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Volatile Zirconium Bis(acetylacetonato)bis(alcoholato) Complexes Containing Heterosubstituted Alcoholato Ligands

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Two new heteroleptic compounds $Zr(acac)_2(OR)_2$, R = $SiMe_3$ and $CH(CF_3)_2$, have been synthesized by high-yield synthetic routes. $Zr(acac)_2(OSiMe_3)_2$, **1**, is formed by a salt elimination reaction between $Zr(acac)_2Cl_2$ and lithium trimethylsilanolate in pentane, while $Zr(acac)_2(hfip)_2$, **2**, hfip = $OCH(CF_3)_2$, has been prepared from $Zr(acac)_2Cl_2$ and a mixture of 2 equiv each of 1,1,1,3,3,3-hexafluoroisopropanol and diethylamine in pentane. The reactions are very selective; the formation of products with other than the 2:2 stoichiometry was not observed under the conditions applied. Both the liquid **2** and the low-melting solid **1** are monomeric and distillable or sublimable in a vacuum. A measured dipole moment of 3.94 D together with spectroscopic data of **1** confirms a cis-octahedral structure, with the metal in a six-coordinated environment. Both substances show an improved hydrolysis stability over homoleptic tetraalcoholates such as Zr(O-*t*-Bu)$_4$, while being much more volatile than β-diketonates such as $Zr(thd)_4$ or $Zr(hfac)_4$. According to preliminary experiments, $Zr(acac)_2(hfip)_2$ is a promising precursor for metal−organic chemical vapor deposition (MOCVD) of zirconia thin films.

Introduction

In the design of precursors for metal−organic chemical vapor deposition (MOCVD), one often has to deal with two major problems limiting the usefulness of a compound: a lack of either volatility or chemical stability.

A good example to illustrate this dilemma is the situation in zirconia CVD. Zirconia, ZrO_2, is a very important material for a number of modern thin-film devices. Examples include oxygen-conductive membranes for use in fuel cells[1−3] and oxygen sensors,[4−6] high-temperature thermal barrier coatings,[7−9] hard protective layers,[10,11] ferroelectrics,[12,13] optical coatings,[14] and more. For most applications, the yttrium-stabilized tetragonal and cubic phases are used due to their superior mechanical properties.

Today, zirconia MOCVD is commonly carried out using β-diketonato derivatives such as tetrakis(tetramethylheptanedionato)zirconium, $Zr(thd)_4$. These homoleptic acetylacetonates are fairly air-stable due to their high coordinative saturation, but have to be heated to quite high temperatures (130−190 °C) in order to achieve a vapor pressure sufficient for CVD.[15−17] Furthermore, a significant carbon incorporation into layers grown from these precursors has been observed in a number of cases, which appears to be an inherent problem according to thermodynamic calculations.[18]

On the other hand, some homoleptic fluoroalcoholato complexes[19−21] and especially the liquid compound tetrakis(*tert*-butanolato)zirconium[22,23] show an excellent volatility. Their main drawback is an extreme hydrolysis sensitivity, which renders handling and long-term storage problematic.[22,24] Consequently, there is ongoing research for alternatives to these two precursor families.

Ideally, one would like to combine the desirable properties of the two ligand types, alcoholato and acetylacetonato, in one molecule. This contribution deals with the synthetic access to two heteroleptic compounds of the 2:2 stoichiometric combination, $Zr(acac)_2(OR)_2$, and their characterization.

Experimental Section

General Procedures. All compounds were handled under a dry nitrogen atmosphere by means of the Schlenk technique. Glassware

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was heated in a vacuum before use. Solvents, including deuterated solvents, were freshly distilled from $LiAlH_4$ (ethers) or CaH_2 (hydrocarbons).

All chemicals except $ZrCl_4$ (99.9%, Aldrich Chemicals) were obtained from Fluka Chemicals, Switzerland, and dried and distilled before use where necessary. Lithium trimethylsilanolate was used as received. Bis(acetylacetonato)dichlorozirconium was freshly prepared from $ZrCl_4$ and acetylacetone.[25,26] Recrystallization was found to be unnecessary if the reflux time was shortened from 12 to 4 h.

Analysis. Microelementary data were obtained at the Laboratory for Organic Chemistry, ETH Zürich, on LECO CHN-900 (C, H) and LECO RO-478 (O) instruments. Zirconium was quantified using ICP-AES (Zeiss, PlasmaQuant 110); sample solutions were prepared by careful hydrolysis with diluted p.a. hydrochloric acid. Melting points were determined in closed capillaries and are uncorrected. Molecular mass was measured in dichloromethane using vapor pressure osmometry. NMR spectra were recorded on Bruker DRX 400 [compound **1**, 400.13 (^{1}H) and 100.62 (^{13}C) MHz] and AC 200 instruments [compound **2**, 200.13 (^{1}H), 188.31 (^{19}F), and 50.32 (^{13}C) MHz], IR spectra (2 cm^{-1} resolution) were recorded on a Nicolet Magna 550 FTIR spectrometer, and MS data (EI+) were collected on a VG Tribrid instrument at 70 eV ionization energy.

Bis(acetylacetonato)bis(trimethylsilanolato)zirconium, 1. $Zr(acac)_2Cl_2$ (8.42 g, 23.37 mmol) is suspended in 100 mL of pentane at room temperature and magnetically stirred. Two equivalents of lithium trimethylsilanolate (4.49 g, 46.73 mmol) in 125 mL of pentane are added by means of a dropping funnel over a period of 2 h. Lithium chloride precipitation is observed, and the color of the solution changes to pale yellow. The reaction mixture is kept stirring overnight, and then the LiCl is filtered off. The precipitate is washed with a total of 60 mL of pentane, the filtrates are combined, and the solvent is removed in vacuo. The residue is a pale yellow viscous oil, 9.25 g (19.77 mmol) corresponding to 84.6% yield of crude product. Upon storage at −25 °C for 2 days, the product crystallizes. Sublimation from the melt at 75 °C/10^{-2} mbar (coldfinger temperature: −20 °C) yields a colorless solid, 6.83 g, 17.25 mmol, 73.8% yield. Mp: 28 °C.

Elemental anal. $C_{16}H_{32}O_6Si_2Zr$: $M = 467.82$ g/mol (found in CH_2Cl_2: $M = 446.7 \pm 25.6$ g/mol). Calcd: C, 41.08; H, 6.89; Zr, 19.5. Found: C, 41.17; H, 6.89; Zr, 19.1 (O interferes with Si).

