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Metal-catalysed Polymerisation

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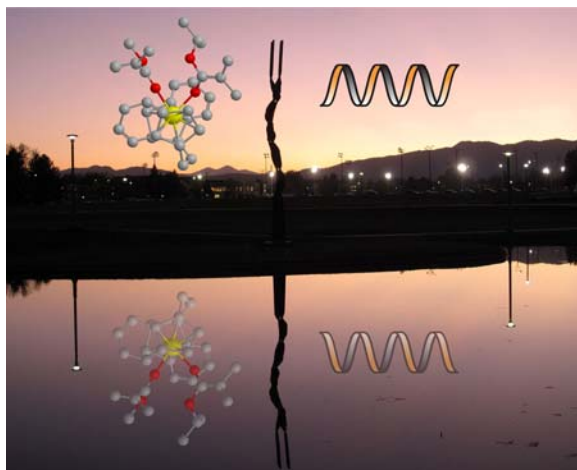


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Zirconium and hafnium complexes of the thio(bisphenolato) ligand: synthesis, structural characterization and testing as 1-hexene polymerization catalysts†

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Thio(bisphenolato) complexes of the type $[M_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2\text{Cl}_4]$ [$M = \text{Zr } 1, \text{Hf } 2$ and $\text{tbop} = 2,2'$ -thiobis{4-(1,1,3,3-tetramethyl-butyl)phenolate}] were prepared by HCl elimination from tbopH_2 and MCl_4 . Substitution of the chlorides in **1** and **2** by 2,6-diisopropylphenolato groups (dipp) generates new compounds $[M_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2(\text{dipp})_4]$ ($M = \text{Zr } 3, \text{Hf } 4$). The structures of **1–4** were confirmed by NMR spectroscopy; complexes **3** and **4** were further investigated by X-ray crystallography. These studies showed **1–4** to be dimers either in the solid state or in solution and to have metal centers adopting distorted octahedral geometry. However treatment of MCl_4 with $[\text{Al}_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2]$ or $[\text{Al}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2\text{Me}_2]$ gave heterotrinnuclear complexes $[\text{M}(\text{tbop-}\kappa^3\text{O,S,O})_2\text{-Cl}_2(\mu\text{-AlX}_2)_2]$ ($M = \text{Zr}, \text{X} = \text{Cl } 5, \text{X} = \text{Me } 7$ and $M = \text{Hf}, \text{X} = \text{Cl } 6, \text{X} = \text{Me } 8$) for which the single-crystal X-ray diffraction analysis showed zirconium and hafnium centers to have eight-coordinate dodecahedral geometry. Complexes **1–6** after activation with aluminium alkyls and supporting on MgCl_2 showed a lack of activity in the ethene polymerization process and moderate activity towards 1-hexene producing high molecular weight atactic poly(1-hexenes).

Introduction

In recent years there is a growing recognition that non-metallocene complexes hold great promise as homogenous olefin polymerization catalysts.¹ Systematic ligand design has explored new families of group IV metal monoanionic phenoxides,¹ bis(phenoximines)² and phosphanylphenoxides³ in highly active systems. The most successful developments in terms of catalysis has appeared using chelating bis-phenoxide ligands,⁴ in particular tridentate and tetradentate having additional neutral donors.^{1d,1e,5–21} However, there is growing evidence that softer second-row donors like sulfur may offer beneficial stabilization of the highly reactive metal center in homogenous catalysis.^{3e,7e,19g,20–22}

With this in mind we have explored group IV metal complexes containing the 2,2'-thiobis{4-(1,1,3,3-tetramethyl-butyl)phenolato} (tbop) ligand as potential precursors in the α -olefin heterogeneous polymerization process. As a result heteroleptic, aryloxo-bridged $[\text{Ti}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2\text{L}_2]$ ($\text{L} = \text{Cl}$, diisopropylphenolato, $=\text{NR}$) and alkoxo-bridged $[\text{Ti}_2(\mu\text{-OR})_2(\text{OR})_2(\text{tbop-}\kappa^3\text{O,S,O})_2]$ ($\text{R} = \text{Me}, \text{Et}$) as well as homoleptic $[\text{M}(\text{tbop-}\kappa^3\text{O,S,O})_2]$ ($M = \text{Ti}, \text{Zr}, \text{Hf}$) complexes have been obtained and characterized.²³ Among them only heteroleptic titanium compounds when activated with aluminium alkyls and supported on MgCl_2 showed to be effective, well-defined, single-site heterogeneous ethene polymerization catalysts.^{23a–c} It has been proved that during the ethene polymerization process, the tbop ligand does not migrate to the aluminium atom of the activator

and generation of active centers occurs *via* the abstraction of coligands from the titanium atom. On the contrary, homoleptic $[\text{M}(\text{tbop-}\kappa^3\text{O,S,O})_2]/\text{aluminium alkyl}$ systems demonstrate a lack of catalytic activity towards ethene. It has been found and well documented that treatment of $[\text{M}(\text{tbop-}\kappa^3\text{O,S,O})_2]$ with AlMe_3 leads to the formation of the coordinatively saturated $[\text{M}(\text{tbop-}\kappa^3\text{O,S,O})_2\text{Me}_2(\mu\text{-AlMe}_2)_2]$ species.^{23d} In this context inactivity demonstrated for octahedral $[\text{Zr}(\text{tbmp-}\kappa^3\text{O,S,O})\text{Cl}_2]$ [$\text{tbmp} = 2,2'$ -thiobis(6-*tert*-butyl-4-methylphenolato)] in ethene as well as in the 1-hexene polymerization process is surprising, and to this date no explanation has been found. In comparison, the corresponding double sulfur donor system $[\text{Zr}(\text{dtbmp-}\kappa^4\text{OSSO})(\text{bn})_2]/\text{B}(\text{C}_6\text{F}_5)_3$ [$\text{dtbmp} = 2,2'$ -ethanedithiobis(6-*tert*-butyl-4-methylphenolato); $\text{bn} = \text{benzyl}$] having the same substituents at the phenolate group like the tbmp ligand in $[\text{Zr}(\text{tbmp-}\kappa^3\text{O,S,O})\text{Cl}_2]$, effectively polymerizes 1-hexene.^{22e} Because of this we have been tried to extend our investigation on the tbop-based group IV metal systems to the 1-hexene polymerization process. Here we report on homodinuclear octahedral and heterotrinnuclear dodecahedral zirconium and hafnium complexes with the tbop ligand, as well as their behavior towards 1-hexene after activation with aluminium alkyls.

