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Preparation and characterization of some structural variants of Cp*Ti(1,2-propandiolato) complexes

Alexander Snell [1], Gerald Kehr, Olga Kataeva [2], Roland Fröhlich [3], Gerhard Erker *

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

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Abstract

1,2-Propandiol reacts with $Cp^*Ti(CH_3)_3$ by rapid liberation of methane to yield a dimetallic complex **6** of the net composition $(Cp^*Ti)_2$(1,2-propandiolato)$_3$. The X-ray crystal structure analysis revealed an unsymmetrical bridging between the [Cp*Ti(1,2-propandiolato)] and [Cp*Ti(1,2-propandiolato)$_2$] subunits. Cp^*TiCl_3 reacts with 1,2-propandiol in a 1:1 stoichiometry in the presence of excess pyridine by replacement of two chlorides by a 1,2-propandiolato ligand. The resulting product was isolated as a dimer **8** and characterized by X-ray diffraction. It exhibits a central Ti_2O_2 ring that was formed by bridging between the two [Cp*TiCl(1,2-propandiolato)] subunits using the oxygen atoms of the primary end of the ligand. From the reaction mixture a more complicated condensation product **9** was isolated in a small yield that contains two [Cp*TiCl(1,2-propandiolato)] units connected in a similar way by a Cp*-free [Ti(1,2-propandiolato)$_2$] moiety as revealed by its X-ray crystal structure analysis. Complex [Cp*TiCl(1,2-propandiolato)]$_2$ (**8**) gives an active catalyst for the syndiotactic polymerization of styrene upon treatment with excess methylalumoxane in toluene solution.

Keywords: Preparation; Characterization; Cp*Ti(1,2-propandiolato); Alkoxide-bridged complexes

1. Introduction

Group 4 oxametallacycles exhibit a structural variety that is due to the specific coordination features of the endocyclic M–O– bond. In the three- and four-membered ring systems the oxygen atom has a very pronounced tendency to bridge between metal atoms [1–3]. The metallatricyclic structure of e.g. the (η^2-formaldehyde)zirconocene dimer (**1**) is a typical example (see Scheme 1) [1]. Six-membered and larger ring systems tend to be monomeric [4,5] because the oxygen atom can, with increasing ring size, more easily undergo ligand to metal back-bonding [6]. Consequently, such systems (e.g. **2**) are characterized by large bonding angles at oxygen and rather short Group 4 metal to oxygen bond lengths. The five-membered ring systems represent borderline cases. We had shown previously that the (tartrato)zirconocene complexes **3** attain dimetallatricyclic structures **3a**, that contain tricoordinate bridging oxygen atoms, that equilibrate with their monocyclic dimetallic 10-membered ring isomers **3b**. Both isomer types were characterized by X-ray diffraction [7].

The coordinatively unsaturated Cp-free (tartrato)titanium complexes **4**, that serve as the precursors of the 'Sharpless-epoxidation catalysts', show similar structures, only that here some of the ester substituents are involved in bonding of the ligands to the otherwise highly coordinatively unsaturated metal centers [8]. We have become interested in the structural chemistry of the intermediate mono-Cp* titanium-derived systems [9] and prepared a variety of the respective 1,2-propandiolato complexes. The absence of stabilizing ester substituents has caused some interesting structural variations in these systems, necessary to avoid a high coordinative unsaturation in these systems. We will describe the structural features of three representative examples and briefly discuss some use of a typical

* Corresponding author.
E-mail address: erker@uni-muenster.de (G. Erker).
[1] This work is part of Alexander Snell's doctoral thesis.
[2] X-ray crystal structure analyses.
[3] X-ray crystal structure analyses.

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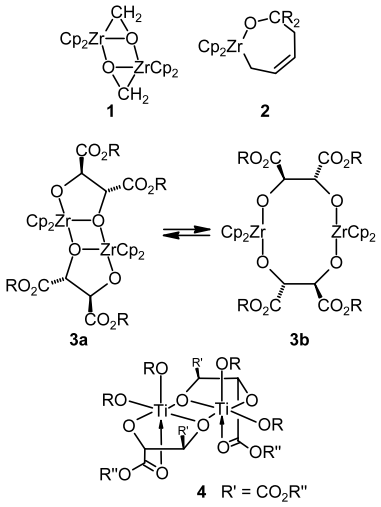


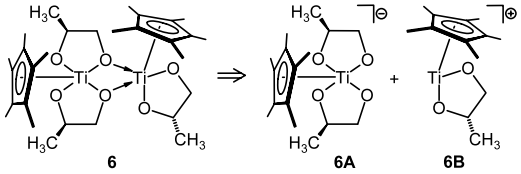
Scheme 1.

example as a catalyst precursor for syndiotactic polystyrene formation.