^{1}H NMR (C_6D_6): 5.20 (s, $\mathrm{C}H$, 2 H), 1.59 (s, $\mathrm{C}H_3$, 12 H), 0.30 (s, $\mathrm{Si}(\mathrm{C}H_3)_3$, 18 H). ^{13}C{^{1}H} NMR (C_6D_6): 191.4 ($C\mathrm{O}$), 103.9 ($C\mathrm{H}$), 26.3 ($C\mathrm{H}_3$), 2.4 ($\mathrm{Si}(C\mathrm{H}_3)_3$).

IR, $\tilde{\nu}$ in pentane and C_6D_6: *2956* s $\nu_{as}(CH_3)$ [silyl], *2925* w $\nu(CH_3)$ [acac], *2897* w $\nu_s(CH_3)$ [silyl], 1612 and 1589 vs $\nu_s(C{=}O)$, 1527 vs $\nu_{as}(C{=}C)$, *1432* m $\delta_{as}(CH_3)$ [acac and silyl], *1375* vs $\delta_s(CH_3)$, $\nu_{as}(C{=}O)$ [acac], 1277 m $\delta_s(CH_3{-}(Si))$, 1263 vw unassigned, 1246 m $\delta_s(CH_3)$ [silyl], 1189 vw unassigned, 1025 m $\nu_{as}(Si{-}O)$?, 986 s $\nu_{as}(Si{-}O)$, 931 and 921 $\nu_s(Si{-}O)$, 839 s $\rho_{as}(CH_3({-}Si))$, 777 and 751 m $\rho_s(CH_3({-}Si))$, 683 vw $\nu_{as}(SiC_3)$, 662 w $\nu_s(SiC_3)$, 538 w ring def, 438 m $\nu_{as}(Zr{-}O(acac))$, 405 vw $\delta_{oop}(C{-}H)$ [acac].

MS (EI+, 70 eV): 451 ($M^+ - CH_3$, 100), 377 ($M^+ - OSiMe_3$, 10), 367 (M^+ − acac, 7), 353 ($[Zr(acac)(OSiMe_3)(OSiMe_2H)]^+$, 15), 279 ($[ZrMe(acac)(OSiMe_2H)]^+$, 24), 255 ($[ZrMe(OSiMe_2H)_2]^+$, 33), 218 ($M^{2+} - 2\ CH_3$, 38), 199 ($[ZrMe(OSiH_3)_2]^+$, 13), 181 ($[ZrMe_2(OSiMeH_2)]^+$, 11), 169 $[Zr(acac)(OSiMe_3)(OSiMe)]^{2+}$, 11), 75 ($SiMe_2OH^+$, 85), 73 ($SiMe_3^+$, 21), 45 ($SiOH^+$, 12), 43 ($SiMe^+$ or $[C_2H_3O]^+$, 26).

All dipole moment measurements were done at 298 K in dry benzene. Measurements of solution dielectric constants were performed on a WTW DK-06 Multidekameter calibrated with *n*-hexane, cyclohexane, benzene, and di(*n*-butyl) ether. Densities were determined on a PAAR DMA-48 digital densitometer, and refractive indices were collected using a ZEISS Abbe-type refractometer. The results for **1** are as follows. (a) Guggenheim−Smith method: $P_O = 317.4 \pm 6.8$ $cm^3\ mol^{-1}$, $\mu = 3.94 \pm 0.03$ D. (b) Halverstadt−Kumler method: $\alpha = 4.41 \pm 0.07$, $\beta = -0.273 \pm 0.02$, $\gamma = 7.01 \times 10^{-3} \pm 0.18 \times 10^{-3}$; $P_T = 510.5 \pm 11.6$ $cm^3\ mol^{-1}$, $P_D = 121.3 \pm 0.3$ $cm^3\ mol^{-1}$; atomic polarization neglected, $P_O = 389.2 \pm 11.6$ $cm^3\ mol^{-1}$, $\mu = 4.36 \pm 0.06$ D; atomic polarization $P_A = 60.7$ $cm^3\ mol^{-1}$, $P_O = 328.5 \pm 11.6$ $cm^3\ mol^{-1}$, $\mu = 4.01 \pm 0.07$ D.

Bis(acetylacetonato)bis(1,1,1,3,3,3-hexafluoroisopropanolato)zirconium, 2. A mixture of 4.2 mL (6.80 g, 40.49 mmol) of 1,1,1,3,3,3-hexafluoroisopropanol and 2.80 g (40.49 mmol) of diethylamine in 70 mL of pentane is added dropwise to a stirred suspension of 6.65 g (18.45 mmol) of $Zr(acac)_2Cl_2$ in 100 mL of pentane over a period of $2^1/_2$ h. The suspension soon transforms to a thick slurry, but becomes well stirrable again toward the end of the addition. The reaction mixture is kept stirring overnight and is subsequently filtered, and the $[NH_2Et_2]Cl$ precipitate is washed with 30 mL of pentane. Removal of solvent from the combined filtrates at room temperature leaves the crude product, which is purified by distillation at an 80 °C bath temperature/10^{-3} mbar (coldfinger at −15 °C). Pure $Zr(acac)_2[OCH(CF_3)_2]_2$ is obtained as a pale yellow, viscous liquid in a 10.39 g (90.3%) yield.

Elemental anal. $C_{16}H_{16}O_6F_{12}Zr$: $M = 623.50$ g/mol (found in CH_2Cl_2: $M = 637.3 \pm 19.5$ g/mol). Calcd: C, 30.82; H, 2.59; O, 15.40; Zr, 14.6. Found: C, 30.88; H, 2.71; O, 15.26; Zr, 14.6.

^{1}H NMR (C_6D_6): 5.27 (s, $\mathrm{C}H(COCH_3)_2$, 2 H), 4.71 (sept, $\mathrm{OC}H(CF_3)_2$, $^3J_{HF} = 6.20$ Hz, 2 H), 1.61 (s, $\mathrm{C}H_3$, 12 H). ^{13}C{^{1}H} NMR (C_6D_6): 192.5 (s, $C\mathrm{O}$), 122.6 (q, $C\mathrm{F}_3$, $^1J_{CF} = 285.5$ Hz), 104.7 (s, $C\mathrm{H}$ (acac)), 75.8 (sept, $C\mathrm{H}(CF_3)_2$, $^2J_{CF} = 32.9$ Hz), 25.5 (s, $C\mathrm{H}_3$). ^{19}F{^{1}H} NMR (C_6D_6): −76.5 (s, $\mathrm{C}F_3$).

