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Studies on Mixed *β*-Diketonate/Isopropoxide Compounds of Zirconium and Hafnium, the X-ray Single-Crystal Structures of [$M_2(OPr^i)_6(tmhd)_2$] (M = Zr, Hf): Some Chemistry Important in the MOCVD of Oxides

Kirsty A. Fleeting,[1a] **Paul O'Brien,***[,1a] **David J. Otway,**[1a] **Andrew J. P. White,**[1a]
David J. Williams,[1a] **and Anthony C. Jones***[,1b]

Department of Chemistry, Imperial College of Science, Technology and Medicine,
South Kensington, London, SW7 2AY, U.K., and Inorgtech, 25 James Carter Road,
Mildenhall, Suffolk, IP28 7DE, U.K.

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Reactions of the homoleptic alkoxides [$M(OPr^i)_4{\cdot}(Pr^iOH)$] (M = Zr or Hf) with different stoichiometric amounts of the *β*-diketone ligand tmhd-H (2,2,6,6-tetramethylheptane-3,5-dione) have been investigated. Crystalline, but powdery, materials with a stoichiometry close to [$M(OPr^i)_2(tmhd)_2$] have been isolated by reacting 2 mol of the *β*-diketone with 1 mol of the metal alkoxide; we present a full explanation based on the ^{1}H NMR results for their behavior in solution. The compounds [$M_2(OPr^i)_6(tmhd)_2$] [M = Zr **(1b)**, and Hf **(2b)**] have been obtained from the exhaustive recrystallization of the above reaction mixture or as the products of the 3:1 *stoichiometric* reaction between [$M(OPr^i)_4.(Pr^iOH)]_2$ and tmhd-H. Compounds **1b** and **2b** have been shown by X-ray crystallography to be isomorphous and are useful precursors for the deposition of the metal oxides by methods such as liquid injection CVD. The symmetrical, dimeric structure of the compounds, with one *β*-diketonate attached to each half of the dimer, may explain why the compounds show little or no tendency toward adventitious homogeneous reaction in MOCVD studies.

Introduction

There is a considerable current effort to develop the chemistry of zirconium alkoxides and their derivatives so as to provide better precursors for the deposition of various materials. Lead−zirconium titanate, $Pb(Zr,Ti)O_3$ (PZT), is potentially an important dielectric for use in nonvolatile computer memories (e.g., DRAM's).[2] PZT is thought to be a promising material[3] because of its ferroelectric properties, and high dielectric constant ($\epsilon \leq 1000$).[4] Several synthetic routes to PZT have been investigated, including sol−gel methods, hydrothermal synthesis, RF sputtering, laser ablation, and metal−organic chemical vapor deposition (MOCVD).[5]

MOCVD is an excellent technique for the deposition of PZT[4,6−8] as it offers the potential for large area growth, good film uniformity, high film densities, high deposition rates, and controllable composition, stoichiometry, and structure. Another advantage of MOCVD is that the step coverage of PZT films by MOCVD is significantly better than that of films produced by other techniques.[9] However, there are some current difficulties in the growth of thin films of PZT by MOCVD, most notably the currently available zirconium precursors are all rather air sensitive or decompose at too high a temperature for the MOCVD process to be viable on device structures. Hence, we have initiated a program of work aimed at developing novel zirconium precursors.

The precursors typically used for MOCVD include zirconium alkoxides,[10] *β*-diketonates,[11,12] and fluorinated *β*-diketonates.[12,13] Zirconium alkoxides usually contain an unsaturated (5- or 6-coordinate metal) center and are in general highly air/moisture sensitive. Stringent anaerobic and anhydrous storage and/or utilization conditions are needed to avoid decomposition during storage or use, and prereaction during growth can be a major problem. Metal *β*-diketonates, such as [$Zr(tmhd)_4$], can be used to deposit pure ZrO_2[11,14,15] but tend to be too thermally stable and cannot be used at the low growth temperatures (<500 °C) required for deposition onto preprocessed microelectronic circuits. More volatile zirconium *β*-diketonates, or their related fluorine derivatives, can have problems in growth experiments due to carbon and/or fluorine contamination.[16] Herein we report on a continuation of our studies on the modification of the

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Table 1. Crystal Data, Data Collection, and Refinement Parameters for $[Zr_2(OPr^i)_6(tmhd)_2]$ (**1b**) and $[Hf_2(OPr^i)_6(tmhd)_2]$ (**2b**)[a]

data	$[Zr_2(OPr^i)_6(tmhd)_2]$ **(1b)**	$[Hf_2(OPr^i)_6(tmhd)_2]$ **(2b)**	data	$[Zr_2(OPr^i)_6(tmhd)_2]$ **(1b)**	$[Hf_2(OPr^i)_6(tmhd)_2]$ **(2b)**
chemical formula	$C_{40}H_{80}O_{10}Zr_2$	$C_{40}H_{80}O_{10}Hf_2$	formula weight	903.5	1078.0
a/Å	10.629(2)	10.580(1)	space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
b/Å	11.204(2)	11.176(1)	T/K	203	203
c/Å	11.858(2)	11.844(1)	λ/Å	0.71073	0.71073
α/deg	69.73(1)	69.37(1)	ρ_{calcd}/g cm^{-3}	1.214	1.465
β/deg	74.41(1)	74.17(1)	μ/mm^{-1}	0.47	4.29
γ/deg	71.47(1)	71.41(1)	R_1[c]	0.041	0.040
V/Å^3	1235.9(4)	1221.7(2)	wR$_2$[d]	0.098	0.092
Z	1[b]	1[b]			

