NO_2F_{12}Sn$: C, 24.84; H, 1.33; N 2.63. Found: C, 24.50; H, 1.02; N, 2.19.

^{1}H NMR (C_6D_6): δ 7.93 (m, 2, *o*-py), 6.71 (m, 1, *p*-py), 6.37 (m, 2, *m*-py), 4.69 (septet, 2, $^3J_{HF} = 6.3$ Hz, OCH(CF$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): 145.4 (2, *o*-py), 140.4 (1, *p*-py), 125.2 (2, *m*-py), 124.0 (q, 4, $^1J_{CF} = 288$ Hz, OCH(CF$_3$)$_2$), 71.0 (septet, 2, $^2J_{CF} = 33$ Hz, OCH(CF$_3$)$_2$). IR (Nujol, KBr, cm^{-1}): 1611 s, 1289 s, 1262 2, 1207 s, 1188 s, 1134 s, 1089 s, 1040 s, 1015 s, 891 s, 855 s, 758 w, 743 s, 685 s, 636 s.

Ge(OR$_f$)$_2$(py). R$_f$OH (1.20 g, 7.1 mmol) was added dropwise to a cold (−30 °C) yellow solution of Ge(N(SiMe$_3$)$_2$)$_2$ (1.4 g, 3.6 mmol) in toluene (25 mL). The solution became colorless during the addition. The reaction mixture was warmed slowly to room temperature and then left to stir for an additional 30 min. The volatile components were removed under vacuum leaving a colorless liquid. Diethyl ether (15 mL) was added to the liquid followed by the dropwise addition of pyridine (0.57 g, 7.1 mmol). After 10 min of stirring the solution was stripped in vacuo to give a viscous liquid, which solidified upon standing overnight in the glovebox. The white solid was extracted with toluene (3 × 5 mL), and the extracts were combined and filtered. The filtrate volume was reduced in vacuo (to 3 mL). Cooling the solution at −35 °C for 18 h produced small colorless crystals (yield 1.4 g, 82%). The product can be sublimed in vacuo (45−50 °C, 0.1 mmHg) as a white powder. Anal. Calcd for $C_{11}H_7NO_2F_{12}Ge$: C, 27.20; H, 1.45; N, 2.88. Found: C, 27.29; H, 1.24; N, 2.70.

^{1}H NMR (C_6D_6): δ 8.00 (m, 2, *o*-py), 6.61 (m, 1, *p*-py), 6.27 (m, 2, *m*-py), 4.61 (br s, 2, OCH(CF$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): 144.2 (2, *o*-py), 140.9 (1, *p*-py), 125.2 (2, *m*-py), 123.3 (q, 4, $^1J_{CF} = 283$ Hz, OCH(CF$_3$)$_2$), 70.1 (septet, 2, $^2J_{CF} = 32$ Hz, OCH(CF$_3$)$_2$). IR (Nujol, KBr, cm^{-1}): 1615 m, 1283 m, 1202 m, 1186 s, 1123 m, 1098 s, 1067 m, 1044 m, 1015 m, 891 m, 860 m, 748 m, 685 m, 642 m.

Ge(OR$_f$)$_2$(H$_2$NPh). R$_f$OH (0.26 g, 1.6 mmol) was added dropwise to a cold (−30 °C) yellow solution of Ge(N(SiMe$_3$)$_2$)$_2$ (0.30 g, 0.76 mmol) in Et_2O (10 mL). The solution became colorless during the addition. The reaction mixture was allowed to warm to room temperature and then left to stir for an additional 40 min. The volatile components were removed under vacuum leaving a colorless liquid. Diethyl ether (10 mL) was added to the liquid, the resulting solution was cooled to 0 °C, and aniline (0.070 g, 0.76 mmol) was added dropwise to the cold solution. The ice bath was removed, and the solution was stirred for an additional 5 min. The solution was stripped in vacuo leaving a white solid. The solid was crystallized as colorless blocks from diethyl ether/hexanes (2:1) at −35 °C (yield 0.27 g, 71%). Anal. Calcd for $C_{12}H_9NO_2F_{12}Ge$: C, 28.84; H, 1.82; N 2.80. Found: C, 28.61; H, 1.53; N, 2.60.

^{1}H NMR (C_6D_6): δ 6.84 (m, 2, *o*-Ph), 6.75 (m, 1, *p*-Ph), 6.24 (m, 2, *m*-Ph), 4.36 (br s, 2, OCH(CF$_3$)$_2$), 3.70 (br s, 2, H_2NPh). ^{13}C{^{1}H} NMR (C_6D_6): 135.5 (s, 1, *ipso*-Ph), 129.7 (s, 2, *m*-Ph), 126.1 (s, 1, *p*-Ph), 120.6 (s, 2, *o*-Ph), 123.1 (q, 2, $^1J_{CF} = 284$ Hz, OCH(CF$_3$)$_2$), 69.8 (septet, 1, $^2J_{CF} = 33$ Hz, OCH(CF$_3$)$_2$). IR (Nujol, KBr, cm^{-1}): 3270 m, 3223 m, 3138 m, 1588 sh, 1495 m, 1289 s, 1270 m, 1215 s, 1190 s, 1115 s, 1099 s, 895 m, 864 m, 748 m, 689 m, 664 w, 649 w.

