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Homo- and Heterometallic Aluminum and Titanium Complexes of Tridentate (OSO) Ligand: Synthesis, Structure, and Catalytic Activity

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The tridentate (OSO-functions) biphenol, 2,2′-thiobis{4-(1,1,3,3-tetramethylbutyl)phenol} (tbopH$_2$), reacts with AlMe$_3$ to give [Al$_2$(μ-tbop-κ^3O,S,O)$_2$Me$_2$] (**1**). Alcoholysis of **1** results in the formation of [Al$_2$(μ-OEt)$_2$(tbop-κ^3O,S,O)$_2$] (**2**). The reaction of **2** with TiCl$_4$ gives the trimeric complex [Ti$_3$(μ-OEt)$_2$(μ-tbop-κ^3O,S,O)$_2$Cl$_6$] (**3**)·C$_6$H$_{14}$. Alkylation of **3**·C$_6$H$_{14}$ with LiMe produces two dimeric complexes, [Ti$_2$(μ-tbop-κ^3O,S,O)$_2$Me$_4$] (**4**) and [Ti$_2$(μ-OE)$_2$(tbop-κ^3O,S,O)$_2$Me$_2$] (**5**)·Et$_2$O. Treatment of [Ti$_2$(μ-OEt)$_2$(tbop-κ^3O,S,O)$_2$(OEt)$_2$] with AlMe$_3$ and EtOH afforded the heterobimetallic species, [Ti$_2$Al$_2$(μ-OEt)$_6$(μ-tbop-κ^3O,S,O)$_2$(OEt)$_4$] (**6**). The structures of **1**−**6** were confirmed by NMR spectroscopy; complexes **1**, **3**·C$_6$H$_{14}$, **5**·Et$_2$O, and **6** were further investigated by X-ray crystallography. Compounds **3**−**6**, when supported on MgCl$_2$ and activated with aluminum alkyls, effectively polymerize ethene.

Introduction

Investigation of nonmetallocene transition metal catalysts has become very popular in recent years. A new trend has been the incorporation of ancillary ligands, such as amido and alkoxo/aryloxo, and related polydentate ligands.[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, or S).[2] Titanium complexes, [Ti$_2$(μ-X)$_2$X$_2$(tbmp-κ^3O,S,O)$_2$], derived from the sulfide-linked bisphenol tbmpH$_2$ [tbmpH$_2$ = 2,2′-thiobis(6-*tert*-butyl-4-methylphenol); X = Cl, O-*i*Pr], activated with methylalumoxane (MAO), were first reported by Kakugo et al. to be highly active for the homogeneous polymerization of ethene, propene, styrene, and dienes, as well as the copolymerization of ethene with styrene.[3] Theoretical calculations predicted that the sulfur bridge in bisphenolates plays an important role in lowering insertion barriers for ethene.[4] Although the Ti−S interaction in thiobis(aryloxide) titanium complexes is weak, it is likely to be of importance in stabilizing the active cationic species, facilitating its formation from the former and MAO, and making the coordination of the counterion less tight.[5]

The conventional Ziegler−Natta (Z−N) catalysts used in industrial production of polyolefins are heterogeneous, referring not only to the insolubility of the catalyst in the polymerizing medium but also to its multisited nature. The result is catalysts that produce complex mixtures with widely varying molecular weights and microstructures. Our goal was to create highly active, single-site heterogeneous systems for the ethene polymerization process. The use of the tridentate (OSO-functions) ligand, 2,2′-thiobis{4-(1,1,3,3-tetramethylbutyl)phenolato} (tbop), allowed us to obtain a family of titanium complexes, such as alkoxo-bridged, [Ti$_2$(μ-OR)$_2$(X)$_2$(tbop-κ^3O,S,O)$_2$] (R = Me, Et; X = OR or Me), and aryloxo-bridged, [Ti$_2$(μ-tbop-κ^3O,S,O)$_2$Cl$_4$], [Ti$_2$(μ-tbop-κ^3O,S,O)(μ-tbop-κ^2O,O)(tbop-κ^3O,S,O)Cl$_2$], [Ti$_2$(μ-tbop-κ^3O,S,O)$_2$Cl$_2$(dipp)$_2$] (dipp = 2,6-diisopropylphenolato), [Ti$_2$(μ-tbop-κ^3O,S,O)$_2$(N-*t*Bu)$_2$(NH$_2$-*t*Bu)$_2$], as well as monomeric species, [Ti(tbop-κ^3O,S,O)Cl(OSiMe$_3$)(NH$_2$-*t*Bu)] and [NH$_2$-*i*Pr$_2$][TiCl$_3$(tbop-κ^3O,S,O)], have been created and structurally characterized.[6,7] These com-

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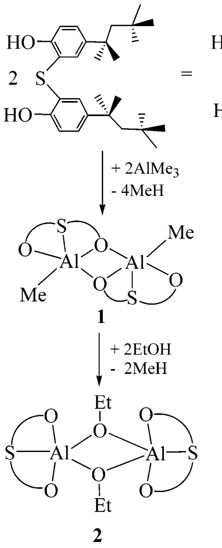
Scheme 1



plexes supported on $MgCl_2$, which is a widely used support in conventional Z−N catalysts, and activated with aluminum alkyls are highly effective ethene polymerization catalysts. Narrow molecular weight distribution for these systems ($M_w/M_n \sim 3$) suggests that the operation of heterogeneous well-defined single-site catalysts occurs. We have been exploring the use of the tbop ligand for preparation of further titanium complexes that might serve as catalysts for the polymerization of ethene. Especially, the interaction of titanium compounds with aluminum derivatives was of great interest to us for understanding the high activity of titanium sulfur-bridged aryloxides in ethene polymerization process.

Herein, we report a structurally characterized new family of complexes supported by the tbop ligand. The investigation of ethoxo−tbop−aluminum derivatives, $AlMe_3$ and LiMe, with titanium precursors has led us to synthesize and characterize trinuclear $[Ti_3(\mu\text{-OEt})_2(\mu\text{-tbop-}\kappa^3O,S,O)_2Cl_6]$, heterometallic tetranuclear $[Ti_2Al_2(\mu\text{-OEt})_6(\mu\text{-tbop-}\kappa^3O,S,O)_2(OEt)_4]$, and dinuclear alkyl $[Ti_2(\mu\text{-tbop-}\kappa^3O,S,O)_2Me_4]$ and $[Ti_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3O,S,O)_2Me_2]$ complexes. Additionally, their activity toward ethene polymerization has been studied.

Results and Discussion

Reaction of a toluene solution of $AlMe_3$ with $tbopH_2$ at a 1:1 molar ratio leads to vigorous evolution of methane, and the monomethyl air- and moisture-sensitive complex, $[Al_2(\mu\text{-tbop-}\kappa^3O,S,O)_2Me_2]$ (**1**), is formed (Scheme 1). Compound **1** does not react further with $tbopH_2$ under ambient conditions. The ^1H and ^{13}C NMR spectra of **1** are in good agreement with the crystal structure obtained from X-ray diffraction techniques. There is no OH resonance, indicating loss of hydroxyl protons. The alkyl groups attached to the metal centers are equivalent and are in the expected chemical shift ranges, with both the ^1H and ^{13}C signals shifted slightly from the starting $AlMe_3$. One set of resonances for the tbop ligand was observed, as well. These observations suggest that compound **1** has the same structure in solution and in the solid state.

