Titanium Complexes of Chelating, Dianionic O,S,O-Bisphenolato Ligands: Syntheses, Characterisation, and Catalytic Activity

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Titanium complexes based on 2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenolato] (tbop) are prepared by reaction of $TiCl_4$ or $Ti(NMe_2)_4$ with the parent biphenol. Three new complexes are reported: $[Ti_2(\mu\text{-tbop-}\kappa^3O,S,O)(\mu\text{-tbop-}\kappa^2O,O)(\text{tbop-}\kappa^3O,S,O)Cl_2]$ (**1**)·2CH_3CN, $[Ti_2(\mu\text{-tbop-}\kappa^3O,S,O)_2Cl_4]$ (**2**) and $[Ti(\text{tbop-}\kappa^3O,S,O)_2]$ (**3**). Substitution of the chlorides in **1** and **2** by 2,6-diisopropylphenolato and imido (N*t*Bu) ligands generates the new compounds $[Ti_2(\mu\text{-tbop-}\kappa^3O,S,O)_2Cl_2(dipp)_2]$ (**4**)·Et_2O and $[Ti_2(\mu\text{-tbop-}\kappa^3O,S,O)_2(N\text{t}Bu)_2(NH_2\text{t}Bu)_2]$ (**5**), respectively. Treatment of **5** with crude Me_3SiCl, containing Me_3SiOH, produces $[Ti(\text{tbop-}\kappa^3O,S,O)Cl(OSiMe_3)(NH_2\text{t}Bu)]$ (**6**). Reaction of **2** with an excess of $NHiPr_2$ provides a mixture of compounds: ionic $[NH_2iPr_2][Ti(\text{tbop-}\kappa^3O,S,O)Cl_3]$ (**7**)·CH_2Cl_2 and molecular $[Ti_2(\mu\text{-tbop-}\kappa^3O,S,O)_2Cl_2(NiPr_2)_2]$ (**8**). The structures of **1**–**8** were confirmed by NMR spectroscopy; complexes **1**, **5**, **6** and **7** were further investigated by X-ray crystallography. Compounds **1**, **2**, **4** and **5**, when supported on $MgCl_2$ and activated with alkylaluminiums, effectively polymerise ethene.

Introduction

Titanium complexes $[Ti_2(\mu\text{-}X)_2X_2(\text{tbmp-}\kappa^3O,S,O)_2]$ derived from the sulfide-linked bisphenol $\text{tbmp}H_2$ [$\text{tbmp}H_2$ = 2,2′-thiobis(6-*tert*-butyl-4-methylphenol); X = Cl, O*i*Pr] were first reported by Kakugo et al. to be highly active for the polymerisation of ethene, propene, styrene and dienes, as well as the copolymerisation of ethene with styrene, upon activation with methylalumoxane (MAO).[1–3] These titanium complexes were found to be an order of magnitude more active than the methylene-bridged chelating aryloxide complexes of the type $[TiX_2(\text{mbmp})]$ [mbmp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato)].[4] This is in qualitative agreement with theoretical studies that showed the S-bridged chelating phenolates to have lower insertion barriers than their methylene-bridged or directly bridged analogues.[5–7] Although the Ti–S interaction in $[Ti_2(\mu\text{-}X)_2X_2(\text{tbmp-}\kappa^3O,S,O)_2]$ 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.[8] Bisphenolato- and bisnaphtholatotitanium complexes have been well characterised both structurally and spectroscopically, and the kinetics and thermodynamics of intra- and intermolecular rearrangement in bisnaphtholates has been described as well.[9,10] However, there are very few reports of structural data on S-bridged titanium analogues, especially of their ligand modifications.[5,11,12] This encouraged us to investigate the titanium compounds with the tridentate O,S,O-thiobisphenolato ligand 2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenolato] (tbop). In addition to the S bridge, the tbop ligand seemed to have one more attractive feature: the long, sterically hindered auxiliary group on the thiobisphenolato ligand sufficiently increases solubility of the catalyst in hydrocarbons.

Recently we described the synthesis and structural characterisation of the mixed-ligand complexes $[Ti_2(\mu\text{-}OR)_2(X)_2(\text{tbop-}\kappa^3O,S,O)_2]$ (R = Me, Et; X = OR or Me).[13] In these complexes the tbop ligand was found to coordinate to the titanium in a *fac* fashion. $[Ti_2(\mu\text{-}OR)_2(X)_2(\text{tbop-}\kappa^3O,S,O)_2]$ complexes supported on $MgCl_2$ and activated with $AlEt_2Cl$ or $AlEt_2Cl/AlEt_3$ show very high activity in ethene polymerisation. The narrow molecular-weight distribution obtained for these systems is indicative of the operation of typical heterogeneous single-site catalyst behaviour.

We have been exploringthe use of the tbop ligand for the preparation of new titanium complexes that might serve as catalysts for the ethene polymerisation process. We report here their syntheses and structures, along with catalytic behaviour in ethene polymerisation.

Results and Discussion

The reaction between $TiCl_4$ and $\text{tbop}H_2$ in *n*-hexane, depending on the stoichiometry (1:1.5 and 1:1), produces

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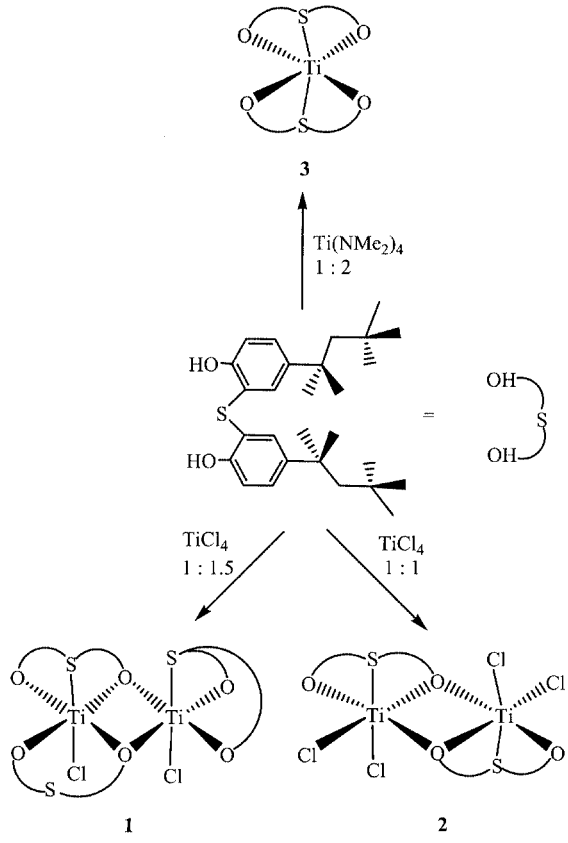
compounds [Ti_2(μ-tbop-κ^3O,S,O)(μ-tbop-κ^2O,O)(tbop-κ^3O,S,O)Cl_2] (**1**·2CH_3CN and [Ti_2(μ-tbop-κ^3O,S,O)$_2Cl_4$] (**2**) with concomitant elimination of three and two equivalents of HCl, respectively (Scheme 1). Surprisingly, reaction of $TiCl_4$ with two equivalents of $tbopH_2$ in diethyl ether did not lead to the anticipated [Ti(tbop-κ^3O,S,O)$_2$] (**3**) but to a good yield of complex **2**. Fortunately, compound **3** is available by simple addition of $tbopH_2$ to [$Ti(NMe_2)_4$]. When the reaction of $tbopH_2$ with neat $TiCl_4$ is carried out in toluene, a mixture of **1**, **2** and **3** is formed, from which only compound **1** could be isolated as an analytically pure product. The IR spectra of **1** and **2** show characteristic modes for terminal coordinated chlorides at 380 and 378 cm^{-1}, respectively.



