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Dialkyl titanium complexes that contain a sulfur-linked bis(phenolato) ligand: The structure of an olefin polymerization catalyst precursor

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Abstract

The sulfur-linked bis(phenol) 2,2′-thiobis(2-*tert*-butyl-4-methylphenol), tbmpH_2, reacted cleanly with titanium tetrachloride to give the orange titanium dichloro complex [Ti(tbmp)Cl_2]$_2$ in virtually quantitative yield. Reaction of the dichloro complex [Ti(tbmp)Cl_2]$_2$ with methyllithium at low temperature gave the unexpectedly thermally robust, yellow dimethyl complex [Ti(tbmp)Me_2]. The reaction of the dichloro complex with benzyl Grignard reagent in pentane afforded the highly crystalline dibenzyl complex [Ti(tbmp)$(CH_2Ph)_2$] as a 1,4-dioxane adduct. The single crystal X-ray crystallography revealed a centrosymmetric 1,4-dioxane-bridged molecule that contains two fragments containing six-coordinate titanium centers with the tridentate tbmp ligand in a facial fashion and two η^1-benzyl ligands. When [Ti(tbmp)Me_2] was activated with $B(C_6F_5)_3$ in toluene, ethylene was polymerized.

Keywords: Titanium; Phenolato ligands; Alkyl complexes; Polymerization catalysts

1. Introduction

Among the ancillary ligand systems introduced to develop non-metallocene α-olefin polymerization catalysts [1], the sulfur-linked dianionic ligand based on 2,2′-thiobis(2-*tert*-butyl-4-methylphenol), tbmpH_2, was one of the earliest examples [2]. Titanium complexes that contain a tbmp ligand were shown to be remarkably versatile olefin polymerization catalysts precursors when activated by methylaluminoxane [3,4]. Theoretical calculations have suggested that the titanium–sulfur interaction in the putative intermediate [Ti(tbmp)Me($H_2C{=}CH_2$)]$^+$ results in the relative decrease of the olefin insertion barrier, thus higher polymerization activity [5]. Although the thioether coordination of the tbmp ligand was recognized in various titanium complexes [6–8], experimental data for the actual catalysts remains relatively scarce. This is partly due to the difficulty to prepare, to isolate, and to structurally characterize the dialkyl derivatives of the type [Ti(tbmp)R_2], not to mention the alkyl cations. We report here the synthesis and structure of two dialkyl complexes [Ti(tbmp)R_2] (R = Me, CH_2Ph) that contain a tbmp ligand, along with experiments aimed at generating the alkyl cations [Ti(tbmp)R]$^+$.

2. Results and discussion

As was previously reported [3,6], the reaction of titanium tetrachloride in toluene with 2,2′-thiobis(2-*tert*-butyl-4-methylphenol), tbmpH_2, results in the clean formation of dark brown dichloro complex [Ti(tbmp)Cl_2] (**1**) which is dimeric according to an X-ray structure analysis [6e]. In contrast to the sparingly soluble dinuclear di(isopropoxy) derivative [Ti(tbm-

