Dimethyl Group IV Metal Complexes of the OSO-Type Ligand Bearing $AlMe_2$ Moieties

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Summary: Complexes having two ancillary $(tbop)^{2-}$ *ligands where* $tbopH_2$ *= 2,2′-thiobis{4-(1,1,3,3-tetramethylbutyl)phenol}, viz.,* $[M(tbop\text{-}\kappa^3O,S,O)_2]$ *(M = Ti,* **1***; M = Zr,* **2***; M = Hf,* **3***), have been prepared in good yields by amine or HCl elimination from* $tbopH_2$*. The* ^1H *and* ^{13}C *NMR studies showed that complexes* **1**−**3** *adopt in solution mononuclear structures. Treatment of* **1**−**3** *with 2 equiv or an excess of* $AlMe_3$ *generates heterometallic* $[M(\mu\text{-}tbop\text{-}\kappa^3O,S,O)_2Me_2(\mu\text{-}AlMe_2)_2]$ *(M = Ti,* **4***; M = Zr,* **5***; M = Hf,* **6***) complexes. The structures of* **4**−**6** *were confirmed by NMR spectroscopy; complexes* **5** *and* **6** *were further investigated by X-ray crystallography. These studies showed* **4**−**6** *to be trimers either in the solid state or in solution. The crystals of* $\mathbf{5}\cdot CH_2Cl_2$ *and* $\mathbf{6}\cdot CH_2Cl_2$ *consist of eight-coordinate dimethyl Zr or Hf centers and two* $AlMe_2$ *moieties attached to oxygen atoms of the tbop ligands. The saturated coordination sphere of the metal centers in* **1**−**6** *makes them inactive in ethene polymerization.*

Introduction

Commercial single-site catalysts in the polyolefin industry are based on metallocene complexes comprising group IV metal centers. In recent years there is a growing recognition that nonmetallocene complexes hold great promise as olefin polymerization catalysts.[1] Most successful developments in terms of catalysis have appeared using chelating bis(aryloxide) ligands, in particular with tridentate and tetradentate ligands having an additional coordinating heteroatom (N, O, S).[2] Theoretical computations predicted that $[TiMe\{2\text{-}C_6H_4O)_2S\}]^+$ species acts as "breathing catalysts", with the S atom moving in and out from the metal center, leading to a lower ethene insertion barrier.[3] We have been exploring the use of the S-bridged 2,2′-thiobis{4-(1,1,3,3-tetramethylbutyl)phenolato} (tbop) ligand for the preparation of early transition complexes, in particular titanium complexes, that might serve as catalysts for the polymerization of α-olefins. The tbop ligand was placed on Ti, and several heteroleptic, alkoxo- and aryloxo-bridged complexes containing coligands such as chlorides, imides, and monoaryloxides have been created and structurally characterized.[4−6] These complexes when activated with aluminum alkyls are highly effective heterogeneous, well-defined, single-site ethene polymerization catalysts. It has been proved that during the polymerization process the tbop ligand does not migrate to the aluminum atom of the activator and generation of active centers occurs via the abstraction of coligands from the titanium atom. In this context, it seems most likely that activation of a homoleptic $[Ti(tbop\text{-}\kappa^3O,S,O)_2]$ compound with aluminum alkyls should not create an effective catalyst. Therefore, we thought it would be informative to explore complexes that contain two tbop ligands on titanium, zirconium, and hafnium and to define the ability of homoleptic $[M(tbop\text{-}\kappa^3O,S,O)_2]$ compounds to interact with aluminum alkyls. The objectives of this work were to prepare of $[M(tbop\text{-}\kappa^3O,S,O)_2]$ [(M = Ti (**1**), Zr (**2**), Hf (**3**)] compounds and heterometallic, alkyl species $[M(\mu\text{-}tbop\text{-}\kappa^3O,S,O)_2Me_2(\mu\text{-}AlMe_2)_2]$ [M = Ti (**4**), M = Zr (**5**), M = Hf (**6**)], to study their X-ray crystal structures as well as to examine their ethene polymerization properties.