Scheme 1.

The structure of **1** (Figure 1) consists of discrete molecules of dimer [Ti_2(μ-tbop-κ^3O,S,O)(μ-tbop-κ^2O,O)(tbop-κ^3O,S,O)Cl_2] together with two MeCN molecules of crystallisation. The coordination environment about the Ti centres bridged by two oxygen atoms of tbop ligands is best described as highly distorted octahedral. The major distortions from idealised octahedral geometry are for the O(41)–Ti(1)–O(61), O(21)–Ti(1)–S(1), O(31)–Ti(2)–O(61), O(41)–Ti(2)–O(61) and O(61)–Ti(2)–S(3) angles, with values of 71.88(11)°, 75.72(9)°, 149.18(12)°, 71.54(10)° and 74.19(8)°, respectively. Two tbop ligands in **1** bridge titanium centres and the third one is facially coordinated to Ti(1). All the oxygen atoms of the tbop ligands are engaged in the formation of the equatorial planes, while the terminal chlorides and two sulfur links [S(1), S(3)] of the tbop ligands occupy the apical sites. The third sulfur atom [S(2)] isnot bonded to any Ti atom. The average titanium–sulfur bond length of 2.735(2) Å is longer than those found in other complexes, for example[Ti_2(μ-O*i*Pr)$_2$(O*i*Pr)$_2$(tbmp-κ^3O,S,O)$_2$] [tbmp = 2,2′-thiobis(6-*tert*-butyl-4-methylphenolato; 2.719(1) Å],[Ti(tbmp-κ^3O,S,O)($C_6H_4CH_2NMe_2$-2-κ^2C,N)Cl] [2.704(1) Å]and [Ti(tbmp-κ^3O,S,O)Cl(O*i*Pr)(HO*i*Pr)] [2.693(1) Å],[5,11] and shorter than those in [Ti_2(μ-OEt)$_2$(OEt)$_2$(tbop-κ^3O,S,O)$_2$] [2.800(1) Å] and [{Ti_2(μ-OEt)$_2$(tbop-κ^3O,S,O)$_2$}$_2$-(μ-O)$_2$] [2.762(2) Å].[13] The average Ti–O distances of 1.832(3) Å and 2.040(3) Å are in the expected range for Ti^{IV} complexes with non-bridging and bridging aryloxo ligands, respectively.[4] The terminal Ti–Cl distances of 2.254(2) Å and 2.265(2) Å are slightly shorter (by less than 0.01 Å) than those in [Ti_2(μ-Cl)$_2Cl_2$(tbmp-κ^3O,S,O)$_2$].[12]

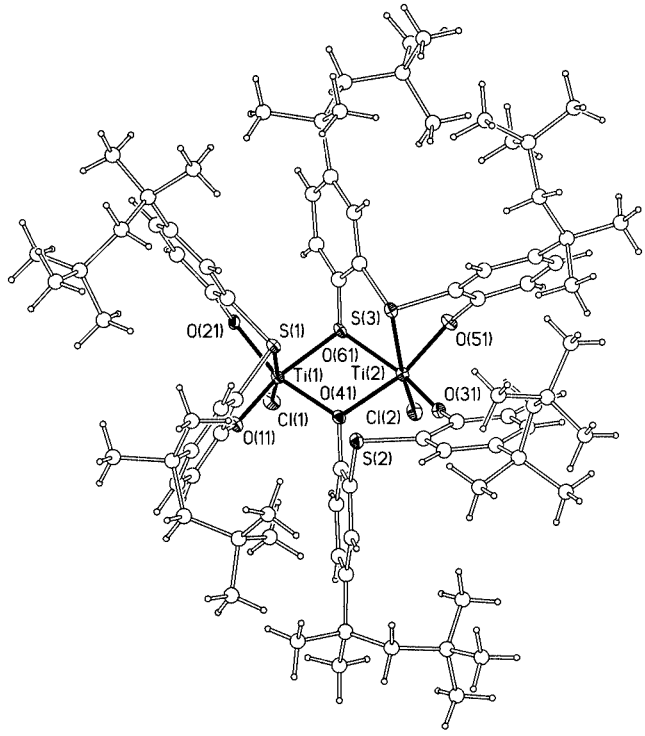
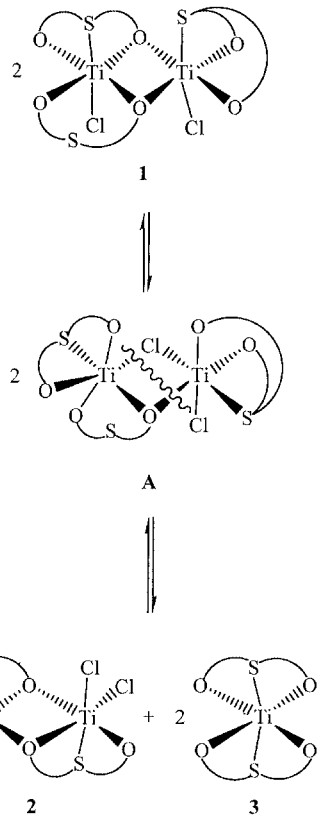


Figure 1. Molecular structure of **1**·2CH_3CN. Selected bond lengths [Å] and angles [°]: Ti(1)–O(11) 1.833(3), Ti(1)–O(21) 1.839(3), Ti(1)–O(41) 2.024(3), Ti(1)–O(61) 2.048(3), Ti(1)–Cl(1) 2.254(2), Ti(1)–S(1) 2.752(2), Ti(2)–Cl(2) 2.265(2), Ti(2)–O(31) 1.793(3), Ti(2)–O(41) 2.041(3), Ti(2)–O(51) 1.863(3), Ti(2)–O(61) 2.048(3), Ti(2)–S(3) 2.728(2); O(41)–Ti(1)–O(61) 71.88(11), O(21)–Ti(1)–S(1) 75.72(9), O(31)–Ti(2)–O(61) 149.18(12), O(41)–Ti(2)–O(61) 71.54(10), O(61)–Ti(2)–S(3) 74.19(8).

