

Synthesis and Thermolytic Behavior of Mixed-Valence Homo- and Heterometallic Group 14 Alkoxides

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The mixed-valence molecule $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ is conveniently synthesized and is shown to exchange bridging and terminal alkoxides in solution in its $\text{Sn}(\mu\text{-O}^i\text{Pr})_3\text{Sn}(\text{O}^i\text{Pr})_3$ structure. $\text{Pb}_3\text{SnO}(\text{O}^i\text{Pr})_8$ is synthesized and shown to undergo an intramolecular fluxional process in solution. Both molecules are sufficiently volatile for CVD study, and comparison of CVD behaviors of these and of $\text{M}(\text{O}^i\text{Pr})_2$ ($\text{M} = \text{Sn}, \text{Pb}$), $\text{Sn}(\text{O}^i\text{Pr})_4$, $\text{SnZr}(\text{O}^i\text{Pr})_6$, and $\text{Pb}_3\text{-ZrO}(\text{O}^i\text{Pr})_8$ shows the reducing capacity of the isopropoxide moiety dominates the thermolytic behavior of all these species, giving metallic Sn or Pb in all cases. Only Zr, when it is present, forms ZrO_2 . The oxide in $\text{Pb}_3\text{SnO}(\text{O}^i\text{Pr})_8$ yields PbO (and 2 Pb^0 and 1 Sn^0), in contrast to the relative electropositivity of Sn and Pb, a fact attributed to kinetic control of CVD behavior.

Introduction

At present, there are many examples of heterometallic alkoxides which can be used as single-source precursors for thin-film synthesis. Some of the many different types of alkoxides which exist include homoleptic ($\text{MM}'(\text{OR})_a$), heteroleptic ($\text{MM}'(\text{OR})_a(\text{X})_b$ where $\text{X} = \text{OAc}, \text{OR}', \text{halide}$), and oxo alkoxide species ($\text{MM}'\text{O}(\text{OR})_a$ or $\text{MM}'(\text{OR})_a(\text{X})_b$). These can have a number of different metal combinations and can also contain up to three different metals¹ in a single molecule. However, we believe that no homometallic, mixed-valence molecular alkoxides have yet been found, and these could have unusual properties. One mixed-valence group 14 oxo alkoxide species, $\text{PbSn}_2\text{O}(\text{O}^t\text{Bu})_4(\text{OAc})_4$,² has been isolated. Our intent was to synthesize new homo- or heterometallic, mixed-valence group 14 alkoxide species and study properties such as sublimation temperature, NMR characteristics, and thermolysis.

A number of studies involving $\text{Sn}(\text{OR})_4$ have shown that Sn^{IV} exhibits behavior similar to that of Zr^{IV} .^{3–6} For example, $\text{M}(\text{O}^t\text{Bu})_4$ is monomeric for both Sn^{IV} ⁵ and Zr^{IV} .^{7,8} Dimeric $[\text{M}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})_2]$ is also formed for either metal,^{5,6,9} and both species have very similar ¹H NMR and solid-state structures. Further, the alcoholates lose the pendant HO^iPr at the same temperature to give $[\text{M}(\text{O}^i\text{Pr})_4]$. The analogous $[\text{Sn}_2(\text{O}^i\text{Pr})_9^-]$ and $[\text{Zr}_2(\text{O}^i\text{Pr})_9^-]$ building blocks have been reported.⁴

Since we have already reported many characteristics of the $\text{M}^{\text{II}}\text{M}^{\text{IV}}(\text{OR})_6$ ¹⁰ and $\text{M}^{\text{II}}\text{M}^{\text{IV}}\text{O}_c(\text{OR})_d$ ($\text{M}^{\text{IV}} = \text{Zr}$) systems,^{11,12} we decided to prepare their Sn^{IV} -containing mixed-valence

analogues. Among numerous reactions attempted, we report here $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ and $\text{Pb}_3\text{SnO}(\text{O}^i\text{Pr})_8$ as direct analogues of $\text{Sn}^{\text{II}}\text{Zr}^{\text{IV}}(\text{O}^i\text{Pr})_6$ ¹⁰ and $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Pr})_8$.¹¹

Experimental Section

All manipulations were carried out under a dry nitrogen or argon atmosphere using oven-dried glassware. Solvents (and HO^iPr) were rigorously dried by freshly distilling them under argon from appropriate drying agents (sodium for Et_2O and THF) and storing them under nitrogen over activated molecular sieves. $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$,¹³ $[\text{Sn}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})_2]$,⁵ $\text{SnZr}(\text{O}^i\text{Pr})_6$ ¹⁰ and $\text{Pb}_3\text{Zr}^{\text{IV}}\text{O}(\text{O}^i\text{Pr})_8$ ¹¹ were prepared according to literature methods. $[\text{Pb}(\text{O}^i\text{Pr})_2]$ was prepared according to a modification of a literature procedure.¹⁴ Synthesis at -40°C in pentane afforded a white, flocculent precipitate, which was washed three times with pentane and dried 12 h under dynamic vacuum (10^{-2} Torr). To obtain $[\text{Sn}(\text{O}^i\text{Pr})_4]$, all HO^iPr was removed from $[\text{Sn}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})_2]$ by heating it to 100°C under dynamic vacuum until the resulting liquid no longer bubbled. ¹⁷O-enriched (40 atom %) water was obtained from Iso-Yeda Corp., Rehovot, Israel. ¹H and ¹³C NMR spectra were recorded on a 300 MHz Varian Gemini 2000 spectrometer at 300 and 75.6 MHz, respectively. ¹⁷O NMR, ¹¹⁹Sn NMR, and ²⁰⁷Pb NMR spectra were recorded on a Varian Unity Inova 400 MHz spectrometer at 54, 149, and 84 MHz, respectively. Spectra were recorded in either C_6D_6 or $\text{C}_6\text{D}_5\text{CD}_3$. ¹H spectra were referenced to the protio impurity resonance of the deuterated solvent (7.15 ppm for C_6D_6 and 2.09 ppm for the upfield resonance of $\text{C}_6\text{D}_5\text{CD}_3$), and ¹³C spectra were referenced to the resonance of the deuterated solvent (128.0 ppm for C_6D_6 and 20.4 ppm for the upfield resonance of $\text{C}_6\text{D}_5\text{CD}_3$). ¹⁷O spectra were referenced to an external sample of ¹⁷O-enriched (5 atom %) H_2O (neat, 0.0 ppm), ¹¹⁹Sn spectra were referenced to an external sample of SnMe_4 (neat, 0.0 ppm), and ²⁰⁷Pb spectra were referenced to an external sample of neat PbEt_4 (73.3 ppm).¹⁵ Elemental analyses were performed in-house on a Perkin-Elmer 2400 Series II CHNS/O analyzer. All

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chemical vapor deposition experiments were carried out under dynamic vacuum (10^{-2} Torr) in a glass apparatus having a separately heated source zone and thermolysis zone. Volatile organic thermolysis products were trapped in a liquid-nitrogen-cooled trap and were vacuum-transferred to an NMR tube containing $C_6D_5CD_3$ prior to analysis. Films were deposited on amorphous glass slides, and the identity of the crystalline material contained in the films was determined through X-ray diffraction experiments on a Scintag XDS-2000 diffractometer using Cu K α radiation and a solid-state Ge detector in the parallel-beam thin-film geometry.