2. Results and discussion

We first used Cp*Ti(CH_3)$_3$ (**5**) as a starting material [10]. The reactive organometallic substrate was treated with racemic 1,2-propandiol in dichloromethane-d_2 at room temperature. When stoichiometric amounts of the diol were used the reaction was not clean, but a single reaction product **6** was obtained when the propylene glycol reagent was reacted with a slight excess of **5**. Complex **6** crystallized from a pentane extract at −30 °C. The new dimetallic complex was isolated in a yield of 37%. The X-ray crystal structure analysis revealed that all three methyl groups were removed from each Cp*Ti unit. Thus, two molecules of the Cp*Ti(CH_3)$_3$ starting material had apparently reacted with three equivalents of 1,2-propandiol to form the product **6** under the applied reaction conditions. The X-ray crystal structure analysis revealed that a dimetallic complex was formed with bridging alkoxides. The coordination is unsymmetric in that way that one 1,2-propandiolato ligand is coordinated to a single titanium atom (Ti1) to form a genuine dioxatitanacyclopentane ring system, whereas the other Cp*Ti unit (Ti2) bears two such ligands to form a pair of such five-membered metallacycles. The overall framework can *formally* be described in such a way that an electrophilic [Cp*Ti(1,2-propandiolato)]$^+$ subunit is coordinated to two oxygen atoms of a [Cp*Ti(1,2-propandiolato)$_2$]$^-$ nucleophile, that serves as a chelate ligand (see Scheme 2, Fig. 1) [11].

Starting from *rac*-1,2-propandiol one introduces three carbon chirality centers into this structure. At this specific framework a total of 64 stereoisomers could in principle be formed, some of which are pairwise



Scheme 2. Formal construction of the framework of **6**.

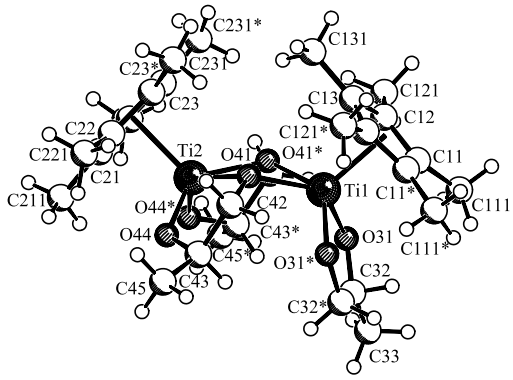


Fig. 1. A view of the molecular structure of complex **6**. Selected bond lengths (Å) and angles (°): Ti1–O31 1.872(2), Ti1–O41 2.060(2), Ti2–O41 2.060(2), Ti2–O44 1.863(2), O31–C32 1.374(4), C32–C33 1.379(7), C32–C32* 1.432(8), O41–C42 1.434(3), C42–C43 1.513(4), C43–O44 1.409(3), C43–C45 1.508(4); O31–Ti1–O31* 81.5(1), O41–Ti–O41* 69.8(1), O31–Ti1–O41 86.3(1), O31–Ti1–O41* 133.1(1), O41–Ti2–O41* 69.8(1), O44–Ti2–O44* 95.9(1), O41–Ti2–O44 79.0(1), O41–Ti2–O44* 131.1(1), Ti1–O31–C32 117.6(2), O31–C32–C33 120.0(5), O31–C32–C32* 111.6(2), C32*–C32–C33 128.4(4), Ti1–O41–Ti2 106.1(1), Ti1–O41–C42 123.8(2), Ti2–O41–C42 111.4(2), O41–C42–C43 106.6(2), C42–C43–O44 105.7(2), C42–C43–C45 114.6(2), C45–C43–O44 111.2(2), Ti2–O44–C43 121.4(2).

identical or enantiomeric. Remarkably, out of the remaining large manifold of possible stereoisomers only a single one was isolated (as a racemate). It is characterized by the relative stereochemistry of the carbon chirality centers as R*,R*,S*. The square pyramidal subunit **6A** (see Scheme 2) thus represents an achiral meso moiety. It represents the regioisomer that has both secondary propandiolate centers oriented towards the same side at the base of the square pyramid and it has both methyl substituents oriented towards (i.e. *syn* with) the Cp* apex (see Fig. 1).

