New dinuclear fluorine-containing bis(salicylidene)imine titanium complex: synthesis and catalytic properties in polymerization of ethylene and propylene

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New dinuclear titanium(IV) dichloride complex with the chelating bis-4,4´-bis-imine-(3,5-di-*tert*-butylsalicylidene)octafluorobiphenyl ligand was synthesized. In the presence of polymethylaluminoxane (MAO), the complex showed high catalytic activity in ethylene polymerization leading to high-molecular (M_n ~2500000) linear polyethylene with a high polydispersity index (M_w/M_n ~7.0) and high melting point (142 °C). The catalytic activity in propylene polymerization in a medium of liquid monomer is substantially lower, and the polypropylene formed is a high-molecular atactic elastomer.

Key words: titanium, phenoxy imine complexes, homogeneous catalysts, polymerization, olefins, polyethylene, polypropylene.

Discovery[1] of a novel class of catalysts for olefin polymerization based on diimine complexes of Group VIII transition metals gave an impetus to fast development of a scientific area called as a «postmetallocene» catalysis of olefin polymerization.[2—4] The development[5—9] of chelated phenoxyimine complexes of titanium and zirconium $MCl_2\{\eta^2\text{-}1\text{-}[C(H){=}NPh^R]{-}2\text{-}O{-}Ph^{R'}\}_2$ is among last achievements in this area of catalysis. The catalysts based of these complexes (FI catalysts Mitsui) are comparable to or excell in activity the most efficient metallocene catalysts for ethylene polymerization. The catalytic performance and resistance to deactivation of the above complexes can be varied in a wide range by a choice of substituents in the chelated ligand and the temperature of polymerization, including high temperatures and living polymerization, to afford the polymer products with different compositions and a broad spectrum of properties.

Experimental studies of the catalytic activity of the phenoxyimine precursor complexes as a function of their nuclearity are of keen interest for elucidation of the mechanism of catalysis by postmetallocene catalysts. An increase in the number of virtual active sites in the catalyst can manifest itself in the cooperative interaction phenomenon, in arising of synergetic effect, and in other features of the process. For instance, a number of specific features have been found for dinuclear metallocene complexes,[10—16] which determine their catalytic performance and the properties of polyolefins formed, the features being different from those for the mononuclear analogs.

In this work, we report on the synthesis of a new dinuclear titanium(IV) chloride complex with bis(salicylidene)imine (**1**) and the study of its catalytic performance in the polymerization of ethylene and propylene upon activation with polymethylaluminoxane (MAO). The catalytic performance of complex **1** was compared with that of the earlier studied mononuclear complex **2**.[17]

Results and Discussion

Dichloride titanium(IV) complex with the bis(salycilidene)imine ligand was prepared from titanium dichlorodiisopropylate and the corresponding ligand in dry meth-

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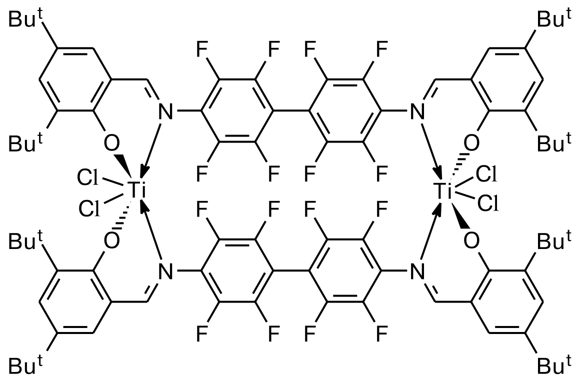

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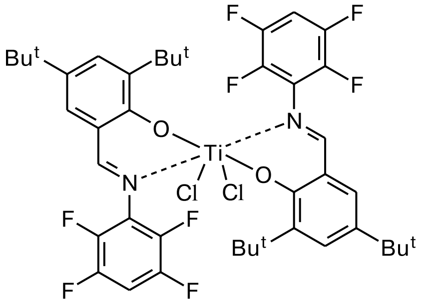