Synthesis of $Sn^{II}Sn^{IV}(O^iPr)_6$. $Sn[N(SiMe_3)_2]$ (2.77 g, 6.30 mmol) was dissolved in 20 mL of Et_2O , and neat HO^iPr (0.58 mL, 7.6 mmol) was added dropwise to this solution to give a clear, light orange solution. $[Sn(O^iPr)_4(HO^iPr)]_2$ (2.62 g, 3.61 mmol) dissolved in 20 mL of Et_2O was added dropwise at 25 °C to give a clear, colorless solution. After 10 min of stirring the solution was dried in vacuo and dissolved in a minimal amount of pentane. Colorless crystals (2.98 g, 65% yield)¹⁶ formed upon cooling the solution to -15 °C. This compound can be sublimed at 70 °C and 10^{-2} Torr to a cold-finger apparatus. 1H NMR ($C_6D_5CD_3$, -20 °C): δ 4.94 (septet, 3 H; d septet satellites, $^3J_{Sn-H} = 27$ Hz),¹⁷ 4.61 (septet, 3 H; d septet satellites, $^3J_{Sn-H} = 53$ Hz),¹⁷ 1.46 (d, 18 H), 1.23 (d, 18 H). 1H NMR ($C_6D_5CD_3$, 25 °C): δ 4.91 (br septet, 3 H), 4.57 (br septet, 3 H), 1.40 (br d, 18 H), 1.24 (br d, 18 H). 1H NMR ($C_6D_5CD_3$, 50 °C): δ 4.89 (br, 3 H), 4.56 (br, 3 H), 1.32 (br, 36 H). 1H NMR ($C_6D_5CD_3$, 70 °C): δ 4.70 (v br, 6 H), 1.31 (br d, 36 H). 1H NMR ($C_6D_5CD_3$, 90 °C): δ 4.70 (br, 6 H), 1.30 (d, 36 H). $^{13}C\{^1H\}$ NMR (C_6D_6 , 25 °C): δ 68.9 (s, $OCH(CH_3)_2$; d satellites, $^2J_{Sn-C} = 18$ Hz), 65.2 (s, $OCH(CH_3)_2$; d satellites, $^2J_{Sn-C} = 38$ Hz), 28.0 (s, $OCH(CH_3)_2$; d satellites, $^3J_{Sn-C} = 28$ Hz), 27.7 (s, $OCH(CH_3)_2$; d satellites, $^3J_{Sn-C} = 34$ Hz). ^{119}Sn NMR ($C_6D_5CD_3$, 25 °C): δ -344 (s; d satellites, $^2J_{Sn-Sn} = 610$ Hz), -584 (br s; br d satellites, $^2J_{Sn-Sn} = 630$ Hz). $^{119}Sn\{^1H\}$ NMR ($C_6D_5CD_3$, 25 °C): δ -344 (s; d satellites, $^2J_{Sn-Sn} = 610$ Hz), -584 (s; d satellites, $^2J_{Sn-Sn} = 610$ Hz). Anal. Calcd for $Sn_2O_6C_{18}H_{42}$: C, 36.53; H, 7.15. Found: C, 37.23; H, 7.15. MS (EI, 15 eV): m/z^+ $Sn(O^iPr)^+$ (61%), $Sn(O^iPr)_3^+$ (17%), $Sn(O^iPr)_4^+$ (17%), $Sn_2(O^iPr)_3^+$ (83%), $Sn^{II}Sn^{IV}(O^iPr)_5^+$ (29%).

$Sn^{II}Sn^{IV}(O^iPr)_6$ can also be synthesized by reaction of equimolar $[Sn(O^iPr)_2]$ and $[Sn(O^iPr)_4]$ in C_6D_6 . Both 1H and $^{13}C\{^1H\}$ NMR data are identical to those for the species synthesized by the above method. $[Sn(O^iPr)_2]$ is made in high yield by dropwise addition of excess HO^iPr to $Sn[N(SiMe_3)_2]$ in Et_2O , followed by removal of the solvent. The colorless, powdery compound sublimes at 120 °C and 10^{-2} Torr. Unlike polymeric $[Pb(O^iPr)_2]$, the compound is very soluble in most hydrocarbon solvents.

Synthesis of $Pb_3Sn^{17}O(O^iPr)_8$. $[Pb(O^iPr)_2]$ (2.00 g, 6.15 mmol) was suspended in 35 mL of THF, and the suspension was heated to reflux. A solution of $^{17}OH_2$ (38.7 μ L, 2.08 mmol) in 10 mL of THF was added dropwise to give a clear, colorless solution. After a 5 min reflux, $[Sn(O^iPr)_4(HO^iPr)]_2$ (0.851 g, 1.02 mmol) dissolved in 20 mL of THF was added, and the resulting solution was refluxed for 10 min. The solution was cooled, and the solvent was removed in vacuo, leaving a waxy solid, which was transferred to a sublimation apparatus. The solid was sublimed at 128 °C and 10^{-2} Torr to leave a waxy, crystalline deposit (2.04 g, 81%) on a 0 °C cold-finger apparatus. During sublimation of this compound, it is necessary to chill the cold-finger apparatus near 0 °C for the vaporized material to condense as a waxy substance. Otherwise, it will simply reflux as a viscous liquid. 1H NMR¹⁸ ($C_6D_5CD_3$, 25 °C): δ 5.05 (septet, 3 H), 5.00 (septet, 4 H; d septets satellites, $^3J_{Sn-H} = 40.8$ Hz), 4.61 (septet, 1 H; d septets satellites, $^3J_{Sn-H} = 51.6$ Hz), 1.52 (d, 6 H; d septet satellites, $^3J_{Sn-H} = 3.5$ Hz), 1.41 (d, 24 H), 1.15 (d, 18 H). 1H NMR ($C_6D_5CD_3$, 50 °C): δ 4.97 (br, 7 H), 4.54 (septet, 1 H; d septets satellites, $^3J_{Sn-H} = 50.1$ Hz), 1.41 (d, 6 H), 1.34 (br, 24 H), 1.17 (br, 18 H). 1H NMR ($C_6D_5CD_3$, 70 °C): δ 4.98 (br,

Table 1. CVD Conditions

compound	source temp (°C)	oven temp (°C)	compound	source temp (°C)	oven temp (°C)
$[Sn(O^iPr)_2]$	79	295	$Pb_3Sn^{17}O(O^iPr)_8$	130	295
$[Sn(O^iPr)_4]$	110	350	$Pb_3Zr^{17}O(O^iPr)_8$	135	325
$Sn^{II}Sn^{IV}(O^iPr)_6$	105	295	$[Pb(O^iPr)_2]$	127	295
$SnZr(O^iPr)_6$	75	315			

Table 2. CVD Products

compound	acetone found (calc)	HO^iPr found (calc)	propene found (calc)	other found	Pb	Sn	PbO	ZrO ₂
$[Sn(O^iPr)_2]$	100 (100)	97 (100)	0	0	X			
$[Sn(O^iPr)_4]$	100 (100)	97 (100)	0	0	X			
$Sn^{II}Sn^{IV}(O^iPr)_6$	100 (100)	98 (100)	0	0	X			
$SnZr(O^iPr)_6$	33 (33)	100 (100)	79 (66)	a	X			X
$Pb_3Sn^{17}O(O^iPr)_8$	100 (100)	98 (100)	0	0	X	X	X	
$Pb_3Zr^{17}O(O^iPr)_8$	59 (75)	100 (100)	16 (25)	0	X			X
$[Pb(O^iPr)_2]$	98 (100)	100 (100)	0	0	X			

^a See Experimental Section.

