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Hydrolytic Synthesis of Lead Oxo Isopropoxides and Their Reaction with $M(O^iPr)_4$ (M = Ti, Zr): Comparisons and Contrasts

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Hydrolysis of $[Pb(O^iPr_2]$ using selected stoichiometries yields $[Pb_4O(^iPr)_6]$ or $[Pb_6O_4(O^iPr)_4]$, and stoichiometric $[Pb(O^iPr)_2]$ converts $[Pb_6O_4(O^iPr)_4]$ to $[Pb_4O(O^iPr)_6]$. $[Pb_4O(O^iPr)_6]$ does not have the T_d structure of its O^tBu analogue. Reaction of electrophilic $M(O^iPr)_4$ (M = Ti or Zr) with $Pb_4O(O^iPr)_6$ yields $Pb_3MO(O^iPr)_8$, by "displacement" of $[Pb(O^iPr)_2]$. However, reaction of the seemingly more accessible oxide in $Pb_6O_4(O^iPr)_4$ with $M(O^iPr)_4$ gives $Pb_3MO(O^iPr)_8$, *together with* other metal oxo alkoxides.

Introduction

Various routes have been reported to yield Pb oxo alkoxides ($Pb_aO_b(OR)_c$).[1−5] Some of the routes studied involve the anodic oxidation of Pb in the presence of HOR,[1] the reaction of $Pb(OAc)_2$ with NaOR,[3,4] or even the thermolysis of $Pb(OR)_2$ in refluxing solvent or during sublimation.[2−4] While there are many routes which can lead to the same products, some of these routes involve many steps, may not be reproducible, require tedious workup, or give unattractive yields. Further, the use of alkoxide/acetate or alkoxide/halide metathesis reactions may lead to mixed-metal (e.g., $Na_aPb_bO_c(OR)_d$) or mixed-ligand (e.g., $Pb_aO_b(OR)_c(X)_d$, X = OAc, Br, F) products.[1] We hoped that the most direct route to a high yield of Pb oxo alkoxide products would be the controlled hydrolysis of $Pb(OR)_2$, requiring only pure $Pb(OR)_2$, stoichiometric water, a polar solvent such as THF (for miscibility with water), and an efficient means of purification (i.e., crystallization). This method also serves as a convenient way to introduce a ^{17}O label (i.e., oxide) into the molecule to use as a spin-active ($I = {}^5/_2$) NMR probe.

We have shown[5] that this method is useful in the synthesis of both homometallic ($Pb_4O(O^tBu)_6$ and $Pb_6O_4(O^tBu)_4$) and heterometallic alkoxides ($Pb_3ZrO(O^tBu)_8$) at room temperature. Since our interests involve the systematic synthesis of homo- and heterometallic alkoxide systems having smaller and more reactive alkoxides, we decided to extend the controlled-hydrolysis pathway to the synthesis of alkoxides of type $Pb_aM^{IV}{}_bO_c(O^iPr)_d$ (M^{IV} = Zr, Ti). Here we report rational, high-yield syntheses for $Pb_4O(O^iPr)_6$, $Pb_6O_4(O^iPr)_4$, and $Pb_3ZrO(O^iPr)_8$ and their characterization, including extensive multinuclear NMR data. This permits some systematic conclusions about the influence of M and R in $Pb_3MO(OR)_8$ species on their structure and dynamics. We also include data for $Pb_3TiO(O^iPr)_8$, which is a new Pb/Ti oxoalkoxide with a metal ratio different from that of $Pb_2Ti_2O(O^iPr)_{10}$.[6]

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 their fresh distillation under argon from appropriate drying agents and storage under nitrogen over activated molecular sieves. $Pb[N(SiMe_3)_2]_2$[7] was prepared according to the literature method. $[Pb(O^iPr)_2]$ was prepared according to a modification of a literature procedure.[8] Synthesis at −40 °C in pentane afforded a white, flocculant precipitate, which was washed three times with pentane and dried for 12 h under dynamic vacuum (10^{-2} Torr). $[Zr(O^iPr)_4(HO^iPr)]_2$ was purchased from Aldrich and recrystallized from HO^iPr/pentane; all HO^iPr can be removed from the solid alcohol adduct under dynamic vacuum (1 h at 100 °C) to leave $[Zr(O^iPr)_4]$.[9] $Ti(O^iPr)_4$ was purchased from Aldrich and used as received. ^{17}O-enriched (40 atom %) water was obtained from Iso-Yeda Corp., Rehovot, Israel. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz Varian Gemini 2000 spectrometer at 300 and 75.6 MHz, respectively. ^{17}O NMR and ^{207}Pb NMR spectra were recorded on a Varian Unity Inova 400 MHz spectrometer at 54 and 84 MHz, respectively. Spectra were recorded in $C_6D_5CD_3$ or $CDCl_3$. ^1H spectra were referenced to the protio impurity resonance of the deuterated solvent (2.09 ppm for the upfield resonance of $C_6D_5CD_3$ and 7.24 ppm for $CDCl_3$), and ^{13}C spectra were referenced to the resonance of the deuterated solvent (20.4 ppm for the upfield resonance of $C_6D_5CD_3$ and 77.0 ppm for $CDCl_3$). ^{17}O spectra were referenced to an external sample of ^{17}O-enriched (5 atom %) H_2O (neat, 0.0 ppm), and ^{207}Pb spectra were referenced to an external sample of neat $PbEt_4$ (73.3 ppm).[10] Elemental analyses were performed in-house on a Perkin-Elmer 2400 series II CHNS/O analyzer. Thermogravimetric analyses (TGA) were recorded on a TA Instruments 951 thermogravimetric analyzer at ambient pressure in a He-filled glovebox. All measurements were run at 5 °C/min from ambient temperature to 700 °C with a 40 mL/min He purge of the sample chamber.

Synthesis of $Pb_4{}^{17}O(O^iPr)_6$ (Eq 1). $Pb[N(SiMe_3)_2]_2$ (6.00 g, 11.4 mmol) was dissolved in 30 mL of THF, and neat HO^iPr (2.0 mL, 26 mmol) was added dropwise to this solution to give a white precipitate in a colorless solution. The reaction mixture was heated to reflux, and $^{17}OH_2$ (55.5 μL, 2.98 mmol) in 10 mL of THF was added dropwise to

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give a clear, colorless solution. After a 1 h reflux, the solvent was removed in vacuo and the resulting cream-colored solid was suspended in a minimal amount of HO^{i}Pr. The solid dissolved upon heating, and colorless, plate-like crystals were grown by allowing the hot solution to cool to room temperature. Two crops of crystals gave 2.68 g (79 %)[11] of product, which can be sublimed at 105 °C and 10^{-2} Torr. ^{1}H NMR ($C_6D_5CD_3$, 25 °C): δ 4.95 (br septet), 1.30 (d); ($C_6D_5CD_3$, −30 °C) δ 5.03 (br m, 2 H), 4.79 (br, 1 H), 1.32 (br septet, 18 H); ($C_6D_5CD_3$, −90 °C) δ 5.08 (br septet, 2 H), 4.80 (septet, 1 H), 1.41 (d, 6 H), 1.36 (br d, 6 H), 1.31 (d, 6 H); ($C_6D_5CD_3$, −100 °C) δ 5.19 (br, 1 H), 5.10 (br septet, 1 H), 4.81 (septet, 1 H), 1.41 (br, 12 H), 1.32 (br d, 6 H). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$, 25 °C): δ 65.2 (s, O*C*H(CH_3)$_2$), 29.6 (s, OCH(*C*H$_3$)$_2$). ^{17}O NMR ($C_6D_5CD_3$, 95 °C): δ 244.4 (br, $\nu^{1/2} = 317$ Hz); ($C_6D_5CD_3$, 25 °C) δ 243.3 (v br, $\nu^{1/2} = 705$ Hz); ($C_6D_5CD_3$, −30 °C) δ 247.4 (s, $\nu^{1/2} = 12$ Hz; d satellites, $^{1}J_{Pb-O} = 361$ Hz; d satellites, $^{1}J_{Pb-O} = 405$ Hz; t satellites, $^{1}J_{Pb-O} = 368$ Hz; t satellites, $^{1}J_{Pb-O} = 405$ Hz), 234.5 (br, $\nu^{1/2} = 462$ Hz). ^{207}Pb NMR ($C_6D_5CD_3$, 25 °C): δ 1368 (br, $\nu^{1/2} = 158$ Hz), 1015 (br, $\nu^{1/2} = 342$ Hz), 650 (br, $\nu^{1/2} = 321$ Hz); ($C_6D_5CD_3$, −30 °C) δ 1356 (s, $\nu^{1/2} = 52$ Hz; d satellites, $J_{Pb-Pb} = 260$ Hz), 996 (s, $\nu^{1/2} = 87$ Hz), 637 (s, $\nu^{1/2} = 81$ Hz; d satellites, $J_{Pb-Pb} = 260$ Hz). MS (EI, 15 eV): *m/z*$^{+}$ Pb(O^{i}Pr)$^{+}$ (100), Pb$_2$^{17}O(O^{i}Pr)$^{+}$ (36), Pb$_3$^{17}O(O^{i}Pr)$_3$$^{+}$ (50), Pb$_4$^{17}O(O^{i}Pr)$_5$$^{+}$ (32). Anal. Calcd for $PbO_7C_{18}H_{42}$: C, 18.02; H, 3.53. Found: C, 18.02; H, 3.39.

