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# First example of cationic titanium (III) complexes with crown ether as catalysts for ethylene polymerization

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# ABSTRACT

Complex cations with a vacant coordination site are considered as the most plausible catalytically active centers of metallocene and post-metallocene polymerization catalysts. For the first time we demonstrated that cationic titanium (III) complexes stabilized with crown ether can be used as pre-catalysts for ethylene polymerization. In the presence of alkyl aluminum chlorides and MgBu<sub>2</sub> as cocatalysts, these complexes catalyze ethylene polymerization to produce Ultra High Molecular Weight Polyethylene (UHMWPE) with productivity up to  $4650 \text{ kg}_{PE}$ / mol <sub>Ti</sub> h-atm and molecular weight up to  $1.8 \cdot 10^6$  Da. UHMWPE powders were processed by the solid-phase method with subsequent orientation drawing into high-strength (1.4–2.1 GPa) and high-modulus (91–118 GPa) films.

# 1. Introduction

Intensive research in the field of classical Ziegler, metallocene and post-metallocene catalysis over the past decades has led to the improvement of known and to the development of new types of catalytic systems, as well polymers and oligomers with improved properties. At the same time, the theoretical aspects of this branch of chemistry are still undeveloped. The most important is the work by T. J. Marks et al. [1], who using the ionic complex  $[Cp_2Zr^{(IV)}R]^+$  [X]<sup>-</sup> elegantly proved the assumption by A. Shilov et al. [2] that the active center in metallocene catalysts for olefin polymerization is a cation  $[Cp^2M^{(IV)}R]^+$ , where M is an atom of 4 group metal. At present, this point of view has become generally accepted for all types of Ziegler systems with groups 4, 5, 8-10 metals, even despite their radical differences and some results that contradict this theory. For example, the catalytic activity of the anionic nickel complex [3], quantum-chemical calculations that do not exclude the possibility of catalytic process on neutral titanium(IV) complexes [4-7]. Another contradictory fact is that the titanium (IV) is easily reduced to Ti(III) compounds during the activation of precatalysts with organoaluminum compounds (OAC). However, all proposed mechanisms of Ziegler catalysis suffer from poor understanding of transformation of the pre-catalyst in the presence of co-catalyst (activator), monomer and a solvent. Nevertheless, the proposed mechanism of metallocene and, with certain corrections, post-metallocene catalysis with a cationic complex of a transition metal as an active center do not contradict to the available experimental data and has a certain predictive potential that sets the main development vector for experimental and theoretical work on Ziegler catalysis.

Thus, in the majority of modern studies in the field of Ziegler catalysis, the postulated role of cationic metal alkyl species is accepted as a proven fact [1] and that does not require additional discussion. This point of view, with certain limitations, is admissible for systems based on zirconium and hafnium compounds, the reduction potential of which is substantially more negative than the redox-potential of organoaluminum activators. For example, for metallocenes Cp<sub>2</sub>MCl<sub>2</sub>:  $-E_{1\backslash 2} =$  1.4 (Ti), 1.6–2.3 (Zr)  $\mu$  2.7 (Hf) [8–10] and for titanium and zirconium

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complexes with an oxopyran ligand:  $-E_{1\setminus 2} = 0.48$  (Ti), 1.3 (Zr) [11]. As a result, the atoms of zirconium and especially hafnium can maintain their oxidation state (+4) throughout the entire catalytic process. At the same time, titanium (IV) compounds are easily reduced to titanium (III) and even lower that was established almost immediately after the discovery of catalysts of this type [see bibliography in the book by N.M. Chirkov et al. [12] and was repeatedly confirmed in later works, for example in [13]. Therefore, the direct analogy of the mechanism of their action with zirconium compounds should be used with great caution. However, the ionic titanium (III) complexes can be obtained independently as well-defined compounds and used directly for the formation of catalytic systems for olefin polymerization.

Based on this paradigm, the use of well characterized ionic complexes of titanium(III) as pre-catalysts for olefin polymerization was studied in this work.

# 2. Experimental section

All manipulations with air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in oven-dried Schlenk glassware on a dual manifold Schlenk line equipped with a high-vacuum line. Some operations were carried out in a Braun M glove box under argon atmosphere. Argon and ethylene of special-purity grade (Linde gas) were dried by purging through a Super Clean<sup>TM</sup> Gas Filters. Dimethoxyethane and diethyl ether were purified by boiling and following distillation over sodium benzophenone ketyl. Hexane was boiled and distilled over Na/K alloy. 15-Crown-5 was dried over 4 Å molecular sieves, degassed in vacuum, and stored under argon. The reagent  $3TiCl_3$ ·AlCl<sub>3</sub> was purchased from Aldrich and used without purification. Titanium(IV) complexes - TiCl<sub>3</sub> 3THF and {2-[ $\alpha,\alpha$ -bis(trifluoromethyl)methanolato]-4,6-di-*tert*-butyl-phenolato}dichlorodi(propan-2-ol)titanium, were synthesized according to [14–15]; their properties corresponded to literature data.