The ^1H NMR spectra of **1** in C_6D_6 show more peaks corresponding to the tbop ligand than would be expected from the crystal structure. These data suggest that the structure of **1** does not stay intact in solution at room temperature. It is most likely that compound **1** undergoes an intramolecular rearrangement in solution probably to the chloride- and oxygen-bridged dinuclear derivative **A** (Scheme 2). This closely corresponds to the well-documented mechanism for intramolecular exchange in [(R_2bino)Ti(O*i*Pr)$_2$]$_2$

(R_2bino = 3,3′-disubstituted-1,1′-bi-2-naphtholates)[10] and [(tartrate)Ti(O*i*Pr)$_2$]$_2$ proposed by Sharpless and Finn.[14]

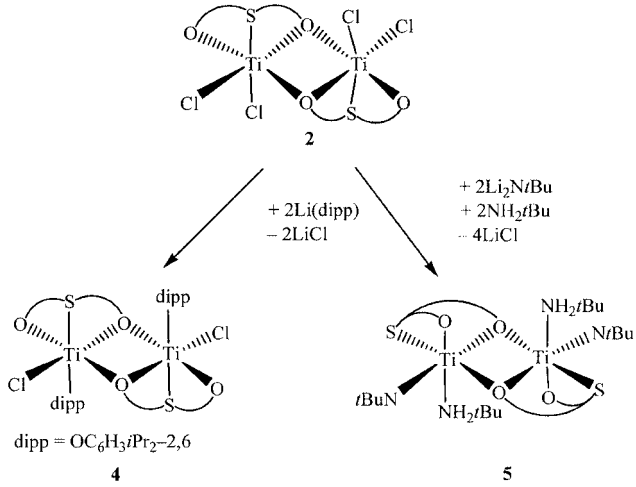


Scheme 2.

Fragmentation of **A** through the interruption of chloride and oxygen bridges would produce compounds [Ti$_2$(μ-tbop-κ^{3}O,S,O)$_2$Cl$_4$] (**2**) and [Ti(tbop-κ^{3}O,S,O)$_2$] (**3**). All these compoundscould participate in a facile equilibrium involving the interconversion of chemically distinct compounds. Partial confirmation of this hypothesis is the fact that compound **1** gives the same products upon substitution of its chlorides as **2** (described below). The presence of compound **3** was confirmed from the ^{1}H NMR spectrum.

Attempts to grow crystals of **2** suitable for X-ray diffraction proved unsuccessful. Therefore, we tried to examine its structure by indirect methods, by investigating the products of substitution of the chlorides in **2** (Scheme 3).

We found that the reaction of **2** with Li(dipp) (dipp = 2,4-diisopropylphenolato) in diethyl ether provides orange-red crystals of [Ti$_2$(μ-tbop-κ^{3}O,S,O)$_2$Cl$_2$(dipp)$_2$] (**4**)·Et$_2$O in good yield. The ^{1}H NMR spectrum of **4** contains septet and doublet resonances for the isopropyl substituents of the dipp groups and similar resonance sets for the tbop ligand to those detected for **2**, together with resonances corresponding to the free diethyl ether. Single-crystal X-ray diffraction of **4** showed it to be composed of dimeric [Ti$_2$(μ-tbop-κ^{3}O,S,O)$_2$Cl$_2$(dipp)$_2$] and one Et$_2$O molecule of crystallisation. Two titanium centres are linked by a double bridge formed from the oxygen atoms of the tbop ligands. The chloride atoms and dipp ligands are terminally coordinated to each titanium atom to complete the octahedral



Scheme 3.

coordination sphere. Unfortunately, the poor-quality X-ray data for **4** do not allow a discussion of bond lengths and angles.[15]

Treatment of **2** with one equivalent of Li$_2$N*t*Bu and NH$_2$*t*Bu per titanium atom in diethyl ether produced [Ti$_2$(μ-tbop-κ^{3}O,S,O)$_2$(N*t*Bu)$_2$(NH$_2$*t*Bu)$_2$] (**5**) in high yield. The coordination of both amine (NH$_2$*t*Bu) and imido (N*t*Bu) ligands to the titanium centres is implied by the presence of two inequivalent *t*Bu groups and the broad resonance for the NH$_2$ group in the ^{1}H NMR spectrum and by ν(NH) bands in the IR spectra (see Experimental Section). Single-crystal X-ray diffraction clearly confirms (Figure 2) that **5** contains an approximately linear Ti=N*t*Bu linkage [166.4(3)°], with a Ti–N$_{imido}$ distance [1.710(3) Å] consistent with a formal metal–nitrogen triple bond ($\sigma^2\pi^4$),[16] and a

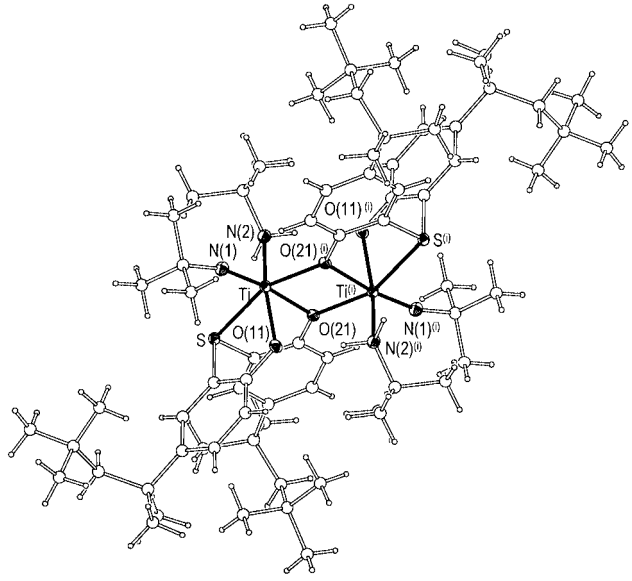


Figure 2. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: Ti–N(1) 1.710(3), Ti–O(11) 2.013(2), Ti–O(21)^i 2.010(3), Ti–N(2) 2.255(3), Ti–O(21) 2.298(2), Ti–S 2.587(2); Ti–N(1)–C(51) 166.4(3), Ti–N(2)–C(61) 126.5(2). Symmetry operation: (*i*) –*x* + 1, –*y*, –*z*.

bent Ti–NH_2tBu unit with a Ti–N bond length and a Ti–N–C angle of 2.255(3) Å and 126.5(2)°, respectively.