Synthesis of Pb$_6$^{17}O$_4$(O^{i}Pr)$_4$ (Eq 2). Pb[N(SiMe$_3$)$_2$]$_2$ (2.00 g, 3.79 mmol) was dissolved in 30 mL of THF, and neat HO^{i}Pr (0.8 mL, 10 mmol) was added dropwise to this solution to give a white precipitate in a colorless solution. The reaction mixture was heated to reflux, and ^{17}OH$_2$ (16.5 μL, 2.56 mmol) in 10 mL of THF was added dropwise to give a clear, colorless solution. After a 1 h reflux, the solution was concentrated until a precipitate formed. The solid dissolved upon heating, and colorless, octagon-shaped crystals were grown by allowing the hot solution to cool to room temperature. Three crops of crystals gave 0.800 g (85%)[11] of product. Decomposition to a yellow powder which eventually turned brown resulted upon attempted sublimation at 110 °C and 10^{-2} Torr. ^{1}H NMR (CDCl$_3$, 25 °C): δ 4.74 (septet), 0.99 (d). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 62.2 (s, O*C*H(CH$_3$)$_2$), 24.3 (s, OCH(*C*H$_3$)$_2$). ^{17}O NMR (CDCl$_3$, 25 °C): δ 240.5 (br m,[12] $^{1}J_{Pb-O} = 440$ Hz). ^{207}Pb NMR (CDCl$_3$, 25 °C): δ 1967 (s). MS (EI, 15 eV): *m/z*$^{+}$ Pb$_4$^{17}O$_3$(O^{i}Pr)$^{+}$ (30), Pb$_5$^{17}O$_4$(O^{i}Pr)$^{+}$ (22), Pb$_6$^{17}O$_4$(O^{i}Pr)$_3$$^{+}$ (100). Anal. Calcd for $Pb_6O_8C_{12}H_{28}$: C, 9.32; H, 1.83. Found: C, 9.41; H, 1.84. X-ray analysis (−165 °C): tetragonal cell, $a = b = 11.786(4)$ Å; $c = 17.652(5)$ Å.

Synthesis of Pb$_3$Zr^{17}O(O^{i}Pr)$_8$ (Method 1) (Eq 3). For a one-pot synthesis, Pb[N(SiMe$_3$)$_2$]$_2$ (3.00 g, 5.68 mmol) was dissolved in 20 mL of Et$_2$O and cooled to 0 °C. Neat HO^{i}Pr (1.0 mL, 13 mmol) was added dropwise to this solution to give a white precipitate. The solvent was removed in vacuo, and the precipitate was dried under dynamic vacuum for 2 h at 40 °C. To the powdery solid was added 35 mL of THF, and the suspension was heated to reflux. While some solid remained undissolved in the refluxing THF, this quickly went into solution upon dropwise addition of ^{17}OH$_2$ (35.8 μL, 1.92 mmol) in 10 mL of THF. The resulting solution was refluxed for 5 min, and [Zr(O^{i}Pr)$_4$(HO^{i}Pr)]$_2$ (0.734 g, 0.947 mmol) in 20 mL of THF was added. After a 10 min reflux, the solvent was removed in vacuo to give a waxy material, which was transferred to a sublimation apparatus. There, it sublimed at 125 °C and 10^{-2} Torr to leave a waxy, *crystalline* deposit (1.64 g, 71%) on a 0 °C cold finger.[13] ^{1}H NMR ($C_6D_5CD_3$, −20 °C): δ 5.09 (septet, 3 H), 4.80 (septet, 4 H), 4.61 (septet, 1 H), 1.45 (d, 6 H), 1.41 (d, 24 H), 1.18 (d, 18 H); ($C_6D_5CD_3$, 10 °C) δ 5.09 (septet, 3 H), 4.78 (br septet, 4 H), 4.58 (br, 1 H), 1.38 (d, 30 H), 1.18 (d, 18 H); ($C_6D_5CD_3$, 30 °C) δ 5.09 (br, 3 H), 4.74 (br, 5 H), 1.35 (br d, 30 H), 1.18 (br, 18 H); ($C_6D_5CD_3$, 70 °C) δ 4.81 (v br, 8 H), 1.27 (br, 48 H); ($C_6D_5CD_3$, 90 °C) δ 4.84 (br, 8 H), 1.27 (d, 48 H). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$, 25 °C): δ 70.2 (v br, O*C*H(CH$_3$)$_2$), 68.2 (br s, O*C*H(CH$_3$)$_2$), 65.2 (s, O*C*H(CH$_3$)$_2$), 29.6 (s, OCH(*C*H$_3$)$_2$), 28.4 (br s, OCH(*C*H$_3$)$_2$). ^{17}O NMR ($C_6D_5CD_3$, 65 °C): δ satellite intensity (calcd; obsd)[14] 235.6 (2.9; 5.3), 231.5 (20.5; 20.8), 227.4 (53.0; 50.9) ($\nu^{1/2} = 93$ Hz; $^{1}J_{Pb-O} = 428$ Hz), 223.5 (20.5; 18.5), 219.8 (2.9; 4.5). ^{207}Pb NMR ($C_6D_5CD_3$, 25 °C): δ 986.5 (s, 2 Pb), 986.1 (s, 1 Pb); ($C_6D_5CD_3$, 50 °C) δ 1000 (s). Anal. Calcd for $Pb_3ZrO_9C_{24}H_{56}$: C, 23.98; H, 4.70. Found: C, 23.93; H, 4.62. MS (EI, 15 eV): *m/z*$^{+}$ Pb(O^{i}Pr)$^{+}$ (25), Pb$_2$^{17}O(O^{i}Pr)$^{+}$ (58), Pb$_3$^{17}O(O^{i}Pr)$_3$$^{+}$ (100), Pb$_3$Zr^{17}O(O^{i}Pr)$_7$$^{+}$ (80).

Synthesis of Pb$_3$Zr^{17}O(O^{i}Pr)$_8$ (Method 2) (Eq 7). A solution of Pb$_4$^{17}O(O^{i}Pr)$_6$ (0.0900 g, 75.0 μmol) in 0.25 mL of $C_6D_5CD_3$ was added to a solution of [Zr(O^{i}Pr)$_4$] (0.0246 g, 75.1 μmol) in 0.25 mL of $C_6D_5CD_3$. The resulting solution was agitated for 3 min and then placed in an NMR tube. After the solution was heated to reflux for 3 min, a white precipitate formed. ^{1}H NMR ($C_6D_5CD_3$, 25 °C): δ 5.08 (br, 3 H), 4.76 (br, 5 H), 1.37 (d, 30 H), 1.21 (br d, 18 H). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$, 25 °C): δ 70.2 (v br, O*C*H(CH$_3$)$_2$), 68.2 (br s, O*C*H(CH$_3$)$_2$), 65.2 (s, O*C*H(CH$_3$)$_2$), 29.7 (s, OCH(*C*H$_3$)$_2$), 28.4 (br s, OCH(*C*H$_3$)$_2$). ^{17}O NMR ($C_6D_5CD_3$, 65 °C): δ 226.4 (multiplet[15]). ^{207}Pb NMR ($C_6D_5CD_3$, 25 °C): δ 980.9 (s, 2 Pb), 980.5 (s, 1 Pb).

Synthesis of Pb$_3$Ti^{17}O(O^{i}Pr)$_8$ (Method 1) (Eq 5). A suspension of [Pb(O^{i}Pr)$_2$] (1.787 g, 5.49 mmol) in 30 mL of THF was warmed to reflux, and ^{17}OH$_2$ (31.9 μL, 1.92 mmol) in 10 mL of THF was rapidly added, resulting in a clear, colorless solution. After a 5 min reflux, Ti(O^{i}Pr)$_4$ (0.520 g, 1.83 mmol) in 20 mL of THF was added. The solution was refluxed for an additional 10 min, and the solvent was removed in vacuo, leaving a waxy material. After the wax was dissolved in pentane and the solution was filtered, the solvent was removed in vacuo and 1.813 g (86%) of light-brown wax remained. Attempted vacuum sublimation resulted in partial decomposition of the compound. At 100 °C and 10^{-2} Torr, equimolar Pb$_3$Ti^{17}O(O^{i}Pr)$_8$ and Ti(O^{i}Pr)$_4$ condensed on a 0 °C cold finger apparatus (^{1}H NMR evidence). ^{1}H NMR ($C_6D_5CD_3$, 25 °C): δ 5.06 (septet), 1.29 (d); ($C_6D_5CD_3$, −70 °C): δ 5.13 (septet, 7 H), 4.93 (septet, 1 H), 1.42 (d, 6 H), 1.33 (d, 42 H); ($C_6D_5CD_3$, −90 °C) δ 5.15 (septet, 7 H), 4.95 (septet, 1 H), 1.45 (d, 6 H), 1.36 (br, 42 H); ($C_6D_5CD_3$, −100 °C) δ 5.16 (br septet, 7 H), 4.96 (septet, 1 H), 1.46 (d, 6 H), 1.43 (br, 24 H), 1.27 (br, 18 H). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$, 25 °C): δ 68.6 (br, O*C*H(CH$_3$)$_2$), 28.5 (br, OCH(*C*H$_3$)$_2$). ^{17}O NMR ($C_6D_5CD_3$, 65 °C): δ satellite intensity (calcd; obsd)[14] 260.9 (2.9; 3.3), 257.0 (20.5; 19.6), 252.9 (53.0; 55.0) ($\nu^{1/2} = 68$ Hz; $^{1}J_{Pb-O} = 442$ Hz), 248.9 (20.5; 19.1), 244.6 (2.9; 3.0). ^{207}Pb NMR ($C_6D_5CD_3$, 25 °C): δ 882.1 (s, 2 Pb), 881.7 (s, 1 Pb). MS (EI, 15 eV): *m/z*$^{+}$ Ti(O^{i}Pr)$_3$$^{+}$ (92), Pb(O^{i}Pr)$^{+}$ (100), Pb$_2$^{17}O(O^{i}Pr)$^{+}$ (18), Pb$_3$^{17}O(O^{i}Pr)$_3$$^{+}$ (27), Pb$_3$Ti^{17}O(O^{i}Pr)$_8$$^{+}$ (19). Anal. Calcd for $Pb_3TiO_9C_{24}H_{56}$: C, 24.88; H, 4.87. Found: C, 25.09; H, 4.99.