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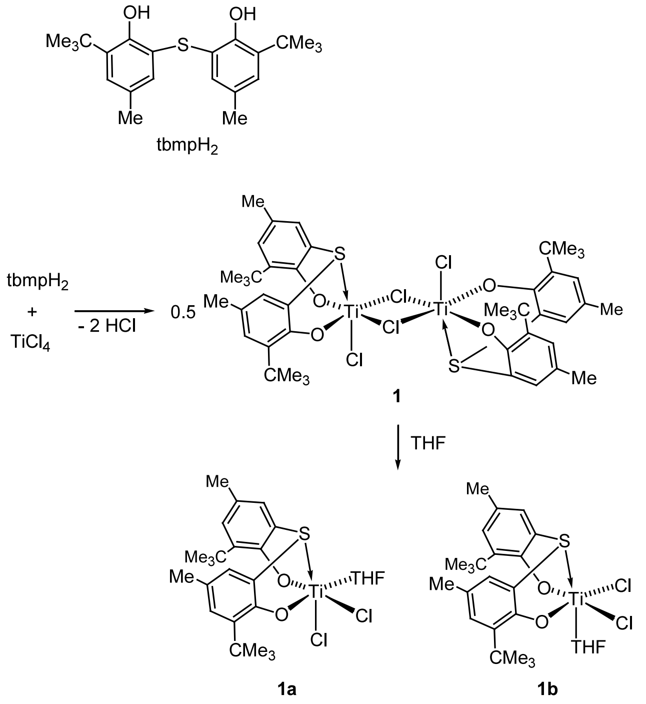
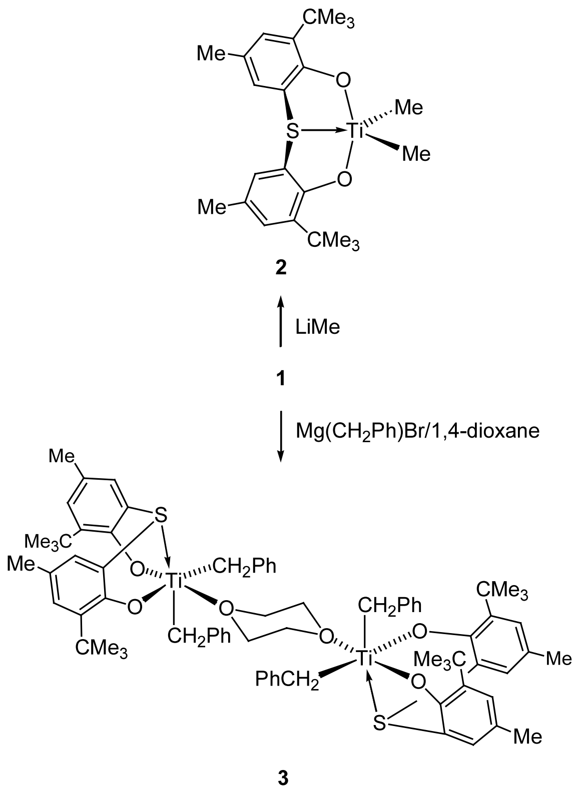
p)(O*i*Pr)$_2$]$_2$ [6a,6b,7], the dichloro complex **1** readily dissolves in basic solvents such as THF and DMSO. Previously **1** was isolated as a diethyl ether solvate [3]. By carefully removing the solvent from THF solutions of **1**, analytically pure mono(THF) adduct [Ti(tbmp)Cl$_2$(THF)] (**1a** or **1b**) could be isolated in quantitative yield (Scheme 1). Although structural characterization was not performed, we give preference to the cis isomer **1a**, since in the trans isomer **1b** the strong π-donor ligands O and Cl would be trans to each other.

The reaction of the dichloro complex [Ti(tbmp)Cl$_2$] (**1**) with methyllithium below -40 °C in pentane–diethyl ether gave an orange solution that decomposed rapidly above 0 °C to a black intractable reaction mixture of unknown composition. Continued experimentation, however, eventually resulted in the isolation of yellow crystalline dimethyl complex [Ti(tbmp)Me$_2$] (**2**). It was crucial to perform the work-up as quick as possible. The dimethyl complex **2** appears to be somewhat stabilized in ethereal solutions and unexpectedly robust in pure state. In solution, it started to decompose only above 70 °C. The NMR spectra of **2** indicate a structure with C_s-symmetry in solution (Scheme 2). The two methyl groups are inequivalent, giving rise to two singlets at 1.22 and 1.51 ppm in the ^{1}H-NMR spectra and to two quartets at 64.1 ($^1J_{CH} = 122$ Hz) and 66.4 ppm ($^1J_{CH} = 124$ Hz) in the ^{13}C-NMR spectra. No coalescence of these signals was observed up to 70 °C, suggesting that an exchange of the two methyl position is associated with a high energy barrier.



Scheme 1.



Scheme 2.

The dimethyl complex **2** could be crystallized from aliphatic hydrocarbons, but the single crystal that was obtained showed only very poor diffraction of X-rays. Data collection was performed at -80 °C. The crystal solution showed a structure between a trigonal biypramid and square pyramid with a titanium center bearing a tridentate tbmp ligand and two inequivalent methyl groups [9]. The titanium–sulfur bond distance of over 2.8 Å is among the longest in titanium complexes containing the tbmp ligand [6,7]. Compared with the dimethyl titanium complex that contain the methylene-bridged bis(phenolato) ligand [{2,2′-CH$_2$(OC$_6$H$_2$-4-Me-6-*t*Bu)$_2$}TiMe$_2$] [10], however, the presence of a titanium–sulfur interaction is evident from the conformation of the eight-membered chelate ring. Due to the very low quality of the experimental data, details from the structure analysis are not discussed further.

