Titanium Complexes Stabilized by a Sulfur-Bridged Chelating Bis(aryloxo) Ligand as Active Catalysts for Olefin Polymerization

Zofia Janas,[a] Lucjan B. Jerzykiewicz,[a] Katarzyna Przybylak,[a] Piotr Sobota,*[a] and Krzysztof Szczegot[b]

Keywords: Titanium / O,S,O ligands / Polymerization / X-ray diffraction / Aluminum

The mixed-ligand complexes [$Ti_2(\mu\text{-}OR)_2(OR)_2(\kappa^3\text{-tbop})_2$] (**1a**) for R = Me and (**1b**) R = Et were prepared by the reaction of $Ti(OR)_4$ and H_2tbop {H_2tbop = 2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol]} in methanol. Treatment of **1a** and **1b** with $AlMe_3$ led to the substitution of terminal alkoxy groups to create the organometallic compounds [$Ti_2(\mu\text{-}OR)_2(\kappa^3\text{-tbop})_2(Me)_2$] (**2a**) for R = Me and (**2b**) for R = Et. Controlled hydrolysis of **2b** causes the evolution of methane and the formation of the titanoxane compounds [$\{Ti_2(\mu\text{-}OEt)_2(\kappa^3\text{-tbop})_2\}_2(\mu\text{-}O)_2$]·$2CH_2Cl_2$ (**3**). Structures of **1a**, **1b**, **2a**, **2b**, and **3** were confirmed by NMR spectroscopy; **1b** and **3** were further investigated with X-ray crystallography. Compounds **1a**, **1b**, **2a**, and **2b** were supported on $MgCl_2$ and when activated with aluminum alkyls, found to effectively polymerize ethylene.

Introduction

Titanium complexes with the formula [Ti(tbmp)X_2] which is derived from the sulfide-linked bis(phenol) H_2tbmp [tbmp = 2,2′-thiobis(6-*tert*-butyl-4-methylphenolato); X = Cl, O*i*Pr] and activated with methylaluminoxane (MAO), were first reported by Kakugo et al. to be highly active in the polymerization of ethylene, propylene, styrene, and dienes, as well as the copolymerization of ethylene with styrene.[1−3] These titanium complexes were found to be more active than the methylene-bridged chelating aryloxide complexes of the type [Ti(mbmp)X_2] [mbmp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato)].[4] This is in qualitative agreement with theoretical studies that showed S-bridged chelating alkoxides to have lower insertion barriers than their methylene-bridged or directly bridged analogues.[5−7] Although the Ti−S interaction in [Ti(tbmp)X_2] is weak, it is likely to be of importance in stabilizing the active cationic species, facilitating its formation from [Ti(tbmp)X_2] and MAO, making the coordination of the counterion more flexible.[8] Titanium bis(phenolato) and bis(naphtholato) complexes are well characterized either structurally or spectroscopically in addition to the kinetics and thermodynamics of the intra- and intermolecular rearrangement in bis(naphtholates) which are also described.[9−10] It is worth noting that molybdenum derivatives containing these ligands have also been intensively investigated and employed for asymmetric olefin metathesis[11] as well as for various ring-closing reactions.[12] However, structural data on thio analogues, especially of their ligand modifications, are still limited.[5,13]

Our work is primarily concerned with the synthesis and structural characterization of titanium compounds with the tridentate (OSO-function) thiobis(phenolato) ligand: 2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenolato] (tbop; Scheme 1). Except for the S-bridge, the tbop ligand appeared to have an extra attractive feature, that is, the long sterically hindered auxiliary group 4-(1,1,3,3-tetramethylbutyl) on the thiobis(phenolato) ligand. This substituent sufficiently increases solubility of the catalyst in hydrocarbons. It was interesting for us to see whether these features of the tbop ligand would help create highly active catalytic systems in the heterogeneous ethylene polymerization process.

Results and Discussion

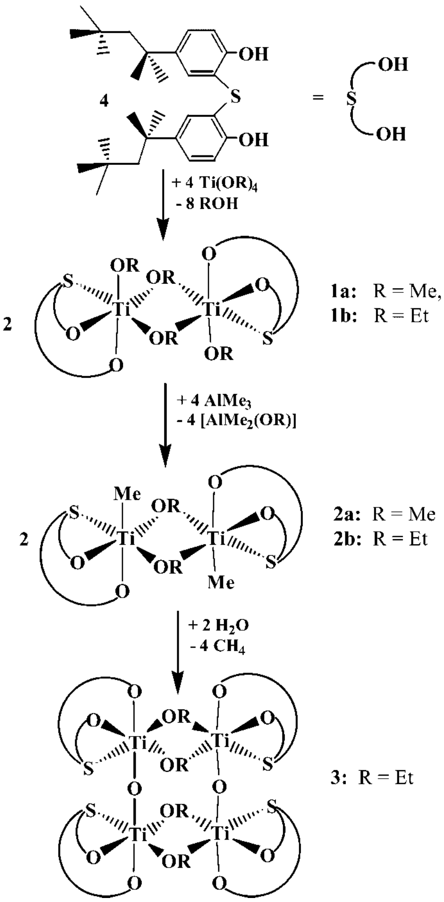
The thiobis(phenol) H_2tbop reacts smoothly with $Ti(OR)_4$ (R = Me, Et) in an appropriate alcohol producing **1a** and **1b**, which are sparingly soluble in alcohols, but readily soluble in common organic solvents (such as toluene, hexane, CH_2Cl_2 and tetrahydrofuran) to give yellow crystals of the complexes [$Ti_2(\mu\text{-}OR)_2(OR)_2(\kappa^3\text{-tbop})_2$] (**1a**) for R = Me, (**1b**) for R = Et (Scheme 1).

