



Zirconium and hafnium *tert*-butoxides and *tert*-butoxo- β -diketonate complexes – Isolation, structural characterization and application in the one-step synthesis of 3D metal oxide nanostructures

Gerald I. Spijksma^{a,b}, Gulaim A. Seisenbaeva^a, Henny J.M. Bouwmeester^b, Dave H.A. Blank^b, Vadim G. Kessler^{a,*}

^a Department of Chemistry, BioCenter, Swedish University of Agricultural Sciences, Box 7015, 75007 Uppsala, Sweden

^b Inorganic Materials Science, Fac. of Science & Technology, and Mesa⁺ Research Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands

ARTICLE INFO

Article history:

Received 7 September 2012

Accepted 18 January 2013

Available online 10 February 2013

Keywords:

Metal alkoxides

β -Diketonate complexes

ZrO₂

HfO₂

Metal–organic decomposition (MOD)

ABSTRACT

Long term storage of the pure commercial Zr(O^{*t*}Bu)₄ in a sealed ampoule results in crystallization of a new high symmetry phase of Zr₃O(O^{*t*}Bu)₁₀ (**1**). Modification of Zr(O^{*t*}Bu)₄ and Hf(O^{*t*}Bu)₄ with 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd) produces dependent on the stoichiometry two types of derivatives, M(O^{*t*}Bu)₂(thd)₂ (**2**, **3**) and M(O^{*t*}Bu)(thd)₃ (**4**, **5**) M = Zr(**2**, **4**), Hf(**3**, **5**), which have all been characterized by NMR and mass-spectral studies and for **4** and **5** also by complete X-ray single crystal studies. The latter failed for **2** and **3** in the view of their poor X-ray reflectivity. Addition of minor amounts of *n*-C₅H₁₁OH to **3** resulted in isolation of an unusual heteroleptic complex Hf₂(OH)(O^{*n*}C₅H₁₁)(O^{*t*}Bu)₂(thd)₄ (**6**). Thermal decomposition of compounds **1** and **3** in nitrogen atmosphere was studied for different thermal regimes by TGA-FTIR approach, revealing in all cases the formation of tetragonal ZrO₂ and monoclinic HfO₂ respectively, along with iso-butene, butanol and water for **1** and the same mixture including also Hthd for **3**. Decomposition of **3** occurred always through intermediate melting, while higher heating rate for **1** permitted to achieve decomposition on in situ evaporation resulting in 3D hedgehog nanostructures according to SEM.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Zirconium and hafnium dioxide 3D nanostructures are highly requested today as materials for catalysis [1–5], metal–oxide nanocomposites with improved mechanical properties (elastic modulus) [6], sensors [7–9], and electrolytes for solid oxide fuel cells [10,11]. The approaches to oxides are often exploiting metal–organic precursors such as metal alkoxides and heteroleptic metal alkoxides and are based on Soft Chemistry techniques, such as Metal Organic Chemical Vapor Deposition (MOCVD) and Metal Organic Decomposition (MOD). For both approaches the choice of precursor compound is rather crucial. In case of MOCVD the solution stability and thermal stability during vapor phase transport are extremely critical for process reproducibility. For MOD the principal requirement is the ability of precursor to decompose in solid state without melting in order to produce nanostructure in the resulting product. It may even seem obvious that the precursor composition does not change during storage after its preparation and before it is used, e.g., the precursor is shelf stable.

The application of commercial zirconium alkoxide precursors is complicated and thus a relatively unattractive option. The zirconium has an unsaturated coordination and this makes the precursors extremely sensitive to hydrolysis and pyrolysis (low thermal and hydrolytic stability). Another drawback of unmodified precursors (e.g., zirconium isopropoxide) is their relative low volatility, requiring high deposition and substrate temperatures and leading to the formation of carbon contamination.

A general method used to improve the thermodynamic stability and volatility of alkoxide precursors is by replacing (part) of the alkoxide ligands by chelating organic ligands [12–14].

In the present work we report isolation and structural characterization of zirconium *t*-butoxide complexes with and without modification by bulky 2,2,6,6-tetramethylheptanedione chelating ligands and the study of their thermal decomposition as a potential source of zirconia and hafnia nanostructures.

2. Experimental

2.1. Materials and methodology

All manipulations were carried out in a dry nitrogen atmosphere using the Schlenk technique or a glove box. Hexane and

* Corresponding author.

E-mail address: vadim.kessler@kemi.slu.se (V.G. Kessler).

toluene (Merck, p.a.) were dried by distillation after refluxing with LiAlH_4 . 2,2,6,6-Tetramethyl-3,5-heptanedione (Hthd) was purchased from Aldrich. ^1H NMR spectra were recorded in CDCl_3 for all compounds on a Bruker 400 MHz spectrometer at 243 K. Mass-spectral studies were carried out with JEOL JMS-SX/SX-102A mass-spectrometer applying electron beam ionization ($U = 70$ eV) with direct probe introduction. Thermal decomposition of the samples was investigated with Perkin-Elmer Pyris 1 TGA instrument coupled with Spectrum 100 FTIR spectrometer for simultaneous analysis of outgoing gases. The produced oxide materials were characterized by powder X-ray diffraction in sealed capillaries taking 360° rotation photos using Bruker SMART Apex-II diffractometer using EVA-12 software [15] and by SEM-EDS studies using Hitachi TM-1000- $\mu\text{-DeX}$ tabletop electron microscope.

2.2. General synthetic procedure

Zirconium *t*-butoxide (99.999%) and hafnium *t*-butoxide (99.99%) were purchased from Aldrich and used as received. All the different precursors were modified with various equivalent amounts of the modifier according to the techniques described below. The exact composition of the single crystals **1**, **4**, **5** and **6** was established with single crystal X-ray crystallography.