The oxygen atoms at the *cis*-oriented primary ends of the two propandiolato ligands both are involved in bridging the two parts of the dinuclear complex. They coordinate to the titanium center of the formal subunit **6B** (see Scheme 2). The methyl substituent of the **6B** unit is oriented away (i.e. *anti*) from the Cp* unit at titanium.

A projection of the molecular structure of complex **6** is depicted in Fig. 1. It features the two Cp* ligands in a *cis*-arrangement at the tris(1,2-propandiolato)dititanium framework. The Ti–κO bonds inside the five-membered rings are markedly shorter (e.g. Ti1–O31: 1.872(2) Å, Ti2–O44: 1.863(2) Å) than the Ti–μO

linkages (Ti1–O41: 2.060(2) Å, Ti2–O41: 2.060(2) Å). The central Ti_2O_2 four-membered ring is slightly puckered. The endocyclic angles at the titanium atoms amount to ca. 70° (O41–Ti1–O41*: 69.8(1)°, O41–Ti2–O41*: 69.8(1)°), whereas the corresponding angles at oxygen are much larger (Ti2–O41–Ti1: 106.1(1)°). It appears that the selective formation of the specific isomer **6** is thermodynamically controlled. In solution, complex **6** is highly dynamic and gives rise to only one averaged set of propandiolate ^{1}H-NMR signals and one averaged Cp* methyl group singlet in the expected overall stoichiometric intensity ratio.

We next reacted Cp^*TiCl_3 (**7**) [12] with propylene glycol. This reaction followed a more predictable course. We treated **7** with one molar equivalent of *rac*-$CH_3CH(OH)CH_2(OH)$ in ether at room temperature in the presence of excess pyridine to trap the formed HCl [13]. Workup including crystallization from pentane gave single crystals of the product **8** that were suited for characterization by an X-ray crystal structure analysis. It showed that the product was formed by displacement of two chlorides from titanium by an 1,2-propandiolato ligand. One chloride remained coordinated to titanium (Ti1–Cl1: 2.332(1) Å, Ti2–Cl2: 2.316(1) Å). The resulting Cp*TiCl(1,2-propandiolato) complex then had undergone a dimerization reaction to yield the obtained product **8** (see Fig. 2). Dimerization has again occurred by using the oxygen atoms at the primary ligand end for bridging. This results in an overall arrangement of two distorted square pyramidal Cp^*TiL_4 units that are edge sharing. Of the several framework geometries possible in such a situation the isomer is found that contains the two (apical) Cp* ligands in a *cis*-orientation at the framework, whereas the two chloride ligands are arranged *trans* to each other. The framework is of idealized C_2-symmetry (but not crystallographically). This characteristic symmetric situation extends itself to the stereochemistry of the chiral centers of the two ligands: in the crystal we find the homochiral dimer (R*,R*) that has both CH_3-substituents at the propandiolato ring system *syn*-oriented with the Cp* rings at titanium.

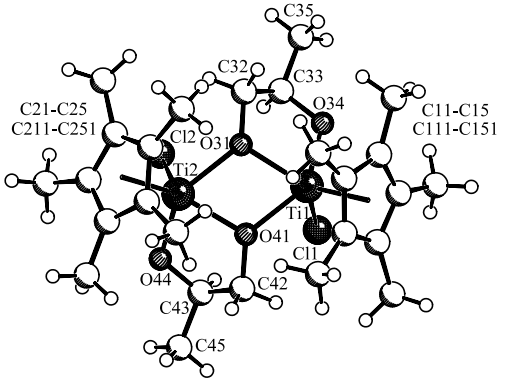
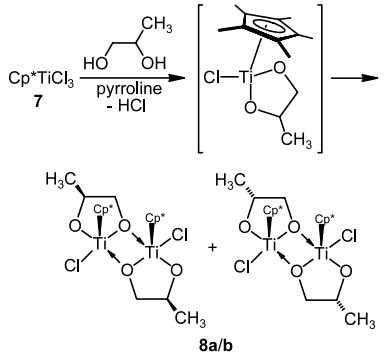


