# Monomeric malonate precursors for the MOCVD of HfO<sub>2</sub> and ZrO<sub>2</sub> thin films<sup>†</sup>

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Received 24th June 2008, Accepted 29th September 2008 First published as an Advance Article on the web 21st November 2008 DOI: 10.1039/b810528f

New Hf and Zr malonate complexes have been synthesized by the reaction of metal amides with different malonate ligands (L = dimethyl malonate (Hdmml), diethyl malonate (Hdeml), di-tert-butyl malonate (Hdbml) and bis(trimethylsilyl) malonate (Hbsml)). Homoleptic eight-coordinated monomeric compounds of the type  $ML_4$  were obtained for Hf with all the malonate ligands employed. In contrast, for Zr only Hdmml and Hdeml yielded the eight-coordinated monomeric compounds of the type ML<sub>4</sub>, while using the bulky Hdbml and Hbsml ligands resulted into mixed alkoxo-malonato six-coordinated compounds of the type [ML2(OR)2]. Single crystal X-ray diffraction studies of all the compounds are presented and discussed, and they are found to be monomeric. The complexes are solids and in solution, they retain their monomeric nature as evidenced by NMR measurements. Compared to the classical  $\beta$ -diketonate complexes,  $[M(acac)_4]$  and  $[M(thd)_4]$  (M = Hf, Zr; acac: acetylacetonate; thd: tetramethylheptadione), the new malonate compounds are more volatile, decompose at lower temperatures and have lower melting points. In particular, the homoleptic diethyl malonate complexes of Hf and Zr melt at temperatures as low as 62 °C. In addition, the compounds are very stable in air and can be sublimed quantitatively. The promising thermal properties makes these compounds interesting for metal-organic chemical vapor deposition (MOCVD). This was demonstrated by depositing HfO<sub>2</sub> and ZrO<sub>2</sub> thin films successfully with two representative Hf and Zr complexes.

# Introduction

Silicon dioxide  $(SiO_2)$  has conventionally been used as the dielectric in metal oxide semiconductor field effect transistors (MOSFETs).<sup>1</sup> However, further downscaling of the dielectric thickness will lead to direct electron tunneling and high leakage currents which can degrade the device performance<sup>1</sup> High permittivity (high-k) insulators which give higher gate capacitances with physically thicker dielectric films are needed to address this issue.1,2 Research studies in the last few years identified Hf and Zr based dielectrics (e.g. oxides, silicates, aluminates) as the most promising high-k materials to replace SiO<sub>2</sub> in CMOS applications.<sup>1-3</sup> Metalorganic chemical vapor deposition (MOCVD) has been established as a very useful fabrication process for the deposition of high quality thin films. It has several advantages such as growth of uniform layers on large substrates, high growth rates, good composition control, conformal coverage on substrates with complex geometries etc. The success of MOCVD process relies strongly on the precursors employed. The availability of volatile metalorganic precursors possessing sufficient vapor pressure, thermal stability during the evaporation process and lower decomposition temperature are some of the features desired.

Metal-organic compounds such as metal halides, classical or functional alkoxides,  $\beta$ -diketonates, alkylamides and metal nitrates are some of the commonly used precursors for MOCVD of Hf and Zr oxide thin films.<sup>4,5</sup> There are certain drawbacks associated with some of these precursors such as lower volatility, higher evaporation and decomposition temperatures, carbon and halogen incorporation in the films and high air and moisture sensitivity. Our earlier approach of modifying the existing class of precursors, for example, usage of different chelating ligands in combination with Hf and Zr alkoxides, showed promise in terms of improved thermal properties, moisture sensitivity etc.6 In a continuation of our efforts to develop precursors with improved properties, in terms of precursor volatility, ease of handling, thermal stability, reduction in decomposition temperature in order to achieve film growth at reduced substrate temperatures, we pursued our work further. In this work, our main objective was to synthesise complexes of Hf and Zr with malonates as alternative chelating ligands with a goal to obtain precursors, which are more volatile and have lower decomposition temperature than the classical  $\beta$ diketonates like [M(acac)<sub>4</sub>] or [M(thd)<sub>4</sub>], and easier to handle than the parent alkoxides or amides. The structural and thermal properties of malonate based Hf and Zr compounds are discussed in detail. As a representative example, compounds [Hf(dmml)<sub>4</sub>] and  $[Zr(dbml)_2(OBu^t)_2]$  (Hdmml = dimethyl malonate, Hdbml = di-tert-butyl malonate) are tested for the MOCVD growth of HfO2 and ZrO<sub>2</sub> respectively and the thin film properties are investigated.

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<sup>†</sup> Electronic supplementary information (ESI) available: Molecular structures, <sup>1</sup>H NMR spectra, mass spectra, TG curves and crystallographic data. CCDC reference numbers 692629-692636. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b810528f

## **Results and discussion**

As a part of our research to develop improved precursors for  $HfO_2$  and  $ZrO_2$ , we used malonates as chelating ligands, since these ligands saturate the metal centre and can also lead to the formation of monomeric compounds, which is important in terms of volatility. The other advantage is that, the presence of the ester groups in the molecule can act as cleavage points, which can trigger decomposition at low temperatures enabling film growth at reduced substrate temperatures. In this study, the bulkiness of the malonates was also varied (by changing the substituent on malonate) to study its effect on product formation, crystallization, volatility and decomposition. We have thus synthesized a series of Hf and Zr malonate complexes through the amide route by substituting amide groups on metal with chelating malonate ligands. Though in principle it is possible to synthesize all the complexes through alkoxide or salt metathesis routes, the amide route was chosen for the following reasons. In alkoxide route, the alcohol, formed during the reaction, can facilitate some other transformation (or product decomposition).<sup>7</sup> The salt metathesis route includes the heterogeneous reaction of metal salt suspension and the metal salt formed as a byproduct could possibly contaminate the precursor. In the amide route, the amines formed as side products can easily be removed by applying vacuum since their boiling points are lower than alcohols.

The reaction of Hf amide with four equivalents of different malonates resulted in the formation of eight-coordinated monomeric Hf complexes  $[Hf(dmml)_4]$  (1),  $[Hf(deml)_4]$  (2),  $[Hf(dbml)_4]$  (3) and  $[Hf(bsml)_4]$  (4) (Hdmml = dimethyl malonate, Hdeml = diethyl malonate, Hdbml =di-*tert*-butyl malonate, Hbsml = bis(trimethylsilyl) malonate) (Scheme 1).