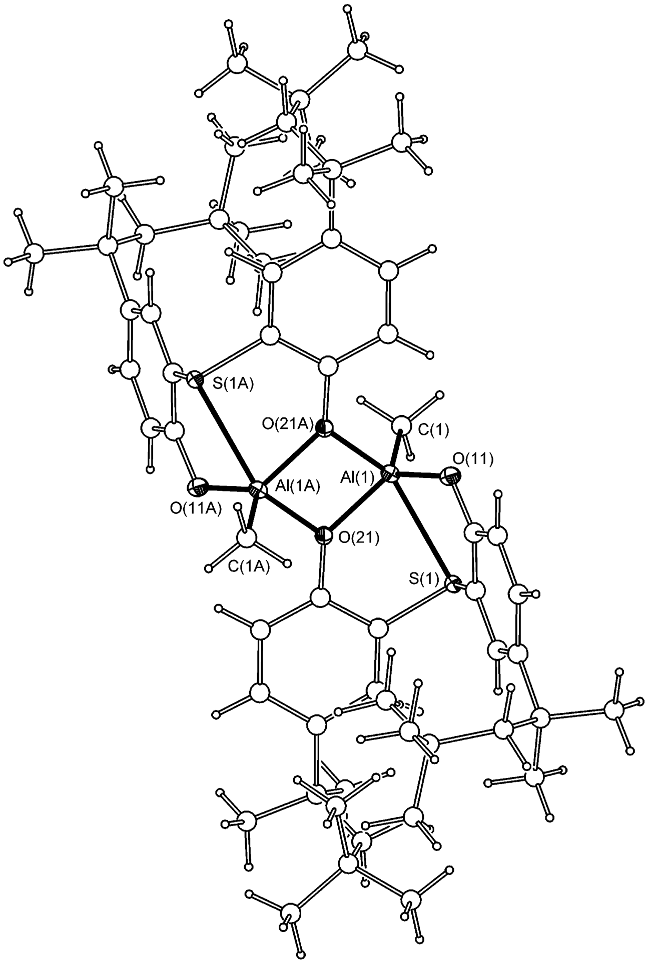


Figure 1. Molecular structure of **1**. Selected bond lengths (Å): Al(1)−C(1) 1.867(5), Al(1)−O(11) 1.761(3), Al(1)−O(21) 1.853(3), Al(1)−O(21A) 1.910(4), Al(1)−S(1) 2.675(2). Symmetry transformations used to generate equivalent atoms: $-x$, $-y + 1$, $-z$.

In the solid state, compound **1** forms dimeric molecules (Figure 1). The central, nearly planar four-membered ring is composed of two aluminum atoms and two bridging oxygen atoms [O(21), O(21A)] of the tbop ligand. This type of bridging has been frequently observed in phenolate aluminum compounds.[8] Each metal atom is coordinated in a distorted trigonal bipyramidal fashion by oxygen [O(21), O(21(A)] in axial and equatorial positions, and sulfur atoms of the tbop groups in axial position, and methyl groups and oxygen atoms [O(11), O(11A)] of the tbop ligands in equatorial position.

The Al−O bond lengths are similar to those found in other structures of five-coordinated aluminum aryloxides.[8e,f] The Al−C bond length of 1.867(5) Å is clearly within the range expected for Al−C terminal bond distances.[9] The Al−S distance of 2.675(2) Å is similar to that found in the five-coordinate monomeric complex,

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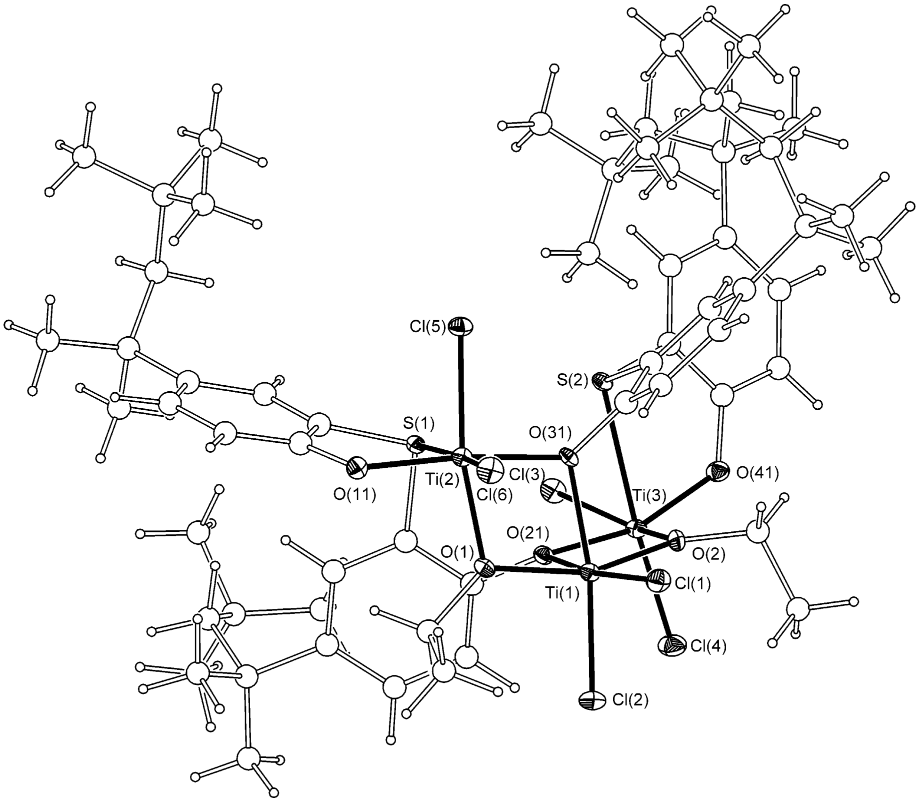

Figure 2. Molecular structure of **3**$\cdot C_6H_{14}$. Selected bond lengths (Å): Ti(1)−Cl(1) 2.252(2), Ti(1)−Cl(2) 2.237(2), Ti(1)−O(1) 1.953(5), Ti(1)−O(2) 1.955(3), Ti(1)−O(21) 2.051(4), Ti(1)−O(31) 2.060(4), Ti(2)−Cl(5) 2.260(2), Ti(2)−Cl(6) 2.236(2), Ti(2)−S(1) 2.723(2), Ti(2)−O(1) 2.016(4), Ti(2)−O(11) 1.825(5), Ti(2)−O(31) 2.019(5), Ti(3)−Cl(3) 2.268(2), Ti(3)−Cl(4) 2.230(2), Ti(3)−S(2) 2.725(2), Ti(3)−O(2) 2.011(4), Ti(3)−O(21) 2.022(5), Ti(3)−O(41) 1.824(5).

