# Titanium Complexes Containing a Disulfide-Bridged Bis(phenolato) Ligand: Synthesis and Structural Characterization of Three Different Bonding Modes

Jun Okuda,*[a] Stefan Fokken,[a] Thomas Kleinhenn,[a] and Thomas P. Spaniol[a]

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A series of titanium(IV) complexes containing the 2,2′-dithiobis(6-*tert*-butyl-4-methylphenolato) ligand (dtbmp) were synthesized and characterized. Treatment of titanium tetra(isopropoxide) with 2,2′-dithiobis(6-*tert*-butyl-4-methylphenol) (dtbmpH$_2$) gave, regardless of the molar ratio of the starting materials, a $C_2$-symmetric dinuclear complex [Ti$_2$(O*i*Pr)$_2$(μ$_2$-O*i*Pr)$_2$(dtbmp)]. According to the results of a single crystal X-ray analysis, the two Ti(O*i*Pr)$_2$ fragments in this complex are bridged by a dtbmp ligand and two isopropoxide ligands. The disulfide link of the dtbmp ligand is bonded to each of the titanium centers [Ti–S 2.795(1) and 2.768(1) Å], thus completing an octahedral coordination sphere around titanium. Reaction of [Ti$_2$(O*i*Pr)$_4$(μ$_2$-O*i*Pr)$_2$(dtbmp)] with Me$_3$SiX (X = Br, I) gave the mononuclear complex Ti(dtbmp)X$_2$. Crystallographic study revealed a distorted octahedral coordination with the disulfide link of the dtbmp dihapto-bonded through a relatively short Ti–S distance of 2.637(1) Å (X = Br) or 2.645(2) Å (X = I). Finally, the reaction of titanium tetra(*n*-butoxide) with dtbmpH$_2$ gave a $C_i$-symmetric dimer [Ti$_2$(O*n*Bu)$_2$(μ$_2$-O*n*Bu)$_2$(dtbmp)$_2$] that exhibits a monohapto coordination of the disulfide bridge in the dtbmp ligand with Ti–S bond lengths of 2.692(1) Å and 2.694(1) Å in the crystal.

## Introduction

As precursors for homogeneous α-olefin polymerization catalysts, titanium complexes with bulky bisphenolato ligands such as the 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato) ligand (mbmp)[1] are attracting some interest as alternatives for both the *ansa*-metallocenes[2] and the chelating diamido complexes.[3] Following the remarkable finding by Kakugo et al.[1c] that in such catalyst precursors the replacement of a methylene bridge[4] by a sulfide group imparts a significant increase in the polymerization activity when activated with methylaluminoxane, crystallographic[5] and computational studies[6] have indicated that the sulfide donor plays an active role. In the putative alkyl cation, the weakly coordinating sulfide is thought to decrease the activation barrier for the olefin insertion into the alkyl−titanium bond. More recently, we noted that nine-membered chelate complexes of titanium are formed with remarkable ease with the ethylene-bridged bisphenolato ligand 2,2′-ethylenebis(6-*tert*-butyl-4-methylphenolato) ligand (ebmp).[5b,7] They copolymerize ethylene with styrene with significant incorporation of the bulky monomer styrene.[8] Since no examples for titanium complexes of 2,2′-dithiobis(6-*tert*-butyl-4-methylphenol) were known in the literature,[9] we decided to study its coordination at tetravalent titanium centers. In this contribution, we describe the synthesis and structural characterization of titanium complexes incorporating the disulfide analogue of the ebmp ligand, 2,2′-dithiobis(6-*tert*-butyl-4-methylphenolato) (dtbmp).

## Results and Discussion

When titanium tetrachloride was reacted with one equivalent of 2,2′-dithiobis(6-*tert*-butyl-4-methylphenol) (dtbmpH$_2$)[9] in hexane for 4 h, the dichloro complex Ti(dtbmp)Cl$_2$ (**1**) could be isolated in 78% yield as a dark red powder. Analytical, mass and $^1$H and $^{13}$C NMR spectroscopic data are consistent with a mononuclear structure with two terminal chloro ligands in which the dtbmp ligand acts as a chelating ligand. Upon complexation, all $^1$H and $^{13}$C NMR signals are shifted to lower field. In contrast to the sparingly soluble dichloro titanium complexes with the chelating bridged bisphenoxy ligands of the type [Ti{Z(OC$_6$H$_2$-4-Me-6-*t*Bu)$_2$}Cl$_2$] (Z = S,[5] SO,[10] and SO$_2$),[5b] but similar to the methylene- and ethylene-linked derivatives [Ti(mbmp)Cl$_2$][4a] and [Ti(ebmp)Cl$_2$],[7] hexane-soluble **1** appears to be mononuclear in solution.