[Pb(μ-OR$_f$)(OR$_f$)(*p*-pyNMe$_2$)]$_2$. R$_f$OH (0.32 g, 1.9 mmol) was added dropwise to a cold (−78 °C) yellow solution of Pb(N(SiMe$_3$)$_2$)$_2$ (0.50 g, 0.95 mmol) in Et_2O (15 mL). The solution became colorless during the addition. After the addition was complete, the mixture was allowed to warm slowly to room temperature. The volatile components were removed in vacuo, leaving a white solid. Diethyl ether (5 mL) was added to dissolve the solid, followed by 4-(dimethylamino)pyridine (0.10 g, 0.86 mmol). A white solid began to precipitate from the solution within 5 min. After being stirred overnight, the suspension was stripped in vacuo and the resulting white solid was rinsed with cold Et_2O (5 mL). The solid was dissolved in warm CH_2Cl_2 (ca. 5 mL), and as the solution cooled to room temperature, colorless crystals appeared, which were isolated by decanting the mother liquor. Cooling the mother liquor to −35 °C afforded a second crop of colorless crystals (total yield 0.42 g, 67% based on Pb). Anal. Calcd for $C_{26}H_{24}N_4O_4F_{24}Pb_2$: C, 23.54; H, 1.82; N 4.22. Found: C, 23.67; H, 1.79; N, 4.09.

^{1}H NMR (CD_3CN): δ 8.21 (d, 4, *o*-Ph), 6.70 (d, 4, *m*-Ph), 5.35 (septet, 4, $^3J_{HF} = 6.8$ Hz, OCH(CF$_3$)$_2$), 3.03 (s, 12, NMe_2). ^{13}C{^{1}H} NMR (CD_3CN): 156.9 (s, 2, *p*-Ph), 147.9 (s, 4, *o*-Ph), 126.5 (q, 8, $^1J_{CF} = 286$ Hz, OCH(CF$_3$)$_2$), 108.4 (s, 4, *m*-Ph), 73.0 (septet, 4, $^2J_{CF} = 31$ Hz, OCH(CF$_3$)$_2$), 39.9 (s, 4, NMe_2). IR (Nujol, KBr, cm^{-1}): 1609 s, 1545 s, 1535 s, 1286 s, 1227 s, 1184 s, 1099 s, 1063 s, 1005 s, 951 w, 887 s, 853 s, 810 s, 739 s, 683 s.

{[Me$_2$NH$_2$][Pb(μ-OR$_f$)(OR$_f$)$_2$]}$_2$. [Pb(NMe$_2$)$_2$]$_2$ (0.30 g, 0.51 mmol) and Et_2O (10 mL) were added to a Schlenk flask wrapped with aluminum foil. The mixture was cooled to −78 °C, and R$_f$OH (0.51 g, 3.0 mmol) was added dropwise. The mixture was warmed slowly to room temperature and then stirred for another 30 min. The mixture was stripped in vacuo, leaving a white solid. The solid crystallized as colorless blocks from ether/hexanes (2:1) solution at −35 °C (yield 0.47 g, 61%). Anal. Calcd for $C_{22}H_{22}N_2O_6F_{36}Pb_2$: C, 17.51; H, 1.47; N 1.86. Found: C, 17.17; H, 1.13; N, 1.54.

^{1}H NMR (C_6D_6): δ 6.17 (s, 4, H_2NMe$_2$), 4.57 (septet, 6, $^3J_{HF} = 6.5$ Hz, OCH(CF$_3$)$_2$), 1.71 (s, 12, H$_2$NMe_2). ^{13}C{^{1}H} NMR (C_6D_6): 124.6 (q, 12, $^1J_{CF} = 286$ Hz, OCH(CF$_3$)$_2$), 71.3 (septet, 6, $^2J_{CF} = 32$ Hz, OCH(CF$_3$)$_2$), 34.9 (s, 4, H$_2$NMe_2). IR (Nujol, KBr, cm^{-1}): 1647 s, 1510 w, 1279 s, 1254 s, 1206 s, 1181 s, 1123 s, 1086 s, 1032 w, 887 s, 855 s, 741 s, 687 s, 629 w.

X-ray Crystallography. Crystal data are presented in Table 1, and final atomic coordinates for the significant atoms are presented in Table 2.