7 H), 4.53 (septet, 1 H; d septets satellites, $^3J_{Sn-H} = 50.1$ Hz), 1.39 (d, 6 H), 1.26 (br, 42 H). 1H NMR ($C_6D_5CD_3$, 90 °C): δ 4.97 (br septet, 7 H), 4.52 (septet, 1 H; d septets satellites, $^3J_{Sn-H} = 48.3$ Hz), 1.38 (d, 6 H), 1.25 (br d, 42 H). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 25 °C): δ 65.5 (s, $OCH(CH_3)_2$), 65.4 (s, $OCH(CH_3)_2$), 65.0 (s, $OCH(CH_3)_2$), 26.4 (s, $OCH(CH_3)_2$),¹⁹ 28.6 (s, $OCH(CH_3)_2$),¹⁹ 27.8 (s, $OCH(CH_3)_2$). $^{119}Sn\{^1H\}$ NMR ($C_6D_5CD_3$, 25 °C): δ satellite intensity (calcd; obsd)²⁰ -585.8 (20.5%; 21.5%), -586.8 (53.0%; 54.5%) ($^2J_{Sn-Pb} = 308$ Hz), -587.8 (20.5%; 23.9%). ^{17}O NMR ($C_6D_5CD_3$, 25 °C): δ satellite intensity (calcd; obsd)²⁰ 219.7 (2.9%; 3.2%), 215.5 (20.5%; 21.6%), 211.4 (53.0%; 53.6%) ($\nu_{1/2} = 17$ Hz; $^1J_{Pb-O} = 453$ Hz, $^1J_{Sn-O} = 111$ Hz), 207.2 (20.5%; 19.5%), 203.0 (2.9%; 2.1%). ^{207}Pb NMR ($C_6D_5CD_3$, 25 °C): δ 963 (s; d satellites, $^2J_{Pb-Sn} = 305$ Hz). Anal. Calcd for $Pb_3SnO_9C_{24}H_{56}$: C, 23.44; H, 4.59. Found: C, 23.08; H, 4.53. MS (EI, 15 eV): m/z^+ $Pb(O^iPr)^+$ (13%), $Pb_2O(O^iPr)^+$ (17%), $Pb_3O(O^iPr)_3^+$ (100%), $Pb_3SnO(O^iPr)_7^+$ (62%).

Thermolysis Experiments. All CVD experiments were performed by first drying all glassware and slides in a 110 °C oven overnight before use. Approximately 0.25 g of precursor was loaded into a deposition tube in a drybox, and the tube was closed to retain the inert atmosphere. The tube was then removed from the drybox and attached to a CVD apparatus consisting of a vacuum pump (10^{-2} Torr), a source heater (for sample vaporization), and a tube furnace (for sample thermolysis). After the atmosphere of the tube was evacuated for 1 h, the furnace was heated to the appropriate temperature (see Table 1) and allowed to stabilize for 1 h. The source was then heated to a temperature where vapor transport was appreciable (see Table 1), and the vaporized compound was passed through the thermolysis zone where the metal products were deposited. All volatile decomposition products were trapped in a liquid-nitrogen-cooled trap. After the experiment was complete, the hot zones were allowed to cool slowly (ca. 4 h) to 25 °C, and trapped volatiles were vacuum-transferred to an NMR tube and analyzed. The resulting metal-containing films were analyzed by X-ray diffraction. The results of this study are shown in Table 2.

Thermolysis of $[Sn(O^iPr)_2]$. Analysis of the films by X-ray diffraction showed only sharp peaks for elemental Sn (JCPDS No. 04-0673) and a very broad peak attributable to amorphous glass. Acetone (100%) and HO^iPr (97%) were the only volatile products of the thermolysis detected by 1H NMR.

Thermolysis of $[Sn(O^iPr)_4]$. Analysis of the films by X-ray diffraction showed that they consisted mostly of Sn (JCPDS No. 04-0673) metal as evidenced by sharp peaks. A trace amount of SnO_2 (JCPDS No. 21-1250) was found in the baseline. By 1H NMR, the volatiles consisted only of acetone (100%) and HO^iPr (97%).

(16) This yield is limited only by the high solubility of the compound in the crystallization solvent.

(17) Decoupling the appropriate methyl protons simplifies this methine signal to a singlet having measurable doublet satellites.

(18) Due to the overlapping of the multiplets in the methine region, the methyl protons must be decoupled to simplify the methine signals. Once this is accomplished, the chemical shifts, satellites, and coupling can be accurately determined.

(19) This signal is broad at its base relative to other signals in its spectrum, indicating averaged Pb-C coupling.

(20) Fewer than the expected seven lines could be resolved due to a limited signal-to-noise ratio.

Thermolysis of $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$. The films contained mainly Sn metal (JCPDS No. 04-0673) with only trace SnO_2 (JCPDS No. 21-1250) detected by X-ray diffraction. The volatiles contained only acetone (100%) and HO^iPr (98%) as determined by ^1H NMR.

Thermolysis of $\text{SnZr}(\text{O}^i\text{Pr})_6$. Only Sn metal (JCPDS No. 04-0673) was detected by X-ray diffraction, but a broad, rolling baseline was a sign that amorphous material (probably ZrO_2) was present. The volatile organic products were acetone (33%), HO^iPr (100%), and propene (79%) as found by ^1H NMR. A small amount of colorless material had condensed past the decomposition zone. This was completely dissolved in C_6D_6 and analyzed. ^1H NMR (C_6D_6 , 25 °C): δ 4.62 (septet, 8 H; $[\text{Zr}(\text{O}^i\text{Pr})_4]$), 4.56 (septet, 3 H; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$),¹¹ 4.46 (septet, 3 H; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 4.42 (septet, 3 H; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 4.39 (septet, 1 H; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 1.63 (d, 6 H; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 1.47 (d, 18 H; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 1.44 (d, 48 H; $[\text{Zr}(\text{O}^i\text{Pr})_4]$), 1.342 (d, 18 H; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 1.340 (d, 18 H; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C): δ 71.9 (s, $\text{OCH}(\text{CH}_3)_2$; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 71.4 (s, $\text{OCH}(\text{CH}_3)_2$; $[\text{Zr}(\text{O}^i\text{Pr})_4]$), 71.3 (s, $\text{OCH}(\text{CH}_3)_2$; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 71.0 (s, $\text{OCH}(\text{CH}_3)_2$; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 70.5 (s, $\text{OCH}(\text{CH}_3)_2$; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 27.0 (s, $\text{OCH}(\text{CH}_3)_2$; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 26.8 (s, $\text{OCH}(\text{CH}_3)_2$; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 26.7 (s, $\text{OCH}(\text{CH}_3)_2$; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$), 26.5 (s, $\text{OCH}(\text{CH}_3)_2$; $[\text{Zr}(\text{O}^i\text{Pr})_4]$), 26.0 (s, $\text{OCH}(\text{CH}_3)_2$; $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$).

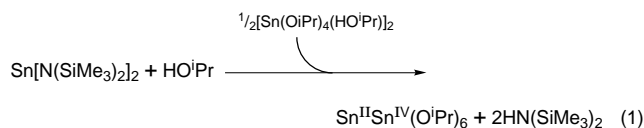
Thermolysis of $\text{Pb}_3\text{Sn}^{17}\text{O}(\text{O}^i\text{Pr})_8$. X-ray diffraction gave sharp lines which indicated the presence of Pb (JCPDS No. 04-0686), PbO (JCPDS No. 38-1477), and Sn (JCPDS No. 04-0673) in the films. By ^1H NMR, the volatiles consisted of only acetone (100%) and HO^iPr (98%).

