Synthesis and Structure of Novel Group IV Tridentate Alkoxide Complexes and Ceramic Thin Films Derived Therefrom. X-ray Structures of (H3CC(CH2-μ3-O)(CH2-μ-O)2)2Ti4(OCH(CH3)2)10, (H3CCH2C(CH2-μ3-O)(CH2-μ-O)2)2Ti4(OCH(CH3)2)10, and (H3CC(CH2-μ-O)3)2Zr4(μ-OCH(CH3)2)2(OCH(CH3)2)8[1]

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An alcoholysis exchange between tris(hydroxymethyl)ethane (THME-H3) or tris(hydroxymethyl)propane (THMP-H3) and group IV metal isopropoxides yields compounds of the general formula (THMR)2M4(OCHMe2)10 [M = Ti (R = E, 1; P, 2); Zr (R = E, 3; P, 4)]. 1 and 2 are formed in toluene, at ambient glovebox temperatures, and adopt a typical fused-M3O12 structure where each titanium atom is surrounded by six oxygens in a slightly distorted face-shared bioctahedral arrangement. All of the oxygens of the central core are from the THMR ligand, present as μ-O and μ3-O oxygen bridges. Generation of 3 or 4 requires heating in toluene at reflux temperatures. The zirconium atoms of 3 possess an extremely distorted edge-shared bioctahedral geometry where the central core consists of a Zr4O8 ring (eight oxygens: six from THME ligands and two from isopropoxide ligands). Each of the zirconium atoms is six-coordinated with four bridging oxygens and two terminal isopropoxide ligands. Spin-cast deposited films generated from toluene solutions of 1 and 3 indicate that increased uniformity of the films and decreased hydrolysis occur in comparison to the cases of Ti(OCHMe2)4, 5, and [Zr(OCHMe2)4·HOCHMe2]2, 6, respectively. 1 crystallized from toluene at 25 °C in the space group $P2_1/n$ with $a = 11.9127(10)$ Å, $b = 14.5313(14)$ Å, $c = 15.4676(15)$ Å, $\beta = 106.191(7)°$, $V = 2571.4$ (4) Å^3, and $D_{calcd} = 1.313$ Mg/m^3 for $Z = 2$. Least-squares refinement of the model based on 5481 reflections ($|F_o| > 2.0\sigma(|F_o|)$) converged to a final $R_F = 3.3\%$. 2 crystallized from toluene at 25 °C in the space group $P2_1/n$ with $a = 13.989(3)$ Å, $b = 10.806(2)$ Å, $c = 18.468(4)$ Å, $\beta = 99.26(2)°$, $V = 2755.4(10)$ Å^3, and $D_{calcd} = 1.259$ Mg/m^3 for $Z = 2$. Least-squares refinement of the model based on 5448 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 3.7\%$. 3 crystallized from toluene at 25 °C in the space group $P\bar{1}$ with $a = 11.5203(11)$ Å, $b = 21.705(2)$ Å, $c = 25.145(2)$ Å, $\alpha = 65.520(7)°$, $\beta = 86.015(8)°$, $\gamma = 78.304(7)°$, $V = 5602.6(9)$ Å^3, and $D_{calcd} = 1.412$ Mg/m^3 for $Z = 4$. Least-squares refinement of the model based on 9029 reflections ($|F_o| > 4.0\sigma(|F_o|)$) converged to a final $R_F = 6.52\%$. For 6, parameters different from those previously reported were determined.

Introduction

Both physical and chemical methodologies exist for the production of ceramic thin films.[2-7] Chemical methods are of

interest due to the flexibility of controlling the resulting products and usually involve either sol-gel[4-6] or metallo-organic decomposition[7] procedures. Another chemical method employed is metallo-organic chemical vapor-phase deposition (MOCVD); however, at present, there are relatively few reports of using metal alkoxides as precursors for MOCVD methodologies.[8] It has been hypothesized that polymetallic alkoxides are potential precursors to polycomponent oxides,[9] thus making them of interest for the production of ceramic materials, such as the perovskite phase of lead zirconate titanate (PZT).[2-7]

Typically, the complex ceramic precursors used for thin films have been synthesized using commercially available metal alkoxides and acetates.[4-6] These compounds are of interest since the organic fractions of the resulting products can be cleanly removed by sintering the films at relatively low temperatures.[4] Also of key importance is the fact that these precursors are easily isolated (or obtained), stable over a long period of time, and highly soluble in organic solvents.[1-10] However, for the successful use of these precursors in thin film

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applications, control of film densification and crystallization behavior is required.[3-7,10] Therefore, development of an understanding of the relationships among chemical precursors, solution processing, film fabrication conditions, and film properties is essential.

Thin film devices are frequently based on multicomponent systems. We have chosen to initially investigate single-component materials before undertaking a more complex ternary system. Studying these *simpler* systems will ultimately assist in controlling the film characteristics of more complex systems of interest. Furthermore, these single-component ceramic oxide thin films also have a wide variety of applications.[11] To generate suitable precursors for production of property-controlled thin films, synthesis and characterization of the starting materials both in solution *and* the solid state are essential. The tridentate ligands 1,1,1-tris(hydroxymethyl)ethane (THME-H_3) and 1,1,1-tris(hydroxymethyl)propane (THMP-H_3) were chosen to generate such compounds. The reactions of THME-H_3 and THMP-H_3 with group IV metal isopropoxides and the properties of the thin films generated from these reaction products are reported.

Experimental Section

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk, vacuum line, and glovebox techniques. All solvents were freshly distilled and dried from sodium benzophenone ketyl prior to use.[12] Solution NMR spectra were obtained on a Bruker AC-250 and referenced against the residual protons in toluene-d_8 or benzene-d_6.[13] FT-IR data were obtained on a Nicolet Magna System 550 spectrometer. TGA/DTA experiments were performed on a Polymer Laboratories STA 1500 instrument. The changes in film thickness and refractive index at room temperature as a function of drying time were measured by ellipsometry on a Gaertner L116-C ellipsometer. Elemental analysis was performed at Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside, NY 11377−2495. 1,1,1-Tris(hydroxymethyl)ethane (Aldrich), 1,1,1-tris-(hydroxymethyl)propane (Alfa), and [Zr(OCHMe₂)₄·HOCHMe₂]₂ (Alfa, Aldrich) were used as received. Ti(OCHMe₂)₄ (Aldrich) was purified by vacuum distillation immediately prior to use.

Thermogravimetric Analysis and Differential Thermal Analysis (TGA/DTA). All samples were of crystalline purity or were freshly distilled. The compounds were loaded in air into a preweighed alumina boat. Sample sizes ranged from 8 to 15 mg. The boat was transferred to the TGA/DTA instrument which was purged with either UHP oxygen or UHP argon. The temperature was ramped at 5 °C/min from ambient temperature to 600 °C and was then held at 600 °C for 1 min.

(H_3CC(CH₂-μ₃-O)(CH₂-μ-O)₂)₂Ti₄(OCH(CH₃)₂)₁₀, 1. In a glovebox, THME-H_3 (0.844 g, 7.03 mmol) was slurried in THF (10 mL) and the slurry was added dropwise to a stirring solution of Ti(OCHMe₂)₄ (4.00 g, 14.1 mmol) in toluene (30 mL). Each drop produced a white precipitate which was quickly redissolved. The reaction mixture was stirred for 12 h, after which the solvent was partially removed by rotary evaporation. With approximately 8 mL of solution remaining, crystalline material was observed to have formed on the sides of the flask. The mixture was removed from the rotary evaporator and left to stand overnight, resulting in clear colorless crystals that proved to be (H_3-CC(CH₂-μ₃-O)(CH₂-μ-O)₂)₂Ti₄(OCH(CH₃)₂)₁₀, **1**. Successive recrystallizations from toluene gave an 83.1% (2.97 g) yield. ¹H NMR (C₇D₈, 250 MHz): δ 5.03 (2H, sept, J_{CH} = 6.00 Hz, OC*H*Me₂), 4.55, 4.47 (7H, mult, OC*H*Me₂, (OC*H₂*)₃CMe), 1.44 (42H, d, J_{CH} = 6.15 Hz, OCH*Me₂*), 1.38 (12H, d, J_{CH} = 6.18 Hz, OCH*Me₂*), 1.31 (6H, d, J_{CH} = 6.07 Hz, OCH*Me₂*), 1.25 (26H, d, J_{CH} = 6.07 Hz, OCH*Me₂*), 0.540

(6H, s, (OCH₂)₃C*Me*). ¹³C NMR (C₇D₈, APT [attached proton test]): δ 80.0 (OC*H*Me₂), 79.3 (OC*H*Me₂), 78.8 (OC*H*Me₂), 72.2 (OC*H*Me₂), 71.2 (OC*H*Me₂), 71.0 (OC*H*Me₂), 70.8 (OC*H*Me₂), 37.5 ((OC*H₂*)₃CMe), 28.2 (OCH*Me₂*), 27.5 (OCH*Me₂*), 26.4 (OCH*Me₂*), 26.2 (OCH*Me₂*), 26.4 (OCH*Me₂*), 16.8 ((OCH₂)₃C*Me*). IR (KBr pellet, cm⁻¹): 2964 (s), 2919 (s), 2870 (s), 1458 (s), 1387 (m), 1370 (s), 1359 (s), 1326 (s), 1163 (s), 1123 (s), 1048 (s), 1020 (s), 1000 (s), 985 (s), 837 (s), 641 (b, s), 502 (b, s). DTA/TGA (oxygen, 17.40 mg): 74.0% weight loss, conversion to TiO₂ = 68.6% weight loss; 88 °C (endotherm, small), 277 °C [exotherm, large (recoalescence peak)]. All events observed in the DTA coincided with changes in the TGA. Anal. Calcd for C₄₀H₈₈O₁₆Ti₄: C, 47.25; H, 8.72; Ti, 18.84. Found: C, 47.29; H, 8.90; Ti, 19.05.