[a] Details in common: graphite monochromated Mo Kα radiation, ω-scans, Siemens P4/PC diffractometer, 203 K, refinement based on F^2. [b] The molecule has crystallographic C_i symmetry. [c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

reactivity of zirconium alkoxides by reaction with β-diketone ligands[17] and report the successful isolation and structural characterization of the compound $[Zr_2(OPr^i)_6(tmhd)_2]$ **(1b)**. The use of this dimer eliminates some of the problems found in growth experiments with simpler metal alkoxides or β-diketonates.[18] The analogous (isomorphous) hafnium compound, $[Hf_2(OPr^i)_6(tmhd)_2]$ **(2b)**, has also been synthesized and structurally characterized.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of dry (molecular sieves) nitrogen using standard glovebox (Miller-Howe FF 160 with double-recirculator system) and Schlenk techniques. Elemental analyses were performed by the Microanalytical Department of Imperial College. The melting points were measured under argon in sealed capillaries and are uncorrected.

Physical Techniques. Infrared spectra were recorded on a Matteson Polaris FT-IR spectrometer as Nujol mulls between NaCl plates. The Nujol was dried with 4 Å molecular sieves prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL GS 270 MHz spectrometer, using the proton impurities of the deuterated solvent as a reference for ^1H (270 MHz) and the ^{13}C resonance of the solvent as a reference for $^{13}C\{^1H\}$ (67.94 MHz) spectra. All chemical shifts are reported positive to high frequency of the standard. Mass spectrometry studies were performed on a VG Autospec-Q (Imperial College Mass Spectrometry Service) operating in electron impact (positive) mode (70 eV) using a direct insertion probe and operating over the temperature range 50−200 °C.

Synthesis. All reactions were performed with dry solvents obtained from Aldrich Chemical Co. (and used without further purification), and all reagents were obtained from Inorgtech of Mildenhall, Suffolk, U.K.

Preparation of $[Zr(OPr^i)_2(tmhd)_2]$ (1a). $Zr(OPr^i)_4 \cdot (Pr^iOH)$ (3.64 g, 9.4 mmol) was dissolved in *n*-hexane (30 mL), and tmhdH (3.91 mL, 18.8 mmol) was added. The solution was stirred at reflux for 1 h, after which time all volatiles were removed in vacuo to yield a white solid. This was redissolved in a minimum of hot *n*-hexane (ca. 8 mL) and left to stand overnight at 0 °C. Colorless crystals of **(1a)** were filtered off. No crystals suitable for X-ray diffraction were obtained. Yield: 3.12 g, 74%. Anal. Calcd for $C_{28}H_{52}O_6Zr$; C, 58.43; H, 9.04. Found: C, 56.86; H, 8.30%. Mp: 110−111 °C. Note: Both the ^1H and $^{13}C\{^1H\}$ NMR spectra show that there is a mixture of compounds in solutions obtained from this material (see the Results and Discussion for details). Exhaustive recrystallization of this material from *n*-hexane led to the isolation of crystals of $[Zr_2(OPr^i)_6(tmhd)_2]$ (vide infra) **(1b)** and/or $[Zr(tmhd)_4]$ **(1c)**.

Preparation of $[Zr_2(OPr^i)_6(tmhd)_2]$ (1b). $Zr(OPr^i)_4 \cdot (Pr^iOH)$ (2.93 g, 7.6 mmol) was dissolved in *n*-hexane (30 mL), and tmhdH (1.51 mL, 7.6 mmol) was added. The reaction conditions and workup were as for **1a**. Colorless crystals of **1b** were filtered off. Yield: 3.31 g, 97%. Anal. Calcd for $C_{40}H_{80}O_{10}Zr_2$: C, 53.2; H, 8.9. Found: C, 53.30; H, 9.07. Mp: 160−163 °C. ^1H NMR (C_6D_6, 270 MHz, 25 °C): δ (ppm) 1.15, 1.26 (36H, s, Me_{tmhd}), 1.42 (36H, s br, Me_{OPr^i}), 3.71, 4.62 (6H, m, CH_{OPr^i}), 5.92, 6.00 (2H, s, CH_{tmhd}). $^{13}C\{^1H\}$ (C_6D_6, 67.94 MHz, 25 °C): δ (ppm) 25.74, 26.88 (Me_{OPr^i}), 28.15, 28.31 (Me_{tmhd}), 40.80, 40.88 (CMe_3), 64.02, 70.87 (CH_{OPr^i}), 92.97, 93.15 (CH_{tmhd}), 200.12, 200.59 (CO).