Table 1. Crystal Data

	compound			
	$Ge(OCH(CF_3)_2)_2(H_2NPh)$	$Sn(OCH(CF_3)_2)_2(HNMe_2)$	$[Pb(OCH(CF_3)_2)_2(p\text{-}pyNMe_2)]_2$	$\{[Me_2NH_2][Pb(OCH(CF_3)_2)_3]\}_2$
empirical formula	$C_{12}H_9NO_2F_{12}Ge$	$C_8H_9NO_2F_{12}Sn$	$C_{26}H_{24}N_4O_4F_{24}Pb_2$	$\{2[C_2H_8N]^+\}[C_{18}H_6O_6F_{36}Pb_2]^{2-}$
fw	499.81	497.87	1326.92	1508.84
crystal dimens (mm)	0.50 × 0.40 × 0.30	0.35 × 0.40 × 0.50	0.10 × 0.50 × 0.50	0.20 × 0.35 × 0.45
radiation (Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73
space group	$P\bar{1}$ (triclinic)	$P2_1/n$ (monoclinic)	$P\bar{1}$ (triclinic)	$P2_1/c$ (monoclinic)
a, Å	9.093(2)	9.957(3)	9.252(2)	11.498(3)
b, Å	10.629(4)	13.859(6)	9.742(2)	10.976(4)
c, Å	11.183(2)	11.808(5)	11.141(3)	17.196(4)
α, deg	115.13(2)		75.92(2)	
β, deg	94.52(2)	104.05(3)	77.04(2)	105.09(2)
γ, deg	109.60(2)		87.34(2)	
temp, °C	−50	−50	−50	−50
Z	2	4	1	2
V, Å^3	890	1581	949	2095
D_{calcd}, g/cm^3	1.86	2.09	2.32	2.39
μ, cm^{-1}	18.2	17.47	90.8	82.8
R, R_w[a]	0.041, 0.032	0.041, 0.038	0.037, 0.039	0.032, 0.031

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = [\sigma(F)]^{-2}$.

Table 2. Atomic Coordinates ($\times 10^4$) for the Significant Atoms in $Ge(OR_f)_2(H_2NPh)$, $Sn(OR_f)_2(HNMe_2)$, $[Pb(\mu\text{-}OR_f)(OR_f)(p\text{-}pyNMe_2)]_2$, and $\{[Me_2NH_2][Pb(\mu\text{-}OR_f)(OR_f)_2]\}_2$

atom	x	y	z
	$Ge(OR_f)_2(H_2NPh)$		
Ge	1976(1)	4272(1)	4762(1)
O(1)	2873(4)	4746(3)	3481(3)
O(2)	2931(3)	2905(3)	4579(3)
N	4082(5)	6021(4)	6251(4)
	$Sn(OR_f)_2(HNMe_2)$		
Sn	6166(1)	1455(1)	5472(1)
O(1)	5966(5)	2603(3)	4335(4)
O(2)	4063(4)	1106(3)	4800(4)
N	6727(7)	630(5)	3997(7)
	$[Pb(\mu\text{-}OR_f)(OR_f)(p\text{-}pyNMe_2)]_2$		
Pb	5078(1)	6410(1)	6109(1)
O(1)	3834(5)	4521(5)	6025(5)
O(2)	3290(6)	6628(6)	7804(6)
N(1)	3564(8)	7955(7)	4943(7)
	$\{[Me_2NH_2][Pb(\mu\text{-}OR_f)(OR_f)_2]\}_2$		
Pb	5566(1)	6354(1)	5794(1)
O(1)	7351(5)	7477(5)	5922(3)
O(2)	6721(5)	5294(5)	6838(3)
O(3)	6185(5)	5172(5)	4916(3)
N(1)	8899(6)	6458(7)	7180(4)

Crystals of $Ge(OR_f)_2(H_2NPh)$, $Sn(OR_f)_2(HNMe_2)$ and $\{[Me_2NH_2][Pb(\mu\text{-}OR_f)(OR_f)_2]\}_2$ are colorless blocks, and crystals of $[Pb(\mu\text{-}OR_f)(OR_f)(p\text{-}pyNMe_2)]_2$ are colorless flat plates. The $Ge(OR_f)_2(H_2NPh)$ crystals were handled under hexanes, and the others, under mineral oil. The samples were placed in a cold nitrogen stream for data collection on a Nicolet R3m/V diffractometer. The θ:2θ scan technique was used to collect data for the Ge and Sn compounds, and the ω scan technique was used for the two Pb complexes. In each case, two standard reflections were monitored after every 2 h or every 100 data collected. The data for $\{[Me_2NH_2][Pb(\mu\text{-}OR_f)(OR_f)_2]\}_2$ showed a linear decay of 9% over the course of the experiment, which was corrected for by applying a normalization factor as a function of X-ray exposure time. Data for the other three compounds did not show significant decay. During data reduction, Lorentz and polarization corrections were applied, as well as a semi-empirical absorption correction based on ψ scans of 10 reflections having χ angles between 70 and 90°.

Refinement of $Ge(OR_f)_2(H_2NPh)$ and $Sn(OR_f)_2(HNMe_2)$. In each case, interpretation of the Patterson map revealed the position of the heavy main group element. Remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement followed. The hydrogen atoms attached to carbon were entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor for all of them. The amino hydrogens were located in a difference map and allowed to refine independently. Final difference maps showed maximum peaks of about 0.7 (Ge) and 1.2 (Sn) e/Å^3.