A sample of zirconium *t*-butoxide (weight: 0.86 g (2.25 mmol)) in 2 ml hexane was modified with 0.41 g Hthd (2.25 mmol). Crystallization occurred during cooling at -30°C over night. Under a microscope the presence of two or three different types of crystals was observed. An attempt was made to separate the different compounds by adding 1 ml of toluene to the sample and subsequently removing the liquid phase from the flask. The remaining crystals were dissolved in 2.5 ml toluene and placed in the freezer at -30°C for crystallization. The obtained crystals in this fraction were identified as **3**. The flask with the liquid phase removed was also placed in the freezer but no successful structural determination was performed on the formed crystals.

2.2.1. $\text{Zr}_3\text{O}(\text{O}^t\text{Bu})_{10}$ (**1**)

Liquid zirconium butoxide was sealed in a glass ampoule under vacuum and stored in a freezer for over 2 years time yielding needle-shaped crystals of **1** through massive crystallization (yield about 30%).

2.2.2. $\text{Zr}(\text{O}^t\text{Bu})_2(\text{thd})_2$ (**2**)

Zirconium *t*-butoxide (weight: 0.90 g (2.35 mmol)) was dissolved in 2 ml hexane. After addition of 0.87 g (4.7 mmol) of Hthd, i.e., 2 mol equivalents the sample was placed over night at -30°C for crystallization. The solution was decanted from the obtained block-shaped almost cubic colorless crystals (1.62 g, yield 91%) that were identified as **2**.

2.2.3. $\text{Hf}(\text{O}^t\text{Bu})_2(\text{thd})_2$ (**3**)

Hafnium *t*-butoxide (weight: 1.56 g (3.31 mmol)) was dissolved in 2 ml toluene. After addition of 1.22 g (6.62 mmol) of Hthd, i.e., 2 mol equivalents a white precipitate was formed. After addition of 6 ml hexane a clear solution was obtained and the sample was placed over night at -30°C for crystallization. The solution was decanted from the obtained block-shaped colorless crystals identified as **3** (yield: 1.97 g, 86%).

2.2.4. $\text{Zr}(\text{O}^t\text{Bu})(\text{thd})_3$ (**4**)

Zirconium *t*-butoxide (weight: 0.77 g (2.0 mmol)) was dissolved in 2 ml hexane. After the addition of 1.10 g (6.0 mmol) of Hthd, i.e., 3 mol equivalents, the sample was placed over night at -30°C for crystallization. The obtained crystals were not of X-ray quality. The sample was dried under vacuum (0.1 mmHg) and the dried product was re-dissolved in 1.5 ml toluene. Crystallization occurred

during cooling at -30°C over night and the crystals were identified as **4** (yield: 0.66 g, 35%).

2.2.5. $\text{Hf}(\text{O}^t\text{Bu})(\text{thd})_3$ (**5**)

Hafnium *t*-butoxide (weight: 1.30 g (2.76 mmol)) was dissolved in a mixture of 2 ml hexane and 5 ml toluene. After addition of 1.53 g (8.3 mmol) of Hthd, i.e., 3 mol equivalents, the sample was placed over night at -30°C for crystallization. The solution was decanted from the obtained crystals and the crystals were identified as **5** (yield: 1.65 g, 58%).

2.2.6. $\text{Hf}_2(\text{OH})(\text{O}^n\text{C}_5\text{H}_{11})(\text{O}^t\text{Bu})_2(\text{thd})_4$ (**6**)

Rod-shaped crystal of **6** was discovered in the batch of large cube-shaped crystals of **3** and identified by single crystal X-ray diffraction study. The small amount of this by-product precluded other characterization.

2.3. X-ray crystallography

Data collection for single crystals of compounds **4** and **5** was carried out at 22°C on a SMART CCD 1 k diffractometer and of compounds **1** and **6** on a SMART Apex-II diffractometer both with graphite monochromated $\text{Mo K}\alpha$ radiation. All structures were solved by standard direct methods. The coordinates of the metal atoms as well as the majority of other non-hydrogen atoms were obtained from the initial solutions and for all other non-hydrogen atoms found in subsequent difference Fourier syntheses. The structural parameters were refined by least squares using first isotropic and then, also anisotropic approximations. The coordinates of the hydrogen atoms were calculated geometrically and were included into the final refinement in isotropic approximation for all the compounds. All calculations were performed using either SHELXTL-NT or SHELXTL-6.31 program package [16,17] on an IBM PC.

2.3.1. Compound **1**

The data have been collected from a crystal displaying merohedral twinning with the twinning matrix 0 1 0 1 0 0 0 0 1 making the true Laue group 6/m to resemble 6/mmm. The introduction of the twinning law decreases strongly the apparent thermal disorder in this structure. The structure is also strongly disordered geometrically. The positional disorder has been modeled with two partly overlapping configurations for the terminal and doubly bridging alkoxide C_4H_9 -residues. The triply-bridging alkoxide group is disordered in practically perfect statistics with the triply-bridging oxo-ligand. The hydrogen atoms could be located only for the triply-bridging alkoxide (defined by C(2) and C(9) atoms). The impossibility to locate other H-atoms (quite numerous!) leads to apparent discrepancy between the reported and the calculated molecular weights. The structure of **1** contains considerable solvent-accessible voids ($682 \text{ \AA}^3$), but they lack electron density and do not contain any solvent according to the results of TGA-experiments reported in this paper.

2.3.2. Compound **4**

This structure does not display any positional disorder but a pronounced thermal disorder inflicting on the quality of the room-temperature data. The compound is also apparently unstable under X-ray beam, which required elimination of one data series of **3** in merging of the data in order to obtain reliable results. This explains some incompleteness in the reported coverage of the space (2σ full 0.887 for the total angle range).