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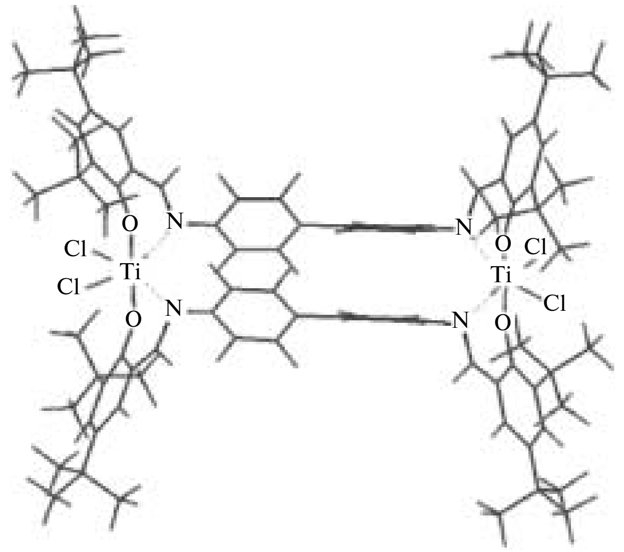

Fig. 1. Proposed structure of complex **1** calculated by the molecular mechanics method (MM2); the Ti—Cl, Ti—N, and Ti—O bond lengths are 2.33, 2.40, and 1.95 Å, respectively; the O—Ti—O, N—Ti—N, and Cl—Ti—Cl bond angles are 175.00, 108.40, and 86.53°, respectively.

ylene chloride according to a known procedure.[18] By analogy with the structures of oxoimine chloride complexes one can suggest that complex **1** has a similar structure. The data of elemental analysis and NMR and IR spectroscopies confirm this suggestion. For instance, no essential difference was observed in a long-wave region of the IR spectra of complexes **1** and **2**. In both cases (unlike the spectra of the starting ligands), two bands of the Ti—Cl stretching vibrations (420 and 397 cm^{-1}) were found, confirming the *cis*-position of Cl atoms in these molecules. A dinuclear structure of the synthesized compound is supported by the results of cryoscopic measurement of its molecular weight. The calculated molecular weight of the dimer is 1755, whereas the measured values are 1680 in benzene and 1810 in nitrobenzene.

The most probable structure of dimeric complex **1** calculated by the molecular mechanics method (MM2) is presented in Fig. 1. As was found for structural analogs,[19—21] both metal atoms in the complex have an octahedral environment with two *cis*-arranged Cl atoms and two bidentate [O,N]-ligands in which O atoms are *trans*-positioned to each other.

The conditions and results of experiments for ethylene polymerization in toluene and bulk polymerization of propylene in the presence of complexes **1** and **2** are shown in Table 1.

Complex **1** is much less soluble in toluene at room temperature (~$6 \cdot 10^{-4}$ mol L^{-1}) than complex **2**. Com-

Table 1. Polymerization of ethylene and propylene in the presence of catalysts **1** and **2** with MAO as cocatalyst

Entry	Catalyst	Monomer	$[Ti] \cdot 10^6$ /mol	Al_{MAO}/Ti (mol mol^{-1})	M.p. /°C	t /min	Y^a /g	A^b
1	**1**	Ethylene^c	1.55	980	12	13	0.47	1516
2	**1**	Ethylene^c	1.55	980	30	14	0.38	1051
3	**2**	Ethylene^c	0.63	600	30	8	0.57	6786
4	**1**	Ethylene^c	1.55	500	90	10	0.05	—
5	**1**	Propylene^d	4.55	1000	50	240	1.17	64.3
6	**2**	Propylene^d	4.72	2000	50	90	6.9	974.6

[a] The yield of polymer.

[b] Specific activity in kg PE (mol Ti)$^{-1}$ h^{-1}.

[c] Solvent is toluene.

[d] Polymerization was carried out in liquid propylene.

plex **1** in solution has a bright crimson color, which rapidly changes to lemon-yellow after the introduction of MAO and the saturation of the solution with ethylene, the color change being accompanied by the formation of polyethylene.

Ethylene polymerization in the presence of complex **1** was carried out at three temperatures (see Table 1). The catalytic activity based on the concentrations of the catalyst and monomer is nearly the same at the reaction temperatures 12 and 30 °C (Fig. 2, *a*, curves *1*, *2*). The rate of the catalyst deactivation during ethylene polymerization is also nearly the same, which fact is displayed by simultaneous decrease in the rate of gas uptake with time. The catalyst deactivates almost immediately at 90 °C (see Table 1, run *4*).

A comparison of the catalytic performances of complexes **1** and **2** in ethylene polymerization shows that, the other conditions being equal, dinuclear complex **1** is 6—7 times less active than mononuclear complex **2** (*cf.* entries *2* and *3* in Table 1). In addition, the latter is more stable during the catalytic reaction (*cf.* Figs 2, *a, b*).

The activities of complex **1** and the earlier synthesized[17] complex **2** in propylene polymerization, when taking into account the monomer concentration in the reaction medium, are substantially lower than those in ethylene polymerization (see Table 1). However, in this case, a comparison of the activities of the catalysts **1** and **2** in propylene polymerization in a liquid monomer medium also shows that, the other conditions being equal, the mononuclear titanium catalyst is ~15 times higher active than the dinuclear catalyst. A comparison of the catalytic performancies of the mono- and dinuclear metallocene complexes having the same ligand environment showed in some cases a significant decrease in activity on going from the mononuclear to dinuclear catalyst.[10—14] As a rule, a decrease in activity is accompanied by an increase in molecular weights and the broadening of the molecular-weight distribution of polyolefins.

Polyethylene formed in the presence of complex **1** corresponds in its characteristics to the polymer prepared in the presence of complex **2**, and in both cases, high-molecular linear polymers are formed. The GPC-measured average-number molecular weight of the polyethylene obtained in run *2* (see Table 1) is ~$2.5 \cdot 10^6$ g mol^{-1}, and its polydispersity index M_w/M_n is very high (~7.0). The polyethylene corresponds in its characteristics to the PE samples formed in the presence of complex **2** (see Table 1, entry *3*, $M_n \approx 2.5 \cdot 10^6$ g mol^{-1}, $M_w/M_n \approx 7.2$).[17] The melting points of the polyethylene samples are equally high, namely, 142 °C. These results suggest that the active sites of the catalysts formed in the **1**—MAO and **2**—MAO systems have the same structure and, hence, the mechanisms of chain propagation and chain transfer in ethylene polymerization are the same. The main differences between these catalysts for ethylene polymerization are the less specific activity of complex **1** and its faster deactivation.

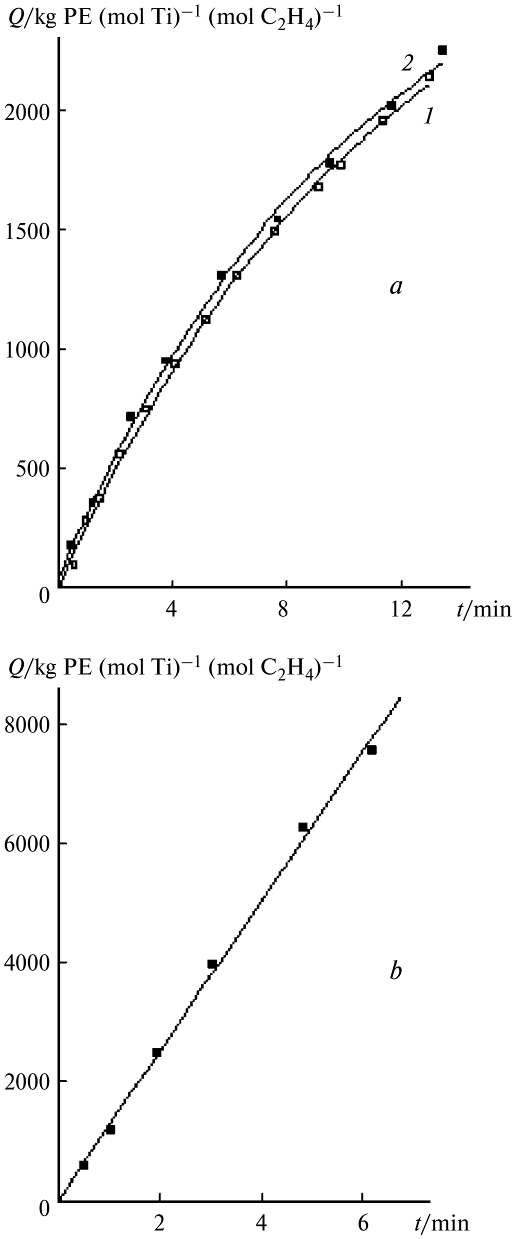

Fig. 2. Yield of polyethylene (*Q*) during polymerization in the presence of catalyst **1** (*a*) (based on the catalyst and ethylene concentrations) *vs.* duration of reaction at 12 (*1*) and 30 °C (*2*) and similar plot for ethylene polymerization in the presence of catalyst **2** (*b*) (toluene, [Ti] = $0.63 \cdot 10^{-6}$ mol, ethylene pressure is 0.97 atm, 30 °C, Al_{MAO}/Ti = 600 mol mol^{-1}).