MS (EI+, 70 eV): 622 (M^+, 1), 607 ($M^+ - CH_3$, 0.6), 554 ($[acac_3Zr(hfip)]^+$, 1), 523 (M^+ − acac, 0.3), 475 ($[acac_2Zr(hfip)HF]^+$, 3), 455 (M^+ − hfip, 56), 387 ($[acac_3Zr]^+$, 2), 378 (unassigned, 8), 307 ($[acac_2ZrF]^+$, 100), 227 ($[acacZrF_2]^+$, 60), 209 ($[acacZrHF]^+$, 3), 187 (unassigned, 2), 146 (unassigned, 5), 99 ($acac^+$ or $[CF_3CH{=}OH]^+$, 2), 43 ($[C_2H_3O]^+$, 3).

IR, $\tilde{\nu}$ in pentane (assignments based on IR/Raman studies of $M(acac)_nX_{4-n}$, X = Cl, Br; $n = 2, 3, 4$; M = Zr, Hf,[27] $Zr(acac)_2(O\text{-}i\text{-}Pr)_2$,[28] and $(CF_3)_2CHOH$[29]): 1602 and 1581 s $\nu_s(C{=}O)$, 1559 m (unassigned acac), 1532 vs $\nu_{as}(C{=}C)$, 1435 m, br $\delta_{as}(CH_3)$, 1370 vs $\delta_{as}(CH)$ [hfip], 1299 s $\nu_{as}(CF_3)$, 1284 m $\delta_s(CH)$ (hfip) and $\nu_s(C{=}C)$, 1264 m $\delta_s(CH)$ (hfip), 1227 and 1217 vs $\nu_{as}(CF_3)$, 1191 and 1184 vs $\nu_s(CF_3)$ and $\delta(C{-}H)$ [acac], 1106 s $\nu_s(CF_3)$, 1029 m $\rho(CH_3)$, 933 w $\nu(C{-}C(H_3))$, 892 m $\nu_{as}(C{-}C{-}C)$ (hfip), 848 m $\nu(CO)$ [hfip], 784 w $\delta(CH)$ (765), 753 w, sh and 749 m $\nu_s(C{-}C{-}C)$ (hfip), 688 s $\delta_{as}(CF_3)$, 665 w $\delta(C{-}CH_3)$ or δ(ring), 540, 531, 519 w $\delta_s(CF_3)$, 447 m, sh and 440 m $\nu(Zr{-}O[acac])$, 409 w $\delta_{oop}(C{-}H)$ [acac].

Bis(acetylacetonato)bis(*tert*-butanolato)zirconium. This compound was prepared from $Zr(acac)_2Cl_2$ and a mixture of *tert*-butanol and diethylamine following the procedure given in ref 30 except that we used pentane instead of toluene as the solvent. After distillation at a 90−95 °C bath temperature and 10^{-3} mbar, a pale yellow viscous liquid was obtained which tends to darken upon storage at ambient temperature. Purity was checked by NMR spectroscopy. Yield: 84.4% (lit.[30] 95%).

^{1}H NMR (C_6D_6): 5.27 (s, $\mathrm{C}H$, 2 H), 1.67 (s, $\mathrm{C}H_3$, 12 H), 1.40 (s, $\mathrm{C}(\mathrm{C}H_3)_3$, 18 H). ^{13}C{^{1}H} NMR (C_6D_6): 190.8 ($C\mathrm{O}$), 103.2 ($C\mathrm{H}$), 75.7 ($C(\mathrm{CH}_3)_3$), 32.5 ($\mathrm{C}(C\mathrm{H}_3)_3$), 26.6 ($C\mathrm{H}_3$).

Results and Discussion

Existing Synthesis Routes. Defined zirconium mixed acetylacetonato−alcoholato coordination compounds were first described in 1970 independently by Mehrotra et al.[21] and Puri.[31] Both groups reacted $Zr(O\text{-}i\text{-}Pr)_4{\cdot}i\text{-}PrOH$ with the desired stoichiometric amount of acetylacetone in refluxing benzene to obtain a range of isomers $Zr(acac)_x(O\text{-}i\text{-}Pr)_{4-x}$, $x = 1{-}3$, with different degrees of isopropanolato substitution. By subsequent reaction of $Zr(acac)_x(O\text{-}i\text{-}Pr)_{4-x}$ with *tert*-butanol, Mehrotra et

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al. were also able to obtain the *tert*-butanolato derivatives:

$$\mathrm{Zr(O\text{-}\mathit{i}\text{-}Pr)_4{\cdot}\mathit{i}\text{-}PrOH} \xrightarrow[n\,=\,1-3]{n\ \mathrm{Hacac}} \mathrm{Zr(acac)_{\mathit{n}}(O\text{-}\mathit{i}\text{-}Pr)_{4-\mathit{n}}} + n\ \mathit{i}\text{-}\mathrm{PrOH} \quad (1)$$

$$\mathrm{Zr(acac)_{\mathit{n}}(O\text{-}\mathit{i}\text{-}Pr)_{4-\mathit{n}}} \xrightarrow{\mathit{t}\text{-}\mathrm{BuOH}} \mathrm{Zr(acac)_{\mathit{n}}(O\text{-}\mathit{t}\text{-}Bu)_{4-\mathit{n}}} + (4\text{-}n)\ \mathit{i}\text{-}\mathrm{PrOH} \quad (2)$$

Both $Zr(acac)_2(O\text{-}t\text{-}Bu)_2$ and $Zr(acac)_2(O\text{-}i\text{-}Pr)_2$ are stable liquids and distillable at 130 °C at 0.5 mbar.[28,31] Out of the range of isomers, these properties favor the 2:2 compounds $Zr(acac)_2(OR)_2$ over the less volatile solids $Zr(acac)_3(OR)$ as candidates for zirconia MOCVD. The same synthetic approach, alcohol exchange in $Zr(acac)_2(O\text{-}i\text{-}Pr)_2$, was used for the synthesis of the alkoxysilanolato derivative $Zr(acac)_2[OSi(O\text{-}t\text{-}Bu)_3]_2$.[32] In contrast to its predecessors, this compound turned out to be a comparatively unvolatile (bp 210 °C/1 Torr) solid, probably due to its high molecular weight.

These early syntheses rely on Bradley's three-step access to zirconium isopropoxide originating from the early 1950s:[33]

$$\mathrm{ZrCl_4} \xrightarrow[\mathrm{NH_3}]{\mathrm{EtOH}} \mathrm{Zr(OEt)_4{\cdot}EtOH} \xrightarrow{\mathit{i}\text{-}\mathrm{PrOH}} \mathrm{Zr(O\text{-}\mathit{i}\text{-}Pr)_4{\cdot}\mathit{i}\text{-}PrOH} \quad (3)$$

Since that time, a direct route to $Zr(O\text{-}i\text{-}Pr)_4{\cdot}i\text{-}PrOH$ has been found.[24] Nonetheless, it is preferable to avoid having to use this extremely moisture- and oxygen-sensitive[22,24] tetraalcoholate as a synthetic intermediate.