Compounds **1a** and **1b** are very stable and can be stored for a long time in air. The ^1H NMR spectra are invariant over a wide temperature range and show two singlets of OCH_3 (δ = 4.61, 4.29 ppm) for **1a** and two sets of CH_3

---

[a] Faculty of Chemistry, University of Wrocław,
14 F. Joliot-Curie Street, 50-383 Wrocław, Poland
Fax: (internat.) + 48-71-3282348
E-mail: plas@wchuwr.chem.uni.wroc.pl
[b] Institute of Chemistry, University of Opole,
48 Oleska Street, 45-052 Opole, Poland

DOI: 10.1002/ejic.200300768



Scheme 1

(t, δ = 1.49; 1.37 ppm) and CH_2 (q, δ = 4.88; 4.78 ppm) resonances of OCH_2CH_3 for **1b** of terminal- and bridging-coordinated alkoxy groups , respectively, suggesting dimeric structures of these complexes exist in solution. A single-crystal X-ray diffraction study for **1b** in the solid state confirmed the structure deduced from ^1H NMR spectroscopy (Figure 1).

The crystal structure of **1b** comprises 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(1)$^{(i)}$] forming the equatorial plane, while the O(2) oxygen atom of the terminal OEt ligand and the sulfur link of the tbop group occupy the apical sites. The two Ti−O(aryloxide) distances of 1.896(2) and 1.916(2) Å are in the expected range for Ti^{IV} complexes with nonbridging aryloxide ligands.[4] The Ti−O(ethoxide) distances of 1.762(2) and 2.009(2) Å are different according to their terminal and bridging nature, respectively, and are typical of $Ti_2(\mu\text{-}OR)_2(OR)$ moieties.[14] The Ti−S bond length of 2.800(1) Å is one of the longest so far reported in the literature;[15] this is substantially longer than Ti−S single bonds (typically 2.3−2.4 Å).[16] Shorter Ti−S bond lengths were reported in the following complexes: for example, $[Ti_2(\mu\text{-}O\mathit{i}Pr)_2(O\mathit{i}Pr)_2(\kappa^3\text{-tbmp})_2]$, where tbmp = 2,2′-thiobis(6-*tert*-butyl-4-methylphenolato) 2.719(1) Å, $[Ti(\kappa^3\text{-tbmp})\{\kappa^2\text{-}C_6H_4(CH_2NMe_2)_2\}Cl]$ 2.704(1) Å, and $[Ti(\kappa^3\text{-tbmp})Cl(O\mathit{i}Pr)(HO\mathit{i}Pr)]$ 2.693(1) Å.[5,13] The geometry of the Ti−S interaction in **1b** is characterized by the angle of 0.7° between the normal of the plane defined by S, C(12), C(22); the Ti−S direction is somewhat smaller than that found in $[Ti_2(\mu\text{-}O\mathit{i}Pr)_2(O\mathit{i}Pr)_2(\kappa^3\text{-tbmp})_2]$ (4°),[5] and is due to the interaction of one of the sulfur lone pairs with the electrophilic Ti atom. However, if the Ti−S interaction is disregarded the coordination can be described as a distorted square-based pyramid with an eight membered ring which has boat-boat conformation.

Reaction of complexes **1a** and **1b** with an excess of $AlMe_3$ in toluene produces light-yellow crystals of the thermally stable organometallic compounds $[Ti_2(\mu\text{-}OR)_2(\kappa^3\text{-tbop})_2(Me)_2]$ (**2a** for R = Me and **2b** for R = Et). Unfortunately, the poor quality of the X-ray data for **2b** prevents us from discussing the bond lengths and angles in detail.[17] Nonetheless, the central core of **2b** is clearly visible as a dimer similar to compound **1b** where the terminal ethoxides are substituted by methyl groups (Scheme 1). The $[Ti_2(\mu\text{-}OMe)_2(Me)_2]$ unit has been observed in the $[Ti_2(\mu\text{-}OMe)_2(\text{tritox})_2(Me)_4]$ (tritox = $\mathit{t}Bu_3CO^-$) complex obtained by controlled interaction of O_2 with the $[Ti(\text{tritox})(Me)_3]$ complex.[18] The presence of the Ti−C bonds was confirmed by the ^1H NMR spectra at room temperature as a singlet (δ = 2.22 ppm for **2a**; δ = 2.23 ppm for **2b**). For comparison, two singlets (δ = 1.38 and 1.36 ppm) of $Ti{-}CH_3$ for $[Ti(\kappa^2\text{-mbp})(CH_3)_2]$ [mbp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato)][4a] and one singlet (δ = 1.22 ppm) for $[Ti(CH_3)_4]{\cdot}Et_2O$ were detected.[19] Additional evidence for the formation of the Ti−C bond was achieved during controlled hydrolysis of **2b**. Treatment of **2b** with an excess of water in toluene resulted in the evolution of methane detected by GC-MS method and the changing color of the reaction mixture from yellow to orange-red. After workup of the post-reaction mixture, red crystals of $[\{Ti_2(\mu\text{-}OEt)_2(\kappa^3\text{-tbop})_2\}_2(\mu\text{-}O)_2]{\cdot}2CH_2Cl_2$ (**3**) were isolated. The solid-state structure of **3** is shown in Figure 2.