The reaction of **1** with benzyl Grignard reagent Mg(CH$_2$Ph)Br in pentane resulted in the clean formation of the dibenzyl complex [Ti(tbmp)(CH$_2$Ph)$_2$] which could only be isolated as a 1,4-dioxanate [Ti(tbmp)(CH$_2$Ph)$_2$]$_2$(μ-C$_4$H$_8$O$_2$) (**3**) (Scheme 2). Well-formed crystals could be readily isolated from pentane solutions and a crystal structure analysis was performed. Fig. 1 shows an ORTEP diagram and Table 1 lists selected bond parameters. In the lattice, two [Ti(tbmp)(CH$_2$Ph)$_2$] fragments are connected by a 1,4-dioxane molecule in a

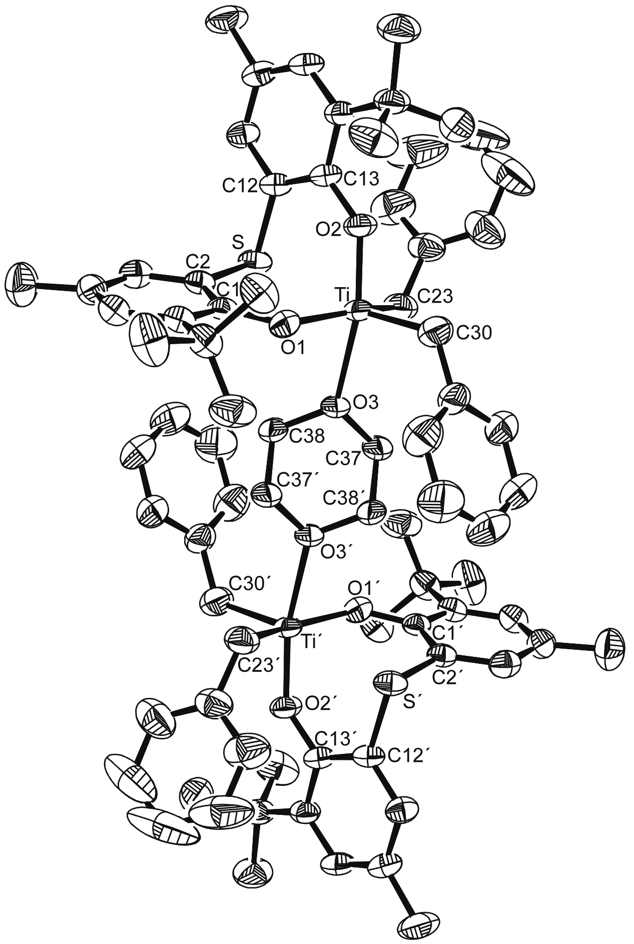


Fig. 1. ORTEP drawing of the molecular structure of **3**. Hydrogen atoms are omitted for clarity. Key atoms are labeled.

Table 1
Selected bond lengths (Å) and angles (°) for $[Ti(tbmp)(CH_2Ph)_2]_2(\mu\text{-}C_4H_8O_2)$ (**3**)

Bond lengths			
Ti–O1	1.893(1)	Ti–O2	1.822(1)
Ti–O3	2.233(1)	Ti–C23	2.170(3)
Ti–C30	2.115(2)	Ti–S	2.8699(6)
Bond angles			
O1–Ti–O2	94.47(6)	O1–Ti–O3	81.41(5)
O1–Ti–C23	149.17(9)	O1–Ti–C30	104.6(1)
O1–Ti–S	72.30(4)	O2–Ti–O3	165.86(6)
O2–Ti–C23	95.68(7)	O2–Ti–C30	95.22(8)
O2–Ti–S	74.66(4)	O3–Ti–C23	81.69(7)
O3–Ti–C30	98.91(8)	O3–Ti–S	91.21(4)
C23–Ti–S	82.48(8)	C30–Ti–S	168.90(8)
C23–Ti–C30	103.4(1)	C24–C23–Ti	116.1(2)
C31–C30–Ti	121.8(2)		