Refinement of $[Pb(OR_f)_2(p\text{-}pyNMe_2)]_2$. Since the unitary structure factors displayed centric statistics, space group $P\bar{1}$ was assumed from the outset. Interpretation of the Patterson map revealed the position of the Pb atom in the asymmetric unit, consisting of one-half molecule situated about an inversion center. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which the hydrogen atoms attached to carbon were entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor for all of them. The final difference map showed a maximum peak of about 1.5 e/Å^3 located near Pb. The color of the crystal changed to bright pink during data collection, and the color persisted for more than 24 h after the X-rays were turned off.

Refinement of $\{[Me_2NH_2][Pb(\mu\text{-}OR_f)(OR_f)_2]\}_2$. Interpretation of the Patterson map revealed the position of the Pb atom in the asymmetric unit, consisting of one-half molecule situated about an inversion center. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which the hydrogen atoms attached to carbon were entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor for the cation hydrogens and a separate variable for the anion hydrogens. The final difference map showed a maximum peak of about 1.3 e/Å^3 located near Pb.

Results and Discussion

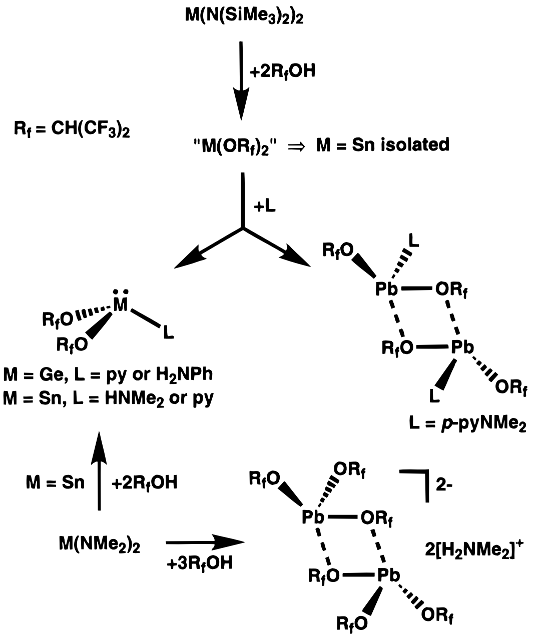
Synthesis. A summary of our synthetic results is presented in Scheme 1. $Sn(N(SiMe_3)_2)_2$ reacts with R_fOH to yield a cloudy viscous liquid. Dissolving the liquid in hexanes and cooling produces colorless flakes that turn to a white powder on drying in vacuo. The exceedingly air-sensitive powder appears to melt near room temperature, and the presence of impurities causes it to partially liquify. NMR, IR, and analytical data indicate the powder is amine-free $Sn(OR_f)_2$, and a molecular weight determination (isothermal distillation)[24] gives the formulation $[Sn(OR_f)_2]_{2.4\pm0.2}$. On this basis and by analogy to the known compounds $[Sn(\mu\text{-}O\text{-}2,6\text{-}Ph_2C_6H_3)(O\text{-}2,6\text{-}Ph_2C_6H_3)]_2$,[25]

---

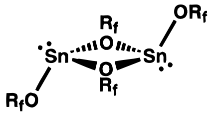
(24) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

(25) Stewart, J. L.; Huffman, J. C. unpublished results quoted in: Kras, L. H.; Euvrard, A.; Grassl, Y. N.; Ronda, S. M.; Stewart, J. L. *Main Group Met. Chem.* **1994**, *17*, 409.

Scheme 1



$[Sn(\mu\text{-O-}t\text{-Bu})(O\text{-}t\text{-Bu})]_2$,[26] $[Sn(\mu\text{-O-}t\text{-Bu})(N(SiMe_3)_2)]_2$,[27] and $[Sn(\mu\text{-NMe}_2)(NMe_2)]_2$,[23] structure **I** is proposed for "$Sn(OR_f)_2$."



I

Proton NMR spectra in the range −90 to 23 °C show only a single septet instead of the two signals expected for **I**. If the dimer formulation and proposed structure are correct, then the observation of only one kind of alkoxide ligand in the low-temperature NMR suggests there is a facile process (e.g., a dimer−monomer equilibrium or an intramolecular turnstile-type mechanism) to effect bridge−terminal alkoxide exchange.

The amido complex $Sn(NMe_2)_2$ reacts with R_fOH to give extremely air-sensitive $Sn(OR_f)_2(HNMe_2)$ in high yield (83%) after vacuum sublimation at 50−55 °C. Alternatively, $Sn(OR_f)_2(HNMe_2)$ can be prepared from $Sn(N(SiMe_3)_2)_2$ by reacting R_fOH with $Sn(N(SiMe_3)_2)_2$ to form $Sn(OR_f)_2$ and then adding excess $HNMe_2$. The py complex, $Sn(OR_f)_2(py)$, an air-sensitive volatile solid, is prepared similarly.