Results and discussion

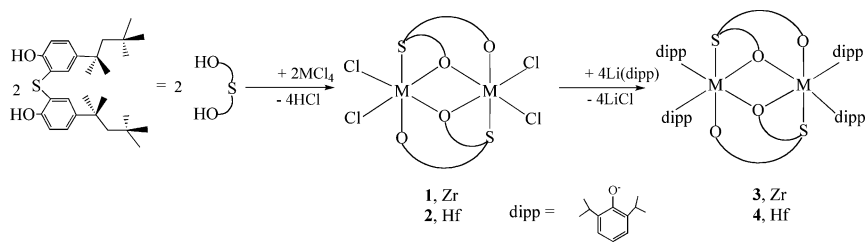
Synthesis and crystallographic studies of homometallic zirconium and hafnium complexes

The preparation of new thio(bisphenolato) zirconium and hafnium dichloride compounds was carried out by employing a method based on the σ -bond metathesis reaction between an appropriate thio(bisphenol) and a homoleptic metal precursor such as MCl_4 enabling HCl elimination. The reaction of MCl_4 where $M = \text{Zr}, \text{Hf}$ and a stoichiometric amount of tbopH_2 in

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†CCDC reference numbers 721082–721085. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b907560g



Scheme 1 Synthesis of zirconium and hafnium complexes **1–4**.

toluene leads to the formation of microcrystalline products [$M_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2\text{Cl}_4$] (**1**) for $M = \text{Zr}$ and (**2**) for $M = \text{Hf}$ (Scheme 1).

The IR spectra of **1** and **2** show characteristic modes for terminally coordinated chlorides at 356, 380 and 320, 338 cm^{-1} , respectively. The ^1H NMR spectra of **1** and **2** contain one set of resonances due to the tbop ligand and are similar to the previously described, well characterized $[\text{Ti}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2\text{Cl}_4]$.^{23b} Attempts to grow crystals of **1** and **2** suitable for X-ray diffraction proved unsuccessful. However we have found that the 1:2 σ -bond metathesis reaction of **1** and **2** with $\text{Li}(\text{dipp})$ ($\text{dipp} = 2,6$ -diisopropylphenolato) in diethyl ether proceeded readily and selectively to yield colorless crystals of $[\text{M}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2(\text{dipp})_4]$ where $M = \text{Zr}$ (**3**) and Hf (**4**). The ^1H NMR spectra of **3** and **4** contain septet and doublet resonances for the isopropyl substituents at the dipp groups and one resonance set of the tbop ligand similar to those detected for **1** and **2**. The molecular structures of the two isostructural complexes **3** and **4** were determined by X-ray crystallography. Fig. 1 shows complex **3**, and selected structural parameters for the two complexes are given in the figure caption.

Crystals of **3** and **4** are composed of dimeric $[\text{M}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2(\text{dipp})_4]$ molecules in which two distorted octahedral metal centers are linked by a double bridge formed through the oxygen atoms of the tbop ligands in a manner shown in Scheme 1. These oxygen atoms together with both oxygen atoms of the dipp groups are situated in equatorial positions whereas the sulfur and the second oxygen atom of the tbop ligand occupy the axial sites. The dipp ligands are terminally coordinated to the metal centers in *cis* positions. The $\text{M}-\text{O}$ distances are very similar and within the expected ranges for Zr and Hf aryloxides.^{7d,17d,21a,23d} However, there is a significant decrease in the metal–sulfur bond distance on going from Zr to Hf. This structural feature presumably reflects a decrease in oxophilicity on descending group IV, although the influence of the crystal packing is not excluded. The molecular structures of **3** and **4** suggest that complexes **1** and **2** may have also in the solid state dimeric nature with terminally coordinated chloride atoms.

Synthesis and crystallographic studies of heterometallic zirconium, hafnium and aluminium complexes

Treatment of MCl_4 with $[\text{Al}_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2]$ ^{23c} at 2:1 molar ratio in toluene leads after workup to colorless crystals of $[\text{M}(\text{tbop-}\kappa^3\text{O,S,O})_2\text{Cl}_2(\mu\text{-AlCl}_2)_2]$ (**5**)- $0.5\text{C}_6\text{H}_{14}$ for $M = \text{Zr}$ and (**6**) for $M = \text{Hf}$ in 82% and 84% yield, respectively (Scheme 2).

The molecular structure of **5**· $0.5\text{C}_6\text{H}_{14}$ was determined by X-ray crystallography and is shown in Fig. 2. The structure of **5** reveals an eight-coordinate Zr center with a dodecahedral

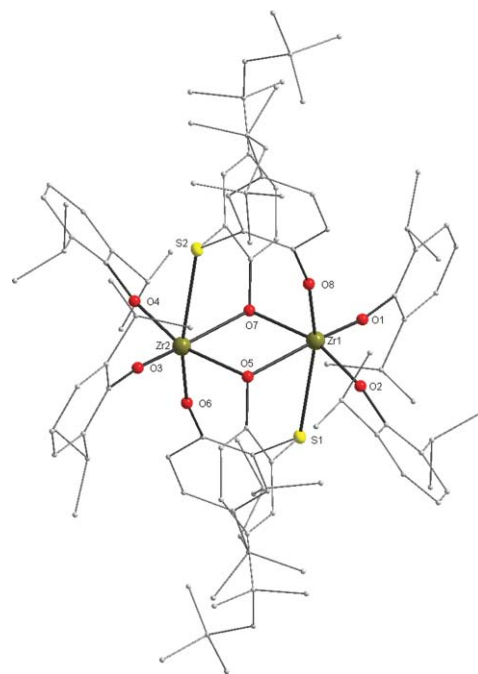
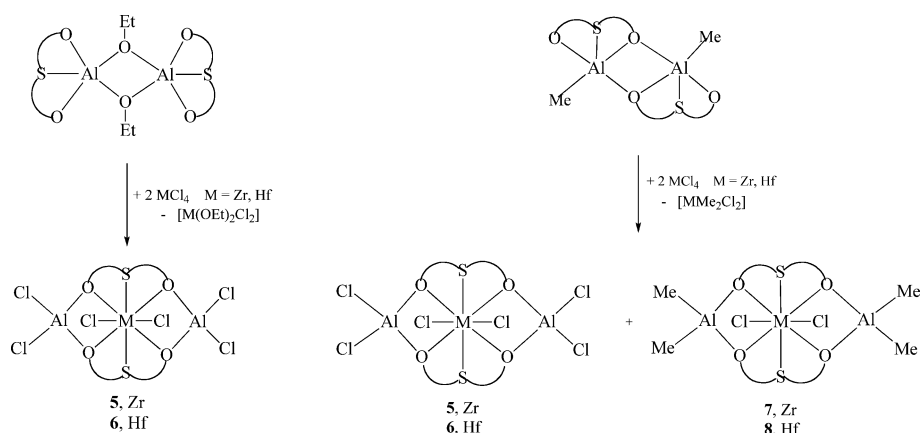