Thermolysis of $\text{Pb}_3\text{Zr}^{17}\text{O}(\text{O}^i\text{Pr})_8$. Only Pb metal (JCPDS No. 04-0686) was detected by X-ray diffraction, but broad peaks in the baseline indicated that amorphous material (probably ZrO_2) was present. Unlike the thermolysis of Zr-containing $\text{SnZr}(\text{O}^i\text{Pr})_6$, no solid was detected past the hot zone. The volatiles (measured at low temperature) contained acetone (59%), HO^iPr (100%), and propene (16%) as determined by ^1H NMR.

Thermolysis of $\text{Pb}(\text{O}^i\text{Pr})_2$. X-ray diffraction showed very sharp signals for Pb metal (JCPDS No. 04-0686). HO^iPr (100%) and acetone (98%) were the only volatiles found by ^1H NMR.

Results

$\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$. The synthesis of $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ involves the in-situ generation of “[$\text{Sn}(\text{O}^i\text{Pr})(\text{N}(\text{SiMe}_3)_2)_2$]²¹ in ether followed by the addition of $[\text{Sn}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})_2]$, which bears the final equivalent of alcohol necessary to complete the Brønsted acid–base reaction (eq 1). The presence of HN-



$(\text{SiMe}_3)_2$ does not appear to have any effect on the association of the two $\text{Sn}(\text{OR})_x$ species. The resulting compound, which is very soluble in both polar and nonpolar solvents, can be crystallized from a concentrated pentane solution. However, X-ray-quality crystals could not be obtained either by this method or by sublimation in a sealed tube under vacuum. A Lewis acid–base reaction of equimolar $[\text{Sn}(\text{O}^i\text{Pr})_2]$ and $[\text{Sn}(\text{O}^i\text{Pr})_4]$ in C_6D_6 gives the same product.

The ^1H NMR spectrum at -20 °C has two equal-intensity peaks in both the methyl and methine regions. Two 1:1 environments are consistent with the structure of the $\text{MM}'(\text{OR})_6$ class¹⁰ (**I**; here $\text{M} = \text{Sn}^{\text{II}}$, $\text{M}' = \text{Sn}^{\text{IV}}$, and $\text{OR} = \text{O}^i\text{Pr}$). By NMR, this class of species shows two equal-intensity chemical environments arising from bridging and terminal alkoxides. The upfield methine septet in the $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ spectrum shows doublet satellite septets ($^2J_{\text{Sn-H}} = 53$ Hz) whereas the downfield septet does not immediately reveal coupling. Decoupling the

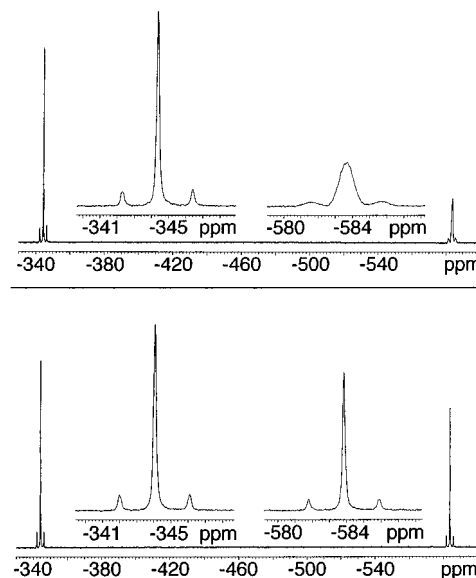
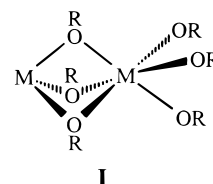


Figure 1. ^{119}Sn NMR spectra of $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ at 25 °C in toluene-d_8 showing two equal-intensity Sn environments where satellites on each peak indicate that the metal centers couple to one another. The upper spectrum shows broadening of the upfield signal due to ^1H coupling whereas the lower spectrum (with ^1H decoupling) shows equally sharp signals.

protons of the upfield methyl group reveals a singlet with doublet satellites ($^2J_{\text{Sn-H}} = 27$ Hz). Thus, the doublet satellite septets were buried under the main septet. Coupling from Sn to the methyl protons was not detected. The Sn–H coupling is most apparent in the ^{119}Sn NMR spectrum which shows equal-intensity peaks (Figure 1) for the two M and M' environments (see **I**). Both peaks exhibit doublet satellites due to Sn–Sn

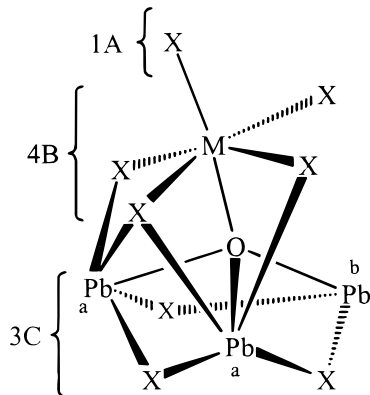


coupling ($^2J_{\text{Sn-Sn}} = 610$ Hz), and the upfield peak, and its satellites, are broadened by coupling to the methine protons. While completely decoupling the methine protons gives equally sharp peaks in the ^{119}Sn NMR spectrum, selectively decoupling either of the methine regions does not simplify the coupling to quartets (arising from coupling to only three of the six possible methine protons) as would be expected. This may be the consequence of the alkoxides exchanging terminal and bridging roles at a rate which is relatively fast on the ^{119}Sn NMR time scale but slow on the ^1H NMR time scale (since two sharp methine septets can be resolved at -20 °C). Already at 25 °C, the ^1H NMR spectrum shows broadening in the methine region due to this exchange. The process occurs fast enough at 70 °C that only one signal is found in each of the methine and methyl regions. At 25 °C, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum also has two equal-intensity peaks in each of the two carbon regions. Unlike the ^1H NMR spectrum, all of these environments show detectable carbon coupling to Sn; both the methine ($^2J_{\text{Sn-C}} = 18$ and 38 Hz) and methyl carbons ($^3J_{\text{Sn-C}} = 28$ and 34 Hz) show doublet satellites of differing magnitudes.

The compound sublimes intact at 70 °C and 10^{-2} Torr to a cold-finger apparatus as a powdery solid, and its mass spectrum shows $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_5^+$, $\text{Sn}(\text{O}^i\text{Pr})^+$, $\text{Sn}(\text{O}^i\text{Pr})_3^+$, $\text{Sn}(\text{O}^i\text{Pr})_4^+$ and $\text{Sn}_2(\text{O}^i\text{Pr})_3^+$.

(21) Compare to $[\text{Sn}(\text{O}^i\text{Bu})(\text{N}(\text{SiMe}_3)_2)_2]$: McGeary, M. J.; Foltling, K.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 4051.