The homologous dark red dibromo and black diiodo complexes **2** and **3** were prepared by reaction of the novel tri(isopropoxy) derivative [Ti$_2$(O*i*Pr)$_4$(μ$_2$-O*i*Pr)$_2$(dtbmp)] (**4**), described below, with an excess of Me$_3$SiX (X = Br, I) in ca. 40% yield. Since the analytical, mass, and $^1$H and $^{13}$C NMR spectroscopic data of **2** and **3** are similar to those of **1**, a structure analogous to that of **1** can be implied for both. Single crystals obtained by slow crystallization from pentane solutions could be analyzed by X-ray diffraction. The two complexes are isomorphous. The crystallographic data are summarized in Table 1 and an ORTEP diagram of the diiodo complex **3** is depicted in Figure 1. The molecule resides on a crystallographically imposed $C_2$ axis. The coordination sphere around the tetravalent titanium center can be described as strongly distorted octahedral. Whereas the two halo ligands and the two sulfur atoms of the disulfide bridge form a sort of equatorial plane [dihedral angle be-

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[a] Institut für Anorganische Chemie und Analytische Chemie,
Johannes Gutenberg-Universität,
Duesberg-Weg 10−14, D-55099 Mainz, Germany

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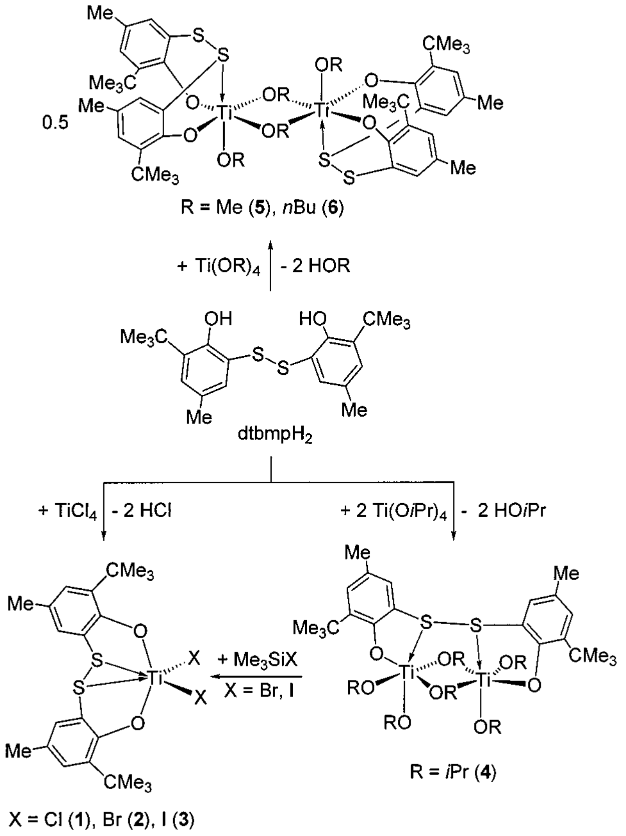

Scheme 1

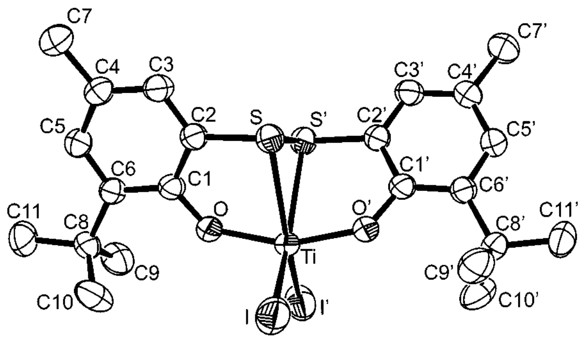

Figure 1. ORTEP diagram of the molecular structure of Ti(dtbmp)$I_2$ (**3**); thermal ellipsoids are drawn at 50% probability level; hydrogen atoms are omitted for the sake of clarity; selected bond lengths (Å) and angles (°): Ti−I 2.6225(6), Ti−O 1.847(2), Ti−S 2.637(1), S−S′ 2.137(2); I−Ti−I 111.00(3), O−Ti−O 158.2(1), C1−O−Ti 135.9(2), C2−S−S′ 99.8(1), S−Ti−S′ 47.82(4)

tween the $TiI_2$ and $TiS_2$ planes 12.68(2)°], the phenoxy oxygen atoms can be considered as adopting the apical sites [O−Ti−O 158.2(1)°]. While the titanium−iodine bond lengths are within the expected range of 2.65 Å,[11] the titanium−sulfur bond of 2.637(1) Å is shorter than that observed in most other tbmp titanium complexes.[5] In agreement with a stronger titanium−disulfide interaction, the sulfur−sulfur distance of 2.137(2) Å is significantly longer than that in dtbmp$H_2$ (2.086 Å).[9b] The angles at the phenoxy oxygen atoms are 135.9(2)° and are considerably smaller than the corresponding values in Ti(ebmp)$Br_2$[5b,7]