Fig. 2. A projection of the molecular structure of complex **8**. Selected bond lengths (Å) and angles (°): Ti1–Cl1 2.332(1), Ti2–Cl2 2.316(1), Ti1–O31 2.035(3), Ti1–O34 1.846(3), Ti1–O41 2.036(2), Ti2–O31 2.061(3), Ti2–O41 2.037(2), Ti2–O44 1.849(3), O31–C32 1.416(4), C32–C33 1.512(6), C33–O34 1.413(5), C33–C35 1.513(6), O41–C42 1.433(4), C42–C43 1.516(6), C43–O44 1.424(5), C43–C45 1.516(5); Cl1–Ti1–O31 120.3(1), Cl1–Ti1–O34 91.0(1), Cl1–Ti1–O41 88.5(1), O31–Ti1–O34 78.4(1), O31–Ti1–O41 69.0(1), O34–Ti1–O41 141.7(1), Cl2–Ti2–O41 120.1(1), Cl2–Ti2–O44 92.1(1), Cl2–Ti2–O31 88.1(1), O41–Ti2–O44 78.6(1), O41–Ti12–O31 68.4(1), O44–Ti2–O31 141.6(1), Ti1–O31–Ti2 108.1(1), Ti1–O41–Ti2 109.0(1), Ti1–O31–C32 114.0(2), Ti2–O31–C32 127.1(2), O31–C32–C33 105.4(3), C32–C33–O34 103.9(3), C32–C33–C35 113.9(4), O34–C33–C35 110.1(3), Ti1–O34–C33 118.4(2), Ti2–O41–C42 114.1(2), Ti1–O41–C42 127.0(2), O41–C42–C43 105.2(3), C42–C43–O44 104.1(3), C42–C43–C45 112.9(4), O44–C43–C45 109.7(3), Ti2–O44–C43 118.8(2).

In complex **8** the central Ti_2O_2 ring system is characterized by rather long titanium–oxygen bond lengths (e.g. Ti1–O31: 2.035(3), Ti2–O31: 2.061(3), Ti1–O41: 2.036(2), Ti2–O41: 2.037(2) Å), whereas the adjacent Ti–κO bonds are markedly shorter (e.g. Ti1–O34: 1.846(3), Ti2–O44: 1.849(3) Å) [14]. Inside the Ti_2O_2 moiety the bonding angles at Ti are small (O31–Ti1–O41: 69.0(1), O31–Ti2–O41: 68.4(1)°); the corresponding angles at the μ-oxygen atoms are much larger (Ti1–O31–Ti2: 108.1(1), Ti1–O41–Ti1: 109.0(1)°).

The pentane extract contained two isomers of **8**, the complexes **8a** and **8b**, in a ca. 1:1 ratio. The NMR spectra showed that both are probably C_2-symmetric in solution. So, we assume that one is equivalent to the product that was characterized in the crystal by X-ray diffraction. The isomers show very similar NMR spectra. The largest deviations occur at the signals of the $-CH_2-CH(CH_3)-$ moieties. Thus, the propandiolato methyl ^{1}H-NMR resonance of **8a** was registered at δ 0.96 whereas that of **8b** was found at δ 0.86. Similarly, the corresponding **8a** ^{13}C-NMR signal of that methyl group is observed at a larger δ value (δ 20.8) than that of **8b** (δ 18.8, in benzene-d_6). We assume that we have here observed the other possible C_2-symmetric *cis*-isomer of **8** that is characterized by having both propandiolato CH_3 groups anti to the Cp* ligands, although we cannot rigorously exclude that one isomer



Scheme 3.

is a C_i-symmetric (R*,S*)-*trans*-(Cp*Ti)$_2$ diastereomer (Scheme 3).

Under the reaction conditions complex **8** is apparently not completely stable for a prolonged period of time. After leaving the original reaction mixture at room temperature for ca. 12 h fractional crystallization gave single crystals of the trinuclear condensation product **9** in a very low yield (ca. 4%). Formally, **9** is formed by a ligand disproportionation reaction of **8** proceeding with cleavage of e.g. $Cp^*_2TiCl_2$, but the mechanism of formation of this product must await further studies.

Complex **9** contains two [Cp*TiCl(1,2-propandiolato)] subunits that are connected with a central Cp*-free [Ti(1,2-propandiolato)$_2$] substructure by means of a total of four primary μ-propandiolato-oxygen bridges. The complex is trinuclear. It contains a central Ti atom that is part of two Ti_2O_2 subunits in a 'spiro' arrangement and two five-membered 1,2-propandiolato ring systems, both of which share one oxygen atom with the Ti_2O_2 units (see Fig. 3). The central titanium atom shows a distorted octahedral coordination geometry. The stereogenic carbon centers at the four individual 1,2-propandiolato units that are used to construct the framework of **9** are pairwise equivalent (R*,R*,R*,R* diastereoisomer). In addition, the two Ti–Cl vectors and the Ti–Cp* units are arranged such, that an overall chiral structure of idealized C_2-symmetry results, although the exact crystallographic symmetry is lower. There is a molecule of pyridine in the crystal. The characteristic Ti–κO and Ti–μO bonding features of **9** are similar to those of **6** and **8**; for details see Fig. 3. In solution complex **9** is highly dynamic. It shows only one set of propandiolato signals and Cp* resonances in the expected intensity ratio in the ^{1}H- and ^{13}C-NMR spectra (Scheme 4).