centrosymmetric fashion. In each of the fragment the tbmp ligand is bonded to the octahedral titanium(IV) center in a facial fashion with a titanium–sulfur distance of 2.8699(6) Å. This bond distance is only surpassed by the value of 2.907(1) Å found in $[Ti(tbmp)(\eta^5\text{-}C_5H_5)Cl]$ [6f]. The titanium–oxygen bond distances are 1.822(1) and 1.893(1) Å and comparable with the bond length of average 1.892(2) Å found in $[Ti(tbmp)(O\mathit{i}Pr)_2]_2$ [6a,6b,7] or 1.865(2) Å in $[\{2,2'\text{-}N(CH_2CH_2OMe)(OC_6H_2\text{-}4,6\text{-}\mathit{t}Bu_2)_2\}Ti(CH_2Ph)_2]$ [11]. The relatively large difference in the two bond lengths is due to the *trans*-influence of the benzyl group. A similar situation was previously found in $[Ti(tbmp)\{C_6H_4(CH_2NMe_2)\text{-}2\}Cl]$ (1.831(3), 1.879(3) Å) [6a,6b]. The two monohapto bonded benzyl groups are arranged in a *cis*-position with titanium–carbon bond lengths of 2.170(3) and 2.115(2) Å. They are somewhat longer than titanium–carbon distances found in other dibenzyl titanium complexes such as $[Ti\{2,2'\text{-}(OC_6H_2\text{-}6\text{-}\mathit{t}Bu\text{-}4\text{-}OMe)_2\}(CH_2Ph)_2\}]$ (2.08(1) Å) [3] and $[Ti\{2,2'\text{-}CH_2OCH_2(OC_6H_2\text{-}6\text{-}\mathit{t}Bu\text{-}4\text{-}Me)_2\}(CH_2Ph)_2]$ (2.086(5) and 2.109(4) Å) [12]. The angles at the α-carbon atoms are remarkably large with 116.1(2) and 121.8(2)° and may reflect the considerable steric crowding of the ligand sphere around the octahedral titanium center.

According to the solution NMR spectra in $CDCl_3$ at room temperature, the 1,4-dioxane molecule is engaged in a fast dissociative equilibrium on the NMR time scale, as can be seen from the sharp singlet at 3.66 ppm for all six protons. Furthermore, the two benzyl groups at the five-coordinate ligand sphere give rise to two separate sets of signals. Thus, two sharp singlets are recorded at 25 °C in C_6D_6 at 3.24 and 3.29 ppm. They remain inequivalent up to 65 °C, when the two singlets of the benzylic coalesce. The observation that the benzylic methylene protons are singlets further corroborates the presence of a C_s-symmetric $[Ti(tbmp)(CH_2Ph)_2]$ species. All attempts at isolating a pure Lewis-base free $[Ti(tbmp)(CH_2Ph)_2]$ failed, although a dark red oil of this composition was previously reported [3].

The reaction of the dimethyl complex **2** with the Lewis-acidic activators $B(C_6F_5)_3$, $[NPhMe_2H][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ in bromobenzene or dichloromethane remained inconclusive due to considerable decomposition above −20 °C. However, the dark red solution formed in such reactions reproducibly polymerized ethylene, albeit in low yield. Even at −80 °C was it not possible to record reasonable NMR spectra, since only broad, featureless signals were observed. At this time we conclude that the tetra-coordinated alkyl cation $[Ti(tbmp)Me]^+$ as the putative catalyst must be extremely electrophilic and unstable. The five-coordinate, 10-electron dialkyl complexes $[Ti(tbmp)R_2]$ ($R = Me$, CH_2Ph) themselves exhibit high Lewis-acidity and easily add a Lewis-base such as an ether molecule to form octahedral, 12-electron complexes. Finally, we note that the related five-coordinate bis(anilido) dimethyl complex $[\{(\mathit{t}Bu\text{-}d_6\text{-}\mathit{N}\text{-}\mathit{o}\text{-}C_6H_4)_2O\}TiMe_2]$ exhibits a trigonal biyramidal structure in the solid state, but is fluxional in solution [13].

3. Experimental

3.1. General considerations

All manipulations were carried out under Ar atmosphere in a glovebox or by using the standard Schlenk techniques in oven-dried glassware. The solvents Et_2O, $C_6H_5CH_3$, THF, n-C_6H_{14} and n-C_5H_{12} were dried by refluxing over sodium–bezophenone and CH_2Cl_2 over CaH_2 under an inert gas and distilled freshly before use. Titanium tetrachloride was purchased from Acros and used without further purification. $tbmpH_2$ was prepared according to literature [14]. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H: 400 MHz; ^{13}C: 100 MHz) at 25 °C. C_6D_6, THF-d_8, C_6D_5Br and $CDCl_3$ were purchased from Deutero and purified by conventional methods before use. The chemical shifts were referenced internally according to the residual solvent resonances and reported relative to Me_4Si. Mass spectra were obtained on a Finnigan 8230 spectrometer. Elemental analysis was performed by the Microanalytical Laboratory of this department.