NMR spectra were recorded on Bruker DPX 300 and Bruker AMX-400 instruments. Elemental analysis (C, H, Cl) was performed by the microanalytical laboratory at A. N. Nesmeyanov Institute of Organoelement Compounds on Carlo Erba-1106 and Carlo Erba-1108 instruments. The contents of Ti were performed by X-ray fluorescence analysis on the VRA-30 device (Karl Zeiss, Germany).

# 2.1. TiCl<sub>2</sub>•2 DME]<sup>+</sup> [TiCl<sub>4</sub>•DME]<sup>-</sup> (I)

**Method 1.** Dark violet {TiCl<sub>3</sub> 0.33AlCl<sub>3</sub>} powder (1.0 g) was suspended in dimethoxyethane (30 ml). The suspension was stirred for 1 h, after which the undissolved precipitate was filtered off, the solution was concentrated to a half of initial volume and left overnight at 5 °C. The precipitated black powder was washed with diethyl ether and dried in a vacuum. Found (%): C 24.72; H 5.13; Cl 36.67; Ti 16.49. Calculated for C<sub>12</sub>H<sub>30</sub>O<sub>6</sub>Cl<sub>6</sub>Ti<sub>2</sub> (%): C 24.89; H 5.19; Cl 36.77; Ti 16.56. <sup>1</sup>H NMR (300 MHz, acetonitrile-*d*<sub>3</sub>, 20 °C, ppm): 3.48 (s, 3H); 3.68 (s, 2H). One crystal was selected for X-ray diffraction study.

**Method 2.** Light green powder TiCl<sub>3</sub> 3THF (1.00 g, 2.7 mmol), obtained by treating {TiCl<sub>3</sub> 0.33AlCl<sub>3</sub>} with tetrahydrofuran was suspended in dimethoxyethane (10 ml). The suspension was stirred until dissolved and the solution was left overnight at 5 °C. The black precipitate that formed was filtered off, washed with diethyl ether and dried in a vacuum. Calculated (%) for  $C_{12}H_{30}O_6Cl_6Ti_2$  (578.82): C 24.89; H 5.19; Cl 36.77; Ti 16.56. Found (%): C 24.83; H 5.15; Cl 36.70; Ti 16.51.

# 2.2. Reduction of titanium (IV) saligenin complex

A solution of 1.1 mmol of AlH<sub>3</sub> produced by the Schlesinger reaction in 11 ml of diethyl ether was added dropwise over 30 min under stirring to a solution of the complex LTi(iPrOH)<sub>2</sub>Cl<sub>2</sub> - {2-[ $\alpha,\alpha$ -Bis(trifluoromethyl)methanolato]-4,6-di-*tert*-butyl-phenolato}dichlorodi (propan-2-ol)titanium, [9] (0.6 g, 1 mmol) in 50 ml of dimethoxyethane at room temperature under argon atmosphere. The mixture was stirred at room temperature for one day until the red color of the solution turned dark green. The solution was evaporated in vacuo to 20 ml, diethyl ether (10 ml) was added and left overnight at a temperature of 5 °C. The precipitated black crystals of complex I - [TiCl<sub>2</sub>•2 DME]<sup>+</sup> [TiCl<sub>4</sub>•DME]<sup>-</sup> (47 mg) were filtered off, washed with diethyl ether (1 ml) and dried in a vacuum. Calculated (%) for C<sub>12</sub>H<sub>30</sub>O<sub>6</sub>Cl<sub>6</sub>Ti<sub>2</sub> (578.82): C 24.89; H 5.19; Cl 36.77; Ti 16.56. Found (%): C 24.68; H 5.08; Cl 36.98; Ti 16.42.

The filtrate was evaporated in vacuum to a volume of 10 ml, filtered, 10 ml of hexane was added and left to stand at a temperature of 5 °C. The precipitated brown crystals of complex **II (L<sub>2</sub>Ti dme)** (85 mg, ~ 20%) were separated, washed with cold hexane (1 ml) and dried in a vacuum. Calculated (%) for C<sub>12</sub>H<sub>30</sub>O<sub>6</sub>Cl<sub>6</sub>Ti<sub>2</sub> (578.82): C 24.89; H 5.19; Cl 36.77; Ti 16.56. Found (%): C 24.68; H 5.08; Cl 36.98; Ti 16.42. <sup>1</sup>H NMR (300 MHz, benzene- $d_8$ , 20 °C),  $\delta$ : 1,23 (s, 9H); 1,47 (s, 9H); 3,22 (br.s., 6H); 3,53 (br.s.,4H); 7,47 (s, 1H); 7,53 (d, 1H, J = 2,1 Hz); 8,06 (br.s.,1H).

# 2.3. [TiCl<sub>2</sub>·15-Crown-5]<sup>+</sup>[AlCl<sub>4</sub>]<sup>-</sup> (III)

**Method 1.** TiCl<sub>4</sub> (0.55 ml, 5 mmol) was added to a solution of 15crown-5 (1.1 g, 5 mmol) in 10 ml of tetrahydrofuran. The reaction mixture was stirred at room temperature for 3 h, then was cooled to  $-40^{\circ}$  C and 1 M solution of Et<sub>2</sub>AlCl in toluene (10 ml, 10 mmol) was added dropwise. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. Part of the solvent was evaporated in vacuo and 2 ml of hexane was added. The slightly blue precipitate that formed was filtered off and recrystallized from a mixture of THF: hexane = 1: 2. Yield - 1.54 g of crystalline substance (54%). Calculated (%) for C<sub>10</sub>H<sub>20</sub>AlCl<sub>6</sub>O<sub>5</sub>Ti (507.83): C 23.65; H 3.97; O 15.75; Al 5.31; Cl 41.89; Ti 9.43. Found (%): C 23.61; H 3.94; Cl 41.85; Ti 9.38. Some crystals were selected for X-ray structural study.