Crystals of **3** consist of two $[Ti_2(\mu\text{-}OEt)_2(\kappa^3\text{-tbop})_2]$ units linked by two μ-O(oxo) atoms coordinated to the titanium atoms with two CH_2Cl_2 solvent molecules of crystallization. The four titanium atoms in **3** have equivalent distorted octahedral geometry. Also the individual Ti−μ-O(oxo) bond lengths are broadly similar and are in the range observed for titanoxanes; for example $[Ti_2(\mu\text{-}O)Cl_2(\text{guaiacolato})_4]$,[20] $[Ti_4(\mu\text{-}O)_4(\text{guaiacolato})_8]$,[20] and $[Ti_4(\mu\text{-}O)_4Cl_8(MeCN)_6]$[21] are formed in situ by controlled hydrolysis of the titanium species. The formation of compound **3** upon hydrolysis of **2b** with an excess of H_2O confirms particular stability of the μ-OR bridges. In contrast, upon deliberate hydrolysis of the monomeric compound $[Ti(\text{mbmp})(O\mathit{i}Pr)_2]$ [mbmp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolato)] with one equivalent of water, the formation of $[Ti(\text{mbmp})_2]$ as a main product was observed and crystallographically confirmed.[4c]

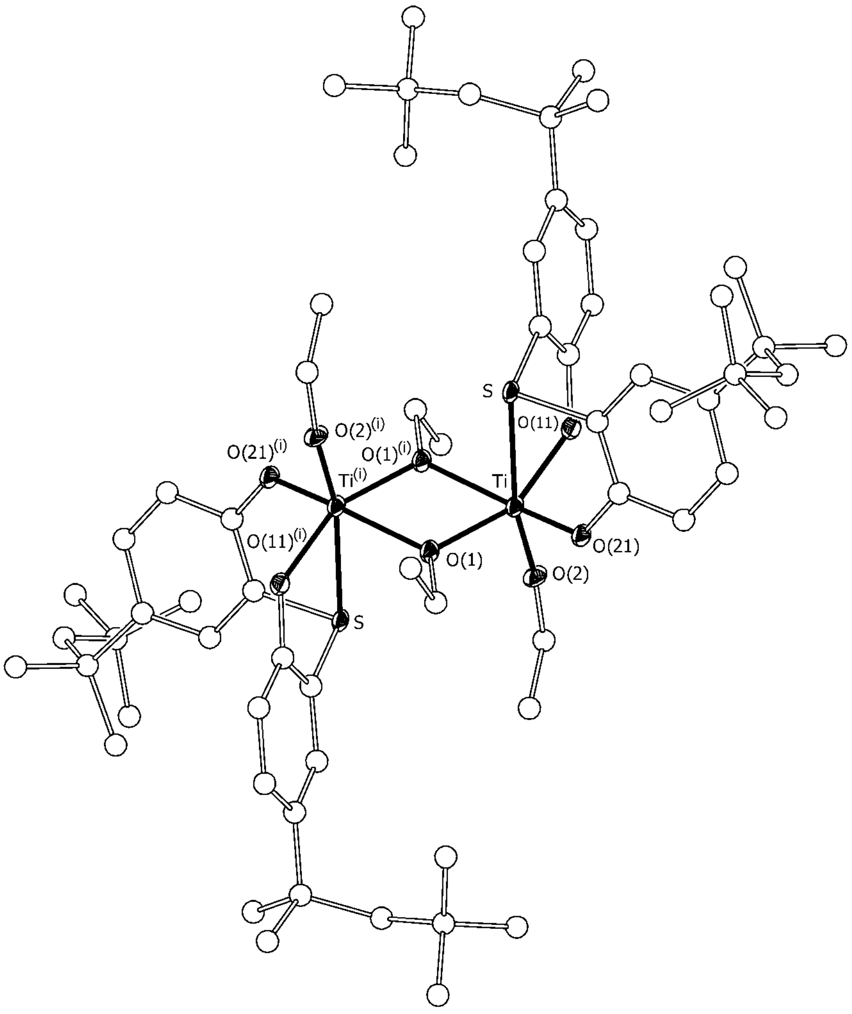


Figure 1. The molecular structure of **1b**; hydrogen atoms and second positions of disordered carbon atoms are omitted for clarity; the displacement ellipsoids are drawn at the 50% probability level; C atoms are represented by open circles of an arbitrary radii. Ti−Ti$^{(i)}$ 3.232(2), Ti−S 2.800(1), Ti−O(1) 2.009(2), Ti−O(2) 1.762(2), Ti−O(11) 1.896(2), Ti−O(21) 1.916(2); O(2)−Ti−O(11) 98.8(1), O(2)−Ti−O(21) 99.1(1), O(11)−Ti−O(21) 99.2(1), O(2)−Ti−O(1) 101.5(1), O(11)−Ti−O(1) 155.8(1), O(21)−Ti−O(1) 90.5(1), O(2)−Ti−O(1)$^{(i)}$ 102.4(1), O(11)−Ti−O(1)$^{(i)}$ 89.6(1), O(21)−Ti−O(1)$^{(i)}$ 155.2(1), O(1)−Ti−O(1)$^{(i)}$ 73.3(1), O(2)−Ti−S 169.5(1), O(11)−Ti−S 74.9(1), O(21)−Ti−S 74.1(1), O(1)−Ti−S 86.8(1), O(1)$^{(i)}$−Ti−S 86.1(1); symmetry transformations used to generate equivalent atoms: $^{(i)}$ $-x + 1$, $-y + 2$, $-z$

Catalysts based on complexes **1a**, **1b**, **2a**, and **2b** are highly active systems for the polymerization of ethylene. They were prepared in *n*-hexane by milling (see Exp. Sect.) a slurry of $MgCl_2(THF)_2$ with one equivalent of the titanium compound and $AlEt_2Cl$ or $AlEt_2Cl/AlEt_3$ (1:1) as the cocatalysts. Ethylene polymerization results; the polymer characterization data are summarized in Table 1.