In the case of Zr, only Hdmml and Hdeml yielded homoleptic eight-coordinated monomeric complexes [Zr(dmml)<sub>4</sub>] (5) and [Zr(deml)<sub>4</sub>] (6) (Scheme 1). However, when bulkier di*tert*-butyl and bis(trimethylsilyl) malonates were used as ligands, only six-coordinated mixed alkoxide-malonate of Zr compounds [Zr(dbml)<sub>2</sub>(OBu<sup>1</sup>)<sub>2</sub>] (7) and [Zr(bsml)<sub>2</sub>(OSiMe<sub>3</sub>)<sub>2</sub>] (8) were obtained (Scheme 2). The alkoxide/siloxide ions on Zr were generated during thermal activation of malonic diester (malonate).<sup>8,9</sup>

The products were purified by crystallization in toluene or toluene/acetonitrile mixture. Except for **3**, **4** and **7**, all the other compounds crystallize with toluene in the crystal lattice. However, toluene can be removed from the crystal lattice by prolonged evacuation at reduced pressure. Crystal and data collection parameters for all compounds are given in Table S1 in the ESI.<sup>†</sup> Compound **1** was crystallized in toluene at 5 °C and it crystallizes in the monoclinic  $P_{2_1}/c$  space group with a toluene molecule in the crystal lattice. The coordination geometry around the Hf ion is square antiprism (Fig. 1).<sup>10</sup> Eight oxygen atoms of the four chelating malonate ions are coordinated to the central Hf ion with the average Hf–O bond length of 2.169 Å, which is shorter than average Hf–O bond length (2.178 Å) in [Hf(acac)<sub>4</sub>].<sup>11</sup> The bite angles of Hf and malonates are wider in **1** (av. 75.58°) compared to the same in [Hf(acac)<sub>4</sub>] (av. 75.12°).

Compound **2** was crystallized in toluene at -30 °C. Similar to **1**, compound **2** crystallizes in a monoclinic  $P2_1/c$  space group with toluene molecule in the crystal lattice (Fig. S1†). The coordination polyhedron of Hf ion is identical to that of **1**. The average Hf–O bond length (2.172 Å) is comparable to the same in **1** and shorter than the same in [Hf(acac)<sub>4</sub>] (av. 2.178 Å). However, the bite angles (av. 75.37°) are narrow compared to the same in **1** (av. 75.58°). As the size of the alkyl group on malonate was increased from ethyl to *tert*-butyl, it was not possible to crystallize the product [Hf(dbml)<sub>4</sub>] (**3**) in toluene. However, X-ray quality crystals were obtained for this compound **3** crystallizes in tetragonal space



Scheme 1 Synthesis of eight-coordinated Hf and Zr malonates.



Scheme 2 Synthesis of six-coordinated mixed alkoxide-malonates of Zr.



Fig. 1 Molecular structure (left) and coordination polyhedron (right) of  $[Hf(dmml)_4]$  (1). (Hydrogen atoms and toluene molecule are removed for clarity.) Selected bond lengths (Å) and angles (°); Hf(1)-O(11) 2.146(2), Hf(1)-O(25) 2.153(2), Hf(1)-O(45) 2.155(2), Hf(1)-O(31) 2.158(2), Hf(1)-O(41) 2.174(2), Hf(1)-O(21) 2.186(2), Hf(1)-O(15) 2.190(2), Hf(1)-O(35) 2.192(2), O(45)-Hf(1)-O(41) 75.35(8), O(25)-Hf(1)-O(21) 75.78(7), O(11)-Hf(1)-O(15) 75.74(8), O(31)-Hf(1)-O(35) 75.44(8).

group of P4/ncc with no solvent molecule in it (Fig. S2†). The coordination polyhedron of Hf is a square antiprism.<sup>10</sup> The molecule has  $C_4$  symmetry and the Hf–O bond lengths (av. 2.176 Å) are close to the same in [Hf(acac)<sub>4</sub>] and are comparable to that of **1** and **2**.

However, it is longer than Hf–O distances observed in [Hf(thd)<sub>4</sub>] (av. 2.146 Å).<sup>7</sup> Hf-malonate bite angle (79.02(8)°) is wider than the same in other Hf malonate compounds reported here. Though it is an eight-coordinated compound, its bite angle is comparable to the same in six-coordinated [Hf(NEt<sub>2</sub>)<sub>2</sub>(dbml)<sub>2</sub>] and [Hf(N(MeEt)<sub>2</sub>(dbml)<sub>2</sub>].<sup>12,13</sup> Solvent free [Hf(bsml)<sub>4</sub>] (**4**) was crystallized in tetragonal  $I4_1/a$  space group in toluene (Fig. 2). There are two types of Hf–O bonds, which differ in their lengths (Hf(1)-O(1) 2.105(2) and Hf(1)-O(5) 2.262(2) Å). It indicates that Hf is strongly coordinated to O(1) compared to O(5). As



Fig. 2 Molecular structure of  $[Hf(bsml)_4]$  (4) (hydrogen atoms are removed for clarity). Selected bond lengths (Å) and angles (°); Hf(1)-O(1) 2.105(2), Hf(1)-O(5) 2.262(2), C(2)-O(1) 1.282(4), C(4)-O(5) 1.250(4), C(2)-C(3) 1.376(4), C(3)-C(4) 1.400(4), O(1)-Hf(1)-O(5) 76.85(8).

a consequence, C(2)-O(1) bond length (1.282(4) Å) is longer than C(4)-O(5) bond length (1.250(4) Å).

This resulted in the shortening of C(2)-C(3) (1.376(4) Å) bond length compared to C(3)-C(4) (1.400(4) Å) bond length. The bonding here can be best explained as intermediate position between **a** and **b** shown in Scheme 3, as formation of position **b** is important for McLafferty rearrangement.



Scheme 3 View of bonding situation in  $[Hf(bsml)_4]$  (4).

Very similar to 1 and 2,  $[Zr(dmml)_4]$  (5) and  $[Zr(deml)_4]$  (6) were crystallized in toluene. Compound 5 (Fig. S3<sup>†</sup>) was crystallized at 5 °C, but compound 6 (Fig. 3) was crystallized at -30 °C. Both crystallize in a monoclinic  $P2_1/c$  space group with toluene molecule in the crystal lattice. Also in both cases, eight oxygen atoms of the four chelating malonate ions are coordinated to the central Zr ion with the average Zr–O bond length of 2.18 Å, which are comparable to Zr–O bond lengths in  $[Zr(acac)_4]$  and other eight coordinated Zr compounds.<sup>14,16</sup>

However, the coordination geometry around Zr ion in **6** is very close to square antiprism (Fig. 3) than the geometry in **5**. The bite angles of Zr and malonates are wider in **5** (av.  $75.36^{\circ}$ ) compared to the same in **6** (av.  $75.13^{\circ}$ ). Overall Zr malonate bite angles in **5** and **6** are narrower than Hf malonates **1** and **2**. All other structural features of **5** and **6** are very similar to their Hf analogues **1** and **2**.