Synthesis of Pb$_3$Ti^{17}O(O^{i}Pr)$_8$ (Method 2) (Eq 9). A white precipitate formed immediately upon mixing of a solution of Pb$_4$^{17}O(O^{i}Pr)$_6$ (0.0900 g, 75.0 μmol) in 0.25 mL of $C_6D_5CD_3$ with a solution of Ti(O^{i}Pr)$_4$ (0.0213 g, 74.9 μmol) in 0.25 mL of $C_6D_5CD_3$. The resulting suspension was transferred to an NMR tube. ^{1}H NMR ($C_6D_5CD_3$, 25 °C): δ 5.07 (septet), 1.29 (d). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$, 25 °C): δ 68.5 (br, O*C*H(CH$_3$)$_2$), 28.5 (br, OCH(*C*H$_3$)$_2$). ^{17}O NMR ($C_6D_5CD_3$, 65 °C): δ 253.0 (multiplet[15]). ^{207}Pb NMR ($C_6D_5CD_3$, 25 °C): δ 882.0 (s, 2 Pb), 881.6 (s, 1 Pb).

Attempted Synthesis of Pb$_2$Ti$_2$^{17}O(O^{i}Pr)$_{10}$ via Hydrolysis (Eq 11). A solution of ^{17}OH$_2$ (40.2 μL, 2.42 mmol) in 15 mL of THF was added to a refluxing suspension of [Pb(O^{i}Pr)$_2$] (1.50 g, 4.61 mmol) in 30 mL of THF. After a 5 min reflux, Ti(O^{i}Pr)$_4$ (1.31 g, 4.61 mmol) in 20 mL of THF was added. The solution was refluxed for an additional 4 h, and the solvent was removed in vacuo, leaving a precipitate suspended in an oil. A portion of the resulting material was analyzed. ^{207}Pb NMR

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[11] The isolated yield suffers somewhat due to the fairly high solubility of the compound in the crystallization solvent.

[12] Only three of the expected seven lines were detected due to the broadness of the lines. Chemical shifts, coupling constants, and intensities of the satellites could not be accurately determined.

[13] During sublimation of this compound, it is necessary to chill the cold-finger apparatus to near 0 °C for the vaporized material to condense as a waxy substance. Otherwise, it will simply reflux as a viscous liquid.

[14] Satellite intensities are calculated for ^{17}O coupling to three “equivalent” Pb atoms at natural abundance. Only five of the expected seven lines could be resolved due to limited signal-to-noise.

[15] The multiplicity, coupling constants, and intensities of the satellites duplicate those cited above. Only the chemical shift of the central line is shown here.

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($C_6D_5CD_3$, 25 °C): δ 882.7 and 882.3 (s; $Pb_3Ti^{17}O(O^iPr)_8$), 178.9 (s; $Pb_2Ti_2{}^{17}O(O^iPr)_{10}$). ^{17}O NMR($C_6D_5CD_3$, 65 °C): δ 554.5 (s, $Ti_3{}^{17}O(O^iPr)_{10}$); satellite intensity (calcd; obsd)[17] 333.7 (17.2; 17.2), 331.2 (63.1; 65.6) ($\nu^{1/2} = 16$ Hz; $^1J_{Pb-O} = 272$ Hz; $Pb_2Ti_2{}^{17}O(O^iPr)_{10}$), 328.7 (17.2; 17.2); 295 (v br; $Ti(O^iPr)_4$), 252.9 (multiplet;[15] $Pb_3Ti^{17}O(O^iPr)_8$).

Conversion of $Pb_6{}^{17}O_4(O^iPr)_4$ to $Pb_4{}^{17}O(O^iPr)_6$ (Eq 15). $[Pb(O^iPr)_2]$ (0.0800 g, 246 μmol) and $Pb_6{}^{17}O_4(O^iPr)_4$ (0.0380 g, 24.6 μmol) were washed into an NMR tube with 0.5 mL of $C_6D_5CD_3$. Heating the resulting suspension to reflux for 5 min gave a clear solution. ^1H NMR ($C_6D_5CD_3$, 25 °C): δ 5.00 (br), 1.29 (d). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 25 °C): δ 65.2 (s, O*C*H$(CH_3)_2$), 29.6 (s, OCH$(\mathit{C}H_3)_2$).

Reaction of $Pb_6{}^{17}O_4(O^iPr)_4$ with $[Zr(O^iPr)_4]$ (Eq 8). $Pb_6{}^{17}O_4(O^iPr)_4$ (0.0400 g, 25.9 μmol) was washed into an NMR tube with a solution of $[Zr(O^iPr)_4]$ (0.0763 g, 233 μmol) in 0.5 mL of $C_6D_5CD_3$. Heating the resulting suspension to reflux for 3 min gave a clear solution. ^{207}Pb NMR ($C_6D_5CD_3$, 25 °C): δ 981.5 (s, 2 Pb), 981.1 (s, 1 Pb). ^{17}O NMR ($C_6D_5CD_3$, 65 °C): δ 411 (s; $Zr_3{}^{17}O(O^iPr)_{10}$), 272 (v br; $Zr(O^iPr)_4$), 263 (multiplet;[15] $Pb_3Zr^{17}O(O^iPr)_8$).

Reaction of $Pb_6{}^{17}O_4(O^iPr)_4$ with $Ti(O^iPr)_4$ (Eq 13). $Pb_6{}^{17}O_4(O^iPr)_4$ (0.0500 g, 32.3 μmol) was washed into an NMR tube with a solution of $Ti(O^iPr)_4$ (0.0828 g, 291 μmol) in 0.5 mL of $C_6D_5CD_3$. Agitating the resulting suspension at 25 °C for 3 min gave a clear solution. ^{207}Pb NMR($C_6D_5CD_3$, 25 °C): δ 884.4 and 884.0 (s; $Pb_3Ti^{17}O(O^iPr)_8$), 156.4 (s; $Pb_2Ti_2{}^{17}O(O^iPr)_{10}$). ^{17}O NMR ($C_6D_5CD_3$, 65 °C): δ 554 (s; $Ti_3{}^{17}O(O^iPr)_{10}$), 334.5 (multiplet;[15] $Pb_2Ti_2{}^{17}O(O^iPr)_{10}$), 295 (v br; $Ti(O^iPr)_4$), 253.3 (multiplet;[15] $Pb_3Ti^{17}O(O^iPr)_8$).

Reaction of $[Pb(O^iPr)_2]$ with $^{17}OH_2$ (3:1) (Eq 4). HO^iPr (0.32 mL, 4.19 mmol) was added dropwise to a solution of $Pb[N(SiMe_3)_2]_2$ (1.00 g, 1.89 mmol) in 20 mL of THF, giving a white precipitate. The solution was warmed to reflux, and a solution of H_2O (11.9 μL, 0.661 mmol) in 10 mL of THF was added. The resulting clear solution was refluxed for another 5 min, and then the solvent was removed in vacuo. Toluene was added to the solid, and the solution was cannula-transferred to another flask. The solvent was removed in vacuo, and a portion of the solid material was analyzed. ^1H NMR ($C_6D_5CD_3$, 25 °C): δ 4.92 (br; $Pb_4{}^{17}O(O^iPr)_6$), 4.74 (br; $Pb_6{}^{17}O_4(O^iPr)_4$), 1.29 (d; $Pb_4{}^{17}O(O^iPr)_6$), 1.06 (br d; $Pb_6{}^{17}O_4(O^iPr)_4$). The solid that did not dissolve in toluene was dried in vacuo, and a portion of it was analyzed. ^1H NMR ($CDCl_3$, 25 °C): δ 4.76 (septet; $Pb_6{}^{17}O_4(O^iPr)_4$), 1.03 (d; $Pb_6{}^{17}O_4(O^iPr)_4$).

Reaction of $[Pb(O^iPr)_2]$ with $^{17}OH_2$ (2:1) (Eq 12). HO^iPr (0.32 mL, 4.19 mmol) was added dropwise to a solution of $Pb[N(SiMe_3)_2]_2$ (1.00 g, 1.89 mmol) in 20 mL of THF, giving a white precipitate. The solution was warmed to reflux, and a solution of H_2O (17.9 μL, 0.998 mmol) in 10 mL of THF was added. The resulting clear solution was refluxed for another 5 min, and then the solvent was removed in vacuo. A portion of the resulting material was analyzed. ^1H NMR ($C_6D_5CD_3$, 25 °C): δ 4.90 (br; $Pb_4{}^{17}O(O^iPr)_6$), 4.73 (br; $Pb_6{}^{17}O_4(O^iPr)_4$), 1.29 (d; $Pb_4{}^{17}O(O^iPr)_6$), 1.06 (br d; $Pb_6{}^{17}O_4(O^iPr)_4$). The solid which did not dissolve in toluene was dried in vacuo, and a portion of it was analyzed. ^1H NMR ($CDCl_3$, 25 °C): δ 4.75 (septet; $Pb_6{}^{17}O_4(O^iPr)_4$), 1.02 (d; $Pb_6{}^{17}O_4(O^iPr)_4$).

Results

$Pb_4{}^{17}O(O^iPr)_6$. The synthesis of $Pb_4O(O^iPr)_6$ proceeds by the addition of stoichiometric (1:4) water to in situ formed $[Pb(O^iPr)_2]$ in refluxing THF (eq 1). The presence of $HN(SiMe_3)_2$,

$$4[Pb(O^iPr)_2] + {}^{17}OH_2 \rightarrow Pb_4{}^{17}O(O^iPr)_6 + 2HO^iPr \quad (1)$$

a Brønsted-basic coproduct during the synthesis of $[Pb(O^iPr)_2]$, has no effect on the hydrolysis. The resulting compound can be crystallized in the form of plates by slowly cooling a hot, concentrated HO^iPr solution to room temperature. The compound is *very* soluble in many aliphatic solvents and can be sublimed intact at 105 °C and 10^{-2} Torr. Its ^1H and $^{13}C\{^1H\}$ spectra at 25 °C in $C_6D_5CD_3$ are deceptively simple and suggest that there is only one chemical environment for the alkoxides and oxo functionality. This could easily lead to the conclusion that the solution structure is of the type found for $Pb_4O(O^tBu)_6$,[3-5] (**I**) which, due to its T_d symmetry, has six equivalent alkoxides and four equivalent metals. It is only under further examination of the molecule by ^{207}Pb NMR and variable-temperature multinuclear NMR that it becomes apparent that the structure is different.