Pb₃Sn¹⁷O(OⁱPr)₈. The synthesis of Pb₃Sn¹⁷O(OⁱPr)₈ first involves the partial hydrolysis (with ¹⁷OH₂) of polymeric [Pb(OⁱPr)₂] in refluxing THF to give a clear solution. The addition of [Sn(OⁱPr)₄(HOⁱPr)₂] and removal of the solvent leave a sticky solid that can be purified by sublimation. We have evaluated the NMR data in comparison to those for Pb₃ZrO(OR)₈ (OR = OⁱPr,¹¹ O^tBu¹²) reported earlier and find the solution structure to be that of **II** (here, M = Sn and X = OⁱPr). Its ¹H NMR

**II**

spectrum shows three environments which integrate to 1:4:3 (compare to 1A:4B:3C in **II**) in both the methine and methyl regions. This oversimplified spectrum thus indicates that residual fluxionality is present. In the methine region, the septets arising from alkoxides bound directly to Sn (i.e., 4B and 1A) have doublet satellites (³J_{Sn-H} = 40.8 Hz and ³J_{Sn-H} = 50.6 Hz, respectively). When a sample in C₆D₅CD₃ is warmed to 50 °C, the methine region simplifies with the coalescing of the 4B and 3C regions. The methyl region also reflects a dynamic exchange of these environments with the broadening of their corresponding peaks while the doublet of the unique alkoxide remains sharp. Increasing the temperature to 70 °C results in coalescing of the already broad methyl peaks while the single unique alkoxide shows sharp multiplets in both regions. By 90 °C, the methyl and methine regions each show two multiplets which integrate to 1:7. Throughout the range of temperatures, the unique alkoxide peak remains equally sharp and this alkoxide maintains its coupling to Sn (i.e., remains bound to Sn). In its ¹³C{¹H} NMR spectrum, three environments were detected in both the methine and methyl carbon regions. While coupling to Pb was not immediately apparent, broadening in the baseline (i.e., broad doublet satellites) of the two greater intensity peaks in the methyl region suggests averaged coupling to Pb due to a fluxional process. Only three of the expected seven lines arising from coupling to multiple Pb (²J_{Sn-Pb} = 308 Hz) atoms were detected in its ¹¹⁹Sn{¹H} NMR spectrum due to signal-to-noise limitations. The intensities of these three lines resemble those of a pattern expected for a single Sn coupling to three Pb atoms at natural abundance. The ¹⁷O NMR spectrum shows the same coupling pattern (¹J_{Pb-O} = 453 Hz), but five of the seven expected lines are found. Further, each of the peaks shows doublet satellites due to coupling to Sn (¹J_{Sn-O} = 111 Hz) (Figure 2). The sharp central line ($\nu_{1/2}$ = 17 Hz) indicates a highly symmetrical distribution of the electron density around the quadrupolar nucleus consistent with the proposed structure. Only a singlet with doublet Sn satellites (²J_{Pb-Sn} = 305 Hz) was found in the ²⁰⁷Pb NMR spectrum. While ¹⁷O NMR showed Sn and Pb coupling, the ²⁰⁷Pb and ¹¹⁹Sn NMR spectra did not show ¹⁷O coupling

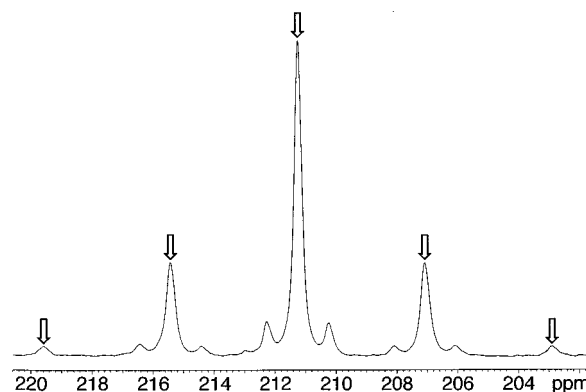


Figure 2. ¹⁷O NMR spectrum of Pb₃Sn¹⁷O(OⁱPr)₈ showing five of the seven expected lines arising from coupling to three Pb atoms at natural abundance. Each of these signals shows doublet satellites due to coupling to one Sn atom. The sharp central line indicates the high symmetry of electron density around O.

coupling owing to a combination of the multiplicity (six equal-intensity singlets) arising from nuclear spin of ¹⁷O ($I = 5/2$) and signal-to-noise limitations.

This species sublimes intact as a colorless, *crystalline* wax to a 0 °C cold-finger apparatus. Its mass spectrum shows Pb₃¹⁷O(OⁱPr)₃⁺, Pb(OⁱPr)⁺, Pb₂¹⁷O(OⁱPr)⁺, and Pb₃Sn¹⁷O(OⁱPr)₇⁺.

Chemical Vapor Deposition. (a) [Sn(OⁱPr)₂]. Only pure Sn metal was deposited upon the thermolysis of [Sn(OⁱPr)₂] at 295 °C. The volatiles consisted of nearly equal amounts of acetone (100%) and HOⁱPr (97%).

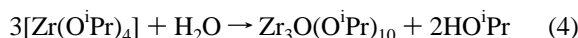
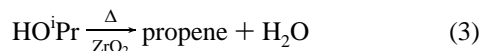
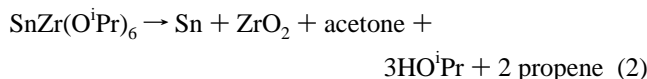
(b) [Sn(OⁱPr)₄]. The thermolysis of [Sn(OⁱPr)₄] at 350 °C deposited spheres of light gray Sn metal on amorphous glass substrates. Trace SnO₂ was detected by X-ray diffraction, but its source is unknown. The volatiles collected, consisting only of acetone (100%) and HOⁱPr (97%), did not show any indication of C–O bond heterolysis which would give an oxide product. We can thus only suggest the possibility that adventitious water, or trace oxo alkoxide impurity, was the source of the SnO₂.

(c) Sn^{II}Sn^{IV}(OⁱPr)₆. Decomposition of Sn^{II}Sn^{IV}(OⁱPr)₆ occurred at 295 °C, 55 °C lower than that of [Sn(OⁱPr)₄], leaving mostly spheres of Sn metal with only trace SnO₂ detected by X-ray diffraction. The volatiles contained only acetone (100%) and HOⁱPr (98%), indicating that reduction occurred at both metal centers to give elemental Sn.

(d) SnZr(OⁱPr)₆. While the decomposition of Sn^{II}Sn^{IV}(OⁱPr)₆ was very clean and left only Sn metal, the presence of oxophilic Zr resulted in an increase in the decomposition temperature to 315 °C due to a different decomposition pathway. The mere presence of [Sn(OⁱPr)₂] was not enough to trigger the lower temperature (295 °C) decomposition of the compound overall as seen for Sn^{II}Sn^{IV}(OⁱPr)₆. Only Sn metal was detected by X-ray diffraction, but broad peaks in the baseline were a sign that amorphous material was present. It is believed that the deposition temperature (315 °C) was not high enough for crystalline ZrO₂ to form.²² A small amount of unthermolized solid, which had condensed past the hot zone, indicated that decomposition was not complete. NMR analysis of this colorless solid revealed that it was a mixture of [Zr(OⁱPr)₄] and Zr₃O(OⁱPr)₁₀ in a ratio of 2:1. The volatile organic products were acetone, HOⁱPr, and propene in a ratio of 0.3:1.0:0.8. The

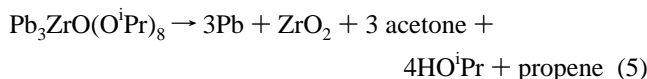
(22) Crystalline ZrO₂ is reportedly deposited by thermolysis of Zr(O^tBu)₄ only well above 300 °C: Omura, T.; Ichimura, H.; Kobayashi, K. *Kagaku Kogaku Ronbunshu* **1990**, *16*, 494.

observed amount of propene was slightly higher than that predicted (see eq 2). Some of the 2-propanol was thus dehydrated by the freshly produced ZrO_2 surface⁷ to give water and propene (eq 3), and water reacted with the unthermolized $[Zr(O^iPr)_4]$ to produce $Zr_3O(O^iPr)_{10}$ and more HO^iPr (eq 4).