The isolation of the $Sn(OR_f)_2$(amine) complexes prompted us to attempt the synthesis of analogous Ge and Pb compounds. Thus, $M(N(SiMe_3)_2)_2$, M = Ge and Pb, reacts with R_fOH and amine, L, to give $Ge(OR_f)_2L$, L = py or H_2NPh, and $Pb(OR_f)_2(p\text{-pyNMe}_2)$. Proton NMR spectra of the crude products from the reactions between $M(N(SiMe_3)_2)_2$ and R_fOH suggest that amine-free $M(OR_f)_2$ compounds are formed, but no attempt was made to isolate or further characterize the compounds. An attempted preparation of $Pb(OR_f)_2(HNMe_2)$ failed, perhaps because dimethylamine is not held tightly enough to $Pb(OR_f)_2$ to permit the isolation of the adduct.

The lead compound $Pb(OR_f)_2(p\text{-pyNMe}_2)$ has only limited solubility in hexane, benzene, and toluene, and for this reason it was initially thought to be a salt. As discussed in the next section, the crystal structure shows it is in fact a neutral dimer, $[Pb(\mu\text{-OR}_f)(OR_f)(p\text{-pyNMe}_2)]_2$. In contrast to the tin and germanium compounds, it is only moderately air sensitive.

The reaction of $Pb(NMe_2)_2$ with R_fOH takes a different course from those involving $Pb(N(SiMe_3)_2)_2$. Thus, the reaction of $Pb(NMe_2)_2$ with 2 equiv of R_fOH produces low yields of the salt $\{[Me_2NH_2][Pb(\mu\text{-OR}_f)(OR_f)_2]\}_2$, where the dimer formulation is based on the X-ray crystal structure (see the next section). By using a stoichiometric amount of R_fOH in the reaction, the salt is isolated in 61% yield. The compound is insoluble in hexanes but is moderately soluble in benzene. It is interesting that the lead salt is formed in the presence of $HNMe_2$ but not in the company of the weaker base $HN(SiMe_3)_2$, both of which are released during alcoholysis of $Pb(NR_2)_2$. The deprotonation of the alcohol by $HNMe_2$ must involve the lead in some way, presumably as an alcohol adduct, because $HNMe_2$ does not deprotonate free R_fOH and a salt is not formed from R_fOH and $M(NMe_2)_2$ for M = Ge or Sn.

We have not been able to extract detailed solution structural information for the amine adducts and the lead salt from NMR spectra. Carbon-13 NMR spectra for the $M(OR_f)_2L$ compounds show only one quartet for the CF_3 groups instead of the expected two quartets that would be consistent with the solid-state structures of the tin dimethylamine and germanium aniline adducts (see the next section). Similarly, room- and low-temperature (to −70 °C) ^{19}F NMR spectra for $M(OR_f)_2L$ (M = Sn, L = $HNMe_2$; M = Ge, L = py) show only a single doublet. Also, the ^1H NMR spectra for the two Ge derivatives show a slightly broadened peak for the alkoxide protons instead of the expected sharp septet, but the ^{13}C spectra are sharp at room temperature.

Proton NMR spectra recorded at room temperature for $[Pb(\mu\text{-OR}_f)(OR_f)(p\text{-pyNMe}_2)]_2$ show three resonances arising from the p-pyNMe$_2$ ligand and one from the alkoxide methine protons in the expected intensity ratio. As the NMR sample (CD_3CN) is cooled, the methine resonance becomes broader and at −40 °C appears to be resolving into two broad humps. At room temperature, the ^1H NMR spectrum of $\{[Me_2NH_2][Pb(\mu\text{-OR}_f)(OR_f)_2]\}_2$ shows a single sharp septet resonance for the alkoxide methine protons as well as two sharp singlet resonances arising from the ammonium cation, all in the expected intensity ratios, but an attempt to obtain a low-temperature-limiting spectrum was not successful. As a sample in toluene-d_8 was cooled, the three resonances observed at room temperature broadened and the N−H protons shifted downfield to ≈8.5 ppm. At −90 °C, the methine protons gave rise to two ill-defined broad humps, the ammonium N−H protons to two broad humps, and the Me groups a broad singlet.

Rapid exchange processes must be responsible for our inability to obtain low-temperature-limiting spectra for the new compounds. Given the extreme sensitivity of the compounds to traces of moisture, it is possible that rapid alcohol/alkoxide exchange from contamination of the NMR samples with free alcohol produced by inadvertant hydrolysis is the source of the problem. The difficulties in obtaining solution structure information from NMR studies prompted us to carry out several X-ray crystal structure determinations.

X-ray Structure Determinations. Plots of $Ge(OR_f)_2(H_2NPh)$, $Sn(OR_f)_2(HNMe_2)$, $[Pb(\mu\text{-OR}_f)(OR_f)(p\text{-pyNMe}_2)]_2$, and $\{[Me_2NH_2][Pb(\mu\text{-OR}_f)(OR_f)_2]\}_2$ are shown in Figures 1−4, respectively. Selected bond distances and angles for the Ge, Sn, and neutral Pb compounds are presented in Table 3 and for the Pb salt compound in Table 4.