Preparation of $[Zr(tmhd)_4]$ (1c). $Zr(OPr^i)_4 \cdot (Pr^iOH)$ (4.60 g, 11.9 mmol) was dissolved in *n*-hexane (40 mL), and tmhdH (9.90 mL, 47.5 mmol) was added. The reaction conditions and workup were as for **1a**. Colorless crystals of **1c** were filtered off. Yield: 8.19 g, 84%. Anal. Calcd for $C_{44}H_{76}O_8Zr$: C, 64.11; H, 9.29. Found; C, 63.98; H, 9.37. Mp: >320 °C. ^1H NMR (C_6D_6, 270 MHz, 25 °C): δ (ppm) 1.24 (72H, s, Me), 5.90 (4H, s, CH). $^{13}C\{^1H\}$ (C_6D_6, 67.94 MHz, 25 °C): δ (ppm) 28.72 (Me), 40.51 (CMe_3), 91.71 (CH), 196.88 (CO).

Preparation of $[Hf(OPr^i)_2(tmhd)_2]$ (2a). $Hf(OPr^i)_4 \cdot (Pr^iOH)$ (5.57 g, 11.7 mmol) was dissolved in *n*-hexane (50 mL), and tmhdH (4.90 mL, 23.5 mmol) was added. The reaction conditions and workup were as for **1a**. Colorless crystals of **2a** were filtered off. Yield: 5.69 g, 76%. Anal. Calcd for $C_{28}H_{52}O_6Hf$: C, 41.37; H, 8.14. Found: C, 39.03; H, 7.96. Mp: 138−142 °C. Note: Both the ^1H and $^{13}C\{^1H\}$ NMR spectra show that there is a mixture of compounds in solution (see Results and Discussion for details).

Preparation of $[Hf_2(OPr^i)_6(tmhd)_2]$ (2b). $Hf(OPr^i)_4 \cdot (Pr^iOH)$ (4.12 g, 8.7 mmol) was dissolved in *n*-hexane (50 mL), and tmhdH (1.81 mL, 8.7 mmol) was added. The reaction conditions and workup were as for **1a**. Colorless crystals of **2b** were filtered off. Yield: 5.87 g, 63%. Anal. Calcd for $C_{40}H_{80}O_{10}Hf_2$: C, 44.61; H, 7.43. Found: C, 44.48; H, 7.27. Mp: 159−164 °C. ^1H NMR (C_6D_6, 270 MHz, 25 °C): δ (ppm) 1.14, 1.26 (36H, s, Me_{tmhd}), 1.39 (36H, d br, Me_{OPr^i}), 3.72, 4.69 (6H, m, CH_{OPr^i}), 5.90, 5.99 (2H, s, CH_{tmhd}). $^{13}C\{^1H\}$ (C_6D_6, 67.94 MHz, 25 °C): δ (ppm) 25.67, 27.63 (Me_{OPr^i}), 28.31, 28.47 (Me_{tmhd}), 41.03, 41.10 (CMe_3), 64.20, 70.66 (CH_{OPr^i}), 93.73, 94.13 (CH_{tmhd}), 200.64, 201.14 (CO).

Preparation of $[Hf(tmhd)_4]$ (2c). $Hf(OPr^i)_4 \cdot (Pr^iOH)$ (11.84 g, 24.9 mmol) was dissolved in *n*-hexane (70 mL), and tmhdH (20.81 mL, 99.7 mmol) was added. The reaction conditions and workup were as for **1a**. Colorless crystals of **2c** were filtered off. Yield: 20.3 g, 89%. Anal. Calcd for $C_{44}H_{76}O_8Hf$: C, 57.98; H, 8.40. Found: C, 60.09; H, 8.29. Mp: > 320 °C. ^1H NMR (C_6D_6, 270 MHz, 25 °C): δ (ppm) 1.24 (72H, s, Me), 5.88 (4H, s, CH). $^{13}C\{^1H\}$ (C_6D_6, 67.94 MHz, 25 °C): δ (ppm) 28.72 (Me), 40.55 (CMe_3), 92.04 (CH), 196.98 (CO).

X-ray Crystallography of $[Zr_2(OPr^i)_6(tmhd)_2]$ (1b) and $[Hf_2(OPr^i)_6(tmhd)_2]$ (2b). Table 1 provides a summary of the crystal data, data collection, and refinement parameters for $[Zr_2(OPr^i)_6(tmhd)_2]$ **(1b)** and $[Hf_2(OPr^i)_6(tmhd)_2]$ **(2b)**. The structures were solved by direct methods and were refined by full-matrix least-squares based on F^2. In each structure, disorder was found in the position of one of the terminal isopropoxide ligands; this was resolved into two partial occupancy orientations, the major occupancy non-hydrogen atoms of which were refined anisotropically. The remaining non-hydrogen atoms in both structures were refined anisotropically. In each structure the C−H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}$ (C-Me)], and