Results and Discussion

Generally, two routes are used to achieve neutral $[M(diaryloxides)_2]$ complexes: (a) σ-bond metathesis reaction between the bisphenols and an appropriate homoleptic metal precursor enabling either alkane, alcohol, amine, or HCl elimination; (b) salt elimination reactions between an alkali metal diaryloxide salt and MCl_4. The convenient route to prepare $[Ti(tbop\text{-}\kappa^3O,S,O)_2]$ (**1**) as an orange-red solid was shown to be the σ-bond metathesis reaction between the $tbopH_2$ and $[Ti(NMe_2)_4]$ in a 2:1 molar ratio and has been described earlier.[5] Both zirconium and hafnium analogues **2** and **3**, respectively, were prepared efficiently by the reaction of 2 equiv of the $tbopH_2$ with MCl_4 under reflux in toluene as colorless, air- and moisture-sensitive compounds with concomitant elimination of 4 equiv

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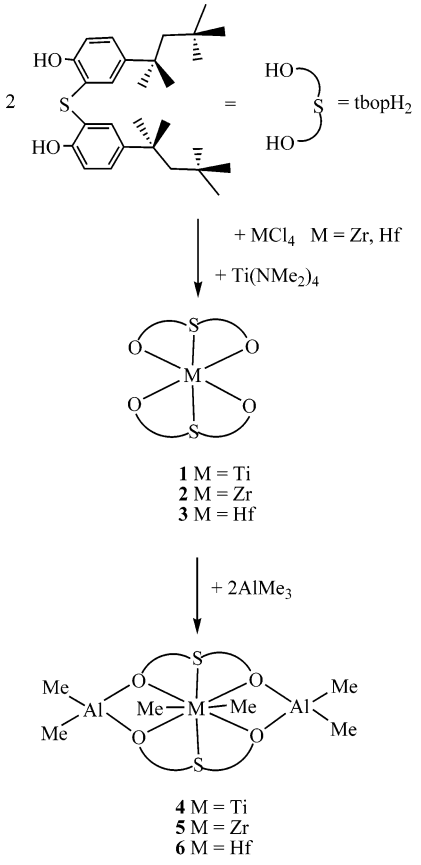
Scheme 1. Preparation of Complexes 1−6



of HCl (Scheme 1). In the same conditions $TiCl_4$ forms the dimeric, heteroleptic complex [Ti_2(μ-tbop-κ^3O,S,O)(μ-tbop-κ^2O,O)(tbop-κ^3O,S,O)Cl_2], which in solution dissociates to [Ti(tbop-κ^3O,S,O)$_2$] (**1**) and [Ti_2(μ-tbop-κ^3O,S,O)$_2$$Cl_2$].[5] Complexes **2** and **3** are well soluble in organic solvents, and attempts to obtain them in crystalline form failed. They were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The ^{1}H and ^{13}C NMR spectra of **2** and **3** are similar to those of **1** and contain one set of resonances from the coordinated tbop ligands. This suggests that in solution complexes **1**−**3** exist as the *trans*-isomers with *fac* conformation of the ligand. In the absence of X-ray studies, we cannot exclude the *fac-cis* or *mer-trans* structures for **1**−**3** in the solid state. It is notable that, for example, well-characterized octahedral compounds [Zr(OOO)$_2$][2e] where OOO = 2,2′-O(OC_6H_2-6-*t*Bu-4-Me)$_2$ and [Hf_2(ONO)$_2$][7] where ONO = amine bis(phenolate)s exist as the *cis*-isomers in the solid state and the *trans*-isomer was proved in solution of [Zr(OOO)$_2$].