Compound 7 crystallizes in triclinic space group  $P\overline{1}$  (Fig. 4). There are two types of Zr in the crystal lattice, which differ slightly in their coordination geometry. In each molecule, two di*tert*-butyl malonates and two *tert*-butoxy ligands are octahedrally coordinated to the central Zr ion. Two *tert*-butoxy groups on each



Fig. 3 Molecular structure of  $[Zr(deml)_4]$  (6) (Hydrogen atoms and toluene molecule are removed for clarity). Selected bond lengths (Å) and angles (°); Zr(1)-O(45) 2.159(2), Zr(1)-O(15) 2.162(2), Zr(1)-O(31) 2.182(2), Zr(1)-O(35) 2.184(2), Zr(1)-O(41) 2.185(2), Zr(1)-O(25) 2.188(2), Zr(1)-O(21) 2.188(2), Zr(1)-O(11) 2.214(2), O(31)-Zr(1)-O(35) 75.13(8), O(45)-Zr(1)-O(41) 75.18(8), O(25)-Zr(1)-O(21) 75.07(8), O(15)-Zr(1)-O(11) 75.15(7).



Fig. 4 Molecular structure of  $[Zr(dbml)_2(OBu')_2]$  (7) (Hydrogen atoms are removed for clarity). Selected bond lengths (Å) and angles (°); Zr(2)-O(51) 1.917(2), Zr(2)-O(61) 1.928(2), Zr(2)-O(21) 2.119(2), Zr(2)-O(29) 2.122(2), Zr(2)-O(25) 2.185(2), Zr(2)-O(210) 2.218(2), O(51)-Zr(2)-O(61) 100.9(1), O(51)-Zr(2)-O(21) 97.7(1), O(61)-Zr(2)-O(21) 94.2(1), O(51)-Zr(2)-O(29) 94.0(1), O(61)-Zr(2)-O(29) 99.3(1), O(21)-Zr(2)-O(29) 160.21(9), O(51)-Zr(2)-O(25) 166.3(1), O(61)-Zr(2)-O(25) 91.6(1), O(21)-Zr(2)-O(25) 86.91(9), O(29)-Zr(2)-O(25) 78.35(9), O(51)-Zr(2)-O(210) 88.48(9), O(61)-Zr(2)-O(210) 168.96(9), O(21)-Zr(2)-O(210) 78.60(9), O(29)-Zr(2)-O(210) 85.77(9), O(25)-Zr(2)-O(210) 79.76(9).

Zr ion are *cis* to each other. Both *tert*-butyl groups on Zr(1)-O are disordered. However, there is no such disorder observed in the Zr(2) based molecules. Zr–O bond lengths for the *tert*-butoxy groups are in the range of 1.917–1.928 Å (av. 1.922 Å), which are shorter than the Zr–O bond lengths of malonate ligands (2.119–2.218 Å (av. 2.162 Å)). Among the two sets of Zr–O bond lengths of malonates on each Zr, one (av. 2.198 Å) which is *trans* to Zr–OBu<sup>t</sup> is longer than other set of Zr–O bond lengths (av. 2.126 Å) due to the *trans* effect of alkoxides on the metal. All the O–Zr–O bond angles strongly deviate from the ideal octahedral angle which varies from 78.4 to 100.9° for *cis* and from 159.1 to 169.0° for *trans*. Among the *cis* angles, 'BuO-Zr-OBu<sup>t</sup> angles (100.4 and 100.9° for Zr(1) and Zr (2) respectively) are wider than other *cis* angles (78.4 to 99.6°) which could be due to the steric effect of 'Bu group. Also the small bite angles of two malonate esters (78.4–79.0°) facilitate

the widening of O–Zr–O angle of the *tert*-butoxy groups. All these structural features are very similar to the related six-coordinated mixed alkoxide-ketoester and mixed amide-malonate compounds reported by our group earlier.<sup>6</sup>

Compound **8** crystallizes with toluene in crystal lattice in the monoclinic space group C2/c forming a distorted octahedral environment at the Zr centre (Fig. S4<sup>†</sup>). Since the toluene molecule was highly disordered, it was squeezed out with the program Platon 1.13.<sup>17</sup> The Zr molecule has  $C_2$  symmetry. Zr–O bond length of siloxy groups (1.949(3) Å) is longer than Zr–O bond length of *tert*-butoxy groups (1.917–1.928 Å with av. 1.922 Å) in 7. It shows that Zr–O bond of siloxide in **8** is weak compared to Zr–O bond of *tert*-butoxy group in 7. It results in the reduced *trans* influence on Zr–O bonds of malonate which are *trans* to OSiMe<sub>3</sub>, and hence its bond length (2.175 Å) is shorter than the Zr–O bond lengths of malonate (2.185–2.218 Å with av. 2.198 Å) which are *trans* to OBu<sup>1</sup> in 7. All other structural features are similar to compound **7**.

Apart from being monomer in solid state, all these compounds (1-8) retain their mononuclearity in solution too. This was confirmed by solution state 1H and 13C NMR spectroscopic studies in  $C_6 D_6$ . <sup>1</sup>H NMR spectra of dimethyl malonates of Hf (1) and Zr (5) show only two singlets with the intensity ratio of 6:1 ( $\delta$  3.40, 4.95 ppm respectively for 1 and  $\delta$  3.45, 4.99 ppm respectively for 5) corresponding to CH<sub>3</sub> and CH of dimethyl malonates respectively (Fig. S5<sup>†</sup>). It clearly shows that only one type of dmml is present in the solution. This fact is also confirmed in <sup>13</sup>C NMR spectra, as they exhibit only three peaks at  $\delta$  51.31, 68.17 and 175.52 ppm for 1; at  $\delta$  51.29, 68.39 and 175.28 ppm for 5 corresponding to OCH<sub>3</sub>, CH and C=O respectively. <sup>1</sup>H NMR spectra of diethyl malonates of Hf (2) and Zr (6) exhibit one triplet (at  $\delta$  1.08 ppm for 2 and at  $\delta$  1.07 for 6) for CH<sub>3</sub>, one quartet (at  $\delta$  4.16 ppm for 2 and at  $\delta$ 4.11 ppm for 6) for CH<sub>2</sub> and one singlet (at  $\delta$  5.02 ppm for 2 and at  $\delta$  4.99 for 6) for CH. <sup>13</sup>C NMR spectra show four peaks at  $\delta$ 14.89, 60.33, 68.54 and 175.08 ppm for **2**; at  $\delta$  14.90, 60.30, 68.73 and 174.83 ppm for 6 corresponding to CH<sub>3</sub>, CH<sub>2</sub>, CH and C=O respectively.

