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Stabilization and destabilization of zirconium propoxide precursors by acetylacetone†

Gerald I. Spijksma,[a] Henny J. M. Bouwmeester,[a] Dave H. A. Blank[a] and Vadim G. Kessler*[b]

[a] *Inorganic Materials Science, Faculty of Science & Technology, and Mesa+ Research Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands. E-mail: G.I.Spijksma@utwente.nl; Fax: +31 53 4894683; Tel: +31 53 489299*

[b] *Department of Chemistry, SLU, Box 7015, 75007 Uppsala, Sweden. E-mail: Vadim.Kessler@kemi.slu.se; Fax: +46 18 673476; Tel: +46 18 671541*

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The stabilizing and destabilizing mechanism in the action of acetylacetone on zirconium propoxide precursors is revealed; the nature of heteroleptic intermediates provides an explanation.

The application of unmodified zirconium precursors in for instance MOCVD (Metal Organic Chemical Vapour Deposition) or sol–gel is a difficult task, due to extreme moisture sensitivity. A generally applied method to moderate the reactivity is the exchange of the alkoxide ligands by chelating organic ligands.[1] In sol–gel studies, acetic acid and acetylacetone are most often applied for this purpose.[2] Both complexing ligands are bidentate, but acetic acid can be bridging or chelating, while acetylacetone is only chelating. The literature on the application of acetylacetone (Hacac) as a complexing agent for the controlled processing of zirconium alkoxide precursors is abundant.[3]

To the best of our knowledge, no reports have been published on zirconium precursor structures formed upon modification. The only proposed model for stabilization is that by Ribot *et al.*[4] however, it is extracted from work performed on cerium(IV) isopropoxide. The authors proposed that the precursor structure in propyl alcohol, $[Ce_2(O^iPr)_8(^iPrOH)_2]$, is altered upon addition of 0.5, 1 or 2 mol equivalents of Hacac to give $[Ce_2(O^iPr)_7(acac)(^iPrOH)]$, $[Ce_2(O^iPr)_6(acac)_2(^iPrOH)_2]$ and $[Ce(O^iPr)_2(acac)_2]$ respectively. In the present study, we attempted to isolate and characterize the stabilized modifications of different zirconium propoxide precursors to confirm the mechanism proposed by Ribot *et al.*[4]

The precursors utilized in this study are commercially available zirconium *n*-propoxide, zirconium isopropoxide, and a mixed-ligand precursor $[Zr_2(O^nPr)_2(O^iPr)_6(^iPrOH)_2]$ that was obtained according to ref. 5. Modification of precursors was performed with commercial grade acetylacetone. All structures presented in this communication were obtained using zirconium isopropoxide as starting reagent. The proton NMR data, however, clearly indicate that the more reactive *n*-propoxide and mixed-ligand precursors are modified by acetylacetone in an analogous manner. In order to obtain crystals of the 1 : 1 Hacac modified zirconium precursor, the zirconium isopropoxide was dissolved in a mixture of hexane and toluene (in a volume ratio of 2 : 1). After addition of an equivalent amount of acetylacetone the sample was dried and, subsequently, re-dissolved in hexane. Crystallization occurred during cooling at −30 °C overnight; a single crystal was mounted in inert oil and transferred to the diffractometer. The structure was characterized as $[Zr(O^iPr)_3(acac)]_2$ (**1**),‡ depicted in Fig. 1.

Following an analogous preparation procedure, but adding two mol equivalents of Hacac to zirconium isopropoxide, crystals of a new unexpected compound $Zr(O^iPr)(acac)_3$ (**2**)§ were obtained, depicted in Fig. 2.

The NMR spectra of the dried crystals of **2** are in agreement with the determined structure, *e.g.*, the signal of the C*H* proton of the central carbon in acetylacetone was nicely split in the expected ratio of 2 : 1. In cases where normal or mixed-ligand zirconium propoxide precursors were used, only needle shaped crystals were obtained. XRD and NMR showed these to have the composition $Zr(acac)_4$. The higher precursor reactivity apparently leads to an even less stable tri-substituted precursor structure.