Treatment of **1**−**3** with 2 equiv or an excess of $AlMe_3$ in *n*-hexane leads after workup to the formation of [M(μ-tbop-κ^3-O,S,O)$_2$$Me_2$($\mu$-$AlMe_2$)$_2$] (M = Ti (**4**), M = Zr (**5**)•CH_2Cl_2, M = Hf (**6**)•CH_2Cl_2) in high yield (Scheme 1). The molecular structures of the two isostructural complexes **5**•CH_2Cl_2 and **6**•CH_2Cl_2 were determined by X-ray crystallography. Figure 1 shows **6**, and selected structural parameters for the two complexes are given in the figure caption. The structures of both complexes reveal eight-coordinate Zr or Hf metal centers with a dodecahedral geometry and tetrahedral aluminum atoms linked via oxygen atoms of the tbop ligands. The M−O distances are very similar in both complexes and as expected significantly longer than those for terminal Zr and Hf aryloxides[2a,d−f,8] Also M−S and M−C bond lengths in both **5** and **6** display similar trends and do not reveal unusual features.[2d,f,g,j,l,9] The Al−O bond lengths are close to those found in other structures of the aluminum aryloxides.[5,10] The Al−C bond lengths are clearly within the range expected for the terminal Al−C bond distances.[6,11]

The ^{1}H and ^{13}C NMR spectra of **5** and **6** are in good agreement with the crystal structure obtained from X-ray diffraction techniques. The methyl groups attached to the Zr or Hf centers are equivalent, whereas methyl groups at aluminum are inequivalent and are in the expected chemical shift ranges, with both the ^{1}H and ^{13}C signals shifted slightly from the starting $AlMe_3$. One set of resonances for the tbop ligand was observed as well. The same sequence of resonances was detected for **4** (see Experimental Section). These observations suggest that compounds **4**−**6** have the same structure in solution and in the solid state and indicate that **4** is their structural analogue.

To our knowledge complexes **4**−**6** are the first examples of dimethyl eight-coordinate group IV metal complexes bearing additionally $AlMe_2$ moieties to form trinuclear heterometallic species. Likely, the formation of compounds **4**−**6** occurs via the migration of Me groups to the central transition metal atoms, and as a result coordination numbers of eight are reached, whereas two $AlMe_2$ moieties undergo addition to the oxygen atoms of the tbop ligands to achieve tetrahedral geometry.

In contrast to previously reported heteroleptic tbop-Ti catalysts,[3−5] preliminary polymerization results showed that complexes **1**−**6** when activated with aluminum alkyls were inactive in ethene polymerization. The lack of catalytic activity can explain the fact that formally considered 16-electron complexes **4**−**6** are coordinatively saturated species and there is no vacancy for the incoming olefin. Even an excess of aluminum alkyls is not able to abstract one of the two tbop ligands from the metal site to generate the cationic unsaturated species, generally considered as the active centers. On the contrary, in the titanium catalytic systems containing one tbop ligand and coligands such as alkoxides, chlorides, and imides, aluminum cocatalysts cause the abstraction of coligands to form dialkyl {Ti(tbop)R_2} intermediates, which initiate cationic active center production.[4−6] In this context inactivity demonstrated for [Zr(tbmp)Cl_2] [tbmp = 2,2′-thiobis(6-*tert*-butyl-4-methylphenolate)] is surprising and up to date no explanation has been found.[2k] The same trend has also been