2.3.3. Compound **5**

No positional, but considerable thermal disorder has been observed for this compound, resulting in enhanced temperature factors for terminal carbon atoms.

2.3.4. Compound 6

No positional, but considerable thermal disorder has been observed for this compound, resulting on enhanced temperature factors for terminal carbon atoms.

3. Results and discussion

3.1. Synthetic comments

Long term storage of liquid zirconium *t*-butoxide at $-18\text{ }^{\circ}\text{C}$ resulted in crystallization with relatively high yield of about 30% of a new hexagonal modification of zirconium oxo-*tert*-butoxide, constructed of the same $\text{Zr}_3\text{O}(\text{O}^i\text{Bu})_{10}$ molecules as the monoclinic one earlier reported by Turova and co-workers [18]. Separation of an oxoalkoxide through crystallization at lower temperature is not surprising as the admixtures of oxospecies in the commercial samples of zirconium alkoxides are fairly common in the view of the hydrolysis sensitivity of these species [19]. Low temperature conditions favor, apparently, formation of a higher symmetry packing.

Interaction of zirconium *t*-butoxide with 1–2 mol equivalent of Hthd produced block shaped crystals (almost cubes) of one and the same compound. The crystals turned out to be poorly reflecting and long exposure times were required to obtain a maximum number of reflections. The experiments permitted the determination of the unit cell of the compound but the quality of the data was not sufficient to refine the structure.

The proper structure refinement was not possible because of complex disorder between the *t*-butoxide ligands and the thd-ligands, but it was clear that this compound was the di-substituted derivative $\text{Zr}(\text{O}^i\text{Bu})_2(\text{thd})_2$ (**2**). The hafnium analogue of this compound, $\text{Hf}(\text{O}^i\text{Bu})_2(\text{thd})_2$ (**3**), was prepared according to the procedure described in the experimental section. Single crystal X-ray diffraction experiments were also performed on this compound. The reflectivity of the compound was better than that of **2**, but the data did not allow refining the structure either.

In the sample produced with 3 mol equivalent of Hthd only one type of crystals was present. They were characterized as $\text{Zr}(\text{O}^i\text{Bu})_1(\text{thd})_3$ (**4**) displaying the molecular structure analogous to other tris-substituted β -diketonato-alkoxides of zirconium, $\text{Zr}(\text{acac})_3(\text{O}^i\text{Pr})$ [20], $\text{Zr}(\text{thd})_3(\text{OPr})$, where $\text{Pr} = ^i\text{Pr}$, ^nPr [21]. The hafnium analogue of this compound, $\text{Hf}(\text{thd})_3(\text{O}^i\text{Bu})$ (**5**), was prepared according to the procedure described in the experimental section.

3.2. Crystal and molecular structures

The non-centrosymmetric hexagonal structure of compound **1** (see Table 1 and Fig. 1), $\text{Zr}_3(\mu_3\text{-O})(\mu_3\text{-O}^i\text{Bu})(\mu\text{-O}^i\text{Bu})_3(\text{O}^i\text{Bu})_6$, is highly disordered with one position for oxygen and zirconium atoms but several for each carbon atom. Even the triply bridges alkoxide group is in statistical disorder with the triply bridged oxo-atom. The Zr–oxygen distances follow the sequence defined by the ligand function: $\text{Zr}-\mu_3\text{OR}(3\text{A})\ 2.38(2) > \text{Zr}-\mu_2\text{O}(1)\ 2.172(7) > \text{Zr}-\mu_3\text{O}(3)\ 2.056(11) > \text{Zr}-\text{O}(2)\ 1.938(8)\text{ \AA}$ and fall into the commonly observed intervals. The observed distances are also very close to those observed in the other earlier reported modification that was lacking positional disorder [18], where the bond lengths of 2.39, 2.166, 2.107 and 1.938 $\text{\AA}$ were reported for the same type of Zr–O contacts (see Fig. 2).

Structures (**4**) and (**5**) exhibit centrosymmetric monoclinic structures resulting from packing of mononuclear molecules. The latter contain one alkoxide and three thd ligands each with a selection of the bond lengths listed in Table 2. The metal–oxygen bond length of the alkoxide ligand are coinciding for these two compounds within the experimental error, i.e., 1.874(7) and

1.888(9) $\text{\AA}$ for (**4**) and (**5**), respectively. The bond lengths to the thd oxygen opposite the alkoxide ligand have the same length in both compounds, i.e., 2.030(9) $\text{\AA}$. The other metal oxygen bond lengths also have comparable values. When these compounds are compared with their isopropoxide analogs [21], i.e., $\text{Zr}(\text{O}^i\text{Pr})(\text{thd})_3$ and $\text{Hf}(\text{O}^i\text{Pr})(\text{thd})_3$, a remarkable trend is observed. The metal–oxygen bond length of the alkoxide ligand are shorter in the propoxide compounds, i.e., 1.847 and 1.820 $\text{\AA}$ for $\text{Zr}(\text{O}^i\text{Pr})(\text{thd})_3$ and $\text{Hf}(\text{O}^i\text{Pr})(\text{thd})_3$, respectively. One would expect that the metal–oxygen bond length of the alkoxide would decrease with the increasing branching and thus donor capacity of the alkoxide ligands. In the work on the modification of zirconium propoxides [21] this trend was clearly present; the metal–oxygen bond length of a *n*-propoxide ligand is 1.924 $\text{\AA}$, while that of the isopropoxide ligand is 1.847 $\text{\AA}$. The deviation of the metal–oxygen bond lengths of the alkoxide ligands in **4** and **5** is due to the sterical hindrance in these compounds. From Table 2 it can be seen that most of the other metal–oxygen bond lengths are also shorter for the propoxide compounds, which also supports the sterical hindrance in **4** and **5** as major cause of the observed structural features.