[Al(tbmp-κ^3O,S,O)Et(Et_2O)] [2.6603(10) Å],[10] and longer than those detected in the tetrahedral structures of [Al_2(tbmp-κ^3O,S,O)Et_4] [2.453(3) Å][10] and [Al(Metbmp-κ^2O,S)Et_2] [2.4926(11) Å].[10]

Compound **1** further reacts with ethanol, giving the ethoxo-bridged aluminum dimer [$Al_2(\mu$-OEt$)_2$(tbop-κ^3O,S,O$)_2$] (**2**). Alternatively, **2** can also be prepared directly by treatment with commercially available Al(OEt)$_3$ with tbopH_2 in toluene. Alkoxo character of bridges in **2** was deduced from the ^{1}H NMR spectra (see Experimental Section). Additionally, the presence of ethoxo bridges in **2** was confirmed chemically. Addition of pyridine to a solution of **2** does not break the dimeric structure. The formation of alkoxo bridges by alcoholysis of aluminum alkyls has been previously reported; for example, when precisely 2 equiv of 2-propanol is added to an etheral solution of the alkyl [Al(mbmp)R]$_2$ [mbmp = 2,2′-methylene(6-*tert*-butyl-4-methylphenolato); R = Me, Et], the isopropoxide [Al(mbmp)(μ-O-*i*Pr)]$_2$ is formed.[8h]

Compound **2** has been shown to be a useful precursor to polynuclear titanium compounds. When a hexane suspension of **2** was treated with $TiCl_4$ at a 1:3 molar ratio, the formation of the trimer [$Ti_3(\mu$-OEt$)_2(\mu$-tbop-κ^3O,S,O$)_2Cl_6$] (**3**)$\cdot C_6H_{14}$ was observed. The IR spectra of **3** show characteristic modes for terminal-coordinated chlorides at 418 cm^{-1}. The ^{1}H NMR spectra of **3** contain an expected set of resonances due to a coordinated tbop ligand and one set for OCH_2CH_3 protons. However, the OCH_2 groups are manifested as two closely spaced multiplets consistent with the presence of diastereotopic methylene groups. The fact that two resonances are not observed for the protons of OCH_2CH_3 groups may be attributed to an averaging process or coincidence resonances. Thus, it is likely that the compound **3** is not interconverting to other species in solution. The structure of **3**$\cdot C_6H_{14}$, shown in Figure 2, consists of discrete trimeric molecules of [$Ti_3(\mu$-OEt$)_2(\mu$-tbop-κ^3O,S,O$)_2Cl_6$] together with one hexane molecule of crystallization.

Three octahedral titanium atoms in **3** are double bridged by oxygen atoms of the tbop and the ethoxo ligands to form a Ti_3O_4 core. The sulfur atom and the second oxygen atom of each tbop ligand are coordinated to the peripheral titanium atoms. Additionally, the octahedral coordination sphere of titanium atoms is completed by two chloride atoms situated in cis positions. The Ti−O and Ti−μ−O distances of the tbop ligands range from 1.824(5) to 2.055(4) Å and are in the expected range for Ti(IV) complexes with nonbridging

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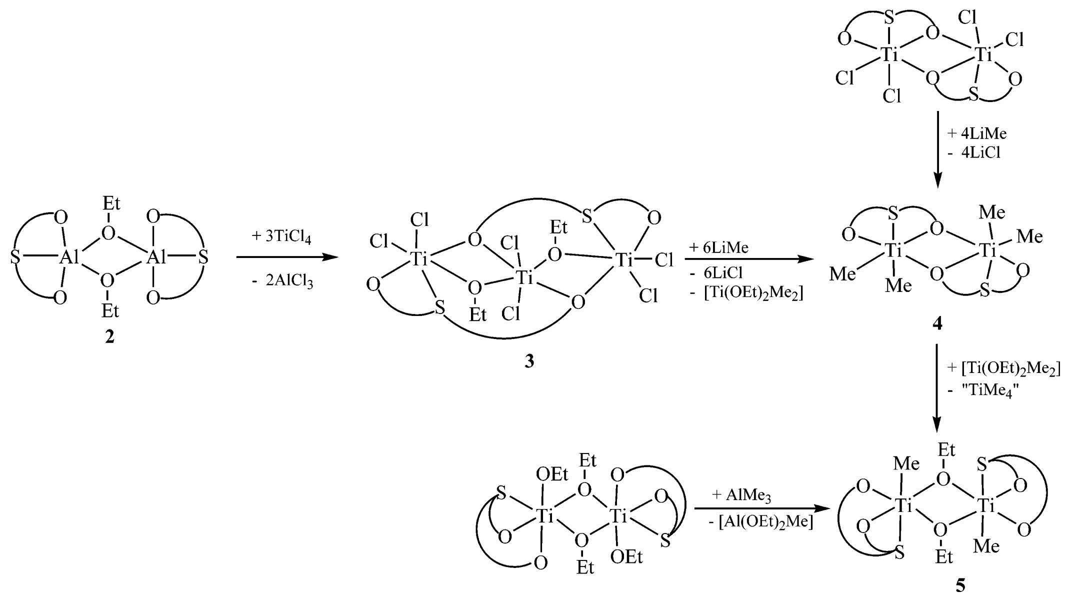
Scheme 2



and bridging aryloxo ligands, respectively.[11] The average titanium–sulfur bond length of 2.724(2) Å is similar to that found in the $[Ti_2(\mu\text{-O-}i\text{Pr})_2(\text{O-}i\text{Pr})_2(\text{tbmp-}\kappa^3\text{O,S,O})_2]$ complex, where tbmp = 2,2′-thiobis(6-*tert*-butyl-4-methylphenolato) [2.719(1) Å],[12] and slightly longer than those detected in $[Ti(\text{tbmp-}\kappa^3\text{O,S,O})(C_6H_4CH_2NMe_2\text{-2-}\kappa^2\text{C,N})Cl]$ [2.704(1) Å] and $[Ti(\text{tbmp-}\kappa^3\text{O,S,O})Cl(\text{O}i\text{Pr})(\text{HO}i\text{Pr})]$ [2.693(1) Å][4a,12] but significantly shorter than those found in $[Ti_2(\mu\text{-OEt})_2(\text{OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2]$ [2.800(1) Å] and $[\{Ti_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2\}_2(\mu\text{-O})_2]$ [2.762(2) Å].[6] The Ti–Cl distances are in the expected range for octahedral Ti(IV) complexes with terminal chlorides.