**Method 2.** According to [16], 1.7 g (5 mmol) of crystalline TiCl<sub>3</sub> 3THF was added to a solution of 15-crown-5 (1.1 g, 5 mmol) in 15 ml of tetrahydrofuran, and after stirring for 30 min and cooling to -10 °C anhydrous AlCl<sub>3</sub> (0.7 g 5 mmol) was added. Part of the solvent was evaporated in vacuo and 3 ml of hexane was added. The resulting blue precipitate was filtered and recrystallized from a mixture of THF: hexane (1:2) to afford 1.8 g of fine green–blue crystalline substance. Calculated (%) for C<sub>10</sub>H<sub>20</sub>AlCl<sub>6</sub>O<sub>5</sub>Ti (507.83): C 23.65; H 3.97; O 15.75; Al 5.31; Cl 41.89; Ti 9.43. Found (%): C 25.22; H 4.62; Cl 40.60; Ti 9.14.

# 2.4. X-ray crystal structure determination

Experimental data for I were collected on a Bruker D8 Venture machine using graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$ Å) at the Center of Shared Equipment of IGIC RAS. Absorption corrections based on measurements of equivalent reflections were applied [17] The structures were solved by direct methods and refined by full matrix least-squares on  $F^2$  with anisotropic thermal parameters for all nonhydrogen atoms [18] All hydrogen atoms were placed in calculated positions and refined using a riding model.

The single-crystal X-ray diffraction data for **II** were collected a threecircle Bruker D8 QUEST PHOTON-III CCD diffractometer using  $\varphi$  and  $\omega$ scan mode. The data were indexed and integrated using the SAINT program [19] and then scaled and corrected for absorption using the SADABS program [20]. For details, see Table S1. The structure was solved by direct methods and refined by a full-matrix least square technique on  $F^2$  in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters  $[U_{iso}(H) = 1.5U_{eq}(C)$  for the methyl groups and  $1.2U_{eq}(C)$  for the other groups]. All calculations were carried out using the SHELXTL program suite [21]. Details of X-ray studies are listed in tables S1-S2. The crystallographic data for **I** and **II** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications under the



Scheme 1. Reduction of saligenin Ti(IV) complex.

CCDC numbers 2,128,039 and 2142742.

#### 2.5. Ethylene polymerization

Because of poor solubility of ionic complexes in arenes and alkanes, in which the olefin polymerization process is traditionally carried out, all compounds of this type were tested for catalytic activity in three modes:

**Mode A** - An individual compound was loaded into the reactor together with activators (the conventional way);

**Mode B** - Required amounts of all components of the catalytic system were loaded into the reactor without preliminary isolation of the precatalyst in an individual state (*in situ* mode);

**Mode C** – Pure titanium complexes were preliminary activated with a binary mixture of Et<sub>2</sub>AlCl and Bu<sub>2</sub>Mg. In the latter case, the required amount of the studied complex and 8–10 ml of toluene was introduced into a 50 ml Schlenk flask with 3–4 glass beads in an argon atmosphere, after which the activator components were added in the ratio [Al]/[Mg]/[Ti] – 300/100/1. The Schlenk flask was placed on a shaker and the mixture was shaken for 3–5 h. As a result, a gel-like suspension was formed, which was then completely transferred into the polymerization reactor in a glove box as a ready-made active form of the polymerization catalyst.

The polymerization was carried out in a 150 ml steel reactor (Parr Company). Before starting the experiment, the reactor was evacuated at a temperature of about 90 °C for 40 min, then it was filled with purified argon. A solvent (toluene) and a pre-catalyst with a titanium content of  $5 \cdot 10^{-6}$  mol were introduced. The total volume of the solvent did not exceed 100 ml. The slurry was stirred and ethylene was fed to the reactor under pressure of 0.7 atm (10 psi) for 30 min with vigorous stirring (600 rpm) at temperature of 30 °C, which was maintained with a thermostat. At the end of the experiment, the reaction mixture was cooled, and 20 ml of ethyl alcohol and 20 ml of 1 M HCl solution were added to the reactor to deactivate unreacted organoaluminum compounds. The resulting polymer was filtered and treated with mixture of 200 ml of alcohol and 20 ml of 1 M HCl solution for 30-40 min at 60 °C under stirring. After that, the suspension was settled at room temperature for 2 days, the precipitate was filtered off, washed with distilled water, alcohol and dried in vacuum for 3-4 h at 70 °C.

#### 2.6. Polymer evaluation methods

DSC was performed by a differential scanning calorimeter DSC-822e (Mettler-Toledo, Switzerland) at a heating rate  $10 \degree C min^{-1}$  in air and in argon.