(H_3CCH₂C(CH₂-μ₃-O)(CH₂-μ-O)₂)₂Ti₄(OCH(CH₃)₂)₁₀, 2. Experimental conditions identical with those for **1** were repeated using THMP-H_3 (0.300 g, 2.23 mmol) in THF (2.5 mL) which was added to Ti(OCHMe₂)₄ (1.27 g, 4.46 mmol) in toluene (10 mL). Yield of (H_3-CCH₂C(CH₂-μ₃-O)(CH₂-μ-O)₂)₂Ti₄(OCH(CH₃)₂)₁₀, **2**: 71.7% (0.84 g). ¹H NMR (C₆D₆, 250 MHz): δ 5.07 (3.5H, sept, J_{CH} = 6.2 Hz, OC*H*Me₂), 4.87 (2.5H, sept, J_{CH} = 6.1, OC*H*Me₂), 4.71−4.64, 4.579−4.40 (11H, mult, (OC*H₂*)₃CCH₂Me, OC*H*Me₂), 4.24 (1.25H, s, (OC*H₂*)₃-CCH₂Me), 1.46 (20H, d, J_{CH} = 6.1 Hz, OCH*Me₂*), 1.40 (9H, d, J_{CH} = 6.2 Hz, OCH*Me₂*), 1.32 (10.5H, d, J_{CH} = 6.1 Hz, OCH*Me₂*), 1.25 (11H, d, J_{CH} = 6.0 Hz, OCH*Me₂*), 1.10−0.95 (2.75H, m, (OCH₂)₃CC*H₂*Me), 0.87 (1.5H, t, J_{CH} = 7.5 (OCH₂)₃CCH₂*Me*), 0.68 (1.5H, t, J_{CH} = 7.5, (OCH₂)₃CCH₂*Me*). ¹³C{¹H} NMR (C₆D₆, APT): δ 82.4 ((OC*H₂*)₃-CCH₂Me), 79.0 (OC*H*Me₂), 78.3 ((OC*H₂*)₃CCH₂Me), 77.6 (OC*H*Me₂), 76.9 (OC*H*Me₂), 76.4 (OC*H*Me₂), 49.9 ((OC*H₂*)₃CCH₂Me), 40.0 ((OC*H₂*)₃CCH₂Me), 26.8 (OC*H*Me₂), 26.5 (OC*H*Me₂), 26.0 (OC*H*Me₂), 8.2 ((OCH₂)₃CCH₂*Me*), 8.0 ((OCH₂)₃CCH₂*Me*). IR (KBr pellet, cm⁻¹): 2973 (s), 2927 (s), 2855 (s), 2696 (w), 2617 (w), 1470 (m), 1450 (m), 1373 (m), 1355 (m), 1323 (m), 1170 (b, s), 1130 (b, s), 1057 (b, s), 1005 (b, s), 944 (s), 845 (s), 844 (s), 802 (s), 780 (s), 642 (s), 622 (s), 590 (s). DTA/TGA (oxygen, 12.09 mg): 82.5% weight loss, conversion to TiO₂ = 69.4% weight loss; 92.3 °C (endotherm, small), 272 °C [exotherm, large (recoalescence peak)]. All events observed in the DTA coincided with changes in the TGA. Anal. Calcd for C₄₂H₉₂O₁₆Ti₄: C, 48.28; H, 8.87; Ti, 18.34. Found: C, 48.29; H, 8.83; Ti, 18.44.

(H_3CC(CH₂-μ-O)₃)₂Zr₄(μ-OCH(CH₃)₂)₂(OCH(CH₃)₂)₈, 3. In a glovebox, THME-H_3 (0.62 g, 5.2 mmol) was dissolved in THF (10 mL) and the mixture was added dropwise to a stirring solution of [Zr-(OCHMe₂)₄·HOCHMe₂]₂ (4.00 g, 5.2 mmol) in toluene (30 mL). A reflux condenser was then attached to the flask, and the reaction mixture was left to stir for 12 h at toluene/THF reflux temperatures. After cooling of the mixture to room temperature, the solvent was removed *in vacuo*. The resulting off-white powder was redissolved in a minimum amount of toluene, and the small insoluble fraction was removed by centrifugation. The concentrated solution was allowed to stand overnight at glovebox ambient temperature. Colorless crystals of (H_3CC(CH₂-μ-O)₃)₂Zr₄(μ-OCH(CH₃)₂)₂(OCH(CH₃)₂)₈, **3**, were produced in 85% yield (2.61 g). ¹H NMR (C₇D₈): δ 4.86 (1H, sept, J_{CH} = 6.27 Hz, OC*H*Me₂), 4.69, 4.52, 4.31(13H, mult, OC*H*Me₂, (OC*H₂*)₃-CMe), 1.54 (7.5H, d, J_{CH} = 6.26 Hz, OCH*Me₂*), 1.29 (35.5H, d, J_{CH} = 6.04 Hz, OCH*Me₂*), 0.405 (4H, s, (OCH₂)₃C*Me*). ¹³C NMR (C₇D₈, APT): δ 77.9 ((OC*H₂*)₃CMe), 72.0 (OC*H*Me₂), 71.0 (OC*H*Me₂), 70.8 (OC*H*Me₂), 70.3 (OC*H*Me₂), 68.5 ((OC*H₂*)₃CMe), 38.8 ((OC*H₂*)₃CMe), 28.0 ((OC*H₂*)₃CMe), 27.8 (OC*H*Me₂), 26.5 (OCH*Me₂*), 26.0 (OCH*Me₂*). IR (KBr pellet, cm⁻¹): 2966 (s), 2911 (s), 2855 (s), 2811 (w), 1461 (m), 1400 (m), 1372 (s), 1355 (s), 1333 (m), 1150 (b, s), 1061 (s), 1011 (s), 944 (m), 844 (m), 822 (w), 616 (m). DTA/TGA (oxygen, 18.20 mg): 56.0% weight loss, conversion to ZrO₂ = 58.6% weight loss; 235 °C [large exotherm (recoalescence peak)], 279 °C (exotherm, medium). All events observed in the DTA coincided with changes in the TGA. Anal. Calcd for C₄₀H₈₈O₁₆Zr₄: C, 40.37; H, 7.45; Zr, 30.66. Found: C, 37.37; H, 7.22.

(H_3CCH₂C(CH₂-μ-O)₃)₂Zr₄(μ-OCH(CH₃)₂)₂(OCH(CH₃)₂)₈, 4. Experimental conditions identical with those for **3** were repeated using THMP-H_3 (0.30 g, 2.23 mmol) in THF (2.5 mL) added to [Zr-(OCHMe₂)₄·HOCHMe₂]₂ (1.71 g, 4.46 mmol) in toluene (30 mL). Yield of (H_3CCH₂C(CH₂-μ-O)₃)₂Zr₄(μ-OCH(CH₃)₂)₂(OCH(CH₃)₂)₈, **4**: 68.4% (0.921 g). ¹H NMR (C₆D₆, 250 MHz): δ 4.92 (2H, sept, J_{CH} = 6.10

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(13) Deuterated solvents were predried over Na/K for 24 h and filtered prior to use.

Hz, OCHMe$_2$), 4.65–4.58 (12H, mult, OCHMe$_2$, (OCH_2)$_3$CCH$_2$Me), 4.52–4.45 (8H, mult, OCHMe$_2$, (OCH_2)$_3$CCH$_2$Me), 1.59 (12H, d, J_{CH} = 6.10 Hz, OCHMe$_2$), 1.36 (48H, d, J_{CH} = 5.96 Hz, OCHMe_2), 0.99 (6H, t, J_{CH} = 6.53 Hz, (OCH$_2$)$_3$CCH$_2$Me), 0.85 (6 H, t, J_{CH} = 6.53 Hz, (OCH$_2$)$_3$CCH$_2$Me). ^{13}C{^{1}H}NMR (C$_7$D$_6$, APT): δ 78.0 ((OCH$_2$)$_3$CCH$_2$-Me), 72.0 (OCHMe$_2$), 71.0 (OCHMe$_2$), 70.9 (OCHMe$_2$), 69.9 (OCHMe$_2$), 68.6 (OCHMe$_2$), 38.9 ((OCH$_2$)$_3$CH$_2$Me), 28.0 (OCHMe_2), 27.8 (OCHMe_2), 26.3 (OCHMe_2), 25.7 (OCHMe_2), 9.1 ((OCH$_2$)$_3$CCH$_2$$Me$), 8.3 ((OCH$_2$)$_3CCH_2$$Me$). IR (KBr pellet, cm^{-1}): 2967 (s), 2926 (s), 2859 (s), 2797 (w), 2705 (w), 2623 (w), 1465 (m), 1401 (w), 1377 (s), 1360 (m), 1335 (m), 1259 (w), 1178 (b, s), 1144 (b, s), 1115 (b, s), 1076 (s), 1056 (s) 1014 (b, s), 943 (s), 848 (m), 828 (w), 828 (m), 801 (w), 774 (w), 613 (m), 559 (s), 510 (s). DTA/TGA (oxygen, 18.99 mg): 56.0% weight loss, conversion to ZrO$_2$ = 59.6% weight loss; 90 °C (endotherm, small), 240 °C [exotherm, large (recoalescence peak)], 284 °C [exotherm, medium]. All events observed in the DTA coincided with changes in the TGA. Anal. Calcd for C$_{42}$H$_{92}$O$_{16}$Zr$_4$: C, 41.42; H, 7.61; Zr , 29.96. Found: C, 38.67; H, 7.35; Zr, 28.48.

Ti(OCHMe$_2$)$_4$, 5 (Aldrich). ^{1}H NMR (C$_6$D$_6$, 250 MHz) δ 4.47 (1H, sept), 1.26 (6H, d, J_{CH} = 6.07 Hz). DTA/TGA (oxygen, 14.80 mg): 83.8% weight loss, conversion to TiO$_2$ = 72.0% weight loss.; 40 °C (endotherm, small), 130 °C (exotherm, small), 245 °C (exotherm, small), 250 °C (exotherm, small), 375 °C (exotherm, small). All events observed in the DTA coincided with changes in the TGA.