Due to their very similar solubility (and often distillation) properties, isomeric mixtures of $Zr(acac)_x(OR)_{4-x}$ are difficult to separate. Since the formation of byproducts, especially $Zr(acac)_4$, has frequently been observed,[30] the above-described synthetic approach cannot be considered sufficiently selective. Furthermore, it does not provide access to a broader range of alcoholates.

A more recent procedure[34] uses the reaction of $Zr(acac)_4$ with 2 equiv of NaOMe in cyclohexane in the presence of a large excess of methanol as an additive. $Zr(acac)_2(OMe)_2$ is selectively obtained in over 80% yield, but with the exception of $Zr(acac)_2(O\text{-}i\text{-}Pr)_2$, this direct procedure does not work for different alcohols. Derivatives of these could, however, be obtained in high (66−97%) yields by exchanging the methanolato group in $Zr(acac)_2(OMe)_2$ for a number of C_3 (OPr, O-*i*-Pr) and C_4 (OBu, O-*i*-Bu, O-*t*-Bu) alcoholato ligands in benzene or cyclohexane at room temperature.[34]

The fastest and most general access to $Zr(acac)_2(OR)_2$ so far has been developed by Hüsges and Kruck.[30] These authors predetermined the desired stoichiometry using the synthetical intermediate $Zr(acac)_2Cl_2$, in which the chlorine atoms are then replaced by a range of branched aliphatic alcohols such as isopropanol, *tert*-butanol, or neopentanol. Whereas this procedure proved very reliable in the synthesis of $Zr(acac)_2(OR)_2$, only the two solids $Zr(thd)_2(O\text{-}t\text{-}Bu)_2$ and $Zr(thd)_2(O\text{-}neopent)_2$, thd = 2,2,6,6-tetramethylheptane-3,5-dione, could be obtained free of the dismutation product $Zr(thd)_4$.[30]

In view of the previous synthetic work, we aimed at extending the use of $Zr(acac)_2Cl_2$ to generate $Zr(acac)_2(OR)_2$ derivatives containing heterosubstituted alcoholato groups, whose successful synthesis had not previously been reported. Introducing fluorine atoms (dipole repulsive forces) and silyl groups (lowering the polarity) into ligands has generally proven a successful strategy for raising the volatility of organometallic and coordination compounds.[19] The positive influence on volatility and dismutation stability reported for bulky alcoholato ligands[34,35] suggests using heterosubstituted alcoholates containing α-branched backbones. Therefore, we have chosen to study the impact of the hfip (1,1,1,3,3,3-hexafluoroisopropanolato) and trimethylsilanolato ligands on volatility and chemical stability of $Zr(acac)_2(OR)_2$.

New Synthetic Pathways. The starting point of the synthetic approach reported hereupon is dichlorobis(acetylacetonato)zirconium, $Zr(acac)_2Cl_2$. This stable compound is conveniently and selectively prepared by reaction of zirconium(IV) chloride with an excess of acetylacetone in refluxing ether.[25,26] There are at least two possible ways to replace the chlorine atoms in $Zr(acac)_2Cl_2$ by OR ligands in the following step: first, reaction with equimolar amounts each of the appropriate alcohol and diethylamine,[30] and second, reaction with an alkaline metal alcoholate, which has not previously been reported.

Bis(acetylacetonato)bis(trimethylsilanolato)zirconium. For the synthesis of the silylated derivative $Zr(acac)_2(OSiMe_3)_2$, it is more convenient to start from the commercially available lithium trimethylsilanolate than from the unstable[36] trimethylsilanol. Upon dropwise addition of lithium trimethylsilanolate to a finely dispersed suspension of bis(acetylacetonato)dichlorozirconium in pentane at room temperature, LiCl elimination takes place and bis(acetylacetonato)bis(trimethylsilanolato)zirconium is formed:

$$\mathrm{Zr(acac)_2Cl_2} + 2\mathrm{LiOSiMe_3} \xrightarrow{\mathrm{pentane}} \mathrm{Zr(acac)_2(OSiMe_3)_2} + 2\mathrm{LiCl} \quad (4)$$

The raw product left after filtration of the reaction mixture and evaporation to dryness is then purified by vacuum sublimation from the melt. The colorless solid thus obtained was identified by spectroscopy and elemental analysis as $Zr(acac)_2(OSiMe_3)_2$. The 75% yield of pure product already successfully demonstrates the potential of this new, two-step synthetic route.

The substance appears to exhibit an unlimited solubility in virtually any hydrocarbon solvent, indicating a very low polarity. Despite a certain hydrolysis sensitivity, it may be handled in air for short periods of time without notable decomposition. By molecular weight determination, **1** was found be monomeric in solution, like $Zr(acac)_2(O\text{-}t\text{-}Bu)_2$ and $Zr(acac)_2(O\text{-}i\text{-}Pr)_2$.[28,31] The situation is different among the 4-coordinated homoleptic alcoholates, all of which have been shown to form dimers or even trimers in solution,[20−22] except for the monomeric $Zr(O\text{-}t\text{-}Bu)_4$. This decreases their vapor pressure significantly.

According to preliminary vapor pressure measurements, bis(acetylacetonato)bis(trimethylsilanolato)zirconium reaches a vapor pressure of 10^{-2} mbar already at 70 °C. This value places the compound between the homoleptic zirconium-β-diketonates and tetrakis(*tert*-butanolato)zirconium, respectively. This observation is not unexpected, taking into account that the medium coordination number of 6 results in a fairly effective shielding of the strongly polarized M−O bonds, while keeping the number of acac ligands and thus the molecular weight low. As has been shown,[19,22,35] this shielding is particularly important for the volatility of alcoholato-containing compounds.

Both the acetylacetone and trimethylsilanol[36] NMR signals of **1** undergo a slight low-field shift upon coordination. Besides

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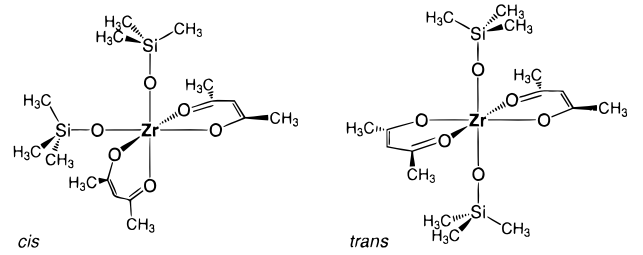

Figure 1. Possible isomeric structures of $Zr(acac)_2(OSiMe_3)_2$.

this general effect, it is interesting to take a closer look at the acetylacetone C$-$H signal. Compared to a number of neutral, nonpolar acetylacetonates $M(acac)_n$[37], a significant deshielding of this resonance on the order of 0.20 ppm is observed. The same effect has been reported for a broad range of structurally related compounds $M(acac)_2X_2$, (M = Sn, Ti, Zr, Hf; X = Hal) and attributed to a molecular dipole electric field effect.[37] To explain the occurrence of such a dipole, it has to be pointed out that, within the six-coordinated octahedral structure of **1**, two stereoisomers may be present, as shown in Figure 1.