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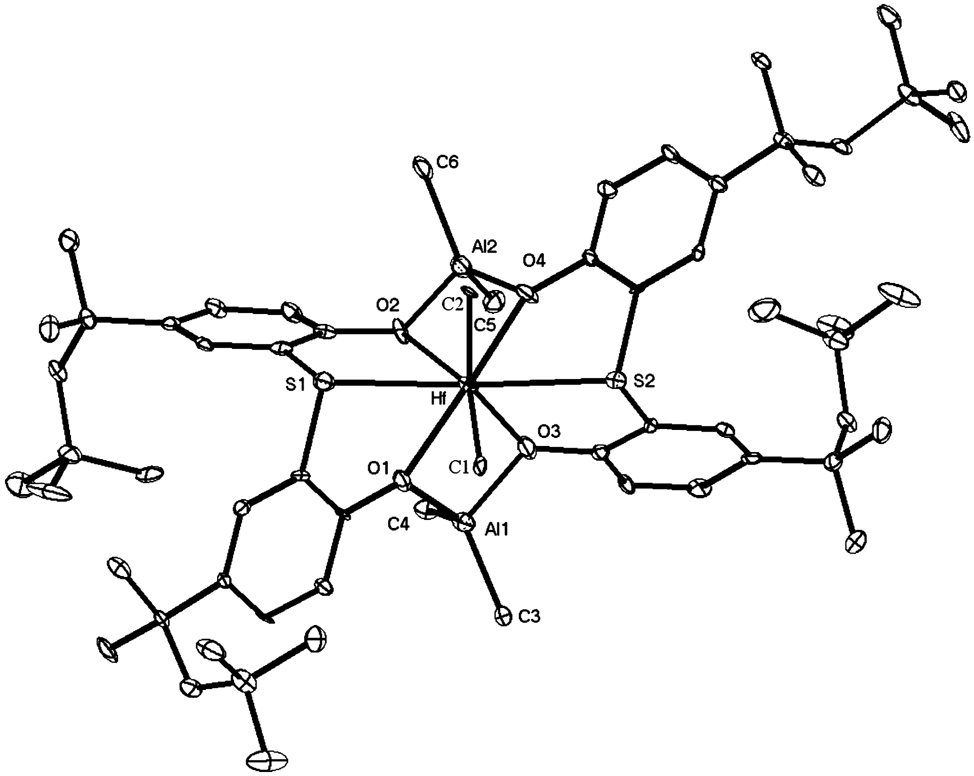

Figure 1. Molecular structure of [M(μ-tbop-κ^3O,S,O)$_2$Me$_2$(AlMe$_2$)$_2$] [where M = Zr (**5**) or Hf (**6**)] (**6** shown, hydrogen atoms omitted for clarity). Selected bond lengths (Å): **5**, Zr−O(1) 2.307(3), Zr−O(2) 2.225(3), Zr−S(1) 2.794(2), Zr−C(1) 2.286(4), Zr−C(2) 2.283(4), Al(1)−O(1) 1.847(3), Al(1)−O(3) 1.856(3), Al(1)−C(3) 1.959(4), Al(1)−C(4) 1.954(4); **6**, Hf−O(1) 2.306(6), Hf−O(2) 2.196(6), Hf−S(1) 2.796(4), Hf−C(1) 2.246(9), Hf−C(2) 2.260(9), Al(1)−O(1) 1.818(7), Al(1)−O(3) 1.886(6), Al(1)−C(3) 1.956(9), Al(1)−C(4) 1.934(9).

observed for our [M(tbop)$_2$Cl$_2$] (M = Zr, Hf) systems,[12] in contrast to the titanium analogue [Ti(tbop)$_2$Cl$_2$], which when activated with aluminum alkyls showed very high activity in the ethene polymerization process (465 kgPE/g Ti/h).[5]

In summary, we have demonstrated the synthesis of homoleptic, neutral group IV complexes of the tridentate ligand 2,2′-thiobis{4-(1,1,3,3-tetramethylbutyl)phenolato} [(tbop)$^{2-}$] and their reactivity toward AlMe$_3$. An effective route for the preparation of zirconium and hafnium [M(tbop-κ^3O,S,O)$_2$] species was based on the direct reaction between MCl$_4$ and 2 equiv of tbopH$_2$ in toluene. Those complexes have been identified by NMR spectroscopy as monomeric *trans*-isomers with *fac* conformation of the ligand in solution. Treatment of **1**−**3** with AlMe$_3$ leads to the formation of mixed metal complexes **4**−**6**, in which by the shift of the methyl groups the transition metal atoms reach an eight-coordination sphere, whereas AlMe$_2$ moieties are attached to the oxygen atoms of the ligands. Complexes **1**−**6** activated with aluminum alkyls were shown to be inactive in ethene polymerization.