The amine and imido groups are terminally coordinated to the titanium centres. A similar coordination of both amine and imido groups to the titanium centres is found in the tetramer $[Ti_4(\mu\text{-}Cl)_4(\mu^3\text{-}Cl)_2Cl_2(NtBu)_4(NH_2tBu)_4]$, which is obtained from the direct reaction of $TiCl_4$ and four equivalents of tBuN(H)$SiMe_3$.[17] The octahedral titanium centres in **5** are bridged by two oxygen atoms [O(21), O(21)$^{(i)}$] of the tbop ligands. These two oxygens form the equatorial planes together with sulfur and imido nitrogen atoms, while the remaining oxygens [O(11), O(11)$^{(i)}$] and amine nitrogens [N(2) and N(2)$^{(i)}$] occupy the apical sites. The Ti–S bond length of 2.587(2) Å is significantly shorter than that in **1** and is one of the shortest Ti–S lengths so far reported in the literature of titanium S-bridged bisaryloxo complexes.[5,11–13] Typically, it is observed that the Ti-μ-O_{Ar} distances are a minimum of 0.1 Å longer than terminal Ti–O_{Ar} bonds, as was found for **1**. However, the Ti–O bond distances in **5** do not reveal this tendency and show a significant variation. These variations could be caused by the *trans* interactions of bridging O(21) and O(21)$^{(i)}$ atoms with imido N(1), N(1)$^{(i)}$ atoms and S, S$^{(i)}$ atoms, respectively, as well as terminal O(11) and O(11)$^{(i)}$ atoms situated in axial positions with amine N(2) and N(2)$^{(i)}$ atoms, respectively. On the other hand, an increased axial Ti–O distance is expected, because axial ligands generally engender more severe steric interactions and experience greater competition for empty dπ-bonding orbitals than analogous equatorial ligands.[18] These two effects sufficiently influence the variation in Ti–O bond distances, although the influence of crystal packingcannot be excluded.

On the basis of structures **4** and **5** it seems most likely that complex **2** is a dimer in which the titanium centres are doubly bridged by oxygen atoms of the tbop ligands and the chlorides are coordinated terminally. This is in contrast to $[Ti_2(\mu\text{-}Cl)_2Cl_2(tbmp\text{-}\kappa^3O,S,O)_2]$, reported by Nakamura and Okuda, which has a chloro-bridged binuclear structure with tbmp ligands facially coordinated to each titanium centre,[12] probably because of the bulky tBu substituents in the tbmp ligands.

Addition of four equivalents of crude Me_3SiCl to **5** in diethyl ether led unexpectedly to yellow crystals of [Ti(tbop-κ^3O,S,O)Cl($OSiMe_3$)(NH_2tBu)] (**6**) in low yield. The X-ray structure of **6** (Figure 3) displays a distorted octahedral geometry around the titanium centre with the tbop ligand coordinated in a *fac* fashion. The oxygen atom [O(3)] of the $OSiMe_3$ ligand and the sulfur atom of the tbop group occupy the apical positions, while oxygens atoms O(1) and O(2) of the tbop ligand, together with the nitrogen atom of NH_2tBu, occupy the equatorial plane. The Ti–S distance of 2.757(1) Å is similar to those found in **1** and significantly longer than those detected in **5**. The Ti–$O_{aryloxo}$ [av. 1.87(2) Å], Ti–O_{alkoxo} [1.7758(2) Å] and Ti–Cl [2.385(1) Å] distances are in the expected range for Ti^{IV} complexes with non-bridging aryloxo[4] and alkoxo ligands[12] and terminal chlorides.Interestingly, intramolecular N–H···Cl [d(N···Cl): 3.4179 Å; N–H–Cl: 169.00°] and C(44)–H(44C)···O(2) [d(C···O): 3.3033 Å; C–H–O: 136.00°]hydrogen bonds are observed. One may suppose that compound **6** might be an-intermediate species in the Ti=NtBu linkage formation.

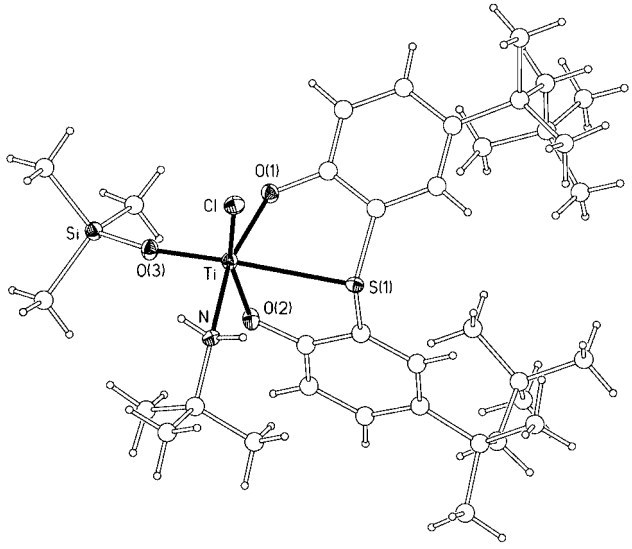
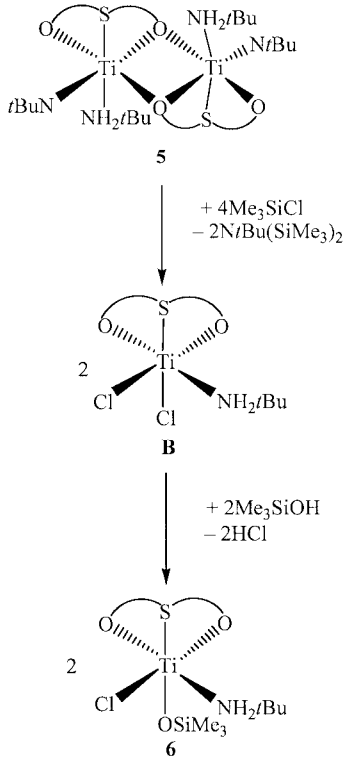


Figure 3. Molecular structure of **6**. Selected bond lengths [Å] and angles [°]: Ti–Cl 2.385(1), Ti–S(1) 2.757(1), Ti–N 2.232(2), Ti–O(1) 1.866(2), Ti–O(2) 1.874(2), Ti–O(3) 1.7758(2); S(1)–Ti–O(3) 174.32, O(2)–Ti–Cl 159.18(6), N–Ti–O(1) 158.69(9), Ti–N–C(41) 130.43(17).