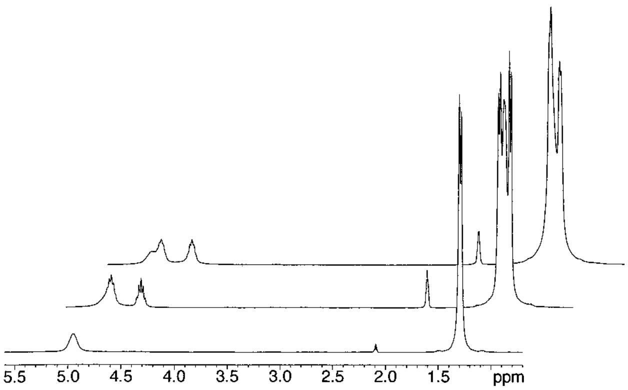
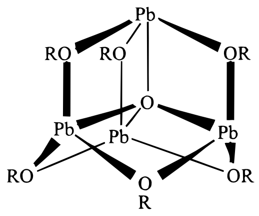


Figure 1. Stacked plot of 300 MHz ^1H NMR spectra of $Pb_4{}^{17}O(O^iPr)_6$ in d_8-toluene at 25 °C (lower), −90 °C (middle), and −100 °C (upper). The signal at 2.1 ppm is due to residual toluene methyl protons.



I

At 25 °C, its ^1H NMR spectrum shows a broadened methine signal and sharp methyl doublet (Figure 1). Upon cooling to −30 °C, the methine region shows two broad lines integrating to 2:1 whereas the methyl region has one broad peak. Further cooling to −90 °C shows no change in the methine region whereas the methyl region shows three equal-intensity doublets. At −100 °C, three equal-intensity multiplets are found in the methine region. The room temperature $^{13}C\{^1H\}$ NMR spectrum also has two equal-intensity peaks in the methine and two in the methyl regions. The ^{207}Pb NMR spectrum at 25 °C has three broad peaks integrating to approximately 1:4:3, but these peaks completely broaden into the baseline on warming to 100 °C. At −30 °C (Figure 2), doublet satellites were detected at two (the signals with intensities of 1 and 3) of the three signals. The signal with the lowest intensity appears to have two more outer satellites that are barely detectable due to signal-to-noise limitations. This could indicate that this Pb couples to three equivalent Pb atoms (based on satellite intensity) at natural abundance. Further, the other signal appears to only couple to one Pb atom (based on satellite intensity). Thus, the signal of intensity 1 shows coupling to three Pb atoms, and the signal of intensity 3 shows coupling to one Pb atom. The relative intensities of all three signals in the spectrum are unchanged on further cooling of the sample. It is therefore possible that all signals are due to one species in solution. This is somewhat hard to support with the ^{17}O NMR evidence found. At 25 °C (and above), the ^{17}O NMR spectrum has only one broad signal (Figure 3). However, the −30 °C spectrum shows decoalesence into a set of sharp, complex multiplets centered around one line

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[17] Satellite intensities are calculated for ^{17}O coupling to two equivalent Pb atoms at natural abundance.

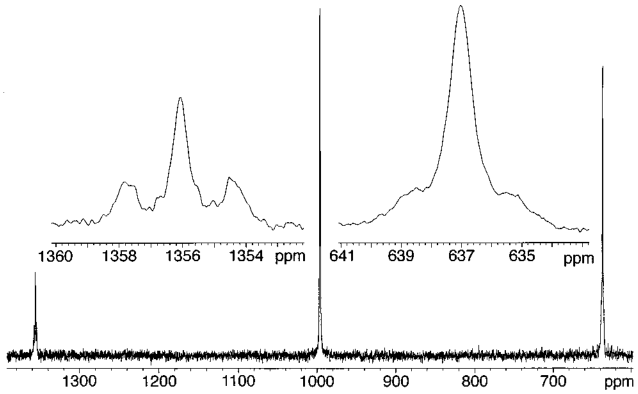


Figure 2. ^{207}Pb NMR spectrum (84 MHz) of $Pb_4O(O^iPr)_6$ in d_8-toluene at −30 °C. Insets (above, left and right) show satellites due to Pb/Pb coupling.

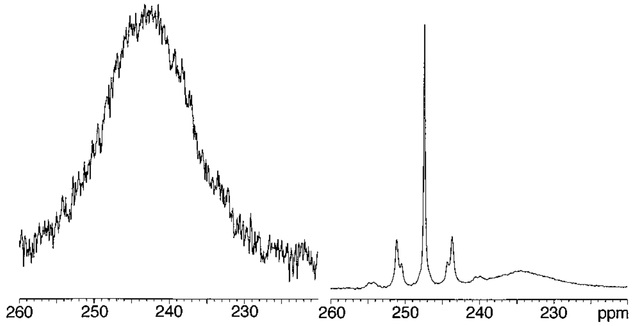


Figure 3. ^{17}O NMR spectra (54 MHz) of $Pb_4{}^{17}O(O^iPr)_6$ in d_8-toluene at 25 °C (left) and −30 °C (right).

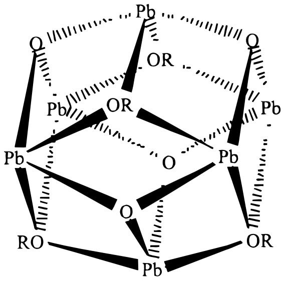
(247 ppm), in addition to a broad signal (234 ppm). The 247 ppm multiplet shows (at least) three different coupling constants with doublet and triplet satellites of differing intensities. These satellites, to a certain extent, are consistent with the coupling found by ^{207}Pb NMR where one unique Pb couples to three equivalent Pb atoms. However, the broad peak in the ^{17}O NMR spectrum indicates either a molecule with low symmetry about the μ_x-O or the occurrence of a fluxional process. At −100 °C, the broad peak disappears into the baseline while the sharp peak broadens only slightly. While a comprehensive explanation of these spectra is lacking, the ^{1}H, ^{207}Pb, and ^{17}O NMR spectra at −30 °C are certainly not consistent with structure **I**.

The mass spectrum of $Pb_4{}^{17}O(O^iPr)_6$ shows $Pb_4{}^{17}O(O^iPr)_5{}^+$, $Pb(O^iPr)^+$, $Pb_2{}^{17}O(O^iPr)^+$, and $Pb_3{}^{17}O(O^iPr)_3{}^+$. Higher oligomers of $[Pb_4{}^{17}O(O^iPr)_6]_n$ were not detected in the *gas phase*.

$Pb_6{}^{17}O_4(O^iPr)_4$. The controlled hydrolysis of in situ formed $[Pb(O^iPr)_2]$ in refluxing THF (eq 2) proceeds by addition of stoichiometric (6:4) $^{17}OH_2$ to give $Pb_6{}^{17}O_4(O^IPr)_4$. This species

$$6[Pb(O^iPr)_2] + 4^{17}OH_2 \rightarrow Pb_6{}^{17}O_4(O^iPr)_4 + 8HO^iPr \quad (2)$$

begins to crystallize upon cooling of the THF solution to room temperature. After the solution is concentrated and warmed to dissolve the precipitate, high-quality crystals form upon cooling of the solution slowly to room temperature. This species is poorly soluble in nearly all solvents at room temperature except $CHCl_3$, in which it is very soluble. Its ^{1}H, $^{13}C\{^1H\}$, ^{17}O, and ^{207}Pb NMR spectra in $CDCl_3$ each show only one chemical environment and are consistent with the general $Pb_6O_4(OR)_4$ structure type (**II**).[1] The T_d symmetry of the molecule causes it to have six equivalent metals, four equivalent alkoxides, and four equivalent oxo groups.

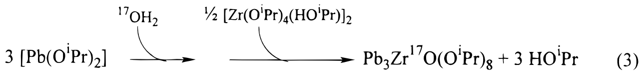


II

Both ^{1}H and $^{13}C\{^1H\}$ NMR show only one environment in the methyl and also in the methine region. Its ^{207}Pb NMR chemical shift (1967 ppm) is approximately the same as that of $Pb_6O_4(O^tBu)_4$ (2015 ppm),[5] and its ^{17}O NMR spectrum displays a splitting pattern (the same as found for the O^tBu analogue) which is indicative of three Pb atoms (at natural abundance) coupling to one oxygen. Further, the broadness of the lines shows a somewhat symmetric (C_{3v}) electron density distribution about the oxo functionality. X-ray analysis at −174 °C gave a unit cell which was nearly the same as that found previously,[1] but the cell was slightly smaller, due to the temperature difference.

Although attempted sublimation at 110 °C and 10^{-2} Torr resulted in decomposition to an intractable brown solid, the mass spectrum (approximately 10^{-5} Torr) showed $Pb_6{}^{17}O_4(O^iPr)_3{}^+$, $Pb_5{}^{17}O_4(O^iPr)^+$, and $Pb_4{}^{17}O_3(O^iPr)^+$.