Experimental Section

General Considerations. All operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques. All the solvents were distilled under dinitrogen from the appropriate drying agents prior to use. The compounds [Ti(NMe$_2$)$_4$], ZrCl$_4$, HfCl$_4$, AlMe$_3$, and 2,2′-thiobis{4-(1,1,3,3-tetramethylbutyl)phenol} (tbopH$_2$) were obtained from Aldrich Chemical Co. and used without further purification unless stated otherwise. [Ti(tbop-κ^3O,S,O)$_2$] (**1**) was prepared according to the literature procedure.[4] Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer in Nujol mulls. NMR spectra were performed on a Brüker ARX 300 spectrometer. Microanalyses were conducted with a ASA-1 (GDR, Karl-Zeiss-Jena) instrument (in-house).

[Zr(tbop-κ^3O,S,O)$_2$] (2). To a suspension of ZrCl$_4$ (1.20 g; 5.15 mmol) in toluene (60 mL) was added tbopH$_2$ (4.56 g; 10.30 mmol). The mixture was refluxed until the evolution of HCl had ceased (48 h). Then the cloudy solution was filtered off, and all volatile components were removed from the filtrate in vacuo to give a light yellow solid. Yield: 2.73 g (55%). Anal. Calcd for C$_{56}$H$_{80}$O$_4$S$_2$Zr: C, 69.16; H, 8.29; S, 6.59. Found: C, 69.55; H, 8.56; S, 6.08. ^{1}H NMR (C$_6$D$_6$): δ 7.89−6.95 (m, 12H, C$_6$*H*$_3$); 1.69 [s, 8H, C(CH$_3$)$_2$C*H*$_2$C(CH$_3$)$_3$]; 1.36 [s, 24H, C(C*H*$_3$)$_2$CH$_2$C(CH$_3$)$_3$]; 0.88 [s, 36H, C(CH$_3$)$_2$CH$_2$C(C*H*$_3$)$_3$]. ^{13}C NMR (C$_6$D$_6$): δ 154.2, 142.7, 129.7, 126.1, 122.2, 115.3 (*C*$_6$H$_3$); 56.1 [C(CH$_3$)$_2$*C*H$_2$C(CH$_3$)$_3$]; 31.2, 30.3, 30.8, 29.3 [*C*(*C*H$_3$)$_2$CH$_2$*C*(*C*H$_3$)$_3$].

[Hf(tbop-κ^3O,S,O)$_2$] (3). This complex was prepared in an analogous manner to that employed for **2** from HfCl$_4$ (1.36 g; 4.25 mmol) and tbopH$_2$ (3.76 g; 8.50 mmol). Yield: 3.17 g (82%). Anal. Calcd for C$_{56}$H$_{80}$O$_4$S$_2$Hf: C, 63.37; H, 7.60; S, 6.03. Found: C, 63.69; H, 7.27; S, 5.88. ^{1}H NMR (C$_6$D$_6$): δ 7.76−7.12 (m, 12H, C$_6$*H*$_3$); 1.70 [s, 8H, C(CH$_3$)$_2$C*H*$_2$C(CH$_3$)$_3$]; 1.36 [s, 24H, C(C*H*$_3$)$_2$CH$_2$C(CH$_3$)$_3$]; 0.89 [s, 36H, C(CH$_3$)$_2$CH$_2$C(C*H*$_3$)$_3$]. ^{13}C NMR (C$_6$D$_6$): δ 156.6, 147.5, 139.2, 136.9, 129,8 118.0 (*C*$_6$H$_3$); 56.8 [C(CH$_3$)$_2$*C*H$_2$C(CH$_3$)$_3$]; 31.9, 30.6, 30.1, 29.5 [*C*(*C*H$_3$)$_2$CH$_2$*C*(*C*H$_3$)$_3$].

[Ti(μ-tbop-κ^3O,S,O)$_2$Me$_2$(AlMe$_2$)$_2$] (4). To a solution of [Ti(NMe$_2$)$_4$] (0.73 g; 3.25 mmol) in toluene was added tbopH$_2$ (2.88 g; 6.50 mmol), and the mixture was refluxed for 12 h. Then all volatiles were removed in vacuo, and an orange sticky material was dissolved in *n*-hexane. After cooling to −40 °C the stirred solution was treated with AlMe$_3$ (3.25 mL, 2 M in toluene; 6.50 mmol), then allowed to warm to room temperature and stirred for an additional 18 h. The orange-red solid was collected by filtration, washed with *n*-hexane (2 × 5 mL), and dried in vacuo. Yield: 1.46

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[12] Wiśniewska, D.; Janas, Z.; Sobota, P. Unpublished results.