The existence of a field effect suggests that the complex preferentially adopts the cis configuration, since the trans isomer has no permanent dipole moment and thus the resulting electric field vanishes. Experiments to determine the constitution of bis(acetylacetonato)bis(trimethylsilanolato)zirconium are described in the stereochemistry section below.

While the molecular peak could not be detected, the intense $M^+ - CH_3$ peak at m/z 451 dominates the mass spectrum of $Zr(acac)_2(OSiMe_3)_2$, even at 70 eV ionization energy. Except for the high-mass signals $M^+ - OSiMe_3$ and $M^+ -$ acac, most of the peaks are attributable to rearranged fragments containing Si$-$H bonds. Both rearrangement processes and the lacking of M^+ are commonly observed even for stable organic silyl compounds such as silyl ethers.[38] A further characteristic feature is the appearance of two intense double-ionized peaks at m/z 218 ($M^{2+} - 2CH_3$) and m/z 169 ($(Zr(acac)(OSiMe_3)(OSiMe)^{2+})$), easily identified by their compressed isotope pattern.

The IR spectrum of $Zr(acac)_2(OSiMe_3)_2$ in pentane and C_6D_6 shows the characteristic vibrations of both ligands, the sharp and intense trimethylsiloxy bands[39,40] as well as the strong acac C=O and C=C modes.[28] The two symmetrical acac C$-$O stretching bands at 1589 and 1612 cm^{-1} appear at the borderline of the ketonic binding regime (1600$-$1750 cm^{-1}). This situation may be interpreted in terms of a slightly asymmetric binding of the acac ligand. From the metal$-$ligand stretching vibrations, only M$-$O(acac) at 438 cm^{-1} could be detected within the investigated wavenumber range. Its position compares well with ν_{as}(Zr$-$O) in $Zr(acac)_4$, which is found at 421 cm^{-1}, as well as with a number of similar compounds.[27,28,30] By comparison with alcoholato-free related compounds such as $Zr(acac)_2Cl_2$,[27] the other low-frequency vibration at 405 cm^{-1} could be assigned to the acac ring C$-$H out-of-plane deformation mode.

Bis(acetylacetonato)bis(1,1,1,3,3,3-hexafluoroisopropanolato)zirconium. Besides silylation, replacement of aliphatic alcohols with their partially or even entirely fluorinated counterparts has also proven to be a very effective means of promoting the volatility of alcoholato complexes. Two related cases to illustrate this effect are the pairs $Zr(O\text{-}i\text{-}Pr)_4$ (bp 110 °C/10^{-4} mbar)/$Zr(hfip)_4$ (bp 110 °C/1 mbar)[20,22] and $Zr(OEt)_4$ (120 °C/10^{-4} mbar) and its perfluoro counterpart $Zr(OCH_2CF_3)_4$ (146 °C/1 mbar).[21,22]

The fluoro alcoholato compound $Zr(acac)_2(hfip)_2$ was therefore expected to show a similarly improved evaporation behavior as compared to the unsubstituted isopropanolato derivative. The substance could successfully be synthesized by carefully adding a mixture of 1,1,1,3,3,3-hexafluoroisopropanol and diethylamine to a suspension of bis(acetylacetonato)dichlorozirconium in pentane at room temperature:

$$Zr(acac)_2Cl_2 + 2(CF_3)_2CHOH + 2NHEt_2 \xrightarrow{\text{pentane}} Zr(acac)_2[OCH(CF_3)_2]_2 + 2[NH_2Et_2]Cl \quad (5)$$

Pentane instead of toluene was chosen as solvent because of its facile and more complete removal from the reaction mixture. In the case of $Zr(acac)_2(O\text{-}t\text{-}Bu)_2$, we obtained about the same reaction yield as in the literature[30] using this modified procedure. To capture the HCl, diethylamine is preferred over ammonia since its dosing may be more precisely controlled in solution. Care has to be taken to premix the amine and the strongly acidic[41] alcohol under controlled conditions, since exothermic formation of an adduct occurs. The association enthalpy of a related system, hexafluoroisopropanol and triethylamine, has been determined to lie between 37 and 65 kJ mol^{-1}, depending on the solvent.[42]

Pure bis(acetylacetonato)bis(hexafluoroisopropanolato)zirconium was obtained after short-path vacuum distillation as a slightly yellow, monomeric liquid in an excellent yield of more than 90% on the 10 g scale. The observed distillation temperature of 80 °C at 10^{-3} mbar is slightly higher than that of **1**. In comparison, tetramethylheptanedionato derivatives such as $Zr(thd)_2(O\text{-}t\text{-}Bu)_2$ and $Zr(thd)_2(O\text{-}i\text{-}Pr)_2$ appear to be only slightly more volatile than $Zr(thd)_4$.[30,43] This is probably due to the doubled molecular weight contribution of the tetramethylheptanedionato compared to the acetylacetonato ligand.

Upon contact with air, $Zr(acac)_2(hfip)_2$ hydrolyzes more rapidly than $Zr(acac)_2(OSiMe_3)_2$, forming large colorless needlelike crystals. Both substances, however, are by far more stable toward hydrolysis than $Zr(O\text{-}t\text{-}Bu)_4$. In neither of the ^1H NMR spectra of the two substances was the free alcohol OH signal ever observed, and the elemental analysis results agreed very well with the calculated values.

The NMR spectra of **2** show the expected coordination deshielding of both ligands. This effect is especially pronounced for the hfip CH septet ($\Delta\delta = 1.26$ ppm), but not for the trifluoromethyl ^{19}F resonance, which basically appears at the same chemical shift as in free hexafluoroisopropanol. The same trend is observed for the corresponding ^{13}C nuclei.