$Pb_3Zr^{17}O(O^iPr)_8$. The synthesis of $Pb_3Zr^{17}O(O^iPr)_8$ first involves the reaction of stoichiometric $^{17}OH_2$ (3:1 $[Pb(O^iPr)_2]$:$^{17}OH_2$) with in situ formed $[Pb(O^iPr)_2]$ in refluxing THF. The reaction is completed with the addition of $[Zr(O^iPr)_4(HO^iPr)]_2$ followed by removal of the solvent in vacuo (eq 3). The hydrolyzed lead solution contains not one species but is instead a mixture of $Pb_4O(O^iPr)_6$ and $Pb_6O_4(O^iPr)_4$ (eq 4) as determined independently by ^{1}H NMR. The wax resulting from eq 3 was purified by sublimation. In its ^{1}H NMR spectrum at −20 °C (Figure 4), both the methine and methyl regions contain sharp multiplets which integrate to 1:4:3. The integration pattern suggests that the structure is that of $Pb_3MO(X)_8$ (**III**), which has been observed for $Pb_3Zr^{17}O(O^tBu)_8$.[5] Only three chemical environments are found due to residual facile fluxionality (not yet decoalesced) which scrambles the alkoxides of type B, and likewise of type C. Warming to 10 °C gives three peaks (one sharp and two broad) in the methine region while the methyl region only contains two sharp doublets; the smallest and largest peak in the methyl region have coalesced. At 30 °C, the largest and smallest peaks in the methine region are coalesced, and only two broad lines in each of its methine and methyl regions, integrating to 3:5, are observed. Another fluxional process becomes apparent at 70 °C where all peaks have coalesced to give only a single broad line in each of its methine and methyl regions. Warming to 90 °C gives a broad methine signal and a sharp methyl doublet. At 25 °C, three peaks are seen by $^{13}C\{^1H\}$ NMR in the methine region while only two are seen in the methyl region; coupling to Pb is not detected in any of



$$3\,[Pb(O^iPr)_2] \xrightarrow{^{17}OH_2} \xrightarrow{\frac{1}{2}\,[Zr(O^iPr)_4(HO^iPr)]_2} Pb_3Zr^{17}O(O^iPr)_8 + 3\,HO^iPr \quad (3)$$

$$30[Pb(O^iPr)_2] + 10^{17}OH_2 \rightarrow 6Pb_4{}^{17}O(O^iPr)_6 + Pb_6{}^{17}O_4(O^iPr)_4 \quad (4)$$

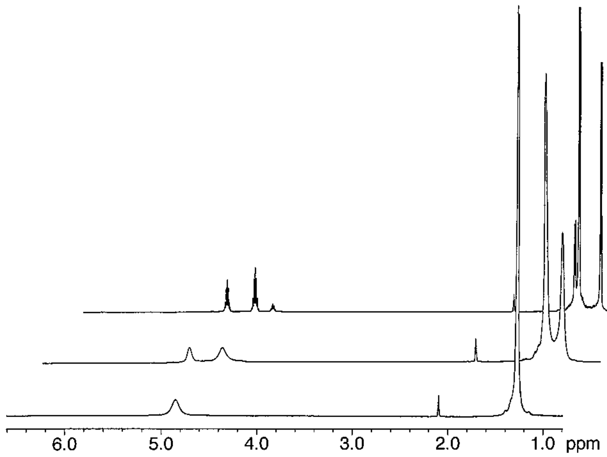
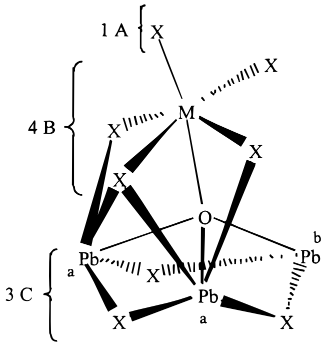


Figure 4. Stacked plot of 300 MHz ^{1}H NMR spectra of $Pb_3Zr^{17}O(O^iPr)_8$ in d_8-toluene at 90 °C (lower), 30 °C (middle), and −20 °C (upper). The signal at 2.1 ppm is due to residual toluene methyl protons.

the peaks. Five lines detected by ^{17}O NMR at 65 °C represent the pattern expected for coupling ($^1J_{Pb-O} = 428$ Hz) to three "equivalent" Pb atoms at natural abundance. The relatively sharp lines ($\nu^{1/2} = 93$ Hz) show a fairly symmetrical distribution of electron density around the μ_4-O. Two lines integrating to 2:1 are detected at 25 °C by ^{207}Pb NMR, and these lines coalesce, upon raising the temperature to 50 °C, to a single, sharp peak with no observed satellites. The observance of two types of Pb is consistent with **III**, which has two Pb atoms of type a and one of type b.



III

This species sublimes intact at 125 °C and 10^{-2} Torr to leave a colorless, *crystalline* wax on a 0 °C cold-finger apparatus. Its mass spectrum shows $Pb_3Zr^{17}O(O^iPr)_7^+$, $Pb_3{}^{17}O(O^iPr)_3^+$, $Pb(O^iPr)^+$, and $Pb_2{}^{17}O(O^iPr)^+$.

$Pb_3Ti^{17}O(O^iPr)_8$. Reacting stoichiometric $^{17}OH_2$ with $[Pb(O^iPr)_2]$ in refluxing THF, followed by the addition of $Ti(O^iPr)_4$ (eq 5), gives $Pb_3Ti^{17}O(O^iPr)_8$. At 25 °C, the ^{1}H NMR spectrum

$$3\,[Pb(O^iPr)_2] \xrightarrow{^{17}OH_2} \xrightarrow{Ti(O^iPr)_4} Pb_3Ti^{17}O(O^iPr)_8 + 2\,HO^iPr \qquad (5)$$

in $C_6D_5CD_3$ shows only a sharp methine septet and a sharp methyl doublet (Figure 5). Upon cooling the sample to −70 °C, both regions show two multiplets (integrating to 1:7), and cooling further to −100 °C gives two signals in the methine region (1:7) whereas the methyl region shows three signals (1:4:3). Thus, by ^{1}H NMR the solution structure is also **III**. Five lines detected by ^{17}O NMR at 65 °C represent the same pattern found for $Pb_3Zr^{17}O(O^iPr)_8$ where one oxygen couples ($^1J_{Pb-O} = 442$ Hz) to three Pb atoms at natural abundance. The relatively sharp lines ($\nu^{1/2} = 68$ Hz) show a symmetrical distribution of electron density around the μ_4-O. Two lines integrating to 2:1 are detected at 25 °C by ^{207}Pb NMR but do not coalesce, even upon heating to 90 °C. No other species, such as $Pb_2Ti_2O(O^iPr)_{10}$[6] or $Pb_4Ti_4O_3(O^iPr)_{18}$, were found as contaminants on the basis of all NMR experiments.

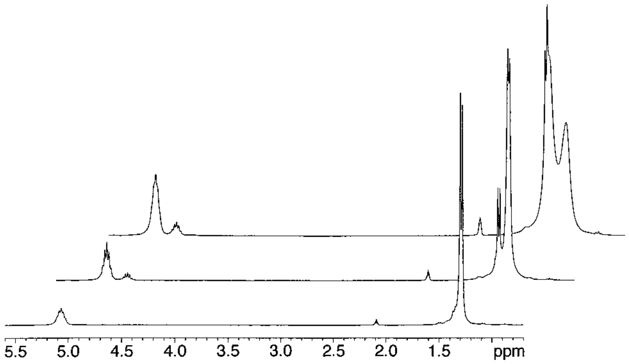


Figure 5. Stacked plot of 300 MHz ^{1}H NMR spectra of $Pb_3Ti^{17}O(O^iPr)_8$ in d_8-toluene at 25 °C (lower), −70 °C (middle), and −100 °C (upper). The signal at 2.1 ppm is due to residual toluene methyl protons.

The compound undergoes partial decomposition during sublimation. Approximately equal amounts of $Pb_3Ti^{17}O(O^iPr)_8$ and $Ti(O^iPr)_4$ sublimed at 100 °C and 10^{-2} Torr to a 0 °C cold-finger apparatus (NMR evidence). Its mass spectrum shows the presence of $Pb_3Ti^{17}O(O^iPr)_8^{\bullet+}$, $Pb_3{}^{17}O(O^iPr)_3^+$, $Ti(O^iPr)_3^+$, $Pb_2{}^{17}O(O^iPr)^+$, and $Pb(O^iPr)^+$.

Mechanistic Studies. We reported earlier that $Pb_4O(O^tBu)_6$ reacts with $Zr(O^tBu)_4$ (eq 6) to give two different heterometallic species at 25 °C in the time of mixing.[5] We decided to

$$Pb_4{}^{17}O(O^tBu)_6 + 2Zr(O^tBu)_4 \xrightarrow[\text{toluene}]{25\ °C} Pb_3Zr^{17}O(O^tBu)_8 + PbZr(O^tBu)_6 \qquad (6)$$

investigate the usefulness of this synthetic route using the O^iPr analogues. Reaction according to eq 7 in toluene forms a precipitate, $[Pb(O^iPr)_2]$, after brief (3 min) heating to reflux.

$$Pb_4{}^{17}O(O^iPr)_6 + [Zr(O^iPr)_4] \xrightarrow{\Delta} Pb_3Zr^{17}O(O^iPr)_8 + [Pb(O^iPr)_2] \qquad (7)$$

Also formed is a species whose NMR spectra are those of independently synthesized $Pb_3Zr^{17}O(O^iPr)_8$. A related reaction, starting with $Pb_6{}^{17}O_4(O^iPr)_4$, was investigated. We found that eq 8 gave $Pb_3Zr^{17}O(O^iPr)_8$ and $Zr_3{}^{17}O(O^iPr)_{10}$, which were identifiable by their ^{17}O NMR chemical shifts and the presence or absence of Pb satellites (263 and 411 ppm, respectively).

$$Pb_6{}^{17}O_4(O^iPr)_4 + 9[Zr(O^iPr)_4] \xrightarrow[\text{toluene}]{\Delta} 2Pb_3Zr^{17}O(O^iPr)_8 + 2Zr_3{}^{17}O(O^iPr)_{10} + [Zr(O^iPr)_4] \qquad (8)$$

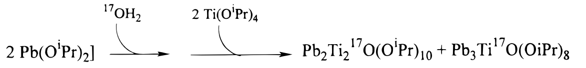
In an experiment similar to eq 7, we attempted the synthesis of the heterometallic oxo alkoxide $Pb_3Ti^{17}O(O^iPr)_8$ in $C_6D_5CD_3$ using $Ti(O^iPr)_4$ (eq 9). A precipitate of $[Pb(O^iPr)_2]$ is

$$Pb_4{}^{17}O(O^iPr)_6 + Ti(O^iPr)_4 \xrightarrow[\text{toluene}]{25\ °C} Pb_3Ti^{17}O(O^iPr)_8 + [Pb(O^iPr)_2] \qquad (9)$$