For comparison of catalyst activities, titanocene dichloride ($[Cp_2TiCl_2]$) was used as a reference under the same conditions (Table 1, Entry 9). It turned out that the catalyst based on the complex **2b** (Entry 7) exhibited the highest catalytic activity (204,760 g·PE·mmol^{-1}·h^{-1}) for ethylene polymerization. This is about fourfold more than with catalysts based on $[Ti_2(\mu\text{-}OEt)_2(OEt)_4(\kappa^2\text{-maltolato})_2]$ (54,630 g·PE·mmol^{-1}·h^{-1}, 50 °C, 0.5 MPa, catalyst 0.01 mmol, $AlEt_2Cl/AlEt_3$ 5 mmol, in *n*-hexane)[20] and the species formulated as $[Ti(tbmp)X_2]$ (47,620 g·PE·mmol^{-1}·h^{-1}; 20 °C, 3 MPa, catalyst 0.2 mmol, MAO 25 mmol, in toluene),[2b] but is less than for $[Ti(tbmp)X_2]$/MAO (390,476 g·PE·mmol^{-1}·h^{-1} for X = Cl and 356,315 g·PE·mmol^{-1}·h^{-1} for X = O*i*Pr; 20 °C, 3 MPa, catalyst 0.001 mmol, MAO 5.17 mmol, toluene) originally reported by Kakugo.[1b,1c] Molecular weights of the polymers produced employing complexes **1a**, **1b**, **2a**, and **2b** under these conditions range from 637,000 to 1,010,000. Polydispersities M_w/M_n for **1a**, **1b**, **2a**, and **2b** (see Table 1) are much narrower than those reported for ethylene polymerization with catalysts based on $[Ti_2(\mu\text{-}OEt)_2(OEt)_4(\kappa^2\text{-maltolato})_2]$ (6.11)[20] and $[Ti(tbmp)X_2]$ (11.9).[2b] It would appear that for polymerization of ethylene, activation at least those systems with $M_w/M_n < 3$ (Entries 3, 4, 7) does afford a single well-defined active species. This indicates that the cocatalyst does not abstract the tbop ligand from the titanium center. In fact, this was confirmed by the results of the interaction of **1a** and **1b** with $AlMe_3$ that showed only the migration of the terminal OR groups to aluminium atoms (Scheme 1). The

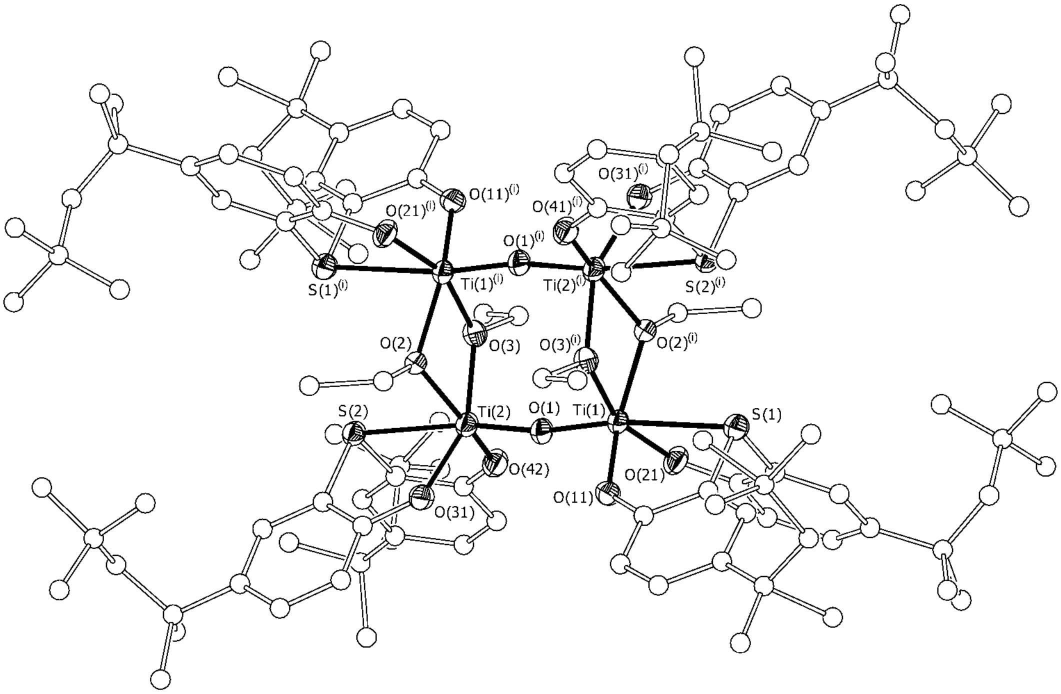


Figure 2. The molecular structure of **3** without solvent molecules with atom numbering scheme; the displacement ellipsoids are drawn at the 50% probability level; H atoms are excluded for clarity; C atoms are represented by circles of an arbitrary radii; selected bond lengths (Å): Ti(1)−Ti(2)$^{(i)}$ 3.204(2), Ti(1)−S(1) 2.762(2), Ti(1)−O(1) 1.816(3), Ti(1)−O(2)$^{(i)}$ 2.000(3), Ti(1)−O(3)$^{(i)}$ 2.011(3), Ti(1)−O(11) 1.878(4), Ti(1)−O(21) 1.866(3), Ti(2)−S(2) 2.770(2), Ti(2)−O(1) 1.795(3), Ti(2)−O(2) 2.017(3), Ti(2)−O(3) 2.004(3), Ti(2)−O(31) 1.878(4), Ti(2)−O(41) 1.870(4); O(1)−Ti(1)−O(21) 99.1(2), O(1)−Ti(1)−O(11) 98.4(2), O(21)−Ti(1)−O(11) 98.7(2), O(1)−Ti(1)−O(2)$^{(i)}$ 101.6(2), O(21)−Ti(1)−O(2)$^{(i)}$ 92.5(2), O(11)−Ti(1)−O(2)$^{(i)}$ 155.2(2), O(1)−Ti(1)−O(3)$^{(i)}$ 99.1(2), O(21)−Ti(1)−O(3)$^{(i)}$ 158.5(2), O(11)−Ti(1)−O(3)$^{(i)}$ 89.9(2), O(2)$^{(i)}$−Ti(1)−O(3)$^{(i)}$ 72.7(2), O(1)−Ti(1)−S(1) 171.4(2), O(21)−Ti(1)−S(1) 75.6(2), O(11)−Ti(1)−S(1) 76.0(2), O(2)$^{(i)}$−Ti(1)−S(1) 85.6(1), O(3)$^{(i)}$ −Ti(1)−S(1) 87.5(1); symmetry transformations used to generate equivalent atoms: (i) $-x + 1, -y + 1, -z$