Treatment of **3** with precisely 6 equiv of LiMe in diethyl ether results in the formation of light yellow, very thin, needlelike crystals of $[Ti_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2Me_4]$ (**4**) in good yield (Scheme 2). Compound **4** can also be obtained in the reaction of $[Ti_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2Cl_4]$[7] with 4 equiv of LiMe in diethyl ether. Absence of ν(Ti–Cl) frequencies in the IR spectra of **4** indicates that chlorides were substituted with methyl groups. The methyl groups at each titanium center are equivalent, giving rise to one singlet at 1.34 ppm in the ^{1}H NMR spectra and to one resonance at 64.3 ppm in the ^{13}C NMR spectra. Also, one set of resonances due to the tbop ligand, slightly shifted from that detected for $[Ti_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2Cl_4]$,[7] was observed. For this reason, we suggest that compound **4** has dimeric structure with titanium atoms double-linked by oxygen atoms of the tbop ligand. Although the structure of the $[Ti_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2Cl_4]$ complex has not been crystallographically characterized, its dimeric nature with aryloxo-bridged titanium centers has been well documented.[7]

When the postreaction mixture of **3** with LiMe, after separation of LiCl was left for 2 weeks at 277 K, a mixture of two kinds of yellow crystals, needles of **4** and prisms of $[Ti_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2Me_2]$ (**5**)·Et$_2$O, was formed (Scheme 2). This result suggests that compound **4** reacts further with the ethoxo–titanium byproduct and that the substitution of one methyl group on each titanium atom in **4** by an ethoxo ligand occurs. To confirm this suggestion, the reaction of **4** with $Ti(OEt)_4$ at a 1:1 molar ratio in Et$_2$O was carried out, which gave compound **5**·Et$_2$O (see Experimental Section). Compound **5** has been previously obtained as **5**·toluene in the reaction of $[Ti_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2(\text{OEt})_2]$ with $AlMe_3$ in toluene, but because of the poor quality of the crystals, the X-ray diffraction data showed only its model.[6]

Crystals of **5**·Et$_2$O suitable for an X-ray structure determination were separated by hand from the mixture. The molecular structure of **5**·Et$_2$O is shown in Figure 3. Crystals of **5**·Et$_2$O comprise a centrosymmetric dimer with a planar Ti_2O_2 core. The coordination sphere around the titanium center can be described as octahedral, with the oxygen atoms of the tbop ligand [O(11), O(21)] and of two bridging OEt groups [O(1), O(1A)] forming the equatorial plane, while the carbon atom [C(1)] of the methyl group and the sulfur link of the tbop ligand occupy the apical sites. The two Ti–O(aryloxo) distances of 1.896(2) and 1.916(2) Å are in the expected range for Ti(IV) complexes with facially coordinated bisaryloxo ligands.[6,7,11] The Ti–μ–O(ethoxo) distance of 1.992(2) Å is typical for $Ti_2(\mu\text{-OR})_2$ moieties.[6,13] The Ti–C distance of 2.078(4) Å is similar to those observed in $[Ti_2(\mu\text{-OMe})_2Me_2(\text{tritox})_2]$ [2.063(10) Å][14] and $[Ti(\text{mbp})Me_2]$ (mbp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato) [2.090(9) and 2.030(10) Å].[11a] The Ti–S bond length of 2.985(1) Å is the longest among titanium complexes containing the sulfide-linked bisphenolato ligands.[2f,g,i,11e,12a]

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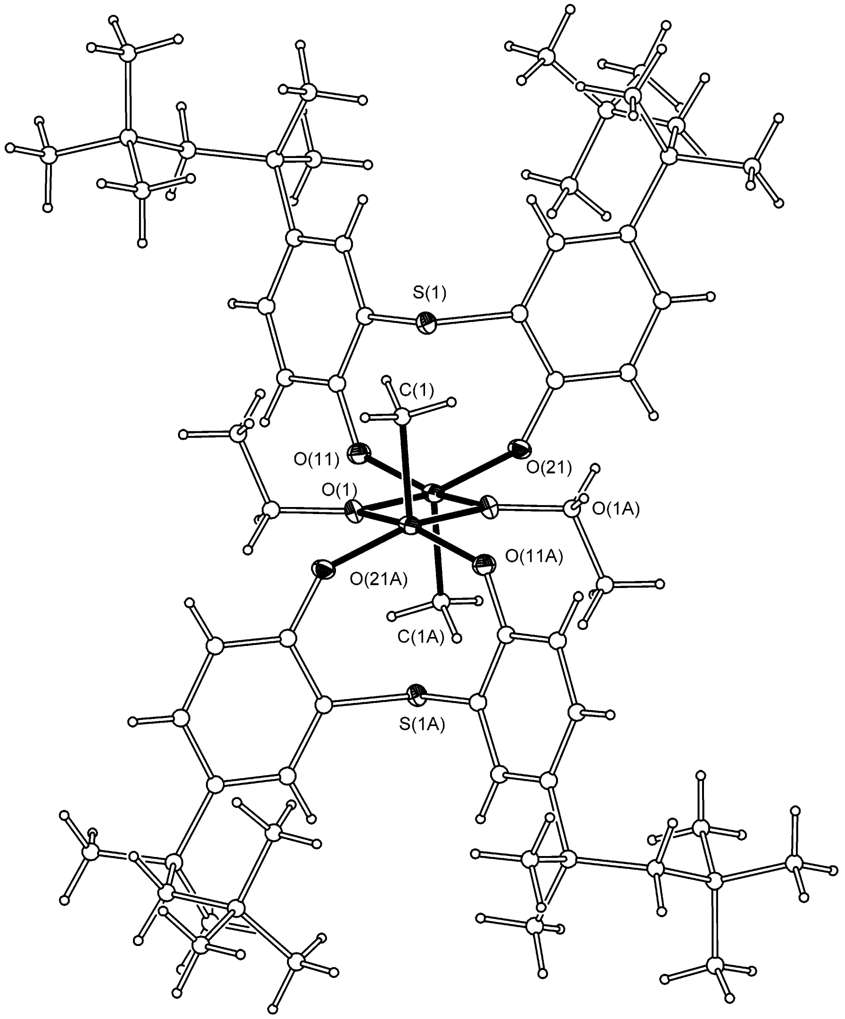
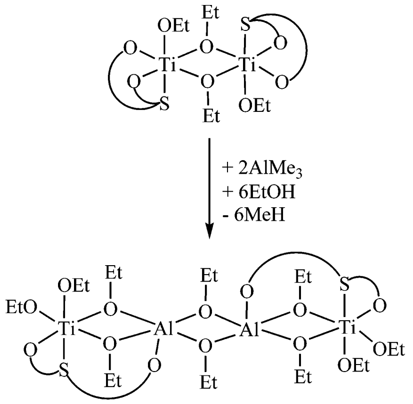


Figure 3. Molecular structure of $\mathbf{5}\cdot Et_2O$. Selected bond lengths (Å): Ti(1)−O(1) 1.992(2), Ti(1)−O(11) 1.861(2), Ti(1)−O(21) 1.851(2), Ti(1)−C(1) 2.078(4), Ti(1)−O(1A) 2.004(2). Symmetry transformations used to generate equivalent atoms: $-x + 1$, $-y$, $-z + 1$.