[Zr(OCHMe$_2$)$_4$·HOCHMe$_2$]$_2$, 6 (Alfa).[29] ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ 4.55 (1H, b s) 1.37 (6H, d, J_{CH} = 6.09 Hz). DTA/TGA (oxygen, 18.10 mg): 70.0% weight loss, conversion to ZrO$_2$ = 67.4% weight loss; 88 °C (endotherm, small), 133 °C (exotherm, small), 283 °C (exotherm, medium). All events observed in the DTA coincided with changes in the TGA. Crystals suitable for X-ray crystallographic studies were grown from a stoichiometric mixture of [Zr-(OCHMe$_2$)$_4$·HOCHMe$_2$]$_2$ and THME-H$_3$ in toluene/THF. The mixture was stirred for 12 h, and the resulting clear solution was concentrated and allowed to sit at ambient temperatures. Over a 1 week period, crystals suitable for X-ray crystallographic studies were isolated (data collection was similar to that described below).[14–19] These crystals proved to be recrystallized [Zr(OCHMe$_2$)$_4$·HOCHMe$_2$]$_2$, **6**; however, the crystal structure solved had parameters[29a,c] different from those previously reported.[29b]

X-ray Data Collection and Solution, and Refinement of the Crystal Structure. (CH$_3$C(CH$_2$O)$_3$)$_2$Ti$_4$(OCHMe$_2$)$_{10}$, 1. A colorless crystal of approximate dimensions 0.40 × 0.40 × 0.46 mm was oil-mounted[14] on a glass fiber and transferred to a Syntex P2$_1$ automated four-circle diffractometer which is equipped with a modified LT-1 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried

Table 1. Collection Data for (THME)$_2$Ti$_4$(OCHMe$_2$)$_{10}$, **1**, (THMP)$_2$Ti$_4$(OCHMe$_2$)$_{10}$, **2**, and (THME)$_2$Zr$_4$(OCHMe$_2$)$_{10}$, **3**

	1	2	3
formula	C$_{40}$H$_{88}$O$_{16}$Ti$_4$	C$_{42}$H$_{92}$O$_{16}$Ti$_4$	C$_{40}$H$_{88}$O$_{16}$Zr$_4$
crystal size (mm)	0.40 × 0.40 × 0.46	0.36 × 0.40 × 0.50	0.13 × 0.23 × 0.41
fw	1016.7	1044.8	1190.99
temp (K)	163	163	163
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ [C^5_{2h}, No.14]	$P2_1/n$ [C^5_{2h}, No.14]	$P\bar{1}$ [C^1_i, No. 2]
a (Å)	11.9127(10)	13.989(3)	11.5203(11)
b (Å)	14.5313(14)	10.806(2)	21.705(2)
c (Å)	15.4676(15)	18.468(4)	25.145(2)
α (deg)			65.520(7)
β (deg)	106.191(7)	99.26(2)	86.015(8)
γ (deg)			78.304(7)
V (Å^3)	2571.4(4)	2755.4(10)	5602.6(9)
Z	2	2	4
D_{calc} (Mg/m^3)	1.313	1.259	1.412
λ (Mo Kα) (Å)	0.710 730	0.710 730	0.710 730
μ(Mo Kα) (mm^{-1})	0.65	0.61	0.779
$R_F{}^a$ (%)	3.3	3.7	6.52 (12.3 for all data)
$R_{wF}{}^b$ (%)	4.8	4.1	
wR2^c (%)			17.75 (for all data)
goodness of fit	1.19	1.80	1.021

^{a} $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| \times 100$. ^{b} $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/ \Sigma w|F_o|^2]^{1/2} \times 100$. ^{c} wR2 $= [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma(w|F_o|^2)^2]^{1/2} \times 100$.

out by previously described methods similar to those of Churchill.[15] Intensity data were collected at 163 K using a θ–2θ scan technique with Mo Kα radiation under the conditions described in Table 1. All 6481 data were corrected for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was 2/m with systematic absences 0k0 for k = 2n + 1 and h0l for h + l = 2n + 1. The centrosymmetric monoclinic space group $P2_1/n$, a non-standard setting of $P2_1/c$ [C^5_{2h}, No. 14] is therefore uniquely defined.

All crystallographic calculations were carried out using either the UC-Irvine modified version of the UCLA Crystallographic Computing Package,[16] the SHELTEX PLUS program set,[17] or the SHELXL-93 refinement program.[18] The analytic scattering factors for neutral atoms

(14) The crystal was immersed in a lube-oil additive which allows for manipulation on the bench-top and prevents decomposition due to air or moisture. The crystal was secured to a glass fiber (the oil acts as the adhesive) which is attached to an elongated brass mounting-pin. Further details appear in: Hope, H. *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series No. 357; American Chemical Society: Washington, DC, 1987.

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were used throughout the analysis;[19] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[19] were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0010(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were located from a difference-Fourier synthesis and included with isotropic thermal parameters. The molecule is a dimer which is located about an inversion center (0, 0, 1). Refinement of positional and thermal parameters led to convergence with $R_F = 3.3\%$, $R_{wF} = 4.8\%$, and GOF = 1.19 for 448 variables refined against those 5481 data with $|F_o| > 2.0\sigma(|F_o|)$. A final difference-Fourier synthesis was featureless, $\varrho(max) = 0.46$ e Å^{-3}.

(CH$_3$CH$_2$C(CH$_2$O)$_3$)$_2$Ti$_4$(OCHMe$_2$)$_{10}$, 2. A colorless crystal of approximate dimensions 0.36 × 0.40 × 0.50 mm was handled as above for **1**. Data were collected on a Siemens P3 diffractometer which is equipped with a modified LT-2 low-temperature system. A semiempirical (ψ scan) absorption correction was applied. The space group is $P2_1/n$. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0002(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were located from a difference-Fourier synthesis and included with isotropic thermal parameters. The molecule is a dimer which is located about an inversion center. Refinement of positional and thermal parameters led to convergence with $R_F = 3.7\%$, $R_{wF} = 4.1\%$, and GOF = 1.80 for 465 variables refined against those 5448 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features, ϱ-(max) = 0.41 e Å^{-3}.

(CH$_3$C(CH$_2$O)$_3$)$_2$Zr$_4$(OCHMe$_2$)$_{10}$, 3. A colorless crystal of approximate dimensions 0.13 × 0.23 × 0.41 mm was handled as above for **1**. Low-temperature (163 K) intensity data were collected via an ω scan technique with Mo Kα radiation. All 14 738 data were corrected for absorption[20] and for Lorentz and polarization effects and placed on an approximately absolute scale. The two possible triclinic space groups were the noncentrosymmetric $P1$ [C_1^1, No. 1] and the centrosymmetric $P\bar{1}$ [C_i^1, No. 2]. Refinement of the model using the centrosymmetric space group proved $P\bar{1}$ was the correct space group. There were two independent molecules per asymmetric unit cell.

The structure was solved by direct methods (SHELXTL PLUS). Initial refinement of the structure was carried out by blocked full-matrix least-squares methods. This refinement (anisotropic displacement parameters for Zr and O atoms, isotropic displacement parameters for C atoms, H atoms included in idealized positions and refined by the riding model) converged to R1 = 0.0652 for 9029 data with ($|F_o| > 4.0\sigma(|F_o|)$), R1 = 0.1229 for all 14 738 data, and wR2 = 0.1775 for all data. Inspection of the results showed large variations in chemically equivalent bond distances, presumably a consequence of the limited number and low intensity of the diffraction data.

For this reason, the final refinement was based on a restrained model with the use of the SHELXL-93 refinement program.[18] Each of the three types of ligands (terminal OCHMe$_2$, μ-OCHMe$_2$, and THME) was constrained to have bonding and nonbonding distances identical to within 0.03 Å in all of its occurrences. The sole exception was for the group bound via O(33), where there was evidence for disorder. Atoms of that group were refined individually, with two alternative positions for each β-carbon atom. The sum of the occupancies of these alternative atom sets was constrained to unity. Treatment of displacement parameters and hydrogen atoms was identical to that described above.

The restrained refinement was based on F^2 and utilized all but six of the 14 738 measured data. Six intense low-angle data were omitted from the refinement because of systematic errors. This refinement yielded an R value comparable to that of the individual-atom refinement (R1 = 0.0652 for 9029 data with $I > 2.0\sigma(I)$) and lower esd's for all structural parameters. Reported results are those from the restrained refinement.

Film Generation. Due to the solubility limitation of (THME)$_2$Ti$_4$-(OCHMe$_2$)$_{10}$, **1**, all the solutions {(THME)$_2$Zr$_4$(OCHMe$_2$)$_{10}$, **3**; Ti-(OCHMe$_2$)$_4$, **5**; [Zr(OCHMe$_2$)$_4$·HOCHMe$_2$]$_2$, **6**} were prepared at a concentration of 0.07 M in toluene, with either crystalline or freshly distilled starting materials. The solvent of choice was freshly dried
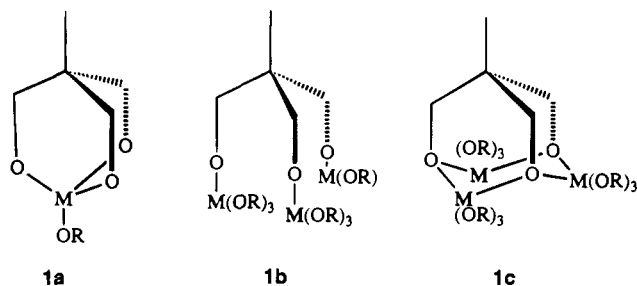

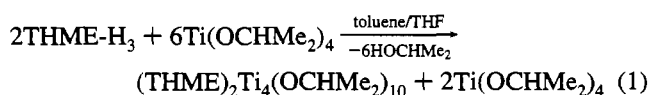**Figure 1.** Possible binding modes for the THME ligand: (a) chelating, (b) monodentate, and (c) tridentate bridging.

toluene for two reasons: (i) the NMR solution studies were run in toluene-d_8 and (ii) previous results[21] indicated that toluene would be a solvent amenable to drying, resulting in uniform films. Due to the low concentration of the reagents, it was decided to spin-cast deposit these films in air for 20 s at 1500 rpm. The substrates used were silicon wafers that were cleaned with filtered methanol and dried at 400 °C for 10 min, immediately prior to deposition.[22] The changes in film thickness and refractive index at room temperature as a function of time were followed by ellipsometry. Topographical surface pictures were then obtained by optical microscopy. After film thickness had stabilized at room temperature, the film was then heated at 10 °C/min to 650 °C and then fired at this temperature for 30 min. Thickness and refractive index data were once again obtained. Photomicrographs were also acquired to record any visual alterations in the surface microstructure.
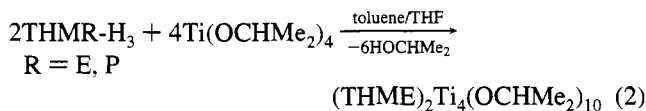
Discussion

This work focused on synthesizing well-characterized group IV tridentate alkoxide complexes which are similar to starting materials that are typically used as precursors for lead zirconate titanate (PZT) ceramic compounds. The tridentate ligands chosen were tris(hydroxymethyl)ethane (THME-H$_3$) and tris-(hydroxymethyl)propane (THMP-H$_3$), since these alkoxides are saturated alkyls, easily obtained, stable, and easily derivatized,[23] which allows for fine tuning of any system developed. It was further thought that the nuclearity of the synthesized precursors could be systematically controlled due to the variety of binding modes possible (Figure 1).[24–28] On the basis of previous work, it was determined that these sterically bulky ligands would also reduce the susceptibility of the precursors to attack by ambient humidity.[21] Finally, there is a paucity of tridentate alkoxide structures reported in the literature for early transition metals;[24,26–28] however, Chen and Zubieta have written a comprehensive review of structurally characterized polyoxomolybdates and vanadate compounds which contain these ligands.[24]

Synthesis. Initially, it was thought that by using the tridentate ligands as chelating agents (Figure 1a) the degree of hydrolysis of the generated products would be limited. Therefore, the 1:1 stoichiometric reactions of THME-H$_3$ with group IV metal isopropoxides were undertaken. The products of these reactions were white powders which were insoluble in a wide variety of solvents. Therefore, these compounds were not considered appropriate materials for the generation of ceramic films and further characterization was not pursued. Instead, the stoichiometry was increased to a 1:3 THME:Ti ratio, in hopes of generating trinuclear monodentate complexes as pictured in Figure 1b.