(e) **$Pb_3Sn^{17}O(O^iPr)_8$** . The thermolysis of $Pb_3Sn^{17}O(O^iPr)_8$ gave elemental Pb, PbO, and elemental Sn. The absence of the SnO_x in the film indicates that Sn^{IV} was completely reduced to Sn metal. The oxide present in $Pb_3Sn^{17}O(O^iPr)_8$ preferentially forms PbO (and Sn) instead of forming SnO_x (and Pb). The volatiles consisted of only acetone (100%) and HO^iPr (98%) produced during the reduction of Sn^{IV} to Sn and Pb^{II} to Pb. The absence of propene indicates that the oxo ligand is the only source of metal oxide during CVD.

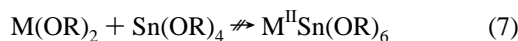
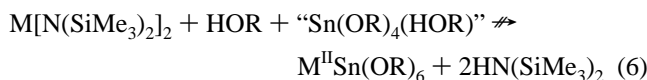
(f) **$Pb_3Zr^{17}O(O^iPr)_8$** . The complete thermolysis of $Pb_3Zr^{17}O(O^iPr)_8$ at 325 °C (i.e., no residue survived the hot zone) gave crystalline Pb metal and ZrO_2 (not detected by X-ray diffraction). While reduction of Pb occurred due to β -hydrogen abstraction, the C–O bond of one O^iPr group was cleaved and ZrO_2 and propene resulted. The volatiles contained amounts of acetone (59%), HO^iPr (100%), and propene (16%) close to those calculated (eq 5) for thermolysis giving only Pb metal and ZrO_2 .



(g) **$[Pb(O^iPr)_2]$** . The decomposition of $[Pb(O^iPr)_2]$ at 295 °C gave cleanly crystalline Pb metal, HO^iPr (100%), and acetone (98%).

Discussion

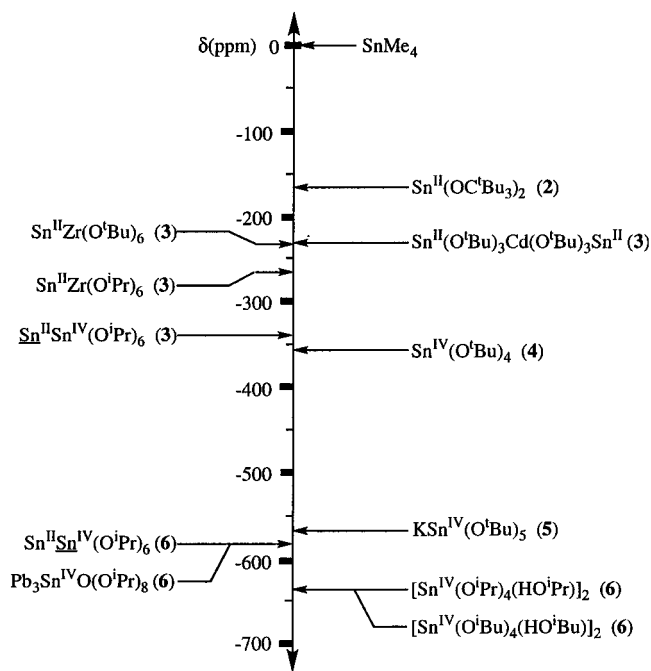
$Sn^{II}Sn^{IV}(O^iPr)_6$. A number of attempts were made to isolate compounds of formula $M^{II}Sn^{IV}(OR)_6$ ($M^{II} = Pb, Sn$; $OR = O^tBu, O^iPr$) as analogues of $M^{II}Zr(OR)_6$ ¹⁰ species we have already studied. Attempts were made using both Brønsted (eq 6) and Lewis (eq 7) acid–base reactions. All reactions, except



that giving $Sn^{II}Sn^{IV}(O^iPr)_6$, were unsuccessful and resulted in unreacted homometallic alkoxides. On the other hand, $Sn^{II}Sn^{IV}(O^iPr)_6$ can be made by both eqs 6 and 7. The difference between Sn^{IV} and Zr^{IV} may originate from the size or the oxophilicity (i.e., need for more ligands) of the metals. Since $PbZr(O^tBu)_6$ but not $PbSn(O^tBu)_6$ has been made, steric bulk of the ligand apparently prevents Sn^{IV} from being six-coordinate. In fact, Sn^{IV} does not often bind six alkoxide ligands^{5,23} unless

(23) Veith, M.; Reimers, M. *Chem. Ber.* **1990**, *123*, 1941.

Scheme 1



they are less sterically demanding (e.g., O^iPr ^{5,6} or O^tBu ²⁴). The attempt to prepare " $PbSn(O^iPr)_6$ " gave only $[Sn(O^iPr)_4]$ and polymeric $[Pb(O^iPr)_2]$. This shows the preference of the large Pb atom to be four-coordinate (as in $[Pb(O^iPr)_2]$ ¹⁴) instead of three-coordinate (as in " $PbSn(O^iPr)_6$ ") when the smaller O^iPr ligand is used.

All NMR spectra of $Sn^{II}Sn^{IV}(O^iPr)_6$ are consistent with its solution structure being **I**. Its ¹H NMR spectrum at -20 °C shows doublet (of septets) satellites on both methine multiplets due to coupling to one Sn. By ¹¹⁹Sn NMR, *only one* of the two equal-intensity signals is broad due to coupling to the methine. Exchange of the terminal and bridging alkoxides is apparent at 25 °C in $Sn^{II}Sn^{IV}(O^iPr)_6$. At 70 °C, this exchange occurs fast enough that only one signal is found in each of the methine and methyl regions by ¹H NMR. The other $MM'(OR)_6$ species showed no evidence of this process, even at higher temperatures.

Previous reports have shown that there is a correlation in ¹¹⁹Sn NMR between the chemical shift and the coordination number of Sn.^{10,25} Typically, a chemical shift found further upfield indicates a higher coordination number (Scheme 1,²⁶ where coordination number is shown in bold). By comparison of chemical shifts to those of other homoleptic alkoxide species whose structure has been identified (by X-ray diffraction, molecular weight measurements, etc.), one can find the ap-

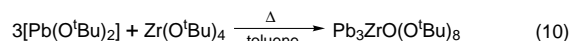
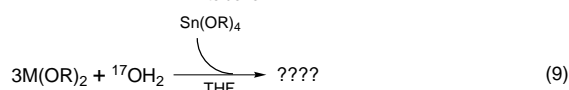
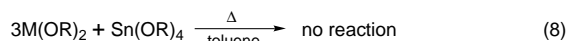
(24) Chandler, C. D.; Caruso, J.; Hampden-Smith, M. J.; Rheingold, A. L. *Polyhedron* **1995**, *14*, 2491.

(25) Hampden-Smith, M. J.; Wark, T. A.; Brinker, C. J. *Coord. Chem. Rev.* **1992**, *112*, 81.

(26) Coordination number of the Sn is in parentheses. New compounds synthesized here appear on the left side of the bar. Compounds on the right side of the bar are in the following references. $Sn(OC^tBu)_2$: Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Smith, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 939. $Sn(\mu-O^tBu)_3Cd(\mu-O^tBu)_3Sn$: Veith, M.; Hans, J.; Stahl, L.; May, P.; Huch, V.; Sebald, A. Z. *Naturforsch.* **1991**, *46B*, 403. $Sn(O^tBu)_4$: Bradley, D. C.; Caldwell, E. A. U.; Wardlaw, W. J. *Chem. Soc. A* **1957**, 4775. Marie, J.-C. *Ann. Chim.* **1961**, 969. Also see ref 5. $KSn(O^tBu)_5$: Veith, M.; Reimers, M. *Chem. Ber.* **1990**, *123*, 1941. $[Sn(O^iPr)_4(HO^iPr)_2]$: Reuter, H.; Kremser, M. Z. *Anorg. Allg. Chem.* **1991**, *598/599*, 259. Also see ref 5. $[Sn(O^tBu)_4(HO^tBu)_2]$: Chandler, C. D.; Caruso, J.; Hampden-Smith, M. J.; Rheingold, A. L. *Polyhedron*, **1995**, *14*, 2491.

proximate coordination number of a Sn atom and use this to predict a solution structure. From our assignment of the solution structure of $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$, we expect to find by ^{119}Sn NMR one signal in the three-coordinate range and one in the six-coordinate range.²⁶ The observed chemical shifts (-344 and -584 ppm) are in the three-coordinate and the six-coordinate regions. Of the two signals in the ^{119}Sn NMR spectrum of $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$, the one found upfield (i.e., six-coordinate) shows coupling to the methine protons. Both signals also show doublet satellites arising from strong $^2J_{\text{Sn}-\text{Sn}}$ (610 Hz) coupling through the μ_2 -OⁱPr groups.

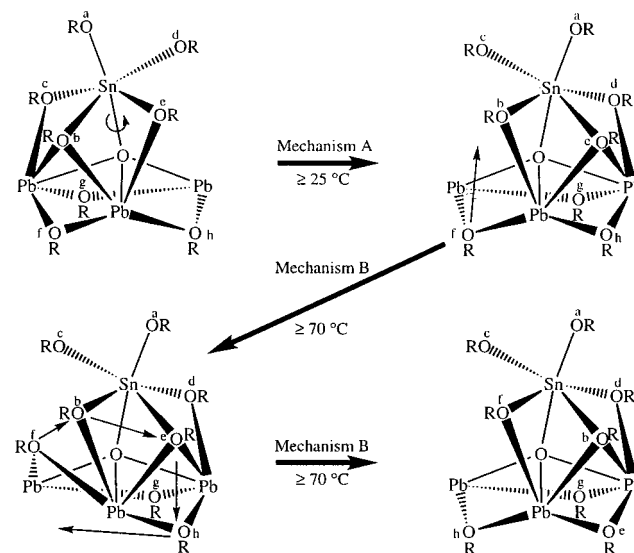
$\text{Pb}_3\text{Sn}^{17}\text{O}(\text{O}^i\text{Pr})_8$. A series of attempts were made to isolate $\text{M}_3\text{Sn}^{\text{IV}}\text{O}(\text{OR})_8$ ($\text{M} = \text{Pb}, \text{Sn}$; $\text{OR} = \text{O}^i\text{Bu}, \text{O}^i\text{Pr}$) compounds using two different methods. These included thermolysis (eq 8) and hydrolysis (eq 9).¹² For example, thermolysis of a 3:1 mixture of $[\text{Pb}(\text{O}^i\text{Bu})_2]$ and $\text{Zr}(\text{O}^i\text{Bu})_4$ gives $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$ (eq 10). The formation of this complex is made possible by C–O



bond cleavage of one OⁱBu ligand to form an oxo alkoxide and an alkene. Thermolysis in the same manner (eq 8) fails to give analogous heterometallic oxo alkoxides; unchanged reagents are recovered. This might be due to the difference in the oxophilicity of Sn vs Zr, since we believe that oxophilic Zr^{IV} is necessary for the thermolysis to proceed as it did in eq 10. The less oxophilic Sn^{IV} center thus did not show the same reactivity. Hydrolyses were also attempted according to eq 9 in refluxing THF. Except for the formation of $\text{Pb}_3\text{Sn}^{17}\text{O}(\text{O}^i\text{Pr})_8$, all other reactions were unsuccessful and only gave homometallic oxo alkoxides and unreacted species. In the case of the hydrolysis of $\text{Sn}(\text{OR})_2$, a light yellow solution was obtained before the addition of $\text{Sn}(\text{OR})_4$, but the oxo alkoxides were not observed by ^1H NMR. We believe that some $\text{Sn}(\text{OR})_2$ was converted to a “ $\text{Sn}_a\text{O}_b(\text{OR})_c$ ” aggregate with a very low alkoxide content (i.e., less visible by ^1H NMR), or it may have been converted completely to SnO. However, the complete hydrolysis to SnO is unlikely since no precipitate formed.

The reaction giving $\text{Pb}_3\text{Sn}^{17}\text{O}(\text{O}^i\text{Pr})_8$ proceeds in the same manner as in the synthesis of the other $\text{Pb}_3\text{MO}(\text{O}^i\text{Pr})_8$ ($\text{M} = \text{Ti}, \text{Zr}$)¹¹ analogues we have synthesized. All three species are formed by reacting polymeric $[\text{Pb}(\text{O}^i\text{Pr})_2]$ with $^{17}\text{OH}_2$ in a 3:1 ratio in refluxing THF followed by the addition of a “ $\text{M}(\text{O}^i\text{Pr})_4$ ” source. All compounds are waxy solids and thus do not form high-quality crystals which can be analyzed by X-ray diffraction. Solution structural methods are especially useful since most elements in $\text{Pb}_3\text{Sn}^{17}\text{O}(\text{O}^i\text{Pr})_8$ have an abundance easily detectable by NMR. The ^1H NMR spectrum shows three signals integrating to 1:4:3 at 25 °C. These intensities are too simple to be consistent with the static structure **II**, and thus a fluxional mechanism is causing the alkoxides to scramble on the NMR time scale. One possible mechanism that creates three environments is the “rocking” of the $\text{Sn}(\text{O}^i\text{Pr})_5$ unit above the $\text{Pb}_3\text{O}(\text{O}^i\text{Pr})_3$ base causing a “precession” of the O–Sn–OⁱPr vector (Scheme 2, mechanism A). This causes an exchange in the bridging roles of the equatorial alkoxides on Sn so that all four OⁱPr groups experience terminal, μ_2 , and μ_3 roles. This “precession” occurs without ever scrambling with the unique OⁱPr group which is trans to the μ_4 -O. The alkoxides in the

Scheme 2



$\text{Pb}_3(\text{O}^i\text{Pr})_3$ base become equivalent but remain different from the equatorial alkoxides at 25 °C. Further, the Pb atoms become equivalent and only one ^{207}Pb NMR signal is found. This is unlike the fluxionality observed for the $\text{Pb}_3\text{MO}(\text{O}^i\text{Pr})_8$ (where $\text{M} = \text{Ti}, \text{Zr}$)¹¹ species which yields the same three alkoxide environments but *does not scramble* the two Pb environments. On warming of a sample of $\text{Pb}_3\text{Sn}^{17}\text{O}(\text{O}^i\text{Pr})_8$, the alkoxide environments begin to exchange. The ^1H NMR spectrum at 70 °C shows two signals which integrate to 1:7 in each of the methine and methyl regions. The two signals indicate that alkoxides in two of the three chemical environments are scrambling, and this can be achieved by mechanism B (Scheme 2). This mechanism successfully interchanges the equatorial ligands on Sn with the ligands in the $\text{Pb}_3(\text{O}^i\text{Pr})_3$ base to make seven of the eight alkoxides coalesce, without involving the unique ligand trans to the μ_4 -O. This alkoxide remains unique even at 100 °C, making the fluxional mechanism different from the mechanisms of the $\text{Pb}_3\text{MO}(\text{O}^i\text{Pr})_8$ ($\text{M} = \text{Ti}, \text{Zr}$) analogues which have the trans alkoxide mixing with other alkoxides at lower temperatures (10 °C for $\text{M} = \text{Zr}$ and 50 °C for $\text{M} = \text{Ti}$).¹¹