Table 1. Ethylene polymerization

Entry	Complex[a]	Cocatalyst	Activity[b]	M_w/M_n	D(g·cm^3)
1	**1a**	$AlEt_2Cl$	116,660	4.35	0.963
2	**1a**	$AlEt_2Cl/AlEt_3$ [c]	132,220	4.06	0.967
3	**1b**	$AlEt_2Cl$	120,590	2.94	0.960
4	**1b**	$AlEt_2Cl/AlEt_3$ [c]	150,590	2.77	0.957
5	**2a**	$AlEt_2Cl$	110,160	3.09	0.962
6	**2a**	$AlEt_2Cl/AlEt_3$ [c]	77,540	3.38	0.965
7	**2b**	$AlEt_2Cl$	204760	2.65	0.964
8	**2b**	$AlEt_2Cl/AlEt_3$ [c]	111,900	4.43	0.963
9	Cp_2TiCl_2	$AlEt_2Cl$	30,000	2.44	0.965

[a] Polymerization conditions: $[Ti]_0$ = 0.005 mmol·dm^{-3}, [Al] = 5 mmol·dm^{-3}, Mg/Ti = 10. [b] Units of activity are g·PE·mmol^{-1}·h^{-1}. [c] $AlEt_3Cl/AlEt_3$, 1:1.

preliminary polymerization results on our Ziegler−Natta-like systems are promising on account of the production of a polymer with sufficiently narrow particle-size distributions. To obtain polymers with satisfactory polydispersity properties and high bulk densities we are now investigating the properties of the new catalysts based on modified titanium complexes described here.

Conclusions

The reaction of $Ti(OR)_4$ with H_2tbop in 1:1 molar ratio results in the formation of dimeric mixed-ligand complexes **1a** and **1b**. Treatment of **1a** and **1b** with an excess of $AlMe_3$ leads to the substitution of only terminal alkoxides by methyl groups to form organometallic compounds **2a** and **2b**. The Ti−C bond in **2a** and **2b** is thermally stable but very sensitive to moisture. The reaction of **2b** with water affords the titanoxane species **3**. In fact, the μ-OR bridges in **2a** and **2b** are very stable and do not undergo substitution either by $-CH_3$ groups or alkoxy oxygen atoms. Compounds **1a**, **1b**, **2a**, and **2b** supported on $MgCl_2$ and activated with $AlEt_2Cl$ or $AlEt_2Cl/AlEt_3$ show very high activity in ethylene polymerization. Narrow molecular weight distribution for these systems indicates that the operation of heterogeneous single-site catalysts occurs.

Experimental Section

General Remarks: All operations were carried out under dry nitrogen, using standard Schlenk techniques. All the solvents were distilled under nitrogen from the appropriate drying agents prior to use. The compounds $Ti(OMe)_4$, $Ti(OEt)_4$, $AlMe_3$, $AlEt_2Cl$, and 2,2′-

thiobis{4-(1,1,3,3-tetramethylbutyl)phenol} (H_2tbop) were obtained from the Aldrich Chemical Co. and used without further purification unless stated otherwise. Infrared spectra were recorded with a Perkin−Elmer 180 spectrophotometer as Nujol mulls. NMR spectra were performed with a Bruker ARX 300 spectrometer. Microanalysis were conducted with a ASA-1 (GDR, Karl- Zeiss-Jena) instrument (in-house).

Synthesis of [$Ti_2(\mu\text{-}OMe)_2(OMe)_2(\kappa^3\text{-}tbop)_2$] (1a): $Ti(OMe)_4$ (1.40 g, 8.1 mmol) was added to a solution of H_2tbop (3.60 g, 8.1 mmol) in methanol (50 mL); the mixture was stirred at room temperature for 12 h . A yellow microcrystalline solid was filtered off, washed with methanol, and dried under vacuum. Yield 4.25 g (95 %). $C_{60}H_{92}O_8S_2Ti_2$: calcd. C 65.44, H 8.42, S 5.82; found C 65.12, H 8.25, S 6.12. IR (Nujol mulls, cm^{-1}): $\tilde{\nu}$ = 440 (w), 454 (w), 546 (vs), 576 (vs), 629 (s), 672 (s), 730 (s), 758 (s), 825 (vs), 866 (s), 880 (s), 888 (s), 1028 (s), 1070−1098 (br., s), 1122 (vs), 1208 (w), 1280 (w), 1249 (s), 1280 (vs), 1298 (vs), 1323 (w), 1362 (s), 1344 (w), 1396 (m), 1594 (w). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.76−6.60 (12 H, C_6H_3), 4.61 (s, 6 H, μ-OCH_3), 4.29 (s, 6 H, OCH_3), 1.68 [s, 8 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.35 [s, 24 H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.82 [s, 36 H, $C(CH_3)_2CH_2C\ (CH_3)_3$] ppm. ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ = 165.9, 142.2, 131.9, 129.8, 127.2, 115.9 (C_6H_3), 68.2, 63.0 (OCH_3), 57.1, 38.2, 32.5, 32.0, 31.8 [$C(CH_3)_2CH_2C\ (CH_3)_3$] ppm.