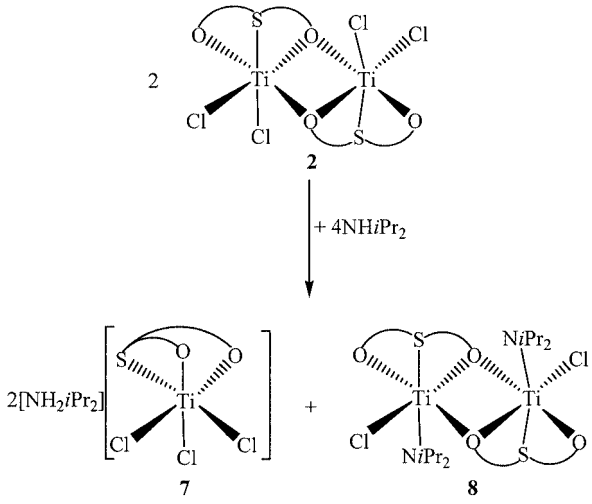
We suggest that the interaction of **5** with crude Me_3SiCl generates a monomeric compound **B** (Scheme 4), which immediately reacts with Me_3SiOH (a product of the hydrolysis of Me_3SiCl that is present in the crude sample) to form **6**



Scheme 4.

with elimination of HCl. However, when freshly distilled Me_3SiCl was used, no formation of **6** was observed and a mixture of **B**, $NH_2tBu{\cdot}HCl$, amido and imido products was identified by ^1H NMR and IR spectroscopy.

The reaction of **2** with two equivalents of $NHiPr_2$ in diethyl ether results in the formation of two products: the ionic complex $[NH_2iPr_2][TiCl_3(tbop\text{-}\kappa^3O,S,O)]$ (**7**) and the molecular complex $[Ti_2(\mu\text{-}tbop\text{-}\kappa^3O,S,O)_2Cl_2(NiPr_2)_2]$ (**8**) (Scheme 5).



Scheme 5.

Crystals of **7** consist of $[NH_2iPr_2]^+$ cations and $[Ti(tbop\text{-}\kappa^3O,S,O)Cl_3]^-$ anions in a 1:1 ratio and one CH_2Cl_2 molecule of crystallisation. The molecular structure of the $[Ti(tbop\text{-}\kappa^3O,S,O)Cl_3]^-$ anion in **7** is shown in Figure 4. This anion evidently maintains a mononuclear octahedral environment with a facially capped tbop ligand. The oxygen atom O(12) of the tbop ligand and chloride Cl(2) occupy an apical coordination sphere, while the remaining donor atoms form the equatorial plane. The Ti–O distances of 1.863(2) and 1.884(2) Å are relatively short and comparable to the terminal aryloxide oxygens found in **1** and **5**. The Ti–Cl bond lengths, disposed *trans* to Ti–O and Ti–S, vary from 2.270(2) to 2.380(2) Å, presumably due to the *trans* influence. The structure of the cation $[NH_2iPr_2]^+$ is well known.[19]

The ^1H NMR spectrum of compound **8** shows similar sets of resonances for the tbop ligand to **5** and additional resonances (septet and doublet) for the deprotonated amido $NiPr_2$ groups. The IR spectrum of **8** also confirms the lack of the ν(NH) frequencies in the expected region. In compounds **1**–**7** thetitanium atom prefers to be six-coordinate. This suggests that complex **8**, which is isolated from non-donor solvents, might be a dimer, as shown in Scheme 5. By analogy to **5**, we propose that the titanium atoms in **8** are joined through the oxygen donors of the tbop ligand rather than the amido $NiPr_2$ groups. Terminal coordination of the amido $NiPr_2$ group to the titanium centre has been observed and crystallographically characterised in $[CpTiCl_2(NiPr_2)]$[20] and $[Li(tmeda)][TiPh_2(NiPr_2)_2]$.[21]

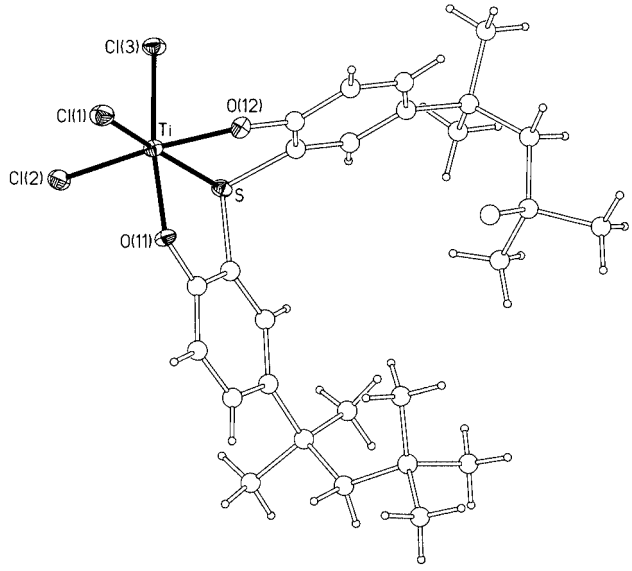


Figure 4. Molecular structure of the $[Ti(tbop\text{-}\kappa^3O,S,O)Cl_3]^-$ anion in **7**·CH_2Cl_2. Selected bond lengths [Å]: Ti–Cl(1) 2.270(2), Ti–Cl(3) 2.369(2), Ti–Cl(2) 2.380(2), Ti–S 2.652(2), Ti–O(11) 1.863(2), Ti–O(12) 1.884(2).

Complexes **1**, **2**, **4** and **5** were tested in ethene polymerisation. 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 $AlEt_2Cl$ as cocatalyst. Prior to the polymerisation, ethene was passed through a suspension of the catalyst. Then, an additional amount of organoaluminium compound [$Al(iBu)_3$ or MAO] was added to the catalyst dispersed in the prepolymer to form a highly active catalyst. Thus, the polymerisation 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 polymerisation) was to prepare granules of polymer containing dispersed catalyst. These granules act as a "microreactor" in the second step of the polymerisation with a high rate (Granular Reactor Technology). This method gave PE yields twice as high as those obtained with a one-stage activation process. The ethene polymerisation results and polymer characterisation data are summarised in Table 1.

Table 1.Ethylene polymerisation.[a]

Entry	Complex	Cocatalyst	Activity[b]	M_w/M_n
1	**1**	MAO	110	3.73
2	**1**	$Al(iBu)_3$	345	4.23
3	**2**	MAO	465	4.36
4	**2**	$Al(iBu)_3$	322	4.67
5	**4**	MAO	357	3.05
6	**4**	$Al(iBu)_3$	707	5.48
7	**5**	MAO	207	3.32
8	**5**	$Al(iBu)_3$	402	4.74
9	$[Cp_2TiCl_2]$	MAO	137	2.80
10	$[Cp_2TiCl_2]$	$Al(iBu)_3$	123	3.16

[a] Polymerisation conditions: for MAO $[Ti]_0$ = 0.05 mmol dm^{-3}, [Al]/[Ti] = 4000; for $Al(iBu)_3$ $[Ti]_0$ = 0.01 mmol dm^{-3}, [Al]/[Ti] = 2000, time 30 min. [b] kg PE/g Ti/h.

For comparison of catalyst activities, titanocene dichloride [Cp_2TiCl_2] was used as a reference under the same conditions (Table 1, entries 9 and 10). It turned out that the catalyst based on complex **4** (entry 6) exhibits the highest catalytic activity (707 kg PE/g Ti/h) for ethene polymerisation. This is about two- and sevenfold more than catalysts basedon[$Ti_2(\mu\text{-}OEt)_2(Me)_2(tbop\text{-}\kappa^3O,S,O)_2$] (344 kg PE/g Ti/h; 323 K, 0.5 MPa, 0.005 mmol catalyst)[13]and the species formulated as [Ti(tbmp)X_2] (100 kg PE/g Ti/h; 293 K, 3 MPa, 0.2 mmol catalyst, 25 mmol MAO, toluene),[2b] respectively, but is comparable with [Ti(tbmp)X_2]/MAO (820 kg PE/g Ti/h for X = Cl and 677 kg PE/g Ti/h for X = O*i*Pr; 293 K, 3 MPa, 0.001 mmol catalyst, 5.17 mmol MAO, toluene) originally reported by Kakugo.[1b,1c] The molecular weights of the polymers produced with complexes **1**, **2**, **4** and **5** under these conditions range from 924 000 to 1 269 000.The polydispersities, M_w/M_n, for **1**, **2**, **4** and **5** (see Table 1) are narrower than those reported for ethylenepolymerisation with catalysts based on [$Ti_2(\mu\text{-}OEt)_2(OEt)_4$-(maltolato-$\kappa^2O,O)_2$] (6.11)[22] and [Ti(tbmp)X_2] (11.9).[2b] It would appear that for polymerisation of ethene, activation of these systems affords a single, well-defined active species. This indicates that the cocatalyst does not abstract the tbop ligand from the titanium centre.

The preliminary polymerisation results on our Ziegler–Natta-like systems are promising on account of the production of a polymer with a sufficiently narrow particle-size distribution.

Conclusions

Reaction of $TiCl_4$ with $tbopH_2$ results in the formation of dimeric, mixed-ligand complexes **1** and **2** depending on the stoichiometry. Analytically pure compound **3** can be only obtained by the protonolysis reaction of $tbopH_2$ with [$Ti(NMe_2)_4$]. The extremely high solubility of **3** makes its isolation in the solid state difficult. Treatment of **1** and **2** with Li(dipp) or Li_2NtBu leads to the partial or complete substitution of chlorides to form dimeric compounds **4** and **5**, respectively. The monomeric complex **6** is a casual product of the reaction of **5** with crude Me_3SiCl containing Me_3SiOH. The use of the secondary amine $NHiPr_2$ in the reaction with **2** produces a mixture of the ionic compound **7** and the molecular species **8**. The solid-state crystal structures of **1**, **4** and **5** showthat their dimeric nature is due to oxygen bridges from the tbop ligands. This is in contrast to the complexes containing a tbmp ligand. It is likely that the bulky substituents in the *ortho* positions of the tbmp ligand are the main reason why chloride bridges are favoured in [$Ti_2(\mu\text{-}Cl)_2Cl_2(tbmp\text{-}\kappa^3O,S,O)_2$].

The complexes **1**, **2**, **4** and **5** are highly effective ethene polymerisation catalysts upon activation with alkylaluminium compounds. The narrow molecular-mass distribution for these systems suggests the operation of heterogeneous, well-defined, single-site catalysts.

Experimental Section

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 $TiCl_4$, $Al(iBu)_3$, MAO, NH_2tBu, $NHiPr_2$, Me_3SiCl and 2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol] ($tbopH_2$) were obtained from the Aldrich Chemical Co. and 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. Microanalysis was conducted with a ASA-1 (GDR, Carl-Zeiss-Jena) instrument (in-house).

[$Ti_2(\mu\text{-}tbop\text{-}\kappa^3O,S,O)(\mu\text{-}tbop\text{-}\kappa^2O,O)(tbop\text{-}\kappa^3O,S,O)Cl_2$](1)·2$CH_3CN$: $tbopH_2$ (6.05 g, 13.67 mmol) was addedto a solution of $TiCl_4$ (1.73 g, 9.11 mmol) in *n*-hexane (60 mL), and the mixture was stirred at room temperature until the evolution of HCl had ceased (48 h). All volatiles were then removed under reduced pressure. The resulting brown solid was washed with *n*-hexane (60 mL), and then the brown precipitate was filtered off, washed with *n*-hexane (3 × 5 mL) and dried under vacuum. The resultant solid was dissolved in warm CH_3CN, from which bright-red crystals suitable for the structure determination were isolated after standing at room temperature for two days. Yield: 5.83 g (86%). $C_{84}H_{120}Cl_2O_6S_3Ti_2$ (1488.67): calcd. C 67.80, H 8.13, Cl 4.70, S 6.45; found C 68.01, H 8.26, Cl 5.32, S 6.13. IR (Nujol mull): $\tilde{\nu}$ = 380 (s), 412 (w), 438 (s), 454 (w), 488 (w), 546 (m), 580 (s), 628 (s), 682 (m), 734 (w), 766 (m), 828 (s), 890 (m), 1060 (w), 1100 (w), 1144 (w), 1250 (s), 1288 (s), 1592 (w) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.78–5.98 (m, 3 H, C_6H_3), 1.54–0.71 [multiplet, signals of $C(CH_3)_2$-$CH_2C(CH_3)_3$] ppm. The crystal structure shows the presence of two CH_3CN molecules in the unit cell. However, the elemental analysis indicates that these are absent from the powder sample analysed; they are presumably removed by the vacuum drying to which the sample was subjected.

[$Ti_2(\mu\text{-}tbop\text{-}\kappa^3O,S,O)_2Cl_4$] (2): $tbopH_2$ (4.05 g, 9.11 mmol) was added to a solution of $TiCl_4$ (1.73 g, 9.11 mmol) in Et_2O or *n*-hexane (60 mL) and the mixture was refluxed until the evolution of HCl had ceased (48 h). The resulting dark-red solid was filtered off, washed with cold Et_2O (3 × 5 mL), and dried under vacuum. Yield: 4.07 g (80%). $C_{56}H_{80}Cl_4O_4S_2Ti_2$ (1118.99): calcd. C 60.20, H 7.22, Cl 12.53, S 5.73; found C 60.86, H 6.96, Cl 12.02, S 5.92. IR (Nujol mull): $\tilde{\nu}$ = 324 (vw), 340 (vw), 378(vs, sh), 420 (s), 448 (m), 466 (m), 500 (w), 542 (w), 568 (m), 578 (m), 628 (vw), 670 (vw), 720 (m), 748 (w), 780 (m), 824 (s), 840 (vs), 888 (m), 916 (m), 936 (vs), 1048 (w), 1064 (w), 1100 (w), 1150 (w), 1192 (m), 1262 (vs), 1324 (m), 1588 (w) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.71–6.89 (m, 12 H, C_6H_3), 1.58 [s, 8 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.19 [s, 24 H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.77 [s, 36 H, $C(CH_3)_2$-$CH_2C(CH_3)_3$] ppm.