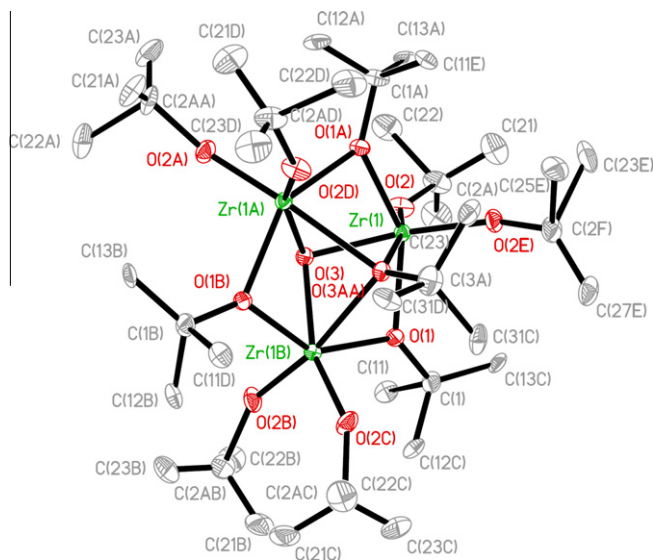
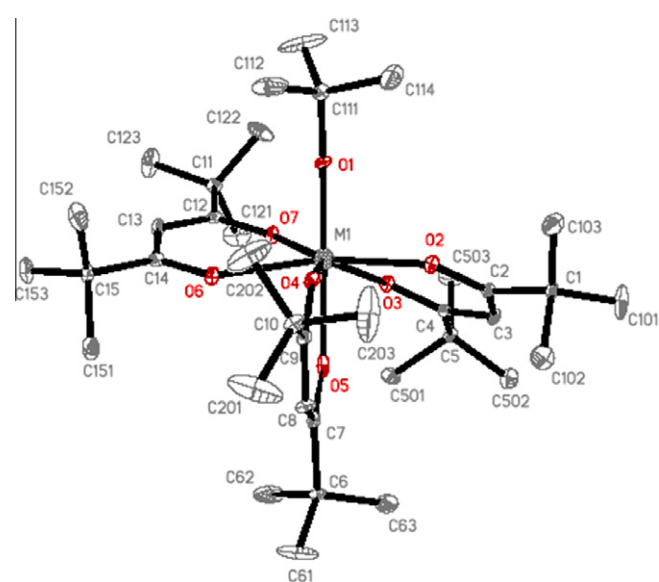
The centrosymmetric triclinic structure of **6** (Fig. 3) is built up by highly unusual (and unexpected) non-centrosymmetric molecules $\text{Hf}_2(\mu\text{-OH})(\mu\text{-O}^n\text{C}_5\text{H}_{11})(\text{O}^i\text{Bu})_2(\text{thd})_4$. The most peculiar feature lies, of course, in the presence of an *n*-pentyl ligand, originating, apparently, from a minor impurity in the obtained sample of hafnium *t*-butoxide complex. The presence of a hydroxo-group is not surprising in the view of the known trend of such compounds to hydrolysis, a related complex $\text{Hf}_2(\mu\text{-OH})_2(\text{O}^i\text{Pr})_2(\text{thd})_4$ being the only isolable di-thd substituted iso-propoxide derivative [21]. The atoms of Hf are heptacoordinated with the coordination sphere composed of two oxygen atoms of the bridging groups, OH and $\text{O}^n\text{C}_5\text{H}_{11}$, one terminal O^iBu group and 4 oxygen atoms of the thd-ligands. The shortest bond lengths are observed with the terminal alkoxide ligands, $\text{Hf}(1)\text{-O}(7)\ 1.931(3)\text{ \AA}$ and $\text{Hf}(2)\text{-O}(10)\ 1.935(4)\text{ \AA}$, the contacts to the (practically symmetrically) bridging hydroxo group is slightly longer, $\text{Hf}(1)\text{-O}(2)$ and $\text{Hf}(2)\text{-O}(2)\ 2.104(4)$ and $2.103(4)\text{ \AA}$, respectively. The bond lengths to the thd ligands are intermediate in length falling into the commonly observed range 2.153(3)–2.221(4) $\text{\AA}$. The longest in average are, surprisingly, the bonds to the oxygen atom of the bridging alkoxide ligand, $\text{Hf}(1)\text{-O}(1)$ and $\text{Hf}(2)\text{-O}(1)\ 2.200(3)$ and $2.193(3)\text{ \AA}$, respectively, as caused, again most probably by the steric effects.

3.3. Solution stability and reactivity

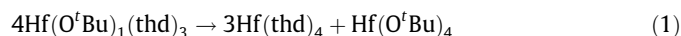
In the view of generally limited solution stability of zirconium and hafnium alkoxide β -diketonates [19–21] it appeared interesting to follow the behavior of the corresponding *tert*-butoxide derivatives. It was not possible to isolate crystals of any other compounds from the sample of zirconium *t*-butoxide with 1 mol equivalent of Hthd than those of the di-substituted derivatives, **2** and **3**. The mixed-ligand complexes **2–5** were studied by ^1H NMR to evaluate their stability and to confirm that no mono-substituted compound exit. The obtained spectra display only signals in the region 1–1.3 ppm and 5.5–5.8 ppm. The first chemical shift is typical for CH_3 while the latter region represents the *CH* of the thd ligand. A selection of the obtained spectra is displayed in Fig. 4. It should be noted that no difference is observed in the chemical shift of the same hafnium and zirconium compounds. The spectrum of freshly prepared **4** is depicted in Fig. 4a and the same sample is recorded again $\sim 5\text{ h}$ later. Between the experiments, which were performed at 243 K, the sample was stored at room temperature. The signals due to **4** are marked with (*) and they are in the expected ratio of 1:18:3 for respectively *CH* and CH_3 of thd and CH_3 of the *t*-butoxide ligand. The position of the signals for the unmodified precursor and $\text{Zr}(\text{thd})_4$ were obtained by measuring a refer-

Table 1Data collection and refinement details for compounds **1**, **4**, **5**, **6**.