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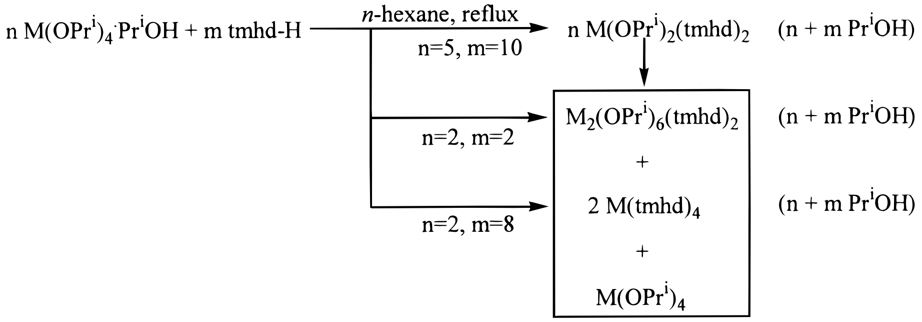
Table 2. Selected Bond Lengths (Å) and Angles (deg) for [$Zr_2(OPr^i)_6(tmhd)_2$] (**1b**) and [$Hf_2(OPr^i)_6(tmhd)_2$] (**2b**)

	1b [M = Zr]	**2b** [M = Hf]		**1b** [M = Zr]	**2b** [M = Hf]
M−O(1)	2.153(2)	2.121(5)	M−O(3)	2.190(2)	2.169(5)
M−O(4)	2.119(2)	2.102(5)	M−O(4′)	2.219(2)	2.192(5)
M−O(5)	1.931(2)	1.927(6)	M−O(6)	1.944(2)	1.953(6)
O(1)−C(1)	1.283(3)	1.281(10)	C(1)−C(2)	1.387(4)	1.384(12)
C(2)−C(3)	1.403(4)	1.397(12)	C(3)−O(3)	1.264(3)	1.270(10)
M···M′	3.508(1)	3.476(1)			
O(5)−M−O(6)	98.09(10)	97.7(3)	O(5)−M−O(4)	99.31(8)	99.2(2)
O(6)−M−O(4)	103.96(9)	103.2(2)	O(5)−M−O(1)	95.31(9)	95.7(2)
O(6)−M−O(1)	88.21(9)	88.4(2)	O(4)−M−O(1)	159.36(7)	159.7(2)
O(5)−M−O(3)	87.37(9)	88.0(2)	O(6)−M−O(3)	164.00(8)	164.9(2)
O(4)−M−O(3)	89.87(8)	89.6(2)	O(1)−M−O(3)	76.27(8)	77.1(2)
O(5)−M−O(4′)	167.34(8)	167.9(2)	O(6)−M−O(4′)	93.09(9)	92.5(2)
O(4)−M−O(4′)	72.07(8)	72.0(2)	O(1)−M−O(4′)	90.95(7)	91.1(2)
O(3)−M−O(4′)	83.43(8)	83.7(2)	M−O(4)−M′	107.93(8)	108.0(2)

Scheme 1. Synthesis of Compounds **1a−c** and **2a−c**



allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system.[19] Selected bond lengths and angles are given in Table 2.

Results and Discussion

Several reactions of zirconium alkoxides with β-diketones or fluoro-β-diketones have been previously reported, and the structure of zirconium tetrakisacetylacetonate, as prepared by the complete substitution reaction, has been determined on several occaisions.[20−22] However, the reactions of alkoxides such as [$Zr(OPr^i)_4$·(Pr^iOH)] with fewer equivalents of the β-diketone (1, 2, or 3) are not well documented. Puri reported monoisopropoxidetris-β-diketonate derivatives with acetylacetone, benzoylacetone, methylacetoacetate, and phenylsalicylate, all of which were monomeric in boiling benzene.[23] Bharara et al.[24] reacted zirconium isopropoxide with some fluoro-β-diketones (hexafluoroacetylacetone, benzoyltrifluoroacetone and 2-thionyltrifluoroacetone) and found the products to be white to yellow crystalline solids, all of which were monomeric in boiling benzene. The products of the reaction between zirconium isopropoxide and various molar ratios of β-diketones (e.g., hexafluoroacetylacetone, acetylacetone, 1,3-diphenylpropane-1,3-dione, 1-phenylpropane-1,3-dione) and β-ketoesters were studied by Saxena et al., and several monomeric zirconium β-diketonates were obtained.[24] These tris-isopropoxide-mono-β-diketonate derivatives were found to be dimeric by cryoscopy. A 6-coordinate, dimeric structure was suggested with the two isopropoxide groups bridge two metal centers, a suggestion that is now confirmed by our crystallographic studies.[25]

The crystalline metal isopropoxides [$M(OPr^i)_4$·(Pr^iOH)] (M = Zr or Hf) react rapidly, under reflux conditions (*n*-hexane), with tmhd-H to give clear colorless solutions; see Scheme 1. Crystals of **1a** and **2a** were isolated from such solutions. On exhaustive recrystallization, solutions of the compounds [$M(OPr^i)_2(tmhd)_2$] [M = Zr **1a** and Hf **2a**] gave crystals of [$M_2(OPr^i)_6(tmhd)_2$] (**1b** and **2b**) as the most stable products and [$M(tmhd)_4$] (**1c** and **2c**) crystallized from the mother liquor remaining after the removal of **1b** and **2b**. Although the parent compounds (**1a** and **2a)** appeared as a crystalline mass in the flask, no single crystals suitable for X-ray study could be isolated. Crystals of **1b** and **2b** were found to be suitable for single-crystal structure determination.