As expected for a mononuclear compound, the <sup>1</sup>H NMR spectrum of compound 3 exhibits one singlet at  $\delta$  1.54 ppm for CH<sub>3</sub> of *tert*-butyl group and one singlet at  $\delta$  4.88 ppm for CH of malonate. The <sup>13</sup>C NMR spectrum also confirms this fact as it shows only four peaks at  $\delta$  29.66, 73.73, 79.46 and 174.70 ppm corresponding to CH<sub>3</sub>, OC, CH and C=O respectively. There are two singlets for <sup>1</sup>H NMR spectrum of compound 4 (at  $\delta$  0.37 ppm for SiMe<sub>3</sub> and at  $\delta$  4.86 ppm for CH). The <sup>13</sup>C NMR spectrum shows three peaks at  $\delta$  0.92, 74.80 and 173.44 ppm corresponding to SiMe<sub>3</sub>, CH and C=O respectively. The <sup>1</sup>H NMR spectrum of compound 7 exhibits three singlets of equal intensity at  $\delta$  1.42, 1.46 and 1.53 ppm for tert-butyl groups. It indicates that the two tertbutyl groups on each malonate are different due to the trans effect of 'BuO on Zr and hence gives two singlets. This phenomenon also supports the trans effect observed in X-ray crystal structure. The third singlet is due to the tert-butoxy group on Zr. The singlet at  $\delta$  4.86 ppm is due to the presence of CH of malonates. This *trans* effect is also seen in <sup>13</sup>C NMR spectrum, as it shows two peaks at  $\delta$  28.96 and 29.05 ppm for CH<sub>3</sub> of *tert*-butyl groups of malonate, two peaks at  $\delta$  79.83 and 79.96 ppm for CCH<sub>3</sub> of *tert*-butyl groups of malonate, two peaks at  $\delta$  175.66 and 175.85 ppm for C=O of malonates, and one peak at  $\delta$  71.42 ppm for CH of malonates.<sup>13</sup>

 Table 1
 Melting points of Hf and Zr compounds

Compound	Compound Mp/°C Compound		Mp∕°C	
[Hf(acac)₄]	19315,18	[Zr(acac)₄]	194 <sup>15,18</sup>	
[Hf(thd)]	> 32019	$[Zr(thd)_4]$	>32019	
[Hf(tbaoac) <sub>4</sub> ]	$180-210^{20},^{a}$	[Zr(tbaoac)₄]	$>260^{6},^{b}$	
$[Hf(dmml)_4](1)$	139–140	$[Zr(dmml)_4]$ (5)	139-140	
$[Hf(deml)_4](2)$	62	$[Zr(deml)_4]$ (6)	62	
$[Hf(dbml)_4]$ (3)	194	$[Zr(dbml)^{2}(OBu^{t})_{2}](7)$	197	
$[Hf(bsml)_4]$ (4)	147-152	$[Zr(bsml)_2(OSiMe_3)_2]$ (8)	>270	

<sup>*a*</sup> Sublimes at 180–210 °C,  $2.5 \times 10^{-4}$  Torr. <sup>*b*</sup> Decomposes without melting at 260 °C.

The <sup>1</sup>H NMR spectrum of compound **8** exhibits one broad signal at  $\delta$  0.31 ppm corresponding to the Me<sub>3</sub>Si on malonates, followed by one sharp singlet of half of its intensity due to the presence of Me<sub>3</sub>SiO on Zr (Fig. S6†). As expected, CH of malonates shows one singlet at 5.00 ppm. The <sup>13</sup>C NMR spectrum shows two peaks at  $\delta$  0.33 and 2.61 ppm for SiMe<sub>3</sub>, one peak at  $\delta$  73.91 ppm for CH and one peak at  $\delta$  175.66 ppm for C=O. These data indicate the presence of only one type of malonate ligands and also supports the reduced *trans* influence of OSiMe<sub>3</sub> on malonates as discussed in the crystal structure description. The above data confirm the mononuclearity of compounds **7** and **8** in solution.

The melting points of all the compounds were measured in sealed capillaries (listed in Table 1) and compared with melting points reported for the classical β-diketonates of Hf and Zr. It was observed that the melting points of the new compounds are relatively lower compared to the related analogues known in the literature, especially with the methyl and ethyl malonate ligands. For example, the difference between  $[Zr(acac)_4]$  and  $[Zr(dmml)_4]$ is only the substitution on carbonyl group. In  $[Zr(acac)_4]$ , methyl group is bonded to carbonyl group, whereas in [Zr(dmml)<sub>4</sub>], methoxy group is bonded to carbonyl group. However, the melting point of [Zr(dmml)<sub>4</sub>] (139–140 °C) is much lower compared to the same for [Zr(acac)<sub>4</sub>] (194 °C). The same trend also exists between  $[Hf(acac)_4]$  and  $[Hf(dmml)_4]$ , and  $[Hf(thd)_4]$  and  $[Hf(dbml)_4]$ . Apart from compound 8, all the other compounds melted at temperatures below 200 °C. A striking observation is that the melting point values of the [Hf(deml)] (2) and [Zr(deml)] (6) are as low as 62 °C. This shows that a slight change in the substituent on the malonates results in a drastic change in the melting point. This could be due to the difference in packing of the molecule in the crystal lattice.

EI mass spectra were recorded for the compounds **1**, **2**, **5**, **6** and **7**. These data provide information about the fragmentation characteristics of the complexes under gas phase ionization conditions. The utilization of mass spectral data to predict the possible mechanism for CVD processes has been previously established.<sup>21</sup> As has been discussed in the literature, care must be taken in extrapolating any fragmentation information from mass spectral data to the CVD process since the latter is thermally induced.<sup>22</sup> Nevertheless, mass spectral data have provided insights into probable fragmentation patterns of the Hf and Zr malonate precursors.