Fig. 1 Molecular structure of $[\text{M}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2(\text{dipp})_4]$ [where $M = \text{Zr}$ (**3**) or Hf (**4**)] (**3** shown, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): **3**, $\text{Zr}(1)\text{-S}(1)$ 2.848(1), $\text{Zr}(1)\text{-O}(1)$ 1.948(2), $\text{Zr}(1)\text{-O}(8)$ 1.954(2), $\text{Zr}(1)\text{-O}(7)$ 2.206(2), $\text{O}(2)\text{-Zr}(1)\text{-S}(1)$ 75.70(6), $\text{O}(1)\text{-Zr}(1)\text{-O}(5)$ 157.14(7), $\text{S}(1)\text{-Zr}(1)\text{-O}(8)$ 160.53(6). **4**, $\text{Hf}(1)\text{-S}(1)$ 2.820(2), $\text{Hf}(1)\text{-O}(1)$ 1.940(3), $\text{Hf}(1)\text{-O}(5)$ 2.186(2), $\text{Hf}(1)\text{-O}(8)$ 1.960(2), $\text{S}(1)\text{-Hf}(1)\text{-O}(1)$ 74.99(7), $\text{O}(2)\text{-Hf}(1)\text{-O}(5)$ 155.97(9), $\text{S}(1)\text{-Hf}(1)\text{-O}(8)$ 160.92(7).

geometry and two tetrahedral aluminium atoms linked *via* oxygen atoms of the tbop ligands. The $\text{Zr}-\text{O}$ and $\text{Zr}-\text{S}$ distances are very similar to those in $[\text{Zr}(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2\text{Me}_2(\mu\text{-AlMe}_2)_2]$ ^{23d} and as expected slightly shorter than those detected for the octahedral complex **3**. The $\text{Al}-\text{O}$ and $\text{Al}-\text{Cl}$ bond lengths are close to those found in other structures of aluminium aryloxides and chlorides respectively.^{23b,c,24,25}

The ^1H NMR spectra of **5** and **6** were similar and afforded a single set of resonances for the tbop ligand in accordance with the ground-state structure established by crystallography. Compounds **5** and **6** are the chloride analogues of the previously described methyl derivatives $[\text{M}(\text{tbop-}\kappa^3\text{O,S,O})_2\text{Me}_2(\mu\text{-AlMe}_2)_2]$ ($M = \text{Ti}$, Zr , Hf) obtained in the reaction of $[\text{M}(\text{tbop-}\kappa^3\text{O,S,O})_2]$ with two equivalents of AlMe_3 .^{23d}

The reaction of MCl_4 with organoaluminium precursor $[\text{Al}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2\text{Me}_2]$ ^{23c} at 2:1 molar ratio in toluene resulted in the formation of colorless solids (**A**) for $M = \text{Zr}$ and (**B**) for



Scheme 2 Synthesis of zirconium and hafnium complexes **5–8**.

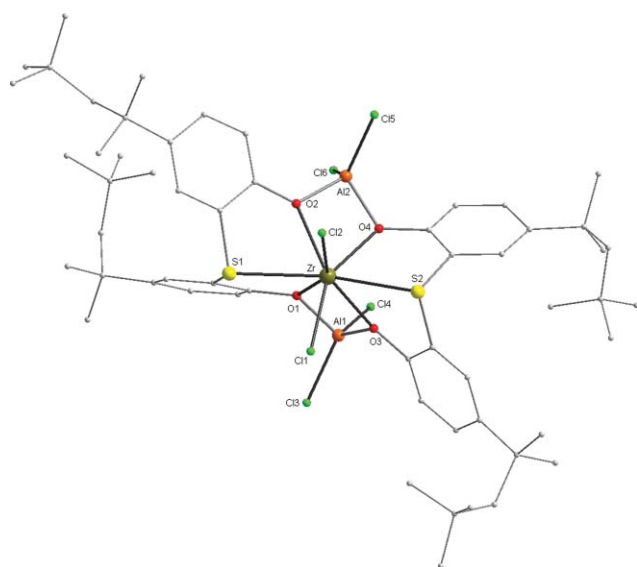


Fig. 2 Molecular structure of $[\text{Zr}(\text{tbp}-\kappa^3\text{O,S,O})_2\text{Cl}_2(\mu\text{-AlCl}_2)_2]$ (**5**)·0.5C₆H₁₄ (hydrogen atoms and C₆H₁₄ omitted for clarity). Selected bond lengths (Å) and angles (°): Zr–S(1) 2.765(2), Zr–S(2) 2.780(2), Zr–O(1) 2.198(2), Zr–O(2) 2.338(2), Zr–Cl(1) 2.400(2), Al(1)–O(1) 1.799(2), Al(1)–O(3) 1.777(2), Al(1)–Cl(3) 2.096(2), Al(1)–Cl(4) 2.087(2), S(1)–Zr–S(2) 150.00(3), O(1)–Zr–O(2) 77.11(8), O(1)–Zr–O(4) 89.17(8), O(3)–Zr–Cl(2) 146.06(6), Cl(2)–Zr–Cl(1) 92.77(3), O(3)–Al(1)–O(1) 85.45(11), O(3)–Al(1)–Cl(4) 112.84(11), O(1)–Al(1)–Cl(3) 110.14(9).

M = Hf. The ¹H NMR spectra of **A** and **B** show signals at –0.01 and –0.03 ppm for **A**, and –0.02 and –0.06 ppm for **B** indicating inequivalent methyl groups attached to aluminium atoms and two sets of resonances due to the tbp ligand. These may suggest that **A** and **B** are a mixture of chemically different compounds in solution.

The solid state structure of crystals obtained by recrystallization of **B** from CH₂Cl₂ showed it to be the cocrystallite of $[\text{Hf}(\text{tbp}-\kappa^3\text{O,S,O})_2\text{Cl}_2(\mu\text{-AlCl}_2)_2]$ (**6**) and $[\text{Hf}(\text{tbp}-\kappa^3\text{O,S,O})_2\text{Cl}_2(\mu\text{-AlMe}_2)_2]$ (**8**) species in a 3:2 ratio (Scheme 2) (Fig. 3).