The Ge and Sn compounds are monomers in the solid state, and the Pb compounds are dimers with crystallographically imposed centers of inversion. All four compounds have

---

(26) Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Smith, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 939.

(27) McGeary, M. J.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 4051.

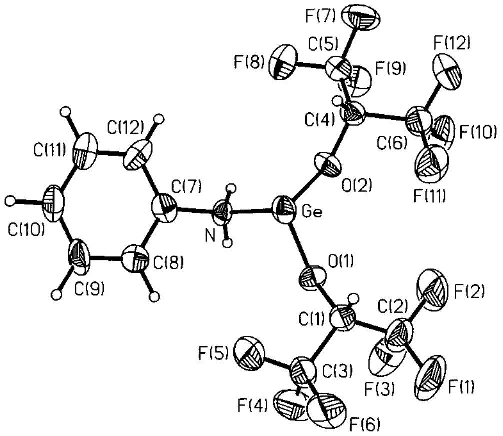


Figure 1. View of Ge(OR$_f$)$_2$(H$_2$NPh), showing the atom-numbering scheme (40% probability ellipsoids with the hydrogens as spheres of arbitrary diameter).

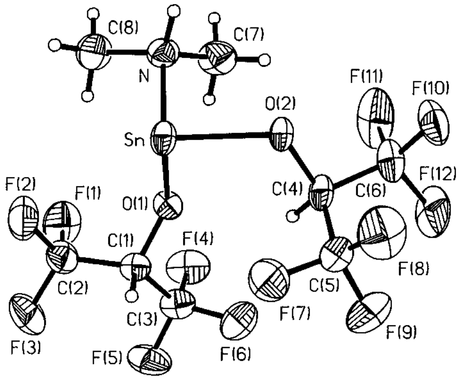


Figure 2. View of Sn(OR$_f$)$_2$(HNMe$_2$), showing the atom-numbering scheme (40% probability ellipsoids with the hydrogens as spheres of arbitrary diameter).

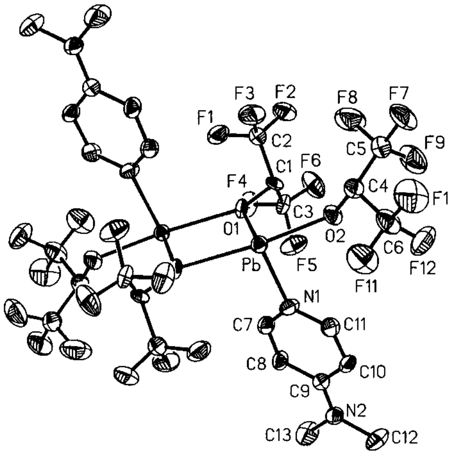


Figure 3. View of [Pb(μ-OR$_f$)(OR$_f$)(p-pyNMe$_2$)]$_2$, showing the atom-numbering scheme (40% probability ellipsoids).

remarkably similar trigonal pyramidal structures in their local metalloid coordination spheres. The three ligands that define the pyramid triangular face opposite the metalloid apex are O(1), O(2), and N in the Ge, Sn, and neutral Pb compounds and O(1), O(2), and O(3) in the Pb salt. The angles between the three M−L legs are within 6° of 90° for all four compounds. In the Pb dimers, each Pb atom interacts weakly with a terminal alkoxide ligand of the other Pb atom. The interaction results in asymmetic bridge bonds with one Pb−O$_{\mathrm{bridge}}$ distance >0.3 Å longer than the other. The long Pb−O$_{\mathrm{bridge}}$ bond makes an angle of ≈155° with respect to one of the terminal ligands and 87° (neutral compound) or 105° (salt compound) with the other.

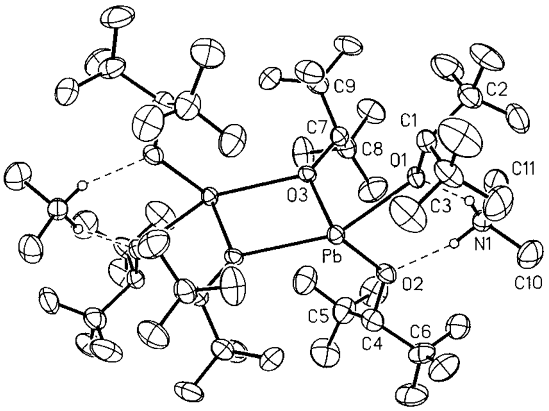


Figure 4. View of {[Me$_2$NH$_2$][Pb(μ-OR$_f$)(OR$_f$)$_2$]}$_2$, showing the atom-numbering scheme (30% probability ellipsoids with the ammonium hydrogens as spheres of arbitrary diameter).