Dimethyl and diethyl malonates of Hf and Zr (1, 2, 5 and 6) exhibit similar fragmentation pattern. None of these four compounds shows a molecular ion peak. However, peaks corresponding to the subsequent fragments viz. M<sup>+</sup> – ROC(O)CHC(O),

 
 Table 2
 Overview of fragments of malonate based complexes of Hf and Zr detected by mass spectrometry

	Mass, $m/z$ (relative intensity, %)				
Fragments	1	2	5	6	
$M^+ - ROC(O)CHC(O)$	604 (<1)	702(1)	514(1)	612(1)	
M+ - L	573 (2)	657 (43)	483 (8)	567 (97)	
$M^+ - L - ROC(O)CHC(O)$	473 (2)	543 (100)	383 (26)	453 (100)	
$M^+ - L - 2ROC(O)CHC(O)$	373 (2)	429 (69)	283 (31)	339 (82)	
$M^+ - L - 3ROC(O)CHC(O)$	273 (1)	315 (5)	183 (20)	225 (12)	
L <sup>+</sup>	132 (4)	160 (4)	132 (4)	160 (4)	
ROC(O)CHC(O)+	101 (100)	115 (90)	101 (100)	115 (93)	
L = dmml and deml.					

 $M^+ - L$ ,  $M^+ - L - ROC(O)CHC(O)$ ,  $M^+ - L - 2ROC(O)CHC(O)$ ,  $M^+ - L - 3ROC(O)CHC(O)$  and  $L^+ROC(O)CHC(O)^+$  were observed. It clearly indicates that malonate ligands on metal decompose into (metal) alkoxide and ROC(O)CHC(O). It also explains the abundance of ROC(O)CHC(O) ions in the spectra.Table 2 gives an overview of the fragments observed in the spectra for dimethyl and diethyl malonates of Hf and Zr. This shows that the decomposition mechanism here is different from thd-based Hf and Zr compounds. During fragmentation in thd based Hf and Zr compounds, diketone part (RC(O)CHC(O)) of RC(O)CHC(O)R is intact with the metal.<sup>7,23</sup> In malonate based Hf and Zr compounds, the diketone part (ROC(O)CHC(O)) of ROC(O)CHC(O)OR is not intact with metal, but only the "OR" part of ROC(O)CHC(O)OR is intact with metal.

The EI mass spectrum of compound 7 clearly shows the decomposition of each *tert*-butyl group into isobutene gas. A schematic view of proposed mechanism of fragmentation of  $[Zr(dbml)_2(OBu^t)_2]$  is shown in the Scheme 4. It shows a molecular ion peak at m/z 666. This is followed by stepwise loss of two isobutene molecules as there are two consecutive peaks at m/z 610 (a) and 554 (b).<sup>24</sup> These two isobutene molecules are most probably from two *tert*-butoxy groups on the metal as the following step is the elimination of water.<sup>25</sup> It is more likely (or more feasible) that two hydroxyl groups on the metal, which are *cis* to each other, condense to eliminate water than two hydroxyl groups on malonates.<sup>7</sup>

Hence, the peak at m/z 537 could be assigned to  $[Zr(O)(dbm])_2]^+$ (c). The following four steps (at m/z 480, 424, 368 and 313) could be due to the elimination of four isobutene molecules (through McLafferty rearrangement) from four *tert*-butyl groups on malonates.<sup>12,13,20,26</sup> This leads to the formation of  $[Zr(O){HO_2CCHCO_2H}_2]$  (at m/z 313) (d). The highest intensity peak (base peak) corresponds to isobutene molecular ion at m/z 57. The overview of fragments of compound **7** is shown in Table 3.

# Thermal characterization

In order to assess the suitability of the Hf and Zr malonate complexes for MOCVD, the thermal characteristics were studied by thermogravimetric (TG) analysis and the results are shown in Fig. 5. The homoleptic Hf methyl (1) and ethyl malonates (2) volatalise in the temperature range of 50–150 °C. This is followed by two shoulders at 187 °C (75 weight%) and 334 °C (50 weight%) for compound 1, and at 225 °C (65 weight%) and 277 °C (50 weight%) for compound 2. A final residue of around



Scheme 4 Proposed mechanism of fragmentation of [Zr(dbml)<sub>2</sub>(O<sup>t</sup>Bu)<sub>2</sub>] (7).

 Table 3
 Overview of fragments of compound 7 detected by mass spectrometry

Fragments	Mass, $m/z$ (relative intensity, %)		
M <sup>+</sup>	666 (3)		
M <sup>+</sup> – isobutene	610 (6)		
M <sup>+</sup> – 2isobutene	554 (3)		
$M^+$ – 2isobutene – $H_2O$	537 (8)		
$M^+$ – 3isobutene – $H_2O$	480 (26)		
$M^+ - 4$ isobutene $- H_2O$	424 (34)		
$M^+$ – 5isobutene – $H_2O$	368 (44)		
$M^+$ – 6isobutene – $H_2O$	313 (9)		
Isobutene	57 (100)		

40% for compound 1 and 35% for compound 2 is left behind. For compound 3, the volatilisation begins at higher temperature (>150 °C), but the residue left behind is much lower (25%). Similar trends were observed in the evaporation behaviour of Zr compounds 5–7 (Fig. 5). Higher residues were obtained for the Zr methyl (5) and ethyl (6) malonates compared to the mixed alkoxide-butyl malonates (7).

A precise analysis of the residues hasn't been carried out, however, the steps in the TG curves could be due to the stepwise loss of the different terminal alkyl groups present in the malonates. As discussed earlier, the cleavage points in the ligand structure of malonates could facilitate decomposition reactions at much reduced temperatures in these Hf and Zr complexes compared to the classical  $\beta$ -diketonates. Detailed mechanistic studies are necessary to verify these claims on precursor decomposition mechanism.

Isothermal thermogravimetric measurements at atmospheric pressure were carried out for compounds 1 and 5. From the isothermal curves (Fig. 6), it was observed that  $[Hf(dmml)_4]$  (1) and  $[Zr(dmml)]_4$  (5) sublime at a constant and appreciable rate (2.27 µg min<sup>-1</sup> for compound 1 and 5.06 µg min<sup>-1</sup> for compound 5) for a long period (400 min) at 100 °C. From the thermal analysis, it can be inferred that the compounds are volatile. The linearity in the isothermal TG curves indicates mass transport behaviour of these compounds which is desirable for the MOCVD process.

## MOCVD and characterisation of HfO2 and ZrO2 thin films

The new Hf and Zr complexes have suitable thermal properties as discussed above (low melting point, low decomposition temperature, can be sublimed quantitatively, sufficient temperature window between volatilisation and decomposition). Therefore, it was interesting to test these compounds for thin film deposition by MOCVD and, as a representative example, the homoleptic [Hf(dmml)<sub>4</sub>] (1) was tested for MOCVD of HfO<sub>2</sub>. In the case of Zr, the mixed alkoxide-malonate, [Zr(dbml)<sub>2</sub>(OBu<sup>+</sup>)<sub>2</sub>] (7) was used for MOCVD of ZrO<sub>2</sub>. The HfO<sub>2</sub> and ZrO<sub>2</sub> films grown



Fig. 5 Thermogravimetric analysis curves for the Hf complexes  $\{[Hf(dmml)_4] (1), [Hf(deml)_4] (2) \text{ and } [Hf(dbml)_4] (3)\}$  and Zr complexes  $\{[Zr(dmml)_4] (5), [Zr(deml)_4] (6) \text{ and } [Zr(dbml)_2(OBu^1)_2] (7)\}$ .