Thus, the structure of **6·8**·CH₂Cl₂ is composed of two chemically independent molecules, which are statistically distributed in the crystal and one molecule CH₂Cl₂ of crystallization. The Hf–O and Hf–S bond lengths and angles are in a similar range and

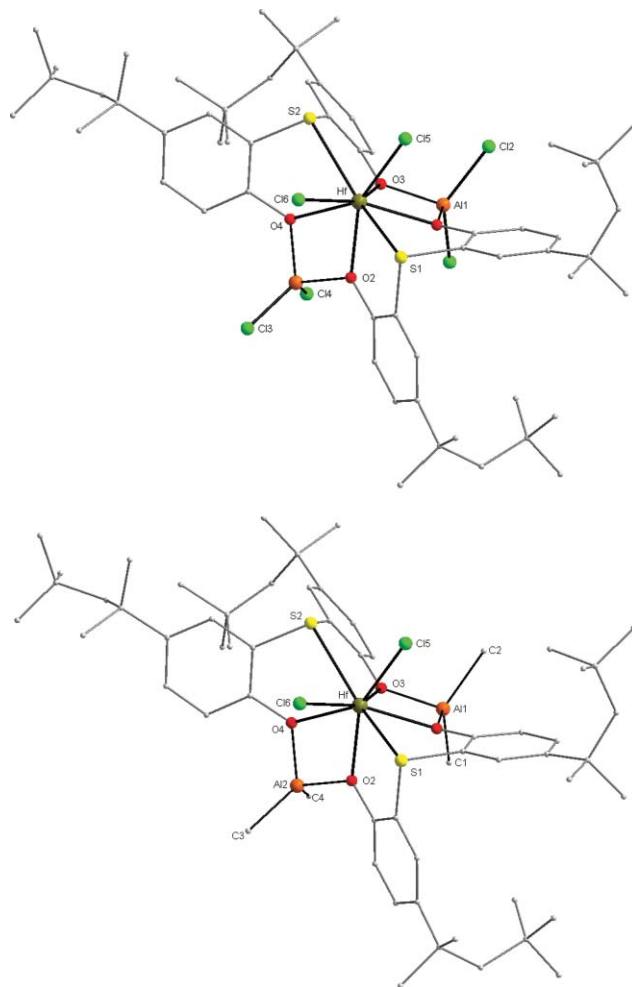


Fig. 3 Molecular structure of the cocrystallite $[\text{Hf}(\text{tbp}-\kappa^3\text{O,S,O})_2\text{Cl}_2(\mu\text{-AlCl}_2)_2]_3[\text{Hf}(\text{tbp}-\kappa^3\text{O,S,O})_2\text{Cl}_2(\mu\text{-AlMe}_2)_2]_2$ (**6·8**)·CH₂Cl₂ (**6** at the top, **8** at the bottom) (hydrogen atoms and CH₂Cl₂ omitted for clarity). Selected bond lengths (Å) and angles (°): Hf–S(1) 2.782(2), Hf–S(2) 2.776(2), Hf–O(1) 2.309(2), Hf–O(2) 2.189(2), Hf–O(3) 2.164(2), Hf–Cl(1) 2.405(2), Al(1)–O(1) 1.796(2), Al(1)–O(3) 1.834(2), S(1)–Hf–S(2) 148.61(3), O(1)–Hf–O(2) 76.47(7), O(1)–Hf–O(4) 125.56(7), O(3)–Hf–Cl(2) 149.23(5), Cl(2)–Hf–Cl(1) 92.05(4), O(3)–Al(1)–O(1) 83.63(10).

close to those of previously reported $[\text{Hf}(\text{tbp}-\kappa^3\text{O},\text{S},\text{O})_2\text{Me}_2(\mu\text{-AlMe}_2)_2]$.^{23d} However, because of disorder at the tetrahedral aluminium atoms arising from unequal distribution of carbon atoms of methyl groups and chlorides at aluminium centers (see Experimental section) discussion of Al–C and Al–Cl distances is impossible. The ^1H NMR spectra of **A** is similar to **B** and suggest it to be also a mixture of **5** and $[\text{Zr}(\text{tbp}-\kappa^3\text{O},\text{S},\text{O})_2\text{Cl}_2(\mu\text{-AlMe}_2)_2]$ (**7**).

The formation of compounds **5**–**8** occurs *via* the substitution of two chlorides at the central transition metal by two tridentate *tbp* groups and as a result zirconium and hafnium reach a coordination number of eight in formed anionic $[\text{M}(\text{tbp}-\kappa^3\text{O},\text{S},\text{O})_2\text{Cl}_2]^-$ species whereas two cationic $[\text{AlCl}_2]^+$ or $[\text{AlMe}_2]^+$ moieties undergo addition to the oxygen atoms of the *tbp* ligands to achieve a tetrahedral geometry. Although compounds **5** and **6** are chloride analogs of methyl derivatives, to our knowledge they represent the first examples of eight-coordinate dichloride zirconium or hafnium complexes bearing AlCl_2 moieties. Unfortunately, attempts to obtain **7** and **8** in a pure form failed.

Polymerization of 1-hexene

To assess the potential of complexes **1**–**6** in α -olefin polymerization catalysis, we performed the preliminarily tests in ethene and 1-hexene polymerization, using both heterogeneous and homogeneous processes with different cocatalysts and under variable conditions. Upon activation of compounds **1**–**6** with aluminium alkyls (Al^iBu_3 , MAO) and supporting on MgCl_2 in *n*-hexane no active catalysts for ethene polymerization had formed whereas the same systems acted as a catalyst in the 1-hexene polymerization process. Catalysts for 1-hexene polymerization were prepared in *n*-hexane by milling a slurry of $[\text{MgCl}_2(\text{thf})_2]$ with the zirconium or hafnium compound (10:1). Then the sample of precatalyst suspension was added to the mixture of 1-hexene and aluminium activator (40:1). The activity of catalysts was found to be practically independent on temperature (293 K or 323 K) and the geometry of zirconium and hafnium sites in precursors and was calculated to be higher (about 40 g mmol^{-1}) for Al^iBu_3 than for MAO as cocatalysts (Table 1). Lower activity or its lack was achieved for systems activated with MAO in homogeneous systems (runs 3, 6, 9, 12, 15, 18, Table 1).

The ^{13}C NMR spectra of poly(1-hexenes) revealed a regioregular and stereoirregular (atactic) structure. The polymers had very high molecular weights in the range $518\,000$ – $937\,000 \text{ g mmol}^{-1}$ and a narrow molecular weight distribution. These results are in contrast to the $[\text{Zr}(\text{tbpmp}-\kappa^3\text{O},\text{S},\text{O})\text{Cl}_2]/\text{MAO}$ system which do not polymerize 1-hexene.^{3a} It has been suggested that the *tbpmp* ligand provides sufficient steric hindrance to suppress 2,1-insertion of 1-hexene. However, the corresponding double sulfur donor system $[\text{Zr}(\text{dtbpm}-\kappa^4\text{OSSO})(\text{bn})_2]/\text{B}(\text{C}_6\text{F}_5)_3$ having the same substituents at the phenolate groups like the *tbpmp*, effectively polymerizes 1-hexene and reveals an atactic structure of poly(1-hexene) with a relatively low molecular weight (7400 g mol).^{22e} In this context the activity of the $[\text{Ti}_2(\text{tbpmp}-\kappa^3\text{O},\text{S},\text{O})_2(\mu\text{-Cl})_2\text{Cl}_2]/\text{MAO}$ system in a specific polymerization of 1-hexene affording atactic poly(1-hexene) is not comprehensible. It is worthy to mention that our heterotrinnuclear titanium complex $[\text{Ti}(\text{tbp}-\kappa^3\text{O},\text{S},\text{O})_2\text{Me}_2(\mu\text{-AlMe}_2)_2]^{23d}$ supported on MgCl_2 upon activation with Al^iBu_3 showed moderate activity in 1-hexene polymerization