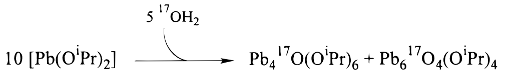
formed immediately in the time of mixing at 25 °C. Also formed is $Pb_3Ti^{17}O(O^iPr)_8$ on the basis of spectra which are the same as those for the species synthesized independently. It has been reported that, in a similar reaction (eq 10, which is not balanced), $Pb_2Ti_2O(O^iPr)_{10}$ is formed in a 64% yield at 20 °C in toluene.[6] We did not find any evidence of the formation

$$Pb_4O(O^iPr)_6 + 4Ti(O^iPr)_4 \rightarrow Pb_2Ti_2O(O^iPr)_{10} \quad (10)$$

of this compound in our reaction (eq 9). We do not believe that the discrepancy is due to a mere difference in stoichiometry (eq 9 vs 10) and thus attempted to synthesize $Pb_2Ti_2{}^{17}O(O^iPr)_{10}$ using a different synthetic pathway. This involved using a different $[Pb(O^iPr)_2]$:$^{17}OH_2$ stoichiometry, which was then reacted with $Ti(O^iPr)_4$ (eq 11). The reaction formed both $Pb_2Ti_2{}^{17}O(O^iPr)_{10}$ and $Pb_3Ti^{17}O(O^iPr)_8$ after a 4 h reflux in THF. Unreacted $Ti(O^iPr)_4$ as well as $Ti_aO_b(O^iPr)_{4a-2b}$ species were detected by ^{17}O NMR using chemical shifts previously reported (eq 11 is not balanced).[18] To better understand the reaction, we isolated the solid from a 2:1 $[Pb(O^iPr)_2]$:$^{17}OH_2$ hydrolysis (cf. eq 11) and identified it as a mixture of $Pb_4{}^{17}O(O^iPr)_6$ and $Pb_6{}^{17}O_4(O^iPr)_4$ (^1H NMR assay). Thus, the hydrolysis in the first step of eq 11 proceeds according to eq 12. It is thus no surprise in eq 11 that two products were formed; two reactants compete for $Ti(O^iPr)_4$. According to eq 9, the species that forms from $Pb_4{}^{17}O(O^iPr)_6$ is $Pb_3Ti^{17}O(O^iPr)_8$. Thus, the formation of $Pb_2Ti_2{}^{17}O(O^iPr)_{10}$ must derive from $Pb_6{}^{17}O_4(O^iPr)_4$. Its reaction with $Ti(O^iPr)_4$ was probed (eq 13) at 25 °C in $C_6D_5CD_3$ (not balanced). Here, both heterometallic oxo alkoxide species were formed (NMR evidence) as well as unreacted $Ti(O^iPr)_4$ and $Ti_aO_b(O^iPr)_{4a-2b}$. Since eq 9 does not make $Pb_2Ti_2{}^{17}O(O^iPr)_{10}$ but eq 13 does, we suggest that the $Pb_4O(O^iPr)_6$, used for the previously reported reaction (eq 10),[6] was contaminated with $Pb_6O_4(O^iPr)_4$. This is further evidenced by the ^{207}Pb NMR chemical shift *reported* for $Pb_4O(O^iPr)_6$ (2021 ppm)[19] being almost the same as that of $Pb_6O_4(O^iPr)_4$ (2024 ppm)[19] and different from that which we report (see Experimental Section).



$$2\,Pb(O^iPr)_2] \xrightarrow{^{17}OH_2} \xrightarrow{2\,Ti(O^iPr)_4} Pb_2Ti_2{}^{17}O(O^iPr)_{10} + Pb_3Ti^{17}O(OiPr)_8 \quad (11)$$



$$10\,[Pb(O^iPr)_2] \xrightarrow{5\,^{17}OH_2} Pb_4{}^{17}O(O^iPr)_6 + Pb_6{}^{17}O_4(O^iPr)_4 \quad (12)$$

$$Pb_6{}^{17}O_4(O^iPr)_4 + 9Ti(O^iPr)_4 \xrightarrow[\text{toluene}]{25\ °C} Pb_2Ti_2{}^{17}O(O^iPr)_{10} + Pb_3Ti^{17}O(O^iPr)_8 \quad (13)$$

The stoichiometric formation of $Pb_3Ti^{17}O(O^iPr)_8$ from $Pb_4O(O^iPr)_6$ and $Pb_6O_4(O^iPr)_4$ (eq 14, which is a more detailed version of eq 5) becomes clearer when one understands the conversion of one Pb/O/O^{i}Pr species to another by reaction with $[Pb(O^iPr)_2]$, a product in eq 9. This conversion (eq 15) occurs upon refluxing the two reactants, which are poorly soluble in toluene, for 5 min to give a toluene-soluble product. Hence, the overall reaction of eq 14 is a composite of both eqs 9 and 15. An analogous statement applies to eq 3 (i.e., a composite of eqs 7 and 15).

$$6Pb_4{}^{17}O(O^iPr)_6 + Pb_6{}^{17}O_4(O^iPr)_4 + 10Ti(O^iPr)_4 \xrightarrow{\Delta} 10Pb_3Ti^{17}O(O^iPr)_8 \quad (14)$$

$$10[Pb(O^iPr)_2] + Pb_6{}^{17}O_4(O^iPr)_4 \xrightarrow[\text{toluene}]{\Delta} 4Pb_4{}^{17}O(O^iPr)_6 \quad (15)$$

Discussion

$Pb_4{}^{17}O(O^iPr)_6$ and $Pb_6{}^{17}O_4(O^iPr)_4$. The controlled hydrolysis of $[Pb(O^iPr)_2]$ in refluxing THF using two different $[Pb(O^iPr)_2]$:$^{17}OH_2$ stoichiometries (4:1 or 6:4) gives two different oxo alkoxide species. Both species are formed when the $[Pb(O^iPr)_2]$:$^{17}OH_2$ ratio differs from 4:1 or 6:4, and these species do not interact at 25 °C in $C_6D_5CD_3$ (NMR evidence). We have observed that, upon adding $^{17}OH_2$ to a hot THF (dilute) solution of $[Pb(O^iPr)_2]$, a white precipitate ("$Pb_a{}^{17}O_b(O^iPr)_{2(a-b)}$") is initially formed and immediately dissolves by further reaction with $[Pb(O^iPr)_2]$. Stoichiometric $[Pb(O^iPr)_2]$ converts $Pb_6{}^{17}O_4(O^iPr)_4$ to $Pb_4{}^{17}O(O^iPr)_6$ (eq 15) after a 5 min reflux in toluene and confirms that $Pb_a{}^{17}O_b(O^iPr)_{2(a-b)}$ (here, $a = 6$ and $b = 4$) does indeed react with $[Pb(O^iPr)_2]$.

Analysis of $Pb_4{}^{17}O(O^iPr)_6$ using ^1H or $^{13}C\{^1H\}$ NMR at 25 °C gave deceptively simple spectra which could result[4] in the mistaken assignment of the solution structure being **I**. It is only when analysis by variable-temperature and multinuclear NMR is performed that it becomes clear that the structure is different. The ^1H NMR spectrum at −30 °C shows two broad lines integrating to 2:1 in the methine region whereas the methyl region has one broad peak. Three equal-intensity peaks are found in the methyl region at −90 °C. The ^{207}Pb NMR spectrum at −30 °C has three peaks integrating to approximately 1:4:3, and the two outer lines show doublets from coupling. On the basis of satellite patterns and intensities, it is believed that these signals arise from one unique Pb coupling to three equivalent Pb atoms. By ^{17}O NMR, the −30 °C spectrum shows a broad signal in the baseline and a sharp signal which is flanked by a complex set of satellites showing at least three different coupling constants. The sharpness of the signal ($\nu^{1/2} = 12$ Hz) indicates very high symmetry around the μ_x-O. Judging from the number of different coupling constants, it appears that there is more than one inequivalent Pb atom bound to the oxo. However, it is hard to explain this result when considering the spectra of the other nuclei.

The fragments found in the mass spectrum confirm that "$Pb_4{}^{17}O(O^iPr)_6$" is present *in the gas phase*, and no masses higher than that of $Pb_4{}^{17}O(O^iPr)_5{}^+$ were detected. While the NMR spectra are inconsistent with **I**, there is a possibility that larger aggregates of $[Pb_4{}^{17}O(O^iPr)_6]_n$ (i.e., $n \geq 2$) might form. Structures **IV** and **V** (X = O^{i}Pr), illustrate two possibilities. The most important feature in the formation of these aggregates is the increase in coordination number at Pb. This typically happens as a result of combining a fairly small ligand with a large metal. For example, $PbZr(OR)_6$ (3-coordinate Pb) forms when O^{t}Bu is used but does not when O^{i}Pr is used. Instead, two $Pb_xZr_y(O^iPr)_{2x+4y}$ species (where $x = 2$ or 4 and $y = 4$ or 2, respectively) are found with Pb being 4-coordinate in both species.[20] Since the multinuclear NMR spectra do not all support a single structural type, we cannot judiciously assign a solution structure to this molecule. We have attempted to grow X-ray quality crystals from many solvents, but the compound is too soluble in almost every solvent chosen. The best crystallization solvent is HO^{i}Pr, but only poor-quality plates are

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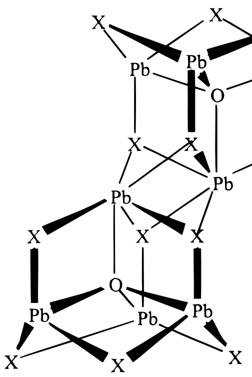
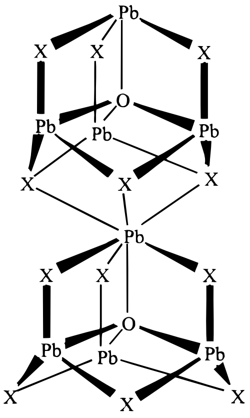
(18) Day, V. W.; Eberspacher, T. A.; Chen, Y.; Hao, J.; Klemperer, W. G. *Inorg. Chim. Acta* **1995**, *229*, 391.