[$Ti_2(\mu\text{-}OEt)_2(OEt)_2(\kappa^3\text{-}tbop)_2$] (1b): This compound was obtained in 90 % yield as a yellow crystalline solid from appropriate quantities of $Ti(OEt)_4$ and H_2tbop by a method similar to that of **1a**. Crystals suitable for the structure determination were obtained from the post-reaction mixture after standing for one day at room temperature. $C_{64}H_{100}O_8S_2Ti_2$: calcd. C 66.42, H 8.71, S 5.54; found C 66.93, H 8.98, S 6.12%. IR (Nujol mulls, cm^{-1}): $\tilde{\nu}$ = 310 (vw), 440 (w), 496 (s), 546 (vs), 580 (s), 622 (s), 680 (s), 740 (s), 764 (s), 834 (vs), 896 (vs), 930 (s), 976 (w), 1028 (s), 1070 (vs), 1122 (vs), 1208 (w), 1248 (s), 1282(vs), 1302 (vs), 1334 (s), 1544 (w), 1596 (m), 1652 (vw). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.76−6.60 (12 H, C_6H_3), 4.98 (q, 4 H, μ-OCH_2CH_3), 4.71 (q, 4 H, OCH_2CH_3), 1.70 [s, 8 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.58 (t, 6 H, μ-OCH_2CH_3), 1.32 [m, 6 H, μ-OCH_2CH_3 and 24 H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.82 [s, 36 H, $C(CH_3)_2CH_2C(CH_3)_3$] ppm. ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ = 166.3, 142.0, 131.9, 129.8, 127.3, 116.0 (C_6H_3), 76.8, 71.4 (OCH_2CH_3), 57.1, 38.1, 32.4, 31.9, 31.7 [$C(CH_3)_2CH_2C(CH_3)_3$], 18.9, 18.4 (OCH_2CH_3) ppm.

[$Ti_2(\mu\text{-}OMe)_2(Me)_2(\kappa^3\text{-}tbop)_2$] (2a): $AlMe_3$ (0.26 g, 3.6 mmol) was added to an orange solution of **1a** (2.00 g, 1.8 mmol) in toluene (50 mL). The brown mixture was stirred for 24 h. The solvent was evaporated off to give an oily residue, after which addition of *n*-hexane (30 mL) and stirring gave a light yellow solid. This was filtered off, washed with *n*-hexane (3 × 5 mL) and dried in vacuo. Yield 1.43 g (74%). $C_{60}H_{92}O_6S_2Ti_2$: calcd. C 67.39, H 8.67, S 6.00; found C 67.12, H 8.62, S 5.89. IR (Nujol mulls, cm^{-1}): $\tilde{\nu}$ = 443 (w), 452 (w), 548 (vs), 572 (vs), 630 (s), 730 (s), 828 (vs), 867 (s), 882 (s), 1030 (s), 1073−1101(br., s), 1126 (vs), 1206 (w), 1282 (w), 1250 (s), 1278 (vs), 1294 (vs), 1320 (w), 1363 (s), 1340 (w), 1398 (m), 1594 (w). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.88−6.69 (12 H, C_6H_3), 4.52 (s, 6 H, μ-OCH_3), 2.23 (s, 6 H, Ti−CH_3), 1.67 [s, 8 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.37 [s, 24 H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.84 [s, 36 H, $C(CH_3)_2CH_2C(CH_3)_3$] ppm. ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ = 165.9, 142.2, 132.0, 130.0, 116.0 (C_6H_3), 68.4, (OCH_3), 57.1, 38.1, 32.4, 32.0, 31.8 [$C(CH_3)_2CH_2C\ (CH_3)_3$], 30.0 (T−CH_3) ppm.

[$Ti_2(\mu\text{-}OEt)_2(Me)_2(\kappa^3\text{-}tbop)_2$] (2b): This compound was obtained in 59 % yield as a light yellow solid from appropriate quantities of **1b** and $AlMe_3$ by a similar method to that used to prepare **2a**. Crystals were obtained from the concentrated reaction mixture after standing for 3 days at room temperature. $C_{62}H_{96}O_6S_2Ti_2$: calcd. C 67.86, H 8.82, S 5.84; found C 67.25, H 8.68, S 5.28. IR (Nujol mulls, cm^{-1}): $\tilde{\nu}$ = 496 (m), 536 (s), 584 (s), 614 (m), 680 (m), 742 (m), 764 (m), 834 (s), 880 (s), 924 (w), 1024 (m), 1060 (m), 1116 (m), 1208 (w), 1250 (m), 1282 (s), 1302 (s), 1544 (vw), 1594 (w). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.77−6.61 (12 H, C_6H_3), 4.78 (q, 4 H, μ-OCH_2CH_3), 2.23 (s, Ti−CH_3), 1.57 [s, 8 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.37 (t, 6 H, μ-OCH_2CH_3), 1.26 [s, 24 H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.84 [s, 36 H, $C(CH_3)_2CH_2C(CH_3)_3$] ppm. ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ = 165.7, 142.6, 132.9, 129.5, 127.3, 115.8 (C_6H_3), 77.0 (OCH_2CH_3), 57.0, 38.1, 32.5, 32.0, 31.7 [$C(CH_3)_2CH_2C(CH_3)_3$], 30.5 (Ti−CH_3), 19.1 (OCH_2CH_3) ppm.