Viscosity-average MW of synthesized UHMWPE samples was calculated with the Mark–Houwink equation:  $M_v=5.37\cdot10^4~[\eta]^{1.37},~[22]$  where  $M_v=viscosity$ -average MW (g mol^-1);  $[\eta]=intrinsic viscosity in decalin at 135 °C (dl g^{-1}); and <math display="inline">[\eta]=(2\eta_{sp}-2ln\eta_r)^{1/2}/0.056~(\eta_{sp},$  specific viscosity decalin at 135 °C;  $\eta_r$ , relative viscosity in decalin at 135 °C;  $\eta_r=\eta_{sp}+1$ ).

The mechanical characteristics of the oriented materials prepared from the synthesized polymers were evaluated using the oriented tapes obtained by a solid-state processing of UHMWPE nascent reactor powders. The monolithic tapes uniform over the entire length (100  $\mu$ m in thickness and 10 mm in width) were formed at a pressure and shear deformation below the polymer melting point (124–126 °C). The tapes were subjected to uniaxial drawing while using a Spinline Daca equipment. The drawing temperature was set 4 °C below the polymer melting point. The mechanical characteristics of the tapes were measured with a Hounsfield H1KS machine at the gauge length of the tested samples 120 mm with 100 mm/min initial deformation rate. The reported values were the average of at least 8 samples.

Scanning electron microscopy investigations of morphologies of nascent reactor powders were carried out with a high resolution Tescan VEGA3 SEM operated at 5 kV. As-polymerized particles were carefully deposited on SEM stubs, and the samples were coated with gold by a sputtering technique.

#### 3. Results and discussion

Ionic titanium(III) compounds can be produced by direct interaction of unsolvated titanium(III) salts, in general, halides with a suitable donor-type solvents via ionization or autocomplexation reactions (Equations 1, 2), via ligand exchange process (Equation 3), upon reduction of molecular compounds of titanium(IV) in the presence of strong Lewis bases (Equation 4), upon reduction and subsequent complexation with a by-product of the reaction (Equation 5) or directly by reaction 6.

$$2TiX_3 + nL ---> 2[TiX_2 \cdot L]^+[X]^-$$
(1)

 $2\mathrm{TiCl}_{3} + \mathrm{nL} - --> [\mathrm{TiCl}_{2} \cdot \mathrm{L}]^{+} [\mathrm{TiCl}_{4} \cdot \mathrm{L}]^{-}$ (2)

$$2\text{TiCl}_{2} \cdot \text{S} + \text{nL} - - > [\text{TiCl}_{2} \cdot \text{L}]^{+} [\text{TiCl}_{4} \cdot \text{L}]^{-} + \text{S}$$
(3)

 $TiCl_4 \bullet L' + nL + kAlH_3 DME - [TiCl_2 \bullet L]^+ [An?]^-$ (4)

$$\text{TiCl}_4 \text{ S} + \text{nL} + \text{nAlR}_2\text{Cl} - - > [\text{TiCl}_2 \cdot \text{L}]^+ [\text{AlCl}_4]^- + \text{S} + \text{Y} + \text{Z} + .??. (5)$$

$$TiCl_3 \cdot S + AlCl_3 + nL - - > [TiCl_2 \cdot L]^+ [AlCl_4]^- + S$$
(6)

where S is a donor-type solvent (usually THF); L-additional ligand; An, Y, Z - unknown products.

We have utilized all the above variants of the synthesis of these compounds, except for reaction 1. In reaction 2, we used the product of the reduction of  $TiCl_4$  with metallic aluminum having the composition  $\{TiCl_3 0.33AlCl_3\}$  as a starting material and dimethoxyethane as a ligand (L):

 $TiCl_3 \bullet 0.33AlCl_3 + DME \rightarrow [TiCl_2 \bullet 2 DME]^+ [TiCl_4 \bullet DME]^- + AlCl_3 \bullet nDME$ (2)

In this reaction, the titanium(III) complex precipitates, while the aluminum chloride remains in solution.



Fig. 1. Structure of the ionic complex [TiCl<sub>2</sub> 2DME]<sup>+</sup> [TiCl<sub>4</sub> DME]<sup>-</sup> (I).



Fig. 2. The structure of the molecular complex [L<sub>2</sub>Ti DME] (II).

In reaction 3, the molecular complex TiCl<sub>3</sub> 3THF and dimethoxyethane as a competing ligand were used:

 $TiCl_{3} \cdot 3THF + DME \rightarrow [TiCl_{2} \bullet 2DME]^{+} [TiCl_{4} \bullet DME]^{-} + 3THF$ (3)

In reaction 4,  $\{2-[\alpha,\alpha-Bis(trifluoromethyl)methanolato]-4,6-di-$ *tert* $butyl-phenolato}dichlorodi(propan-2-ol)titanium (the method of its$ synthesis and structure are described in [15]) was reduced withaluminum hydride in dimethoxyethane (Scheme 1).