[Ti(tbop-$\kappa^3O,S,O)_2$] (3): $tbopH_2$ (2.19 g, 5.44 mmol) was added to a solution of [$Ti(NMe_2)_4$] (0.5 g, 2.72 mmol) in hexane (30 mL). After refluxing the reaction mixture for 6 h, all volatiles were evaporated in vacuo and the residue was dissolved in *n*-hexane (10 mL). The resulting solution was allowed to stand at room temperature for several days, upon which orange microcrystals of **3** separated. Yield: 0.4 g (15.8%). The extremely good solubility of this complex in organic solvents did not allow us to separate pure **3** with higher yield. Removal of solvent under vacuum gave a sticky product. $C_{56}H_{80}O_4S_2Ti$ (929.30): calcd. C 72.38, H 8.68, S 6.90; found C 71.99, H 8.65, S 7.11. IR (Nujol mull): $\tilde{\nu}$ = 446 (m), 460 (m), 502 (w), 539 (w), 566 (m), 575 (m), 627 (vw), 669 (vw), 722 (m), 747 (w), 781 (m), 822 (s), 838 (vs), 882 (m), 915 (m), 934 (vs), 1046 (w),

1060 (w), 1100 (w), 1151 (w), 1190 (m), 1260 (vs), 1320 (m), 1588 (w) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 8.35–6.24 (m, 12 H, C_6H_3), 1.70 [br, 8 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.40 [br, 24 H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.95, 0.90, 0.84 [s, 36 H, $C(CH_3)_2CH_2C(CH_3)_3$] ppm.

[Ti$_2$(μ-tbop-κ^{3}O,S,O)$_2$Cl$_2$(dipp)$_2$] (4)·Et$_2$O: A solution of Li(dipp) (0.50 g, 2.70 mmol) in diethyl ether (20 mL) was added to a solution of **2** (2.52 g, 2.70 mmol) in diethyl ether (30 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 1 week provided red crystals of complex **4**. Yield: 1.24 g (65%). $C_{80}H_{114}Cl_2O_6S_2Ti_2$ (1402.65): calcd. C 68.54, H 8.20, Cl 4.99, S 4.57; found C 67.99, H 8.01, Cl 5.05, S 4.68. IR (Nujol mull): $\tilde{\nu}$ = 350 (m), 386 (s), 416 (m), 428 (m), 456 (m), 488 (m), 544 (w), 572 (m), 588 (m), 616 (w), 628 (w), 640 (w), 684 (m), 724 (s), 736 (s), 748 (s), 796 (m), 830 (s), 890 (m), 922 (s), 976 (w), 1044 (w), 1050 (m), 1100 (m), 1122 (m), 1146 (s), 1194 (s), 1250 (m), 1274(s), 1326 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 8.5–7.15 (m, 18 H, C_6H_3), 3.21 [sept, 4 H, $C_6H_3\{CH(CH_3)_2\}_2$], 1.43 [s, 8 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.35 [d, 24 H, $C_6H_3\{CH(CH_3)_2\}_2$], 0.95 [s, 24 H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.77 [s, 36 H, $C(CH_3)_2CH_2C(CH_3)_3$] ppm. The crystal structure shows the presence of one Et_2O molecule in the unit cell. However, the elemental analysis indicates that this is absent from the powder sample analysed; presumably it is removed by the vacuum drying to which the sample was subjected.

[Ti$_2$(μ-tbop-κ^{3}O,S,O)$_2$(N*t*Bu)$_2$(NH$_2$*t*Bu)$_2$] (5): BuLi (2.19 mL, 3.52 mmol) was added to a cooled (233 K) solution of NH_2tBu (0.13 g, 1.76 mmol) in diethyl ether (40 mL). The mixture was allowed to warm to room temperature. After 3 h of stirring, **2** (0.98 g, 0.88 mmol) was added. The orange mixture was stirred for 24 h and then filtered to remove LiCl. Then, NH_2tBu (0.13 g, 1.76 mmol) was added to the filtrate and stirred for 2 h. Concentration of the reaction mixture to 10 mL gave yellow crystals of **5** after standing at room temperature for 2 d. These were filtered off and dried in vacuo. Yield: 0.86 g (76%). $C_{72}H_{120}N_4O_4S_2Ti_2$ (1265.64): calcd. C 68.33, H 9.56, N. 4.43, S, 5.07; found C 68.98, H 10.16, N 4.31, S 5.37. IR (Nujol mull): $\tilde{\nu}$ = 346 (vw), 402 (w), 420 (w), 444 (w), 492 (w), 530 (w), 560 (w), 574 (w), 604 (w), 672 (m), 748 (m), 758 (m), 824 (vs), 886 (m), 874 (s), 1018 (s), 1060 (s), 1112 (s), 1146 (s), 1194 (m), 1232 (s), 1260 (vs), 1308 (vs), 1536 (w), 1592 (m), 3104 (m), 3180 (w) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.94–6.60 (m, 12 H, C_6H_3), 4.22 [br. s, 4 H, $NH_2C(CH_3)_3$], 1.48 [s, 8 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.27 [s, 18 H, $NH_2C(CH_3)_3$], 1.26 [s, 24 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.04 [s, 18 H, $NC(CH_3)_3$], 0.73 [s, 36 H, $C(CH_3)_2CH_2C(CH_3)_3$] ppm.

[Ti(tbop-κ^{3}O,S,O)Cl(OSiMe$_3$)(NH$_2$*t*Bu)] (6): Crude Me_3SiCl (0.86 g, 7.90 mmol) was added to a solution of **2** (2.5 g, 1.97 mmol) in diethyl ether (30 mL). The reaction mixture was stirred at room temperature, upon which the solution changed colour from orange to dark red. After filtration the solution was concentrated to 10 mL and allowed to stand at room temperature for 4 d. After that time red crystals of **6** suitable for X-ray structural analysis separated. Yield: 1.73 g (72%). $C_{35}H_{60}ClNO_3SiSTi$ (686.34): calcd. C 61.28, H 8.82, Cl 5.10, N 2.04, S 4.67; found C 61.91, H 8.53, Cl 5.28, N 2.16, S 5.03%. IR (Nujol mull): $\tilde{\nu}$ = 340 (vw), 472 (w), 492 (w), 584 (m), 622 (w), 680 (m), 736 (m), 762 (s), 836 (s), 892 (s), 928 (vs), 1028 (m), 1056 (m), 1148 (m), 1248 (s), 1280 (s), 1296 (s), 1568 (m), 3216 (s), 3280 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.38–6.79 (m, 6 H, C_6H_3), 4.15 [br. s, 2 H, $NH_2C(CH_3)_3$], 1.47 [s, 4 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.21 [s, 9 H, $NH_2C(CH_3)_3$], 1.09 [s, 12 H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.65 [s, 18 H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.13 [s, 9 H, $Si(CH_3)_3$] ppm.