Single-Crystal X-ray structures of [$Zr_2(OPr^i)_6(tmhd)_2$] (1b) and [$Hf_2(OPr^i)_6(tmhd)_2$] (2b). The structure of [$Zr_2(OPr^i)_6(tmhd)_2$] **(1b)** is illustrated in Figure 1; selected bond lengths (Å) and angles (deg) are shown in Table 2. The molecules are dimeric comprising two metal atoms, two tmhd, and six isopropoxide ligands positioned about an inversion center. In the zirconium compound, the Zr···Zr distance is nonbonding at 3.508(1) Å and is at the long end of the range reported in the literature for dimers (3.31−3.50 Å).[26] The zirconium centers are 6-coordinate, comprising a chelating η^2-tmhd, two terminal isopropoxide ligands, and two μ_2-isopropoxide bridging ligands in a distorted octahedral geometry. The cis angles at Zr are in the range 72.07(8)−103.96(9)°. The Zr−O bond distances fall into three distinct groups, with those involving the terminal isopropoxide molecules being 1.931(2) and 1.944(2) Å (average 1.938 Å); these values are slightly shorter than those reported for [$Zr_2(OPr^i)_8(Pr^iOH)_2$][27] (average 2.057 Å) yet are comparable with those reported in the compound [$(thme)_2Zr_4(OCHMe_2)_{10}$][26]

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[19] SHELXTL PC version 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.

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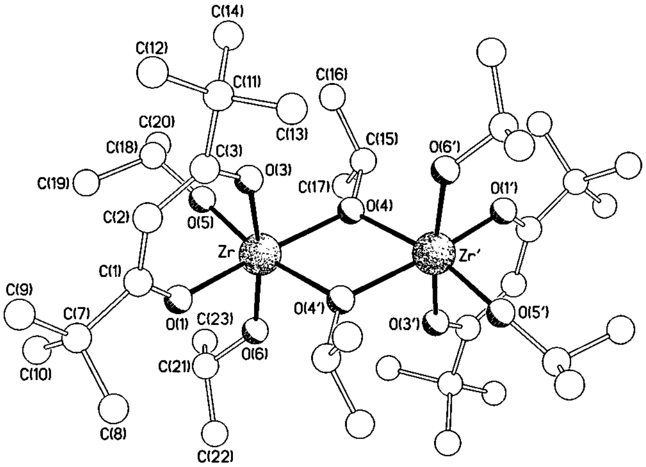

Figure 1. Molecular structure of [Zr$_2$(OPr^i)$_6$(tmhd)$_2$] **(1b)**.

Table 3. Selected IR Data (cm^{-1}) for Compounds **1a**−**c** and **2a**−**c**

compd^a	ν(C=O)	ν(C=C)	ν(C−O)
[Zr(OPr^i)$_2$(tmhd)$_2$] (**1a**)	1598, 1592, 1578	1537, 1528, 1503	1103, 1057
[Zr$_2$(OPr^i)$_6$(tmhd)$_2$] (**1b**)	1600, 1593, 1573	1533, 1527, 1505	1108, 1063
[Zr(tmhd)$_4$] (**1c**)	1573	1505	
[Hf(OPr^i)$_2$(tmhd)$_2$] (**2a**)	1600, 1591, 1573	1537, 1527, 1507	1110, 1061
[Hf$_2$(OPr^i)$_6$(tmhd)$_2$] (**2b**)	1599, 1588	1535, 1527	1113, 1055
[Hf(tmhd)$_4$] (**2c**)	1581	1510	

^{a} Nujol mulls.

(range 1.92−2.00 Å, average 1.94(1) Å) (thme = tris(hydroxymethyl)ethane). Those to the tmhd ligands, which are bonded in an asymmetric chelating manner, are 2.153(2) to O(1) and 2.190(2) Å to O(3) (average 2.172 Å), the longer distance reflecting the greater trans influence of a terminal cf. a bridging isopropoxide ligand.

The third set of Zr−O bonds, those involving the bridging μ_2-isopropoxide molecules, are noticeably asymmetric, being 2.219(2) at O(4′) and 2.119(2) Å at O(4), again reflecting the difference in formal charge of the isopropoxide ligands. The average bridging distance of 2.169 Å is comparable to that for [Zr$_2$(OPr^i)$_8$(Pr^{i}OH)$_2$][27] (average 2.173 Å), though in this latter structure the bridge is essentially symmetric. The Zr−O−Zr bridge angle of 107.93(8)° does not differ significantly from that reported for [Zr$_2$(OPr^i)$_8$(Pr^{i}OH)$_2$][27] [107.2(7)°].

The periphery of the molecule is dominated by the isopropoxide and *tert*-butyl groups of the ligands, creating an almost totally hydrophobic surface. The packing is thus essentially van der Waals in nature.

The single-crystal X-ray structure of [Hf$_2$(OPr^i)$_6$(tmhd)$_2$] **(2b)** is isomorphous to **1b**, there being overall small contractions in the coordination distances reflecting the reduced ionic radius of the metal. There are few, if any, relevant, structurally characterized hafnium compounds to provide a basis for a comparative discussion.