	1	4	5	6
Chemical composition	C ₄₀ H ₉₀ O ₁₁ Zr ₃	C ₃₆ H ₆₆ O ₇ Zr	C ₃₆ H ₆₆ O ₇ Hf	C ₅₇ H ₁₀₆ O ₁₂ Hf ₂
Formula weight	1020.78	714.12	801.39	1532.40
Crystal system	hexagonal	monoclinic	monoclinic	triclinic
Space group	<i>P</i> -31c	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
μ (mm ⁻¹)	0.551	0.304	2.521	3.036
<i>R</i> ₁	0.0640	0.0864	0.0678	0.0349
<i>wR</i> ₂	0.2011	0.2035	0.1646	0.0926
<i>a</i> (Å)	17.906(6)	10.417(4)	10.429(2)	12.675(7)
<i>b</i> (Å)	17.906(6)	21.099(8)	21.137(4)	15.020(9)
<i>c</i> (Å)	10.830(4)	19.256(7)	19.345(4)	20.093(12)
α (°)	90	90	90	84.920(7)
β (°)	90	99.988(13)	99.70(4)	79.653(7)
γ (°)	120	90	90	67.344(6)
<i>V</i> (Å ³)	3008.4(17)	4168(3)	4203.5(14)	3472(3)
<i>T</i> (K)	295	295	295	295
<i>Z</i>	2	4	4	2
Number of independent reflections (<i>R</i> _{int})	1874 (0.0670)	7252 (0.0809)	8175 (0.0523)	13462 (0.0190)
$\theta_{\max}$ (°); completeness (%)	25.53; 99.2	26.00; 88.7	26.00; 99.1	26.00; 98.4
Number of observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	1631	2991	4689	10695

**Fig. 1.** Molecular structure of Zr₃(μ₃-O)(μ₃-O^{*t*}Bu)(μ-O^{*t*}Bu)₃(O^{*t*}Bu)₆ (**1**) with 15% probability ellipsoids. The symmetrically dependent fragments are generated via rotation around a C₃-axis.**Fig. 2.** Molecular structure of the M(thd)₃(O^{*t*}Bu) derivatives, M = Zr(**4**) and Hf(**5**) with 10% probability ellipsoids.

ence sample and from ref 20, respectively. The signals due to these compounds are respectively marked with (□) and (○). It can clearly be seen that upon aging in solution, compound **4** rearranges. The remaining signals that appear upon aging, depicted in Fig. 4b, are due to the formation of **2** and will be discussed below. The rearrangement of **4** seems to involve mainly the formation of tetra-substituted species and unmodified precursors and is represented by Eq. (1).



All the signals in the obtained spectra are corresponding to the isolated and characterized compounds and thus there is no evidence for the existence of a mono-substituted compound. The solid state stability of the compounds is quite high, after storage of the samples for about half a year in the freezer the composition remained unchanged. This is in contrast to the observed relatively poor solution stability.

The ¹H NMR spectra of freshly prepared **2** is depicted in Fig. 4c and of the spectrum of the aged for ~3 days in solution is displayed

Table 2Metal–oxygen bond lengths of **4**, **5**, Zr(O^{*i*}Pr)(thd)₃ and Hf(O^{*i*}Pr)(thd)₃ [20].

	4	5	Zr(O ^{<i>i</i>} Pr)(thd) ₃	Hf(O ^{<i>i</i>} Pr)(thd) ₃
M–O1	1.874(7)	1.888(9)	1.847	1.810
M–O2	2.030(9)	2.030(9)	2.017	2.050
M–O3	2.140(7)	2.137(9)	2.092	2.116
M–O4	2.147(7)	2.143(9)	2.108	2.123
M–O5	2.175(7)	2.180(8)	2.123	2.154
M–O6	2.176(7)	2.183(9)	2.165	2.165
M–O7	2.211(6)	2.198(9)	2.185	2.161

in Fig. 5 2d. The signals in the spectrum of the fresh sample can be assigned to **2** and the unmodified precursor, marked with (●) and (□), respectively. The ratio of the signals due to CH and CH₃ of thd and CH₃ of the *t*-butoxide ligand are about the expected order of magnitude but cannot be determined very accurately, since the signals in the CH₃ region are not resolved. This could be due to the presence of some traces of parent alcohol. Upon aging, the di-substituted compound rearranges by forming mainly compound