Table 1. Crystal Data and Structure Analysis Results for 5·CH₂Cl₂ and 6·CH₂Cl₂

	5·CH_2Cl_2	**6**·CH_2Cl_2
formula	$C_{63}H_{100}Cl_2O_4S_2Al_2Zr$	$C_{63}H_{100}Cl_2O_4S_2Al_2Hf$
fw	1201.66	1288.90
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	14.920(3)	14.908(6)
b, Å	15.693(4)	15.667(6)
c, Å	16.648(4)	16.645(6)
α, deg	73.82(3)	74.06(9)
β, deg	87.06(3)	86.71(9)
γ, deg	62.93(3)	62.80(9)
V, Å^3	3320.4(17)	3314(2)
Z	2	2
cryst size, mm	0.353 × 0.214 × 0.089	0.323 × 0.209 × 0.102
cryst color	colorless	colorless
radiation; λ, Å	0.71073	0.71073
temp, K	100(2)	100(2)
θ range, deg	2.95−27.00	2.88−25.00
data collected		
h	−19 to +19	−16 to +17
k	−19 to +20	−16 to +17
l	−16 to +2	−19 to +19
no. of data collected	33 308	16 978
no. of indep reflns	14 365	10 745
absorp corr	analytical	analytical
final R indices (obsd data)		
R_1 [$I > 2\sigma(I)$]	0.0727	0.0681
wR_2 (all data)	0.1409	0.1577
goodness of fit	1.091	1.027

g (42%). Anal. Calcd for $C_{62}H_{98}O_4S_2Al_2Ti$: C, 69.37; H, 9.20; S, 5.97. Found: C, 69.19; H, 9.08; S, 5.67. ^{1}H NMR (C_6D_6): δ 7.87−6.98 (m, 12H, C_6H_3); 1.96 [s, 6H, Ti−CH_3]; 1.68, 1.66 [d, 8H, $C(CH_3)_2CH_2C(CH_3)_3$]; 1.40, 1.34 [s, 24H, $C(CH_3)_2CH_2C(CH_3)_3$]; 0.78 [s, 36H, $C(CH_3)_2CH_2C(CH_3)_3$]; 0.11, −0.41 (s, 12H, Al−CH_3). ^{13}C NMR (C_6D_6): δ 157.4, 144.3, 130.7, 129.6, 125.1, 117.4 (C_6H_3); 66.3 (Ti−CH_3); 57.3 [$C(CH_3)_2CH_2C(CH_3)_3$]; 32.4, 31.8, 31.6, 31.2 [$C(CH_3)_2CH_2C(CH_3)_3$]; −8.1, −9.9 (Al−CH_3).

[Zr(μ-tbop-κ^3O,S,O)$_2$Me$_2$(μ-AlMe$_2$)$_2$] (5)·CH$_2$Cl$_2$. A stirred solution of **2** (1.60 g; 1.65 mmol) in hexane (30 mL) at −40 °C was treated with $AlMe_3$ (1.65 mL, 2 M in toluene; 3.30 mmol). The mixture was allowed to warm to room temperature and stirred for an additional 18 h. The colorless solid was collected by filtration, washed with *n*-hexane (2 × 5 mL), and dried in vacuo. Yield: 1.6 g (84%). Crystals suitable for X-ray analysis were obtained by recrystallization from a concentrated solution of **5** in CH_2Cl_2 at −40 °C. Anal. Calcd for $C_{63}H_{100}Cl_2O_4S_2Al_2Zr$: C, 62.97; H, 8.39; Cl, 5.90; S, 5.34. Found: C, 63.09; H, 8.15; Cl, 5.81; S, 5.43. ^{1}H NMR (C_6D_6): δ 7.83−6.94 (m, 12H, C_6H_3); 4.39 (s, 2H, CH_2Cl_2); 1.68, 1.62 [d, 8H, $C(CH_3)_2CH_2C(CH_3)_3$]; 1.38, 1.32 [s, 24H, $C(CH_3)_2CH_2C(CH_3)_3$]; 0.86 [s, 6H, Zr−CH_3]; 0.77 [s, 36H, $C(CH_3)_2CH_2C(CH_3)_3$]; 0.19, −0.3 (s, 12H, Al−CH_3). ^{13}C NMR (C_6D_6): δ 156.4, 144.9, 131.5, 129.7, 124.1, 117.6 (C_6H_3); 57.3 [$C(CH_3)_2CH_2C(CH_3)_3$]; 53.4 (CH_2Cl_2); 32.4, 31.8, 31.5, 31.2 [$C(CH_3)_2CH_2C(CH_3)_3$]; 30.7 (Zr-CH_3); −7.8, −10.0 (Al−CH_3).