In reaction 5,  $TiCl_4$  was reduced with diethylaluminum chloride in the presence of 15-crown-5 in THF (equation 5):

# $TiCl_4 \cdot nTHF + Et_2AlCl \rightarrow [TiCl_2 \cdot 15 - Crown - 5]^+ [AlCl_4]^- + THF + [Y,Z](5)$

As a result, in reactions 2' and 3', black powders of the titanium(III) complex with the composition [2TiCl<sub>3</sub> 3DME], poorly soluble in all standard organic solvents, were obtained as the main product. The structure of this ionic compound [TiCl<sub>2</sub> 2DME]<sup>+</sup> [TiCl<sub>4</sub> DME]<sup>-</sup> (I) is shown in Fig. 1. The cation and anion in this complex have an octahedral environment. The distances Ti-O = 2.09-2.11 Å and Ti-Cl = 2.30-2.31 Å in the cation and 2.15-2.16 Å and 2.36-2.40 Å in the anion differ little from those previously determined for other titanium(III) molecular complexes, for example, in TiCl<sub>3</sub> 3THF (2.09-2.18 Å and 2.34-2.36 Å) [23]. Both cation and anion possess slightly distorted octahedral environment with expectedly smallest endocyclic O-Ti-O angles (76.85(12)-77.23(13)°). In the cation, chlorine ligands occupy *cis*-positions with Cl-Ti-Cl angle equal to  $100.49(7)^{\circ}$ . The Ti-O distances range within 2.087 (3)-2.116(3) Å; Ti-Cl separations are 2.2950(15), 2.3144(15) Å. These

values are close to those found for *trans*- $[TiCl_2 \cdot 4THF]^+$  cations (2.064 (8)- 2.126(5) and 2.333(2)-2.361(3) Å).[24–25] In the anion, both Ti-O and Ti-Cl distances are expectedly longer (2.148(3)-2.156(3) Å and 2.3643(14)- 2.3972(14) Å) and somewhat differ from those reported for the only structurally characterized  $[TiCl_4 \bullet DME]^-$  anion in PPN<sup>+</sup> $[TiCl_4 \bullet DME]$  salt (2.171(2)- 2.174(2) and 2.360(1)- 2.383(1) Å) [26].

The complex **I** in its purest form was obtained by reaction 3. The product of reaction 2 contains insignificant-amount of aluminum chloride, most likely in the form of an adduct with DME. Yield (**I**) in reaction 4 is small, since it is complicated by the formation of the bis-ligated titanium(IV) complex **II**, additionally stabilized by DME with the composition [Sal<sub>2</sub>Ti DME], where Sal -2-[ $\alpha$ , $\alpha$ -bis(trifluoromethyl) hydroxymethyl]-4,6-di-*tert*-butyl-phenol.

The structure of complex II was unambiguously established by the Xray diffraction and is shown in Fig. 2 along with the atom numbering scheme. The selected bond lengths and angles are given in Table S2.

Complex II crystallizes in the triclinic space group *P*-1 and possesses the idealized  $C_2$  (2) intrinsic symmetry (the two-fold axis passes through the titanium atom and the middle of the C—C bond of the 1,2-dimethoxyethane ligand). The titanium atom has the distorted octahedral coordination environment formed by the three bidentate chelating ligands. The two 2-(3,5-di-*tert*-butyl-2-oxo-phenyl)-2,2-trifluoromethyl-ethoxy ligands form the six-membered almost planar chelate metallacycles with the bite angles of 87.41(3) and 87.38(3)°, and the DME ligand forms the five-membered metallacycle in the *twist* conformation with the bite

#### Table 1

Ethylene Polymerization by complexes 3-4<sup>a</sup>.

Entry	Pre-Catalyst	Polymeriz. technique <sup>b</sup>	A <sup>c</sup>	Bulk density	m.p. °C	Crystal-linity <sup>d</sup> , %	M <sub>w</sub> *10 <sup>-6 e</sup>
$1^{\mathbf{f}}$	(TiCl <sub>3</sub> ) <sub>2</sub> (DME) <sub>3</sub>	С	1630	0.072	142/139	76.05/ 65.52	1.19
2	15-Crown-5/ TiCl <sub>4</sub> / Et <sub>2</sub> AlCl; 1:1:1	В	3750	0.056	139/134	77.95/ 61.02	1.36
3	15-Crown-5/ TiCl <sub>4</sub> / Et <sub>2</sub> AlCl;	А	1920	0.048	140/135	72.98/ 64.10	1.75
4	1:1:2	В	4530	0.063	137/137	79.33/ 65.57	0.9
5		С	4380	0.063	139/137	78.95/ 60.40	1.6
6	15-Crown-5 /TiCl <sub>4</sub> / Et <sub>2</sub> AlCl; 1:2:1	В	3460	0.058	139/135	79.48/ 53.57	1.63
7	15-Crown-5/ TiCl <sub>4</sub> /Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> ; 1:1:1	В	4650	0.082	136/137	70.28/ 64.14	0.5
8	15-Crown-5/ TiCl <sub>4</sub> ; 1:1	В	2560	0.063	140/137	78.33/ 67.08	1.59
9	15-Crown-5/ TiCl <sub>3</sub> ; 1:1	В	4090	0.075	137/137	73.29/ 62.62	0.65
10	15-Crown-5/ TiCl <sub>3</sub> /AlCl <sub>3</sub> ; 1:1:1	Α	2410	0.056	143/140	71.29/ 67.56	1.8
11	15-Crown-5/ TiCl <sub>3</sub> /AlCl <sub>3</sub> ; 1:1:0.33	В	4540	0.078	137/136	79.46/ 68.70	0.76

<sup>a)</sup> Polymerizations were carried out in 100 ml of toluene with  $5 \times 10^{-6}$  mol of precatalyst at a constant 1 atm excessive ethylene pressure for 15 min., activator - Et<sub>2</sub>AlCl/Bu<sub>2</sub>Mg = 300/100.

