Titanium(IV) chloride complexes with chiral tetraaryl-1,3-dioxolane-4,5-dimethanol ligands as a new type of catalysts of ethylene polymerization

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Titanium complexes of chiral ligands, (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetraphenyl-1,3dioxolane-4,5-dimethanol and its structural analogs, activated by polymethylalumoxane catalyze ethylene polymerization with an activity from 3 to 530 (kg polyethylene) (mol Ti h atm)⁻¹. An increase in the bulk of the aryl substituents results in a decrease in the catalytic activity of the complexes.

Key words: titanium chloride, chiral ligands, structure, homogeneous catalysts, polymerization, ethylene, polyethylene.

The invention of new highly efficient catalysts for olefin polymerization based on Group VIII transition metal complexes with diimine ligands¹ has stimulated intensive development of the field of research referred to as "postmetallocene" catalysis.^{2–4} The main problems solved within the framework of this approach include the search for new ligands that change the geometry and the electronic properties of complexes and the preparation of complexes with metal atoms other than those used previously.^{1–3} Among the most vivid results obtained by now, mention should be made of the synthesis of catalysts with the oxoimine type of ligands and a Group IV metal atom as the complexing center,⁵ catalysts involving chromium,⁶ catalysts for copolymerization of hex-1-ene with ethylene,⁷ and some others.^{8–13}

The use of complexes with chiral ligands in olefin polymerization appears rather attractive and topical. Presumably, these substances would be demanded for the synthesis of stereoregular polypropylene and oligomerization or copolymerization of polar and nonpolar monomers.

Transition metal complexes (especially Ti^{IV} complexes) with 2,2,R,R'-tetraaryl-1,3-dioxolane-4,5-di-

methanol (TADDOL) ligands are known^{14–16} to be unique catalysts for the C–C bond formation in the nucleophilic addition to electrophiles and in the Diels–Alder reaction. The analogy with the formation of C–C bonds upon olefin polymerization suggests that this type of complexes would catalyze equally efficiently synthesis of polyethylene (PE) and polypropylene with high molecular mass. The reason is that the chain transfer reactions resulting in a lower molecular masses of the polymer would be retarded due to the steric strain created by the bulky phenyl substituents in the tetraaryldioxolanedimethanol ligands.

This study deals with the catalytic properties of the titanium complexes with chiral polydentate ligands, *viz.*, (4R,5R)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetraphenyl-1,3-dioxo-lane-4,5-dimethanol and its structural analogs.

Results and Discussion

Ligands **1–3** were synthesized by the known procedure using the reaction of arylmagnesium bromides with tartaric acid esters.^{17,18} Then the dilithium alkoxides ob-

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tained from compounds 1-3 on treatment with BuLi in hexane were mixed with 1 equiv. of TiCl₄ (Scheme 1). The resulting solutions of complexes 4-6 were used, without isolation or purification, as catalysts of ethylene polymerization (in the presence of polymethylalumoxane (MAO) as the co-catalyst).

Scheme 1



Ar = Ph, R = Me (1, 4); Ar = C_6F_5 , R = Me (2, 5); Ar = α -naphthyl, RR = (CH₂)₅ (3, 6)

The reaction of dibenzo[b,d]furan-4,6-dicarbaldehyde with diisopropyl L-tartrate gave 4,6-bis[4,5-di(isoprop-oxycarbonyl)-1,3-dioxolan-2-yl]dibenzo[b,d]-furan (7), which reacts with phenylmagnesium bromide to afford 4,6-bis[4,5-bis[hydroxy(diphenyl)methyl]-1,3-dioxolan-2-yl}dibenzo[b,d]furan (8) (Scheme 2).

The composition and structures of the products were confirmed by data from elemental analysis, NMR spec-



Fig. 1. Structure of 4,6-bis[4,5-di(isopropoxycarbonyl)-1,3-dioxolan-2-yl]dibenzo[*b*,*d*]furan (7).

troscopy and single-crystal X-ray diffraction analysis of the intermediate product 7 (Fig. 1, Table 1).