Meanwhile, the active sites that form in the catalytic **1**—MAO and **2**—MAO systems during propylene polymerization in the liquid monomer medium have more profound differences. Most likely, the differences manifest themselves not only in the lower activity of complex **1** compared to complex **2** but also in the generation of

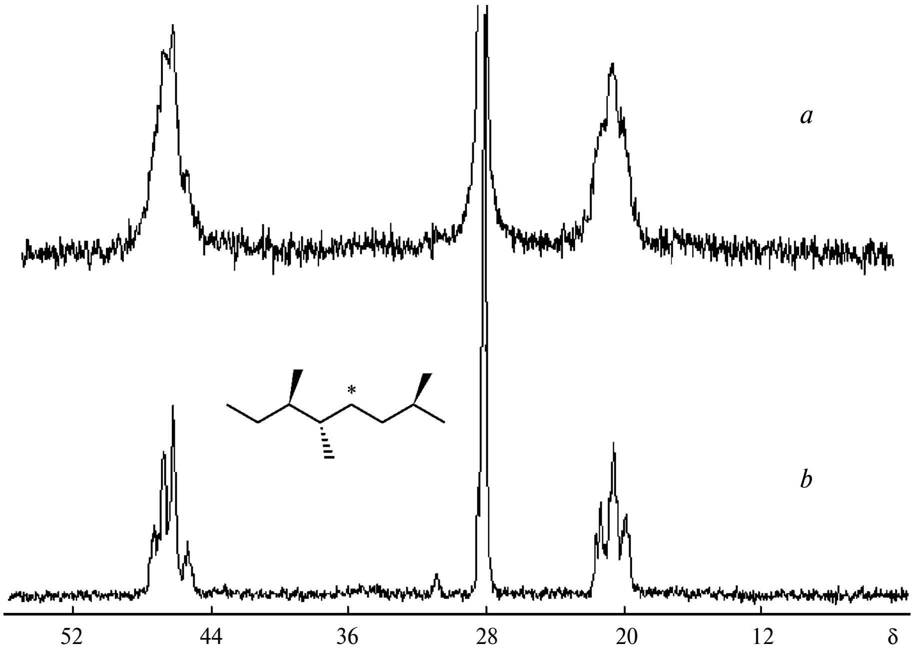

Fig. 3. Regions of the ^{13}C NMR spectra for samples of atactic high molecular elastomeric polypropylene prepared in the presence of complexes **1** (*a*) and **2** (*b*).

regio-errors because of 2,1-addition of the propylene molecules. The data of ^{13}C NMR spectroscopy for the samples of polypropylene (PP) prepared in the presence of catalysts **1** and **2** may serve as an illustration (Fig. 3). The polymer formed in the presence of catalysts **1** and **2** is the X-ray amorphous atactic PP. However, the number of regio-errors (2,1-additions, whose signal is marked by an asterisk in the ^{13}C NMR spectrum) in PP prepared with mononuclear complex **2** is much higher than those with catalyst **1**.

Hence, complex **1** is essentially less active in the polymerization of ethylene and propylene compared to complex **2**.

Experimental

Complexes were prepareded in dry conditions under argon. Dichloromethane, toluene, hexane, benzene, nitrobenzene, and ethyl acetate (chemically pure) were purified according to known procedures.[22] The reagents $TiCl_4$ and $Ti(OPr^i)_4$ (Fluka) were additionally distilled under argon. The complex $TiCl_2(OPr^i)_2$ was prepared as described previously.[23] In the syntheses of the ligands, 1,1´-diaminooctafluorobiphenyl and 3,5-di-*tert*-butylsalicylic aldehyde (Fluka and Aldrich) were used. The molecular weight was measured by cryoscopy according to a reported procedure.[24] The ^{1}H NMR spectra were obtained on Bruker WP-200 and Bruker AMX-400 instruments. The IR spectra were recorded on a Magna-IR 750 spectrophotometer. The ^{13}C NMR spectra of a 7.5 wt.% solution of polypropylene (PP) in 1,1,2,2-tetrachloroethane-d_2 were recorded on a Bruker AC-200 instrument at 110 °C.

X-ray diffraction analyses of PP samples were performed on a DRON-2 diffractometer.

Molecular-mass characteristics (M_w, M_n, M_w/M_n) of PE and PP were measured in solutions of the polymers in 1,2-dichlorobenzene at 135 °C by gel permeation chromatography on a Waters 150-C instrument equipped with a linear column with HT-μ-styragel.

4,4´-Bis-imino-bis(3,5-di-*tert*-butylsalicylidene)octafluorobiphenyl. A solution of 3,5-di-*tert*-butylsalicylaldehyde (0.20 g, 0.85 mmol) in toluene was placed in a two-necked flask and 0.15 g (0.43 mmol) 4,4´-diaminooctafluorobiphenyl and 0.01 g (0.01 mmol) *p*-toluenesulphoacid were added. The mixture was refluxed under stirring for 20 h, filtered off, evaporated, purified on a chromatographic column filled with silica gel (eluent is hexane—ethyl acetate, 5 : 1). The product was obtained as a yellow oil, yield was 82%. Found (%): C, 66.29; H, 5.70; N, 3.62. $C_{42}H_{44}F_8N_2O_2$. Calculated (%): C, 66.31; H, 5.83; N, 3.68. IR (KBr), ν/cm^{-1}: 1690 (C=N). ^{1}H NMR ($CDCl_3$), δ: 1.46 (s, 36 H, Bu^t); 7.05, 7.36 (both s, 2 H, H arom.); 9.84 (s, 2 H, CH=N); 11.79 (s, 2 H, OH).

Bis[4,4´-bis(imino-3,5-di-*tert*-butylsalicylidene)octafluorobiphenyltitanium(IV) dichloride] (1). A solution of 4,4´-bis-imino-bis(3,5-di-*tert*-butylsalicylidene)octafluorobiphenyl (0.08 g, 0.10 mmol) in dichloromethane was placed in a two-neck flask filled with argon and 0.024 g (0.10 mmol) $TiCl_2(OiPr)_2$ was added under stirring. After 20 h, a red precipitate was filtered off, washed with dichloromethane and toluene and dried in a vacuum. Yield was 85%. Found (%): C, 57.40; H, 4.86; Cl, 7.98; N, 3.03; Ti, 5.42. $C_{84}H_{84}Cl_4F_{16}N_4O_4Ti_2$. Calculated (%): C, 57.48; H, 4.82; Cl, 8.08; N, 3.19; Ti, 5.45. IR (KBr), ν/cm^{-1}: 1610 (C=N); 566 (Ti—O); 472 (Ti—N); 420, 397 (Ti—Cl). ^{1}H NMR (toluene-d_8), δ: 1.54 (s, 72 H, Bu^t); 7.05, 7.36 (both s, 4 H, H arom.); 8.93 (s, 4 H, CH=N).

Ethylene polymerization. To study the catalytic ethylene polymerization, toluene (high purity grade) was used. Before runs, solvents were purified from possible admixtures according to a known procedure.[25] Polymethylaluminoxane (Witco) was used as a 10% solution in toluene. Argon and ethylene (high purity grade) were dried by passing the gases through a column filled with molecular sieves 5 Å.

All procedures for pretreating of glassware and the protocol of the pretreating and introduction of complexes and gaseous ethylene into the reactor, as well as the measurement of the polymerization kinetics were described earlier.[26] After complete dissolution of ethylene in a solution of the tested complex, polymerization was started by the introduction of a MAO solution into the reactor and stopped by the treatment of the reactor contents with a 10% solution of HCl in EtOH. The polymeric product was filtered off, washed with alcohol and water, and dried in a vacuum at 50—60 °C to a constant weight.

Propylene polymerization. Polymerization was carried out by complete filling the reactor with liquefied propylene ($p_{C_3H_6} \approx$ 40 atm), purity grade for polymerization (99.7 vol.%), which was used without additional purification. A total procedure of the experiment was reported elsewhere.[27]

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