Spectroscopic Characterization. The infrared spectra of compounds **1a**−**c** and **2a**−**c** were studied as Nujol mulls between NaCl windows. Selected infrared frequencies are listed in Table 3. The IR bands are tentatively assigned on the basis of the infrared data of previously characterized metal alkoxides and β-diketonates.[21,24,28,29] The asymmetric and symmetric ν(C−O) stretches were observed in the region 1200−1100 cm^{-1}. The ν(C- -O) and ν(C- -C) absorption frequencies corresponding to the tmhd ligands were observed in the region 1600−1400 cm^{-1}.

Table 4. Selected ^{1}H NMR Data (δ/ppm) for Compounds **1a**−**c** and **2a**−**c** in C$_6$D$_6$ at 25 °C

		tmhd		OPr^i	
complex	no.	CH	CH$_3$	CH	CH$_3$
[Zr(OPr^i)$_2$(tmhd)$_2$]	**1a**	5.91−6.00	1.13−1.22	4.50−4.78	1.24−1.37
[Zr$_2$(OPr^i)$_6$(tmhd)$_2$]	**1b**	5.92, 6.00	1.15, 1.26	3.71, 4.62	1.42
[Zr(tmhd)$_4$]	**1c**	5.90	1.24		
[Hf(OPr^i)$_2$(tmhd)$_2$]	**2a**	5.86−5.95	1.13−1.23	4.61−4.75	1.28−1.39
[Hf$_2$(OPr^i)$_6$(tmhd)$_2$]	**2b**	5.90, 5.99	1.14, 1.26	3.72, 4.69	1.39
[Hf(tmhd)$_4$]	**2c**	5.88	1.24		

Multinuclear NMR (^{1}H and ^{13}C{^{1}H}) studies were performed on all the compounds; the ^{1}H NMR data are shown in Table 4, and the ^{13}C{^{1}H} NMR signals are summarized in Table 5. The ^{1}H NMR spectrum of **1b** recorded in C$_6$D$_6$ is shown in Figure 2. The solid-state structure of **1b** shows a single centrosymmetric dimer in which all of the isopropoxides on an individual metal are facially arranged if one considers the bridges to be asymmetric. The centrosymmetric arrangement of **1b**, if preserved in solution, would lead to a spectrum with only one environment for the OCH$_{\mathrm{tmhd}}$ resonance, but two are observed (δ 5.92 and 6.00 ppm). The Me$_{\mathrm{tmhd}}$ signals are at δ 1.15 and 1.26 ppm. Both pairs of resonances for OCH$_{\mathrm{tmhd}}$ and Me$_{\mathrm{tmhd}}$ have the same intensity ratio (3:2). The resonances due to the tmhd signals are sharp, which suggests that any exchange of the tmhd ligands is slow. The resonances associated with the alkoxide are all broadened, and suggest that these ligands are in more rapid exchange. The terminal alkoxide OC*H* resonance is assigned at δ 4.64 ppm and the terminal methyl signal at δ 1.42 ppm; both signals have the same fwhm of 18.2 Hz. The bridging isopropoxide resonances are much broader (fwhm = 72.8 Hz). The OC*H* signal at δ 3.69 and the Me signal at δ 0.99 are both upfield in comparison to the terminal isopropoxide ligands. The most logical explanation of these observations is that there is an equilibrium between two dimeric compounds in solution, in which the alkoxide ligands are in exchange at an intermediate rate.

Several geometric isomers are possible for fused octahedra with two chelating ligands. The first compound corresponds to the complex unequivocally identified in the solid state; as the arrangement that places the alkoxides facially (all cis) on each metal center, it is likely to be preferred and predominant. The second is an alternative form but with two alkoxides trans. The third possible arrangement is less likely and involves a cis arrangement of the diketonates, which will probably lead to steric crowding of *tert*-butyl groups and is thus unlikely; it would also lead to many more proton environments than are observed in the NMR. The spectra of the hafnium analogue are exactly analogous.

It is interesting to compare theses results with those obtained by Errington[30] for the related titanium compounds [[Ti(OPr^i)$_3$(acac)]$_2$] and [Ti(OPr^i)$_3$(acac)]. In these systems there is clear evidence for the disproportionation of the mixed species to homoleptic alkoxide and diketonate species, the former is particularly easy to identify in the proton NMR spectrum. This reaction is not observed in our system.

The NMR of the crude product [Zr(OPr^i)$_2$(tmhd)$_2$] **(1a)** is far from simple; however, the results for **1a** help to understand the behavior of this compound in solution. The NMR spectra