To determine whether any titanium precursors, such as $Ti(OR)_4$ where R = alkyl, would be able to generate similar trimeric species to **3**, the reaction of **2** with $Ti(OEt)_4$ (1:3) in toluene at room temperature was curried out. As a result, the formation of well-known dimeric $[Ti_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2(OEt)_2]$[6] was observed. However, when $[Ti_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2(OEt)_2]$ was treated with $AlMe_3$ at a 1:2 molar ratio in toluene, and then the reaction mixture was alcoholized with EtOH, the heterobimetallic tetranuclear species $[Ti_2Al_2(\mu\text{-OEt})_6(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2(OEt)_4]$ (**6**) was isolated (Scheme 3). The ^1H NMR spectrum of **6** indicates the presence of terminal and bridging OEt groups as well as tbop ligands in different environments since multiplet of quartets and triplets are obtained for the CH_2 and CH_3 of OEt groups, respectively, and two sets of resonances due to tbop ligands are observed.

Scheme 3



6

The X-ray crystal structure of **6** (Figure 4) shows that the discrete molecular unit contains a core of two peripheral titanium and two internal aluminum atoms linked by oxygen atoms from the six OEt groups. Remaining four OEt ligands are bonded terminally to the titanium atoms. Two of the tbop ligands are bonded similarly, having one oxygen atom at the titanium and other one at the aluminum coordination sphere. The octahedral environment of each titanium is completed by the sulfur atom of the tbop ligand. The aluminum atoms in **6** have the trigonal bipyramidal geometry. As expected, the average Ti−μ−O(ethoxo) distance of 2.033(3) Å is significantly longer than the terminal ones [av. 1.788 (3) Å]. The Ti−S distance of 2.888(2) Å is shorter than that detected in $\mathbf{5}\cdot Et_2O$ and is only surpassed by the value of 2.907(1) Å found in $[Ti(tbmp)(\eta^5\text{-}C_5H_5)Cl]$.[11e] The average Al−$\mu$−O(ethoxo) distance of 1.858(3) Å is somewhat longer than those found in the tetrahedral structures of dimeric aluminum alkox-

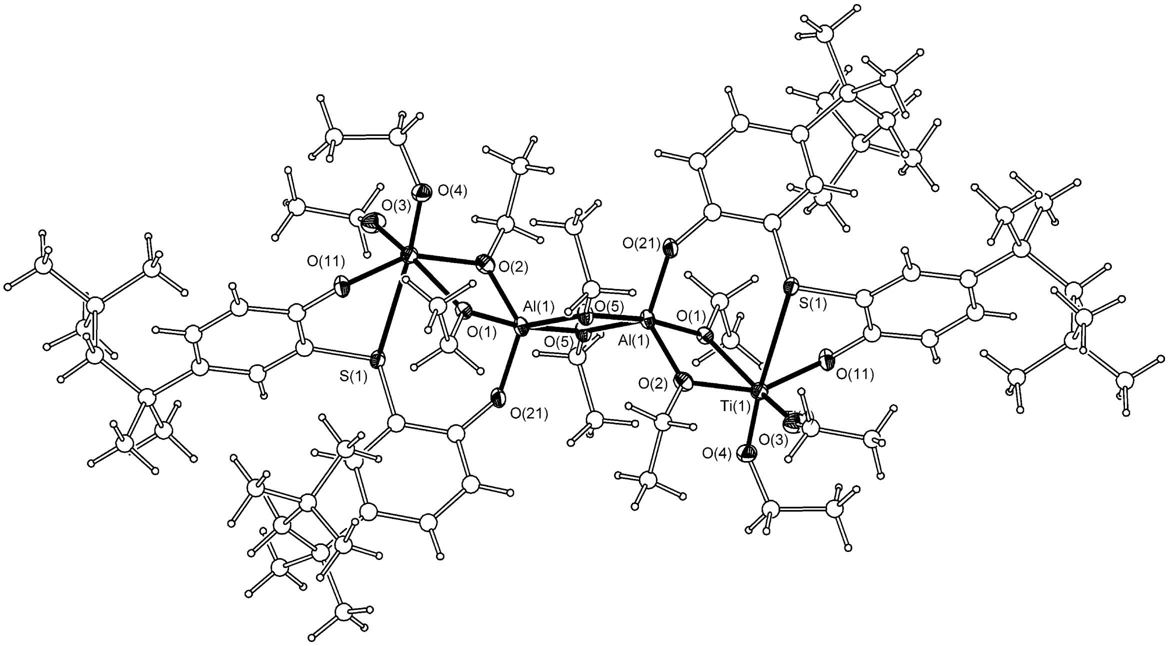


Figure 4. Molecular structure of **6**. Selected bond lengths (Å): Ti(1)−S(1) 2.888(2), Ti(1)−O(1) 2.024(3), Ti(1)−O(2) 2.043(3), Ti(1)−O(3) 1.786(3), Ti(1)−O(4) 1.790(3), Ti(1)−O(11) 1.898(3), Al(1)−O(1) 1.866(3), Al(1)−O(2) 1.808(3), Al(1)−O(5) 1.812(3), Al(1)−O(21) 1.759(3), Al(1)−O(5A) 1.904(3). Symmetry transformations used to generate equivalent atoms: −*x*, −*y*, −*z* + 1.

ides, such as [Al(mbmp)(μ-O-*i*Pr)]$_2$ [1.847(2) Å][8h] and [Al(OC$_6$H$_2$-2,4,6-*t*Bu$_3$)$_2$)(μ-OEt)]$_2$ [1.845(2) Å].[8i] The Al−O(aryloxo) bond length of 1.759(3) Å is similar to that found in **1**.

The formula of **6** suggested that it should also be obtained in the direct reaction of Ti(OEt)$_4$ with **2** or [Ti$_2$(μ-OEt)$_2$(tbop-κ^3O,S,O)$_2$(OEt)$_2$] with Al(OEt)$_3$ at appropriate stoichiometry. Unfortunately, attempts to isolate **6** by these routes failed. It seems, most likely, that **6** is only generated in situ during alcoholysis of intermediates formed during reaction of [Ti$_2$(μ-OEt)$_2$(tbop-κ^3O,S,O)$_2$(OEt)$_2$] with AlMe$_3$.

Complexes **3**−**6** were tested in an ethene polymerization process. Catalysts based on these compounds were prepared in *n*-hexane by milling (see Experimental Section) a slurry of [MgCl$_2$(THF)$_2$] with the titanium compound (10:1) and AlEt$_2$Cl as cocatalyst. Prior to the polymerization, ethene was passed through the suspension of the catalyst. Then, an additional amount of organoaluminum compound [Al(*i*Bu)$_3$ or MAO] was added to the catalyst and dispersed in the prepolymer to form a highly active catalyst. Thus, the polymerization of ethene was performed in a two-step process. The aim of the first step (very low Al:Ti molar ratio, normal pressure of monomer, very low rate of polymerization) was to prepare granules of polymer containing dispersed catalyst. These granules acted as a “microreactor” in the second step of polymerization with a high rate (Granular Reactor Technology). This method gave PE yields 2-fold higher than those obtained with one-stage activation process. The ethene polymerization results and polymer characterization data are summarized in Table 1.