For the titanium reaction (eq 1), the THME-H$_3$ ligand was first slurried in THF, due to its low solubility in other organic

$$2\text{THME-H}_3 + 6\text{Ti(OCHMe}_2)_4 \xrightarrow[-6\text{HOCHMe}_2]{\text{toluene/THF}}$$

$$(\text{THME})_2\text{Ti}_4(\text{OCHMe}_2)_{10} + 2\text{Ti(OCHMe}_2)_4 \quad (1)$$

solvents and then slowly added to a stirring solution of $Ti(OCHMe_2)_4$ in toluene. No precipitate was present after 12 h of stirring. During the removal of the solvent from the reaction mixture, crystals formed, which were acceptable for X-ray studies and proved to be $(H_3CC(CH_2-\mu_3-O)(CH_2-\mu-O)_2)_2$-$Ti_4(OCHMe_2)_{10}$, **1**, $[(THME)_2Ti_4(OCHMe_2)_{10}]$. The reaction was further optimized by altering the stoichiometry to 1:2 (eq 2, R = E). If an excess of $Ti(OCHMe_2)_4$ is used (eq 1 or 2),

$$2THMR\text{-}H_3 + 4Ti(OCHMe_2)_4 \xrightarrow[-6HOCHMe_2]{\text{toluene/THF}}$$
$$R = E, P$$

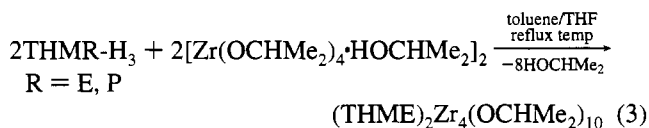$$(THME)_2Ti_4(OCHMe_2)_{10} \quad (2)$$

only **1** is isolated. The solubility limit of **1** is approximately 0.07 M in toluene, and it is stable in solution, at ambient temperature, over an extended period of time; however, **1** is thermally unstable. Warming a toluene solution above 45 °C results in the immediate formation of a white precipitate, which is no longer soluble in a wide variety of solvents.

After the appropriate stoichiometry for the THME-H_3 reaction was determined, an analogous reaction using THMP-H_3 was undertaken (eq 2, R = P). The THMP-H_3 ligand is significantly more soluble than the THME-H_3 ligand. X-ray quality single crystals were isolated by drastically reducing the volume of the reaction mixture and allowing it to stand overnight at ambient temperatures. The isolated product proved to be (H_3-$CCH_2C(CH_2-\mu_3-O)(CH_2-\mu-O)_2)_2Ti_4(OCHMe_2)_{10}$, **2**, $[(THMP)_2$-$Ti_4(OCHMe_2)_{10}]$. **2** demonstrates increased solubility versus **1**, and solutions of **2** in toluene can be warmed slightly (~35 °C) without any noticeable precipitate forming. After cooling, a microcrystalline powder was isolated. The ^1H NMR spectrum of this powder does not differ from that of the crystals.

In an attempt to make the zirconium analog of **1**, a reaction similar to eq 2 was undertaken using $[Zr(OCHMe_2)_4\cdot HOCHMe_2]_2$ instead of $Ti(OCHMe_2)_4$. During this reaction there was no evidence of the transitory precipitate previously observed. After 1 week at ambient temperature, the concentrated reaction mixture yielded colorless crystals that proved to be the starting material $[Zr(OCHMe_2)_4\cdot HOCHMe_2]_2$, **6**;[29] however, unit cell parameters[29a] different from those previously reported[29b] were found.

An identical reaction was then performed as above except the solution was heated at toluene reflux temperatures for 12 h, eq 3 (R = E). The initially clear solution became tinged with

$$2THMR\text{-}H_3 + 2[Zr(OCHMe_2)_4\cdot HOCHMe_2]_2 \xrightarrow[-8HOCHMe_2]{\substack{\text{toluene/THF} \\ \text{reflux temp}}}$$
$$R = E, P$$

$$(THME)_2Zr_4(OCHMe_2)_{10} \quad (3)$$

a slight yellow color. The solvent was removed *in vacuo*, the product was extracted with toluene to remove a small precipitate, and crystals were grown by concentrating the reaction mixture. These crystals proved to be ($H_3CC(CH_2-\mu$-$O)_3)_2Zr_4(\mu\text{-}OCHMe_2)_2(OCHMe_2)_8$, **3**, $[(THME)_2Zr_4(OCHMe_2)_{10}]$. Warming a solution of **3** above 100 °C and cooling back to room temperature results in no change in the room-temperature ^1H NMR spectrum (*vide infra*). The solubility limit of **3** is greater than 0.25 M in toluene, and solutions are stable for several months.

The THMP zirconium derivative was synthesized in a manner analogous to that for **3** (eq 3, R = P). Once again, the heated solution turns slightly yellow. After extraction with toluene, crystals can be formed by drastic reduction of the solvent

Table 2. Atomic Coordinates ($\times 10^5$) for $(THME)_2Ti_4(OCHMe_2)_{10}$, **1**

atom	x	y	z
Ti(1)	14217(2)	13861(2)	95466(2)
Ti(2)	6920(2)	1776(2)	111358(2)
O(1)	−3466(9)	11604(7)	88984(7)
O(2)	−10412(9)	565(7)	101394(7)
O(3)	6834(9)	14203(7)	106654(7)
O(4)	11604(11)	26184(8)	93463(9)
O(5)	19112(10)	10196(9)	85725(8)
O(6)	28559(10)	14376(8)	103101(8)
O(7)	1074(10)	4655(8)	120330(7)
O(8)	22307(10)	293(8)	117234(7)
C(1)	−12138(14)	17968(11)	90140(11)
C(2)	−18314(13)	8023(11)	101638(11)
C(3)	−2605(14)	20311(11)	106534(11)
C(4)	−13985(14)	17559(11)	99577(11)
C(5)	−23415(15)	24530(12)	99975(13)
C(6)	18232(15)	33784(12)	92168(12)
C(7)	15147(23)	42058(15)	97063(16)
C(8)	15906(20)	35602(16)	82199(14)
C(9)	30275(14)	11654(12)	84217(11)
C(10)	28761(18)	12858(14)	74180(13)
C(11)	38356(17)	3643(15)	88096(14)
C(12)	37527(14)	17140(12)	110759(11)
C(13)	33093(18)	24571(14)	115868(13)
C(14)	48079(16)	20349(16)	107794(14)
C(15)	−4385(15)	5072(12)	127424(11)
C(16)	−2371(21)	14478(15)	131832(16)
C(17)	278(20)	−2669(17)	134001(14)
C(18)	28187(14)	−1874(12)	126372(11)
C(19)	30413(16)	6849(13)	131933(12)
C(20)	39552(16)	−6885(15)	126806(14)

volume. Due to the fact that **1** and **2** possess similar structures, it is proposed that **4** in the solid state is similar in structure to **3**.

Solid State. The use of tridentate ligands such as THME-H_3 and THMP-H_3 has not been reported for the early transition metals of Ti or Zr; however, the general structure type obtained for **1** and **2** has been reported for a molybdenum compound (with the identical tridentate ligand), $(THME)_2Mo_4(OEt)_2(O)_8$.[25] Structures of a few other transition metals (M = V,[24,26] Mo,[24−26] Fe,[27a] Cu[27b]) utilizing these tridentate ligands are also reported in the literature. The nuclearity of the vanadium and molybdenum molecules is quite varied and ranges from dimers to oligomers that possess up to 42 metal centers.[24−26] The majority of these oligomers are salts where the THMR (R = H, CH_3[E], CH_2CH_3[P], CH_2OH, NR_2, NO_2) ligands surround, but are not involved in, the central binding of the $[M-O]_n$ core, as observed for **1−3**. The iron compound[27a] isolated is a hexameric species, $OFe_6(THME)_6^{2-}$, which possesses only μ-O oxygens from the THME ligands, and externally supports the internal Fe−O core. The dimer $[CuCl_2(THME)]_2^{27b}$ is interesting, inasmuch as one of the −OH functional groups of the THME ligand remains unreacted. There is one report of a tridentate, ligated alkoxide of titanium that utilizes 1,3,5-cyclohexanetriol (CYHT-H_3) as a chelating ligand.[28] This compound is monomeric and is supported by a cyclopentadienyl coligand, $(\eta^5\text{-}C_5H_4(SiMe_3))$-$Ti(CYHT)$. Attempts in our laboratory to synthesize titanium alkoxides using the CYHT-H_3 ligand have resulted in microcrystalline material only. The NMR spectrum of this powder suggests that the structure is very similar to those of **1** and **2**.[31]

Crystal Structure. Table 1 lists the data collection parameters for $(THME)_2Ti_4(OCHMe_2)_{10}$, **1**, $(THMP)_2Ti_4(OCHMe_2)_{10}$, **2**, and $(THME)_2Zr_4(\mu\text{-}OCHMe_2)_2(OCHMe_2)_8$, **3**. Tables 2−4 list the positional parameters for **1−3**, respectively. Table 5 shows a comparison of selected bond distances and angles for **1, 2**, and the previously characterized compound $Ti_4(\mu_3\text{-}OMe)_2$-

Table 3. Atomic Coordinates ($\times 10^5$) for (THMP)$_2$Ti$_4$(OCHMe$_2$)$_{10}$, **2**

atom	x	y	z
Ti(1)	31063(2)	7871(3)	1689(2)
Ti(2)	45466(2)	−4932(3)	−8842(2)
O(1)	44076(8)	17014(11)	5658(6)
O(2)	57036(8)	6042(11)	−2364(7)
O(3)	37269(8)	9495(11)	−8118(7)
O(4)	24985(9)	22719(13)	−100(7)
O(5)	28465(9)	4330(13)	10841(7)
O(6)	22071(9)	−2498(14)	−2932(7)
O(7)	49133(9)	−844(13)	−17259(7)
O(8)	36495(9)	−16707(12)	−11704(7)
C(1)	46417(14)	28259(17)	2278(10)
C(2)	58125(13)	18341(17)	−5195(11)
C(3)	40250(14)	21308(17)	−10460(10)
C(4)	49106(13)	26449(16)	−5383(10)
C(5)	51453(16)	39480(18)	−8030(12)
C(6)	53398(24)	40725(25)	−15845(15)
C(7)	18272(16)	30055(23)	2959(14)
C(8)	12903(32)	38280(41)	−2903(25)
C(9)	23499(25)	37316(34)	9418(21)
C(10)	19633(15)	−24(23)	12917(12)
C(11)	17911(20)	6652(37)	19774(15)
C(12)	20032(22)	−13863(30)	13871(22)
C(13)	15237(16)	−5574(28)	−9161(14)
C(14)	8311(25)	−14928(36)	−7050(26)
C(15)	9924(26)	6053(40)	−12274(21)
C(16)	54078(15)	−75(22)	−23427(11)
C(17)	48287(22)	7954(31)	−29253(14)
C(18)	55828(21)	−12893(27)	−26111(14)
C(19)	34619(16)	−25620(23)	−17396(13)
C(20)	29105(23)	−19609(41)	−24239(16)
C(21)	29169(23)	−36376(28)	−14810(26)

(μ-OMe)$_4$(OMe)$_{10}$, **7**.[30] Table 6 is a list of important bond distances and angles for **3** and the reported metrical data for [Zr(OCHMe$_2$)$_4$·HOCHMe$_2$]$_2$, **6**.[29b] **1** and **2** crystallized in the space group $P2_1/n$ and **3** crystallized with two molecules in the asymmetric unit cell in the space group $P\bar{1}$.