<sup>b)</sup> Polymerization technique: A – common mode, an individual pre-catalyst was introduced in the reactor, B – pre-catalyst obtained *in situ* was used, C - pre-catalyst was preliminary pre-activated.

<sup>c)</sup> Productivity, in kg<sub>PE</sub>/mol <sub>Ti</sub> h·atm.

<sup>d)</sup> Crystallinity was determined by DSC, the first melting for PE,  $\chi = (\Delta H_m / \Delta H_m^0) \times 100\%$ , where  $\Delta H_m^0 = 293.0 \text{ J/g}$ .

<sup>e)</sup> Molecular weight was determined by the viscosimetric method.

<sup>f)</sup> Polymerizations were carried out for 30 min.



**Fig. 3.** Crystal structure of the complex  $[TiCl_2 \bullet 15$ -Crown-5]<sup>+</sup> [AlCl<sub>4</sub>]<sup>-</sup> (III) [10].

angle of 74.67(3)°. As expected, the Ti–O( $C_{sp}^2$ ) bonds (1.8148(7) and 1.8284(7) Å) are shorter than the Ti–O( $C_{sp}^3$ ) bonds (1.8826(7) and 1.8859(7) Å) (Table 1). The Ti  $\leftarrow$  O coordination bonds to the oxygen atoms of the DME ligand are substantially longer (2.1876(7) and 2.1992 (7) Å) than the covalent Ti–O bonds (Table 1). The O2–Ti1–O4, O1–Ti1  $\leftarrow$  O6 and O3–Ti1  $\leftarrow$  O5 angles of 167.24(3), 161.97(3) and 161.86(3)°, respectively (Table S1), indicate a significant distortion from linearity.

In the crystal, the molecules of **II** are bound by the C–H…F [C…F 3.3316(12) Å, H…F 2.43 Å,  $\angle$ C–H…F 151°] hydrogen bonding and F…F nonvalent (2.6525(10) Å) interactions into puckered ribbons along the crystallographic **b** axis (Figure S1). The ribbons are separated by vander-Waals distances (Figure S2).

Apparently, due to this environment, reduction of Ti(IV) does not occur even when treated with such a powerful reducing agent as aluminum hydride. Similiar effect of strong coordinated ligands on the electrochemical characteristics of complexes of group 4 metals was shown earlier [8–11].

The most interesting and unpredicted results were obtained in the reduction of TiCl<sub>4</sub> in the presence of crown ether (reaction 5). The type of intracavity cation with the composition  $[TiCl_2 15-Crown-5]^+[AlCl_4]^-$  (III) with Ti-Cl, Ti-O and Al-Cl distances equal to 2.369, 2.379 Å, 2.12–2.17 Å, and 2.12–2.15 Å, respectively (Fig. 3), is well known in the supramolecular chemistry of macrocycles [27]. In this case, the complex unexpectedly crystallizes with the tetrahedral anion  $[AlCl_4]^-$  (Fig. 3), which is apparently formed as a by-product during the reduction of Ti (IV) to Ti(III), instead of anticipated  $[TiCl_4]^-$  or  $[TiCl_6]^{2-}$  anions. This compound was obtained earlier by direct interaction of the Ti(III) complex with aluminum chloride in THF medium (Equation 6) [16].

Indeed, even in the first works studying reduction of TiCl<sub>4</sub> by organoaluminum compounds [28-30], it was pointed out that this reaction is rather complex (multichannel) and strongly depends on temperature, nature of the OAC and the solvent, and the ratio of reagents. Only the fact of the reduction of Ti(IV) to Ti(III) remained indisputable, which apparently proceeds through the stages of the formation of unstable alkylhalide complexes of titanium and various alkyl halide compounds of aluminum with strong kinetic hindrances. It was found earlier [31–32] that in the presence of organic ligands the reduction of Ti(IV) occurs in parallel with disproportionation of aluminum alkyl chlorides that leads to the formation of AlCl<sub>3</sub> among other products. In our case, i. e. in the presence of the macrocyclic ligand 15-Crown-5, this reduction reactions results in the formation of the intracavitary Ti(III) complex with a yield of no less than 50%, which reflects the complex nature of this reaction. Due to the lack of information on the structures of all products of this reaction, we, like the authors of early works [31-32], find it difficult to write its stoichiometry.