[Hf(μ-tbop-κ^3O,S,O)$_2$Me$_2$(μ-AlMe$_2$)$_2$] (6)·CH$_2$Cl$_2$. This complex was prepared in an analogous manner to that employed for **5** from **3** (1.8 g; 1.70 mmol) and $AlMe_3$ (1.70 mL, 2 M in toluene; 3.40 mmol). Yield: 1.69 g (87%). Crystals suitable for X-ray analysis were obtained by recrystallization from a concentrated solution of **6** in CH_2Cl_2 at −40 °C. Anal. Calcd for $C_{63}H_{100}Cl_2O_4S_2Al_2Hf$: C, 58.71; H, 7.82; Cl, 5.50; S, 4.97. Found: C, 58.39; H, 7.79; Cl, 5.50; S, 5.17. ^{1}H NMR (C_6D_6): δ 7.79−6.96 (m, 12H, C_6H_3); 4.40 (s, 2H, CH_2Cl_2); 1.67, 1.61 [d, 8H, $C(CH_3)_2CH_2C(CH_3)_3$]; 1.37, 1.31 [s, 24H, $C(CH_3)_2CH_2C(CH_3)_3$]; 0.77 [s, 36H, $C(CH_3)_2CH_2C(CH_3)_3$]; 0.64 [s, 6H, Zr−CH_3]; 0.19, −0.28 (s, 12H, Al−CH_3). ^{13}C NMR (C_6D_6): δ 156.6, 144.8, 131.5, 129.6, 124.3, 118.0 (C_6H_3); 57.4 [$C(CH_3)_2CH_2C(CH_3)_3$]; 53.2 (CH_2Cl_2); 34.8 (Hf−CH_3); 32.4, 31.8, 31.5, 31.1 [$C(CH_3)_2CH_2C(CH_3)_3$]; −7.8, −9.9 (Al−CH_3).

Crystal Structure Determination of 5·CH$_2$Cl$_2$ and 6·CH$_2$Cl$_2$. Crystal data collection and refinement are summarized in Table 1. Preliminary examination and intensity data collection were carried out on a KUMA CCD KM-4 κ-axis diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All data were corrected for Lorentz, polarization, and absorption effects. Data reduction and analysis were carried out with the Kuma Diffraction programs.[13] The structures were solved by direct SHELXTL software methods[14] and refined using full-matrix least-squares on all F^2 data. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions with isotropic thermal parameters. CCDC reference number 611200 for **5**·CH_2Cl_2 and 611201 for **6**·CH_2Cl_2.

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Supporting Information Available: A CIF file giving crystallographic data for the structures of **5**·CH_2Cl_2 and **6**·CH_2Cl_2, reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0608051

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[13] Oxford Diffraction. *CrysAlis CCD* and *CrysAlis RED*, Version 1.171; Oxford Diffraction Ltd: Abingdon Oxfordshire, England, 2004.

[14] Sheldrick, G. M. *SHELXTL*, Version 5.1; Bruker AXS Inc.: Madison, WI, 1998.