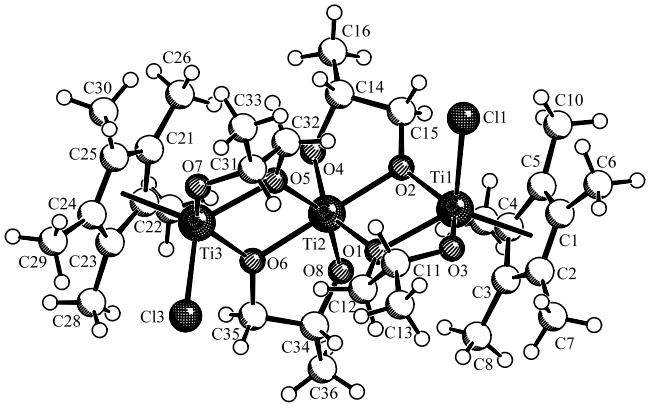


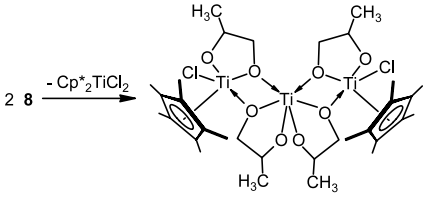
Fig. 3. A view of the molecular structure of **9**. Selected bond lengths (Å) and angles (°): Ti1–Cl1 2.338(2), Ti1–O1 2.021(4), Ti1–O2 2.032(4), Ti1–O3 1.856(5), Ti2–O2 2.014(4), Ti2–O4 1.842(4), Ti2–O6 2.012(4), Ti2–O8 1.826(4), Ti3–Cl3 2.335(2), Ti3–O5 2.015(4), Ti3–O6 2.044(4), Ti3–O7 1.857(4), O1–C12 1.431(7), O3–C11 1.423(7), C11–C12 1.516(9), C11–C13 1.511(9), O2–C15 1.429(7), O4–C14 1.497(11), C14–C15 1.502(12), C14–C16 1.486(12), O5–C32 1.441(6), O7–C31 1.421(6), C31–C32 1.510(9), C31–C33 1.520(8), O6–C35 1.433(6), O8–C34 1.430(15), C34–C35 1.518(17), C34–C36 1.528(15); Cl1–Ti1–O1 121.9(1), Cl1–Ti1–O2 86.2(1), Cl1–Ti1–O3 91.8(1), O1–Ti1–O2 69.7(2), O1–Ti1–O3 78.0(2), O2–Ti1–O3 140.2(2), O1–Ti2–O2 70.0(2), O1–Ti2–O4 149.1(2), O1–Ti2–O5 89.6(2), O1–Ti2–O6 101.6(2), O1–Ti2–O8 93.7(2), O2–Ti2–O4 79.4(2), O2–Ti2–O5 102.5(2), O2–Ti2–O6 169.1(2), O2–Ti2–O8 107.9(2), O4–Ti2–O5 92.9(2), O4–Ti2–O6 108.1(2), O4–Ti2–O8 99.8(2), O5–Ti2–O6 69.8(2), O5–Ti2–O8 148.8(2), O6–Ti2–O8 79.2(2), Cl3–Ti3–O5 122.6(1), Cl3–Ti3–O6 86.7(1), Cl3–Ti3–O7 92.6(1), O5–Ti3–O6 69.3(1), O5–Ti3–O7 78.1(2), O6–Ti3–O7 140.4(2), Ti1–O1–Ti2 110.0(2), Ti1–O2–Ti2 110.0(2), Ti2–O5–Ti3 110.6(2), Ti2–O6–Ti3 109.9(2).

Substituted (cyclopentadienyl)titanium alkoxide complexes have served as components for catalyst systems forming syndiotactic polystyrene [15]. We have, therefore, used the Cp*TiCl(1,2-propandiolato) dimer complex system **8** for generating such an active styrene polymerization catalyst.