Table 1. Crystallographic data for **2**, **3**, **4**, and **6**

| Compound | **2** | **3** | **4** | **6** |
|---|---|---|---|---|
| Empirical formula | $C_{22}H_{28}Br_2O_2S_2Ti$ | $C_{22}H_{28}I_2O_2S_2Ti$ | $C_{40}H_{70}O_8S_2Ti_2$ | $C_{60}H_{92}O_8S_4Ti_2\cdot 0.5C_6H_6$ |
| Formula mass | 596.28 | 690.26 | 838.88 | 1204.43 |
| Crystal color | red | black | orange | orange |
| Crystal size [mm] | 0.9 × 0.5 × 0.4 | 0.6 × 0.3 × 0.3 | 0.6 × 0.4 × 0.3 | 1.10 × 1.04 × 0.94 |
| Crystal system | monoclinic | monoclinic | triclinic | orthorhombic |
| Space group | $C2/c$ | $C2/c$ | $P\bar{1}$ | $Pna2_1$ |
| $a$ [Å] | 14.505(6) | 14.355(2) | 10.249(1) | 19.206(3) |
| $b$ [Å] | 11.949(5) | 12.248(3) | 13.763(1) | 15.614(3) |
| $c$ [Å] | 14.635(5) | 14.949(3) | 19.018(3) | 23.740(2) |
| $\alpha$ [°] | 90 | 90 | 70.495(9) | 90 |
| $\beta$ [°] | 99.08(3) | 95.55(1) | 76.34(1) | 90 |
| $\gamma$ [°] | 90 | 90 | 77.779(8) | 90 |
| $V$ [Å$^3$] | 2505(2) | 2616.0(9) | 2431.2(5) | 7119(2) |
| $Z$ | 4 | 4 | 2 | 4 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.581 | 1.753 | 1.146 | 1.124 |
| $\mu$ [mm$^{-1}$] | 3.714 | 2.862 | 0.456 | 0.387 |
| $F(000)$ | 1200 | 1344 | 900 | 2580 |
| $2\theta_{max}$ [°] | 56 | 60 | 52 | 56 |
| Index ranges | $0 \le h \le 19$ | $-20 \le h \le 20$ | $0 \le h \le 12$ | $0 \le h \le 25$ |
|  | $-10 \le k \le 15$ | $-17 \le k \le 17$ | $-16 \le k \le 16$ | $-20 \le k \le 18$ |
|  | $-19 \le l \le 19$ | $-20 \le l \le 20$ | $-22 \le l \le 23$ | $-31 \le l \le 22$ |
| Transmission (min/max) | 86.68/99.96 | 91.91/100.00 | 96.73/99.85 | 95.39/100.00 |
| Reflections collected | 3307 | 7554 | 10039 | 21760 |
| Independent reflections | 3015 | 3781 | 9480 | 11952 |
|  | $R_{int} = 0.0695$ | $R_{int} = 0.0200$ | $R_{int} = 0.0138$ | $R_{int} = 0.0253$ |
| Observed with $I > 2\sigma(I)$ | 1742 | 2822 | 6770 | 9456 |
| No. of parameters | 188 | 174 | 613 | 730 |
| $R1/wR2/GOF$ [$I > 2\sigma(I)$] | 0.0681/0.1473/1.068 | 0.0366/0.0910/1.083 | 0.0455/0.1127/1.059 | 0.0418/0.1097/1.071 |
| $R1/wR2/GOF$ (all data) | 0.1311/0.1809/1.167 | 0.0564/0.1061/1.081 | 0.0783/0.1323/1.038 | 0.0589/0.1204/1.037 |
| Resid. electron density [eÅ$^{-3}$] | 1.183/−0.603 | 1.363/−1.033 | 0.419/−0.280 | 0.362/−0.259 |

and mononuclear nonchelating phenolato titanium complexes.[12]

Attempts to alkylate the dihalo complexes invariably resulted in the formation of dark intractable material. We suspect that the disulfide bridge is irreversibly cleaved by the reducing alkylating reagents. As anticipated, polymerization tests upon activation with MAO and ethylene were irreproducible and showed no significant activity.

When titanium tetra(isopropoxide) was reacted with one equivalent of dtbmpH$_2$ in toluene for three days, orange crystals of what was initially thought to be $[Ti(dtbmp)(O\textit{i}Pr)_2]$ could be isolated. Analogous reactions of titanium tetra(isopropoxide) with methylene-, ethylene-, thio-, sulfinyl- and sulfone-bridged bisphenol all gave the di(isopropoxy) complexes $[Ti\{Z(OC_6H_2\text{-}4\text{-}Me\text{-}6\text{-}\textit{t}Bu)_2\}](O\textit{i}Pr)_2$ in quantitative yield.[5] However, the elemental analysis and mass spectrum of **4** indicated a dinuclear structure with only one half dtbmp ligand per titanium with a formula corresponding to $[Ti_2(O\textit{i}Pr)_6(dtbmp)]$. The $^1$H NMR spectrum has the rather striking feature of all methyl groups of the six isopropoxy groups being diastereotopic. Accordingly, the $^{13}$C NMR spectrum gives rise to three inequivalent isopropyl groups. The molecule therefore does not contain any mirror plane, although the two halves of the dtbmp ligand are equivalent. This appearance is temperature independent in the range of −80 to +110 °C.