The compound (THME)$_2$Ti$_4$(OCHMe$_2$)$_{10}$, **1** (Figure 2), forms a typical fused-M$_3$O$_{12}$ arrangement.[30,32,33a] The basic constructs of the central core of **1** are very similar to Figure 1c. **1** possesses a crystallographic center of symmetry and consists of a planar, eight-member, rhombohedrally shaped ring with alternating titanium and oxygen atoms. The titanium atoms are octahedrally bound by oxygens, forming distorted, face-shared bioctahedral geometries. All of the bridging oxygen atoms (there are two types: four μ-O and two μ_3-O) are associated with the tridentate THME ligands (one residing above the central core and the other below it). Both THME ligands span the central Ti$_4$O$_6$ core, with two of the bridging oxygens on one side of the central ring associated with the triply bridging oxygen on the opposite side of the ring. The central core is shown in Figure 2b (the carbons of the isopropoxide ligands have been removed for clarity). There are also two types of octahedrally bound titanium metal centers that lie at the corners of the central rhombohedral core. Two of the four titaniums possess three terminal isopropoxides and one interaction with the μ_3-O oxygens of the THME ligands. The other two titanium atoms bind to both of the μ_3-O oxygens

and therefore have only two terminal isopropoxide ligands. The compound (THMP)$_2$Ti$_4$(OCHMe$_2$)$_{10}$, **2** (Figure 3), crystallized in an arrangement and space group identical to those of **1**.

The compound (THME)$_2$Zr$_4$(μ-OCHMe$_2$)$_2$(OCHMe$_2$)$_8$, **3** (Figure 4), is also tetranuclear; however, there are only μ-O oxygens in the structure. **3** has an approximate C_2 axis passing through Zr(2) and Zr(4). The central core consists of a ring of four point-fused Zr$_2$(μ-O)$_2$ rings. Each zirconium atom is in an extremely distorted six-coordinate edge-shared bioctahedral arrangement, with four bridging oxygens and two terminal isopropoxide ligands. The THME ligands are on opposite sides of the Zr$_4$ plane but span only part of the central core as μ-O oxygens, which forces two isopropoxide ligands to bridge. Both μ-OCHMe$_2$ ligands bridge from Zr(4) on opposite sides of the central Zr$_4$ plane. Unlike the case of Zr(4), which possesses two μ-O(OCHMe$_2$) and two μ-O(THME) oxygens, the μ-O oxygens of Zr(2) are solely from the THME ligands. The other two metal centers [Zr(1) and Zr(3)] are coordinated to one μ-O(OCHMe$_2$) and three μ-O (THME) oxygens. Figure 4b shows the basic central core of **3** with the methyl carbons of the isopropoxide ligands removed for clarity.

Metrical Data.[34] **1** and **2** are the first tridentate alkoxide ligated titanium complexes isolated. Since there is a dearth of well-characterized titanium alkoxides (especially those containing the basic Ti$_4$(μ_3-OR)$_2$(μ-OR)$_4$ geometrical arrangement), comparisons of the terminal-O−, μ-O−, and μ_3-O−Ti distances can only be made with a limited number of other titanium alkoxy complexes. Only two homoleptic alkoxide titanium compounds with the nuclearity described have been published: Ti$_4$(μ_3-OMe)$_2$(μ-OMe)$_6$(OMe)$_8$, **7**,[30] and Ti$_4$(μ_3-OEt)$_2$(μ-OEt)$_6$(OEt)$_8$, **8**.[32] Three other reported oligomers of **8** produced by hydrolysis reactions are the titanium oxo alkoxide compounds Ti$_7$O$_4$-(OEt)$_{20}$,[35] Ti$_{10}$O$_8$(OEt)$_{24}$,[36] and Ti$_{16}$O$_{16}$(OEt)$_{32}$.[35] Other alkoxides of titanium that have been crystallographically characterized include heteronuclear isopropoxide,[37] aryl alkoxide,[38] and acetate[39] ligated compounds.

As would be expected, the distances for **1** and **2** (shown in Table 5) are identical, within experimental error. The terminal Ti−OR (R = CHMe$_2$) distances for **1** and **2** range from 1.787−

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(31) Preliminary NMR data for the reaction product ["(CYHT)$_2$Ti$_4$-(OCHMe$_2$)$_{10}$"] from a stoichiometric mixture of 1:2 (CYHT-H$_3$) and Ti(OCHMe$_2$)$_4$. Reaction conditions were identical to those for **1**. ^{1}H NMR (250 MHz, C$_6$D$_6$): δ 5.09 (2H, t, J_{CH} = 2.5 Hz), 4.83 (4H, sept, J_{CH} = 6.09 Hz), 4.44 (1H, b s), 1.28 (36H, d, J_{CH} = 6.09 Hz). ^{13}C NMR (C$_6$D$_6$) δ 77.6, 74.4, 73.2, 38.3, 38.0, 26.5.

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(37) Some examples include: (a) Kuhlman, R.; Vaartstra, B. A.; Streib, W. E.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1993**, *32*, 1272. (b) Hampden-Smith, M. J.; Williams, D. S.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 4076. (c) Eve. D. J.; Niven, M. L. *Inorg. Chim. Acta* **1990**, *174*, 205. (d) Drew, M. G. B.; Eve, D. J. *Acta Crystallogr.* **1977**, *B33*, 2919.

(38) Some examples include: (a) Boyle, T. J.; Barnes, D. L.; Heppert, J. A.; Morales, L.; Takusagawa, F. *Organometallics* **1992**, *11*, 1112. (b) Toth, R. T.; Stephan, D. W. *Can. J. Chem.* **1991**, *69*, 172. (c) Hofmeister, G. E.; Hahn, F. E.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 2318. (d) Sharpless, K. B. *Chem. Scr.* **1987**, *27*, 521. (e) Sharpless, K. B.; Pedersen, S. F.; Dewan, J. C.; Erkman, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1279. (f) Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1996**, 610. (g) Olmstead, M. M.; Sigel, G.; Hope, H.; Xu, X.; Power, P. *J. Am. Chem. Soc.* **1985**, *107*, 8087. (h) Borgias, B. A.; Cooper, S. R.; Koh, Y. B.; Raymond, K. *Inorg. Chem.* **1984**, *23*, 1009. (i) Williams, I. D.; Pedersen, S. F.; Sharpless, K. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 6430. (j) Van de Velde, G. M. H.; Harkena, S.; Gellings, P. J. *Inorg. Chim. Acta* **1974**, *11*, 243. (k) Svetich, G. W.; Voge, A. A. *Acta Crystallogr.* **1972**, *B28*, 1760. (l) Watenpaugh, K.; Caughlan, C. N. *Inorg. Chem.* **1966**, *5*, 1782.

Table 4. Atomic Coordinates ($\times 10^5$) for $(THME)_2Zr_4(OCHMe_2)_{10}$, **3**