3.2. $[Ti(tbmp)Cl_2]_2$ (**1**)

Titanium tetrachloride (5.0 ml, 45.6 mmol) was slowly added to a stirred solution of $tbmpH_2$ (16.4 g, 45.6 mmol) in 60 ml of $C_6H_5CH_3$. Hydrogen chloride formed was vented through a valve. After 15 h the precipitation of the product was complete. The solvent was removed and the product was dried in vacuo to give 20.2 g (42.6 mmol, 93%) of dark brown microcrystals. ^{1}H-NMR (Me_2SO-d_6, 25 °C): δ 1.32 (s, 18H, $C(CH_3)_3$), 2.12 (s, 6H, 4-CH_3), 6.84 (d, $^4J_{HH} = 1.7$ Hz, 2H, C_6H_2-5), 6.94 (d, $^4J_{HH} = 1.7$ Hz, 2H, C_6H_2-3). $^{13}C\{^1H\}$-NMR (Me_2SO-d_6, 25 °C): δ 20.4 (q, $^1J_{CH} = 126.2$ Hz, 4-CH_3), 29.4 (q, $^1J_{CH} = 125.8$ Hz, $C(\mathit{C}H_3)_3$), 34.5 (s, $\mathit{C}(CH_3)_3$), 121.9 (s, C-2), 127.5 (d, $^1J_{CH} = 147.0$ Hz, C-5), 128.7 (s, C-4), 130.7 (d, $^1J_{CH} = 172.9$ Hz, C-3), 137.4 (s, C-6), 151.9 (s, C-1). EI MS: m/z 474 (62%, $[M]^+$), 459 (6%, $[M-CH_3]^+$), 439 (5%, $[M-Cl]^+$), 424 (100%, $[M-CH_3, -Cl]^+$), 222 (15%, $[M-2CH_3]^{2+}$), 204 (22%), 57 (31%, $[C_4H_9]^+$). Anal. Calc. for $C_{22}H_{28}Cl_2O_2STi$: C, 55.59; H, 5.94. Found: C, 55.48; H, 6.04%.

3.3. $[Ti(tbmp)Cl_2(THF)]$ (**1a**)

The adduct was isolated in quantitative yield as dark red crystals by dissolving $[Ti(tbmp)Cl_2]$ (**1**) in THF and removing the solvent at −78 °C in vacuo. ^{1}H-NMR ($CDCl_3$): δ 1.37 (s, 18H, $C(CH_3)_3$), 2.02 (m, 4H, THF), 2.25 (s, 6H, 4-CH_3), 4.41 (m, 4H, THF) 7.04 (d, $^4J_{HH} = 1.7$ Hz, 2H, 5-H) 7.16 (d, $^4J_{HH} = 1.7$ Hz, 2H, 3-H). ^{13}C-NMR ($CDCl_3$): δ 20.9 (q, $^1J_{CH} = 127$ Hz, 4-CH_3), 25.5 (t, $^1J_{CH} = 134$ Hz, THF), 29.4 (q, $^1J_{CH} = 126$ Hz, $C(\mathit{C}H_3)_3$), 35.1 (s, $\mathit{C}(CH_3)_3$), 75.0 (t, $^1J_{CH} = 156$ Hz, THF), 129.9 (s, C-2), 129.9 (d, $^1J_{CH} = 154$ Hz, C-5), 131.4 (d, $^1J_{CH} = 162$ Hz, C-3), 132.1 (s, C-4), 136.8 (s, C-6), 164.8 (s, C-1). Anal. Calc. for $C_{26}H_{36}Cl_2O_3STi$: C, 57.05; H, 6.63. Found: C, 57.09; H, 6.45%.