Fig. 6 Isothermal curves for  $[Hf(dmml)_4]$  (1) and  $[Zr(dmml)_4]$  (5) at 100 °C.

at temperatures below 500 °C were amorphous. XRD analysis revealed that the crystallinity of the films was increased with the increase in substrate temperature. The crystalline films of HfO<sub>2</sub> and ZrO<sub>2</sub> stabilised in the monoclinic phase (JCPDS card 00–043–1017 for HfO<sub>2</sub> and 00–037–1484 for ZrO<sub>2</sub>) as shown in Fig. 7. Similar observations of these materials crystallising in the monoclinic phase have been reported using other Hf and Zr precursors in the same temperature range.<sup>6,27</sup>

The surface morphology of the as-deposited films was analysed by SEM (Fig. 8). There were no distinct surface features on the films grown at temperatures lower than 500  $^{\circ}$ C confirming the amorphous nature of the films obtained.

The SEM micrograph of an HfO<sub>2</sub> film grown at 700 °C (Fig. 8a) shows the formation of fine grains and Fig. 8b shows the cross section of the film (thickness = 60 nm), which reveals the densely packed structure of the film tending towards columnar growth. Similar features were observed in the case of  $ZrO_2$  (Fig. 8c and d), however at the same temperature longitudinal  $ZrO_2$  grains and the columnar growth was much more clearly evident (film thickness = 360 nm). A detailed study on the deposition and characterization



Fig. 7 XRD patterns of  $HfO_2$  (a) and  $ZrO_2$  (b) films deposited from  $[Hf(dmml)_4]$  (1) and  $[Zr(dbml)_2(OBu^i)_2]$  (7) respectively at 600 °C.



**Fig. 8** SEM images of  $HfO_2$  (a and b) and  $ZrO_2$  (c and d) films deposited from  $[Hf(dmml)_4]$  (1) and  $[Zr(dbml)_2(OBut)_2]$  (7) respectively at 700 °C.

of  $HfO_2$  and  $ZrO_2$  films grown varying different CVD process conditions is currently underway. It should be noted that all the compounds reported here are stable in solution and show a high degree of solubility in commonly used organic solvents. Therefore it will be interesting to test them for liquid injection MOCVD applications.

## Summary and conclusions

A series of new Hf and Zr precursors with different chelating malonate ligands (compounds **1–8**) were synthesised in high yields. The Hf and Zr malonate compounds are monomeric. The thermal properties of the precursors are suitable for MOCVD applications. Preliminary MOCVD experiments are carried out to deposit thin films of HfO<sub>2</sub> using [Hf(dmml)<sub>4</sub>] (**1**) and ZrO<sub>2</sub> films using [Zr(dbml)<sub>2</sub>(OBu<sup>1</sup>)<sub>2</sub>] (7). The HfO<sub>2</sub> and ZrO<sub>2</sub> films grown at temperatures above 500 °C crystallize in the monoclinic phase and exhibit columnar grain growth. We have demonstrated that the simple and straightforward synthetic route resulted in significant improvement in the MOCVD precursor development for HfO<sub>2</sub> and ZrO<sub>2</sub>. The new Hf and Zr compounds have improved thermal properties compared to the classical β-diketonate class of compounds like [M(acac)<sub>4</sub>] and [M(thd)<sub>4</sub>]. A detailed MOCVD studies using these compounds are currently in progress.

## Experimental

All reactions were performed using a conventional vacuum/argon line with standard Schlenck techniques. Samples for all analyses were prepared in argon filled glove boxes. Elemental analyses were performed by the analytical service center at faculty of Chemistry at Ruhr-Universität Bochum (CHNSO Vario EL 1998). Electronic ionization (EI) mass spectra were recorded using a Varian MAT spectrometer supplied with an ionizing energy of 70 eV. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on the Bruker Advance DRX-200. Thermal analysis was carried out using a Seiko TG/DTA 6300S11 at ambient pressure (Sample weight ~10 mg, heating rate 5 °C min-1). ZrCl4 (Alfa Aesar), HfCl4 (Alfa Aesar), n-BuLi (Merck), HNEt<sub>2</sub> (Fluka), dimethyl malonate (Acros), diethyl malonate (Janssen Chimica), di-tert-butyl malonate (Fluka) and bis(trimethylsilyl) malonate (Fluka) were used as received. The Zr and Hf amide compounds  $[Zr(NEt_2)_4]$  and  $[Hf(NEt_2)_4]$  were synthesized according to a previously reported procedure.<sup>28</sup> Crystallographic data were collected on a Xcalibur 2 Oxford using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved using the SHELXL-97 software package and refined by full matrix least-squares methods based on  $F^2$  with all observed reflections.

## MOCVD of HfO<sub>2</sub> and ZrO<sub>2</sub>

The screening of the metal-organic precursors was carried out using a self-built horizontal cold wall CVD reactor operating at reduced pressure.<sup>29</sup> Nitrogen (purity 6.0, flow rate: 50 sccm) and oxygen (purity 4.8, flow rate: 50 sccm) were used as carrier gas and oxidant respectively. The flow rates were controlled using mass flow controllers (MKS). The films were grown on Si(100) substrates, which were cleaned prior to deposition. The substrate temperature was varied between 400–700 °C and the temperature of the precursor bubbler was maintained at 100 °C. The reactor pressure was set at 1.00 mbar. The as-grown films were characterised by X-ray diffraction (XRD) using a Bruker D8 Advance AXS diffractometer with Cu-K $\alpha$  radiation (1.5481 Å) with a position sensitive detector (PSD). All the films were analysed in the  $\theta$ -2 $\theta$  geometry. The morphology of the film was studied using a LEO Gemini SEM 1530 electron microscope.