Complex **8** was activated by treatment with a large excess of methylalumoxane (MAO) in toluene solution. After a 5 min preactivation, styrene was added to the reaction mixture and the polymerization was carried out for a period of 1 or 2 h at room temperature. The **8**/MAO system is an active catalyst, especially at high Ti/Al ratios (see Table 1). The obtained polystyrene is highly syndiotactic, as was shown by ^{13}C-NMR spectroscopy [16]. Characteristically the obtained polymer exhibits a single *ipso*-C(Ph) resonance at δ 145.7 (rr, in 1:1 benzene-d_6/1,2,4-trichlorobenzene at 350 K). Complex **8** seems to be a suitable reagent for the generation of active catalysts for syndiotactic polystyrene formation. It shows activities comparable to the Cp*TiCl$_3$/MAO system (see Table 1).

3. Experimental

All reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents, including deuterated solvents for the spectroscopic characterization, were dried and distilled under argon prior to use. For additional general information, including a list of instruments used for spectroscopic and physical characterization of the compounds (see Ref. [17]). The complexes Cp*TiCl$_3$ (**7**) [12] and Cp*Ti(CH$_3$)$_3$ (**5**) [10] were synthesized according to literature procedures.



Scheme 4.

Table 1
Syndiotactic polystyrene formation at the **8**/MAO catalyst system [a]

Compound	Ti/Al	T (h)	g PS	act [b]
8	570	1	3.1	103
8	570	2	4.1	68
8	1135	1	7.9	263
7 [c]	1135	1	3.2	107

[a] In toluene solution at 20 °C, 30 μmol (Ti complex).
[b] Catalyst activity in kg PS mol^{-1} (Ti-cat) h^{-1}.
[c] Cp^*TiCl_3.

3.1. Reaction of $Cp^*Ti(CH_3)_3$ (5) with 1,2-propandiol

3.1.1. Preparation of 6

Dry *rac*-propylene glycol (44.6 mg, 5.87 mmol) was added to a solution of 200 mg (8.80 mmol) of $Cp^*Ti(CH_3)_3$ (**5**) in 10 ml of dichloromethane at ambient temperature. The reaction mixture was kept for 2 h at room temperature (r.t.) with stirring and then the solvent was removed in vacuo. The residue was dissolved in a minimum volume of pentane. At −30 °C yellow crystals of **6** were obtained. Yield of **6**: 1.90 g (37%). Anal. Calc. for $C_{29}H_{48}O_6Ti_2$ (MW 588.5): C, 59.19; H, 8.22. Found: C, 58.19; H, 8.45%. ^{1}H-NMR (benzene-d_6, 600 MHz, 300 K): $\delta = 5.25$ (3H), 4.28 (3H) and 3.82 (3H, ABX, $^2J = 8.5$, $^3J_{trans} = 9.8$, $^3J_{cis} = 4.1$ Hz, –CH–CH_2–), 2.02 (s, 30H, Cp*), 1.13 (d, $^3J = 6.1$ Hz, 9H, CH_3). ^{13}C-NMR (benzene-d_6, 150.8 MHz, 300 K): $\delta = 123.2$ (*ipso*-C of Cp*), 85.1 (O–*C*HMe–), 80.0 (CH_2), 20.2 (CH_3), 11.8 (CH_3 of Cp*). GHSQC (benzene-d_6, 600/156.8 MHz, 300 K): $\delta = 5.25/80.0$ (O–*CH*Me), 4.28/85.1 (–CH_2– [*trans*-H to Me]), 3.82/85.1 (–CH_2– [*cis*-H to Me]), 2.02/11.8 (CH_3 of Cp*), 1.13/20.2 (CH_3). 1D-TOCSY (benzene-d_6, 600 MHz, 300 K): irradiation at δ 4.28 (*trans*-H of CH_2), response at δ 5.25 (OC*H*Me), 3.82 (*cis*-H of CH_2), 1.13 (CH_3); irradiation at δ 3.82 (*cis*-H of CH_2), response at δ 5.25, 4.28, and 1.13. IR (KBr): $\tilde{\nu} = 2960$ (s), 2922 (s), 1440 (m), 1380 (s), 1229 (m), 1124 (br. s), 1091 (m), 854 (m), 722 (s), 591 (s) cm^{-1}.