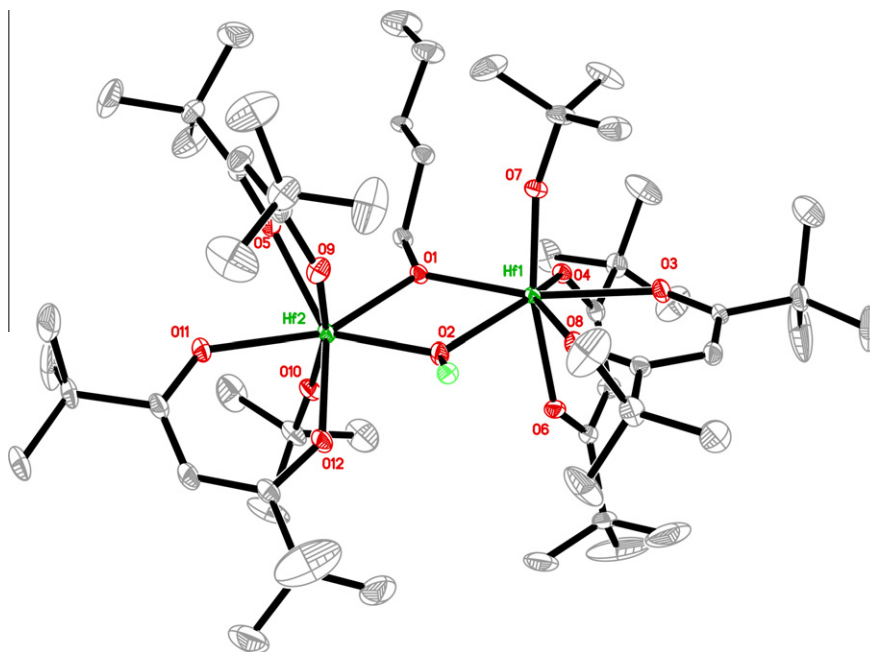


Fig. 3. Molecular structure of $\text{Hf}_2(\mu\text{-OH})(\mu\text{-O}^t\text{C}_5\text{H}_{11})(\text{O}^t\text{Bu})_2(\text{thd})_4$ (**6**) with 10% probability ellipsoids.

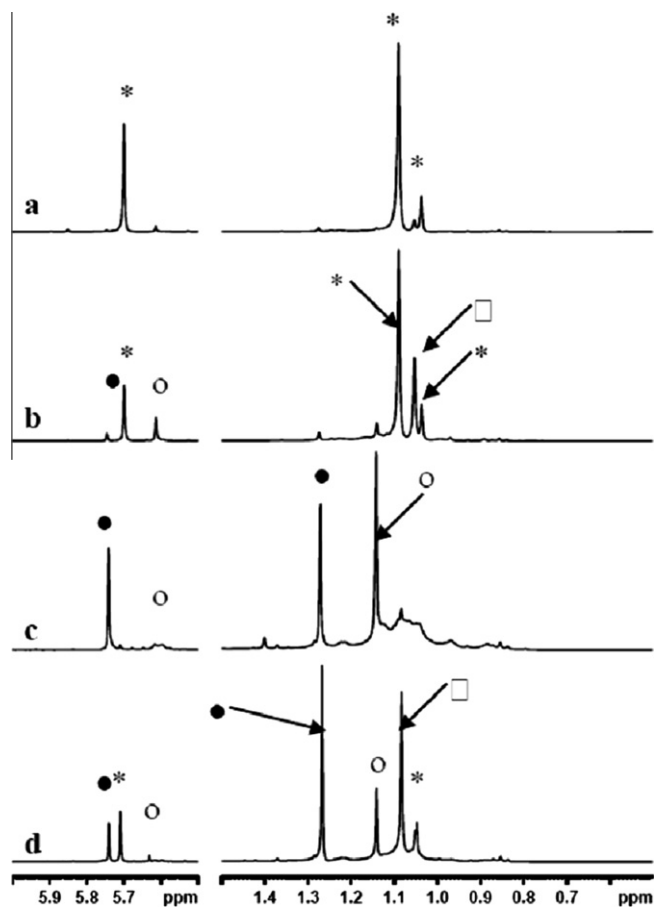
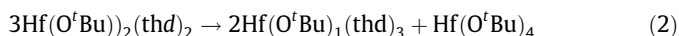


Fig. 4. NMR spectra of fresh **5** (a) and aged **4** (b) and fresh (c) and aged (d) **2**. The signals due to **4** and **5** are marked with (*), those due to **2** and **3** with (●), $\text{Zr}(\text{thd})_4$ with (○), unmodified *t*-butoxide precursor with (□). For reasons of clarity in comparison the intensities of the signals between 6 and 5.5 ppm are increased four times compared to those between 1.5 and 0.5 ppm.

4 and unmodified precursor. The equation of this reaction is as follows:



A sample, of which the NMR spectra are not displayed here, showed a transformation of **3** into the tetra-substituted $\text{Hf}(\text{thd})_4$ in the about the same time (just under 3 days) as displayed in Fig. 4d for **2**. The solution stability of di-substituted compounds seems to be of the same order of magnitude as that of the tri-substituted compounds. The solid state stability of the di-substituted compounds is again, high, after storage of the samples for about half a year in the freezer the composition remained unchanged.

Mass spectrometry experiments were performed on compound **2–5** and the obtained data is summarized in Table 3. It should be noted that for **2**, **3** and **5** dried crystals were used while sample **3** was prepared by removing the solvents of a solution with Hthd and hafnium *t*-butoxide in the appropriate ratios. The obtained data for all samples is in good agreement with their molecular structure. The major fragments in the gas phase are in all cases the initial structure of the compound minus an alkoxide ligand. All four compounds are tremendously volatile; this is illustrated by the unusual detection of the whole molecule in the spectra of **4** and **5**. The spectrum obtained from **2** displays a signal at 727 (26.5%) M/z (1), that is assigned to $\text{Hf}(\text{thd})_3$. This indicates the presence of compound **5** in the sample. This is probably due to the different way of preparation of this sample, as mentioned above, and clearly demonstrates the easy transformation of these compounds in solution (as also has been observed by the NMR experiments). The preparation and characterization of **2** has earlier been described [22]. The mass spectrometry data presented [20] displayed a two large signals, at 639 (25%) and 587 (35%) that are clearly due to the presence of **4**. The formation of **4** is enhanced by the reflux step that was included in their synthesis.