Table 3. Selected Bond Distances (Å) and Angles (deg) for Ge(OR$_f$)$_2$(H$_2$NPh), Sn(OR$_f$)$_2$(HNMe$_2$) and [Pb(μ-OR$_f$)(OR$_f$)(p-pyNMe$_2$)]$_2$

	M = Ge	M = Sn	M = Pb
	Bond Distances[a]		
M−O(1)	1.870(4)	2.061(5)	2.247(6)
M−O(2)	1.878(4)	2.107(4)	2.260(6)
M−N	2.092(3)	2.264(8)	2.363(7)
M−O(1′)			2.716(6)
	Bond Angles[a]		
O(1)−M−O(2)	93.4(2)	90.1(2)	88.2(2)
O(1)−M−N	87.6(1)	83.7(2)	90.9(2)
O(2)−M−N	88.3(2)	90.2(2)	83.9(2)
O(1′)−M−O(2)			153.6(2)
O(1′)−M−N			87.2(2)
O(1′)−M−O(1)			67.1(2)
M−O(1)−M′			112.9(2)
M−O(1)−C(1)	116.3(3)	128.7(4)	118.7(5)
M−O(2)−C(4)	117.2(3)	121.1(4)	118.5(5)
M′−O(1)−C(1)			127.7(5)

[a] In this table, N is N(1) for M = Pb.

Table 4. Selected Bond Distance (Å) and Angles (deg) for {[Me$_2$NH$_2$][Pb(μ-OR$_f$)(OR$_f$)$_2$]}$_2$

	Bond Distances		
Pb−O(1)	2.354(5)	Pb−O(2)	2.258(5)
Pb−O(3)	2.243(6)	Pb−O(3′)	2.659(5)
	Bond Angles		
O(1)−Pb−O(2)	83.0(2)	O(1)−Pb−O(3)	86.8(2)
O(2)−Pb−O(3)	90.7(2)	O(1)−Pb−O(3′)	155.5(2)
O(2)−Pb−O(3′)	105.0(2)	O(3)−Pb−O(3′)	70.2(2)
Pb−O(1)−C(1)	122.1(4)	Pb−O(2)−C(4)	122.3(5)
Pb−O(3)−C(7)	123.3(4)	Pb−O(3)−Pb′	109.8(2)
Pb′−O(3)−C(7)	126.6(5)		

The Pb lone pair does not appear to be stereochemically “active” in either structure.

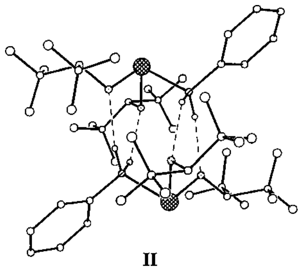
As expected on the basis of their respective atomic radii, the M−O and M−N distances lengthen significantly going down the periodic table column from Ge to Sn to Pb. Bond distances in the compounds are normal. The Ge−O distances, for example, are close to those found in Ge(OC-t-Bu$_3$)$_2$ (1.896(6), 1.832(11) Å),[26] Ge(O-2,6-t-Bu$_2$C$_6$H$_2$-4-Me)$_2$ (1.812(7), 1.802(8) Å),[28] and [Ge(O-t-Bu)$_2$(Ni(CO)$_3$)]$_2$ (1.780(6) Å).[29] The Sn−O bond distances are slightly longer than those found in the tin(II) compounds Sn(OAr)$_2$, Ar = 2,6-t-BuC$_6$H$_2$-4-Me or

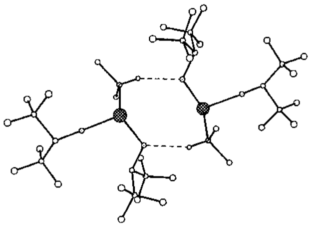
---

(28) Cetinkaya, B.; Gümrükcü, I.; Lappert, M. F.; Atwood, J. L.; Rogers, R. D.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2088.

(29) Grenz, M.; Hahn, E.; Mont, W.-W.; Pickardt, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 61; *Angew. Chem.* **1984**, *96*, 69.

2,4,6-*t*-$Bu_3C_6H_2$ (1.98−2.04 Å),[21,28] $Sn(N(SiMe_3)_2)(O$-2,6-*t*-BuC_6H_2-4-Me) (2.055(2) Å),[30] and [Sn(O-*t*-$Bu)_2]_2$ (1.97(2) Å)[26] as well as related tin(IV) alkoxide complexes (1.90−1.97 Å).[31,32] The Sn−N distance is comparable to those in tin(II) SnR(X), R = $C(SiMe_3)_2$-*o*-py and X = $C(SiMe_3)_2$-*o*-py, Cl, or $N(SiMe_3)_2$,[33] which range from 2.26 to 2.45 Å, and tin(IV) $Sn(OC_6H_3PhC_6H_4)_2(HNMe_2)_2$ (2.32(1) Å).[34] In the crystals of both $Ge(OR_f)_2(H_2NPh)$ and $Sn(OR_f)_2(HNMe_2)$, there is intermolecular hydrogen bonding between the alkoxide oxygen atoms on one molecule and the amine protons on another (d(N···O) ≈ 3.0 Å), making dimers about an inversion center (**II** and **III**, respectively). The hydrogen bonding lengthens the Sn−O(2) bond distance slightly compared to Sn−O(1).