[NH$_2$*i*Pr$_2$][Ti(tbop-κ^{3}O,S,O)Cl$_3$] (7)·CH$_2$Cl$_2$ and [Ti$_2$(μ-tbop-κ^{3}O,S,O)$_2$Cl$_2$(N*i*Pr$_2$)$_2$] (8): $NHiPr_2$ (0.16 mL, 1.94 mmol) was addedto a solution of **2** (1.09 g, 1.94 mmol) in toluene (20 mL) and the mixture was stirred for 12 h. Then, solvent was removed under vacuum and the residue extracted with Et_2O. CH_2Cl_2 (5 mL) was added to the dark-red ether solution, and left at room temperature for a few days. After that time red crystals of **7** suitable for X-ray analysis had settled out. They were filtered off and dried under vacuum. Yield: 0.89 g (66%). $C_{34}H_{56}Cl_3NO_2STi$ (697.10): calcd. C 58.68, H 8.12, Cl 15.09, N 2.01, S 4.60; found C 58.58, H 8.09, Cl 14.89, N 1.96, S 4.48. IR (Nujol mull): $\tilde{\nu}$ = 316 (s), 352 (m), 416 (m), 450 (m), 468 (m), 492 (m), 578 (s), 588 (m), 680 (m), 740 (s), 754 (m), 834 (s), 879 (m), 892 (m), 1100 (w), 1140 (w), 1248 (s), 1258 (s), 1272 (s), 1290 (s), 1334 (s), 1568 (m), 1579 (m) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.75 (br., 2 H, NH_2iPr_2), 7.63–6.50 (m, 6 H, C_6H_3), 2.88 [m, 2 H, $NCH(CH_3)_2$], 1.63 [s, 4 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.28 [d, 12 H, $NCH(CH_3)_2$], 1.25 [s, 12 H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.81 [s, 18 H, $C(CH_3)_2CH_2C(CH_3)_3$] ppm. The crystal structure shows the presence of one CH_2Cl_2 molecule in the unit cell. However, the elemental analysis indicates that this is absent from the powder sample analysed; presumably it is removed by the vacuum drying to which the sample was subjected.

The dark-orange, solid residue from the separation of **7** was dissolved in toluene (20 mL) and Et_2O (20 mL) was added. After standing for 2 d at room temperature, orange microcrystals of **8** precipitated. These were filtered off, washed with Et_2O and dried under vacuum. Yield: 0.58 g (48%). $C_{68}H_{108}Cl_2N_2O_4S_2Ti_2$ (1248.47): calcd. C 65.42, H 8.72, Cl 5.68, N 2.24, S 5.14; found C 65.02, H 8.41, Cl 5.52, N 2.01, S 5.21. IR (Nujol mull): $\tilde{\nu}$ = 338 (w), 456 (m), 486 (m), 576 (s), 625 (w), 675 (m), 735 (s), 750 (s), 799 (s), 879 (s), 890 (m), 1105 (w), 1139 (w), 1245 (s), 1251 (s), 1269 (s), 1287 (s), 1330 (s), 1579 (m) cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.63–6.50, (m, 6 H, C_6H_3), 3.37 [sept, 2 H, $N\{CH(CH_3)_2\}_2$], 1.63 [s, 4 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.28 [s, 12 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.01 [d, 12 H, $N\{CH(CH_3)_2\}_2$], 0.81 [s, 18 H, $C(CH_3)_2CH_2C(CH_3)_3$] ppm.

Polymerisation Test: A slurry of [$MgCl_2(THF)_2$] (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 6 h. Then, the titanium compound (1 mmol) and *n*-hexane (50 mL) were added, and the mixture was milled for a further 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 polymerisation, ethene was passed through the suspension of the catalyst (10 mL) in a Schlenk ampoule for 15 min at room temperature and normal pressure to form the prepolymer (about 1 g). An additional amount of organoaluminium compound [$Al(iBu)_3$ or MAO] was then added to the catalyst dispersed in the prepolymer (Al:Ti = 2000) to form a highly active catalyst. The polymerisation 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 polymerisation was quenched with a 5% solution of HCl in methanol and dried under vacuum.

Crystal Data and Refinement Details for 1·2CH$_3$CN, 5, 6, and 7·CH$_2$Cl$_2$: Preliminary examination and intensity data collections were carried out on a CCD KUMA KM4 κ-axis diffractometer with graphite-monochromated Mo-K_α. Data were corrected for Lorentz, polarisation and absorption effects. The structures were solved by direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL-NT v. 5.1 software package.[23] Carbon-bound hydrogen atoms were included in calculated positions and refined in the riding mode. Other hydrogen

Table 2. Details of data collection and structural refinements for **1**·2CH_3CN, **5**, **6** and **7**·CH_2Cl_2.

	1·2CH_3CN	**5**	**6**	**7**·CH_2Cl_2
Empirical formula	$C_{88}H_{126}Cl_2N_2O_6S_3Ti_2$	$C_{72}H_{120}N_4O_4S_2Ti_2$	$C_{35}H_{60}ClNO_3SSiTi$	$C_{35}H_{58}Cl_5NO_2STi$
M	1570.77	1265.64	686.34	782.03
T [K]	100(1)	100(1)	100(1)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_1/c$
a [Å]	16.029(2)	17.312(5)	10.761(2)	17.770(3)
b [Å]	17.208(2)	23.068(4)	11.943(2)	15.272(2)
c [Å]	18.016(2)	22.075(6)	15.433(2)	15.207(3)
α [°]	110.19(1)	90	78.54(1)	90
β [°]	103.27(1)	112.47(5)	88.54(1)	98.26(1)
γ [°]	92.05(1)	90	82.00(1)	90
D_c [Mg m^{-3}]	1.147	1.029	1.184	1.272
μ [mm^{-1}]	0.355	0.289	0.409	0.618
Reflections collected	31389	17731	13320	26620
Independent reflections (R_{int})	19801 (0.0576)	9489 (0.0483)	8476 (0.0323)	9602 (0.0553)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0717, 0.1292	0.0752, 0.1665	0.0502, 0.1047	0.0734, 0.1200

atoms were located in a difference map and refined free. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data are summarised in Table 2.

CCDC-243718 to -243721 (for **1**·2CH_3CN, **5**, **6**, and **7**·CH_2Cl_2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cam-bridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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