Table 1 1-Hexene polymerization results with complexes **1**–**6**^a

Run	Compound	Activator	Activity [g PH/mmole ⁻¹ h ⁻¹]	$M_w \cdot 10^{-3}$	M_w/M_n
1	1	Al^iBu_3	33	93.7	3.3
2	1	MAO	25	—	—
3 ^b	1	MAO	17	—	—
4	2	Al^iBu_3	37	59.5	3.4
5	2	MAO	14	—	—
6 ^b	2	MAO	0	—	—
7	3	Al^iBu_3	40	63.5	2.6
8	3	MAO	0	—	—
9 ^b	3	MAO	0	—	—
10	4	Al^iBu_3	31	84.7	3.1
11	4	MAO	24	—	—
12 ^b	4	MAO	0	—	—
13	5	Al^iBu_3	32	51.8	2.7
14	5	MAO	16	—	—
15 ^b	5	MAO	14	—	—
16	6	Al^iBu_3	43	55.4	2.4
17	6	MAO	25	—	—
18 ^b	6	MAO	23	—	—

^a Polymerization conditions: $[\text{M}]_0 = 0.1 \text{ mmol dm}^{-3}$, $[\text{Al}] = 2 \text{ mmol dm}^{-3}$, $\text{Mg}/\text{M} = 10$, $T = 293 \text{ K}$. ^b Without MgCl_2 .

to produce atactic poly(1-hexene) ($30 \text{ g mmol}^{-1} \text{ h}^{-1}$). Thus, so far accessible data have not been indicative of factors determining the activity, molecular weight and stereoregularity of 1-hexene polymerization by the sulfur donor based systems and further studies in this area are essential for explanation of this problem.

Conclusions

We have demonstrated the synthesis of a family of neutral zirconium and hafnium complexes of the tridentate thio(bisphenolato) ligand (*tbp*). An effective route for the preparation of $[\text{M}_2(\mu\text{-tbp}-\kappa^3\text{O},\text{S},\text{O})_2\text{Cl}_4]$ ($\text{M} = \text{Zr}$ **1**, Hf **2**) species was based on the direct reaction between MCl_4 and one equivalent of *tbpH*₂ in toluene. Substitution of the chlorides in **1** and **2** by 2,6-diisopropylphenolato groups (*dipp*) generates new dimeric compounds $[\text{M}_2(\mu\text{-tbp}-\kappa^3\text{O},\text{S},\text{O})_2(\text{dipp})_4]$ ($\text{M} = \text{Zr}$ **3**, Hf **4**). The structures of **1**–**4** were confirmed by NMR spectroscopy; complexes **3** and **4** were further investigated by X-ray crystallography. The use of the *tbp*-aluminium precursors $[\text{Al}_2(\mu\text{-OEt})_2(\text{tbp}-\kappa^3\text{O},\text{S},\text{O})_2]$ or $[\text{Al}_2(\mu\text{-tbp}-\kappa^3\text{O},\text{S},\text{O})_2\text{Me}_2]$ in reactions with MCl_4 creates heterotrinnuclear complexes $[\text{M}(\text{tbp}-\kappa^3\text{O},\text{S},\text{O})_2\text{Cl}_2(\mu\text{-AlX}_2)_2]$ ($\text{M} = \text{Zr}$, $\text{X} = \text{Cl}$ **5**, $\text{X} = \text{Me}$ **7** and Hf $\text{X} = \text{Cl}$ **6**, $\text{X} = \text{Me}$ **8**). The single-crystal X-ray diffraction analysis of those complexes showed for zirconium and hafnium centers to have eight-coordinate dodecahedral geometry and aluminium atoms to have tetrahedral surroundings. Complexes **1**–**6** after activation with aluminium alkyls and supporting on MgCl_2 showed a lack of activity in the ethene polymerization process and moderate activity towards 1-hexene producing high molecular weight atactic poly(1-hexenes). Their narrow molecular weight distribution indicates that the operation of heterogeneous single-site catalysts occurs. Similar activities of those systems towards 1-hexene suggests that independently on the geometry of zirconium and hafnium sites in precursors **1**–**6** the same type of active centers are produced during their activation with aluminium alkyls.

Experimental

General remarks

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 ZrCl_4 , HfCl_4 , AlMe_3 , MAO, $\text{Al}(\text{i-Bu})_3$ and 2,2'-thiobis{4-(1,1,3,3-tetramethyl-butyl)phenol} (tbopH_2) were obtained from the Aldrich Chemical Co. and used without further purification unless stated otherwise. $[\text{Al}_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2]$ and $[\text{Al}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2\text{Me}_2]$ were prepared by literature method.^{23c} Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer in Nujol mulls. NMR spectra were performed on a Bruker ARX 300 spectrometer. Microanalysis were conducted with a ASA-1 (GDR, Karl-Zeiss-Jena) instrument (in-house).

$[\text{Zr}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2\text{Cl}_4]$ (1)

To a suspension of ZrCl_4 (1.35 g; 5.79 mmol) in toluene (40 mL) was added tbopH_2 (2.56 g; 5.79 mmol). The mixture was stirred at room temperature until the evolution of HCl had ceased (48 h). Then all volatiles were removed under reduced pressure to obtain a light yellow solid (2.54 g, 73%). (Found: C 55.39; H 6.58; Cl 11.29; S 5.43. $\text{C}_{56}\text{H}_{80}\text{Cl}_4\text{O}_4\text{S}_2\text{Zr}_2$ requires C 55.79; H 6.69; Cl 11.56; S 5.32%. $\nu_{\text{max}}/\text{cm}^{-1}$ 356 (m), 380 (s), 452 (m), 492 (s), 524 (s), 556 (m), 622 (s), 730 (3), 760 (s), 832 (vs), 884 (s), 976 (m), 1062 (s), 1100 (m), 1148 (m), 1252 (vs), 1268 (s), 1324 (s), 1364 (s), 1376 (s), 1402 (m), 1412 (s), 1596 (m) (Nujol). δ_{H} (300 MHz, C_6D_6 , 298 K) 8.53–6.57 (12H, m, C_6H_3), 1.62 [8H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 1.26 [24H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 0.72 [36H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]. δ_{C} (75.5 MHz, C_6D_6 , 298 K) 154.5, 146.9, 130.9, 128.9, 124.2, 117.9 (C_6H_3), 57.1 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 38.2, 32.8, 31.3, 30.3 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$].