3.4. $[Ti(tbmp)Me_2]$ (**2**)

A supension of $[Ti(tbmp)Cl_2]$ (**1**) (2.0 g, 4.2 mmol) in 50 ml of C_5H_{12} was treated with methyllithium in Et_2O (5.3 ml, 8.4 mmol) −44 °C. The reaction mixture was warmed to room temperature (r.t.) and was stirred for 1 h during which time the color turned yellow. After rapid extraction of the residue with 20 ml of C_5H_{12} and filtration, the combined filtrates were concentrated to 15 ml. Cooling to −30 °C afforded 0.5 g of yellow microcrystals (29%). ^{1}H-NMR (C_6D_6): δ 1.56 (s, 18H, $C(CH_3)_3$), 1.59 (s, 3H, $TiCH_3$), 1.73 (s, 3H, $TiCH_3$), 1.97 (s, 6H, 4-CH_3), 7.04 (d, 2H, $^4J_{HH} = 0.5$ Hz, 5-C_6H_2), 7.32 (d, 2H, $^4J_{HH} = 0.5$ Hz, 3-C_6H_2). ^{1}H-NMR ($CDCl_3$): δ 1.22 (s, 3H, $TiCH_3$), 1.51 (s, 3H, $TiCH_3$), 1.52 (s, 18H, $C(CH_3)_3$), 2.26 (s, 6H, 4-CH_3), 7.11 (s, 2H, 5-C_6H_2), 7.35 (s, 2H, 3-C_6H_2). ^{13}C-NMR ($CDCl_3$): $\delta = 20.8$ (pt q, $^1J_{CH} = 126.5$ Hz, $^3J_{CH} = 4.4$ Hz, 4-CH_3), 29.6 (m q, $^1J_{CH} = 126.0$ Hz, $^3J_{CH} = 4.7$ Hz, $C(\mathit{C}H_3)_3$), 35.3 (m, $^2J_{CH} = 3.7$ Hz, $\mathit{C}(CH_3)_3$), 64.1 (q, $^1J_{CH} = 122.4$ Hz, $TiCH_3$), 66.4 (q, $^1J_{CH} = 123.6$ Hz, $TiCH_3$), 125.8 (s, 2-C_6H_2), 129.9 (m d, $^1J_{CH} = 154.3$ Hz, $^3J_{CH} = 4.5$ Hz, 5-C_6H_2), 131.2 (q, $^2J_{CH} = 6.1$ Hz, 6-C_6H_2), 132,7 (m d, $^1J_{CH} = 160.7$ Hz, $^3J_{CH} = 4.4$ Hz, 3-C_6H_2), 136.8 (s, 4-C_6H_2), 164.0 (pt, $^3J_{CH} = 4.4$ Hz, 1-C_6H_2). EI MS: m/z 419 (100%, $[M^+ - Me]$), 404 (89%, $[M^+ - 2Me]$), 358 (54%, $tbmpH_2^+$), 149 (45%, $C_4H_9C_6H_4O^+$), 57 (91%, $C_4H_9^+$). Anal. Calc. for $C_{24}H_{34}O_2STi$ (434.5): C, 66.35; H, 7.89; S, 7.38. Found: C, 65.33; H, 7.80; S, 7.72%.

3.5. $[Ti(tbmp)(CH_2Ph)_2]_2(1,4\text{-}C_4H_8O_2)$ (**3**)

To a solution of $[Ti(tbmp)Cl_2]$ (**1**) (2.0 g, 4.2 mmol) in 50 ml of C_5H_{12} was added a solution of benzyl magnesium bromide (5.8 ml, 1.44 M, 8.4 mmol) in THF at −34 °C. The cooling bath was removed and after stirring for 40 min 1,4-dioxane (0.9 ml, 84 mmol) was added. The dark red solution was stirred for 30 min at r.t. Filtration, concentration to 4 ml, and cooling to −30 °C afforded dark red crystals; yield 1.25 g (51%). ^{1}H-NMR (C_6D_6): δ 1.51 (s, 18H, $C(CH_3)_3$), 2.10 (s, 6H, 4-CH_3), 3.24 (s, 2H, CH_2Ph), 3.29 (s, 2H, CH_2Ph), 3.34 (s, 4H, $C_4H_8O_2$), 6.74 (t, $^3J_{HH} = 7.4$ Hz, 1H, *para*-$CH_2C_6H_5$), 6.91 (d, $^3J_{HH} = 7.1$ Hz, 2H, *ortho*-$CH_2C_6H_5$), 6.97 (pt, $^3J_{HH} = 7.6$ Hz, 3H, *meta*- and *para*-$CH_2C_6H_5$), 7.03 (d, $^4J_{HH} = 1.6$ Hz, 2H, 5-C_6H_2), 7.24 (d, $^4J_{HH} = 1.6$ Hz, 2H, 3-C_6H_2), 7.32 (t, 2H, $^3J_{HH} = 7.4$ Hz, *meta*-$CH_2C_6H_5$), 7.44 (d, 2H, $^3J_{HH} = 7.9$ Hz, *ortho*-$CH_2C_6H_5$). ^{1}H-NMR ($CDCl_3$): δ 1.43 (s, 18H, $C(CH_3)_3$), 2.21 (s, 6H, 4-CH_3), 2.94 (s, 2H,