atom	x	y	z	atom	x	y	z
Zr(1)	436(1)	78(1)	3089(1)	Zr(6)	−5780(1)	−6266(1)	3215(1)
Zr(2)	334(1)	791(1)	1552(1)	Zr(7)	−4412(1)	−5008(1)	3293(1)
Zr(3)	−1098(1)	−543(1)	1648(1)	Zr(8)	−4341(1)	−4255(1)	1767(1)
Zr(4)	−958(1)	−1247(1)	3177(1)	O(21)	−5153(6)	−6442(3)	2440(3)
O(1)	1247(5)	−12(3)	2324(3)	O(22)	−4141(5)	−5876(3)	3060(3)
O(2)	471(6)	−63(3)	1309(2)	O(23)	−4095(5)	−5283(3)	1817(3)
O(3)	86(5)	−1073(3)	2404(3)	C(21A)	−3949(8)	−6811(5)	2449(4)
C(1)	2294(8)	−469(5)	2282(4)	C(22A)	−3040(8)	−6281(5)	3001(4)
C(2)	1580(8)	−505(5)	1364(4)	C(23A)	−3012(8)	−5761(4)	1901(4)
C(3)	1254(8)	−1417(5)	2355(4)	C(21B)	−2986(8)	−6426(4)	2453(4)
C(4)	2060(8)	−925(4)	1983(4)	C(21C)	−1791(9)	−6887(5)	2458(5)
C(5)	3257(9)	−1375(5)	1953(5)	O(24)	−6640(6)	−5451(3)	2435(3)
O(4)	−221(5)	1004(3)	2305(3)	O(25)	−5486(5)	−4454(3)	2513(2)
O(5)	−1315(6)	442(3)	1688(3)	O(26)	−5900(5)	−4416(3)	1421(2)
O(6)	−1199(5)	−157(3)	2926(2)	C(24A)	−7698(8)	−4959(4)	2387(4)
C(6A)	−1408(8)	1377(5)	2304(4)	C(25A)	−6666(8)	−4075(5)	2461(4)
C(7)	−2400(8)	855(5)	1764(4)	C(26A)	−7044(8)	−4032(5)	1461(4)
C(8)	−2300(8)	314(4)	2864(4)	C(24B)	−7486(8)	−4203(4)	2087(4)
C(9)	−2393(7)	984(4)	2310(4)	C(24C)	−8689(8)	−3732(5)	2036(4)
C(10)	−3578(8)	1451(5)	2326(4)	O(27)	−5835(6)	−5595(3)	3659(3)
O(7)	−2089(6)	−995(3)	2430(3)	C(27A)	−6398(9)	−5615(6)	4195(4)
C(7A)	−3174(11)	−1246(7)	2481(7)	C(27B)	−6147(12)	−6332(6)	4657(5)
C(7B)	−4232(9)	−734(6)	2430(5)	C(27C)	−7669(10)	−5318(6)	4088(5)
C(7C)	−3114(15)	−1797(8)	2336(8)	O(28)	−3315(5)	−4542(3)	2555(3)
O(8)	485(6)	−1020(3)	3539(2)	C(28A)	−2230(10)	−4336(6)	2619(5)
C(8A)	1132(12)	−1503(8)	4065(6)	C(28B)	−1177(9)	−4814(6)	2568(5)
C(8B)	2299(10)	−1821(6)	3970(5)	C(28C)	−2304(14)	−3616(6)	2367(7)
C(8C)	618(14)	−1552(9)	4584(6)	O(29)	−4921(7)	−5877(3)	1140(3)
O(9)	1998(6)	60(4)	3342(3)	C(29A)	−4646(18)	−6234(9)	796(7)
C(9A)	3141(11)	66(7)	3483(5)	C(29B)	−5135(12)	−6839(6)	950(5)
C(9B)	3228(14)	111(8)	4043(5)	C(29C)	−4095(12)	−5920(7)	253(5)
C(9C)	3658(15)	569(9)	2998(7)	O(30)	−7307(6)	−5446(4)	1383(3)
O(10)	−420(7)	485(4)	3595(3)	C(30A)	−8104(12)	−5470(7)	1006(6)
C(10A)	−681(18)	814(9)	3964(8)	C(30B)	−8875(14)	−5953(8)	1298(7)
C(10B)	−234(15)	1409(7)	3837(7)	C(30C)	−8715(11)	−4778(6)	610(5)
C(10C)	−1356(11)	490(7)	4470(5)	O(31)	−4912(6)	−7167(3)	3731(3)
O(11)	1879(7)	989(4)	1264(3)	C(31A)	−4866(11)	−7834(5)	4161(5)
C(11A)	2959(13)	1155(8)	1022(6)	C(31B)	−4847(13)	−8330(6)	3897(6)
C(11B)	3007(13)	1294(8)	406(5)	C(31C)	−3833(10)	−8021(6)	4561(5)
C(11C)	3298(17)	1681(10)	1166(8)	O(32)	−7312(6)	−6512(4)	3469(3)
O(12)	−528(7)	1673(3)	991(3)	C(32A)	−8465(13)	−6654(9)	3563(6)
C(12A)	−523(12)	2338(6)	565(5)	C(32B)	−8609(17)	−7185(9)	4126(6)
C(12B)	−513(12)	2837(6)	831(5)	C(32C)	−8801(18)	−6776(12)	3075(7)
C(12C)	−1470(11)	2563(6)	129(5)	O(33)	−5033(7)	−4297(3)	3564(3)
O(13)	−460(7)	−1257(3)	1374(3)	C(33A)	−5390(16)	−3787(9)	3780(8)
C(13A)	−185(10)	−1558(5)	972(4)	C(33B)	−4556(26)	−3320(14)	3614(12)
C(13B)	−883(11)	−2095(6)	1086(5)	C(33X)	−6564(26)	−3557(16)	3802(13)
C(13C)	−300(12)	−1019(6)	361(4)	C(33Y)	−5615(29)	−3076(16)	3224(13)
O(14)	−2466(6)	−147(4)	1125(3)	C(33Z)	−5285(52)	−3863(30)	4280(24)
C(14A)	−3415(11)	244(7)	737(5)	O(34)	−3113(6)	−5462(4)	3851(3)
C(14B)	−2947(15)	675(8)	171(6)	C(34A)	−2149(12)	−5736(6)	4234(6)
C(14C)	−4176(13)	−201(8)	695(7)	C(34B)	−2030(14)	−6473(6)	4581(6)
O(15)	−360(7)	−2227(3)	3480(3)	C(34C)	−2067(17)	−5321(8)	4557(7)
C(15A)	−33(12)	−2942(6)	3764(5)	O(35)	−2988(6)	−4130(3)	1257(3)
C(15B)	248(17)	−3250(9)	3347(7)	C(35A)	−1992(9)	−4166(5)	908(4)
C(15C)	−957(14)	−3223(8)	4184(6)	C(35B)	−1540(11)	−3513(6)	691(5)
O(16)	−2248(7)	−1285(4)	3708(3)	C(35C)	−2287(13)	−4339(7)	436(5)
C(16A)	−3214(14)	−1252(9)	4055(7)	O(36)	−5028(6)	−3283(3)	1483(3)
C(16B)	−3891(13)	−1783(8)	4199(7)	C(36A)	−5336(9)	−2611(5)	1050(4)
C(16C)	−3131(14)	−951(8)	4461(6)	C(36B)	−4545(10)	−2177(5)	1104(5)
Zr(5)	−5747(1)	−5513(1)	1676(1)	C(36C)	−5291(10)	−2618(6)	452(4)

(1) to 1.839(1) Å. When compared to other homo- or heteroleptic titanium alkoxide compounds (Ti−OR (terminal) distances

1.730(4)−2.078(14) Å), both **1** and **2** have distances at the low end of these values. As is typical, the average Ti−OR (terminal), Ti−μ-OR′ (R′ = $(OCH_2)_3CCH_3$ or $(OCH_2)_3CCH_2$-CH_3), and Ti−μ_3-OR′ distances of **1** and **2** become progressively longer 1.81, 2.04, and 2.20 Å, respectively.[40] **7** and **8** have reported Ti−μ-OR distances ranging from 1.96 to 2.08 Å and Ti−μ_3-OR distances of 2.15−2.23 Å.[30,32] Similar ranges are reported for other heteroleptic titanium alkoxide complexes.[37−38] The tridentate ligands have little effect on the bond distances of the other alkoxide ligands.

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Table 5. Bond distances (Å) and Angles (deg) for (THME)₂Ti₄(OCHMe₂)₁₀, **1**, (THMP)₂Ti₄(OCHMe₂)₁₀, **2**, and Ti₄(OMe)₁₆, **7**

Distances (Å)

	1	2	7ᵃ
M---M			
M(1)---M(2)	3.328(1)	3.319(1)	3.353
M(1)---M(2′)	3.337(1)	3.351(1)	3.351
M---C(4) ((CH₃)(CH₂O)₃)	3.629	3.629	
	3.500	3.473	
M−O (terminal) (av)	1.81(3)	1.80(2)	1.75−2.08
M−μ-O (av)	2.04(8)	2.04(8)	1.96−2.08
M−μ₃-O (av)	2.20(3)	2.20(3)	2.13−2.20
μ₃-O---μ₃-O	2.639	2.626	2.595
μ-OR′(1)---μ-OR′(3) (av)ᵇ	2.803	2.694	

Angles (deg)

	1	2	7ᵃ
M−μ-O−M (av)	109(1)	109(1)	112(1)
M−μ₃-O−M			
Ti(1)/Ti(2)	98.9(1)	98.3(1)	100.9(4)
Ti (1)/Ti(2′)	97.5(1)	98.3(1)	100.3(4)
Ti(2)/Ti(2′)	105.6(1)	105.9(1)	106.0(3)
M−μ-O−C (av)	120(1)	119(3)	122(4)
M−μ₃-O−C	114.3(1)	114.2(1)	114.7(7)
	115.9(1)	116.2(1)	114.6(7)
	121.8(1)	121.2(1)	118.3(7)
	78.8(1)	79.0(1)	112.8(5)
μ-O−M−μ-O	156.9(1)	157.1(1)	111.5(5)
μ-O−M−μ₃-O	72.1(1)−84.6(1)	72.5(1)−85.5(1)	73.8(4)−89.6(4)
μ₃-O−M−μ₃-O	74.4(1)	74.1(1)	74.0(3)
μ-O−C−C(4) (av)	113	113	
μ₃-O−C−C(4)	114.3(1)	113.6(2)	

ᵃ Two molecules in the unit cell. ᵇ OR′ = (OCH₂)₃CCH₃ or (OCH₂)₃CCH₂CH₃.

Table 6. Bond Distances (Å) and Angles (deg) for (THME)₂Zr₄(OCHMe₂)₁₀, **3**, and [Zr(OCHMe₂)₄·HOCHMe₂]₂, **6**²⁹ᵇ

Distances (Å)

	3ᵃ	4ᵇ
M---M	3.493(2)−3.530(1)	3.480−3.502
M−OR (av)ᶜ	1.94(1)	1.943
M−μ-OR′ (av)ᵈ	2.16(2)	
M−μ-OR (av)ᶜ	2.171(6)	2.170
μ-O---μ-O′	2.45−2.51	2.76−2.78

Angles (deg)

	3ᵃ	4ᵇ
M−μ-O−M (av)	109(1)	107
M−μ-OR′ (av)ᵈ	122(4)	172
μ-OR′−M−μ-OR′ ᵈ	79.2(2)	
	79.3(2)	
	81.5(2)	
	82.0(2)	
μ-OR′−M−μ-OR (av)ᶜ,ᵈ	70.0(3)	
μ-OR−M−μ-ORᶜ	148.2(2)	72.7
μ-O−M−ORᶜ	94.4(3)−107.9(3)	93.9
μ-O−CH₂−C(4) (av)	113	

ᵃ Two molecules in the asymmetric unit cell. ᵇ Four molecules in the unit cell. ᶜ OR = OCHMe₂. ᵈ OR′ = (OCH₂)₃CCH₃ or (OCH₂)₃CCH₂CH₃.