The main geometric parameters of compound 7 do not differ much from the values expected for this class of compounds. The dioxolane rings have envelope confor-



Scheme 2

Table 1. Selected bond lengths (*d*) and bond angles (ω) in structure **7**

Parameter	Value	Parameter	Value
Bond	d/Å	Bond	d/Å
O(1) - C(4)	1.386(6)	C(3)-C(12)	1.405(6)
O(1) - C(1)	1.399(6)	C(4)—C(9)	1.396(8)
O(2)-C(13)	1.422(7)	C(5) - C(6)	1.372(8)
O(2)-C(14)	1.437(5)	C(6)—C(7)	1.408(7)
O(2')-C(13')	1.391(7)	C(7)—C(8)	1.374(7)
O(2')-C(14')	1.424(6)	C(9)-C(10)	1.371(7)
O(3)-C(13)	1.416(7)	C(10)-C(11)	1.380(8)
O(3) - C(15)	1.431(6)	C(11)-C(12)	1.386(8)
O(3')-C(15')	1.413(6)		
O(3')-C(13')	1.428(7)	Angle	ω/deg
C(1) - C(5)	1.368(7)	C(4) - O(1) - C(1)	105.2(4)
C(1) - C(2)	1.403(7)	C(13) - O(2) - C(14)	102.4(4)
C(2) - C(8)	1.395(8)	C(13') - O(2') - C(14')	109.0(4)
C(2) - C(3)	1.450(8)	C(13) - O(3) - C(15)	103.6(4)
C(3) - C(4)	1.386(8)	C(15')-O(3')-C(13')	107.8(5)

mations in which the C(13) and C(13') atoms deviate from the plane of the dioxolane fragments, the symmetry plane of the dioxolane rings (without consideration of the ester groups) actually coincides with the plane of the dibenzofuran system (see Fig. 1). The carboxylate substituents in the dioxolane rings occupy axial positions. The hydrogen atom at the chiral C(13) center is synperiplanar with respect to the oxygen atom of the dibenzofuran system, whereas the hydrogen atom at C(13') is antiperiplanar. This type of arrangement of the dioxolane fragments gives rise to a number of contracted intramolecular C–H...O contacts (the H...O distances are 2.42-2.44 Å).

Presumably, the positions and the conformation of the dioxolane rings in ligand $\mathbf{8}$ are retained the same as in ester $\mathbf{7}$.

Binuclear complex 9 was prepared by a procedure similar to that used to synthesize mononuclear complexes 4-6 (see Scheme 2).

Ethylene polymerization was carried out in the presence of mononuclear titanium(iv) complexes **4**—**6** and binuclear complex **9**. The catalytic activity was estimated without separation of LiCl; thus, possible changes in the composition and structures of complexes upon isolation and storage can be avoided.

Since in some cases the kinetics of ethylene absorption had an induction period due to the low rate of formation of the active sites and catalyst deactivation processes, the catalytic activity of the system was estimated in terms of two parameters, namely, the integral activity (*A*) expressed in kg PE (moles of the catalyst h atm)⁻¹ and the rate of ethylene absorption (*R*), which takes into account different ethylene concentrations in the solution and the change in the concentration with temperature and expressed in kg PE (mol Ti)⁻¹ ([C₂H₄])⁻¹.



Fig. 2. Yield of polyethylene (*Y*) in ethylene polymerization in the presence of a catalytic system **4**—MAO ([Ti] = $3.2 \cdot 10^{-6}$ mol L⁻¹) vs. reaction time at 30 °C and different Al_{MAO}/Ti molar ratios: 200 (*I*), 310 (*2*), 385 (*3*), and 1050 (*4*).

The catalytic activity of complex 4 in ethylene polymerization was studied for concentrations ranging from $1.1 \cdot 10^{-3}$ to $1.6 \cdot 10^{-4}$ mol L⁻¹ at 30 °C. As shown in Fig. 2, an increase in the Al_{MAO}/Ti molar ratio from 200 to 385 is accompanied by a gradual increase in the activity of the catalytic system from 60 to 500 kg PE (mol Ti h atm)⁻¹. However, further increase in this ratio to 1050 does not increase the activity (430 kg PE (mol Ti h atm)⁻¹). This results in a decrease in the stability of system performance in the catalytic reaction. This type of behavior distinguishes complex 4 from other known post-metallocene and metallocene systems whose activities and stabilities of performance increase with an increase in the Al_{MAO}/M ratio up to 2000–3000.