CH_2Ph), 3.03 (s, 2H, CH_2Ph), 3.66 (s, 4H, $C_4H_8O_2$), 6.71 (d, $^3J_{HH} = 7.1$ Hz, 2H, *ortho*-$CH_2C_6H_5$), 6.76 (t, $^3J_{HH} = 7.4$ Hz, 1H, *para*-$CH_2C_6H_5$), 6.97 (pt, $^3J_{HH} = 7.6$ Hz, 3H, *meta*- and *para*-$CH_2C_6H_5$), 7.03 (d, $^4J_{HH} = 1.6$ Hz, 2H, 5-C_6H_2), 7.21 (d, $^4J_{HH} = 1.6$ Hz, 2H, 3-C_6H_2), 7.25 (m, 4H, *ortho*- and *meta*-$CH_2C_6H_5$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 20.8 (4-CH_3), 29.8 ($C(\mathit{C}H_3)_3$), 35.2 ($\mathit{C}(CH_3)_3$), 67.0 ($C_4H_8O_2$), 90.0 ($\mathit{C}H_2C_6H_5$), 97.4 ($\mathit{C}H_2C_6H_5$), 123.0 (*para*-$CH_2C_6H_5$), 123.5 (*para*-$CH_2C_6H_5$), 126.2 (2-C_6H_2), 127.1 (*meta*-$CH_2C_6H_5$), 127.7 (*meta*-$CH_2C_6H_5$), 128.5 (*ortho*-$CH_2C_6H_5$), 128.6 (*ortho*-$CH_2C_6H_5$) 129.8 (5-C_6H_2), 131.3 (4-C_6H_2), 132.5 (3-C_6H_2), 136.8 (6-C_6H_2), 143.4 (*ipso*-$CH_2C_6H_5$), 146.7 (*ipso*-$CH_2C_6H_5$), 164.6 (1-C_6H_2). EI MS: *m/z* 495 (13%, $[M^+ - C_7H_7]$), 91 (100%, $C_7H_7^+$). Anal. Calc. for $C_{76}H_{92}O_6S_2Ti_2$ (1261.4): C, 72.36; H, 7.35; S, 5.08. Found: C, 72.92; H, 7.05; S, 5.22%.

3.6. X-ray crystal structure analysis of **3**

Single crystals suitable for X-ray crystal structure analysis were obtained by cooling of concd. C_6H_{14} solutions to −30 °C. Crystal data: $C_{76}H_{92}O_6S_2Ti_2$, $M_r = 1261.44$, triclinic, $0.18 \times 0.461 \times 0.795$ mm, $P\bar{1}$ (No. 2), $a = 9.525(1)$, $b = 11.858(1)$, $c = 17.800(2)$ Å, $\alpha = 101.124(2)$, $\beta = 100.815(2)$, $\gamma = 112.274(2)^\circ$, $V = 1748.6(3)$ Å^3, $Z = 2/2$, $\rho_{calc} = 1.198$ Mg m^{-3}, Mo–K$_\alpha$ ($\lambda = 0.71073$ Å), Bruker AXS diffractometer, semi-empirical absorption correction, $T = 193$ K, ω scans, $3^\circ < \theta < 28^\circ$, $F(000) = 672$, μ(Mo–K$_\alpha$) = 0.338 mm^{-1}, number of reflections measured 15 690, 8327 independent reflections. The structure was solved by direct methods (SHELXS-86) [15] and refined (SHELXL-97) [16] against all F^2 data, resulting in $R_1 = 0.0426$ and $wR_2 = 0.099$ for all observed reflections with $I > 2\sigma(I)$, goodness-of-fit = 0.933.

