

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Coordination compounds of titanium (IV) and 2-hydroxymethylphenol derivatives: Their synthesis, structure and catalytic activity in ethylene and 1-hexene polymerization





Vladislav A. Tuskaev ^{a, b, *}, Svetlana Ch Gagieva ^a, Michail V. Solov'ev ^a, Dmitrii A. Kurmaev ^{a, b}, Nikolay A. Kolosov ^a, Ivan V. Fedyanin ^b, Boris M. Bulychev ^a

^a Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119991 Moscow, Russian Federation ^b A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation

ARTICLE INFO

Article history: Received 11 July 2015 Received in revised form 19 August 2015 Accepted 20 August 2015 Available online 29 August 2015

Keywords: Polymerization Titanium Magnesium Polyolefin Ziegler–Natta

1. Introduction

Achievements in post-metallocene catalysis were summarized in several recent reviews [1–5]. It is generally recognized that the most efficient post-metallocene catalysts are the group 4 metals coordination compounds stabilized by phenoxide ligands. Usually, those ligands contain additional donor atoms, such as imine or amine nitrogen [6] (O,N ligands), or sulfur [7] (O,S ligands). There are substantially fewer examples of metal complexes with OO-type ligands used as precatalysts for the olefin polymerization catalysis. And among those saligenin-based complexes (where ligand structure contain both phenol and alcohol hydroxyls) are indeed unique [8,9].

The purpose of present work was to synthesize the Ti (IV) complexes with a variety of saligenin ligands, and to evaluate their structure and catalytic activity in ethylene and 1-hexene polymerization reactions upon activation by different co-catalysts, as well as the impact of non-transition metals salts (Li, Mg) in catalytic activity.

E-mail address: tuskaev@yandex.ru (V.A. Tuskaev).

ABSTRACT

A series of titanium complexes $LTiCl_2 \cdot ({}^{i}PrOH)_2$ **12-18** and heterobimetallic complex $L_2Ti \cdot {}^{i}PrOLi \cdot THF$ **19** bearing saligenin-type $[O,O]^{2-}$ ligands **6-11** were synthesized in high yields from $Cl_2Ti(O^{i}Pr)_2$ or $LiTi(O^{i}Pr)_5$. X-ray structure analyses for **15** and **19** revealed that these complexes adopt a distorted octahedron or distorted tetragonal pyramid geometry. When activated by binary activator $\{3Et_2AlCl + Bu_2Mg\}$, complexes **12-19** exhibited moderate to high activities toward ethylene and 1-hexene polymerization, giving high molecular weight polymers with broad molecular weight distributions. The results of this study show the unique ability of Li and Mg chlorides to improve the catalytic ability of post-metallocene pre-catalysts.

© 2015 Published by Elsevier B.V.

2. Results and discussion

2.1. Ligands and complexes synthesis

When choosing the saligenin benzylic carbon substituents, we have originally favored the fluorine-containing moieties. We expected them to be similar to the phenoxyimines [6,10,11] and TADDOLs complexes [12-14] where introduction of fluorine moiety in ligand structure results in increase of Ti atom acidity and thus improving the catalytic activity of resulting complex.

Ligands **6-9** were synthesized by reacting the 1-(3,5-di-*tert*butyl-2-hydroxyphenyl)-2,2,2-trifluoroethanone with respective metal-organic derivatives (Scheme 1). Ligands without fluorine moieties **10-11** were synthesized by lithiation of 2,4-di-*tert*-butyl-6-bromo-phenol, with subsequent treatment of lithium derivative with respective carbonyl compound.

Titanium complexes **12-18** were synthesized by direct interaction of ligands **6-11** with one equivalent of $TiCl_2(O^{-i}Pr)_2$ in toluene (Scheme 2, path a). The X-ray structure of representative complex **15** is presented on Fig. 1. In **15** titanium atom has a distorted octahedron coordination formed by chlorine atoms, oxygens of original ligand and isopropanol oxygens of leaving isopropoxy groups.

^{*} Corresponding author. Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119991 Moscow, Russian Federation.



a BuLi, CF₂CO₂Me; b NaBH₄, MeOH; c RLi or RMgHal; d BuLi, R₂CO

Scheme 1. Synthesis of ligands 6-11.



Scheme 2. Synthesis of Ti (IV) complexes with saligenines.

In our previous reports [9,12,13,15–17] we have associated a relatively high catalytic activity of OO- or ONO-type ligands Ti complexes to the Li or Mg compounds involved in formation of secondary complexes through ligands oxygens. To evaluate the

possibility of such scenario we have studied the interaction of saligenin-type ligand 6-(1,1,1,3,3,3-hexofluoro-2-hydroxypropane-2-yl)-4,6-di-tert-butylphenol with LiTi($O^{i}Pr_{)5}$. The structure of synthesized heterometallic complex L₂Ti.ⁱPrOLi.TGF (**19**) was resolved by X-ray crystallography (Fig. 1, on the right).

Compound **19** co-crystallizes with a solvate methylene chloride molecule. Ti atom coordination polyhedron is a distorted tetragonal pyramid, where foundation is formed by ligands' oxygens, and the top is formed by an isopropyl fragment oxygen. Lithium coordination polyhedron is a significantly distorted tetragonal pyramid, where foundation is formed by alcohol oxygens O(2) and O(4) as well as fluorine atoms of trifluoromethyl groups F(1) and F(7), and the top is formed by O(1T) – a coordinated tetrahydrofuran oxygen.

Considering the synthetic method, complex **19** structure and composition, serve as a proof of secondary complexation resulting in a molecular heterometallic complex.

2.2. Catalytic activity and polymer properties

Catalytic properties of synthesized compounds in the reaction of ethylene and 1-hexene polymerization are summarized in Tables 1 and 2. All compounds listed in Table 1 cannot be activated by such common co-catalysts as methylalumoxide, trimethylaluminum or diethylalumochloride (MAO, Me₃Al or Et₂AlCl, ratio of Ti/Al \leq 1:500). However, they demonstrate moderate activity in presence of {3Et₂AlCl/MgBu₂} binary co-catalyst [18,19].

For example, complex **3** containing two CF₃ groups [9], demonstrates the highest catalytic activity at [Al]/[Ti] ratio equal to 500 (Table 1, runs 1-2). Substitution of one CF₃ group for hydrogen, methyl, phenyl or pentafluorophenyl groups (compounds **12**, **13**, **14**, **15**) leads to the notable increase of catalytic activity that does not change significantly upon the decrease of [Al]/[Ti] ratio to 300.

The increase of catalytic activity in complexes with a single CF₃ group compared to **3** was unexpected, as we anticipated a contrary effect. Even more surprising was the high catalytic activity displayed by complexes lacking the CF₃ groups altogether. Complex **16** containing two phenyl moieties in benzyl position has catalytic activity that is twice of that for the **3** (Table 1, runs 1 and 13). This difference decreases upon Al/Ti ratio increase to about 500 (Table 1, run 16); and at ratio equal to 1000, the overall system catalytic activity is notably decreased. The kinetics of ethylene catalytic polymerization in presence of this catalyst is stable and the whole system is reasonably thermostable. It is active at both 50 and 80 °C, albeit the increase of temperature results in 2 fold decrease of catalytic activity and increase of the polydispersity index (runs 14 and 15).

The most active compounds of the series were **17** with two methyl groups in benzyl position and **18** that is based on 2,4-di-



Fig. 1. General view of 15 (on the left; only the major component of dis-ordered molecule is shown) and 19 (on the right) in thermal ellipsoid representation (p = 50%). Hydrogen atoms except those of coordinated isopropyl moieties are omitted for clarity.

Table 1
Ethylene Polymerization by LTiCl2*(iPrOH)2-(Et2AlCl:Bu2Mg) Catalyst Systems.a

Run	Pre-catalyst	[Al]/[Ti]	Weight of PE, g	Activity ^b	Tg ^c , (°C)	Mw	Mn	Mw/Mn
1	3	300	2.3	1315	142.7	1.21×10^{6}	2.11×10^{5}	5.73
2	3	500	3.7	2140	144.8	Ins. in TCB		
3	3 ^d	100	0					
4	3 ^e	200	0					
5	12	300	4.9	2800	145.7	Ins. in TCB		
6	12	500	5.0	2850	141.4	1.05×10^{6}	1.66×10^{5}	6.32
7	13	300	4.5	2570	147.0	Ins. in TCB		
8	13	500	4.9	2800	140.0			
9	14	300	2.9	1660	142.0	6.39×10^{5}	7.89×10^4	8.08
10	14	500	4.1	2340	146.9	Ins. in TCB		
11	15	300	4.6	2630	140.0	9.40×10^5	1.57×10^5	5.99
12	15	500	4.6	2630	142.0	0.82×10^6	1.21×10^5	6.78
13	16	300	4.4	2515	146.2	Ins. in TCB		
14	16 ^f	300	1.9	1115	141.7	1.28×10^{6}	1.99×10^5	6.45
15	16 ^g	300	2.1	1230	142.5	$1.39 imes 10^6$	1.21×10^{5}	11.49
16	16	500	4.5	2570	144.2	Ins. in TCB		
17	16	1000	3.7	2115		4.02×10^5	7.30×10^4	5.48
18	17	300	3.9	2170	141.5	1.23×10^{6}	4.90×10^5	2.51
19	17	500	5.7	3170	143.0	1.25×10^{6}	1.84×10^5	6.79
20	18	300	4.7	2690	139.1	1.10×10^{6}	1.42×10^5	7.75
21	18	500	5.2	2970	140.4	0.91×10^{6}	1.10×10^5	8.10
22	19	300	0.4	230	142.0			
23	19	500	1.8	1030	140.3	1.27×10^6	1.68×10^5	7.56

^a Polymerizations carried out in 50 mL of toluene with 5 μ mol of catalyst at a constant 0.7 atm ethylene pressure for 30 min, temperature 30 °C, [Et₂AlCl]/[Bu₂Mg] = 3:1. ^b Kg of PE (mol of Ti atm)⁻¹ h⁻¹.

^c Melting temperatures determined by DSC at second heating of PE samples.

^d $[Et_2AlCl]/[Bu_2Mg] = 1:1.$

 $e [Et_2AlCl]/[Bu_2Mg] = 2:1.$

^f Temperature 50 °C.

^g Temperature 80 °C.

tert-butyl-saligenin. In terms of catalytic activity, either of them surpasses the prototype compound **3**. It is apparent that for this series of post-metallocene complexes, neither the bulk of a benzyl atom substituent nor its acceptor capacity impact the catalytic activity of the resulting system.

Heterometallic complex **19** demonstrates only the traces of activity at [Al]/[Ti] = 300. However, once the activation concentration reaches 500 equivalents, activity of **19** increases about 4.5 times, reaching 1030 kg of PE (mol of Ti atm)⁻¹ h⁻¹. It is possible, that **19** demonstrates such mediocre activity due to two of it bulky bidental ligands that hinder ethylene molecule binding to the catalytic center. Unlike **19**; compounds **3**, **12-18** have octahedral central atom surrounding - they are coordination saturated, but this saturation is achieved through binding of two isopropanol molecules. Those molecules can be relatively easily removed from the coordination environment when the complex is treated with alumo- or magnesium-organic compounds. Mixing complex **12** with preformed $MgCl_2$ ($Bu_2Mg + HCl$) regardless of the origin of the latter does not improve the system activity. It appears that catalytic activity of the system increases only when all components are formed simultaneously in *statu nascendi*.

The polyethylene samples obtained in the above experiments have a high molecular mass as most of them insoluble in trichlorobenzene at 135 °C. The IR spectra of those samples are lacking the 1378 cm⁻¹ band attributed to the deformational vibrations of methyl groups, which means lack of chain branching [20]. Respectively, all samples demonstrate high melting temperatures (139–147°C).

The activities of studied catalysts in reaction of 1-hexene polymerization are generally substantially slower than the ones in ethylene reaction. For that reason for activation we have used the most effective co-catalyst - $\{3Et_2AlCl + MgBu_2\}$. The results of these studies are summarized in Table 2. As evident from Table 2 data, the

Table 2

1-Hexene polymerization by LTiCl ₂	·(ⁱ PrOH) ₂ -(3Et ₂ AlCl/Bu ₂ Mg) Catalyst Systems.
---	--

Run	Pre-catalyst	[Al]/[Ti]	Conversion, (%)	Degree of isotacticity (mmmm) % ^b (mm, mr, rr) [21,22]	Mw ^c	Mn ^c	Mw/Mn
1	3	300	68	61 (0.76, 0.11, 0.13)	6.57×10^5	$9.97 imes 10^4$	6.6
2	3	500	100	54 (0.65, 0.12, 0.23)	5.94×105	$7.25 imes 10^4$	8.2
3	12	300	96	74 (0.83, 0.14, 0.03)	8.20×10^5	$9.8 imes 10^4$	8.4
4	13	300	89	28 (0.56, 0.12, 0.28)	5.82×10^5	$9.54 imes10^4$	6.1
5	14	300	82	36 (0.53, 0.18, 0.29)	4.54×10^5	$6.99 imes 10^4$	6.5
6	15	300	95	75 (0.84, 0.12, 0.05)	6.98×10^5	$1.35 imes 10^4$	5.2
7	16	300	19	31 (0.53, 0.22, 0.25)	5.23×10^5	6.82×10^4	7.7
8	16	300	74	52 (0.60, 0.13, 0.27)	5.72×10^5	$6.94 imes 10^4$	8.2
9	16	500	60	45 (0.55, 0.11, 0.34)	4.84×10^5	$7.20 imes 10^4$	6.7
10	17	300	98	64 (0.71, 0.10, 0.19)	7.20×10^{5}	8.91×10^4	8.1
11	18	300	96	70 (0.78, 0.10, 0.12)	4.90×10^5	$6.70 imes 10^4$	7.3
12	19	300	Traces				

^a Polymerizations carried out in 2 mL of toluene, 6 ml of 1-hexene with 5 µmol of catalyst for 24 h, temperature 5 °C, [Et₂AlCl]/[Bu₂Mg] = 3:1.

^b Determined by ¹³C NMR [21,22].

^c Determined from GPC in 1,2,4-trichlorobenzene using narrow polystyrene standards.

increase of [A1]/[Ti1] ratio with **3** increases the degree of monomer conversion, that reaches 100% at 500 equivalents. However, this change also causes the growth of polymer chain errors, resulting in a decrease of isotacticity from 61% (mm - 0.76) (at 300 equivalents) to about 54% (mm - 0.65). Since in case of 1-hexene resulting polymer stereoregularity is a more essential parameter, the rest of the experiments were carried out with Al/Ti ratio of 300.

Comparison of the results for **3** and **13** demonstrates that substitution of CF₃ for methyl one results in significant decrease of isotacticity. Compounds **14** and **15** that contain phenyl and perfluorophenyl substituents demonstrate good degree of conversion, but significant stereospecificity can only be achieved with perfluorophenyl moiety (**15**, run 6). Compound **16** lacking the perfluorophenyl moiety has demonstrated very modest results in 1hexene polymerization. Thus, the most efficient catalyst was **15**, which demonstrated the degree of 1-hexene conversion of 95% and high level of isotacticity (75%, mm - 0.84). It should be noted as well that all investigated co-catalysts form multi-center systems which is evident from the PDI values of resulting polyhexene samples.

Overall, there are no observed similarities between the polymerization processes for ethylene and 1-hexene in presence of above catalysts.

3. Conclusions

In summary, a series of titanium complexes (**12-18**) and heterobimetallic (Ti–Li) complex **19** bearing saligenin-type $[O,O]^{2-}$ ligands (**6-11**) were synthesized in high yields from $Cl_2Ti(O^iPr)_2$ or LiTi(O^iPr)₅ with corresponding ligands in toluene. The X-ray solid state diffraction study of complexes **15** and **19** was presented. Precatalysts **12-19** are completely inactive in presence of MAO, Me₃Al or Et₂AlCl. When activated by binary activator {3Et₂AlCl + Bu₂Mg}, these complexes exhibited moderate to high activities toward ethylene and 1-hexene polymerization, giving high molecular weight polymers with broad molecular weight distributions. We speculate that observed ability of magnesium chloride (which appears in the catalytic system as the result of the interaction of MgBu₂ with 2AlEt₂Cl) to promote the catalytic process is due to the products of secondary coordination.

Introducing fluorine-containing substituents in benzyl-position of ligands wasn't resulted in significant change on catalytic activities. No notable effect of the steric and electronic parameters of substituents in benzyl-position on the polymerization behavior was revealed. Further modification of these systems to enhance their catalytic performance is underway and will be reported in due course.

4. Experimental section

All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in oven-dried Schlenk glassware on a dual manifold Schlenk line, interfaced to a high-vacuum line. Argon and ethylene of special-purity grade (Linde gas) were dried by purging through a Super CleanTM Gas Filters.

Toluene, *n*-hexane, diethyl ether, and tetrahydrofuran were distilled over Na/benzophenone ketyl. Dichloromethane was distilled over calcium hydride. The water contents of these solvents were periodically controlled by Karl-Fischer coulometry by using a Methrom 756 KF apparatus.

Benzene-d6 was stored over Na/K alloy and was degassed by freeze–pump–thaw cycles before being vacuum transferred directly. CDCl₃ was stored over 4 Å sieves. Unless otherwise noted, all reagents were purchased from Sigma–Aldrich. Polymethylaluminoxane (Witco) was used as a 10% solutions in toluene. Dichlorodiisopropoxytitanium and LiTi(O-ⁱ-Pr)₅ were prepared following literature procedures [23,24]. Ligand **11**, 2,4-di-*tert*-butyl-6-(hydroxydiphenyl-methyl)phenol, was synthesized as described [25], its ