

## Oxide Formation upon Thermolysis of a Pb(II)/Zr(IV) Alkoxide

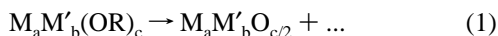
Daniel J. Teff, John C. Huffman, and Kenneth G. Caulton\*

*Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405-4001**Received July 17, 1995. Revised Manuscript Received March 1, 1996*<sup>⊗</sup>

**Abstract:** While  $\text{Pb}(\mu\text{-O}^i\text{Bu})_3\text{Zr}(\text{O}^i\text{Bu})_3$  is stable for days in refluxing toluene, addition of stoichiometric  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  prior to reflux yields  ${}^i\text{BuOH}$ ,  $\text{H}_2\text{C}=\text{CMe}_2$ , and  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$ , which was characterized by multinuclear NMR and X-ray diffraction. Highly pure  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  itself is unchanged in refluxing toluene, although it is slowly converted to  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  by catalytic quantities of  ${}^i\text{BuOH}$ ,  $\text{LiNMe}_2$ , or  $\text{HN}(\text{SiMe}_3)_2$ , but not by Pb metal. Stoichiometric water converts  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  completely to  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$ , which reacts at 25 °C with  $\text{Zr}(\text{O}^i\text{Bu})_4$  to give  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$ . Since  $\text{PbZr}(\text{O}^i\text{Bu})_6$  and  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  show no NMR spectroscopic evidence of reacting at 25 °C in toluene, the mechanism of the formation of  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$  is suggested to involve O/C heterolysis and C–H bond scission as the rate determining step during thermolysis. Convenient syntheses of  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  and  $\text{Pb}_6\text{O}_4(\text{O}^i\text{Bu})_4$  are described, and  ${}^{207}\text{Pb}$  and  ${}^{17}\text{O}$  NMR spectra of all species are described. Crystallographic data for  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$  (at –174 °C) include  $a = 16.663(2)$  Å,  $b = 12.608(1)$ ,  $c = 21.117(2)$ , and  $Z = 4$  in space group  $Pbc2_1$ .

## Introduction

The molecular precursor route to solid metal oxides (eq 1)



from alkoxides demands controlled methods of synthesis of sometimes complex heterometallic aggregates,<sup>1</sup> and then low temperature (e.g.,  $\leq 500$  °C) and selective conversion of such aggregates to the final oxide, with control over product crystallinity, porosity, particle size, microstructure, etc.<sup>2</sup> The major chemical parameter for influencing the latter “processing” is the group R. It is this factor which we have addressed in recent publications.<sup>3</sup> We describe here the course of the earliest step in a thermolytic transformation of such a heterometallic species. This example is characterized by combining a hard and very electrophilic metal ( $\text{Zr}^{\text{IV}}$ ) with a soft metal ( $\text{Pb}^{\text{II}}$ ). The alkoxide,  $\text{O}^i\text{Bu}$ , lacks a  $\beta$ -hydrogen (which in the past has led to reduction of copper in a Cu/Zr isopropoxide), but has a proclivity to C/O bond heterolysis.

Among Pb(II) alkoxides, there have been some examples where decomposition has resulted in oxo-containing homo- or heterometallic aggregates.<sup>4–10</sup> Oxo “contamination” has resulted from a number of synthetic pathways. Reaction of  $\text{Pb}(\text{OAc})_2$  with  $\text{M}(\text{OR})_n$  very often forms oxo products.<sup>6,8,11–13</sup> Further,

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, April 15, 1996.

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it is apparent that decomposition to an oxo species is facilitated by impurities,<sup>14</sup> adventitious water, concentration effects,<sup>5,6</sup> or high temperatures.<sup>5–7</sup> Syntheses of oxo-free lead alkoxides have been reported,<sup>14,15</sup> and conditions which favor their formation are usually lower temperatures (i.e., near 25 °C), with crystallization as the preferred method of purification.

One condition which apparently triggers oxo formation by Pb(II) alkoxide is thermal treatment (i.e., sublimation at excessive temperatures). There are some reports in which pure lead alkoxide compounds, when refluxed in toluene, produced aggregates with  $\mu_4\text{-O}$  functionalities at their center.<sup>4,7</sup> Though major products of thermal decomposition can be isolated and characterized by a number of techniques (i.e., multinuclear NMR, X-ray crystallography, elemental analysis, etc.), the organic products of decomposition often remain poorly characterized,<sup>5,7</sup> or completely uncharacterized.<sup>4,6</sup> There is thus a need for better understanding of the decomposition products and mechanisms. With such fundamental knowledge, this “decomposition” route could become useful in the production of heterometallic precursors containing bridging oxo ligands.

We report here results which are consistent with proton transfer concurrent with O/C bond heterolysis in the rate determining step for oxo formation and that this is facilitated by the presence of electrophilic Zr(IV). It is *not* a facile reaction of Pb(II)/ $\text{O}^i\text{Bu}$  species in the absence of Zr(IV).

## Experimental Section

All manipulations were carried out under an atmosphere of dry nitrogen or argon using standard Schlenk techniques. All solvents were dried appropriately and distilled prior to use and stored over molecular sieves under dry nitrogen. A 5.4 M azeotrope of  $\text{HO}^i\text{Bu}$  in heptane was prepared by distillation of  $\text{HO}^i\text{Bu}$  in excess heptane. This azeotrope was stored under nitrogen over 3 Å molecular sieves prior to use.  $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$  was prepared at room temperature as a slight modification

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to the literature procedure<sup>16</sup> and used in its crystalline form. Zr(O'Bu)<sub>4</sub> was prepared according to a modification of the literature procedure<sup>17</sup> using Zr(NMe<sub>2</sub>)<sub>4</sub>.<sup>18</sup> Coordinated amine was removed by distillation of the product under dynamic vacuum (80 °C, 10<sup>-2</sup> Torr). In all hydrolyses, <sup>17</sup>OH<sub>2</sub> was used (40 atom % enrichment, Iso-Yeda Corp., Rehovot, Israel). Reactions with isotopically normal H<sub>2</sub>O were executed analogously. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian XL300 or a Bruker AM500 spectrometer, and chemical shifts were referenced to the protio impurity or <sup>13</sup>C signal of the solvent, respectively. <sup>17</sup>O NMR was recorded on an AM500 spectrometer at 67.8 MHz with neat H<sub>2</sub>O (δ = 0.0 ppm) as an external reference. <sup>207</sup>Pb NMR spectra were recorded on a Bruker AM500 spectrometer at 104 MHz with chemical shifts referenced to neat PbEt<sub>4</sub> (δ = 73.3 ppm relative to PbMe<sub>4</sub> = 0)<sup>19</sup> as an external standard with positive shifts being to higher frequencies. Elemental analyses were performed by Desert Analytics.

**Synthesis of [Pb(O'Bu)<sub>2</sub>]<sub>3</sub>.** This is a modest modification of the synthesis in ref 14. Pb[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (7.34 g, 13.9 mmol) was dissolved in 5 mL of pentane, and addition of HO'Bu azeotrope (5.6 mL, 30 mmol) resulted in an exothermic reaction producing a clear, colorless solution. The reaction was stirred 5 min, and the volatiles were then removed *in vacuo*. A cold finger was added to the vessel, and [Pb(O'Bu)<sub>2</sub>]<sub>3</sub> (4.74 g, 96%) sublimed at 95 °C and 10<sup>-2</sup> Torr. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.44 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 71.5 (s, C(CH<sub>3</sub>)<sub>3</sub>), 36.1 (s, C(CH<sub>3</sub>)<sub>3</sub>). <sup>207</sup>Pb NMR (toluene-*d*<sub>8</sub>, 60 °C) δ 2050 (v br, Pb<sup>a</sup>, see I); (toluene-*d*<sub>8</sub>, 25 °C) δ 2044 (s, ν<sup>1/2</sup> = 700 Hz, Pb<sup>a</sup>), -417 ppm (s, ν<sup>1/2</sup> = 2260 Hz, Pb<sup>b</sup>); (toluene-*d*<sub>8</sub>, -45 °C) δ 2032 (s, Pb<sup>a</sup>, satellite intensity = 22%, d, <sup>2</sup>J<sub>Pb-Pb</sub> = 690 Hz), -314 (s, Pb<sup>b</sup>, satellite intensity = 43%, d, <sup>2</sup>J<sub>Pb-Pb</sub> = 690 Hz).

We investigated the interaction of Li<sup>o</sup>Bu with [Pb(O'Bu)<sub>2</sub>]<sub>3</sub> and find formation of an adduct, LiPb(O'Bu)<sub>3</sub>, which shows one O'Bu environment by both <sup>1</sup>H and <sup>13</sup>C NMR. The unit cell shows this material to be isomorphous with Li<sub>2</sub>Sn<sub>2</sub>(O'Bu)<sub>6</sub>, whose structure<sup>20</sup> has no terminal alkoxides. Pure Li<sub>2</sub>Pb<sub>2</sub>(O'Bu)<sub>6</sub> was refluxed in toluene for 3 days with no evidence of decomposition (by <sup>1</sup>H NMR).

**Synthesis of Pb<sub>4</sub><sup>17</sup>O(O'Bu)<sub>6</sub>.** A solution of <sup>17</sup>OH<sub>2</sub> (37 μL, 2.2 mmol, 5% stoichiometric excess) in 20 mL of THF was slowly cannula transferred into a solution of [Pb(O'Bu)<sub>2</sub>]<sub>3</sub> (3.00 g, 8.49 mmol) in 20 mL of THF. This gave a clear, colorless solution which was stirred 24 h. The solvent was then removed *in vacuo* to produce a frothy liquid which eventually dried to a white solid. A cold finger was added to the flask, and Pb<sub>4</sub><sup>17</sup>O(O'Bu)<sub>6</sub> (2.13 g, 78% yield) sublimed at 125 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.35 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 70.5 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.7 (s, C(CH<sub>3</sub>)<sub>3</sub>). <sup>207</sup>Pb NMR (toluene-*d*<sub>8</sub>, 25 °C): δ 1166 (s, intensity = 92%; satellite intensity = 8%, sextet, <sup>1</sup>J<sub>Pb-O</sub> = 428 Hz). <sup>17</sup>O NMR (toluene-*d*<sub>8</sub>, 25 °C): δ intensity (calc; obs) 207 (0.4%; 1%), 204, (4.5%; 4.4%), 201, (22.2%, 21.4%), 198, (45.8%; 45.2%) (ν<sup>1/2</sup> = 20 Hz, <sup>1</sup>J<sub>Pb-O</sub> = 428 Hz) 195 (22.2%; 21.4%), 191, (4.5%; 4.4%), 188, (0.4%, 1%). MS (EI, 15 eV): m/z<sup>+</sup> Pb<sub>4</sub>O(O'Bu)<sub>6</sub><sup>+</sup> (18%), Pb<sub>4</sub>O(O'Bu)<sub>5</sub><sup>+</sup> (100%), Pb<sub>3</sub>O(O'Bu)<sub>5</sub><sup>+</sup> (43%). Anal. Calcd for Pb<sub>4</sub>O<sub>7</sub>C<sub>24</sub>H<sub>54</sub>: C, 22.45; H, 4.24. Found: C, 21.30; H, 4.17.

**Synthesis of Pb<sub>6</sub><sup>17</sup>O<sub>4</sub>(O'Bu)<sub>4</sub>.** A solution of <sup>18</sup>OH<sub>2</sub> (99 μL, 6.0 mmol, 5% stoichiometric excess) in 20 mL of THF was slowly cannula transferred into a solution of [Pb(O'Bu)<sub>2</sub>]<sub>3</sub> (3.00 g, 8.49 mmol) in 20 mL of THF. This gave a clear, colorless solution which was stirred 24 h at 25 °C. The solvent was removed *in vacuo* and the resulting solid was dissolved in pentane to give a slightly turbid solution. This was filtered through Celite, and the solvent was removed *in vacuo* to leave Pb<sub>6</sub><sup>17</sup>O<sub>4</sub>(O'Bu)<sub>4</sub> (2.17 g, 96%), a powdery, white solid. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.19 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 69.5 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.8 (s, C(CH<sub>3</sub>)<sub>3</sub>). <sup>207</sup>Pb (toluene-*d*<sub>8</sub>, 25 °C): δ 2015. <sup>17</sup>O NMR (toluene-*d*<sub>8</sub>, 25 °C): δ 228 (ν<sup>1/2</sup> = 440 Hz) with doublet satellites at 231 and 225 ppm. Anal. Calcd for Pb<sub>6</sub>O<sub>8</sub>C<sub>16</sub>H<sub>36</sub>: C, 12.00; H, 2.26. Found: C, 11.86; H, 2.32.

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**Table 1.** Crystallographic Data for Pb<sub>3</sub>ZrO(O'Bu)<sub>8</sub>

chemical formula	Pb <sub>3</sub> ZrO <sub>9</sub> C <sub>32</sub> H <sub>72</sub>	space group	<i>Pbc</i> 2 <sub>1</sub>
<i>a</i> , Å	16.663(2)	<i>T</i> , °C	-174
<i>b</i> , Å	12.608(1)	<i>λ</i> , Å	0.71069
<i>c</i> , Å	21.117(2)	<i>ρ</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.967
<i>V</i> , Å <sup>3</sup>	4436.46	<i>μ</i> (Mo Kα), cm <sup>-1</sup>	117.1
<i>Z</i>	4	<i>R</i>	0.0473
formula wt	1313.74	<i>R</i> <sub>w</sub>	0.0426

<sup>a</sup> *R* = Σ(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)/Σ|*F*<sub>o</sub>|. <sup>b</sup> *R*<sub>w</sub> = [Σw(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)<sup>2</sup>/Σw|*F*<sub>o</sub>|<sup>2</sup>]<sup>1/2</sup> where *w* = 1/σ<sup>2</sup>(|*F*<sub>o</sub>|).

**Synthesis of Pb<sub>3</sub>ZrO(O'Bu)<sub>8</sub>.** [Pb(O'Bu)<sub>2</sub>]<sub>3</sub> (0.69 g, 0.65 mmol) and Zr(O'Bu)<sub>4</sub> (0.25 g, 0.65 mmol) were dissolved together in toluene. After a 24-h reflux, the solvent was removed *in vacuo* to yield a cream-colored solid. Crystallization from ether at -20 °C gave 0.39 g (41%) of colorless rhomboids. X-ray quality crystals were grown from ether in the same manner. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.63 (s, 9H), 1.58 (s, 36H), 1.31 (s, 27). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 75.6 (s, C(CH<sub>3</sub>)<sub>3</sub>), 72.5 (s, C(CH<sub>3</sub>)<sub>3</sub>), 71.0 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.2<sup>21</sup> (s, C(CH<sub>3</sub>)<sub>3</sub>), 34.9<sup>21</sup> (s, C(CH<sub>3</sub>)<sub>3</sub>), 34.0 (s, C(CH<sub>3</sub>)<sub>3</sub>). <sup>207</sup>Pb NMR (toluene-*d*<sub>8</sub>, 25 °C): δ 1066. <sup>17</sup>O NMR (toluene-*d*<sub>8</sub>, 25 °C): δ, intensity (calc; obs) 203 (3%; 3%), 200, (21%; 21%), 197, (53%; 53%) (ν<sup>1/2</sup> = 79 Hz, <sup>1</sup>J<sub>Pb-O</sub> = 429 Hz), 194 (21%; 21%), 191, (3%, 3%). Anal. Calcd for Pb<sub>3</sub>ZrO<sub>9</sub>C<sub>32</sub>H<sub>72</sub>: C, 29.26; H, 5.52. Found: C, 29.36; H, 5.32.

**X-ray Structure Determination of Pb<sub>3</sub>ZrO(O'Bu)<sub>8</sub>.** A small well-formed crystal was cleaved from a larger, nearly square plate. The fragment was then affixed to the end of a glass fiber using silicone grease and transferred to the goniostat where it was cooled to -174 °C for characterization and data collection. Standard inert atmosphere handling techniques were used throughout the investigation. Three different data sets were taken on several different preparations of the sample because of the problems encountered (see below). A systematic search of a limited hemisphere of reciprocal space located a set of reflections with orthorhombic symmetry and systematic absences corresponding to one of the space groups *Pbcm* or *Pbc*2<sub>1</sub>. Subsequent solution and refinement of the structure confirm the noncentrosymmetric *Pbc*2<sub>1</sub> to be the proper space group. Data were collected<sup>22</sup> (6° < 2θ < 45°) using standard moving crystal, moving detector technique with fixed background counts at each extreme of the scan. Data (Table 1) were corrected for Lorentz and polarization terms, as well as absorption (analytical method, transmission factors 0.063–0.225). Early attempts to solve the structure met with no success. While possible metal positions were readily located using both SHELXT-PC and MULTAN78, attempts to refine them were unsuccessful. It was finally possible to attain convergence by using the least squares in SHELX with a damping factor on the refinement. Only the metal atoms were refined anisotropically and hydrogen atoms were placed in fixed, idealized positions for the final cycles of undamped refinement. Attempts to solve and refine the structure in a higher symmetry space group were unsuccessful. The absolute structure was determined for the particular crystal studied; *R* factors for the enantiomorph were 0.0634 and 0.0613. A final difference Fourier was essentially featureless, the largest peak being 0.74 e/Å<sup>3</sup>. The results are shown in Table 2 and supporting information, as well as Figure 1.

## Results

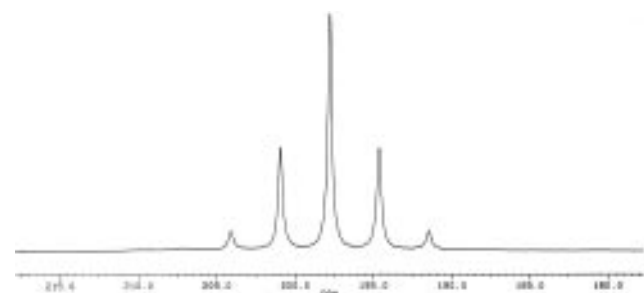
**Stability and Aggregation of [Pb(O'Bu)<sub>2</sub>]<sub>n</sub>.** It has been reported<sup>5</sup> that attempted sublimation of [Pb(O'Bu)<sub>2</sub>]<sub>3</sub> at 200 °C (the compound sublimes in vacuum as low as 90 °C) yields only Pb<sub>4</sub>O(O'Bu)<sub>6</sub>. We have not been able to confirm these findings, and have only observed that pure [Pb(O'Bu)<sub>2</sub>]<sub>3</sub> sublimed unchanged at 200 °C and 10<sup>-2</sup> Torr. It has been subsequently reported that this transformation is not simply thermolysis, but can be impurity-promoted.<sup>14</sup> We find that [Pb(O'Bu)<sub>2</sub>]<sub>3</sub> can be refluxed for 2 days in toluene (110 °C) with essentially no change, and that added Pb metal does not alter this result. However, addition of 90 mol % of <sup>t</sup>BuOH (a

(21) Coupling to <sup>207</sup>Pb is apparent, yet broadened due to fluxionality.

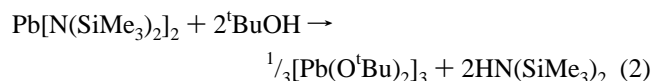
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**Table 2.** Selected Bond Distances (Å) and Angles (deg) for  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$ 

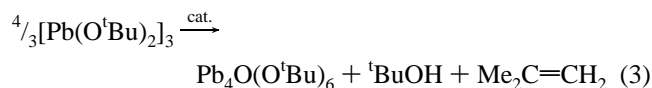
Pb(1)–O(5)	2.26(3)	Pb(2)–O(11)	2.29(3)	Zr(4)–O(5)	2.23(4)
Pb(1)–O(11)	2.28(3)	Pb(2)–O(26)	2.50(3)	Zr(4)–O(6)	2.32(3)
Pb(1)–O(6)	2.55(3)	Pb(2)–O(36)	2.62(4)	Zr(4)–O(16)	2.02(3)
Pb(1)–O(31)	2.51(3)	Pb(3)–O(5)	2.15(4)	Zr(4)–O(21)	1.98(3)
Pb(1)–O(41)	2.67(3)	Pb(3)–O(26)	2.18(3)	Zr(4)–O(36)	2.04(3)
Pb(2)–O(5)	2.26(3)	Pb(3)–O(31)	2.19(3)	Zr(4)–O(41)	2.08(3)
Pb(2)–O(6)	2.53(3)				
O(5)–Pb(1)–O(11)	76.4(10)	O(5)–Zr(4)–O(36)	80.4(13)		
O(5)–Pb(2)–O(11)	76.2(10)	O(5)–Zr(4)–O(41)	83.0(12)		
O(5)–Pb(1)–O(6)	61.0(10)	O(6)–Zr(4)–O(16)	100.3(12)		
O(5)–Pb(1)–O(11)	76.4(10)	O(6)–Zr(4)–O(21)	154.8(14)		
O(5)–Pb(1)–O(31)	69.4(9)	O(6)–Zr(4)–O(36)	81.0(12)		
O(5)–Pb(1)–O(41)	70.2(10)	O(6)–Zr(4)–O(41)	80.8(12)		
O(6)–Pb(1)–O(11)	71.7(10)	O(16)–Zr(4)–O(21)	104.9(13)		
O(6)–Pb(1)–O(31)	129.6(9)	O(16)–Zr(4)–O(36)	97.3(14)		
O(6)–Pb(1)–O(41)	66.0(11)	O(16)–Zr(4)–O(41)	95.7(14)		
O(11)–Pb(1)–O(31)	89.4(10)	O(21)–Zr(4)–O(36)	95.3(14)		
O(11)–Pb(1)–O(41)	135.0(10)	O(21)–Zr(4)–O(41)	96.9(14)		
O(31)–Pb(1)–O(41)	105.7(11)	O(36)–Zr(4)–O(41)	159.2(12)		
O(5)–Pb(2)–O(26)	68.8(12)	Pb(1)–O(5)–Pb(2)	100.8(8)		
O(11)–Pb(2)–O(26)	87.5(11)	Pb(1)–O(5)–Pb(3)	111.2(15)		
O(5)–Pb(2)–O(6)	61.4(10)	Pb(1)–O(5)–Zr(4)	101.0(14)		
O(5)–Pb(2)–O(11)	76.2(10)	Pb(2)–O(5)–Pb(3)	111.6(14)		
O(5)–Pb(2)–O(26)	68.8(12)	Pb(2)–O(5)–Zr(4)	100.9(14)		
O(5)–Pb(2)–O(36)	68.5(11)	Pb(3)–O(5)–Zr(4)	127.8(10)		
O(6)–Pb(2)–O(11)	71.6(10)	Zr(4)–O(6)–C(7)	126.2(28)		
O(6)–Pb(2)–O(26)	129.1(9)	Pb(1)–O(11)–Pb(2)	99.1(11)		
O(6)–Pb(2)–O(36)	66.7(11)	Pb(1)–O(11)–C(12)	127(3)		
O(11)–Pb(2)–O(26)	87.5(11)	Pb(2)–O(11)–C(12)	132(3)		
O(11)–Pb(2)–O(36)	134.7(11)	Zr(4)–O(16)–C(17)	166.7(27)		
O(26)–Pb(2)–O(36)	104.6(9)	Zr(4)–O(21)–C(22)	179(3)		
O(5)–Pb(3)–O(26)	76.9(11)	Pb(2)–O(26)–Pb(3)	102.3(13)		
O(5)–Pb(3)–O(31)	77.8(12)	Pb(2)–O(26)–C(27)	129.6(26)		
O(26)–Pb(3)–O(31)	99.7(11)	Pb(3)–O(26)–C(27)	125.7(26)		
O(5)–Zr(4)–O(6)	65.4(11)	Pb(3)–O(31)–C(32)	125(3)		
O(5)–Zr(4)–O(16)	165.7(10)	Zr(4)–O(36)–C(37)	147(3)		
O(5)–Zr(4)–O(21)	89.4(12)	Zr(4)–O(41)–C(42)	149(3)		

**Figure 1.**  $^{17}\text{O}$  NMR of  $\text{Pb}_4^{17}\text{O}(\text{O}^i\text{Bu})_6$  showing seven of the nine expected lines arising from coupling to four possible  $^{207}\text{Pb}$  atoms at natural abundance.

potential impurity by accidental hydrolysis of  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  catalyzes low conversion (5%) to  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  after 36 h at 110 °C in toluene. Synthesis according to eq 2 gives  $\text{HN}(\text{SiMe}_3)_2$



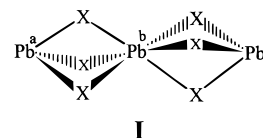
as a product (and thus a possible impurity in  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$ ). We have therefore evaluated 30 mol % of  $\text{HN}(\text{SiMe}_3)_2$  as a catalyst for the conversion in eq 3. We find, after 36 h at reflux in



toluene, even greater conversion to the oxo compound than by  $^t\text{BuOH}$ . Finally, we evaluated possible base catalysis of eq 3

by treating  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  with 20 mol % of  $\text{LiNMe}_2$ . Already at 25 °C, there is  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$ ,  $\text{HNMe}_2$ , isobutylene, and a broad  $^1\text{H}$  NMR signal we assign to the interaction of  $\text{HO}^i\text{Bu}$ ,  $\text{Pb}(\text{O}^i\text{Bu})_2$ , and  $\text{LiO}^i\text{Bu}$ ; subsequent heating gives further conversion to  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$ . Further, there is no sign of thermal decomposition of  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  in the presence of a trace or stoichiometric amount of  $\text{LiO}^i\text{Bu}$  after 3 days of reflux in toluene (see Experimental Section). We therefore suggest that unreacted  $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$  or  $\text{HN}(\text{SiMe}_3)_2$  as impurities can have an undesired effect on the isolation of  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  involving elevated temperature (e.g., sublimation, crystallization from a high-temperature solution).

A previously reported quantitative synthesis<sup>5</sup> of  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  involves reacting  $^t\text{BuOH}$  with a concentrated pentane solution of  $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$  (as in eq 2) at room temperature, whereas pure  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  is reportedly formed at lower temperatures ( $\sim -70$  °C) from dilute solutions. We have found that not only low-temperature dilute solutions but also concentrated solutions at room temperature give predominately pure  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  and suspect that the trace quantities of  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  we detected in our samples result from adventitious water (from solvents, etc.).<sup>23</sup>



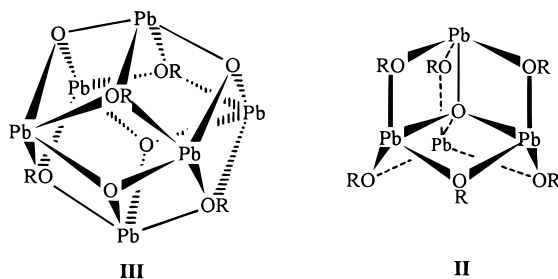
We require knowledge of the degree of aggregation of  $[\text{Pb}(\text{O}^i\text{Bu})_2]_n$  in toluene solution. In the solid state, it has structure **I**.<sup>14,15</sup> Since this trimer has equivalent  $^1\text{H}$  and  $^{13}\text{C}$  environments, these nuclei are not very useful for solution characterization, while the inequivalent lead centers provide a more appealing way to distinguish dimer from trimer. The 41.8-MHz  $^{207}\text{Pb}$  NMR spectrum of  $[\text{Pb}(\text{O}^i\text{Bu})_2]_n$  in toluene solution has been reported<sup>5</sup> to be a singlet at 1191 ppm relative to  $\text{PbMe}_4$ .<sup>24</sup> We find, at a higher frequency (104 MHz), that the spectrum consists of two broad signals at 25 °C; an intense signal is found at 2044 ppm ( $\text{Pb}^a$ ) and a broader, weaker signal is observed at  $-417$  ppm ( $\text{Pb}^b$ ). Both signals show satellites in the  $-45$  °C spectrum due to  $\text{Pb}^a$ – $\text{Pb}^b$  coupling (see **D**), and due to its lower population and the onset of a dynamic process, the  $-417$ -ppm peak is slightly broader than the 2044-ppm peak. In going to higher temperatures, the lines broaden further so that, at  $+60$  °C, the 2044-ppm peak is very broad and the  $-417$ -ppm peak is broadened into the noise. These results are wholly in agreement with the presence in solution of trimer **I**, together with the occurrence of a fluxional process which interchanges the three- and the six-coordinate lead sites.

The nuclearity of  $[\text{Pb}(\text{O}^i\text{Bu})_2]_n$  has been previously reported to be 2.6, measured cryoscopically in benzene,<sup>14</sup> and  $\sim 1.8$  when measured by the Signer method at room temperature in benzene.<sup>5</sup> These data suggest a dimeric species at higher temperature, and an equilibrium between dimer and trimer at lower temperature. At 25 °C and higher, our  $^{207}\text{Pb}$  NMR measurements show an additional sharp signal of low intensity at 1770 ppm which may possibly arise from the presence of  $[\text{Pb}(\text{O}^i\text{Bu})_2]_2$ .

(23) Since  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  and  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  have essentially the same  $^1\text{H}$  NMR chemical shift in  $\text{C}_6\text{D}_6$ , detecting the one in the presence of the other demands  $^{13}\text{C}\{^1\text{H}\}$  NMR (or  $^{207}\text{Pb}$ ) assay. The  $^1\text{H}$  NMR is also less reliable because the chemical shift is somewhat influenced by the presence of free  $^t\text{BuOH}$ .

(24) The actual reported value for  $\text{Pb}(\text{O}^i\text{Bu})_2$  was 4152 ppm with  $\text{Pb}(\text{NO}_3)_2$  as an external zero reference. When calculated with respect to  $\text{PbMe}_4$  as a zero reference ( $\text{Pb}(\text{NO}_3)_2$  is found at  $-2961$  ppm relative to  $\text{PbMe}_4$ —see ref 19), its chemical shift is 1191 ppm.

**Pb/Oxo/Alkoxides.** (a) **Synthesis.** This work offers rational and efficient synthesis to two lead oxoalkoxides by addition of stoichiometric water (with a 5% excess) in THF to a solution of  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$ . The reactions giving  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  (**II**) or  $\text{Pb}_6\text{O}_4(\text{O}^i\text{Bu})_4$  (**III**) remain as clear, colorless solutions through-

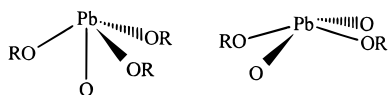


out the addition of  $\text{H}_2\text{O}$ . We have found that, if the order of addition is reversed (i.e., the  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  solution is added to the  $\text{H}_2\text{O}$  solution), the synthesis of each proceeds through a stage where a white precipitate forms, and then dissolves, by further



reaction with  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$ . For the reaction giving  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$ , the precipitate formed dissolves at room temperature. However, in the synthesis of  $\text{Pb}_6\text{O}_4(\text{O}^i\text{Bu})_4$ , a 24-h reflux is required for complete dissolution of the solid. Since the compounds  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  and  $\text{Pb}_6\text{O}_4(\text{O}^i\text{Bu})_4$  trace a steep decline in the  $^i\text{BuO}:\text{Pb}$  ratio, one can imagine that other oxoalkoxide compounds exist at higher aggregation levels, and that one (or more) of these (and not  $\text{PbO}$  itself) is the white precipitate:  $\text{Pb}_a\text{O}_b(\text{OR})_{2(a-b)}$ . In fact, we have not seen any sign of reaction between  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  and  $\text{PbO}$  in independent experiments in polar solvents. To confirm that  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  indeed reacts with an oxoalkoxide of higher aggregation to form one of lower aggregation, we combined the reactants (1:10 mole ratio) as shown in eq 4. After warming these reagents in toluene at  $40^\circ\text{C}$  for 5 min,  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  is indeed formed by an oxo redistribution reaction. This represents conversion of  $\mu_3$ - to  $\mu_4$ -O groups, and demonstrates the residual Lewis basicity of the oxide groups in  $\text{Pb}_6\text{O}_4(\text{O}^i\text{Bu})_4$ .

The two hydrolytic syntheses we report here furnish each of the two products with very little detectable impurity oxoalkoxides. This indicates thermodynamic stability of these aggregates. Both are *closo*, and both have four-coordinate pyramidal geometries for their Pb centers; these geometries are apparently favorable for Pb, in part because they furnish a location for the metal lone pair. Each structure also has equivalent geometries for its 4 or 6 metal centers in solution.



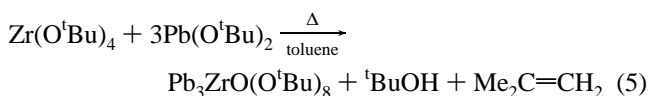
(b) **NMR Spectroscopy.** The  $^{207}\text{Pb}$  NMR spectrum for  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  consists of a single peak at 1166 ppm. This molecule, having  $T_d$  symmetry (**II**), has four equivalent metals and six equivalent alkoxides. When  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  is reacted with  $^{17}\text{OH}_2$  to give  $\text{Pb}_4^{17}\text{O}(\text{O}^i\text{Bu})_6$ , the central  $^{207}\text{Pb}$  NMR signal is flanked by six new equal-intensity signals which result from  $^{207}\text{Pb}-^{17}\text{O}$  ( $I = 5/2$ ) coupling with a spacing of 428 Hz. The  $^{17}\text{O}$  NMR spectrum of the labeled species (Figure 1) shows seven of the nine lines expected for a  $\text{Pb}_4$  species: an overlapping singlet, doublet, triplet, quartet, and quintet centered on 198 ppm. The multiplicity observed arises from statistical combinations of the natural abundance of  $^{207}\text{Pb}$  (22%), and the

intensities found are wholly consistent (see Experimental Section) with four possible Pb centers, present in natural abundance, which couple to the central oxygen. The value of  $J(\text{Pb}-\text{O})$  is 428 Hz. Detecting the outer lines would require a signal-to-noise ratio in excess of 2300:1. The  $^{17}\text{O}$  NMR line width (20 Hz) is quite narrow and indicative of an isotropic (highly symmetric) charge density about the quadrupolar nucleus,  $^{17}\text{O}$ . This is consistent with the symmetry of this molecule.

The  $^{207}\text{Pb}$  NMR spectrum for  $\text{Pb}_6\text{O}_4(\text{O}^i\text{Bu})_4$  (**III**) shows a single strong signal at 2015 ppm. Its  $T_d$  symmetry causes it to have six equivalent metals and four equivalent  $^i\text{Bu}$  groups. Our  $^{207}\text{Pb}$  NMR spectrum also shows two very weak peaks further downfield (2034 and 2038 ppm), which we assign to traces of higher hydrolysis products. This spectrum shows *no* traces of  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  or  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$ . The  $^{17}\text{O}$  NMR spectrum for  $\text{Pb}_6^{17}\text{O}_4(\text{O}^i\text{Bu})_4$  consists of a single chemical shift centered at 228 ppm flanked by two lines of a doublet ( $J(\text{Pb}-\text{O}) = 310$  Hz) due to those isotopomers with one  $^{207}\text{Pb}$  adjacent to the  $\mu_3$ - $^{17}\text{O}$ . The signal arising for this  $\mu_3$ -O is found further downfield than for its  $\mu_4$ -O analog in  $\text{Pb}_4^{17}\text{O}(\text{O}^i\text{Bu})_6$ . Although both of these oxoalkoxides have the same molecular symmetry, the symmetry at the  $\mu_x$ -O is lower ( $C_{3v}$ ) in  $\text{Pb}_6^{17}\text{O}_4(\text{O}^i\text{Bu})_4$ , and this is apparent in its  $^{17}\text{O}$  NMR spectrum. The natural line width here is 440 Hz, and this is consistent with a less symmetric charge density about the  $\mu_3$ -O.

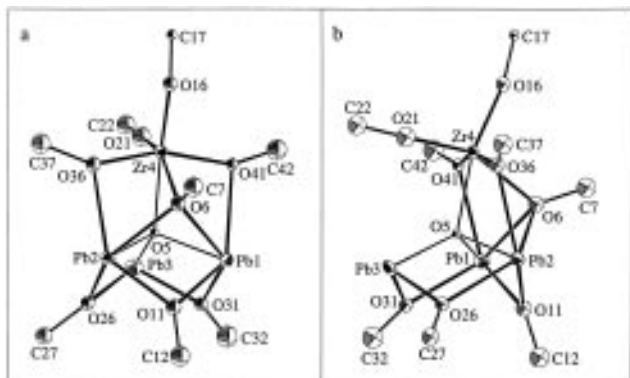
Our  $^{207}\text{Pb}$  NMR spectra of products apparently pure by  $^1\text{H}$  and  $^{13}\text{C}$  NMR criteria showed additional weak peaks, generally due to products of further hydrolysis (e.g.,  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  in  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$ ,  $\text{Pb}_6\text{O}_4(\text{O}^i\text{Bu})_4$  in  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$ ). As the degree of hydrolysis (the  $\mu_x$ -O:Pb ratio) increases, the Pb:OR ratio increases and thus  $^1\text{H}$  and  $^{13}\text{C}$  NMR become less reliable for detecting impurities. We suggest that this, together with the necessity to scan multiple chemical shift "windows" on the very broad  $^{207}\text{Pb}$  chemical shift range ( $\sim 2500$  ppm), is the cause of the disagreement between our  $^{207}\text{Pb}$  chemical shifts and those reported previously<sup>5</sup> for  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  and for  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$ . We are confident about the numbers we report here.

**Thermolytic Heterometallic Oxo Formation.** Refluxing a toluene solution of  $\text{Zr}(\text{O}^i\text{Bu})_4$  and  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  for 24 h causes conversion to a molecule whose  $^1\text{H}$  NMR spectrum shows three singlets of relative intensity 1:4:3 down to  $-80^\circ\text{C}$ . Both isobutylene and  $^i\text{BuOH}$  are also produced ( $^1\text{H}$  NMR evidence). While some of this product results when the Zr:Pb ratio is  $n:3$  with  $n > 1$ , the balanced synthetic reaction is eq 5, and the reaction thus is best carried out with a 1:3 Zr:Pb stoichiometry.



**Structure of  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$ .** The solid-state structure of  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$  shows a molecule with a  $\text{Pb}_3\text{ZrO}$  core which is significantly distorted from tetrahedral geometry (Figure 2). The  $\text{Pb}_3(\text{O}^i\text{Bu})_3$  unit, with three  $\mu_2$ -O $^i\text{Bu}$  groups bridging the lead centers, has approximate  $C_3$  symmetry. This unit is capped by zirconium (thus the oxo ligand has  $\mu_4$  functionality), but the six-coordinate Zr lies off the 3-fold axis (Figure 2) of the Pb unit in a manner which allows it to bridge two Pb centers with three of "its" O $^i\text{Bu}$  ligands: two are  $\mu_2$ -O $^i\text{Bu}$  and one is  $\mu_3$ -O $^i\text{Bu}$ . Since the  $\text{Zr}(\text{O}^i\text{Bu})_5$  unit has three O $^i\text{Bu}$  ligands involved in bridging, two O $^i\text{Bu}$  ligands are terminal, with one being *trans* to the  $\mu_4$ -O and the other *trans* to the  $\mu_3$ -O $^i\text{Bu}$ .

The skeleton of this molecule bears some resemblance to the adamantane framework (**II**) commonly found for homometallic lead oxoalkoxides<sup>4,6</sup> such as  $\text{Pb}_4\text{O}(\text{OSiPh}_3)_6$ .<sup>4</sup> The central  $\mu_4$ -O



**Figure 2.** ORTEP drawing of  $\text{Pb}_3\text{ZrO}(\text{O}^t\text{Bu})_8$ , with methyl groups omitted for clarity. (a) View showing Zr octahedron capping the basal  $\text{Pb}_3$  unit. (b) View of  $\text{Pb}_3\text{ZrO}(\text{O}^t\text{Bu})_8$ , rotated  $90^\circ$  about a vertical axis from (a), showing the geometry about the  $\mu_4$ -O ligand and showing the three-coordinate geometry of the unique  $\text{Pb}_3$ .

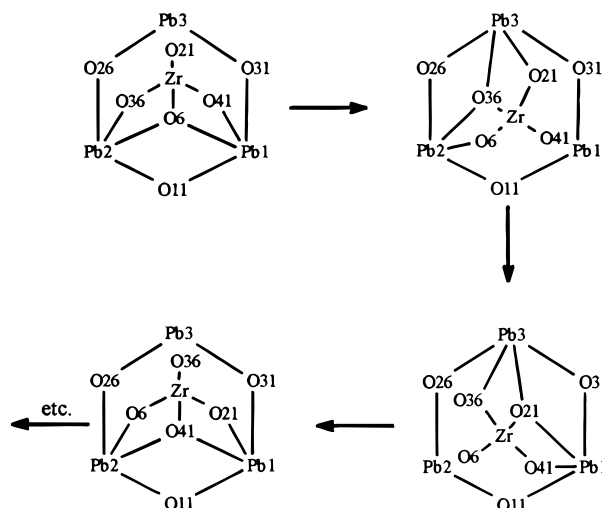
of  $\text{Pb}_3\text{ZrO}(\text{O}^t\text{Bu})_8$  is nearly equidistant (2.15(4)–2.26(3) Å) from all four metals, with distances being quite similar to  $\mu_4$ -O–Pb distances in  $\text{Pb}_4\text{O}(\text{OSiPh}_3)_6$  (2.25(1)–2.31(1) Å). While the  $\mu_4$ -O of  $\text{Pb}_4\text{O}(\text{OSiPh}_3)_6$  is nearly tetrahedral (Pb–O–Pb =  $106.78$ – $112.24^\circ$ ), the central oxygen of  $\text{Pb}_3\text{ZrO}(\text{O}^t\text{Bu})_8$  is more distorted from tetrahedral. Of the angles with the  $\mu_4$ -O at the vertex ( $100.8(8)$ – $111.6(1)^\circ$ ), the largest is from Zr to the unique lead (Zr4–O5–Pb3 =  $126.2(3)^\circ$ ). Due to  $\mu_2$ - and  $\mu_3$ -O<sup>t</sup>Bu bridging to only two of the three leads, coordination numbers at lead are 5 (Pb1), 5 (Pb2), and 3 (Pb3). Pb3 is pyramidal (angles sum to  $254^\circ$ ), indicative of a stereochemically-active lone pair which occupies the fourth site of its distorted tetrahedral environment. Both Pb1 and Pb2 are inverted square-pyramidal (i.e., Pb “below” the base) with equatorial ligands being  $\mu_2$ - and  $\mu_3$ -O<sup>t</sup>Bu groups (angles sum to  $333^\circ$  for ligands on Pb1 and  $331^\circ$  for ligands on Pb1 and Pb2, respectively) and the axial position occupied by the  $\mu_4$ -O.

The two five-coordinate leads are related by an idealized mirror plane of symmetry passing through both terminal alkoxides, Pb3, Zr4, and O5, O6, and O11. With two different lead coordination numbers present, there is a distortion in the  $\text{Pb}_3(\text{O}^t\text{Bu})_3$  six-membered ring. Four shorter (2.18(3), 2.19(3), 2.28(3), and 2.29(3) Å) and two longer (2.50(3) and 2.51(4) Å) Pb–O bonds are present. The longer of these distances are similar to those from lead to the  $\mu_3$ -O<sup>t</sup>Bu group (2.53(4) and 2.55(4) Å). The longest bonds in the molecule are those from lead to O36 and O41 (2.62(4) and 2.67(3) Å) which are bound strongly to Zr.

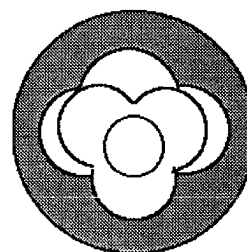
$\text{Pb}_3\text{ZrO}(\text{O}^t\text{Bu})_8$  has a framework similar to  $\text{Pb}_2\text{Ti}_2\text{O}(\text{O}^i\text{Pr})_{10}$ <sup>25</sup> when considering the coordination geometry at Zr and Ti. Around the M(IV) atom, both aggregates have a unique terminal OR ligand *trans* to the  $\mu_4$ -O, and have four equatorial OR groups where one is  $\mu_3$ , two are  $\mu_2$ , and one is terminal. Both molecules closely follow the same trends in bonding, where M– $\mu_3$ -OR bonds (M = Pb, Ti, Zr) are longer than the M– $\mu_2$ -OR bonds which are in turn longer than the M-terminal–OR bonds. In fact, bonds which are comparable between these molecules are systematically within 0.2 Å of each other.

**Solution Structure and Spectroscopy of  $\text{Pb}_3\text{ZrO}(\text{O}^t\text{Bu})_8$ .**  $\text{Pb}_3\text{ZrO}(\text{O}^t\text{Bu})_8$  exhibits three chemical environments of relative intensity 1:4:3 in both its <sup>1</sup>H and <sup>13</sup>C NMR spectra in  $\text{C}_6\text{D}_6$  at 25 °C. These we assign to the unique axial O<sup>t</sup>Bu group on Zr, the equatorial O<sup>t</sup>Bu groups on Zr, and the three O<sup>t</sup>Bu groups contained in the  $\text{Pb}_3(\text{O}^t\text{Bu})_3$  ring. It is particularly interesting

### Scheme 1



### Scheme 2



that intensities of four and three can exist in the same molecule since 4-fold and 3-fold rotational symmetry are mutually incompatible. Some fluxional process is implied.

Averaged <sup>207</sup>Pb coupling to two of the three kinds of methyl carbons (i.e., coupling is seen only in those alkoxides which are connected directly to, or come in contact with, Pb) in the <sup>13</sup>C NMR spectrum of  $\text{Pb}_3\text{ZrO}(\text{O}^t\text{Bu})_8$  indicates that the fluxionality is *intramolecular*. Thus, a possible mechanism (Scheme 1; not shown are the  $\mu_4$ -O and the terminal O<sup>t</sup>Bu) involves “precession” of the ( $\mu_4$ -O)–Zr–Ot vector. This would be accomplished by “rocking” and a small migration of the Zr–(O<sup>t</sup>Bu)<sub>5</sub> unit around the ideal C<sub>3</sub> axis of the  $\text{Pb}_3(\text{O}^t\text{Bu})_3$  ring. This accomplishes a time-averaged signal for the  $\mu_3$ -O<sup>t</sup>Bu,  $\mu_2$ -O<sup>t</sup>Bu, and equatorial t-O<sup>t</sup>Bu ligands without ever exchanging them with the unique terminal O<sup>t</sup>Bu ligand (not shown in Scheme 1) *trans* to the  $\mu_4$ -O. The O<sup>t</sup>Bu groups in the  $\text{Pb}_3(\text{O}^t\text{Bu})_3$  ring and the Pb environments are also averaged by this motion.

Consistent with this conclusion, the 104-MHz <sup>207</sup>Pb NMR spectrum of  $\text{Pb}_3\text{ZrO}(\text{O}^t\text{Bu})_8$  in toluene is a sharp single line (1066 ppm) at 25 °C. By –70 °C, this single line is very broad (~12 ppm half-width), and at –90 °C (our low-temperature limit, based on diminishing solubility), the spectrum is undetectably broad (i.e., is at decoalescence). This is consistent with the fluxional mechanism deduced from the <sup>1</sup>H NMR study, and with a low barrier to such migration. It is of interest that this “4-against-3” motion replicates that of an epitrochoid within a hypotrochoid (IV), the concept upon which the Wankel rotary engine<sup>26</sup> was commercialized (Scheme 2).

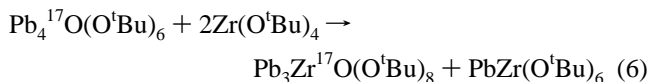
**Mechanism of Formation of  $\text{Pb}_3\text{ZrO}(\text{O}^t\text{Bu})_8$ .**  $\text{Zr}(\text{O}^t\text{Bu})_4$  is unchanged after 2 days reflux in toluene. Likewise,  $[\text{Pb}(\text{O}^t\text{Bu})_2]_3$  is recovered unchanged after 2 days reflux in toluene. The product of a 1:1 reaction between these two,  $\text{PbZr}(\text{O}^t\text{Bu})_6$ , is also unchanged after 2 days reflux in toluene.