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Table 5. Selected $^{13}C\{^1H\}$ NMR Data (δ/ppm) for Compounds **1a**−**c** and **2a**−**c** in C_6D_6 at 25 °C

complex	tmhd				OPr^i	
	***C*O**	***C*H**	C(***C*H**$_3$)$_3$	***C*H**$_3$	***C*H**	***C*H**$_3$
$[Zr(OPr^i)_2(tmhd)_2]$ (**1a**)	198.61−200.57	91.66−92.94	40.49−40.78	28.15−28.70	71.08,71.56	26.13−27.97
$[Zr_2(OPr^i)_6(tmhd)_2]$ (**1b**)	200.12, 200.59	92.97, 93.15	40.80, 40.88	28.15, 28.31	64.02,70.87	25.74, 26.88
$[Zr(tmhd)_4]$ (**1c**)	196.88	91.71	40.51	28.72		
$[Hf(OPr^i)_2(tmhd)_2]$ (**2a**)	196.96−199.17	93.51	40.71−40.55	28.11−28.71	70.24−70.51	27.21−27.26
$[Hf_2(OPr^i)_6(tmhd)_2]$ (**2b**)	200.64, 201.14	93.73, 94.13	41.03, 41.10	28.31, 28.47	64.20,70.66	25.67, 27.63
$[Hf(tmhd)_4]$ (**2c**)	196.98	92.04	40.55	28.72		

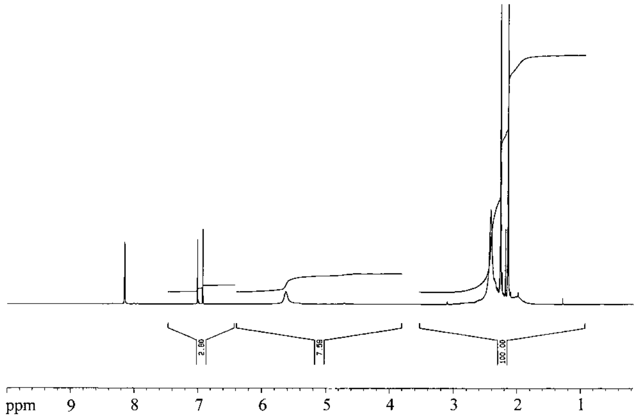

Figure 2. ^1H NMR spectrum of $[Zr_2(OPr^i)_6(tmhd)_2]$ **(1b)** in C_6D_6 at room temperature.

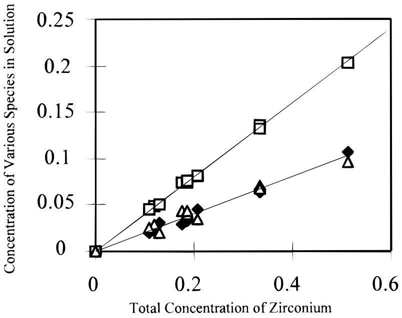

Figure 3. Graph of concentration of various species, where □ = $[Zr(tmhd)_4]$, ◆ = sum of the concentrations of dimeric species (i.e., total integration for $[Zr_2(OPr^i)_6(tmhd)_2]$), and △ = $[Zr(OPr^i)_4]$, vs total concentration of zirconium added (i.e., $[Zr(OPr^i)_2(tmhd)_2]$).

of the best quality samples of **1a** has three C*H* (tmhd) environments between δ 5.91 and 6.00 and an equally congested methyl region, suggesting that this compound forms a mixture of products in solution (C_6D_6 at room temperature) that are in equilibrium on the NMR time scale. The OCH_{tmhd} resonances are well defined. Variable-concentration and variable-temperature ^1H NMR results indicate that the chemistry of the isopropoxide system is complex; our results suggest that the dimerization of $[Zr(OPr^i)_2(tmhd)_2]$ is not a favorable reaction and that the monomer is not observed in solution. The explanations for this observation may lie in the steric crowding of the simple parent dimer pair. The ^1H NMR spectra of **1b** and **1c** (at room temperature) both have sharp resonances associated with the tmhd signals, indicating slow exchange for these ligands and these resonances can be assigned to $[Zr_2(OPr^i)_6(tmhd)_2]$ and $[Zr(tmhd)_4]$. The two resonances assigned to the $[Zr_2(OPr^i)_6(tmhd)_2]$ compound are in a 1:4 ratio. The alkoxide OC*H* resonances are observed as three very broad signals very close to each other with an integration of 10 protons. The resonance at δ 4.61 is a well-defined multiplet, characteristic of the free parent alkoxide. The alkoxide methyl resonances are ill defined, due to fast exchange in solution. However, integration supports our conclusion that the best quality samples we have obtained can be represented by a quantitative disproportionation to the symmetrical dimer $[Zr_2(OPr^i)_6(tmhd)_2]$, tetrakis-tmhd, and the parent alkoxide.

$$5\,[Zr(OPr^i)_2(tmhd)_2] \rightarrow [Zr_2(OPr^i)_6(tmhd)_2] + 2[Zr(tmhd)_4] + [Zr(OPr^i)_4] \quad (1)$$

It appears from our study that little or no $[Zr(OPr^i)_2(tmhd)_2]$ is formed in solution, although accidental degeneracies and broadening could obscure the observation of small quantities of the compound.