Single crystals of **4** obtained by slow cooling of a saturated solution in 2-propanol were studied by X-ray crystallography. The ORTEP diagram of the molecule is shown in Figure 2 and the crystallographic data are listed in Table 1. The results of the diffraction study reveal a dinuclear structure in which two $Ti(O\textit{i}Pr)_2$ fragments are linked by two O*i*Pr groups and one bridging dtbmp ligand. The bulky dtbmp ligand spans the $Ti_2(O\textit{i}Pr)_2$ plane so as to be located in a highly skewed way, rendering the molecule chiral. The coordination geometry around the titanium centers can be regarded as distorted octahedral. The titanium−sulfur distances with 2.7954(9) and 2.768(1) Å are clearly longer than the distance in **3**, whereas the sulfur−sulfur distance is 2.100(1) Å. The coordination mode of the disulfide fragment in **4** is comparable to that found in $[(TiCl_3)_2(\mu\text{-}Cl)_2(\mu\text{-}MeSSMe)]$, for which titanium−sulfur distances of 2.712(3) and 2.742(3) Å and a sulfur−sulfur distance of 2.052(3) Å were reported.[13]

When equimolar mixtures of titanium tetramethoxide and tetra(*n*-butoxide) are reacted with dtbmpH$_2$ in toluene, orange precipitates of the dialkoxo complexes of the formula $[Ti(dtbmp)(OR)_2]$ [R = Me (**5**), *n*Bu (**6**)] are formed. Based on the low solubility of **5** and **6**, a dimeric structure similar to that of $[Ti\{Z(OC_6H_2\text{-}4\text{-}Me\text{-}6\text{-}\textit{t}Bu)_2\}(O\textit{i}Pr)_2]_2$ (Z = S,[7] SO,[10] and SO$_2$[5b]) is inferred. The $^1$H and $^{13}$C NMR spectroscopic data are consistent with a $C_{2h}$ symmetry, since two separate sets of signals for the *n*-butoxy groups are recorded. Most notably, the α-protons of the bridging group are diastereotopic and appear as two higher-order multiplets, whereas those of the terminal *n*-butoxy group give rise to a binomial triplet at 4.87 ppm with $^3J_{HH}$ = 4 Hz. The single crystal structure analysis of **6** confirmed a related dimeric structure (Table 1, Figure 3). The centrosymmetric molecule consists of two $Ti\{S_2(OC_6H_2\text{-}4\text{-}Me\text{-}6\text{-}\textit{t}Bu)_2\}(O\textit{n}Bu)$ fragments bridged by two O*n*Bu groups in the familiar manner. The most striking feature relates to the coordination of the disulfide bridge. Only one sulfur atom is coordinated to the titanium center with a bond length of 2.692(1) and 2.694(1) Å. These distances are somewhat shorter than those in $[Ti\{S(OC_6H_2\text{-}4\text{-}Me\text{-}6\text{-}\textit{t}Bu)_2\}(O\textit{n}Bu)_2]_2$ [2.738(1) Å[5b]] and in other titanium(IV) complexes containing the tbmp ligand,[5] and may reflect a stronger titanium−sulfur bond. The other sulfur atoms of the disulfide links have a distance to the titanium of 3.828(2) and 3.832(2) Å and can be considered to be nonbonding. In agreement with this unsymmetrical bonding situation, the titanium−oxygen bonds Ti1−O4 and Ti2−O7 within the phenoxy moieties with the nonbonding

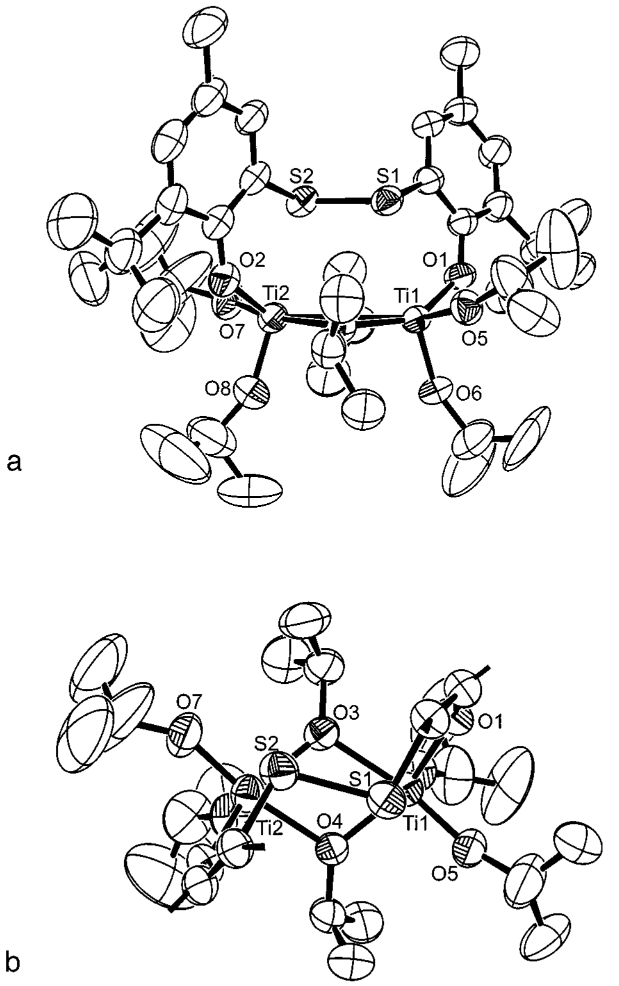

Figure 2. ORTEP diagram of the molecular structure of $Ti_2(O\textit{i}Pr)_4(\mu\text{-}O\textit{i}Pr)_2(dtbmp)$ (**4**): (a) side view; (b) top view; ring carbon atoms except those at the *ipso* and *ortho* positions have been omitted; thermal ellipsoids are drawn at 50% probability level; hydrogen atoms are omitted for the sake of clarity; selected bond lengths (Å) and angles (°): Ti1−O1 1.920(2), Ti1−O5 1.784(2), Ti1−O6 1.773(2), Ti1−O3 2.100(2), Ti1−O4 1.971(2), Ti1−S1 2.7954(9), Ti2−O2 1.923(2), Ti2−O7 1.786(2), Ti2−O3 1.972(2), Ti2−O4 2.087(2), Ti2−O8 1.779(2), Ti2−S2 2.768(1), S1−S2 2.100(1); O6−Ti1−S1 170.95(8), O3−Ti1−O5 164.97(9), O1−Ti1−O4 147.39(8), O3−Ti1−O4 72.26(7), S2−S1−Ti1 100.45(4)

sulfur atoms are significantly shorter than Ti1−O3 and Ti2−O6 and the angles at the oxygen atoms O4 and O7 are larger than those at O3 and O6. The sulfur−sulfur bond length is 2.059(2) Å and significantly shorter not only than that in **3** and **6**, but also that in dtbmpH$_2$. This observation can be explained by a partial sulfur−sulfur double bond character of the disulfide bridge, when only one sulfur atom is coordinated. Finally, the apparent mirror plane in the solution structure can be accounted for by a fast 1,2-shift of the titanium center from one sulfur atom to the other.

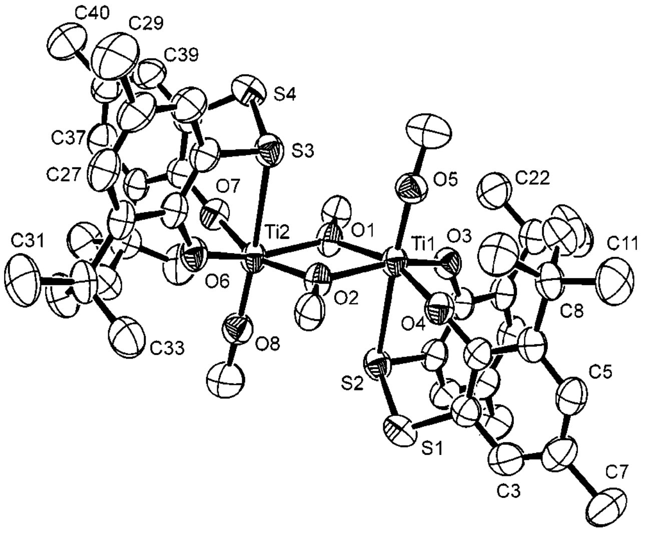

Figure 3. ORTEP diagram of the molecular structure of $Ti_2(OnBu)_2(\mu\text{-}OnBu)_2(dtbmp)_2$ (**6**); thermal ellipsoids are drawn at 50% probability level; carbon atoms of the *n*-butoxy groups except those in the α-positions and hydrogen atoms are omitted for the sake of clarity; selected bond lengths (Å) and angles (°): Ti1−O1 2.038(3), Ti1−O2 1.997(2), Ti1−O3 1.903(2), Ti1−O4 1.855(3), Ti1−O5 1.767(3), Ti1−S2 2.692(1), Ti1−S1 3.828(2), S1−S2 2.059(2), S3−S4 2.063(2), Ti2−S3 2.694(1), Ti2−S4 3.832(2); C2−S1−S2 109.2(2), C2−S1−Ti1 76.3(1), S2−S1−Ti1 42.36(4), O1−Ti1−O2 72.91(9), O3−Ti1−O4 96.8(1) O5−Ti1−S2 171.03(9), Ti2−O1−Ti1 107.0(1), Ti1−O2−Ti2 107.5(1), C13−O3−Ti1 133.3(2), C1−O4−Ti1 153.2(3), C53−O5−Ti1 153.1(4).

In summary, we have synthesized and structurally characterized a series of tetravalent titanium complexes containing a disulfide-linked bis(phenolato) ligand dtbmp. Compared with the ethylene-bridged ligand ebmp, the coordination of the disulfide function at the tetravalent titanium center results in various coordination modes: $\eta^2$-S$_2$ in **2** and **3**, $\mu$-$\eta^1$-S$_2$ in **4**, and $\eta^1$-S$_2$ in **6**. In the literature, most of the disulfide coordination chemistry is confined to that of softer late transition or coinage metals.[13] The facile reduction may, however, limit the application of titanium complexes containing the disulfide-linked bis(phenolato) ligand in polymerization catalysis.

## Experimental Section

**General:** All experiments were performed under argon with standard Schlenk techniques. Solvents were purified, dried and distilled under argon. − $^1$H and $^{13}$C NMR: Bruker DRX 400, AC 200 or AM 400; all spectra in CDCl$_3$ at 25 °C. − Mass Spectra: Finnigan 8230. − Elemental analyses: Microanalytical laboratory of this department.

**2,2′-Dithiobis(6-*tert*-butyl-4-methylphenol) (dtbmpH$_2$):** To a solution of 2-*tert*-butyl-4-methylphenol (126 g, 767 mmol) in 120 mL of toluene was added over a period of 2 h a solution of disulfur dichloride (34.2 mL, 57.7 g, 433 mmol) in 100 mL of toluene at room temperature. The reaction mixture was stirred at 80 °C for an additional 90 min. The solvent was evaporated and the viscous, orange-brown crude product was dissolved in hot ethanol. After cooling and recrystallization from methanol in order to remove 2,2′-trithiobis(6-*tert*-butyl-4-methylphenol), yellow crystals of 2,2′-dithiobis(6-*tert*-butyl-4-methylphenol) were obtained. Yield 53.6 g (36%), m.p. 107 °C. − $^1$H NMR: δ = 1.36 [s, 18 H, C(CH$_3$)$_3$], 2.18 (s, 6 H, 4-CH$_3$), 6.53 (s, 2 H, OH), 6.99 (d, $^4J_{HH}$ = 2 Hz, 2 H, 3-H), 7.11 (d, $^4J_{HH}$ = 2 Hz, 2 H, 5-H). − $^{13}$C{$^1$H} NMR: δ = 20.5 (4-*C*H$_3$), 29.5 [C(*C*H$_3$)$_3$], 35.0 [*C*(CH$_3$)$_3$], 120.6 (C-2), 129.1 (C-4), 131.4 (C-5), 134.0 (C-3), 136.3 (C-6), 153.2 (C-1). − EI MS: *m/z* (%) = 390 (57) [M$^+$], 358 (82) [$C_{21}H_{26}OS_2^+$], 195 (52) [M$^{2+}$], 164 (100) [$C_{11}H_{16}O^+$], 149 (41) [$C_{10}H_{13}O^+$], 91 (17) [$C_7H_7^+$]. − $C_{22}H_{30}O_2S_2$ (390.6): calcd. C 67.65, H 7.74; found C 67.53, H 7.55.

**Dichloro{2,2′-dithiobis(6-*tert*-butyl-4-methylphenolato)}titanium (1):** To a solution of titanium tetrachloride (0.38 mL, 3.48 mmol) in 30 mL of hexane was added slowly a solution of 2,2′-dithiobis(6-*tert*-butyl-4-methylphenol) (1.36 g, 3.48 mmol) in 35 mL of hexane at room temperature. A dark red powder started to precipitate and the reaction mixture was stirred for an additional 4 h. After evaporation of the solvent, the residue was washed with 10 mL of hexane to afford 1.38 g of dark red microcrystals (78%). − $^1$H NMR: δ = 1.49 [s, 18 H, C(CH$_3$)$_3$], 2.33 (s, 6 H, 4-CH$_3$), 7.25 (d, $^4J_{HH}$ = 1.4 Hz, 2 H, 3-H), 7.45 (d, $^4J_{HH}$ = 1.4 Hz, 2 H, 5-H). − $^{13}$C{$^1$H} NMR: δ = 20.9 (4-*C*H$_3$), 29.5 [C(*C*H$_3$)$_3$], 35.4 [*C*(CH$_3$)$_3$], 122.6 (C-2), 127.8 (C-4), 132.0 (C-5), 132.2 (C-3), 137.5 (C-6), 168.0 (C-1). − EI MS: *m/z* (%) = 506 (27) [M$^+$], 471 (32) [M$^+$ − Cl], 194 (52) [$C_{11}H_{14}OS^+$], 91 (100) [$C_7H_7^+$]. − $C_{22}H_{28}Cl_2O_2S_2Ti$ (507.4): calcd. C 52.08, H 5.56; found C 50.98, H 5.41.

**Dibromo{2,2′-dithiobis(6-*tert*-butyl-4-methylphenolato)}titanium (2):** To a solution of **4** (100 mg, 119 μmol) in 15 mL pentane was added bromotrimethylsilane (97.4 μL, 715 μmol) at room temperature. After 2 d dark red crystals precipitated from the solution. Filtration and washing with 2 mL of pentane afforded the product, yield 31 mg (44%). − $^1$H NMR: δ = 1.52 [s, 18 H, C(CH$_3$)$_3$], 2.33 (s, 6 H, 4-CH$_3$), 7.26 (d, $^4J_{HH}$ = 1.4 Hz, 2 H, 3-H), 7.45 (d, $^4J_{HH}$ = 1.4 Hz, 2 H, 5-H). − $^{13}$C{$^1$H} NMR: δ = 20.9 (4-*C*H$_3$), 29.6 [C(*C*H$_3$)$_3$], 35.4 [*C*(CH$_3$)$_3$], 120.6 (C-2), 129.0 (C-4), 131.4 (C-5), 133.9 (C-3), 137.4 (C-6), 168.1 (C-1). − EI MS: *m/z* (%) = 596 (100) [M$^+$], 517 (78) [M$^+$ − Br], 460 (52) [M$^+$ − Br − $C_4H_9$], 196 (12) [$C_{11}H_{16}OS^+$]. − $C_{22}H_{28}Br_2O_2S_2Ti$ (596.3): calcd. C 44.32, H 4.77; found C 44.27, H 4.73.