$[\text{Hf}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2\text{Cl}_4]$ (2)

This complex was prepared in an analogous manner to that employed to **1** from HfCl_4 (1.26 g; 3.93 mmol) and tbopH_2 (1.74 g; 3.93 mmol) as a colorless solid (2.22 g, 82%). (Found C 48.55; H 5.55; Cl 9.85; S 4.68. $\text{C}_{56}\text{H}_{80}\text{Cl}_4\text{O}_4\text{S}_2\text{Hf}_2$ requires C 48.73; H 5.84; Cl 10.28; S 4.65%. $\nu_{\text{max}}/\text{cm}^{-1}$ 320 (m), 338 (vs), 420 (vw), 440 (w), 466 (m), 462 (s), 474 (w), 528 (m), 558 (w), 586 (m), 600 (s), 676 (m), 732 (vs), 736 (s), 756 (vs), 830 (vs), 852 (m), 868 (s), 924 (m), 976 (w), 1056 (vs), 1100 (m), 1140 (m), 1224 (vs), 1250 (vs), 1278 (vs), 1324 (m), 1364 (vs), 1372 (m), 1376 (vs), 1596 (m) (Nujol). δ_{H} (300 MHz, C_6D_6 , 298 K): 8.64–6.96 (12H, m, C_6H_3), 1.68 [8H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 1.29 [24H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 0.82 [36H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]. δ_{C} (75.5 MHz, C_6D_6 , 298 K) 129.2, 128.5, 126.3, 125.6, 125.1, 124.8 (C_6H_3), 56.8 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 38.3, 32.2, 32.0, 31.9 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$] ppm.

$[\text{Zr}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2(\text{dipp})_4]$ (3)

To a solution of **1** (2.62 g; 2.17 mmol) in diethyl ether (30 mL) was added Li(dipp) (1.60 g; 8.70 mmol) dissolved in diethyl ether (20 mL). The mixture was stirred over a period of 12 h and then filtered to remove LiCl. Reduction of the filtrate volume to 10 mL

and storage at 253 K for a one week provided colorless crystals of **3** (2.39 g, 62%). (Found C 73.01; H 8.51; S 3.81. $\text{C}_{104}\text{H}_{148}\text{O}_8\text{S}_2\text{Zr}_2$ requires C 73.10; H 8.73; S 3.75%. $\nu_{\text{max}}/\text{cm}^{-1}$ 446 (m), 478 (s), 525 (m), 568 (m), 631 (m), 739 (m), 762 (s), 839 (vs), 881 (m), 982 (m), 1067 (s), 1120 (m), 1144 (m), 1261 (vs), 1274 (m), 1334 (s), 1358 (s), 1412 (m), 1433 (s), 1591 (m) (Nujol). δ_{H} (300 MHz, C_6D_6 , 298 K) 7.63–6.70 (24H, m, C_6H_3), 3.72 [8H, septet, $\text{C}_6\text{H}_3\{\text{CH}(\text{CH}_3)_2\}_2$], 1.76, 1.68 [8H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 1.33, 1.29 [24H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 1.21 [48H, d, $\text{C}_6\text{H}_3\{\text{CH}(\text{CH}_3)_2\}_2$], 0.84 [36H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]. δ_{C} (75.5 MHz, C_6D_6 , 298 K) 163.6, 140.9, 136.9, 133.9, 131.7, 129.7, 123.8, 123.5, 118.6 (C_6H_3), 56.7 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 37.9, 32.2, 31.5, 27.9 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 27.2 [$\text{C}_6\text{H}_3\{\text{CH}(\text{CH}_3)_2\}_2$], 22.9 [$\text{C}_6\text{H}_3\{\text{CH}(\text{CH}_3)_2\}_2$].

$[\text{Hf}_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2(\text{dipp})_4]$ (4)

This complex was prepared in an analogous manner to that employed to **3** from **2** (1.88 g; 1.36 mmol) and Li(dipp) (1.00 g; 5.45 mmol) as colorless crystals (1.78 g, 67%). (Found C 65.91; H 7.56; S 3.47. $\text{C}_{104}\text{H}_{148}\text{O}_8\text{S}_2\text{Hf}_2$ requires C 66.32; H 7.92; S 3.40%. $\nu_{\text{max}}/\text{cm}^{-1}$ 442 (m), 455 (m), 471 (s), 485 (w), 531 (m), 558 (w), 582 (m), 611 (s), 656 (m), 667 (vs), 725 (s), 738 (s), 764 (vs), 836 (vs), 862 (m), 866 (s), 912 (m), 924 (m), 964 (w), 1071 (vs), 1106 (m), 1128 (m), 1231 (s), 1262 (s), 1270 (vs), 1324 (m), 1362 (vs), 1374 (w), 1581 (m) (Nujol). δ_{H} (300 MHz, C_6D_6 , 298 K) 7.63–6.70 (24H, m, C_6H_3), 3.74 [8H, septet, $\text{C}_6\text{H}_3\{\text{CH}(\text{CH}_3)_2\}_2$], 1.76, 1.68 [8H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 1.34 [24H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 1.25 [48H, d, $\text{C}_6\text{H}_3\{\text{CH}(\text{CH}_3)_2\}_2$], 0.83 [36H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]. δ_{C} (75.5 MHz, C_6D_6 , 298 K) 163.6, 141.1, 133.9, 131.9, 129.75, 123.7, 123.1, 121.2, 119.4 (C_6H_3), 56.6 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 37.9, 32.4, 32.2, 31.5 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 27.3 [$\text{C}_6\text{H}_3\{\text{CH}(\text{CH}_3)_2\}_2$], 22.9 [$\text{C}_6\text{H}_3\{\text{CH}(\text{CH}_3)_2\}_2$].