The dependence of the activity of the catalytic system based on complex 4 on the polymerization temperature is shown in Fig. 3. It can be seen that $30 \text{ }^{\circ}\text{C}$ is the



Fig. 3. Rate of ethylene absorption (*R*) in the presence of a catalytic system **4**—MAO ($[Ti] = 3.2 \cdot 10^{-6} \text{ mol } L^{-1}$, Al_{MAO}/Ti = 310 mol mol⁻¹) *vs.* reaction time at different reaction temperatures: 20 (*I*), 30 (*2*), 60 (*3*), and 70 °C (*4*).



Fig. 4. Yield of polyethylene (*Y*) in ethylene polymerization in the presence of catalysts **4–6** and **9** *vs.* reaction time at 30 °C ([Ti] = $3.2 \cdot 10^{-6}$ mol L⁻¹, Al_{MAO}/Ti = 1050 mol mol⁻¹).

temperature of choice. At 60 °C, catalyst deactivation becomes noticeable (the integral activity is 240 kg PE (mol Ti h atm)⁻¹), while at 70 °C, deactivation predominates (the activity is 40 kg PE (mol Ti h atm)⁻¹).

The activities of the catalytic systems obtained from complexes **4**–**6** and **9** are compared in Fig. 4. It can be seen that the activities of compounds **4** and **5** do not differ much (530 and 650 kg PE (mol Ti h atm)⁻¹, respectively), although the system based on complex **5** is more stable. The step to complex **6** is accompanied by an increase in steric crowding at the metal center and results in a sharp decline of the catalyst activity (170 kg PE (mol Ti h atm)⁻¹). Binuclear complex **9** occupies an intermediate position (its activity is 290 kg PE (mol Ti h atm)⁻¹). Thus, in terms of the activity in the ethylene polymerization, the complexes can be arranged in the following sequence: **5** > **4** > **9** > **6**.

The catalytic properties of binuclear complex 9 display some specific features. At high concentration of the complex and low Al_{MAO}/Ti molar ratio, the rate of formation of catalytic sites is an essential factor. This is apparently responsible for the presence of an induction period in the polymerization. To confirm this hypothesis, we carried out the following experiments. In one of them, ethylene polymerization was carried out over a catalytic system 9—MAO at high catalyst concentration $(1.5 \cdot 10^{-3})$ mol L^{-1}) and with its activation directly in the reaction medium (Al_{MAO}/Ti = 100 mol mol⁻¹). In the second experiment, the catalyst was dissolved together with MAO and the preactivated catalyst was kept for 3.5 h before injection into the reactor. The kinetics of ethylene polymerization with these systems is shown in Fig. 5. It can be seen that the former catalytic system shows a substantial induction period and, during the polymerization, the rate of monomer absorption gradually increases. In the second catalytic system, polymerization proceeds at a constant rate.

It is noteworthy that binuclear complex **9** has a much higher thermal stability than the mononuclear analog **4**,



Fig. 5. Yield of polyethylene (*Y*) in the presence of a catalytic system **9**—MAO *vs.* reaction time on direct introduction of the catalyst into the MAO-containing reaction medium (*I*), and after catalyst pre-activation by keeping it in a toluene solution with MAO for 3.5 h (*2*) (polymerization temperature 30 °C, $p_{C_2H_4} = 0.89$ atm, toluene, [Ti] = $1.5 \cdot 10^{-3}$ mol L⁻¹, Al_{MAO}/Ti = 100 mol mol⁻¹).

although its activity is 1.5-2 times lower than that observed with a catalytic system **4**-MAO, all other factors being the same.

As can be seen from Fig. 6, the catalyst involving complex 9 exhibits rather stable performance at polymerization temperatures of 25–60 °C (curves 1-3), but is deactivated almost completely over a period of 5 min at 70 °C (curve 4).

The IR spectra of the polymers obtained with any of the catalysts exhibit bands at 908 and 995 cm⁻¹, which are indicative of chain transfer through β -H elimination and hydrogen migration to the Ti atom or to the monomer, which yields terminal vinyl groups.¹⁹ The fact that PE is mainly linear and has a relatively high molecular mass is



Fig. 6. Rate of ethylene absorption (*R*) in the presence of a catalytic system **9**—MAO *vs.* reaction time at different temperatures: 25 (*I*), 50 (*2*), 60 (*3*), and 70 °C (*4*) ($p_{C_2H_4} = 0.89$ atm, toluene, [Ti] = $1.74 \cdot 10^{-5}$ mol L⁻¹, Al_{MAO}/Ti = 52 mol mol⁻¹).

indicated by high melting points of the obtained samples (140-142 °C).

Thus, we synthesized a new class of titanium chelates active in ethylene polymerization upon activation by MAO. According to the results obtained, their performance is at the level of the so-called active catalysts (against the activity scale introduced previously²⁰ for post-metallocene type chelates, which is ~200 kg PE (mol Ti h atm)⁻¹). The relatively high stabilities of complexes 5 and 9, especially 9, under polymerization conditions at high temperatures provides grounds for believing that these catalysts can be used in block copolymerization of ethylene with less active (for example, higher) olefins.

Experimental

The complexes were synthesized under argon. Tetrahydrofuran, dichloromethane, toluene, isopropyl alcohol, hexane, and ethyl acetate (chemically pure grade) were additionally purified according to published procedures;²¹ TiCl₄ (Fluka) was distilled under argon; SiO₂ and dibenzo[*b*,*d*]furan (Fluka) were used as received. Diisopropyl L-tartrate and dibenzo[*b*,*d*]furan-4,6dicarbaldehyde were prepared by a previously described procedure.²²

The NMR spectra of solutions of ligands in CDCl₃ were recorded on Bruker WP-200 and Bruker AMX-400 instruments and IR spectra, on a Magna-IR 750 spectrophotometer. The optical rotation was measured on a Perkin—Elmer 241 polarimeter. The elemental analysis was performed on Carlo Erba-1106 and Carlo Erba-1108 instruments.

(4R,5R)-2,2-Dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetraphenyl-1,3-dioxolane-4,5-dimethanol (1) was prepared by a known procedure,¹⁷ m.p. 193 °C (*cf.* Ref. 17: m.p. 192 °C).

(4R,5R)-2,2-Dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis(pentafluorophenyl)-1,3-dioxolane-4,5-dimethanol (2) was prepared by a published procedure,¹⁸ m.p. 106 °C (*cf.* Ref. 18: m.p. 104–105 °C).

(2R,3R)-1,4-Dioxaspiro[4.5]decane- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis(1-naphthyl)-2,3-dimethanol (3) was prepared by a known procedure,¹⁷ m.p. 186 °C (*cf.* Ref. 17: m.p. 192 °C).

4,6-Bis[4,5-di(isopropoxycarbonyl)-1,3-dioxolan-2-yl]dibenzo[b,d]furan (7). A solution of dibenzo[b,d]furan-4,6dicarbaldehyde (1.00 g, 4.46 mmol) in benzene (20 mL), diisopropyl L-tartrate (1.88 mL, 8.92 mmol), and TsOH (0.0154 g, 0.01 mmol) were refluxed for 48 h with the Dean-Stark trap. The reaction mixture was washed with a saturated solution of NaHCO₃, the solvent was evaporated, and the product was recrystallized from methanol. Yield 0.7 g (24%), m.p. 103-105 °C, $[\alpha]_D^{25}$ -49.5 (*c* 1, CHC1₃). Found (%): C, 62.18; H, 6.07. C₃4H₄₀O₁₃. Calculated (%): C, 62.19; H, 6.14. ¹H NMR, δ : 7.98 (d, 2 H, ³J = 7.5 Hz); 7.83 (d, 2 H, ³J = 7.3 Hz); 7.39 (t, 2 H, ³J = 7.3 Hz, ³J = 7.5 Hz); 6.85 (s, 2 H); 5.18 (br.m, 4 H); 4.98, 4.85 (both d, 2 H each, ³J ≈ 3 Hz); 1.36 (d, 12 H, ³J = 5.8 Hz); 1.28, 1.23 (both d, 6 H each, ³J = 6.8 Hz).