**Diiodo{2,2′-dithiobis(6-*tert*-butyl-4-methylphenolato)}titanium (3):** To a solution of **4** (180 mg, 324 μmol) in 20 mL pentane was added iodotrimethylsilane (0.26 mL, 1.92 mmol) at room temperature. After 2 d black crystals precipitated from the solution. Filtration and washing with 5 mL of pentane afforded the product, yield 86 mg (38%). − $^1$H NMR: δ = 1.61 [s, 18 H, C(CH$_3$)$_3$], 2.32 (s, 6 H, 4-CH$_3$), 7.30 (d, $^4J_{HH}$ = 2 Hz, 2 H, 3-H), 7.45 (d, $^4J_{HH}$ = 2 Hz, 2 H, 5-H). − $^{13}$C{$^1$H} NMR: δ = 20.8 (4-*C*H$_3$), 29.7 [C(*C*H$_3$)$_3$], 35.3 [*C*(CH$_3$)$_3$], 122.8 (C-2), 129.0 (C-4), 131.2 (C-5), 131.9 (C-3), 133.7 (C-6), 168.2 (C-1). − EI MS: *m/z* (%) = 564 (13) [M$^+$ − I], 436 (100) [M$^+$ − 2I,], 331 (14) [M$^+$ − 2 I − 2 $C_4H_9$], 127 (96) [I$^+$] − $C_{22}H_{28}I_2O_2S_2Ti$ (690.3): calcd. C 38.28, H 4.09; found C 38.08, H 4.14.

**Tetra(isopropoxy)di(μ-isopropoxy){μ-2,2′-dithiobis(6-*tert*-butyl-4-methylphenolato)}dititanium (4):** To a suspension of 2,2′-dithiobis(6-*tert*-butyl-4-methylphenol) (1.88 g, 4.81 mmol) in 50 mL of dry 2-propanol was added titanium tetra(isopropoxide) (2.84 mL, 9.62 mmol) and the reaction mixture stirred for 2 d at room temperature. During this time the color of the solution changed from yellow to orange. The solution was concentrated to a volume of ca. 30 mL and cooled to −78 °C for 16 h to give orange crystals, yield 2.58 g (64%). − $^{1}$H NMR: $\delta = 0.97$ [d, $^{3}J_{HH} = 6.2$ Hz, 6 H, $\mathrm{CH(C}\mathit{H}_3)_2$], 1.00 [d, $^{3}J_{HH} = 6.2$ Hz, 6 H, $\mathrm{CH(C}\mathit{H}_3)_2$], 1.07 [d, $^{3}J_{HH} = 6.2$ Hz, 6 H, $\mathrm{CH(C}\mathit{H}_3)_2$], 1.22 [d, $^{3}J_{HH} = 6.2$ Hz, 6 H, $\mathrm{CH(C}\mathit{H}_3)_2$], 1.34 [d, $^{3}J_{HH} = 6.2$ Hz, 6 H, $\mathrm{CH(C}\mathit{H}_3)_2$], 1.40 [s, 18 H, $\mathrm{C(CH_3)_3}$], 1.48 [d, $^{3}J_{HH} = 6.2$ Hz, 6 H, $\mathrm{CH(C}\mathit{H}_3)_2$], 2.26 (s, 6 H, 4-$\mathrm{CH_3}$), 4.58 [sept, $^{3}J_{HH} = 6.2$ Hz, 2 H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$], 4.97 [sept, $^{3}J_{HH} = 6.2$ Hz, 2 H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$], 5.06 [sept, $^{3}J_{HH} = 6.2$ Hz, 2 H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$], 7.04 (d, $^{4}J_{HH} = 2$ Hz, 2 H, 3-H), 7.38 (d, $^{4}J_{HH} = 2$ Hz, 2 H, 5-H). − $^{13}$C{$^{1}$H} NMR: $\delta = 20.8$ (4-$\mathit{C}\mathrm{H_3}$), 24.1 [$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$], 24.8 [$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$], 25.7 [$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$], 26.1 [$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$], 26.3 [$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$], 26.3 [$\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$], 29.7 [$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 35.2 [$\mathit{C}\mathrm{(CH_3)_3}$], 74.4 [$\mathit{C}\mathrm{H(CH_3)_2}$], 78.5 [$\mathit{C}\mathrm{H(CH_3)_2}$], 79.8 [$\mathit{C}\mathrm{H(CH_3)_2}$], 118.7 (C-2), 127.0 (C-4), 131.1 (C-5), 133.8 (C-3), 137.0 (C-6), 167.2 (C-1). − EI MS: $m/z$ (%) = 554 (2) [$\mathrm{M^+ - Ti(OC_3H_7)_4}$], 436 (6) [$\mathrm{C_{22}H_{28}O_2S_2Ti^+}$], 269 (100) [$\mathrm{(M^+ - Ti(OC_3H_7)_4 - CH_4)^{2+}}$], 225 (13) [$\mathrm{C_{11}H_{13}OS_2^+}$]. − $\mathrm{C_{40}H_{70}O_8S_2Ti_2}$ (838.9): calcd. C 57.27, H 8.41; found C 57.08, H 9.20.