Surprisingly, the two strongest MS peaks (m/z 307, $[acac_2ZrF]^+$, and 227, $[acacZrF_2]^+$) are related to Zr$-$F-containing rearrangement ions. In contrast, the mass spectra of $Zr(acac)_2(OR)_2$ with conventional alcohols give the fragments $[Zr(acac)_3]^+$ and $[Zr(acac)_2(OR)]^+$ as the most intense signals.[30]

By spectral comparison,[27,28] the vibrational spectrum of $Zr(acac)_2[OCH(CF_3)_2]_2$ in pentane could be completely assigned. For the identification of the six C$-$F vibrations, the spectrum of $(CF_3)_2CHOH$[29] was consulted. As in the case of **1**, the carbonyl stretching modes at 1581/1602 cm^{-1} implicate some

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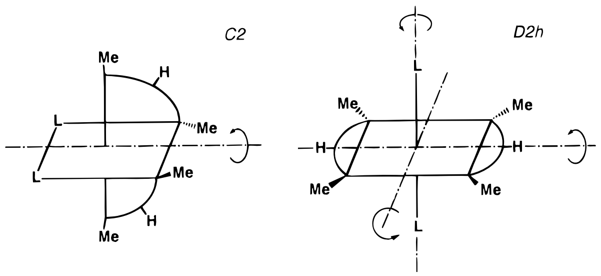

Figure 2. Symmetry of octahedral $Zr(acac)_2L_2$ cis and trans stereoisomers.

asymmetric bonding of the acac ligand. Additionally, splitting of the hfip δ_s(CH) band at 1272 cm^{-1} indicates an asymmetric constitution.

Stereochemistry. Dialkoxobis(acetylacetonato)zirconium compounds have a coordination number of 6 and, in analogy to structurally related compounds $M^{IV}(acac)_2L_2$ (M^{IV} = Ti, Zr, Hf; L = F, Cl, Br; M^{IV} = Ti, L = OR),[27,37,44−46] are expected to have an octahedral structure. In any of these, two stereoisomeric structures are possible, in which the monodentate L ligands (such as halogeno or alkoxide) take cis or trans positions with respect to each other, as shown in Figure 2.

In the absence of any X-ray structural data, stereoisomeric studies have been conducted using vibrational spectroscopy,[27] NMR spectroscopy,[37,44−47] and dipole moment measurements.[37] Without exception, the investigated bis(acetylacetonato)dihalo- and bis(acetylacetonato)bis(alcoholato)titanium complexes as well as bis(acetylacetonato)dichlorozirconium adopt the cis configuration.

Information about the stereochemistry of zirconium bis(acetylacetonato)bis(alcoholato) compounds is currently not available. From basic steric considerations, one intuitively might expect that replacing the chloro ligands in $Zr(acac)_2Cl_2$ by bulky, branched alcoholato groups changes the cis structure into a trans configuration. In contrast, recent molecular mechanics calculations performed by Comba et al.[46] on three similar titanium complexes showed that the cis isomers are sterically less strained.

NMR Studies. Bradley[45] and Fay and co-workers[44] observed a splitting of the acac methyl proton resonance into a doublet at low temperatures for several homologous titanium compounds $Ti(acac)_2(OR)_2$. This was attributed to a cis structure, in which the two methyls have magnetically inequivalent positions as shown in Figure 2. In contrast, low-temperature NMR experiments failed to resolve the magnetically inequivalent acac methyl protons in the case of two zirconium complexes, $Zr(acac)_2(O\text{-}t\text{-}Bu)_2$[30] and $Zr(acac)_2Cl_2$.[26] $Zr(acac)_2Cl_2$, which shows rapid exchange rates at temperatures as low as −130 °C, was later proven to adopt cis symmetry by dipole-moment measurements.[37] In view of these previous results, it was an open question whether the place exchange process could be frozen in any bis(acetylacetonato)bis(alcoholato)zirconium complex. Because of its well-separated acac and trimethylsilanolato methyl group signals, we chose $Zr(acac)_2(OSiMe_3)_2$ for closer investigation.

We collected low-temperature ^1H NMR spectra of **1** in CD_2Cl_2 solution in the 293−173 K range. On the basis of basic symmetry considerations (see Figure 2), a symmetrical splitting of the acac methyl group resonance—but not of the ring proton signal—is expected in the case of a cis complex. In contrast, in an undistorted trans configuration, all acac proton positions should be equivalent. The alcoholato signals, like the acac CH resonance, are expected to remain unaffected in the investigated temperature range.

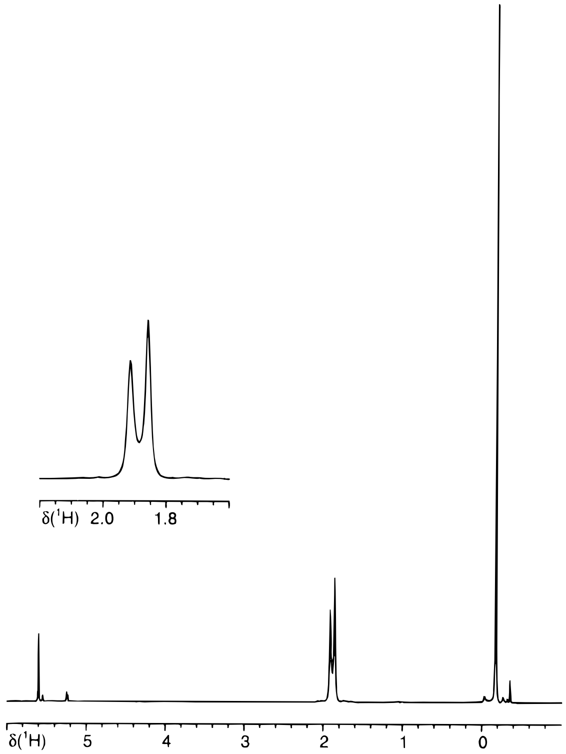

Figure 3. ^1H NMR spectrum of $Zr(acac)_2(OSiMe_3)_2$ in CD_2Cl_2 at 183 K.

When the measurement temperature is decreased, the proton NMR spectrum of $Zr(acac)_2(OSiMe_3)_2$ remains unchanged over a large temperature range. It is not until 203 K that line broadening of the acac methyl signal is observed. At 183 K, finally, the methyl resonance splits up by 22 Hz into a symmetrical doublet centered around 1.89 ppm. As shown in Figure 3, both the Si−CH_3 and the acac ring CH signals remain sharp singlets, which is in complete agreement with a C_2 symmetry, corresponding to the cis isomer.

Further confirmation was obtained from the $^{13}C\{^1H\}$ NMR spectrum at 183 K. A pronounced signal splitting into two equally intense peaks was observed for both the acetylacetone methyl (by 1.15 ppm, 115.9 Hz) and carbonyl (by 5.15 ppm, 518.3 Hz) carbons, whereas, even at that temperature, both the CH and $SiMe_3$ carbon signals did not broaden at all. This is again in excellent agreement with the postulated cis symmetry. Due to the larger signal splitting, low-temperature ^{13}C NMR spectroscopy proved to be a more sensitive probe for this kind of compound than proton NMR. Even at 213 K, a considerable broadening of the acac methyl resonance ($w_{1/2}$ = 55 Hz) could be observed.