The catalytic properties of systems with individual ionic complexes I and III (complex III was obtained by reaction 6, complex II was not

studied due to its small amounts available), were tested in the reaction of ethylene polymerization. In addition, we tested a number of mixtures obtained *in situ* by reduction of TiCl<sub>4</sub> 2THF with diethylaluminum chloride or ethylaluminum dichloride in toluene in the presence of 15-crown-5. It was found that activators conventional for classical Ziegler catalysis - Et<sub>3</sub>Al, Me<sub>3</sub>Al, iBu<sub>3</sub>Al, Et<sub>2</sub>AlCl and polymethylalumoxanes (MAO, MMAO) are practically unable to activate any of the complexes obtained in this work (only trace amounts of polymer were observed). Therefore, we used a  $3Et_2AlCl + Bu_2Mg$  mixture, which has been successfully used to activate classical Ziegler, metallocene, and postmetallocene catalysts [33–34].

Due to their ionic nature, all tested compounds are practically insoluble in aromatic and aliphatic hydrocarbons.

In the standard mode **A** (introduction of an individual precatalyst into the reactor), complex **I** showed no activity. After preliminary activation with {3Et<sub>2</sub>AlCl + Bu<sub>2</sub>Mg} mixture (mode **C**, see Experimental section), the productivity of the system was 1630 kg PE/mol <sub>Ti</sub> h atm (Table 1, entry 1), which is more than twice the productivity of the molecular complex TiCl<sub>3</sub> 3THF under the same condition (728 kg PE/mol <sub>Ti</sub> h atm., [35]). At the same time, the productivity of complex **I** practically does not differ from the productivity of the system formed in mode **B** during the reduction of TiCl<sub>4</sub> 2THF in the presence of Et<sub>3</sub>Al, Et<sub>2</sub>AlCl and Bu<sub>2</sub>Mg – 1668 kg PE/mol <sub>Ti</sub> h atm [35]. In fact, this once again indicates that in both cases an active center with a titanium (+3) atom is formed.

The activity of complex **I**, in which the titanium ion is stabilized by DME, is significantly inferior to all titanium complexes with crown ethers (*vide infra*). This confirms our assumption that macrocyclic ligands - crown ethers are able to effectively stabilize a catalytically active particle.

As mentioned above, the compositions of the products formed during the reduction of titanium tetrachloride depends mainly on the Ti/Al ratio and on the activator composition.

Complex III in this work was obtained by two ways: upon reduction of TiCl<sub>4</sub> 2THF in toluene with one equivalent of Et<sub>2</sub>AlCl in the presence of 15-crown-5 and upon the direct interaction of TiCl<sub>3</sub> 3THF with AlCl<sub>3</sub> in a THF solution of 15-crown-5, as described in [16]. The productivity of the product obtained by the first method (and tested without isolation in the individual state, mode **B**) in the polymerization of ethylene was 3870 kg PE/mol Ti h atm., while the productivity of the product obtained by the second method (mode A) is significantly less  $-2410 \text{ kg PE/mol}_{Ti}$ h atm. (Table 1, entry 11). This difference can be explained by the formation in the first case other, more active forms of precursors, possibly containing alkyl groups in addition to complex III. This possibility follows from the complex nature of the reduction of titanium tetrachloride by organoaluminum compounds [28-32]. Indeed, if the reduction of TiCl<sub>4</sub>·2THF is carried out in the presence of two equivalents of Et<sub>2</sub>AlCl, the activity of the systems (formed in modes B and C) increases to 4380-4530 kg PE / mol Ti h atm. At the same time, when two equivalents of TiCl<sub>4</sub> 2THF are reduced with one equivalent of Et<sub>2</sub>AlCl, the activity drops to 3460 kg PE / mol Ti h atm. The ambiguity of the reduction reaction is also indicated by the data on the catalytic activity obtained on the TiCl<sub>4</sub>·2THF-Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>-15-crown-5 system (mode B). This system showed the maximum productivity in ethylene polymerization - 4650 kg PE / mol Ti h atm. (Table 1, entry 7) and even despite of using less active activator with only one ethyl group.

As can be seen from the data in the Table 1 (entries 11–13), the activity of some systems strongly depends on the amount of aluminum chloride contained in the pre-catalyst: it noticeably increases with its decrease. The system formed *in situ* (mode **B**) by interaction of a suspension of {TiCl<sub>3</sub> 0.33AlCl<sub>3</sub>} in toluene with the crown ether showed comparable productivity – 4540 kg PE/mol<sub>Ti</sub> h atm (Table 1, entry 12), slightly superior to the system that does not contain aluminum chloride – 4100 kg PE/mol<sub>Ti</sub> h atm. (Table 1, entry 9). The data obtained on the TiCl<sub>4</sub> 2THF/15-crown-5 system showed much smaller productivity of 2560 kg PE/mol<sub>Ti</sub> h atm. (Table 1, entry 8). It implies that extracavitary

### Table 2

	Mechanical	properties	of	UHMWPE	oriented	film	tapes
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Entry <sup>a</sup>	Catalytic system	E <sup>b,</sup> GPa	σ <sup>°</sup> GPa	ε <sup>d</sup> %
2	15-Crown-5/TiCl <sub>4</sub> / Et <sub>2</sub> AlCl; 1:1:1	96.9–111.8	1.4–2.0	2.2–2.7
3	15-Crown-5/TiCl <sub>4</sub> / Et <sub>2</sub> AlCl;1:1:2 (Mode <b>A</b> )	105.4–117.9	1.9–2.1	2.1–2.9
5	15-Crown-5/TiCl <sub>4</sub> / Et <sub>2</sub> AlCl;1:1:2 (Mode C)	93.2–105.6	1.5–2.0	1.6–2.2
6	15-Crown-5/TiCl <sub>4</sub> / Et <sub>2</sub> AlCl; 1:2:1	91.7–116.9	1.4–1.8	1.2–1.6

<sup>a</sup> Numbering corresponds to Table 1.