4,6-Bis{4,5-bis[hydroxy(diphenyl)methyl]-1,3-dioxolan-2-yl}dibenzo[*b*,*d***]furan (8).** A solution of ester 7 (0.9 g, 1.37 mmol) in THF (30 mL) was added with cooling (0 °C) and stirring under argon to a solution of PhMgBr prepared from Mg (0.29 g, 12 mmol) and PhBr (1.88 g, 12 mmol) in THF (70 mL). After

warming to room temperature, the reaction mixture was refluxed for 2 h and neutralized with a saturated solution of NH₄Cl. The organic layer was separated, the solvent was evaporated, and the residue was recrystallized from methanol. Yield 0.19 g (14%), dec.p. 232 °C, $[\alpha]_D$ +159.3 (*c* 0.5, CHC1₃). Found (%): C, 80.71; H, 5.42. C₇₀H₅₆O₉. Calculated (%): C, 80.75; H, 5.42. ¹H NMR, δ : 7.82 (d, 2 H, ³*J* = 7.5 Hz); 7.61 (m, 8 H); 7.44 (t, 4 H, ³*J* = 7.5 Hz); 7.39–7.07 (m, 32 H); 6.14 (s, 2 H); 5.54 (d, 2 H, ³*J* = 4.0 Hz); 5.35 (d, 2 H, ³*J* = 4.4 Hz); 3.54, 2.41 (both s, 2 H each). ¹³C NMR, δ : 154.18, 145.40, 145.36, 144.52, 144.16 (2 C each); 128.50, 128.42 (4 CH each); 128.22, 128.17 (2 CH each); 127.90 (2 C); 127.38 (t); 127.17, 127.14 (2 CH each); 126.90, 124.79 (2 C each); 123.25, 122.05 (2 CH each); 121.58 (2 C); 102.47, 82.02, 81.22, 79.65, 79.27 (2 CH each).

Synthesis of complexes 4–6 and 9 (general procedure). A 10 *M* solution of butyllithium in hexane (0.042 mL, 0.42 mmol) was added dropwise with stirring under argon to a cooled (-78 °C) solution of ligand 1–3 or 8 (0.20 mmol) in toluene (10 mL). The temperature of the reaction mixture was slowly brought to ambient temperature, the mixture was stirred for 4 h and cooled to -78 °C. A solution of TiCl₄ (0.024 mL, 0.20 mol) was added and the mixture was again warmed to ambient temperature. After 3 h, the reaction mixture was filtered, the solvent was evaporated, and the product was recrystallized from toluene.

Complex 4. Yield 0.110 g (94%), m.p. 294 °C, $[\alpha]_D$ -90.3 (*c* 1, toluene). Found (%): C, 63.79; H, 4.69; Cl, 12.20; Ti, 8.05. C₃₁H₂₈Cl₂O₄Ti. Calculated (%): C, 63.83; H, 4.84; Cl, 12.16; Ti, 8.21. ¹H NMR (toluene-d₈), δ : 7.20–7.25 (m, 20 H); 4.80 (s, 2 H, CH); 1.57 (s, 6 H, Me).

Complex 5. Yield 0.164 g (87%), m.p. 225 °C, $[\alpha]_D$ +18.4 (*c* 1, toluene). Found (%): C, 39.29; H, 0.92; Cl, 7.29; Ti, 4.95. C₃₁H₈Cl₂F₂₀O₄Ti. Calculated (%): C, 39.48; H, 0.85; Cl, 7.52; Ti, 5.08. ¹H NMR (toluene-d₈), δ : 4.69 (s, 2 H, CH); 1.43 (s, 6 H, Me).

Complex 6. Yield 0.124 g (76%), m.p. 271 °C, $[\alpha]_D$ -39.3 (*c* 1, toluene). Found (%): C, 72.79; H, 4.69; Cl, 8.56; Ti, 5.75. C₅₀H₄₀Cl₂O₄Ti. Calculated (%): C, 72.93; H, 4.86; Cl, 8.63; Ti, 5.80. ¹H (toluene-d₈), δ : 7.16–7.68 (m, 28 H); 4.70 (s, 2 H, CH); 1.50–1.74 (m, 10 H, CH₂).

Complex 9. Yield 0.197 g ($\overline{78\%}$), m.p. 294 °C. Found (%): C, 65.72; H, 4.04; Cl, 11.07; Ti, 7.65. C₇₀H₅₂Cl₄O₉Ti₂. Calculated (%): C, 65.96; H, 4.11; Cl, 11.13; Ti, 7.51. ¹H NMR (toluene-d₈), δ : 7.78 (d, 2 H); 7.61 (m, 8 H); 7.42 (t, 4 H, $^{3}J =$ 7.5 Hz); 7.39–7.07 (m, 32 H); 6.14 (s, 2 H); 5.54 (d, 2 H, $^{3}J =$ 4.0 Hz); 5.35 (d, 2 H, $^{3}J =$ 4.4 Hz); 2.38 (s, 2 H).

Solutions of complexes used for polymerization were prepared by the following procedure. Butyllithium (0.042 mL, 0.42 mmol) was added dropwise with stirring under argon to a cooled (-78 °C) solution of ligand **1–3** and **8** (0.20 mmol) in heptane (10 mL). The temperature of the reaction medium was slowly brought to ambient temperature, the mixture was stirred for 4 h and cooled to -78 °C, and a solution of TiCl₄ (0.024 mL, 0.20 mol) was added. This mixture was used without additional treatment.

Ethylene polymerization. The catalytic polymerization of ethylene was carried out in toluene and heptane (special purity grade), which were purified from possible impurities by the procedure standard for this process.²³ Polymethylalumoxane (Witco) was used as a 10% toluene solution. Argon and ethylene (special purity grade) were dried by passing through a column packed with 5A molecular sieves.

All operations for the setup assembly and the procedures for preparation and injection, into the reaction vessel, of the complexes assayed and ethylene, and measurements of polymerization kinetics are similar to those described previously.²⁴ After complete dissolution of ethylene in a solution of the assayed complex in toluene or heptane, polymerization was initiated by introducing a solution of the catalyst into the reactor and quenched with a 10% solution of HCl in ethanol. The polymeric product was filtered off, washed with ethanol and water, and dried *in vacuo* at 50–60 °C to a constant weight.

The X-ray diffraction experiment for compound 7 ($C_{34}H_{40}O_{13}$) was carried out at 110 K on a Smart CCD 1000K diffractometer (Mo-K α radiation, graphite monochromator, ω -scan mode, $2\theta_{\text{max}} \leq 54^{\circ}$). The crystals are monoclinic, a = 9.944(2) Å, b = 18.315(5) Å, c = 10.470(2) Å, $\beta = 116.099(11)^{\circ}$, V =1712.5(7) Å³, d_{calc} = 1.274 g cm⁻³, M = 656.66, F(000) = 696, $\mu = 0.98 \text{ cm}^{-1}, Z = 2 (Z' = 1)$, space group P2₁. Of the total 6432 measured reflections ($R_{int} = 0.0334$), 3900 independent reflections were used in the subsequent calculations and in the refinement. The structure was solved by the direct method and refined by least-squares method in the full-matrix anisotropic approximation for F^2_{hkl} . The hydrogen atoms were located from difference electron density Fourier syntheses and included in the refinement in the anisotropic approximation. The final R-factors are R = 0.0363 over 2035 reflections with $I > 2\sigma(I)$, $wR_2 = 0.0929$, GOF = 1.099 for all reflections. All calculations were carried out on a SHELXTL PLUS program package.²⁵

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