The ^1H NMR methyl coalescence temperature, 193 K, is much lower than that observed for a number of homologous titanium derivatives *cis*-$Ti(acac)_2(OR)_2$ as well as *cis*-$Ti(acac)_2Cl_2$, which have coalescence temperatures in the range 251−325 K.[44,45] Obviously, the titanium compounds are stereochemically much more rigid. This might be due to the about 10% larger covalent radius of Zr compared to Ti,[48] which results in less steric interaction of the ligands.

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By using 2-dimensional NMR spectroscopy, the correlation between H and C signals could be made. It was found that both methyl and carbonyl high-field signals correlate with the low-field hydrogen signal, and vice versa.

Molecular mechanics calculations for $Ti(bzac)_2(OEt)_2$ and $Ti(bbac)_2(OEt)_2$[46] have shown that the ethanolato groups in these two titanium complexes take exclusively the cis position to each other, in good agreement with experimental NMR data. It was found that this behavior can satisfactorily be explained by steric effects and that the electronic trans-directing effect may not play a key role in this group of compounds. In the absence of similar supporting calculations, however, it cannot be completely excluded that the occurrence of a singlet at room temperature is due to the occurrence of the trans isomer rather than signal coalescence. However, no indication of any equilibrium mixture of cis and trans isomers was ever observed in the intermediate temperature region, so that a cis–trans equilibrium is considered unlikely.

Dipole Moment Studies. In view of the remarks made above it was decided to investigate the dipole moment of **1** at room temperature. The two isomers should be easily distinguishable, because the permanent dipole moment of an ideal octahedral trans isomer must be 0, whereas, in a cis isomer, a permanent dipole moment should be observable.

The dipole moment is not measured directly but usually is calculated from measurements of the dielectric constant ϵ. The most common way to obtain dielectric constants of nongaseous polar substances is measurement in solution. In this case, the contribution of the nonpolar solvent to ϵ has to be separated out, which is done by measuring solutions of different concentrations.

There are two models currently in use for calculating the solute dipole moment from such dielectric constant measurements, the Halverstadt–Kumler method and the Guggenheim–Smith method.[49] The latter is often preferred because, unlike the Halverstadt–Kumler approach, it takes the atomic polarization contribution into account and does not require precise solution density measurements.[49] For comparison purposes, however, the solution density was also determined and the Halverstadt–Kumler results were calculated in addition.

Both methods rely on Debye's equation (eq 6)[49] to calculate the permanent dipole moment μ from the orientation polarization P_O:

$$\mu = \frac{3}{2}\sqrt{\frac{kT}{\pi N_L}P_O} \tag{6}$$

In the Guggenheim method, P_O is obtained directly as the slope of a linear plot of the term $f(\epsilon,n)$ against the concentration c_2 of the polar solute, as described in eq 7.

$$f(\epsilon, n) \equiv \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} - \frac{{n_{12}}^2 - 1}{{n_{12}}^2 + 2} = P_O c_2 + \text{constant} \tag{7}$$

In Figure 4, the experimental results obtained for benzene solutions of **1** under inert measurement conditions are plotted. As can be seen, we did not find any deviation from the linear concentration dependence within the investigated concentration range, between 0.03 and 0.3 mol/L $Zr(acac)_2(OSiMe_3)_2$. (See also Table 1.)

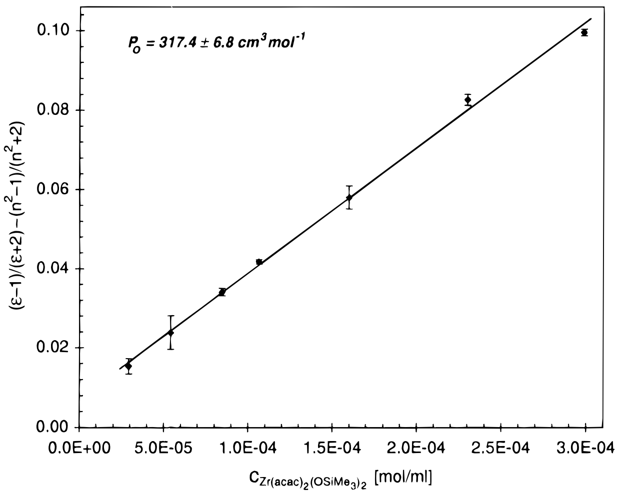

Figure 4. Guggenheim plot of $Zr(acac)_2(OSiMe_3)_2$ (benzene solution, 298 K).

Table 1. Experimental Data of $Zr(acac)_2(OSiMe_3)_2$ Solutions in Benzene at 298 K[a]

c_2 [mol l^{-1}]	ω_2	ρ_{12} [g cm^{-3}]	ϵ_{12}	n_{12}	$\frac{\epsilon_{12}-1}{\epsilon_{12}+2} - \frac{{n_{12}}^2-1}{{n_{12}}^2+2}$
2.915×10^{-2}	0.01555	0.8770	2.340	1.49795	1.534×10^{-2}
5.410×10^{-2}	0.02877	0.8797	2.390	1.49733	2.384×10^{-2}
8.453×10^{-2}	0.04478	0.8831	2.459	1.49810	3.403×10^{-2}
1.064×10^{-1}	0.05619	0.8856	2.510	1.49805	4.173×10^{-2}
1.599×10^{-1}	0.08390	0.8916	2.630	1.49835	5.806×10^{-2}
2.311×10^{-1}	0.11971	0.8988	2.810	1.49855	8.265×10^{-2}
2.984×10^{-1}	0.15388	0.9073	2.943	1.49870	9.961×10^{-2}

[a] Index 1 = solvent, 2 = solute; c = concentration; ω = weight fraction; ρ = solution density; ϵ = dielectric constant; n = refractive index.

Using eqs 7 and 6, the permanent dipole moment of bis(acetylacetonato)bis(trimethylsilanolato)zirconium according to Guggenheim was calculated as $\mu_{Zr(acac)_2(OSiMe_3)_2} = 3.94 \pm 0.03$ D.