The modification of zirconium and hafnium *t*-butoxides with Hthd involves di- and tri-substituted compounds. The presence of a tri-substituted compound is in agreement with the intermediate structures formed upon Hacac and Hthd modification of zirconium and hafnium propoxides [19–21]. The main difference between the **4** and **5** and the propoxide analogs is the metal–oxygen bond length of the alkoxide ligand. Sterical hindrance causes

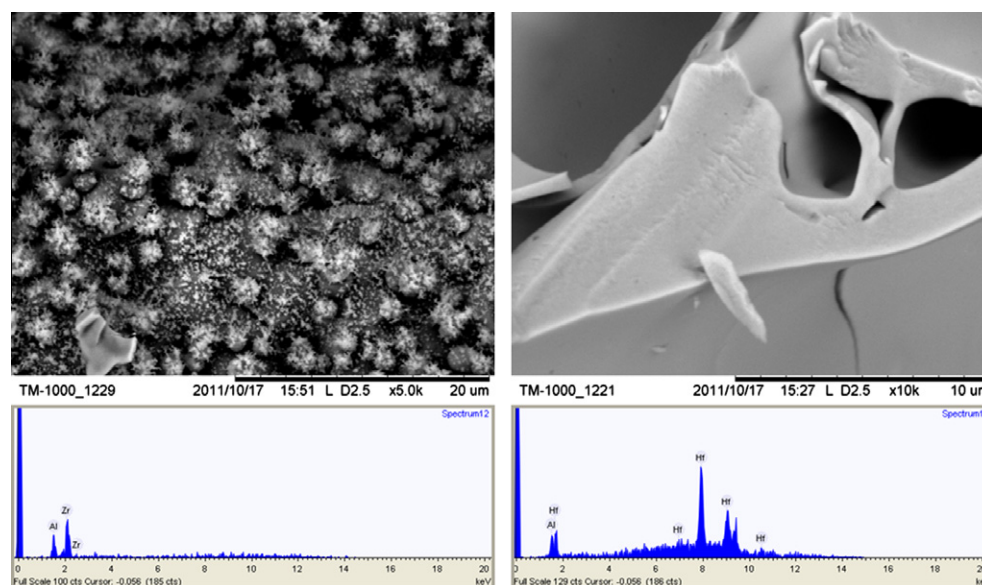


Fig. 5. SEM images and EDS analyzes of the ZrO_2 and HfO_2 produced by decomposition of compounds **1** and **3** respectively (the Al signal originate from the sample holder).

Table 3
Interpretation of $M/z(1)$ spectrum of **2–5**.

	2	3	4	5
$\text{M}(\text{thd})-\text{CH}_4$	257 (7.1)		257 (0.5)	
$\text{M}(\text{OH})(\text{thd})^+$			291 (17.8)	
$\text{M}(\text{OH})_2(\text{thd})$	307 (5.9)		307 (7.5)	
$\text{M}(\text{thd})_2$		544 (5.7)	456 (6.3)	
$\text{M}(\text{OH})(\text{thd})_2$	473 (13.9)	561 (22)	473 (31.5)	561 (15.5)
$\text{M}(\text{O}^i\text{Bu})(\text{thd})_2$	529 (100)	617 (100)	529 (100)	617 (100)
$\text{M}(\text{thd})_3$	639 (3.41)	727 (26.5)	639 (100)	727 (100)
$\text{M}(\text{OH})(\text{thd})_3$			656 (4.6)	744 (5.9)
$\text{M}(\text{O}^i\text{Bu})(\text{thd})_3$			712 (0.5)	799 (2.3)

that the metal–oxygen bonds of the *t*-butoxide ligands in **4** and **5** are longer than that of a propoxide ligands in for instance $\text{Zr}(\text{O}^i\text{Pr})(\text{thd})_3$, $\text{Zr}(\text{O}^i\text{Pr})(\text{thd})_3$ and $\text{Hf}(\text{O}^i\text{Pr})(\text{thd})_3$. The larger *t*-butoxide ligands and the resulting sterical hindrance causes that the mono-nuclear di-substituted compounds **2** and **3** are formed rather than di-nuclear mono-substituted compounds as observed in the modification of zirconium and hafnium propoxides.

3.4. Thermal behavior and the produced oxide materials

Compounds **1** and **3**, possessing potentially highest shelf stability, were subjected to TGA investigation (heating rate $10^\circ\text{C}/\text{min}$) in atmosphere of air under ambient pressure for determination of the character of their decomposition and nature of its products (MOD).

Compound **1** decomposes in a largely four-step process, where the first step below 100°C with the loss of 9 wt.% is associated with evaporation of hexane occlusions, rather sharp one at 160°C stays for 20 wt.% and the second at $272\text{--}310^\circ\text{C}$ accounts for 26 wt.% (both associated with release of mostly butene and water vapor through beta-hydrogen elimination and condensation) and, finally, the combustion of the residual carbon takes place in broad temperature interval $320\text{--}560^\circ\text{C}$ and stays for the loss of additional 13 wt.%. The decomposition of **3** occurs in one major step at 300°C associated with both thermal decomposition and evaporation as the residual mass (18 wt.%) is largely below the theoretical for the decomposition (30.5%).

The decomposition products were identified in both cases as dioxides, tetragonal ZrO_2 and monoclinic HfO_2 respectively (please,

see Suppl.). The appearance of the produced oxide materials is drastically different. While the zirconium dioxide obtained from **1** consists of hedgehog shaped aggregates, the hafnium dioxide obtained from **3** is a dense material with characteristic features of a melt (see Fig. 5). This difference indicates apparently that the decomposition for **1** occurs under applied conditions without phase transition directly as a solid, which for metal–organic precursors is most often associated with formation of the objects described, dependent on the details of their appearance as nano-hedgehogs, nano-raspberries or nano-flowers [23]. The decomposition of **3** proceeds via melting, resulting probably from higher thermal stability typical for β -diketonate substituted alkoxides [22].