**Tetramethoxybis{2,2′-dithiobis(6-*tert*-butyl-4-methylphenolato)}dititanium (5):** A mixture of 2,2′-dithio(6-*tert*-butyl-4-methylphenol) (1.68 g, 4.30 mmol) and titanium tetramethoxide (741 mg, 4.30 mmol) in 25 mL of toluene was stirred for 3 d at room temperature. After the solvent was evaporated, residual titanium tetramethoxide was removed by filtration of chloroform extracts of the reaction mixture. Evaporation of the solvent afforded a yellow powder, yield 894 mg (42%). − $^{1}$H NMR: $\delta = 1.38$ [s, 18 H, $\mathrm{C(CH_3)_3}$], 2.18 (s, 6 H, 4-$\mathrm{CH_3}$), 3.98 [br s, 3 H, $\mathrm{OCH_3}$], 4.55 [3 H, $\mathrm{OCH_3}$(term.)], 6.89 (d, $^{4}J_{HH} = 2$ Hz, 2 H, 3-H), 7.05 (d, $^{4}J_{HH} = 2$ Hz, 2 H, 5-H). − $^{13}$C{$^{1}$H} NMR: $\delta = 20.7$ (4-$\mathit{C}\mathrm{H_3}$), 29.8 [$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 35.1 [$\mathit{C}\mathrm{(CH_3)_3}$], 63.6, 67.1 [$\mathrm{O}\mathit{C}\mathrm{H_3}$], 119.1 (C-2), 128.2 (C-4), 128.7 (C-5), 129.0 (C-3), 129.5 (C-6), 162.8 (C-1). − EI MS: $m/z$ (%) = 390 (65) [$\mathrm{M/2^+ - 2OCH_3 - Ti}$], 195 (52) [$\mathrm{(M/2 - 2OCH_3 - Ti)^{2+}}$], 164 (100) [$\mathrm{C_{11}H_{16}O^+}$], 91 (85) [$\mathrm{C_7H_7^+}$]. − $\mathrm{C_{48}H_{68}O_8S_4Ti_2}$ (997.1): calcd. C 57.82, H 6.87; found C 59.98, H 6.83.

**Tetra(*n*-butoxy){2,2′-dithiobis(6-*tert*-butyl-4-methylphenolato)}dititanium (6):** To a solution of 2,2′-dithio(6-*tert*-butyl-4-methylphenol) (917 mg, 2.35 mmol) in toluene was added titanium tetra(*n*-butoxide) (0.80 mL, 2.35 mmol). The reaction mixture was stirred for 18 h at room temperature. During this time an orange solid precipitated. Filtration and washing with 2 × 10 mL of toluene afforded orange-yellow microcrystals, yield 992 mg (73%). − $^{1}$H NMR: $\delta = 0.44$ (t, 3 H, $\mathrm{CH_2CH_2CH_2C}\mathit{H}_3$), 0.86 (m, 2 H, $\gamma$-$\mathrm{CH_2}$), 1.02 (t, 3 H, $\mathrm{CH_2CH_2CH_2C}\mathit{H}_3$), 1.35 [s, 18 H, $\mathrm{C(CH_3)_3}$], 1.51 (m, 2 H, $\gamma$-$\mathrm{CH_2}$), 1.59 [m, 1 H, $\beta$-$\mathrm{CH_2}$(term.)], 1.65 [m, 1 H, $\beta$-$\mathrm{CH_2}$(term.)], 1.81 (m, 2 H, $\beta$-$\mathrm{CH_2}$), 2.15 (s, 6 H, 4-$\mathrm{CH_3}$), 4.13−4.31 (m, 2 H, $\mathrm{OCH_2}$), 4.87 [t, $^{3}J_{HH} = 4$ Hz, 2 H, $\mathrm{OCH_2}$-(term.)], 6.84 (d, $^{4}J_{HH} = 2$ Hz, 2 H, 3-H), 6.99 (d, $^{4}J_{HH} = 2$ Hz, 2 H, 5-H). − $^{13}$C{$^{1}$H} NMR: $\delta = 13.8$, 14.1 ($\mathrm{CH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 18.3, 19.1 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 20.7 (4-$\mathit{C}\mathrm{H_3}$), 30.0 [$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$], 30.9, 34.5 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 35.1 [$\mathit{C}\mathrm{(CH_3)_3}$], 76.1, 80.1 ($\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 118.7 (C-2), 128.5 (C-4), 129.0 (C-5), 129.3 (C-3), 137.3 (C-6), 163.0 (C-1). − EI MS: $m/z$ (%) = 582 (84) [$\mathrm{M/2^+}$], 550 (100) [$\mathrm{M/2^+ - 2\ CH_4}$], 438 (99) [$\mathrm{M/2^+ - 2\ OC_4H_9}$]. − $\mathrm{C_{60}H_{92}O_8S_4Ti_2}$ (1165.4): calcd. C 61.84, H 7.95; found C 60.89, H 7.84.

**Crystal Structure Determinations of 2, 3, 4, and 6:** Relevant crystallographic data are summarized in Table 1. X-ray data were collected with an Enraf−Nonius CAD4 diffractometer at 296(2) K by using Mo-$K_\alpha$ radiation and ω scans. Data reductions were carried out using the program system MOLEN.[15a] The structures of **2, 4,** and **6** were solved by direct methods (SHELXS-86);[15b] the structure of **3** was solved by isotypic replacement using the coordinates of **2**. All structures were refined by full-matrix least squares against $F^2$ (SHELXL-93).[15c] Non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. All hydrogen atoms in **2** and **3** were located in difference Fourier maps and refined isotropically, whereas in **4** the hydrogen atoms of several methyl groups are included in calculated positions. In **6**, all hydrogen atoms were included into calculated positions. Four of the isopropyl groups in **4** were refined with disordered split positions. The structure of **6** also shows strong disorder of the *n*-butyl groups. Crystallographic data (excluding structure factors) for the structures included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-140742 for **2**, -140743 for **3**, -170744 for **4**, and -140745 for **6**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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