The Kumler–Halverstadt method individually determines the total polarization P_T and the distortion polarization P_D, which accounts for the induced polarization of the molecule due to the applied electric field. The orientation polarization P_O is then obtained from the difference of these two quantities:

$$P_O = P_T - P_D \tag{8}$$

A correction term, P_A, for the atomic polarization, originally not included by Halverstadt and Kumler, may also be subtracted from P_T. It was shown that, especially in metal complexes, neglecting the atomic polarization might introduce some error, and a guess of a P_A contribution as high as $0.5P_D$ was made for metal acetylacetonates.[37] Using this estimation together with the experimentally determined polarizations P_T and P_D, we obtained a dipole moment $\mu_{Zr(acac)_2(OSiMe_3)_2}$ of 4.01 ± 0.07 D, which matches the Guggenheim–Smith value within experimental error. Neglecting the atomic polarization altogether raises the result to 4.36 ± 0.06 D, about 10% above the Guggenheim value. This confirms that P_A should not be neglected in organometallic and coordination compounds.

The pronounced permanent dipole moment observed for bis(acetylacetonato)bis(trimethylsilanolato)zirconium provides direct evidence for a cis configuration, in agreement with the low-

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(48) Values taken from the following: *TAPP Version 2.2;* ES Microware, Inc.: Hamilton, OH, 1995.

(49) See, for example: Sime, R. J. *Physical Chemistry: Methods, Techniques, and Experiments*; Saunders College Publishing: London, 1990 and references cited therein.

temperature NMR findings described above. The presence of a cis–trans mixture at room temperature, which would affect the observed dipole moment because an average value of the two isomers would then be obtained, can be ruled out by the NMR observations.

The value obtained is significantly lower than found for metal(IV) dihalobis(acetylacetonato) complexes ($\mu = 6.2-8.2$ D).[37] This is not due to different stereochemical constitutions, but can rather be understood in terms of the differences between halo and alcoholato ligands. This can be illustrated by calculating the group dipole moment of the Zr–$OSiMe_3$ entity from the molecular dipole moment of **1** according to eq 9. Using an

$$\mu_{\mathrm{Zr-OSiMe_3}} = \frac{1}{\sqrt{2}}[\mu_{\mathrm{Zr(acac)_2(OSiMe_3)_2}} - \mu_{\mathrm{Zr-acac}}] \qquad (9)$$

approximate value of 1.7 D[37] for the Zr–acac moment and assuming ideal cis symmetry, we find a dipole moment of 1.6 D for the Zr–$OSiMe_3$ group. This is very similar to the Zr–acac moment, but much lower than $\mu_{\mathrm{Zr-X}}$ in $Zr(acac)_2Cl_2$ (4.4 D) and $Zr(acac)_2Br_2$ (4.6 D),[37] which is not unexpected in view of the different ligand polarization power.

Apart from stereochemistry, it is interesting to see how the different $Zr(acac)_2L_2$ dipole moments reflect different substance properties. Comparison of $Zr(acac)_2(OSiMe_3)_2$ ($\mu = 3.94$ D) to $Zr(acac)_2Cl_2$ ($\mu = 7.98$ D) reveals some striking differences. **1** melts near room temperature and is volatile and extremely soluble in pentane, whereas the chloro complex is a high-melting, crystalline solid, nonvolatile, and practically insoluble in pentane. These differences can be attributed to stronger intermolecular dipole–dipole forces in $Zr(acac)_2Cl_2$ compared to **1**.

Conclusions

Two convenient high-yield synthetic routes for zirconium bis(acetylacetonato)bis(alcoholato) complexes are now available, both starting from $Zr(acac)_2Cl_2$. The fluorinated liquid $Zr(acac)_2(hfip)_2$, **2**, was obtained in a single step by reacting $Zr(acac)_2Cl_2$ with 2 equiv of a hexafluoroisopropanol/diethylamine mixture, while the new and equally rapid route to the low-melting solid $Zr(acac)_2(OSiMe_3)_2$, **1**, makes use of a salt elimination reaction with lithium trimethylsilanolate. In comparison to most other synthetic approaches, the handling of extremely air-sensitive intermediates such as $Zr(O\text{-}i\text{-}Pr)_4 \cdot i\text{-}PrOH$ is avoided and the exchange step formerly needed to introduce different alcohols into intermediates such as $Zr(acac)_2(O\text{-}i\text{-}Pr)_2$ or $Zr(acac)_2(OMe)_2$ is no longer necessary. Due to the synthetic simplicity and selectivity, synthesis upscaling should be straightforward, an important issue for the use of these complexes as chemical vapor deposition precursors.

The stereochemistry of a zirconium bis(acetylacetonato)bis(alcoholato) complex has been determined for the first time. For $Zr(acac)_2(OSiMe_3)_2$, both low-temperature NMR and room-temperature dipole-moment measurements ($\mu = 3.94$ D) unambiguously confirmed an octahedral cis configuration. This falls in line with both experimental observations and theoretical calculations for related titanium compounds.

The new monomeric substances can easily be purified by distillation (**2**) or sublimation (**1**) at about 80 °C in a mechanical pump vacuum, a big volatility improvement compared to zirconium β-diketonates. In relation to the reference compound $Zr(acac)_2(O\text{-}t\text{-}Bu)_2$, the introduction of silicon or fluorine heteroatoms into the ligand sphere resulted in a 10–20 °C lower boiling point, despite the 7% and 43% increases in molecular weight for **1** and **2**, respectively. Both approaches thus succeeded in raising volatility. Preliminary vapor pressure measurements just being performed indicate that the vapor pressure of **2** is 10^{-2} mbar at 65 °C and 10^{-1} mbar at 90 °C, respectively.

The liquid $Zr(acac)_2(hfip)_2$ has already successfully been tested as a precursor for zirconia MOCVD.[50] Even at moderate deposition temperatures (550–625 °C), we frequently obtain transparent, high-quality films with less than 1 atom % fluorine contamination, according to XPS (X-ray photoelectron spectroscopy) measurements.

The 2:2 stoichiometry in heteroleptic bis(acetylacetonato)bis(alcoholato)zirconium complexes results in a medium coordination number of 6, compared to 4 in homoleptic alcoholates and 8 in acetylacetonates. Since both $Zr(acac)_2(OSiMe_3)_2$ and $Zr(acac)_2(hfip)_2$ were found to be far more stable toward hydrolysis than $Zr(O\text{-}t\text{-}Bu)_4$, this stoichiometry appears to be a good compromise between volatility and air stability: the “best of both (ligand) worlds”.

Acknowledgment. The author is indebted to Prof. N. D. Spencer for his continuing interest and his support of this work. I would also like to thank R. Hüsges of Cologne University, Cologne, Germany, for helpful suggestions regarding the synthetic procedure for compound **2** and K. Matsumoto for translation of ref 34. Support by E. Meister (Lab. Phys. Chem., ETH Zürich) regarding the dipole moment apparatus and H. Rüegger (Lab. Inorg. Chem., ETH Zürich) for NMR measurements is also gratefully acknowledged.

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