4. Conclusions

The modification of zirconium and hafnium *t*-butoxides involves di- and tri-substituted compounds. The size of the *t*-butoxide ligands makes that a di-substituted compound is formed instead of the mono-substituted propoxide compounds. The metal–oxygen bond length of the *t*-butoxide ligands is significant longer compared to that of propoxide in analogous compounds. This clearly underlines the presence of sterical hindrance in these systems.

The solid state stability of the formed compounds is tremendously high, upon storage for half a year no change in composition was observed. In contrast, the solution stability displayed behavior analogous to that of Hthd and Hacac modified zirconium and hafnium propoxides, i.e., concentration of the modifying ligands leading to the formation tetra-substituted and unmodified compounds.

MOD treatment of the obtained precursors provides MO_2 , $\text{M} = \text{Zr}, \text{Hf}$, oxides with nano-hedgehog morphology for $\text{Zr}_3\text{O}(\text{O}^i\text{Bu})_{10}$ as starting material, but a dense melt-shaped for mixed-ligand precursors, most probably due to lower thermal stability of the non-substituted alkoxide.

Acknowledgments

The authors are very grateful to Rolf Andersson for the assistance with the NMR analysis and to Suresh Gohil for performing the mass spectrometry experiments. G.I.S. is grateful to The Netherlands Organization for Scientific Research (NWO) and EXXON-MOBIL Chemical Benelux for facilitating his research at SLU with

a travel grant and travel award, respectively. This work has been carried out at the Department of Chemistry, SLU, in the framework of the project “molecular precursors and molecular models of nanoporous materials” that has in continuation received support from the Swedish Research Council (Vetenskapsrådet).

Appendix A. Supplementary material

Supplementary crystallographic data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers **CCDC 894743–894746** for **1**, **4**, **5** and **6**, respectively. Supplementary data associated with this article (TGA and XPD for compounds **1** and **3**) are available on request from the authors.

References

- [1] Y.W. Li, D.H. He, Z.X. Cheng, C.L. Su, J.R. Li, Q.M. Zhu, *J. Mol. Catal. A: Chem.* 175 (2001) 267.
- [2] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* 829 (1987) 405.
- [3] A. Knell, P. Barnickel, A. Baiker, A. Wokaun, *J. Catal.* 137 (1992) 306.
- [4] X. Zhang, B.Q. Xu, *J. Phys. Chem. B* 109 (2005) 9678.
- [5] A. Magrez, R. Smajda, J.W. Seo, E. Horvath, P. Rebernik Ribic, J.C. Andresen, D. Acquaviva, A. Olariu, G. Laurenczy, L. Forro, *ACS Nano* 5 (2011) 3428.
- [6] C.I. Chang, Y.N. Wang, H.R. Pei, C.J. Lee, X.H. Du, J.C. Huang, *Key Eng. Mater.* 351 (2007) 114.
- [7] C.M.S. Rodrigues, J.A. Labrincha, F.M.B. Marques, *Solid State Ionics* 136–137 (2000) 671.
- [8] H. Kurosawa, Y. Yan, N. Miura, N. Yamazoe, *Solid State Ionics* 79 (1999) 338.
- [9] Y.Z. Wu, F.T. Hu, N. Gan, J.G. Hou, T.H. Li, Y.T. Cao, L. Zheng, *Adv. Mater. Res.* 343–344 (2011) 490.
- [10] C.C. Chao, C.M. Hsu, Y. Cui, F.B. Prinz, *ACS Nano* 5 (2011) 5692.
- [11] T.Z. Sholklapper, H. Kurokawa, C.P. Jacobson, S.J. Visco, L.C. De Jonghe, *Nano Lett.* 7 (2007) 2136.
- [12] A.C. Jones, H.C. Aspinall, P.R. Chalker, R.J. Potter, K. Kukli, A. Rahtu, M. Ritala, M. Leskelä, *J. Mater. Chem.* 14 (2004) 3101.
- [13] L.G. Hubert-Pfalzgraf, *J. Mater. Chem.* 14 (2004) 3113.
- [14] T.J. Leedham, A.C. Jones, P.J. Wright, M.J. Crosbie, D.J. Williams, H.O. Davies, P. O'Brien, *Integr. Ferroelectr.* 26 (1999) 767.
- [15] EVA-12 Reference manual, Bruker-AXS, 2008.
- [16] G.M. Sheldrick, *Acta Crystallogr., Sect. A* 64 (2008) 112.
- [17] SHELXTL-NT reference manual, Bruker AXS, 1998.
- [18] Z.A. Starikova, E.P. Turevskaya, N.I. Kozlova, N.Ya. Turova, D.V. Berdyev, A.I. Yanovsky, *Polyhedron* 18 (1999) 941.
- [19] G.I. Spijksma, G.A. Seisenbaeva, H.J.M. Bouwmeester, D.H.A. Blank, V.G. Kessler, *J. Sol-Gel Sci. Technol.* 51 (2009) 10.
- [20] G.I. Spijksma, H.J.M. Bouwmeester, D.H.A. Blank, V.G. Kessler, *Chem. Commun.* 2004 (1874).
- [21] G.I. Spijksma, H.J.M. Bouwmeester, D.H.A. Blank, A. Fischer, M. Henry, V.G. Kessler, *Inorg. Chem.* 44 (2006) 4938.
- [22] A.C. Jones, T.J. Leedham, P.J. Wright, M.J. Crosbie, P.A. Lane, D.J. Williams, K.A. Fleeting, D.J. Otway, P. O'Brien, *Chem. Vap. Deposition* 4 (1998) 46.
- [23] J.M. Wu, B. Qi, *J. Phys. Chem. C* 111 (2007) 666.