Finally, an attempt to isolate the form with 0.5 mol equivalents of Hacac was made. The preparation was similar to that of the forms with 1 and 2 mol equivalents of Hacac. NMR showed the formation of **1** as shown in Fig. 3, while the isolated crystals were identified by XRD as unmodified precursor. No indication was found that the asymmetric 0.5 equivalent Hacac modified structure, as proposed by Ribot *et al.*,[4] exists.

NMR measurements as a function of time were performed on the mixed-ligand system in order to exclude the existence of other stable forms and to gain information on the stability of the different structures. An experiment was performed by adding 1 mol equivalent of Hacac to the mixed-ligand precursor. The composition of the sample was monitored by NMR as a function of time. Only minor changes occurred after leaving the sample at room temperature (21.4 °C) for several days, indicating that the stability

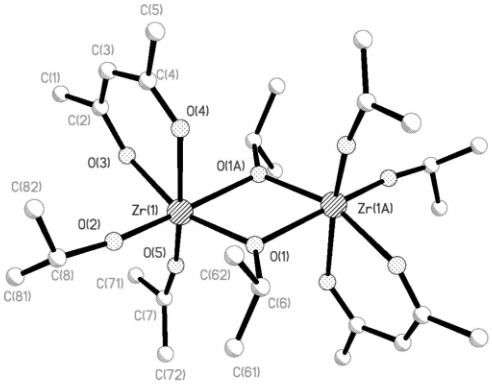

Fig. 1 Molecular structure of $[Zr(O^iPr)_3(acac)]_2$ (**1**).

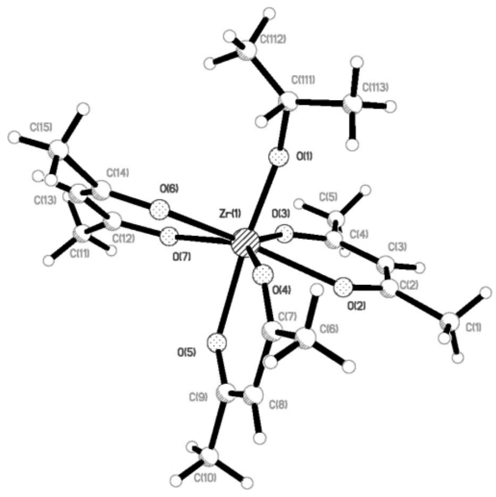

Fig. 2 Molecular structure of $Zr(O^iPr)(acac)_3$ (**2**).

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† Electronic supplementary information (ESI) available: summary of ^1H NMR spectra and CIF files for compounds **1** and **2**. See http://www.rsc.org/suppdata/cc/b4/b406012a/

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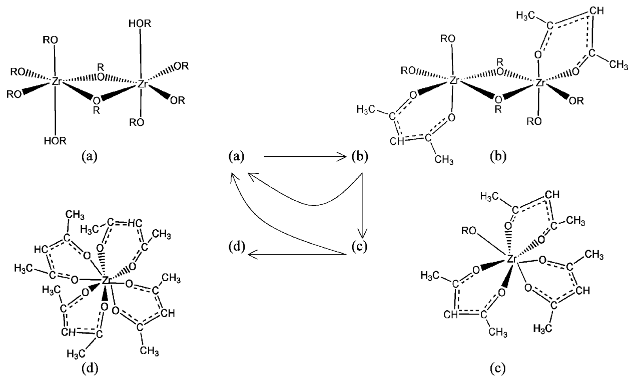

Fig. 3 The proposed mechanism and structures for the stabilization of zirconium propoxide in propanol. Addition of up to 1 mol equivalent of Hacac to the initial precursor (a) leads to (b). Addition of more than 1 mol equivalent leads to a reaction of (b) to (a) and (c). Spontaneous rearrangement of (c) gives (d) and (a). Different reactions are schematically depicted in the center of the figure.

of the mono-substituted structure is fairly high. The addition of excess isopropanol, often facilitating ligand exchange,[6] did not lead to significant structural rearrangements upon monitoring the precursor solution for several days. The stabilization of zirconium and hafnium isopropoxides with 1 eq. of a bulky β-diketonate 2,2,6,6,-tetramethylheptanedione giving structural analogs of compound **1** for MOCVD applications has been reported earlier,[7] but **1** remains so far the first structurally characterized and relatively stable intermediate in sol–gel applications.

After the addition of 2 mol equivalents of Hacac to the mixed-ligand precursor solution, the initial NMR spectra showed multiple peaks at around 5.5 ppm, 10 minutes after the sample was prepared. Distinguishing different structures on the basis of these peaks is rather complicated, since peaks of the mono- and tetra-substituted structures partly or completely overlap with one of the peaks of the tri-substituted derivatives. However, the largest signal was assigned to Zr(acac)$_4$, since only this peak remained after 16 hours. The two minor peaks were attributed to the intermediate tri-substituted structure. The presence and disappearance after 16 hours of peaks assigned to normal and isopropoxide CH_3 groups lend support to the conclusion that the tri-substituted precursor is formed initially in this system. After 16 hours the spectra had also changed with respect to the position of the peaks corresponding to the bridging groups.

The rearrangement from tri- to tetra-substituted structures was also observed on the dried Zr(O^{i}Pr)(acac)$_3$ crystals. After 15 days of storage at room temperature, the NMR data showed that the majority of the sample had transformed to Zr(acac)$_4$.

Recapitulating, upon addition of 2 mol equivalents of Hacac the tri- and tetra-substituted species are formed. The tri-substituted form rearranges in time to the tetra-substituted one and to free alkoxide. No indications were found for the existence of a di-substituted species.

It emerges that the nature of the heteroleptic intermediates on different zirconium propoxides characterized in this study is not in agreement with the proposed mechanism and structures of intermediates for the corresponding cerium system.[4] Upon addition of up to 1 mol equivalent of Hacac, the fairly stable [Zr(O^{i}Pr)$_3$(acac)]$_2$ is formed. When an additional Hacac is added, the [Zr(O^{i}Pr)$_3$(acac)]$_2$ structure is supposedly destabilized leading to the presence of the initial precursor and unstable Zr(O^{i}Pr)(acac)$_3$. Spontaneous rearrangement of Zr(O^{i}Pr)(acac)$_3$ to stable Zr(acac)$_4$ occurs at room temperature. The proposed stabilization and destabilization mechanism together with the accompanying structures of the intermediates are schematically depicted in Fig. 3.

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Notes and references

‡ Crystal data: $C_{28}H_{56}O_{10}Zr_2$, M = 735.17, triclinic, a = 10.004(16), b = 10.696(14), c = 12.27(2) Å, α = 87.74(4)°, β = 67.16(3)°, γ = 64.75(5)°, V = 1081(3) Å^3, T = 295 K, space group $P\bar{1}$, Z = 1, μ = 0.520 mm^{-1}, 5582 reflections measured, 4123 unique (R_{int} = 0.0222 which were used in all calculations. The final discrepancy factors were $R1$ = 0.0469; $wR2$ = 0.1018 for 2261 observed reflections ($I > 2\sigma(I)$).

§ Crystal data: $C_{18}H_{28}O_7Zr$, M = 447.62, orthorhombic, a = 8.5444(17), b = 30.933(6), c = 8.2339(16) Å, V = 2176.3(7) Å^3, T = 295 K, space group $Pna2(1)$, Z = 4, μ = 0.537 mm^{-1}, 8461 reflections measured, 3517 unique (R_{int} = 0.0792) which were used in all calculations. The final discrepancy factors were $R1$ = 0.0681; $wR2$ = 0.1609 for 2279 observed reflections ($I > 2\sigma(I)$).

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