The results of a variable-concentration NMR study quantitatively confirm the above suggestion. In Figure 3, concentrations of the various zirconium-containing complexes, as calculated from the OCH_{tmhd} resonances, in solution are plotted against the total concentration of $[Zr(OPr^i)_2(tmhd)_2]$ **(1a)** added to the sample. If the disproportionation is complete (see eq 1), the required ratio for the concentrations of $[Zr_2(OPr^i)_6(tmhd)_2]$:$[Zr(tmhd)_4]$:$[Zr_2(OPr^i)_4]$ is 1:2:1. Hence, if the disproportionation is complete and the above is true the slope of a plot of $[Zr]_{total}$ vs $[Zr(tmhd)_4]$ should be 0.4 (found 0.40) and for $[Zr_2(OPr^i)_6(tmhd)_2]$ or $[Zr(OPr^i)_4]$ 0.2 (found 0.20 and 0.20, respectively). These values are in excellent agreement with our predictions, and the ratios of the slopes give the expected 1:2:1 ratio for $[Zr_2(OPr^i)_6(tmhd)_2]$:$[Zr(tmhd)_4]$:$[Zr_2(OPr^i)_4]$.

The ^1H NMR of the homoleptic diketonates **1c** and **2c** show, as expected, only one C*H* tmhd environment at 5.90 and 5.88 ppm, respectively. No isopropoxide signals are seen, suggesting the compounds are pure and the $^{13}C\{^1H\}$ NMR spectra are also clean. Similar observations have been made on the related cerium complex.[29]

Electron impact mass spectrometry studies were performed for all compounds, and the major ions observed are shown in Table 6. Compounds **1a** and **2a** exhibited ions of monomeric and dimeric composition and demonstrated patterns of decomposition seen in **1b**, **1c**, **2b**, and **2c**; that is, $[M(tmhd)_2]^+$, $[M(OPr^i)_2(tmhd)]^+$, and $[M_2(OPr^i)_4(tmhd)]^+$ were observed. Mass spectrometry studies of compounds **1b** and **2b** exhibited ions of dimeric composition and subsequently a distinct pattern of decomposition to their monomeric fragments; the fragment $[M(OPr^i)(tmhd)]^+$ was also observed. Similar fragmentation pathways were also observed for compounds **1c** and **2c**; $[M(tmhd)_x]$ where $x = 2-4$ fragments were observed in both spectra.

Conclusion

We have isolated and structurally characterized two new zirconium and hafnium compounds; the zirconium compound shows improved precursor characteristics in MOCVD.[18] The compounds $[M_2(OPr^i)_6(tmhd)_2]$ **(1b** and **2b)** are isomorphous, with 6-coordinate metal atoms and μ_2-bridging isopropoxide ligands. The results for compound **1b** confirm the structure proposed by Saxena et al.[25] for such zirconium isopropoxide-

Table 6. Selected Mass Spectrometry Data (m/z^+) for Compounds **1a**−**c** and **2a**−**c**

compd	$[M(tmhd)_x]^+$	$[M(OPr^i)_x]^+$	$[M(OPr^i)_x(tmhd)]^+$	$[M_2(OPr^i)_x(tmhd)]^+$	$[M_2(OPr^i)_x(tmhd)_2]^+$
$[Zr(OPr^i)_2(tmhd)_2]$ (**1a**)	456(2), 640(3)	208(2) 268(3)	333(1) 391(2)	483(2),601(4)	
$[Zr_2(OPr^i)_6(tmhd)_2]$ (**1b**)		208(2) 268(3)	333(1), 391(2)	601(4), 661(5), 719(6)	607(1), 725(3), 785(4), 843(5)
$[Zr(tmhd)_4]$ (**1c**)	456(2), 640(3), 823(4)				
$[Hf(OPr^i)_2(tmhd)_2]$ (**2a**)	544(2), 727(3)	355(3)	420(2)	657(2), 775(4)	
$[Hf_2(OPr^i)_6(tmhd)_2]$ (**2b**)		295(2)	420(1), 479(2)	774(4), 893(6)	781(1), 840(2), 958(4), 1017(5)
$[Hf(tmhd)_4]$ (**2c**)	544(2), 727(3), 910(4)				

[a] Values of x in parentheses.

β-diketonate compounds. The structures are useful in understanding our previously described MOCVD results.[17] The behavior of the mixtures of composition $[Zr(OPr^i)_2(tmhd)_2]$ is likely to be intermediate between that of the parent alkoxide $[Zr(OPr^i)_4 \cdot (Pr^iOH)]_2$ and the more stable species such as $[Zr(tmhd)_4]$, as is observed in MOCVD experiments.[17] The results of the NMR experiments are useful in assessing which compounds or mixtures are most likely to be reliable MOCVD precursors for solution delivery. The compound $[Zr_2(OPr^i)_6(tmhd)_2]$ is probably the most potentially useful precursor of those reported in this paper. It is a well-defined crystalline compound with better stability than the alkoxide. Two species are generated in solution; however, both of these are likely to be symmetrical isopropoxide bridged dimers, the dissociation of which in the vapor phase is likely to lead to monomeric $[Zr(OPr^i)_3(tmhd)]$. The results of studies of the deposition of ZrO_2 using liquid delivery CVD[18] support this suggestion, and an unusually wide temperature range of 450−600 °C for diffusion controlled growth has been observed.

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Supporting Information Available: X-ray crystallographic files for the structure determinations of $[Zr_2(OPr^i)_6(tmhd)_2]$ and $[Hf_2(OPr^i)_6(tmhd)_2]$ are available on the Internet only. This material is available free of charge via the Internet at http://pubs.acs.org.

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