[{$Ti_2(\mu\text{-}OEt)_2(\kappa^3\text{-}tbop)_2$}$_2$($\mu$-O)$_2$]·2$CH_2Cl_2$ (3): To a solution of **2b** (1.10 g, 0.8 mmol) in toluene (30 mL), 0.03 mL (1.7 mmol) of H_2O was added in one portion. The evolution of a gas was identified as methane by the GC-MS method. The reaction mixture was stirred for 2 h and then all volatiles were evaporated under vacuum. The residue was dissolved in CH_2Cl_2 (10 mL), CH_3CN (5 mL) was added and the mixture was left in a refrigerator. After 2 days, orange-red crystals suitable for X-ray study were isolated. Yield 0.56 g (54%). $C_{122}H_{184}Cl_4O_{14}S_4Ti_4$: calcd. C 62.72, H 7.94, Cl 6.07, S 5.49; found C 63.58, H 8.29, Cl 7.12, S 5.94%. IR (Nujol mulls, cm^{-1}): $\tilde{\nu}$ = 302 (vw), 448 (w), 500 (w), 538 (s), 580 (s), 622 (w), 640 (vw), 680 (m), 736 (s), 758 (s), 808 (vs), 828 (vs), 844 (s), 882 (m), 966 (vw), 1028 (m), 1084 (w), 1148 (vw), 1208 (vw), 1252 (m), 1280(s), 1298 (s), 1324 (w), 1544 (vw), 1594 (vw), 1652 (vw). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.63−6.88 (24 H, C_6H_3), 5.96 (s, 4 H, CH_2Cl_2), 4.89 (q, 8 H, μ-OCH_2CH_3), 1.57 [s, 16 H, $C(CH_3)_2CH_2C(CH_3)_3$], 1.49 (t, 12 H, μ-OCH_2CH_3), 1.26 [s, 48 H, $C(CH_3)_2CH_2C(CH_3)_3$], 0.72 [s, 72 H, $C(CH_3)_2CH_2C(CH_3)_3$] ppm. ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ = 165.8, 142.5, 133.0, 129.8, 127.3, 115.7 (C_6H_3), 76.5 (μ-OCH_2CH_3), 57.2, 37.9, 32.1, 32.1, 31.8 [$C(CH_3)_2CH_2C(CH_3)_3$], 19.3 (μ-OCH_2CH_3).

Polymerization Test: A slurry of $MgCl_2(THF)_2$ (30 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 (5 mmol) and *n*-hexane (50 mL) were added, and the mixture was milled for a further 24 h. The sample of procatalyst suspension (containing 0.01 % titanium) was activated with $AlEt_2Cl$ or $AlEt_2Cl/AlEt_3$ (1:1 molar ratio; 20 mmol) for 15 min at 323 K under argon 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 ethylene pressure. The polymerization was quenched with a 5 % solution of HCl in methanol and dried under vacuum.

X-ray Crystallographic Study for 1b and 3: Crystal data collection and refinement are summarized in Table 2. Preliminary examination and intensity-data collections were carried out on a KUMA KM-4 κ-axis diffractometer with graphite-monochromated Mo-K_α and with a scintillation counter (**1b**) or a CCD camera (**3**). All data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with the Kuma Diffraction programs.[22−23] The structures were solved by direct methods,[24] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97 software.[25] Carbon bonded hydrogen atoms were included in calculated positions and refined in the riding mode using SHELXL-97 default parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. In the structure of **1b** one carbon atom of an ethanol molecule is disordered between two sites — occupancy factors for these two positions were set as 0.65 and 0.35,

Table 2. Crystal data and structure refinement

	1b	**3**
Empirical formula	$C_{64}H_{100}O_8S_2Ti_2$	$(C_{120}H_{180}O_{14}S_4Ti_4)\cdot 2CH_2Cl_2$
Molecular mass	1157.32	2332.3
Habit	block	prism
Space group	$P\bar{1}$	$P\bar{1}$
Crystal system	triclinic	triclinic
Unit cell dimensions		
a (Å)	10.401(2)	13.898(5)
b (Å)	11.778(2)	16.122(4)
c (Å)	14.709(3)	17.841(6)
α (°)	91.00(3)	111.22(3)
β (°)	107.00(3)	92.94(3)
γ (°)	111.00(3)	108.18(3)
V (Å^3)	1593.6(5)	3479.0(19)
Z	1	1
T (K)	100.0(5)	100.0(5)
$D_{calcd.}$ (Mg/m^3)	1.206	1.113
μ (mm^{-1})	0.367	0.410
Crystal size (mm)	0.4 × 0.4 × 0.2	0.3 × 0.2 × 0.1
Absorption correction	none	none
Type of diffractometer	Kuma KM4	Kuma CCD-KM4
Diffraction geometry	ω-2θ scan	ω scan
θ (°)	2.21 to 25.11	3.7 to 28.45
Number of reflections collected	4397	24156
Number of unique reflections	4245	15306
$R_{(int)}$	0.0425	0.0570
Number of observed reflections	3393 [$I > 2\sigma(I)$]	6793 [$I > 2\sigma(I)$]
Refinement method	least-squares on F^2	least-squares on F^2
Number of parameters	361	689
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0367$, $wR = 0.1000$	$R_1 = 0.0884$, $wR = 0.2188$
GooF = S	1.074	0.950
Largest diff. peak and hole eA^{-3}	0.554 and −0.496	0.751 and −0.571

$R_1 = \Sigma\|F_o| - |F_c\| / \Sigma F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $S = \{\Sigma[w(F_o^2-F_c^2)^2] / (n-p)\}^{1/2}$

respectively. In the structure of **3** high temperature factors of some carbon atoms suggest their disorder, which could not be resolved. CCDC-198192 (for **1b**) and -198193 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors thank the State Committee for Scientific Research (Poland) for financial support of this work (grant no. 4 T09A 137 24).