## Synthesis of [Hf(dmml)<sub>4</sub>] (1)

To the solution of  $[Hf(NEt_2)_4]$  (0.467 g, 1 mmol) in 20 ml of diethyl ether, Hdmml (0.528 g, 4 mmol) in 20 ml of diethyl ether was added drop wise over a period of 1 h at room temperature. After stirring for 24 h at ambient conditions, the solvent was removed under reduced pressure yielding a white solid. The resulting solid was dissolved in toluene and kept at 5 °C for 24 h to afford colorless crystals suitable for single crystal X-ray analysis. Yield: 0.633 g (90%). Mp: 139–140 °C. Elemental analysis: calc. for  $C_{20}H_{28}O_{16}Hf$ : C 34.17%, H 4.01%; found: C 33.92%, H 4.06%. <sup>1</sup>H NMR (room temp., 200 MHz,  $C_6D_6$ ):  $\delta_H$  3.40 (24H, s, CH<sub>3</sub>), 4.95 (4H, s, CH). <sup>13</sup>C NMR (room temp., 200 MHz,  $C_6D_6$ ):  $\delta_C$  51.31 (OCH<sub>3</sub>), 68.17 (CH), 175.52 (OCO). EI-MS (70 eV): 604, <1% (M+ -MeOC(O)CHC(O)); 573, 2% (M+ - dmml); 473, 2% (M+ - dmml -MeOC(O)CHC(O)); 373, 2% (M<sup>+</sup> – dmml – 2MeOC(O)CHC(O)); 273, 1% (M<sup>+</sup> - dmml - 3MeOC(O)CHC(O)); 132, 4% (Hdmml); 101, 100% (MeOC(O)CHC(O)).

#### Synthesis of [Hf(deml)<sub>4</sub>] (2)

[Hf(NEt<sub>2</sub>)<sub>4</sub>] (0.467 g, 1 mmol) was dissolved in 20 ml of diethyl ether. To this solution, four equivalents of Hdeml (0.641 g, 4 mmol) in 20 ml of diethyl ether was added drop wise over a period of 1 h at room temperature. The resultant solution was stirred for 24 h at ambient conditions and then the solvent was removed under vacuum. The remaining sticky solid was dissolved in toluene and kept at -30 °C for 24 h to afford colorless crystals suitable for single crystal X-ray analysis. Yield: 0.720 g (88%). Mp: 62 °C. Elemental analysis: calc. for  $C_{28}H_{44}O_{16}Hf$ : C 41.26%, H 5.44%; found: C 41.39%, H 4.98%. <sup>1</sup>H NMR (room temp., 200 MHz,  $C_6D_6$ ):  $\delta_H$  1.08 (24H, t, CH<sub>3</sub>), 4.16 (16H, q, CH<sub>2</sub>), 5.02 (4H, s, CH). <sup>13</sup>C NMR (room temp., 200 MHz,  $C_6D_6$ ):  $\delta_C$  14.89 (CH<sub>3</sub>), 60.33 (OCH<sub>2</sub>), 68.54 (CH), 175.08 (OCO). EI-MS (70 eV): 702, 1% (M<sup>+</sup> -EtOC(O)CHC(O)); 657, 43% (M+ - deml); 543, 100% (M+ - deml -EtOC(O)CHC(O)); 429, 69% (M<sup>+</sup> – deml –2EtOC(O)CHC(O)); 315, 5% (M<sup>+</sup> – deml – 3EtOC(O)CHC(O)); 160, 4% (Hdeml); 115, 90% (EtOC(O)CHC(O)).

## Synthesis of [Hf(dbml)<sub>4</sub>] (3)

A solution of Hdbml (0.865 g, 4 mmol) in 20 ml of toluene was added drop wise to a stirred solution of  $[Hf(NEt_2)_4]$  (0.467 g, 1 mmol) in 20 ml of toluene over a period of 1 h at room temperature. After stirring for 5 h at 110 °C, the solvent was removed under reduced pressure yielding a sticky solid. The obtained solid was dissolved in toluene/acetonitrile mixture and kept at room temperature for 7 days to afford colorless crystals suitable for single crystal X-ray analysis. Yield: 0.865 g (83%). Mp: 194 °C. Elemental analysis: calc. for C<sub>44</sub>H<sub>76</sub>O<sub>16</sub>Hf: C 50.84%, H 7.37%; found: C 50.36%, H 7.32%. <sup>1</sup>H NMR (room temp., 200 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta_{\rm H}$  1.54 (72H, s, CH<sub>3</sub>), 4.88 (4H, s, CH). <sup>13</sup>C NMR (room temp., 200 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta_{\rm C}$  29.66 (CH<sub>3</sub>), 73.73 (C–O), 79.46 (CH), 174.70 (OCO).

# Synthesis of [Hf(bsml)<sub>4</sub>] (4)

To the diethyl ether (20 ml) solution of  $[Hf(NEt_2)_4]$  (0.467 g, 1 mmol), four equivalents of Hbsml (0.994 g, 4 mmol) in 20 ml of diethyl ether was added drop wise over a period of 1 h at room temperature. The resultant solution was stirred for 24 h at room temperature. Removal of the solvent under reduced pressure yielded a slightly sticky solid which was dissolved in toluene and kept at -30 °C for 24 h to afford colorless crystals suitable for single crystal X-ray analysis. Yield: 0.92 g (79%). Mp: 147–152 °C. Elemental analysis: calc. for C<sub>36</sub>H<sub>76</sub>O<sub>16</sub>Si<sub>8</sub>Hf: C 37.01%, H 6.56%; found: C 36.39%, H 6.10%. <sup>1</sup>H NMR (room temp., 200 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta_{\rm H}$  0.37 (72H, s, CH<sub>3</sub>), 4.86 (4H, s, CH). <sup>13</sup>C-NMR (room temp., 200 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta_{\rm C}$  0.92 (CH<sub>3</sub>), 74.80 (CH), 173.44 (OCO).

## Synthesis of [Zr(dmml)<sub>4</sub>] (5)

A solution of Hdmml (0.528 g, 4 mmol) in diethyl ether (20 ml) was added drop wise to a stirred solution of  $[Zr(NEt_2)_4]$  (0.380 g, 1 mmol) in 20 ml of diethyl ether over a period of 1 h at room temperature. After stirring for 24 h at ambient conditions, the solvent was removed under reduced pressure yielding a white solid. The solid obtained was dissolved in toluene and kept at 5 °C for 24 h to afford colorless crystals suitable for single crystal X-ray analysis. Yield: 0.585 (95%). Mp: 139-140 °C. Elemental analysis: calc. for C<sub>20</sub>H<sub>28</sub>O<sub>16</sub>Zr: C 39.02%, H 4.58%; found: C 38.96%, H 4.56%. <sup>1</sup>H NMR (room temp., 200 MHz,  $C_6D_6$ ):  $\delta_H$ 3.45 (24H, s, CH<sub>3</sub>), 4.99 (4H, s, CH). <sup>13</sup>C NMR (room temp., 200 MHz, C<sub>6</sub>D<sub>6</sub>): δ<sub>C</sub> 51.29 (OCH<sub>3</sub>), 68.39 (CH), 175.28 (OCO). EI-MS (70 eV): 514, 1% (M<sup>+</sup> - MeOC(O)CHC(O)); 483, 8% (M<sup>+</sup> - dmml); 383, 26% (M<sup>+</sup> - dmml - MeOC(O)CHC(O)); 283, 31% (M<sup>+</sup> - dmml - 2MeOC(O)CHC(O)); 183, 20% (M<sup>+</sup> dmml - 3MeOC(O)CHC(O)); 132, 4% (Hdmml); 101, 100% (MeOC(O)CHC(O)).