Table 1. Ethene Polymerization[a]

entry	complex	cocatalyst	activity[b]	M_w/M_n
1	**3**	MAO	353	3.02
2	**3**	Al(*i*Bu)$_3$	426	3.71
3	**4**	MAO	42	3.08
4	**4**	Al(*i*Bu)$_3$	400	3.59
5	**5**	MAO	110	2.78
6	**5**	Al(*i*Bu)$_3$	343	3.22
7	**6**	MAO	78	3.05
8	**6**	Al(*i*Bu)$_3$	138	3.31
9	Cp$_2$TiCl$_2$	MAO	137	2.80
10	Cp$_2$TiCl$_2$	Al(*i*Bu)$_3$	123	3.16

[a] Polymerization conditions: for MAO, [Ti]$_0$ = 0.005 mmol dm^{-3}, [Al]:[Ti] = 4000; for Al(*i*Bu)$_3$, [Ti]$_0$ = 0.005 mmol dm^{-3}, [Al]:[Ti] = 2000, time = 30 min. [b] In kg PE g Ti h^{-1};

For comparison of catalyst activities, titanocene dichloride (Cp$_2$TiCl$_2$) was used as a reference under the same conditions (Table 1, entries 9 and 10). It turned out that the catalysts based on the complexes **3**−**5** (entries 1, 2, 4, and 6) exhibited comparable catalytic activity (about 400 kg·PE/g Ti·h^{-1}) for ethene polymerization. This is more than that when compared with catalysts based on the species formulated as [Ti(tbmp)X$_2$] (100 kg PE/g of Ti·h; 293 K, 3 MPa, 0.2 mmol catalyst; 25 mmol MAO, toluene),[2k] but almost 2-fold less than that with [Ti$_2$(μ-tbop-κ^3O,S,O)$_2$Cl$_2$(dipp)$_2$]/Al(*i*Bu)$_3$ (707 kg of PE/g of Ti·h; 323 K, 0.5 MPa, 0.005 mmol catalyst)[7] and [Ti(tbmp)X$_2$]/MAO (820 kg PE/g of Ti·h for X = Cl and 677 kg PE/g of Ti·h for X = OPr^i; 20 °C, 3 MPa, 0.001 mmol catalyst, 5.17 mmol MAO, toluene) systems originally reported by Kakugo.[3] Molecular weights of the polymers, M_w, produced by employing complexes **3**−**6** under these conditions range from 924 000 to 1 369 000. Their polydispersities, M_w/M_n (see Table 1), are narrower than those reported for ethene polymerization with catalysts based on [Ti$_2$(μ-OEt)$_2$(OEt)$_4$(maltolato-κ^2O,O)$_2$] (6.11)[15] and [Ti(tbmp)X$_2$] (11.9).[2k] It would appear that, for polymerization of ethene, activation of systems based on complexes **3**−**6** does afford a single well-defined active species. This indicates that the

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(15) Sobota, P.; Przybylak, K.; Utko, J.; Jerzykiewicz, L. B.; Pombeiro, A. J. L.; Guedes da Silva, M. F. C.; Szczegot, K. *Chem.*−*Eur. J.* **2001**, *7*, 951.

cocatalyst does not abstract the tbop ligand from the titanium center to the aluminum. This is in good agreement with results of the interaction of **3** with $TiCl_4$, which showed the formation of a stable $Ti_3(tbop)_2$ unit via the migration of the tbop group from the aluminum coordination sphere. It means that the titanium center is more acidic for the tbop than for the aluminum. Presented here and previously,[6,7] results showed sufficiently low influence of coligands modifying titanium centers on catalytic activity of catalysts based on tbop−titanium complexes. Comparable catalytic activities obtained for our tbop−titanium complexes suggest that, presumably, aluminum cofactors abstract coligands from the Ti−tbop core and create in all cases similar active centers. The nature of the active center in the catalyst based on the tbop−titanium complexes is currently being investigated.

Conclusions

The reaction of $tbopH_2$ with $AlMe_3$ affords the dimeric aluminum methyl complex **1**, from which after alcoholysis with EtOH, the μ−ethoxo−aluminum compound **2** is formed. Treatment of **2** with $TiCl_4$ leads to the migration of ethoxo and tbop ligands to the titanium center, and the trimeric mixed-ligand complex **3**·C_6H_{14} is produced. The chlorides in **3** can be easily substituted by methyl groups to form a mixture of two products: **4** and **5**·Et_2O. Alcoholysis of one-pot reaction mixture of $[Ti_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2(\text{OEt})_2]$ and $AlMe_3$ generates the heterometallic tetramer **6**.

Complexes **3**−**6** supported on $MgCl_2$ and activated with aluminum alkyls are highly effective ethene polymerization catalysts. Narrow molecular weight distribution for these systems suggests that the operation of heterogeneous well-defined single-site catalysts occurs. Comparable activity of catalysts based on **3**−**6** and on previously described the tbop−titanium complexes suggests that the Ti−tbop moiety plays the most important role in generating catalytic active centers. Modification of titanium coordination sphere by O- and N-donor coligands generally does not sufficiently influence catalytic activity of the tbop−titanium catalysts.

Experimental Section

General Remarks: All operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques. All of the solvents were distilled under dinitrogen from the appropriate drying agents prior to use. The $TiCl_4$, $Ti(OEt)_4$, $AlMe_3$, $Al(i\text{Bu})_3$, MAO, LiMe, 2,2′-thiobis{4-(1,1,3,3-tetramethylbutyl)phenol} ($tbopH_2$), and 2,6-diisopropylphenol (dippH) compounds were obtained from the Aldrich Chemical Co. and were used without further purification unless stated otherwise. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer in Nujol mulls. NMR spectra were performed on a Bruker ARX 300 spectrometer. Microanalyses were conducted with a ASA-1 (GDR, Karl- Zeiss-Jena) instrument (in-house).

$[Al_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2Me_2]$ (1). To a cooled (273 K) solution of $tbopH_2$ (1.77 g, 4.00 mmol) in toluene (60 mL) was added a toluene solution of $AlMe_3$ (2.0 M, 2 mL, 4.00 mmol). The mixture was warmed to room temperature and was stirred for 12 h. A white precipitate was filtered off, washed with hexane (3 × 5 mL), and dried under vacuum. Yield: 1.63 g (84%). The filtrate was concentrated to ca. 30 mL and kept at 293 K; after 1 day, the colorless crystals suitable for the crystal structure determination were obtained. Anal. Calcd for $C_{58}H_{86}O_4S_2Al_2$: C, 72.16; H, 8.98; S, 6.64. Found: C, 72.08; H, 8.92; S, 6.34. ^1H NMR (C_6D_6): δ 7.57−6.48 (m, 12H, C_6H_3), 1.55 [s, 8H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.18 [s, 24H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.55 [s, 36H, $C(CH_3)_2CH_2C(CH_3)_3$], −0.45 (s, 6H, Al−CH_3). ^{13}C NMR (C_6D_6): δ 159.4, 151.9, 145.2, 140.7, 137.8, 132.8 (C_6H_3), 57.0 [$C(CH_3)_2CH_2C(CH_3)_3$], 38.3 (Al−CH_3), 32.4, 32.0 [$C(CH_3)_2CH_2C(CH_3)_3$], 21.2 [$C(CH_3)_2CH_2C(CH_3)_3$].

$[Al_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2]$ (2). To a cooled (273 K) solution of **1** (1.60 g, 1.66 mmol) in toluene (30 mL) was added an excess of dry EtOH (0.5 mL, 8.56 mmol). The mixture was warmed to room temperature and was stirred for 12 h. Then, the reaction mixture was taken to dryness under vacuum to yield a sticky white product. It was solidified by treatment with dry ethanol and stirring at room temperature for 3 h. Next, white solid was filtered off, washed with ethanol (3 × 5 mL), and dried under vacuum. Yield: 1.38 g (81%). Anal. Calcd for $C_{60}H_{90}O_6S_2Al_2$: C, 70.28; H, 8.85; S, 6.25. Found: C, 69.96; H, 8.69; S, 6.01. ^1H NMR (C_6D_6): δ 8.10−6.93 (m, 12H, C_6H_3), 4.33 (m, 4H, CH_3CH_2O), 1.75 [br s, 8H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.43 [br s, 24H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.00 (t, 6H, CH_3CH_2O), 0.84, [br s, 36H, $C(CH_3)_2CH_2C(CH_3)_3$]. ^{13}C NMR (C_6D_6): δ 131.4, 130.4, 128.7, 127.6, 125.0, 121.9 (C_6H_3), 60.1 [$C(CH_3)_2CH_2C(CH_3)_3$], 32.4, 31.9 [$C(CH_3)_2CH_2C(CH_3)_3$], 20.2 [$C(CH_3)_2CH_2C(CH_3)_3$].

$[Ti_3(\mu\text{-OEt})_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2Cl_6]$ (3)·C_6H_{14}. To a solution of **2** (1.67 g, 1.63 mmol) in hexane (50 mL) was added $TiCl_4$ (0.53 mL, 4.90 mmol). The reaction mixture was stirred at room temperature for 12 h. A red−brown solid was formed, which was filtered off, washed with hexane (3 × 5 mL), and dried under vacuum. Yield: 1.93 g (89%). Red crystals suitable for the crystal structure determination were obtained from the filtrate after standing at room temperature for 2 days. Anal. Calcd for $C_{60}H_{90}Cl_6O_6S_2Ti_3$: C, 54.27; H, 6.83; Cl, 16.02; S, 4.82. Found: C, 54.61; H, 7.01; Cl, 15.86; S, 4.77. ^1H NMR (C_6D_6): δ 7.69−6.44 (m, 12H, C_6H_3), 4.41, 4.95 (q, 4H, CH_3CH_2O), 1.66 (t, 6H, CH_3CH_2O), 1.50 [s, 8H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.35−1.31 [m, 8H, $CH_3(CH_2)_4CH_3$], 1.20, 1.12 [d, 24H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.96 [t, 6H, $CH_3(CH_2)_4CH_3$], 0.70, 0.69 [s, 36H, $C(CH_3)_2CH_2C(CH_3)_3$]. ^{13}C NMR (C_6D_6): δ 166.8, 159.7, 147.7, 147.0, 129.8, 128.3, 126.1, 123.9, 122.97, 122.9, 122.0, 113.3 (C_6H_3), 85.3 (OCH_2CH_3), 56.0, 55.9 [$C(CH_3)_2CH_2C(CH_3)_3$], 31.6, 31.2, 30.8, 30.7, 30.4 [$C(CH_3)_2CH_2C(CH_3)_3$], 22.3 [$C(CH_3)_2CH_2C(CH_3)_3$], 15.0, 13.6 (OCH_2CH_3). The crystal structure shows the presence of one hexane 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.

$[Ti_2(\mu\text{-tbop-}\kappa^3\text{O,S,O})_2Me_4]$ (4) and $[Ti_2(\mu\text{-OEt})_2(\text{tbop-}\kappa^3\text{O,S,O})_2Me_2]$ (5)·Et_2O. To a cooled (273 K) suspension of **3** (1.48 g, 1.11 mmol) in Et_2O (40 mL) was added LiMe (1.6 M, 2.79 mL, 4.44 mmol). The reaction mixture was warmed to room temperature and stirred for 2 h. Then, LiCl was filtered off, and the filtrate was concentrated and stored for 1 day at 277 K, yielding light-yellow needle-shaped crystals of **4**. Yield: 0.40 g (61%). Anal. Calcd for $C_{60}H_{92}O_4S_2Ti_2$: C, 69.48; H, 8.94; S, 6.18. Found: C, 69.43; H, 8.47; S, 6.05. ^1H NMR (C_6D_6): δ 7.84−6.80 (m, 12H, C_6H_3), 1.69 [s, 8H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.36 [s, 24H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.34 (s, 12H, Ti−CH_3), 0.82 [s, 36H, $C(CH_3)_2CH_2C(CH_3)_3$]. ^{13}C NMR (C_6D_6): δ 165.8, 142.6, 132.7, 129.5, 128.7, 115.7 (C_6H_3), 64.3 (Ti−CH_3), 56.9 [$C(CH_3)_2CH_2C(CH_3)_3$], 32.4, 32.0, 31.7 [$C(CH_3)_2CH_2C(CH_3)_3$], 18.9 [$C(CH_3)_2CH_2C(CH_3)_3$].

When the reaction mixture without LiCl was left for 2 months at 277 K, a mixture of **4** as yellow needle-shaped crystals and yellow prismatic crystals of **5**·Et_2O was formed. Crystals of **5**·Et_2O were separated by hand for the X-ray diffraction study. Anal. Calcd for $C_{62}H_{96}O_6S_2Ti_2$ (**5**): C, 67.86; H, 8.82; S, 5.84. Anal. Calcd for $C_{66}H_{106}O_7S_2Ti_2$ (**5**·Et_2O): C, 67.67; H, 9.12; S, 5.47.

Table 2. Crystallographic Data for Compounds 1, 3·C_6H_{14}, 5·Et_2O, and 6

compound	**1**	**3**·C_6H_{14}	**5**·Et_2O	**6**
empirical formula	$C_{58}H_{86}Al_2O_4S_2$	$C_{66}H_{104}Cl_6O_6S_2Ti_3$	$C_{66}H_{106}O_7S_2Ti_2$	$C_{76}H_{130}Al_2O_{14}S_2Ti_2$
fw	965.41	1414.10	1171.50	1481.76
T, K	100	100	100(1)	100
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a, Å	11.294(5)	15.478(4)	7.011(3)	9.018(3)
b, Å	12.976(5)	22.140(5)	13.791(6)	21.743(4)
c, Å	13.286(5)	23.719(5)	17.957(5)	21.141(4)
α, deg	96.15(3)	90	79.10(3)	90
β, deg	105.97(3)	97.32(3)	81.80(3)	90.30(2)
γ, deg	111.14(3)	90	78.79(3)	90
V, Å^3	1699.1(13)	8062(3)	1662.3(11)	4145.2(18)
Z	1	4	1	2
ρ_{calcd}, mg/m^3	0.943	1.165	1.170	1.187
μ, mm^{-1}	0.140	0.582	0.351	0.321
θ range, deg	3.03 to 28.48	2.89 to 28.49	2.99 to 28.50	3.52 to 28.57
No. of reflns collected	21840	60448	22259	28734
No. of ind. reflns/$R_{\mathrm{(int)}}$	11536/0.04	18892/0.05	7739/0.04	9539/0.06
No. of parameters	298	748	367	433
R_1 [$I > 2\sigma(I)$]	0.0644	0.0638	0.0510	0.0737
wR_2 [$I > 2\sigma(I)$]	0.0590	0.0780	0.0467	0.0621
GOF (F^2)	1.187	1.141	1.181	1.123

Reaction of 4 with Ti(OEt)$_4$. To a solution of **4** (0.53 g, 0.51 mmol) in Et_2O (20 mL) was added $Ti(OEt)_4$ (0.12 g, 0.51 mmol) in Et_2O (20 mL) at room temperature. The reaction mixture was stirred for 12 h, concentrated to 5 mL, and left at 253 K. After 1 week, prismatic crystals of **5**·Et_2O were separated. Yield: 0.32 g (58%). Anal. Calcd for $C_{62}H_{96}O_6S_2Ti_2$: C, 67.86; H, 8.82; S, 5.84. Found: C, 67.25; H, 8.68; S, 5.28. ^{1}H NMR (C_6D_6): δ 7.77−6.61 (12 H, $C_6\mathit{H}_3$), 4.78 (q, 4H, μ-$OC\mathit{H}_2CH_3$), 2.23 (s, Ti−$C\mathit{H}_3$), 1.57 [s, 8 H, $C(CH_3)_2C\mathit{H}_2C(CH_3)_3$], 1.37 (t, 6 H, μ-$OCH_2C\mathit{H}_3$), 1.26 [s, 24 H, $C(C\mathit{H}_3)_2CH_2C(CH_3)_3$], 0.84 [s, 36 H, $C(CH_3)_2CH_2C(C\mathit{H}_3)_3$]. ^{13}C NMR ($C_6D_6$): δ 165.7, 142.6, 132.9, 129.5, 127.3, 115.8 (C_6H_3), 77.0 ($O\mathit{C}H_2CH_3$), 57.4 [$C(CH_3)_2\mathit{C}H_2C(CH_3)_3$], 38.1, 32.5, 32.1, 31.7 [$\mathit{C}(\mathit{C}H_3)_2CH_2\mathit{C}(\mathit{C}H_3)_3$], 30.5 (Ti−$\mathit{C}H_3$), 19.2 ($OCH_2\mathit{C}H_3$).

[$Ti_2Al_2(\mu$-$OEt)_6(\mu$-tbop-κ^3O,S,O$)_2(OEt)_4$] (6). To a cooled (273 K) solution of [$Ti_2(\mu$-$OEt)_2$(tbop-κ^3O,S,O$)_2(OEt)_2$] (1.97 g, 1.70 mmol) in toluene (40 mL) was added $AlMe_3$ (1.7 mL, 2.0 M, 3.40 mmol). The reaction mixture was warmed to room temperature and was stirred for 12 h. Then, EtOH (0.6 mL, 10.28 mmol) was added to the reaction mixture, and stirring continued for 12 h. Next, the reaction mixture was taken to dryness under vacuum to yield a dark-yellow product. It was washed with hexane and dried under vacuum. Crystals suitable for the crystal structure determination were obtained by recrystallization of the crude product from diethyl ether. Yield: 2.16 g (86%). Anal. Calcd for $C_{76}H_{130}O_{14}S_2Al_2Ti_2$: C, 61.60; H, 6.12; S, 4.33. Found: C, 61.80; H, 6.07; S, 4.44. ^{1}H NMR (C_6D_6): δ 7.98−6.62 (m, 12H, $C_6\mathit{H}_3$), 4.96−3.33 (multiplet of quartets, 20H, $CH_3C\mathit{H}_2O$), 1.65, 1.61 [s, 8H, $C(CH_3)_2C\mathit{H}_2C(CH_3)_3$], 1.38, 1.29 [s, 24H, $C(C\mathit{H}_3)_2CH_2C(CH_3)_3$], 1.27, 1.19, 1.32 (t, 30H, $C\mathit{H}_3CH_2O$), [0.82, 0.78 (s, 36H, $C(CH_3)_2CH_2C(C\mathit{H}_3)_3$]. ^{13}C NMR ($C_6D_6$): δ 160.1, 147.3, 131.2, 129.1, 126.1, 115.3 (C_6H_3), 74.6, 74.3, 70.9, 70.6 ($O\mathit{C}H_2CH_3$), 56.4 [$C(CH_3)_2\mathit{C}H_2C(CH_3)_3$], 31.8, 31.4, 31.3 [$C(\mathit{C}H_3)_2CH_2\mathit{C}(\mathit{C}H_3)_3$], 22.3 [$\mathit{C}(CH_3)_2CH_2C(CH_3)_3$], 19.3, 19.0, 18.2, 17.7, 17.0, 14.8, 13.6 ($OCH_2\mathit{C}H_3$).

Polymerization Test: A slurry of [$MgCl_2(THF)_2$] (10 mmol) in *n*-hexane was milled under argon in a glass mill (250 mL capacity, with 20 balls of 5−15 mm diameter) at room temperature for 6 h. Then, the titanium compound (1 mmol) and *n*-hexane (50 mL) were added, and the mixture was milled for an additional 24 h. The sample of precatalyst suspension (containing 0.01 mmol of titanium) was activated with $AlEt_2Cl$ (Al:Ti = 120) for 15 min at 323 K under argon. Prior to polymerization, ethene was passed through the suspension of the catalyst (10 mL) in a Schlenk ampule for 15 min at room temperature and normal pressure, and the prepolymer was obtained (about 1 g). Then, an additional amount of organoaluminum compound, Al(*i*Bu)$_3$ or MAO, was added to the catalyst and dispersed in the prepolymer (Al:Ti = 2000) to form a highly active catalyst. The polymerization of ethylene was carried out in *n*-hexane at 323 K in a stainless steel reactor (1 L), equipped with a stirrer, at 0.5 MPa pressure. The polymerization was quenched with a 5% solution of HCl in methanol and dried under vacuum.

Crystal Structure Determination 1, 3·C_6H_{14}, 5·Et_2O, and 6: Crystal data collection and refinement are summarized in Table 2. Preliminary examination and intensities data collections were carried out on a KUMA CCD KM-4 κ-axis diffractometer with graphite-monochromated Mo Kα (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. The structures were solved by direct methods using SHELXTL software[16] and were refined using full-matrix least-squares on all *F* data CRYSTALS program.[17] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions with isotropic thermal parameters (CCDC reference number 268294−268297).

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Supporting Information Available: Crystallographic data for structures **1**, **3**·C_6H_{14}, **5**·Et_2O, and **6** reported in this paper. This material is available free of charge via Internet at http://pubs.acs.org.

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