II


III

The two short Pb−O bond distances in the neutral dimer and two of the three short distances in the salt are within 3σ of each other, but Pb−O(1) in the salt is significantly longer than the other distances. The reason why Pb−O(1) is longer in the salt is not obvious; in particular, the longer bond cannot be ascribed to the hydrogen-bonding interaction between the ammonium protons and the O atoms because O(2) is not lengthened by the same interaction. The N···O distances are about the same (O(1), 2.66 Å; O(2), 2.74 Å).

Surprisingly, the short Pb−O_{bridge} bonds, Pb−O(1) in the neutral dimer and Pb−O(3) in the salt, are not significantly lengthened by their involvement in the dative interaction with the other Pb atom. The terminal Pb−O distances in both compounds are close to those in Pb(II) monoglycerolate (average 2.26(3) Å)[35] and Pb(O-2,4-*t*-$Bu_2C_6H_2$-4-Me$)_2$ (average 2.14(1) Å),[21] as well as to the shorter of the asymmetric bridge Pb−O distances in $[Pb(\mu,\eta^1\text{-}OCH_2CH_2OMe)_2]_\infty$ (2.234(4) and 2.440(5) Å) and in $Pb_3(\mu$-O-*t*-$Bu)_6$ (2.17(1) and 2.55(1) Å).[36] The long Pb−O_{bridge} distances in both the neutral and salt compounds are ≈2.7 Å, which is nearly 0.2 Å longer than the dative Pb−O bond in Pb(S-2,4,6-$(CF_3)_3C_6H_2)_2$(THF) (2.495(10) Å).[37] This suggests the Pb−O bridge interactions in the dimers are extremely weak.

Conclusion

Tin(II) $Sn(OR_f)_2$ and the amine adducts $Sn(OR_f)_2L$, L = $HNMe_2$ or py, are prepared in high yield from bis(amido)tin(II) compounds. By analogy to known tin(II) alkoxide and related compounds, $Sn(OR_f)_2$ is proposed to be a dimer with two bridging alkoxide ligands. A crystal structure of $Sn(OR_f)_2(HNMe_2)$ shows it to have a trigonal pyramidal geometry. The new compounds are volatile solids, an important attribute if they are to be used as conventional CVD tin oxide precursors. The results of low and atmospheric pressure chemical vapor deposition studies using $Sn(OR_f)_2$ and $Sn(OR_f)_2(HNMe_2)$ as precursors will be reported shortly.

The analogous germanium(II) compounds, $Ge(OR_f)_2L$, L = py or H_2NPh, and the Pb(II) dimers $[Pb(\mu\text{-}OR_f)(OR_f)(p\text{-}pyNMe_2)]_2$ and $\{[Me_2NH_2][Pb(\mu\text{-}OR_f)(OR_f)_2]\}_2$ are prepared by similar methods. X-ray crystal structures of $Ge(OR_f)_2(H_2NPh)$, $[Pb(\mu\text{-}OR_f)(OR_f)(p\text{-}pyNMe_2)]_2$, and $\{[Me_2NH_2][Pb(\mu\text{-}OR_f)(OR_f)_2]\}_2$ reveal they all have local trigonal pyramidal metalloid coordination geometries similar to $Sn(OR_f)_2(HNMe_2)$. The Pb dimers are held together via long dative Pb−O bonds.

Acknowledgment for support is made to the Environmental Institute of Houston and the Robert A. Welch Foundation. We thank Dr. James Korp for his technical assistance with the crystal structure determinations and his helpful discussions.

Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles and packing diagrams for $Ge(OR_f)_2(H_2NPh)$, $Sn(OR_f)_2(HNMe_2)$, $[Pb(\mu\text{-}OR_f)(OR_f)(p\text{-}pyNMe_2)]_2$, and $\{[Me_2NH_2][Pb(\mu\text{-}OR_f)(OR_f)_2]\}_2$ (28 pages). Ordering information is given on any current masthead page. Tables of observed and calculated structure factors can be obtained from the authors.

IC960293Q

---

(30) Braunschweig, H.; Chorley, R. W.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1992**, 1311.

(31) Hampden-Smith, M. J.; Wark, T. A.; Rheingold, A.; Huffman, J. C. *Can. J. Chem.* **1991**, *69*, 121.

(32) Chandler, C. D.; Caruso, J.; Hampden-Smith, M. J. *Polyhedron* **1995**, *14*, 2491.

(33) Engelhardt, L. M.; Jolly, B. S.; Lappert, M. F.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 336.

(34) Smith, G. D.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1989**, *111*, 750.

(35) Keller, H.-L.; Riebe, H.-J. *Z. Anorg. Allg. Chem.* **1987**, *550*, 102.

(36) Goel, S. C.; Chiang, M. Y.; Buhro, W. E. *Inorg. Chem.* **1990**, *29*, 4640.

(37) Labahn, D.; Brooker, S.; Sheldrick, G. M.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1992**, *610*, 163.