3.1.2. X-ray crystal structure analysis of 6

Formula $C_{29}H_{48}O_6Ti_2$, $M = 588.47$, yellow crystal $0.20 \times 0.15 \times 0.05$ mm, $a = 8.236(1)$, $b = 15.895(1)$, $c = 11.277(1)$ Å, $\beta = 92.04(1)°$, $V = 1475.3(2)$ Å^3, $\rho_{calc} = 1.325$ g cm^{-3}, $\mu = 5.80$ cm^{-1}, empirical absorption correction via SORTAV ($0.893 \leq T \leq 0.972$), $Z = 2$, monoclinic, space group $P2_1/m$ (No. 11), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 5808 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 3108 independent ($R_{int} = 0.044$) and 2211 observed reflections [$I \geq 2\sigma(I)$], 189 refined parameters, $R = 0.047$, $wR^2 = 0.096$, maximum residual electron density 0.26 (−0.28) e Å^{-3}, due to symmetry the atom C33 is splitted in two positions with occupancy 0.5, hydrogens calculated and refined as riding atoms. Data sets were collected with Enraf Nonius CAD4 or Nonius KappaCCD diffractometers, the later one equipped with a rotating anode generator Nonius FR591. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MOLEN (K. Fair, Enraf-Nonius B.V., 1990) and DENZO-SMN (Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307–326), absorption correction for CCD data SORTAV (R.H. Blessing, Acta Crystallogr. A51 (1995) 33–37; R.H. Blessing, J. Appl. Crystallogr. 30 (1997) 421–426), structure solution SHELXS-97 (G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467–473), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

3.2. Reaction of Cp^*TiCl_3 (7) with 1,2-propandiol

3.2.1. Formation of 8 and 9

Propylene glycol (2.66 g, 35.0 mmol, dried over calcium sulfate) and pyridine (8.29 g, 105 mmol) were added to a suspension of Cp^*TiCl_3 (**7**, 10.0 g, 35.0 mmol) in 50 ml of diethyl ether. The resulting yellow suspension was stirred for 4 h at r.t. Solvent was removed in vacuo and the residue continuously extracted with pentane for 8 h. At −30 °C overnight yellow crystals of **8** were obtained from the pentane extract. Yield of **8**: 9.38 g (41%), m.p. 317 °C (dec.). Anal. Calc. for $C_{26}H_{42}Cl_2O_4Ti_2$ (585.3): C, 53.35; H, 7.23. Found: C, 53.95; H, 8.05%. In solution two stereoisomers of **8** were observed in a ca. 1:1 molar ratio: ^{1}H-NMR (benzene-d_6, 600 MHz, 300 K), **8a**: $\delta =$ 4.36 (2H), 4.15 (2H) and 3.86 (2H, ABX, $^2J = 11.5$, $^3J_{trans} = 7.4$, $^3J_{cis} = 2.3$ Hz, OC*H*–C*H*Me–O), 2.07 (s, 30H, Cp*), 0.96 (d, $^3J = 6.6$ Hz, 6H, CH_3); **8b**: $\delta = 4.31$ (m, 2H), 3.85 (m, 4H, OCH_2–C*H*Me–O), 2.06 (s, 30H, Cp*), 0.86 (d, $^3J = 6.6$ Hz, CH_3). ^{13}C-NMR (benzene-d_6, 150.8 MHz, 300 K), **8a**: $\delta = 129.8$ (*ipso*-C of Cp*), 84.2 (O*C*HMe), 82.2 (OCH_2), 20.0 (CH_3), 11.6 (CH_3 of Cp*); **8b**: $\delta = 128.6$ (*ipso*-C of Cp*), 84.4 (O*C*HMe), 82.0 (OCH_2), 18.8 (CH_3), 12.0 (CH_3 of Cp*). GHSQC (benzene-d_6, 600/150.8 MHz, 300 K), **8a**: $\delta = 4.36/84.2$, 4.15/82.2, 3.86/82.2, 2.07/11.6, 0.96/20.0; **8b**: $\delta = 4.31/84.4$, 3.85/82.0, 2.06/12.0, 0.86/18.8. 1D-TOCSY (benzene-d_6, 600 MHz, 300 K), **8a**: irradiation at δ 0.96 (CH_3), response at δ 4.36, 4.15 and 3.86; **8b**: irradiation at δ 0.86 (CH_3), response at δ 4.31, 3.85; irradiation at δ 4.31, response at δ 3.85, 0.86. IR (KBr): $\tilde{\nu} = 2966$ (s), 2920 (s), 2842 (s), 1492 (w), 1440 (m), 1380 (s), 1229 (m), 1124 (br. s), 854 (m), 722 (s), 591 (s) cm^{-1}. During the preparation of **8** we have obtained a small quantity of **9** (413 mg, 4.3%) from the original reaction mixture by fractional crystallization at −30 °C; m.p. 328 °C. Anal. Calc. for $C_{32}H_{54}Cl_2O_8Ti_3 \cdot 0.5C_5H_5N$ (820.9): C, 50.48; H, 6.94; N, 0.82. Found: C, 51.22; H, 7.52; N, 0.56%.