(19) The chemical shift shown here was calculated with respect to $PbMe_4$ as a zero reference. The actual reported value for this compound had $Pb(NO_3)_2$ as an external zero reference ($Pb(NO_3)_2$ is found at −2961 ppm relative to $PbMe_4$; see ref 10).

(20) Teff, D. J.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 2981.



IV



V

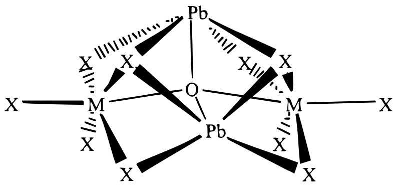
isolated even when using very slow cooling techniques. Some of these crystals were analyzed, but were found to undergo a destructive phase change when cooled below −45 °C. Further, analysis above −45 °C only gave a very poor data set. Sublimation also fails to give high-quality crystals.

In contrast to $Pb_4{}^{17}O(O^iPr)_6$, multinuclear solution NMR spectra of the further-hydrolyzed species, $Pb_6{}^{17}O_4(O^iPr)_4$, are wholly consistent with its reported solid-state structure (**II**; OR = O^iPr).[1] When the size of a ligand is decreased, it is commonly found that the coordination number of the metal can increase. Apparently the combination of the coordination geometry around Pb (see **II**) and oxo content provide a satisfactory amount of electron density and prevent further aggregation at Pb. A change in coordination number is not achieved until another metal, particularly one more oxophilic than Pb (i.e., Ti, Zr), is introduced.

$Pb_3Zr^{17}O(O^iPr)_8$ and $Pb_3Ti^{17}O(O^iPr)_8$. These species can be isolated cleanly as the only product upon the reaction of a correct stoichiometric mixture of $Pb_4{}^{17}O(O^iPr)_6$ and $Pb_6{}^{17}O_4(O^iPr)_4$ (see eqs 3 and 5) with the appropriate $M(O^iPr)_4$ precursor. They are also formed by combining $Pb_4{}^{17}O(O^iPr)_6$ and $M(O^iPr)_4$ (eqs 7 and 9). This reaction is apparent by precipitation of $[Pb(O^iPr)_2]$. In the case of Zr, the reactants must be heated to reflux in toluene for a short time (3 min), perhaps due to the aggregation of $[Zr(O^iPr)_4]_x$ ($x \approx 3$),[21] which creates coordinative saturation of Zr and hinders its reactivity. For $[Ti(O^iPr)_4]_x$, which has a lower molecular complexity ($x \approx 1.4$),[21] the reaction is completed in the time of mixing with a precipitate forming immediately upon combination of the reactants. The two reactions (eqs 7 and 9) cleanly give only two products ($Pb_3M^{17}O(O^iPr)_8$ and $[Pb(O^iPr)_2]$), and no other contaminants (such as $Pb_2M_2O(O^iPr)_{10}$ or $Pb_4M_4O_3(O^iPr)_{18}$) were observed. The reaction can be envisioned as a simple substitution of one $Pb(O^iPr)_2$ unit in **I** with one $M(O^iPr)_4$ giving **III**. Substitution of a $Pb(O^iPr)_2$ unit in **III** with one $M(O^iPr)_4$ might appear to be the most direct route to the formation of $Pb_2M_2{}^{17}O(O^iPr)_{10}$ (**VI**), but it *does not occur* for either Zr or Ti, even in refluxing toluene (eq 16).

$$\underset{\textbf{III}}{Pb_3M^{17}O(O^iPr)_8} + M(O^iPr)_4 \nrightarrow Pb_2M_2{}^{17}O(O^iPr)_{10} + Pb(O^iPr)_2 \quad (16)$$

A common thread to the synthetic transformation described here is the attachment of the electrophile (Ti^{IV} or Zr^{IV}) to an oxide of the Pb oxo alkoxide. The $M(O^iPr)_4$ reagent is also a nucleophile, bringing some of its alkoxide ligands into bridging roles to Pb(II); the coordination number of Pb thus rises. In the present case, $Zr(O^iPr)_4$ *displaces* $Pb(O^iPr)_2$ from the μ_4-oxo species $Pb_4O(O^iPr)_6$. Reaction of an electrophile at the μ_3-oxo ligand in $Pb_6O_4(O^iPr)_4$ might be expected to be more facile since this oxo is "convex", with outwardly directed Lewis basicity. This is supported by the report of an adduct of formula $[Nb(OEt)_5]_4Pb_6O_4(OEt)_4$[22] containing a $Pb_6O_4(O^iPr)_4$ core with one Nb for each oxide. However, this logic fails, in practice here.



VI

Instead, the $Pb_6O_4(O^iPr)_4$ framework does not remain intact, and the only heterometallic oxo alkoxide product detected is $Pb_3Zr^{17}O(O^iPr)_8$. The reaction of $Pb_6{}^{17}O_4(O^iPr)_4$ with $[Zr(O^iPr)_4]$ is apparent when the former, being sparingly soluble in toluene, is dissolved after heating to reflux for 5 min. The Zr analogue of **VI** was not observed, possibly as a consequence of the oxophilicity of Zr. That is, it is possible that the formation of **III** is preferred over **VI** when M = Zr since the structure of **III** has a more electron rich environment for M. In both **III** and **VI**, the coordination geometry at M is the same with M being bound to one μ_4-O, one μ_3-X, two μ_2-X, and two terminal X groups. However, in **III** the electron density of the μ_4-O is not shared by two oxophilic M centers, as it is in **VI**, thus providing more electron donation. Further, **III** has a third electron-rich Pb center, in contrast to **VI**, which also increases the electron density of **III**. This argument may also explain why **III** cannot be converted to **VI** via simple substitution since the oxophilic metals prefer the more electron rich structure over substitution to make **VI**.

The reaction of $Pb_6{}^{17}O_4(O^iPr)_4$ and $Ti(O^iPr)_4$ in toluene results in dissolution of the former at 25 °C. In this case (eq 13), the two species $Pb_3Ti^{17}O(O^iPr)_8$ and $Pb_2Ti_2{}^{17}O(O^iPr)_{10}$ are obtained and a stoichiometric mixture favoring the latter (eq 17) still contains the former (see eq 13) even if attempts are made to drive the reaction by reflux in toluene.

$$Pb_6{}^{17}O_4(O^iPr)_4 + 9Ti(O^iPr)_4 \nrightarrow 3Pb_2Ti_2{}^{17}O(O^iPr)_{10} + Ti_3{}^{17}O(O^iPr)_{10} \quad (17)$$

All evidence found by multinuclear NMR spectrometry suggests that both $Pb_3M^{17}O(O^iPr)_8$ (M = Ti, Zr) species have the same structure (**III**) in solution. By ^1H NMR at room temperature the two species have very different spectra. The Zr analogue shows some decoalesced peaks while the Ti species has a completely coalesced spectrum. For Zr, cooling to −30 °C shows three decoalesced chemical environments (i.e., some residual fluxionality remains) whereas for Ti this is not achieved until −100 °C. Both species show the same types of fluxionality (i.e., similar mechanisms), but the mechanisms governing the fluxional processes occur at different temperatures. Scheme 1 shows a proposed, stepwise set of mechanisms which achieve the different types of alkoxide scrambling seen at different

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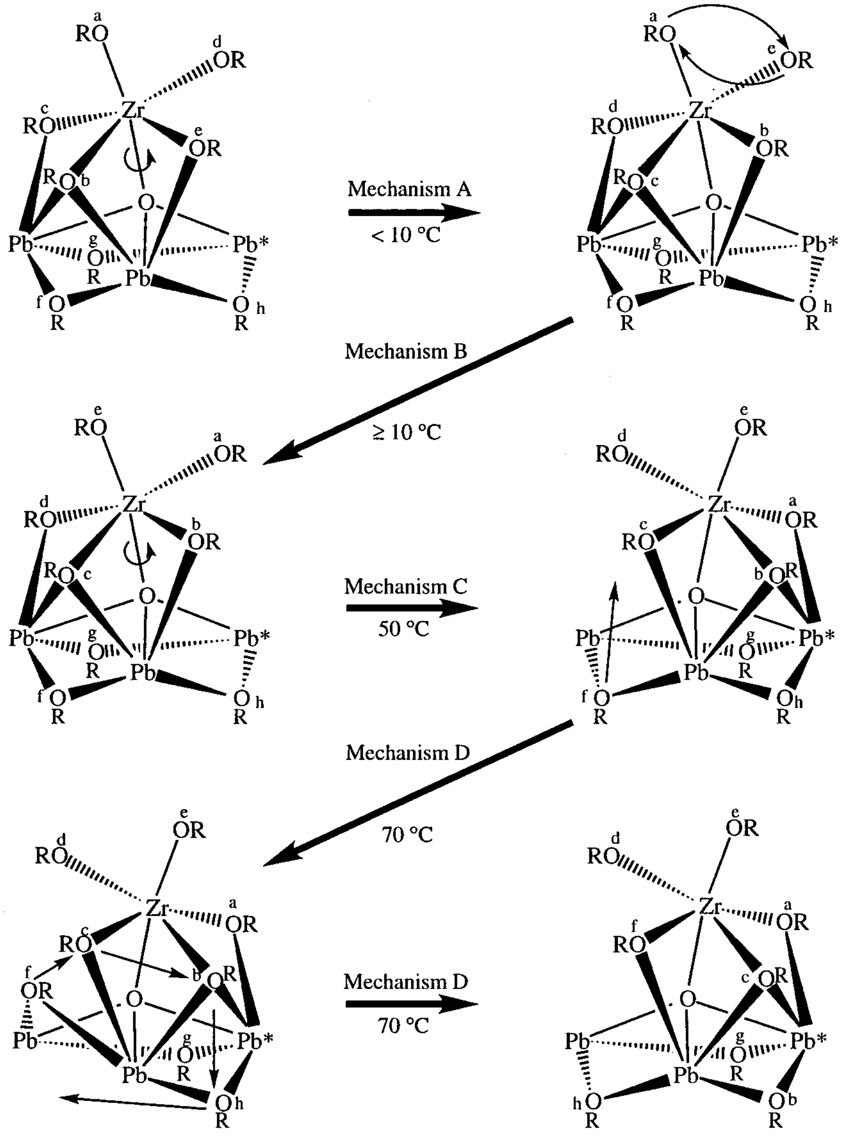
[21] Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic: New York, 1978.

[22] Papiernik, R.; Hubert-Pfalzgraf, L. G.; Daran, J.-C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 695.

Scheme 1



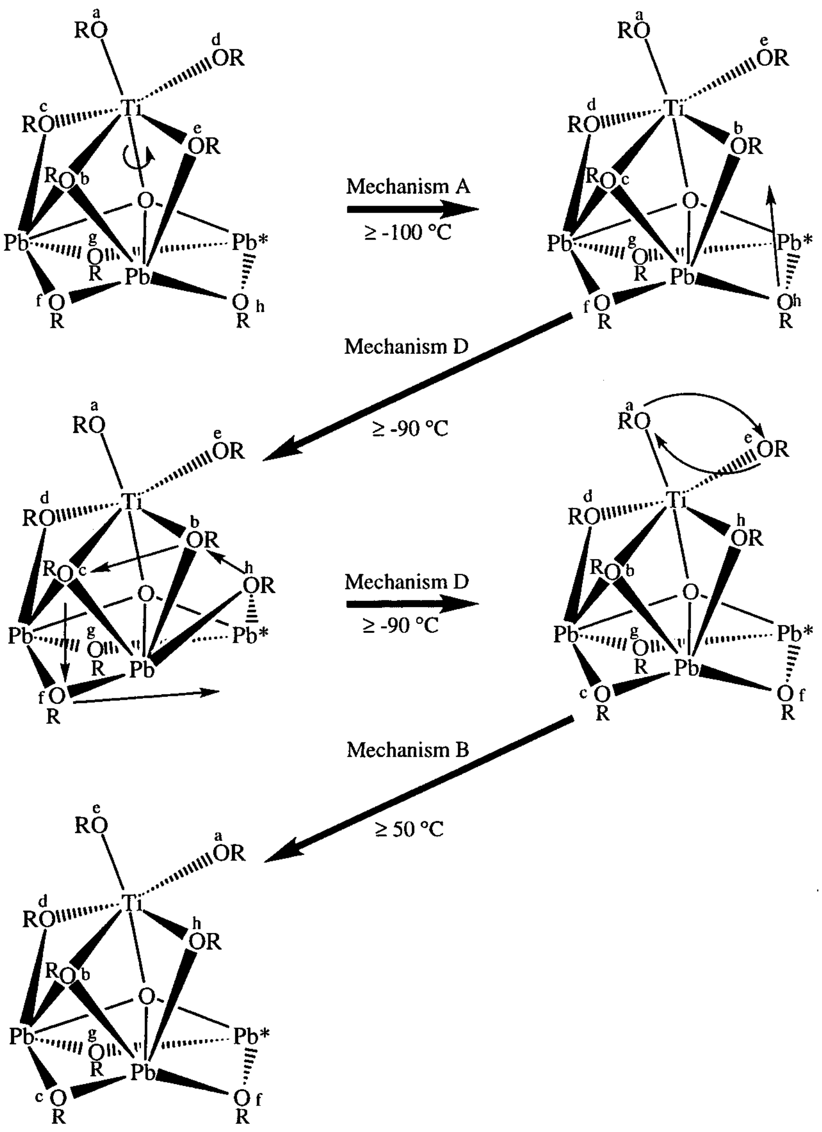
temperatures. For Zr, the proposed mechanism A causes limited residual scrambling of alkoxides, giving three types (1:4:3). Mechanism B, occurring at 10 °C, causes exchange of the terminal alkoxides. At the same time, mechanism A scrambles the four equatorial alkoxides on Zr. These mechanisms leave the 2:1 (compare Pb:Pb* in Scheme 1 below 50 °C) inequivalence of the three Pb atoms as seen in its 25 °C ^{207}Pb NMR spectrum. A small "precession" of the O−Zr−O^{i}Pr vector (mechanism C) at 50 °C scrambles the Pb sites. At 70 °C, mechanism D scrambles the alkoxides in the $Pb_3(O^iPr)_3$ ring with the equatorial alkoxides on Zr. The combination of mechanisms A, B, C, and D at 90 °C successfully scrambles all of the alkoxides, giving only a methine septet and a methyl doublet (i.e., a completely coalesced spectrum) by ^{1}H NMR.

For the Ti analogue, the same mechanisms are believed to operate but are observed at different temperatures (Scheme 2). In its −100 °C ^{1}H NMR spectrum, a residual fluxional mechanism (A) gives only three chemical environments. Unlike the Zr case, the alkoxides in the $Pb_3(O^iPr)_3$ ring scramble with the equatorial alkoxides on Ti *via* mechanism D while the axial alkoxide *trans* to the oxo remains unique at −90 °C. Finally, mechanism B begins to exchange the axial alkoxide with the equatorial alkoxides on Ti, resulting in the exchange of all alkoxides. The 2:1 (compare Pb:Pb* in Scheme 2) inequivalence of the three Pb atoms is seen even at 90 °C by ^{207}Pb NMR, and thus mechanism C (see Scheme 1) has a higher activation energy for the Ti species. This, as well as the difference in coalescence temperatures for the two species, is perhaps explained by the difference in the size of M^{IV}. In the Ti species, the exchange of all alkoxides at 25 °C (by ^{1}H NMR) is a facile process compared to the exchange of alkoxides in Zr analogue. With increased steric congestion (the smaller Ti), it becomes easier for the ligands to migrate (due to a "loose" transition state).

Conclusions

Controlled hydrolysis of polymeric $[Pb(O^iPr)_2]$ with $^{17}OH_2$ in refluxing THF gives the aggregate $Pb_4{}^{17}O(O^iPr)_6$ or $Pb_6{}^{17}O_4(O^iPr)_4$ or gives a mixture of the two when the $[Pb(O^iPr)_2]$:$^{17}OH_2$ ratio differs from 4:1 or 6:4. Stoichiometric $[Pb(O^iPr)_2]$ converts $Pb_6{}^{17}O_4(O^iPr)_4$ to $Pb_4{}^{17}O(O^iPr)_6$ after a short (5 min) reflux in toluene. While the structure of $Pb_6O_4(O^iPr)_4$ is the same as that of its O^{t}Bu analogue by multinuclear NMR, $Pb_4O(O^iPr)_6$ gives too many NMR signals to be consistent with the structure of its O^{t}Bu analogue. We cannot assign a structure due to the complexity of the spectra, but are confident that $[Pb_4O(O^iPr)_6]_n$ building blocks are present on the basis of major

Scheme 2



fragments of this unit (i.e., $Pb_4{}^{17}O(O^iPr)_5{}^+$) found in its mass spectrum. We thus suggest that oligomers of this unit are the source of the complex NMR spectra.

The reactions with Pb^{II} oxo alkoxides presented here show how an oxide ion, even one "encapsulated" in a μ_4 site, can bind electropositive Ti or Zr alkoxides to form "globular" (i.e., *closo*, or quasi-spherical) $M^{IV}/Pb^{II}/O/O^iPr$ aggregates.

This study also allows the following conclusions:

(1) The influence of alkoxide identity on the accessibility of certain precursors (i.e., heterometallic atom ratios) is clarified by these studies. Thus, for R = ^tBu, $Pb^{II}{}_3M^{IV}(OR)_8$ is available for M = Zr but not Ti, apparently for reasons of M^{IV} size. For the smaller substituent R = ^iPr, $Pb_3MO(O^iPr)_8$ is available for both M = Zr and Ti. The size limitation is thus not simply on metal radius, but also on the alkoxide ligand effective size.

(2) These studies reveal unpredictable features of the synthesis of heterometallic species from lead oxo alkoxide sources. Both $M(O^iPr)_4$ species (M = Ti and Zr) react with $Pb_4O(O^iPr)_6$, in spite of the encapsulated nature of the μ_4-oxide in this molecule, to form Ti−oxo or Zr−oxo bonds, but they do so in an unusual *displacement* reaction, with loss of $Pb(O^iPr)_2$. The insolubility of this binary alkoxide may enhance the ΔG for such a displacement. It is quite possible that the *mechanism* of this unusual reaction begins by electrophilic (i.e., M^{IV}) attack on an alkoxide oxygen of $Pb_4O(O^iPr)_6$. However, it is also true that, in the final product $Pb_3ZrO(O^iPr)_8$, Zr provides O^iPr groups to bridge to Pb, so the arriving $Zr(O^iPr)_4$ also behaves as a nucleophile. The coordination number of Pb therefore increases.

(3) In spite of the "exposed" μ_3 and "convex" pyramidal character of the oxide oxygens of $Pb_6O_4(O^iPr)_4$, it reacts with $M(O^iPr)_4$ not simply to form an adduct analogous to $[Nb(OEt)_5]_4Pb_6O_4(OEt)_4$,[22] but rather by fragmentation of the Pb_6 unit. The nondetection of $Pb(O^iPr)_2$ can be understood (if indeed it is produced) since $Pb(O^iPr)_2$ was shown to react readily with $Pb_6O_4(O^iPr)_4$ (eq 15), to give $Pb_4O(O^iPr)_6$, a species which is itself reactive to give established heterometallic oxo alkoxides. One reason for the complexity of $Pb_6O_4(O^iPr)_4$ reactions thus becomes clear. In addition, however, *full oxide abstraction* from Pb^{II} to M^{IV} is observed here, yielding some $(\mu_3\text{-}O)M^{IV}{}_3(O^iPr)_{10}$ (M = Ti and Zr). Finally, the $Pb_3M^{17}O(O^iPr)_8$ species does not react with $M(O^iPr)_4$ to form $Pb_2M_2{}^{17}O(O^iPr)_{10}$ for either Ti or Zr, even in refluxing toluene.

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