For **1** and **2** the central rhombohedral core is planar due to the symmetry of the molecule. The range of the average μ-OR′−Ti−μ-OR′ angles is extremely large (78.8−157.1°) when compared to the μ-OR−Ti−μ-OR angles of **7** (114.6−118.3°, which are within the range of those for other observed bridging alkoxides).²⁹ᵇ,³⁷,³⁸ The distorted octahedral arrangement of the metal centers of **1** and **2** is an indication of the strain enforced by the bite of the THMR (R = E, P) ligands. The μ-O−C−C(1) angle of the THMR ligand for **1** and **2** is
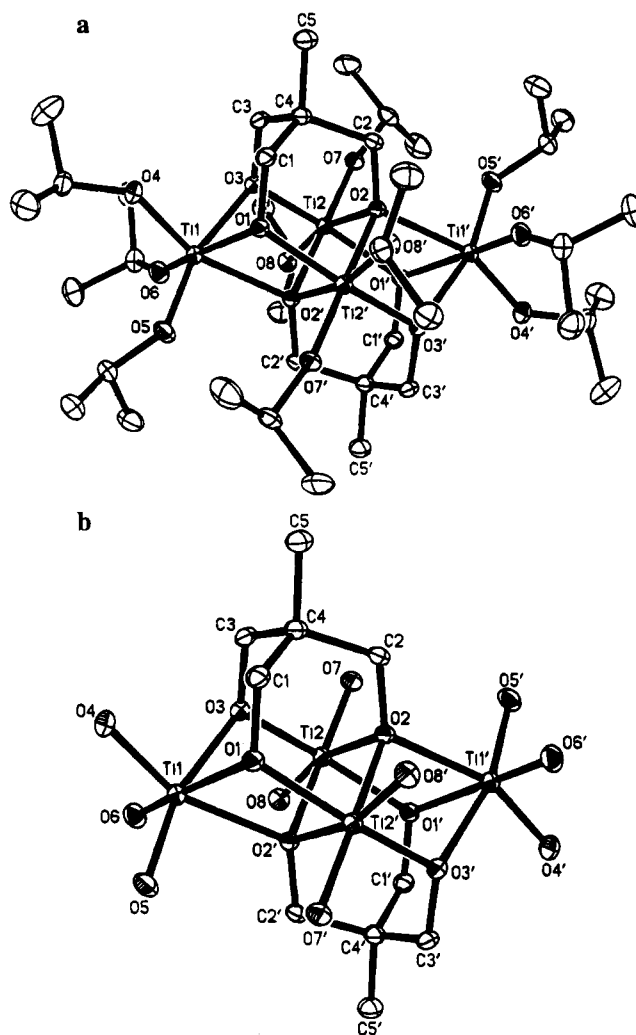

Figure 2. (a) Thermal ellipsoid drawing of (THME)₂Ti₄(OCHMe₂)₁₀, **1**. Thermal ellipsoids are drawn at 50% probability. (b) Thermal ellipsoid drawing of the central core of (THME)₂Ti₄(OCHMe₂)₁₀, **1**. Thermal ellipsoids are drawn at 50% probability. The carbons associated with OCHMe₂ ligands have been omitted for clarity.
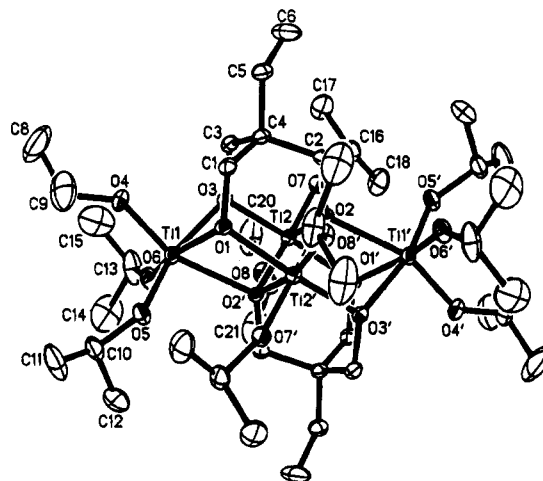

Figure 3. Thermal ellipsoid drawing of (THMP)₂Ti₄(OCHMe₂)₁₀, **2**. Thermal ellipsoids are drawn at 50% probability.

113°, indicating a slight distortion of the methylene carbons. This illustrates how the tridentate ligand is stretched to accommodate the titanium metal centers. The Ti(1)---Ti(2) distances of **1** and **2** (average 3.33 Å) agree with that observed in **7** (average 3.35 Å) and are typical of other polynuclear titanium compounds.
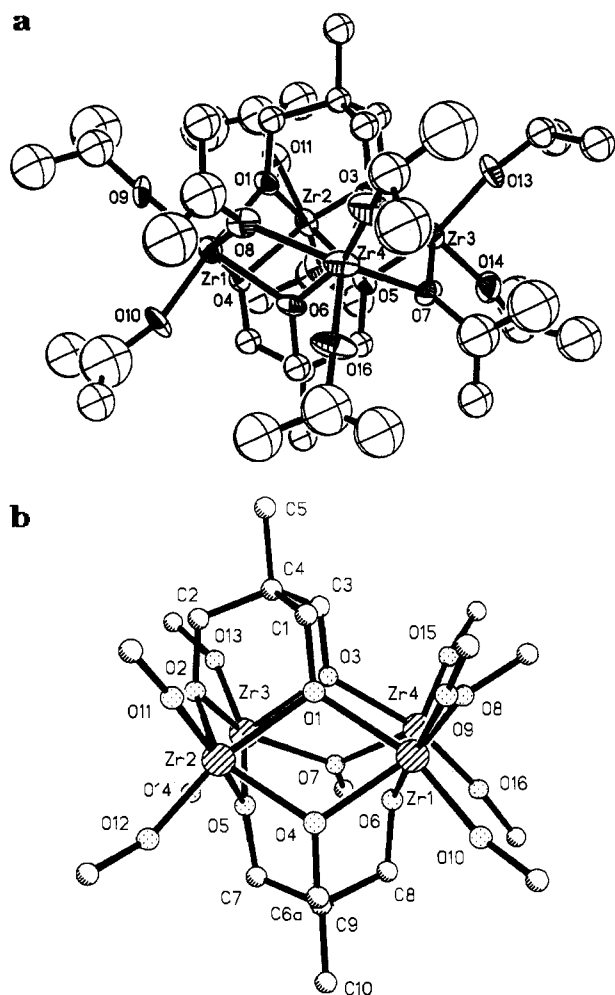
a

b

Figure 4. (a) Thermal ellipsoid drawing of (THME)₂Zr₄(OCHMe₂)₁₀, **3**. Thermal ellipsoids are drawn at 50% probability. (b) Ball and stick drawing of the central core of (THME)₂Zr₄(OCHMe₂)₁₀, **3**. The methyl carbons associated with OCH*Me*₂ ligands have been omitted for clarity.

(THME)₂Zr₄(OCHMe₂)₁₀, **3**, is the first zirconium alkoxide with this M₄(OR)₁₆ edge shared bioctahedral geometry.[33] No tridentate ligands have been reported for this metal. In fact, the structure of only one homo-[28] or heteroleptic[41] zirconium alkoxide has been reported, [Zr(OCHMe₂)₄·HOCHMe₂]₂, **6**.[29] A comparison of some important bond distances and angles for **3** and **6** is shown in Table 6. For **3**, the Zr−μ-OR (OR = OCHMe₂) and Zr−μ-OR' (OR' = (OCH₂)₃CMe) average distances are identical, within experimental error (2.17 Å). The Zr−OR (terminal) average distance of 1.94(1) Å agrees with other reported values ranging from 1.92 to 2.00 Å. The mean deviation from the plane formed by the four zirconium atoms is 0.007 Å. The mean deviation from the plane formed by the Zr₂O₂ rings ranges from 0.10 to 0.15 Å. The average Zr−μ-OR'−Zr angle is 109° and is similar to that of **6** (107°). However, the μ-OR−M−OR (terminal) angles for **3** range from 94.4 to 107.9°; whereas, for **6** the average angle is 93.9°. This variance is due to the strain enforced by the THME ligand on the central core that forces the zirconium metal centers to adopt

an *extremely* distorted octahedral environment. The geometry around the zirconium metal centers can be visualized as an intermediate between trigonal prismatic and octahedral geometry (Figure 4b).[33b] The metal−metal distance is approximately 3.51(2) Å, which is on the long end of the range reported in literature, 3.31−3.50 Å[28a,41] and is due to the bite of the THME ligand. The μ-O−C−C(1) angle of the THME ligand is 113°, again indicating a slight distortion of the methylene carbons and flaring of the THME ligand.

It is noteworthy that **1** and **2** adopt structures different from that of **3**. The size difference between titanium(IV) and zirconium(IV) of 0.1 Å[42] must account for the structural differences between these compounds, since the bond lengths of **1**−**3** are within statistical agreement when this difference is explicated.

Thermal Analysis. Thermal gravimetric analysis/differential thermal analysis (TGA/DTA) experiments on **1**−**4** and the analogous starting materials, Ti(OCHMe₂)₄, **5**, and [Zr-(OCHMe₂)₄·HOCHMe₂]₂, **6**, were undertaken. The spectra of **1**, **3**, **5**, **6** under an atmosphere of oxygen are shown in Figure 5. **5** is a liquid which potentially distills, and any differences can be associated with these characteristics. The TGA/DTA spectra of the analogs **1** and **2** or **3** and **4** are nearly identical. At lower temperatures, spectra of **1**−**4** display a large weight loss recorded in the TGA without corresponding large thermal events observed in the DTA. For **1** and **2**, the weight loss occurs up to ∼300 °C; for **3** and **4**, the weight loss is observed up to ∼250 °C, similar to that observed in **6**; for **5**, the weight loss is complete around 150 °C. In the DTA of these compounds, a very large exothermic recoalescence peak[1,43] is observed (277 °C, **1**; 272 °C, **2**; 235 °C, **3**; 240 °C, **4**), with a corresponding 20−30% weight loss recorded in the TGA. Such recoalescence peaks, indicative of highly exothermic behavior, have been noted previously in thermal analysis studies of ethoxide-derived lithium niobate gels.[44] After the large recoalescence peaks in the spectra of **1** and **2**, there are no more thermal events or weight losses recorded. Since no more events are recorded, this large thermal event is most likely the additive feature of organic pyrolysis and the transformation of the remaining material to the ceramic oxide, TiO₂. For **3** and **4**, around 300 °C (279, **3**; 284, **4**) there appears a second recoalescence peak that coincides with the exothermic peak observed for **6** (283 °C). In these spectra the two exothermic peaks may represent different organic pyrolysis events coupled with conversion of the remaining material to the ceramic oxide, ZrO₂.

The TGA/DTA data indicate that THME ligated compounds, **1**−**4**, behave much differently from **6** in the solid state; however, some characteristic exothermic peaks are carried over. The weight losses of the zirconium-containing compounds (**3** and **4**) are consistent with theoretical losses; however, the titanium compounds (**1** and **2**) vary significantly from ideal conversions to the metal oxide. This can be attributed to the distillation of the small contaminate of Ti(OCHMe₂)₄, **5**, species (ever present with isolation of **1** and **2**). It is of interest to note that the exothermic peaks of **1** and **2** are significantly larger than those observed in the thermal treatment of **3** and **4**.