^{1}H-NMR (benzene-d_6, 600 MHz, 300 K): $\delta = 3.46$ (4H), 3.14 (4H) and 2.98 (4H, ABX, $^2J = 10.7$, $^3J_{trans} = 7.6$, $^3J_{cis} = 3.5$ Hz, O–CH_2–CHMe–O), 2.04 (s, 30H, Cp*), 0.82 (d, $^3J = 6.3$ Hz, 12H, CH_3). ^{13}C-NMR (benzene-d_6, 150.8 MHz, 300 K): $\delta = 127.7$ (*ipso*-C of Cp*), 84.2 (O*C*HMe), 82.2 (O*C*H_2), 20.0 (CH_3), 11.8 (CH_3 of Cp*). 1D-TOCSY (benzene-d_6, 600 MHz, 300 K): irradiation at δ 0.82 (CH_3), response at δ 3.46, 3.14, 2.98; irradiation at δ 3.46, response at δ 3.14, 2.98, 0.82; irradiation at δ 3.44, response at δ 3.46, 2.98, 0.82. IR (KBr): $\tilde{v} = 2920$ (br. s), 2861 (s), 1446 (m), 1381 (s), 1091 (br. s), 979 (m), 735 (s), 624 (s) cm^{-1}.

3.2.2. X-ray crystal structure analysis of **8**

Formula $C_{26}H_{42}Cl_2O_4Ti_2 \cdot C_4H_{10}O$, $M = 659.42$, yellow crystal $0.40 \times 0.25 \times 0.25$ mm, $a = 16.791(1)$, $b = 8.608(1)$, $c = 23.422(2)$ Å, $\beta = 98.28(1)^\circ$, $V = 3350.1(5)$ Å^3, $\rho_{calc} = 1.307$ g cm^{-3}, $\mu = 6.71$ cm^{-1}, empirical absorption correction via SORTAV ($0.775 \leq T \leq 0.850$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 12 604 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.68$ Å^{-1}, 7374 independent ($R_{int} = 0.036$) and 5861 observed reflections [$I \geq 2\sigma(I)$], 357 refined parameters, $R = 0.069$, $wR^2 = 0.168$, maximum residual electron density 0.74 (-0.41) e Å^{-3}, the thermal displacement parameters of the ether molecule indicate some positional disorder, refinement with split positions did not improve the model, hydrogens calculated and refined as riding atoms.

3.2.3. X-ray crystal structure analysis of **9**

Formula $C_{32}H_{54}Cl_2O_8Ti_3 \cdot 1/2C_5H_5N$, $M = 820.90$, yellow crystal $0.25 \times 0.25 \times 0.15$ mm, $a = 15.113(1)$, $b = 15.784(1)$, $c = 19.096(1)$ Å, $\alpha = 79.27(1)$, $\beta = 74.06(1)$, $\gamma = 67.04(1)^\circ$, $V = 4017.0(4)$ Å^3, $\rho_{calc} = 1.357$ g cm^{-3}, $\mu = 7.61$ cm^{-1}, empirical absorption correction via SORTAV ($0.833 \leq T \leq 0.895$), $Z = 4$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 37 097 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 13 995 independent ($R_{int} = 0.083$) and 8151 observed reflections [$I \geq 2\sigma(I)$], 887 refined parameters, $R = 0.067$, $wR^2 = 0.146$, maximum residual electron density 1.20 (-0.50) e Å^{-3} in the region of the disordered solvate molecule, this is refined with constraints and isotropic thermal displacement parameters, two almost identical molecules in the asymmetric unit, atoms C14 (C114) and C34 (C134) refined with split positions, hydrogens calculated and refined as riding atoms.

3.3. Styrene polymerization

The polymerization experiments were all carried out by using 30 mmol samples of the respective catalyst precursor (see Table 1) that were each dissolved in ca. 20 ml of a 10.5 weight (%) methylalumoxane solution in toluene. The catalyst systems were preactivated in a Schlenk flask for 5 min. Then styrene (10 ml, 86.5 mmol) was added and the polymerization reaction allowed to proceed for a specified time (see Table 1). The reaction was quenched by the dropwise addition of 20 ml of a 1:1 mixture of methanol–dilute aqueous HCl. The aqueous phase was separated, extracted with toluene and the combined organic layers were concentrated in vacuo. The isolated polymer was refluxed with 30 ml of acetone to remove atactic polystyrene. The insoluble syndiotactic polystyrene was collected by filtration and dried for 12 h in vacuo.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 199810, 199811 and 199812. 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; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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