Both the ^{119}Sn and ^{17}O NMR spectra of $\text{Pb}_3\text{Sn}^{17}\text{O}(\text{O}^i\text{Pr})_8$ show a coupling pattern consistent with three Pb atoms at natural abundance coupling to the respective nucleus. The ^{17}O NMR spectrum also shows coupling to Sn as doublet satellites. The assigned solution structure of $\text{Pb}_3\text{Sn}^{17}\text{O}(\text{O}^i\text{Pr})_8$, **II**, thus predicts that the ^{119}Sn chemical shift would be found in the six-coordinate Sn region. Not only is the chemical shift (-587 ppm) in the predicted region, but it is only 3 ppm different from that found for the six-coordinate Sn of $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ (-584 ppm).

Thermolysis Experiments. The thermolytic decompositions of $[\text{Sn}(\text{O}^i\text{Pr})_2]$, $[\text{Sn}(\text{O}^i\text{Pr})_4]$, and $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ all result in the deposition of spheres of elemental Sn with acetone and HO^iPr as the only volatile organic products. While these compounds contain Sn having different oxidation states (either Sn^{II} , Sn^{IV} , or both), the decomposition products are the same. At the outset of this investigation, we were curious to know whether Sn^{IV} would lead to deposition of SnO_x , since a previous report showed that the thermolysis of $[\text{Zr}(\text{O}^i\text{Pr})_4]$ gives ZrO_2 , propene, and HO^iPr .⁷ Further, one might imagine that the thermolysis of $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ might serve as a convenient way to make a Sn-doped SnO_x film if the two metal ions of this metal alkoxide decomposed by different pathways (cf. $\text{SnZr}(\text{O}^i\text{Pr})_6$). In fact,

we find that even the hard ion Sn^{IV} prefers to undergo reduction by β -hydrogen abstraction from the O^iPr ligand instead of the C—O bond heterolysis effected by hard, electrophilic Zr. The thermolysis of both $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ and $[\text{Sn}(\text{O}^i\text{Pr})_4]$ did give trace SnO_2 , but this might result from the presence of trace “ $\text{Sn}_a\text{O}_b(\text{O}^i\text{Pr})_c$ ” in the precursors. Since alkenes were not seen in the volatiles, the SnO_2 apparently did not form by C—O bond heterolysis. The decomposition of $[\text{Sn}(\text{O}^i\text{Pr})_4]$ occurs 55 °C higher (350 °C) than that of the divalent or mixed-valence compound. However, we believe that the decomposition pathway (β -hydrogen abstraction) is essentially the same for the three complexes since all three species give the same thermolysis products. It is interesting that $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$, which contains $[\text{Sn}(\text{O}^i\text{Pr})_4]$, can be completely thermolyzed below 350 °C. Apparently, the presence of $[\text{Sn}(\text{O}^i\text{Pr})_2]$ in the mixed-valence species creates a mechanism by which reduction at both metal centers can occur.

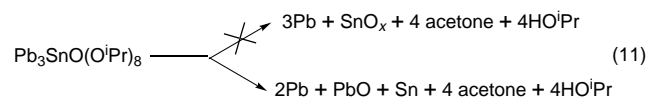
In contrast to the thermolysis of $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ to give metal, that of the Zr analogue, $\text{SnZr}(\text{O}^i\text{Pr})_6$, gives both metal (Sn) and metal oxide (ZrO_2) with only a 20 °C increase in the oven temperature from the $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ case. Since the deposition temperature was below what is needed to give crystalline ZrO_2 ,²² we did not detect zirconia by X-ray diffraction. A broad and rolling baseline did suggest that the film contained amorphous material. The presence of metal oxide in the films is corroborated by finding propene in the volatiles. In fact, the amount of propene detected was more than what was anticipated. This might be explained by the fact that HO^iPr has been shown to dehydrate when passed over a hot, freshly produced ZrO_2 surface⁷ to give water and propene (eq 3). We believe that the water then reacted with unthermolyzed $[\text{Zr}(\text{O}^i\text{Pr})_4]$ to make $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$ and more HO^iPr (eq 4). A ring of waxy material which condensed downstream from the hot zone was shown by ¹H NMR to be $[\text{Zr}(\text{O}^i\text{Pr})_4]$ and $\text{Zr}_3\text{O}(\text{O}^i\text{Pr})_{10}$.

The decomposition of $[\text{Pb}(\text{O}^i\text{Pr})_2]$ gives simply crystalline Pb metal, HO^iPr , and acetone. This shows that the polymeric species can be cleanly sublimed at 127 °C and 10^{-2} Torr into a hot zone where the metal is reduced by β -hydrogen abstraction from the O^iPr ligand.

The presence of Zr and a μ_4 -O in $\text{Pb}_3\text{Zr}^{17}\text{O}(\text{O}^i\text{Pr})_8$ apparently does not alter the fate of Pb in this heterometallic species; Pb metal is still formed and PbO is not detected. The μ_4 -O remains

bound to Zr, the more oxophilic of the two metals. Again, the decomposition temperature was lower than what is needed to form crystalline ZrO_2 , so it was not detected by X-ray diffraction. However, the evolved propene indicated that C—O bond cleavage did occur.

Thermolysis of $\text{Pb}_3\text{Sn}^{17}\text{O}(\text{O}^i\text{Pr})_8$ could involve either the formation of Pb and SnO_x or the formation of Pb, PbO , and Sn (eq 11). Despite the presence of Sn^{IV} , PbO forms in preference



to SnO_x . This is implausible, on the basis of the electropositivity of Sn vs Pb and suggests that these products may form under kinetic control: if Sn^{IV} is reduced to Sn^0 first, then PbO is the only product possible.

Conclusions

We have shown that Sn^{IV} in some instances can be used in place of Zr^{IV} to prepare $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}(\text{O}^i\text{Pr})_6$ and $\text{Pb}_3\text{SnO}(\text{O}^i\text{Pr})_8$ as direct analogues of $\text{Sn}^{\text{II}}\text{Zr}^{\text{IV}}(\text{O}^i\text{Pr})_6$ and $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Pr})_8$. We suggest that the absence of an analogous $\text{Sn}_3\text{M}(\text{O}^i\text{Pr})_8$ originates from the better ability of Pb^{II} than Sn^{II} to adopt the higher coordination number of the basal metals in structure **II**.

The thermolyses of isopropoxides studied here containing the soft, electron-rich, group 14 metals in all cases gave crystalline metal, acetone, and HO^iPr as a result of β -hydrogen abstraction from the ligand. Thus, O^iPr must generally be anticipated as a *reducing* ligand, relative to O^tBu . The precursors containing hard, oxophilic Zr were shown to give ZrO_2 due to the decomposition occurring by C—O bond heterolysis, giving HO^iPr and propene. The thermolysis of $\text{Pb}_3\text{SnO}(\text{O}^i\text{Pr})_8$ produced PbO , Pb, and Sn, and no SnO_x was detected. Since Sn is more oxophilic than Pb, we conclude that these products are not thermodynamic but rather kinetic. This illustrates one of the potential benefits of a *chemical* approach to thin-layer deposition.

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