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On the other hand, addition of  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  (2/3 molar equiv) to  $\text{PbZr}(\text{O}^i\text{Bu})_6$ <sup>27</sup> (1 molar equiv), followed by heating at reflux in toluene for 24 h gives  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$ . Since the 25 °C <sup>1</sup>H NMR spectrum of  $\text{PbZr}(\text{O}^i\text{Bu})_6$  in the presence of  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  shows no new species to be formed, the formation of  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$  must result from species which achieve only low concentration, and only at elevated temperature.

We have also found that, once an oxo ligand is formed, production of  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$  can take place at 25 °C. This is very much like the formation of  $\text{Pb}_2\text{Ti}_2\text{O}(\text{O}^i\text{Pr})_{10}$  at room temperature from  $\text{Pb}_4\text{O}(\text{O}^i\text{Pr})_6$  and  $\text{Ti}(\text{O}^i\text{Pr})_4$ .<sup>24</sup> The reaction in eq 6 is complete within the time of mixing in benzene at 25



°C. This indicates that O/C bond cleavage and C–H bond scission are probably the slow steps in eq 5. We propose that the rapid reaction of  $\text{Zr}(\text{O}^i\text{Bu})_4$  with  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  is initiated by the attack of Lewis acidic monomeric  $\text{Zr}(\text{O}^i\text{Bu})_4$  on a  $\mu_2$ -O<sup>i</sup>Bu oxygen. In contrast,  $\text{PbZr}(\text{O}^i\text{Bu})_6$ , where Zr is six-coordinate, does not react at 25 °C with  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$ . Only after 3 days at 130 °C does  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$  form from the coordinatively saturated  $\text{PbZr}(\text{O}^i\text{Bu})_6$  and  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$ .

The reaction of  $\text{Pb}_4^{17}\text{O}(\text{O}^i\text{Bu})_6$  with  $\text{Zr}(\text{O}^i\text{Bu})_4$  according to eq 6 was investigated by <sup>207</sup>Pb and <sup>17</sup>O NMR. After a solution of the reactants was stirred for 24 h in toluene-*d*<sub>8</sub>, the <sup>207</sup>Pb NMR spectrum showed that  $\text{Pb}_4^{17}\text{O}(\text{O}^i\text{Bu})_6$  no longer remained, and that two new signals, for  $\text{Pb}_3\text{Zr}^{17}\text{O}(\text{O}^i\text{Bu})_8$  and  $\text{PbZr}(\text{O}^i\text{Bu})_6$ , were present in an integral ratio of 3:1, respectively. The <sup>17</sup>O NMR spectrum showed five of the expected seven lines of a  $\text{Pb}_3$  species. Since the molecule is dynamically averaged ( $C_{3v}$  symmetry) at 25 °C, all line spacings are the same, and yield an averaged  $J(\text{Pb}–\text{O})$  value of 429 Hz. The two outermost lines remain unobserved, since they are only 1/500th of the intensity of the central line. The intensities of the observed lines agree with those calculated for three equivalent Pb nuclei, and thus confirm that we do not observe a  $\text{Pb}_n$  species with  $n \neq 3$  as the molecule present in solution. Although the chemical shift and <sup>207</sup>Pb–<sup>17</sup>O coupling (197 ppm, 429 Hz) are quite similar to those of  $\text{Pb}_4^{17}\text{O}(\text{O}^i\text{Bu})_6$  (198 ppm, 428 Hz), the difference is seen in the greater line width of  $\text{Pb}_3\text{Zr}^{17}\text{O}(\text{O}^i\text{Bu})_8$  (compare 79 Hz to 20 Hz). This is apparently due to the lower symmetry (ideally  $C_{3v}$  when the molecule is fluxional) at the  $\mu_4$ -O.

The relevance of the above results is that  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$ , if it is formed (eq 5) at 110 °C in toluene from  $\text{Pb}(\text{O}^i\text{Bu})_2$  and Zr-

(27) Vaartstra, B. A. *Mater. Res. Soc. Symp. Proc.* **1993**, 282, 689. Since  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  reacts immediately with  $\text{Zr}(\text{O}^i\text{Bu})_4$  at 25 °C in benzene to form  $\text{PbZr}(\text{O}^i\text{Bu})_6$ , this experiment is equivalent to mixing equimolar  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  with  $\text{Zr}(\text{O}^i\text{Bu})_4$ .

$(\text{O}^i\text{Bu})_4$ , would be immediately transformed to  $\text{Pb}_3\text{ZrO}(\text{O}^i\text{Bu})_8$ . It is also likely that any oxo lead species formed under these conditions would undergo similar conversion, since  $\text{O}^{2-}$  attached to Pb(II) would be expected to be electron-rich, and thus nucleophilic.

The remaining question is then the mechanism of generation of  $\text{O}^{2-}$ , isobutylene, and <sup>i</sup>BuOH in eq 5. Since proton transfer is implied by the observed products, a Brønsted basic O<sup>i</sup>Bu group is useful. Terminal O<sup>i</sup>Bu on Pb(II) would suffice. Such proton transfer must be concerted with O/C bond heterolysis, which, in turn, would be facilitated by that oxygen being attached to electrophilic metal centers, e.g., several Zr(IV). These ideas explain why  $\text{PbZr}(\text{O}^i\text{Bu})_6$  is thermally robust, since it lacks terminal O<sup>i</sup>Bu on Pb(II). Further mechanistic speculation seems imprudent.

## Conclusions

This work shows that the best routes to the species  $\text{Pb}_4\text{O}(\text{O}^i\text{Bu})_6$  and  $\text{Pb}_6\text{O}_4(\text{O}^i\text{Bu})_4$  employ hydrolysis. Moreover, we concur with an earlier report<sup>14</sup> that pure  $[\text{Pb}(\text{O}^i\text{Bu})_2]_3$  is quite thermally resistant to transformation to oxo species. In retrospect, it might be expected that a Pb(II) alkoxide would be especially sensitive to water, because the low metal oxidation state leaves alkoxide oxygen relatively electron-rich.

On the other hand, this study has shown that a lead-containing oxo species can be generated by thermal decomposition of an O<sup>i</sup>Bu ligand when it is assisted by a strong Lewis acid (Zr). This transformation is selective and thus occurs in good yield. The oxo product and the volatile byproducts of its formation have been fully characterized. NMR studies indicate that the volatile products formed are HO<sup>i</sup>Bu and isobutylene, and thus involve proton transfer from carbon. This is quite consistent with reactivity derived from Zr-assisted O–CMe<sub>3</sub> heterolysis, with proton transfer from a developing Me<sub>3</sub>C<sup>+</sup> ion.

We are currently investigating the reactivity of  $\text{Pb}_6\text{O}_4(\text{O}^i\text{Bu})_4$  with  $\text{Zr}(\text{O}^i\text{Bu})_4$ , hoping to isolate another  $\text{Pb}_a\text{Zr}_b\text{O}_c(\text{O}^i\text{Bu})_d$  product within a Pb:Zr ratio different than that which we have already found.

**Acknowledgment.** This work was supported by the Department of Energy.

**Supporting Information Available:** Full crystallographic details and positional and thermal parameters (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9523606