# Synthesis of [Zr(deml)<sub>4</sub>] (6)

Hdeml (0.641 g, 4 mmol) in 20 ml of diethyl ether was added dropwise to a solution of [Zr(NEt<sub>2</sub>)<sub>4</sub>] (0.380 g, 1 mmol) in 20 ml of diethyl ether over a period of 1 h at room temperature. After stirring for 24 h at ambient conditions, the solvent was removed under reduced pressure yielding a white solid. The resulting solid was dissolved in toluene and kept at -30 °C for 24 h, which yielded colorless crystals suitable for single crystal X-ray analysis. Yield: 0.68 g (93%). Mp: 62 °C. Elemental analysis: calc. for C<sub>28</sub>H<sub>44</sub>O<sub>16</sub>Zr: C 46.20%, H 6.09%; found: C 46.28%, H 5.37%. <sup>1</sup>H NMR (room temp., 200 MHz,  $C_6D_6$ ):  $\delta_H$  1.07 (24H, t, CH<sub>3</sub>), 4.11 (16H, q, CH<sub>2</sub>) 4.99 (4H, s, CH). <sup>13</sup>C NMR (room temp., 200 MHz,  $C_6D_6$ ):  $\delta_C$  14.90 (CH<sub>3</sub>), 60.30 (OCH<sub>2</sub>), 68.73 (CH), 174.83 (OCO). EI-MS (70 eV): 612, 1% (M<sup>+</sup> -EtOC(O)CHCO); 567, 97% (M<sup>+</sup> - deml); 453, 100% (M<sup>+</sup> - deml -EtOC(O)CHC(O)); 339, 82% (M<sup>+</sup> - deml - 2EtOC(O)CHC(O)); 225, 12% (M<sup>+</sup> - deml - 3EtOC(O)CHC(O)); 160, 4% (Hdeml); 115, 93% (EtOC(O)CHCC(O)).

# Synthesis of [Zr(dbml)<sub>2</sub>(O<sup>t</sup>Bu)<sub>2</sub>] (7)

Hdbml (0. 865 g, 4 mmol) in 20 ml of toluene was added dropwise to a solution of  $[Zr(NEt_2)_4]$  (0.380 g, 1 mmol) in 20 ml of toluene over a period of 1 h at room temperature. After

stirring for 5 h at 110 °C, the solvent was removed under reduced pressure yielding a white solid. The resulting solid was dissolved in toluene/acetonitrile mixture and kept at 5 °C for 7 days to afford colorless crystals suitable for single crystal X-ray analysis. Yield: 0.5 g (75% based on [Zr(NEt<sub>2</sub>)<sub>4</sub>]). Mp: 197 °C. Elemental analysis: calc. for C<sub>30</sub>H<sub>56</sub>O<sub>10</sub>Zr: C 53.94%, H 8.45%; found: C 53.32%, H 9.98%. <sup>1</sup>H NMR (room temp., 200 MHz,  $C_6D_6$ ):  $\delta_H$  1.42 (18H, s, CH<sub>3</sub>), 1.46 (18H, s, CH<sub>3</sub>) 1.53 (18H, s, CH<sub>3</sub>) 4.86 (2H, s, CH). <sup>13</sup>C NMR (room temp., 200 MHz,  $C_6D_6$ ):  $\delta_C$  28.96 (CH<sub>3</sub> of mal), 29.05 (CH<sub>3</sub> of mal), 32.91(CH<sub>3</sub> of 'BuO), 71.42 (CH of mal), 75.77 (C-CH<sub>3</sub> of <sup>t</sup>BuO), 79.83 (C-CH<sub>3</sub> of mal), 79.96 (C-CH<sub>3</sub> of mal) 175.66 (OCO), 175.85 (OCO). EI-MS (70 eV): 666, 3% (M+); 610, 6% (M<sup>+</sup> - isobutene); 554, 3% (M<sup>+</sup> - 2isobutene); 537, 8% (M<sup>+</sup> -2isobutene – H<sub>2</sub>O); 480, 26% (M<sup>+</sup> – 3isobutene – H<sub>2</sub>O); 424, 34%  $(M^+ - 4isobutene - H_2O); 368, 44\% (M^+ - 5isobutene - H_2O);$ 313, 9% (M<sup>+</sup> – 6isobutene – H<sub>2</sub>O); 57, 100% (isobutene).

# Synthesis of [Zr(bsml)<sub>2</sub>(OSiMe<sub>3</sub>)<sub>2</sub>] (8)

Four equivalents of Hbsml (0.994 g, 4 mmol) in 20 ml of toluene was added drop wise over a period of 1 h to a solution of  $[Zr(NEt_2)_4]$  (0.380 g, 1 mmol) in 20 ml of toluene at room temperature. After stirring for 5 h at 110 °C, the solvent was removed under reduced pressure yielding a pale yellow solid which was dissolved in toluene and kept at -30 °C for 7 days to afford colorless crystals suitable for single crystal X-ray analysis. Yield: 0.48 g (63% based on  $[Zr(NEt_2)_4]$ ). Mp: >270 °C. Elemental analysis: calc. for  $C_{24}H_{56}O_{10}Si_6Zr$ : C 37.71%, H 7.38%; found: C 30.38%, H 6.50%. <sup>1</sup>H NMR (room temp., 200 MHz,  $C_6D_6$ ):  $\delta_H$  0.31 (36H, s(br), CH<sub>3</sub>), 0.34 (18H, s, CH<sub>3</sub>) 5.00 (2H, s, CH). <sup>13</sup>C NMR (room temp., 200 MHz,  $C_6D_6$ ):  $\delta_C$  0.33 (CH<sub>3</sub>), 2.61 (CH<sub>3</sub>), 73.91 (CH), 175.66 (OCO).

# Acknowledgements

The authors are grateful to the German Science Foundation for funding this work (DFG-CVD-SPP-1119-DE-390–3). One of the authors (RP) thanks the Alexander von Humboldt (AvH) foundation for the fellowship.

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