---

[1] [1a] M. Kakugo, T. Miyatake, K. Mizunuma, *Chem. Express* **1987**, *2*, 445. [1b] T. Miyatake, K. Mizunuma, Y. Seki, M. Kakugo, *Makromol. Chem. Rapid Commun.* **1989**, *10*, 349. [1c] T. Miyatake, K. Mizunuma, M. Kakugo, *Macromol. Symp.* **1993**, *66*, 203.

[2] [2a] C. J. Schaverien, A. J. van der Linden, A. G. Orpen, *Polym. Prepr. (Am. Chem. Polym. Div.)* **1994**, *35*, 672. [2b] A. J. van der Linden, C. J. Schaverien, N. Meijboom, C. Ganter, A. G. Orpen, *J. Am. Chem. Soc.* **1995**, *117*, 3008.

[3] Patent, Mitsui Toatsu Chem. Inc. JP 05230133-A, **1992**.

[4] [4a] C. Floriani, F. Corazza, W. Lesueur, A. Chiesi-Villa, C. Guastini, *Angew. Chem. Int. Engl.* **1989**, *101*, 93. [4b] F. Corazza, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* **1991**, *30*, 146. [4c] J. Okuda, S. Fokken, H-C. Kang, W. Massa, *Chem. Ber.* **1995**, *128*, 221.

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

[6] R. D. J. Froese, D. G. Musaev, T. Matsubara, K. Morokuma, *J. Am. Chem. Soc.* **1997**, *119*, 7190.

[7] R. D. J. Froese, D. G. Musaev, T. Matsubara, K. Morokuma, *Organometallics* **1999**, *18*, 373.

[8] E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391.

[9] [9a] M. Mazzanti, C. Floriani, A. Chesi-Villa, C. Guastini, *J. Chem. Soc., Dalton Trans.* **1989**, 1793. [9b] P. J. Toscano, E. J. Schermerhorn, C. Dettelbacher, D. Macherone, J. Zubieta, *J. Chem. Soc., Chem. Commun.* **1991**, 933.

[10] T. J. Boyle, D. L. Barnes, J. A. Heppert, L. Morales, F. Takusagawa, J. W. Connolly, *Organometallics* **1992**, *11*, 1112.

[11] R. R. Schrock, J. Y. Jamieson, S. J. Dolman, S. A. Miller, P. J. Bonitatebus Jr., A. H. Hoveyda, *Organometallics* **2002**, *21*, 409 and references cited therein.

[12] S. L. Aeilts, D. R. Cefalo, P. J. Bonitatebus Jr., J. H. Houser, A. H. Hoveyda, R. R. Schrock, *Angew. Chem. Int. Ed.* **2001**, *40*, 1452.

[13] [13a] S. Fokken, T. P. Spaniol, H-Ch. Kang, W. Massa, J. Okuda, *Organometallics* **1996**, *15*, 5069. [13b] H-J. Krüger, *Angew. Chem. Int. Ed.* **1999**, *38*, 627. [13c] Y. Nakayama, H. Saito, N. Ueyama, A. Nakamura, *Organometallics* **1999**, *18*, 3149. [13d] P. L. Arnold,

L. S. Natrajan, J. J. Hall, S. J. Bird, C. Wilson, *J. Organomet. Chem.* **2002**, *647*, 205.

[14] [14a] K. Watenpaugh, C. N. Caughlan, *Inorg. Chem.* **1966**, *5*, 1782. [14b] H. Haase, H. H. Hoppe, *Acta Crystallogr., Sect. B* **1968**, *24*, 281. [14c] A. Koshino, Y. Shuto, Y. Iitaka, *Acta Crystallogr., Sect. B* **1970**, *26*, 544.

[15] [15a] M. M. Olmstead, R. M. Kessler, H. Hope, M. D. Yanuck, W. K. Musker, *Acta Crystallogr., Sect. C* **1987**, *47*, 1890. [15b] T. T. Nadasdi, Y. Huang, D. W. Stephan, *Inorg. Chem.* **1993**, *32*, 347.

[16] *International Tables of Crystallography*, vol. C, Kluwer Academic, Dordrecht, **1992**.

[17] Space group $P\bar{1}$, $a = 7.126(5)$ Å, $b = 14.779(6)$ Å, $c = 18.783(6)$ Å, $\alpha = 91.6(3)°$, $\beta = 97.9(4)°$, $\gamma = 93.9(2)°$.

[18] T. V. Labben, P. Wolczanski, *J. Am. Chem. Soc.* **1987**, *109*, 424.

[19] S. Kleinhenz, K. Seppelt, *Chem. Eur. J.* **1999**, *5*, 3573.

[20] P. Sobota, K. Przybylak, J. Utko, L. B. Jerzykiewicz, A. J. L. Pombeiro, M. F. C. Guedes da Silva, K. Szczegot, *Chem. Eur. J.* **2001**, *7*, 951.

[21] G. R. Wille, J. Palin, M. G. B. Drew, *J. Chem. Soc., Dalton Trans.* **1994**, 1799 and references therein.

[22] Kuma Diffraction. KM-4 User's Guide, Version 10.1. Kuma Diffraction, Wrocław, Poland, **1996**.

[23] Kuma Diffraction. KM-4 CCD Software: version 1.161. KUMA Diffraction Instruments GmbH, Poland, **1995−1999**.

[24] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[25] G. M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.

Received October 22, 2003