3.7. Ethylene polymerization by [(tbmp)TiMe$_2$] (**2**)

A Schlenk tube (50 ml) with $B(C_6F_5)_3$ (20 mg, 39 µmol) was evacuated and filled with ethene (1 bar). After addition of 9 ml of $C_6H_5CH_3$ the solution was stirred for 5 min and a solution of complex **2** (10 mg, 23 µmol) in 1.5 ml of $C_6H_5CH_3$ was added. The polymerization was stopped after 5 min by adding 1 ml of methanolic HCl and the polymer was precipitated from MeOH. Filtration and drying overnight in vacuo at r.t. gave 24 mg of polyethylene.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 193062 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428.

[2] (a) T. Miyatake, K. Mizunuma, Y. Seki, M. Kakugo, Macromol. Chem. Rapid Commun. 10 (1989) 349;
(b) T. Miyatake, K. Mizunuma, M. Kakugo, Macromol. Chem. Macromol. Symp. 66 (1993) 203.

[3] A. van der Linden, C.J. Schaverien, N. Meijboom, C. Ganter, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008.

[4] (a) F.G. Sernetz, R. Mülhaupt, S. Fokken, J. Okuda, Macromolecules 30 (1997) 1562;
(b) J. Okuda, E. Masoud, Macromol. Chem. Phys. 199 (1998) 543.

[5] (a) R.D.J. Froese, D.G. Musaev, T. Matsubara, K. Morokuma, J. Am. Chem. Soc. 119 (1997) 7190;
(b) R.D.J. Froese, D.G. Musaev, K. Morokuma, Organometallics 18 (1999) 373.

[6] (a) S. Fokken, T.P. Spaniol, H.-C. Kang, W. Massa, J. Okuda, Organometallics 15 (1996) 5069;
(b) S. Fokken, Doctoral Thesis, University of Marburg, 1995.;
(c) J. Okuda, S. Fokken, H.-C. Kang, W. Massa, Polyhedron 17 (1998) 943;
(d) S. Fokken, T.P. Spaniol, J. Okuda, F.G. Sernetz, R. Mülhaupt, Organometallics 16 (1997) 4240;
(e) Y. Nakayama, K. Watanabe, N. Ueyama, A. Nakamura, A. Harada, J. Okuda, Organometallics 19 (2000) 2498;
(f) F. Amor, S. Fokken, T. Kleinhenn, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 621 (2001) 3.

[7] L. Porri, A. Ripa, P. Colombo, E. Miano, S. Capelli, S.V. Meille, J. Organomet. Chem. 514 (1996) 213.

[8] For a leading reference on transition metal complexes containing the tbmp ligand, see: P.L. Arnold, L.S. Natrajan, J.J. Hall, S.J. Bird, C. Wilson, J. Organomet. Chem. 647 (2002) 205.

[9] The following lattice parameters were found: $a = 24.701(4)$, $b = 8.1540(3)$, $c = 11.903(8)$ Å, $b = 104.112(6)^\circ$, tentative space group $P2_1/c$ (No. 14); T.P. Spaniol, F. Reichwald, J. Okuda, unpublished results.

[10] (a) C. Floriani, F. Corazza, W. Lesueur, A. Chiesi-Villa, C. Guastini, Angew. Chem. Int. Ed. Engl. 28 (1989) 66;
(b) J. Okuda, S. Fokken, H.-C. Kang, W. Massa, Chem. Ber. 128 (1995) 221.

[11] E.Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, Chem. Commun. (2001) 2120.

[12] V. Reimer, T.P. Spaniol, J. Okuda, H. Ebeling, A. Tuchbreiter, R. Mülhaupt, Inorg. Chim. Acta, in press.

[13] (a) R. Baumann, R. Stumpf, W.M. Davis, L.-C. Liang, R.R. Schrock, J. Am. Chem. Soc. 121 (1999) 7822;

(b) R. Baumann, W.M. Davis, R.R. Schrock, J. Am. Chem. Soc. 119 (1997) 3830.

[14] T.K. Prakasha, R.O. Day, R.R. Holmes, J. Am. Chem. Soc. 115 (1993) 2690.

[15] G.M. Sheldrick, SHELXS-86, A Program for Crystal Structure Solution, University of Göttingen, Germany, 1986.

[16] G.M. Sheldrick, SHELXL-97, A Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.