$[\text{Zr}(\text{tbop-}\kappa^3\text{O,S,O})_2\text{Cl}_2(\mu\text{-AlCl}_2)_2]$ (5)·0.5 C_6H_4

A mixture of ZrCl_4 (1.64 g; 7.02 mmol) and $[\text{Al}_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2]$ (3.6 g; 3.51 mmol) in toluene (40 mL) was stirred at room temperature for 18 h. The resulting mixture was filtered to remove $[\text{ZrCl}_2(\text{OEt})_2]$, and the filtrate was evaporated *in vacuo*, leaving a colorless solid, which was washed with *n*-hexane (2 × 5 mL) and dried under vacuum to give a colorless powder (3.57 g, 82%). (Found: C 54.02; H 6.68; Cl 16.96; S 5.33. $\text{C}_{56}\text{H}_{80}\text{Cl}_6\text{O}_4\text{S}_2\text{Al}_2\text{Zr}$ requires C 54.28; H 6.41; Cl 17.16; S 5.17%. $\nu_{\text{max}}/\text{cm}^{-1}$ 379 (s), 451 (m), 484 (s), 536 (s), 557 (m), 632 (s), 728 (3), 762 (s), 832 (vs), 874 (s), 972 (m), 1054 (s), 1101 (m), 1149 (m), 1253 (vs), 1266 (s), 1323 (s), 1364 (s), 1369 (s), 1410 (m), 1434 (s), 1582 (m) (Nujol). δ_{H} (300 MHz, C_6D_6 , 298 K) 7.67–7.09 (12H, m, C_6H_3), 1.63, 1.57 [8H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 1.28, 1.22 [24H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 0.77 [36H, s, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]. δ_{C} (75.5 MHz, C_6D_6 , 298 K) 159.3, 145.5, 140.2, 131.9, 130.1, 117.8 (C_6H_3), 57.5 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$], 38.1, 32.0, 31.8, 30.9 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$].

Crystals suitable for X-ray analysis were obtained by recrystallization from a mixture of *n*-hexane– CH_2Cl_2 (1 : 4) at 258 K.

The crystal structure shows the presence of 0.5 molecule of hexane in the unit cell, however the elemental analysis indicates

that this is absent from the powder sample analyzed, presumably removed by the vacuum drying to which they were subjected.

[Hf(tbp- κ^3 O,S,O)₂Cl₂(μ -AlCl₂)₂] (6)

This complex was prepared as described above for **5** starting from HfCl₄ (0.93 g; 2.92 mmol) and [Al₂(μ -OEt)₂(tbp- κ^3 O,S,O)₂] (1.50 g; 1.46 mmol). Workup afforded a white powder of **6** (1.63 g, 84%). (Found: C 50.01; H 6.01; Cl 15.95; S 4.58. C₅₆H₈₀Cl₆O₄S₂Al₂Hf requires C 50.70; H 6.08; Cl 16.04; S 4.82%). $\nu_{\max}/\text{cm}^{-1}$ 318 (w), 336 (vs), 422 (w), 445 (w), 456 (m), 464 (s), 478 (w), 532 (m), 562 (w), 582 (m), 612 (s), 666 (m), 736 (s), 732 (s), 749 (vs), 832 (s), 849 (m), 862 (s), 920 (m), 966 (w), 1049 (vs), 1105 (m), 1138 (m), 1228 (vs), 1246 (vs), 1282 (vs), 1314 (m), 1358 (vs), 1370 (m), 1374 (vs), 1586 (m) (Nujol). δ_{H} (300 MHz, C₆D₆, 298 K) 7.67–7.09 (12H, m, C₆H₃), 1.63, 1.57 [8H, s, C(CH₃)₂CH₂C(CH₃)₃], 1.28, 1.22 [24H, s, C(CH₃)₂CH₂C(CH₃)₃], 0.68 [36H, s, C(CH₃)₂CH₂C(CH₃)₃]. δ_{C} (75.5 MHz, C₆D₆, 298 K) 159.2, 145.5, 140.2, 131.9, 130.1, 117.8 (C₆H₃); 57.5 [C(CH₃)₂CH₂C(CH₃)₃]; 38.1, 32.9, 31.8, 30.9 [C(CH₃)₂CH₂C(CH₃)₃].

[Zr(tbp- κ^3 O,S,O)₂Cl₂(μ -AlCl₂)₂]₂[Zr(tbp- κ^3 O,S,O)₂Cl₂(μ -AlMe₂)₂]₂ (5·7)

These complexes were prepared as described above for **5** and **6** starting from ZrCl₄ (0.66 g; 2.87 mmol) and [Al₂(tbp- κ^3 O,S,O)₂Me₂] (2.78 g; 2.87 mmol). Workup afforded a white powder which after recrystallization from CH₂Cl₂ gave colorless, microcrystalline product. Yield for white powder: 2.52 g, 73.9% (calc. for starting ZrCl₄). Elemental analysis as well as NMR spectra were identical for both the powder and the crystalline form. (Found C 56.11; H 6.94; Cl 14.01; S 5.38. C₂₈₉H₄₂₆Cl₂₄O₂₀S₁₀Al₁₀Zr₅ requires C 56.74; H 7.02; Cl 13.91; S 5.24%). $\nu_{\max}/\text{cm}^{-1}$ 382 (s), 449 (m), 486 (s), 532 (s), 552 (m), 629 (s), 722 (3), 758 (s), 827 (vs), 879 (s), 966 (m), 1057 (s), 1107 (m), 1152 (m), 1249 (vs), 1262 (s), 1328 (s), 1359 (s), 1366 (s), 1412 (m), 1424 (s), 1586 (m) (Nujol). δ_{H} (300 MHz, C₆D₆, 298 K) 7.94–6.83 (24H, m, C₆H₃), 1.74, 1.68 1.63, 1.57 [16H, s, C(CH₃)₂CH₂C(CH₃)₃], 1.28, 1.22, 1.20, 1.14 [48H, s, C(CH₃)₂CH₂C(CH₃)₃], 0.72, 0.71 [72H, s, C(CH₃)₂CH₂C(CH₃)₃], –0.01, –0.03 (12H, s, Al–CH₃). δ_{C} (75.5 MHz, C₆D₆, 298 K) 155.3, 155.1, 146.9, 146.8, 131.5, 131.4, 130.2, 130.1, 123.7, 123.5, 118.4, 118.2 (C₆H₃), 57.1, 57.0 [C(CH₃)₂CH₂C(CH₃)₃], 32.3, 32.1, 31.9, 31.8, 31.5, 31.4, 31.3, 31.1 [C(CH₃)₂CH₂C(CH₃)₃], 14.3, 10.5 (Al–CH₃).

[Hf(tbp- κ^3 O,S,O)₂Cl₂(μ -AlCl₂)₂]₂[Hf(tbp- κ^3 O,S,O)₂Cl₂(μ -AlMe₂)₂]₂ (6·8)·CH₂Cl₂

These complexes were prepared as described above for **5·7** starting from HfCl₄ (0.72 g; 2.25 mmol) and [Al₂(tbp- κ^3 O,S,O)₂Me₂] (2.18 g; 2.25 mmol). Workup afforded a white powder which after recrystallization from CH₂Cl₂ gave colorless crystals suitable for X-ray analysis. Yield for white powder: 2.29 g, 78.96% (calc. for starting HfCl₄). Elemental analysis as well as NMR spectra were identical for both the white powder and the crystalline form of **6·8**. (Found: C 52.48; H 6.46; Cl 13.12; S 5.01. C₂₈₉H₄₂₆Cl₂₄O₂₀S₁₀Al₁₀Hf₅ requires C 52.96; H 6.55; Cl 12.96; S 4.88%). $\nu_{\max}/\text{cm}^{-1}$ 326 (vw), 336 (s), 422 (w), 452 (m), 458 (s), 478 (w), 542 (m), 556 (w), 581 (m), 611 (s), 672 (m), 744 (s), 758 (vs), 826

(s), 848 (m), 862 (s), 921 (m), 972 (w), 1062 (vs), 1112 (m), 1139 (m), 1234 (vs), 1244 (vs), 1281 (vs), 1326 (m), 1363 (s), 1370 (m), 1374 (s), 1592 (m) (Nujol). δ_{H} (300 MHz, C₆D₆, 298 K) 7.28–6.8 (24H, m, C₆H₃), 1.74, 1.68 1.63, 1.57 [16H, s, C(CH₃)₂CH₂C(CH₃)₃], 1.21, 1.20, 1.16, 1.17 [48H, s, C(CH₃)₂CH₂C(CH₃)₃], 0.67, 0.66 [72H, s, C(CH₃)₂CH₂C(CH₃)₃], –0.02, –0.06 (12H, s, Al–CH₃). δ_{C} (75.5 MHz, C₆D₆, 298 K) 155.6, 155.3, 146.8, 146.6 131.2, 131.1, 130.3, 130.1, 123.8, 123.7, 117.8, 117.6 (C₆H₃), 57.2, 57.1 [C(CH₃)₂CH₂C(CH₃)₃], 38.3, 38.2, 32.3, 32.2, 31.9, 31.8, 31.8, 31.7 [C(CH₃)₂CH₂C(CH₃)₃]; 10.9, 8.5 (Al–CH₃).

The crystal structure shows the presence of one CH₂Cl₂ molecule in the unit cell, however the elemental analysis indicates that this is absent from the powder sample analyzed, presumably removed by the vacuum drying to which they were subjected.

Polymerization of 1-hexene

A slurry of [MgCl₂(THF)₂] (100 mmol) and zirconium or hafnium precatalyst (10 mmol) in *n*-hexane was milled under argon in a glass mill (capacity 250 ml, with 20 balls of diameter 5–15 mm) at room temperature for 24 h. The sample of precatalyst suspension (containing 0.1 mmol of Zr or Hf) was added to the mixture of 1-hexene (80 mmol) and aluminium activator (2 mmol) in *n*-hexane (50 mL). The reaction mixture was stirred at 293 K or 323 K under argon and after 1 h polymerization was terminated by the addition of 20 mL of 5% solution of HCl in ethanol and dried under vacuum at 40 °C for 12 h.

Molecular weight and polydispersities of poly-1-hexene were measured by GPC method (Gel Permeation Chromatography), Waters-150, at 415 K in 1,2,4-trichlorobenzene.

Crystallographic analysis

Crystal data and refinement details for all compounds are given in Table 2.

The crystals were mounted on glass fibers and then flash-frozen to 100(2) K (Oxford Cryosystem-Cryostream Cooler). Preliminary examination and intensities data collections were carried out on a Kuma KM4 CCD κ -axis diffractometer with graphite-monochromated Mo K α radiation. All data were corrected for Lorentz, polarization and absorption effects. Data reduction and analysis were carried out with the Kuma Diffraction programs.²⁶ All structures were solved by direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL software.²⁷ Carbon bonded hydrogen atoms were included in calculated positions and refined in the riding mode using SHELXTL default parameters. Other hydrogen atoms were located in a difference map. All crystals were poorly shaped and weakly diffracting, giving low resolution data and relatively high *R*-values. One reason for this might be the high amount of disorder in the crystal structure. The high temperature factors of the terminal carbon atoms suggest their disorder, which unfortunately, could not be resolved. It was found that the structure of **6·8**·CH₂Cl₂ is composed of two chemically independent [Hf(tbp- κ^3 O,S,O)₂Cl₂(μ -AlCl₂)₂] and [Hf(tbp- κ^3 O,S,O)₂Cl₂(μ -AlMe₂)₂] molecules which are statistically distributed in the crystal. The terminal Cl and Me ligands in these complexes were refined with a 0.6 and 0.4 occupancy, respectively. Moreover the CH₂Cl₂ solvent molecule is split over three sites.

Table 2 Crystal data and collection parameters of complexes **3**, **4**, **5**-0.5C₆H₁₄ and **6**-8-CH₂Cl₂

Compound	3	4	5 -0.5C ₆ H ₁₄	6 -8-CH ₂ Cl ₂
Empirical formula	C ₁₀₄ H ₁₄₈ O ₈ S ₂ Zr ₂	C ₁₀₄ H ₁₄₈ Hf ₂ O ₈ S ₂	C ₅₉ H ₈₇ Al ₂ Cl ₆ O ₄ S ₂ Zr	C _{58.60} H _{86.80} Al ₂ Cl _{6.40} HfO ₄ S ₂
<i>M</i>	1772.78	1947.32	1282.29	1378.73
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	19.830(5)	19.776(5)	14.737(5)	14.802(4)
<i>b</i> /Å	19.186(5)	19.173(5)	15.552(5)	15.571(4)
<i>c</i> /Å	28.187(4)	28.240(4)	16.690(5)	16.625(4)
α /°	90	90	73.73(2)	73.88(3)
β /°	112.15(2)	112.24(2)	86.36(2)	86.93(3)
γ /°	90	90	62.22(2)	62.71(3)
<i>V</i> /Å ³	9933(4)	9911(4)	3239(2)	3259.2(18)
<i>Z</i>	4	4	2	2
<i>D</i> _c /Mg m ⁻³	1.186	1.305	1.311	1.405
Crystal size/mm ³	0.332 × 0.231 × 0.121	0.322 × 0.210 × 0.083	0.32 × 0.17 × 0.11	0.324 × 0.215 × 0.112
μ /mm ⁻¹	0.304	2.188	0.551	1.996
θ /°	2.82 to 27.00	2.83 to 28.53	2.89 to 27.00	2.88 to 27.00
Reflections collected	112 927	26 452	26 815	37 547
Unique reflections, <i>R</i> _(int)	21 660, 0.0529	23 439, 0.032	13 944, 0.0538	14 204, 0.056
Parameters	1073	1081	688	742
Final <i>R</i> ₁ , w <i>R</i> ₂ [<i>I</i> > σ (<i>I</i>)]	0.0647, 0.1063	0.0384, 0.0855	0.0507, 0.0822	0.0343, 0.0534
Final <i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.0924, 0.1140	0.0565, 0.0908	0.0822, 0.0916	0.0572, 0.0568
Goodness-of-fit (<i>S</i>)	1.245	1.080	0.936	0.984

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