<sup>b</sup> E – average tensile modulus, GPa;

 $\sigma$  – tensile strength, GPa;

 $^{d}~\epsilon$  – elongation at break, %.



Fig. 4. Stress-elongation curves for UHMWPE orientated tapes (Tables 1 and 2, entries 2, 3, 5, 6).

complex TiCl<sub>4</sub>/15-crown-5 upon reduction does not transform into an intracavitary Ti(III) complex. These results once again emphasize the complicated and uncertain nature of the transformation of titanium tetrachloride in such complex catalytic systems.

Thus, on the one hand, it is confirmed the reduction of Ti(IV) to Ti (III) during the formation of the catalytic system and subsequent occurrence of the polymerization reaction on the active site with the Ti (III) atom, but, on the other hand, an unambiguous confirmation of the cationic mechanism of this reaction is not obtained, since titanium in homo- and heteronuclear complexes with crown ether is present in both the cation and the anion.

The melting point and degree of crystallinity of all produced polyethylene samples are in the range of 136–143 °C and 70–79 %, respectively (Table 1) and are typical for UHMWPE [22].

The processing of obtained UHMWPE reactor powders into highmodulus oriented films was carried out under pressure and shear deformation at an elevated temperature below polymer melting point with subsequent uniaxial drawing [36] to form monolithic samples. Table 2 shows the mechanical characteristics of film tapes prepared from obtained reactor powders. Stress-strain curves of UHMWPE-orientated film tapes are shown in Fig. 4.

The best mechanical characteristics in this series were recorded for the material obtained on the catalytic system {15-Crown-5/TiCl<sub>4</sub>/ Et<sub>2</sub>AlCl} in a 1: 1: 2 ratio (entry 4, Tables 1 and 2). Any change in this ratio leads to a deterioration in the mechanical properties of oriented films (entries 3 and 7, Table 2). This UHMWPE sample has the maximum molecular weight in this series ( $1.75 \cdot 10^6$  Da). The polymer obtained on a preactivated catalytic system (entry 6) has slightly worse mechanical characteristics.



Fig. 5. SEM images of the surface morphology of UHMWPE powders at lower (top row) and higher (bottom row) magnifications: A - worm-like (Tables 1-2, entry 2), B - cob-web (Tables 1-2, entry 3) and C - broccoli-like (Tables 1-2, entry 6).

It is well known that drawability of UHMWPE highly depends on its supramolecular structure [37–38]. To examine the morphologies of these powders, SEM technique was used (Fig. 5, S15–S18).

As can be seen from the scanning electron micrographs at low magnification, the polymer particles have the irregular shape and porous structure, which determines the low bulk density ( $0.04-0.08 \text{ g/cm}^3$ ) of the obtained samples. At high magnification, samples have different morphology - worm-like, cob-web or broccoli-like.

# 4. Conclusions

In summary, a new cationic titanium (III) complexes stabilized by ligands with ether oxygen donor atoms, including macrocyclic crown ethers have been synthesized. Structure of complexes **I-III** has been established by X-ray diffraction.

All complexes in the presence of a binary co-catalysts {3Et<sub>2</sub>AlCl + Bu<sub>2</sub>Mg} exhibited high productivity towards ethylene polymerization (up to 4651 kg of PE/mol<sub>Ti</sub>·h·atm). The molecular weight of obtained polymer samples reached 1.75  $10^6$  Da.

The activity of complex **I**, in which the titanium ion is stabilized by DME, is significantly lower than all titanium complexes with crown ethers. This confirms our assumption that macrocyclic ligands - crown ethers are able to effectively stabilize a catalytically active center.

It can also be concluded that the differences in the compositions and structures of titanium pre-catalysts and their effect on the catalytic activity of systems are largely leveled out by the method of forming these systems and especially by using the binary activator {3Et<sub>2</sub>AlCl/Bu<sub>2</sub>Mg}.

The UHMWPE nascent reactor powders produced on these catalytic systems were processed by a solvent-free method into high-strength (up to 2.1 GPa) and high-modulus (up to 118 GPa) oriented film tapes.

Comparing the results obtained with previously published data on the neutral TiCl<sub>3</sub>·3THF complex [35], it can be noted that the ionic nature of the precatalysts stabilized by the crown ether significantly increases both the catalytic activity and the mechanical characteristics of oriented films, even for polyethylene samples with relatively low (not exceeding 1.75  $10^6$  Da) molecular weight.

It can also be concluded from these data that the differences in the compositions and structures of titanium pre-catalysts and their effect on the catalytic activity of systems are largely leveled out by the method of forming these systems and especially by using the binary activator  $\{3Et_2AlCl/Bu_2Mg\}$ .

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi. org/10.1016/j.eurpolymj.2022.111166.

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