Solution State. ¹H NMR Spectroscopy. The ¹H NMR spectrum of crystals of **1** dissolved in toluene-*d*₈ shows that in the downfield region (δ 4.4−5.2) three types of protons exist: a clearly defined methine of the OCHMe₂ ligand (δ 5.0), a

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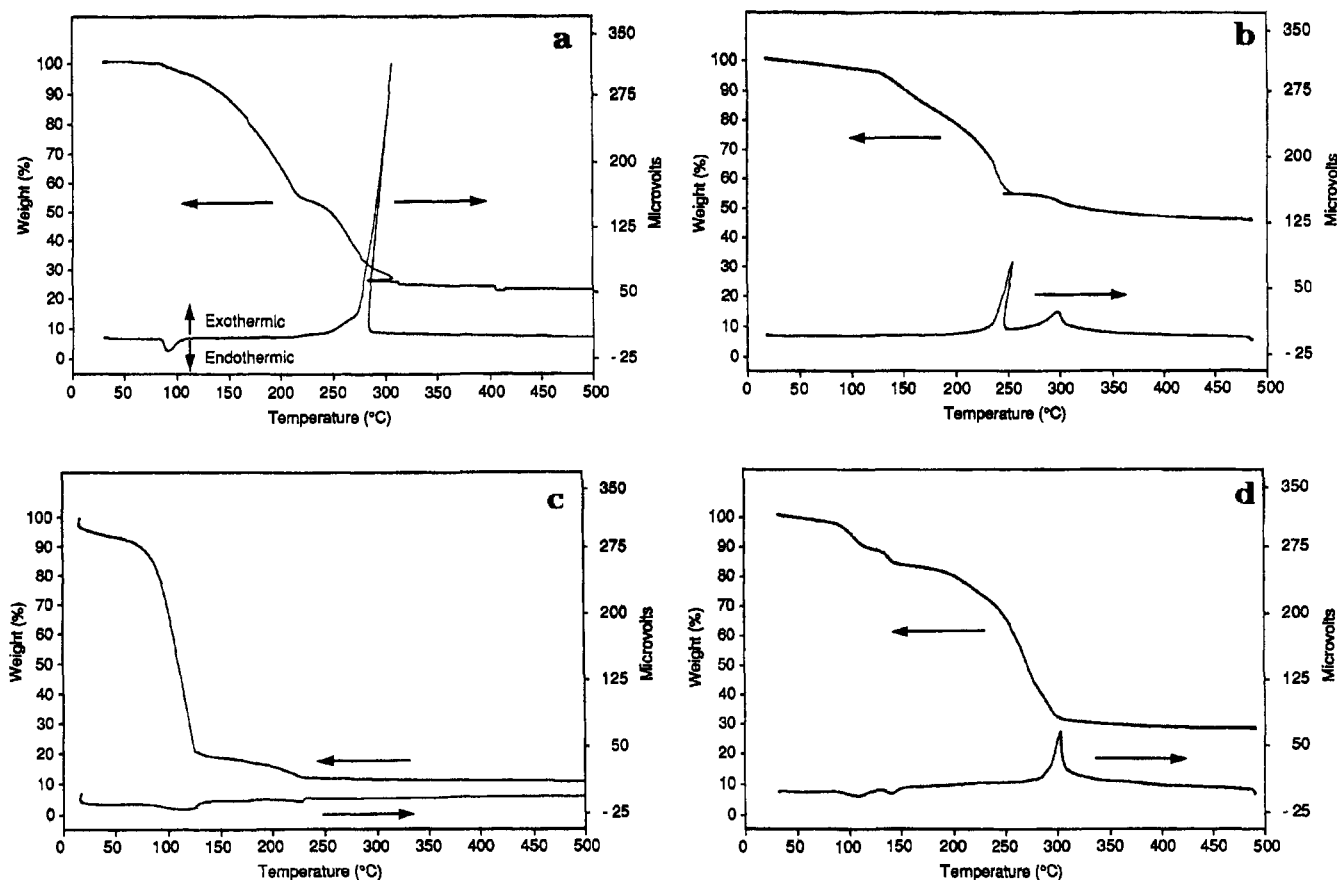(44) Eichorst, D. J.; Payne, D. A. *Mater. Res. Soc. Symp. Proc.* **1988**, *121*, 773.

Figure 5. TGA/DTA (oxygen): (a) $(THME)_2Ti_4(OCHMe_2)_{10}$, **1**; (b) $(THME)_2Zr_4(OCHMe_2)_{10}$, **3**; (c) $Ti(OCHMe_2)_4$, **5**; (d) $[Zr(OCHMe_2)_4 \cdot HOCHMe_2]_2$, **6**.

complex mult (δ 4.5, $OCHMe_2$), and methylene protons of the THME ligand. In the methyl regions there are two major doublets in a ratio of 1:5 and two minor doublets that appear to be a minor impurity. This ratio is not consistent with the structure observed; however, a *slight* excess of $Ti(OCHMe_2)_4$ appears to be present whenever crystals of **1** are isolated and its resonance overlaps with those of the $OCHMe_2$ ligands of **1**. Also present is one singlet that has been assigned as the methyl peak of the THME ligand (δ 0.50). The ^1H NMR spectrum of crystals of **2** (C_6D_6) shows, as expected, a more complexity than that of **1**. The methine region indicates two clearly defined septuplets (δ 5.13, 4.87), followed by a complex multiplet further upfield (δ 4.50). The methyl region, as in **1**, consists of four doublets (δ 1.47, 1.41, 1.34, 1.26) in a ratio of 2:1:1:2 and a complex mult. These overlapping resonances are composed of what appear to be two quartets and two triplets that correspond to the CH_2CH_3 groups of the THMP ligand.

The ^1H NMR spectra of **3** and **4** are less complex than that of **1** or **2**. In both spectra, the downfield region shows a clearly defined $OCHMe_2$ septuplet followed upfield by a complex multiplet that appears to be three methine protons and a methylene resonance for the THMR (R = E, P) ligand. The methyl region has two doublets in a ratio of 1:4. The differences in the spectra of **3** and **4** appear upfield of these two resonances. For **3**, there is one sharp methyl resonance at δ 0.43 associated with the THME ligand. The dynamic behavior of the $OCHMe_2$ ligands was observed at different temperatures (*vide infra*). In contrast, the spectrum of **4** reveals two triplets (δ 0.99, 0.85). These have been assigned as the methyls of the THMP ligands. The expected quartets of the methylene protons may be seen as discernible shoulders on the $OCHMe_2$ doublets.

Variable-Temperature ^1H NMR Spectroscopy. Variable-temperature ^1H NMR studies of **1** and **3** in toluene-d_8 were

undertaken to elucidate any dynamic behavior for these compounds. Little information was obtained about these compounds at lower temperatures due to their decreased solubility.

At higher temperatures (<30 °C) for **1**, the methine, methylene, and methyl resonances rapidly disappear and are replaced by one septuplet in the methine region and a doublet in the methyl region. The solvent peaks have grown in relation to the resonances associated with **1**. The room-temperature ^1H NMR spectrum of **1**, after cooling from 45 °C, resembled $Ti(OCHMe_2)_4$ coupled with the formation of a white precipitate at the bottom of the NMR tube. Apparently the dimer is disrupted at elevated temperatures, forming $Ti(OCHMe_2)_4$ and an insoluble white product, which would be consistent with a 1:1 $Ti(OCHMe_2)_4:THME$ stoichiometric product being formed. For **3**, at higher temperatures (<50 °C) the methine/methylene resonances form a single multiplet and the methyl resonances of the isopropoxide ligands form only one doublet; however, the methyl resonance of the THME ligand does not shift. These spectra indicate that the isopropoxide ligands are undergoing a rapid exchange at this high temperature but the central core is apparently undisturbed. Upon cooling of the heated sample of **3** to room temperature, an identical ambient spectrum is obtained, as before.

Compound **1** has a tendency to precipitate out of solution at low temperatures and to decompose at elevated temperatures; therefore, it is difficult to deduce structural evolution at these extremes. The solution state of **3**, over the temperature range investigated, indicated that, at elevated temperatures, rapid exchange of the terminal and bridging $OCHMe_2$ ligands occurs. The central core of this compound appears to be unaffected, as indicated by the presence of one methyl resonance for the THME ligand throughout the temperature range investigated.

Film Aspects. Ceramic thin films were generated from the newly isolated compounds $(THME)_2Ti_4(OCHMe_2)_{10}$, **1**,[45] and $(THME)_2Zr_4(OCHMe_2)_{10}$, **3**,[45] and the standard starting reagents $Ti(OCHMe_2)_4$, **5**, and $[Zr(OCHMe_2)_4 \cdot HOCHMe_2]_2$, **6**. In general, the films become opaque during deposition. This is presumably due to the susceptibility of **1**, **3**, **5**, and **6** to hydrolysis and condensation reactions initiated by ambient humidity.[46] Due to these condensation reactions, the gel network increases in rigidity and therefore resists the capillary contraction forces associated with drying (solvent volatilization). This results in minimal film shrinkage (as observed by ellipsometry), increased porosity development, and macroscopic cracking.[47]

Films prepared from **1** and **3** displayed less macroscopic cracking and porosity when compared to analogous films prepared from **5** and **6**, respectively. This behavior can be explained by reduced hydrolysis sensitivity of **1** and **3** through the introduction of the tridentate THME ligand. Unfortunately, compounds **1** and **3** are still not suitable for film fabrication due to the nonuniformity of the films generated. The similarity in structure of the THME- and THMP-substituted compounds and in their solution characteristics indicates that analogous film results would be obtained with the THMP derivatives.

Conclusion

The THMR (R = E, P) ligand has demonstrated a propensity for forming a variety of bridging and chelating modes. For the group IV alkoxides synthesized, these tridentate ligands favor formation of tetranuclear complexes which possess the general formula $(THMR)_2M_4(OR)_{10}$. **3** and **4** have a higher degree of solubility and display enhanced thermal stability versus **1** or **2**. Both **1** and **3** appear to be less susceptible to hydrolysis in the film fabrication process than the commonly used starting materials **5** and **6**. Further reductions in the reactivity of the deposited THMR ligated compounds with circumjacent humidity are required to produce uniform films.

Supplementary Material Available: Listings of X-ray experimental details, hydrogen positional parameters, bond distances and angles, and anisotropic thermal parameters for **1**–**3** and selected variable-temperature ^1H NMR spectra of **1** and **3** (37 pages). Ordering information is given on any current masthead page.

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(45) The THMP ligated compounds (**2** and **4**) were *not* used to generate the films investigated due to the more complex solution properties of both **2** and **4** as well as the lack of structural data on **4**.

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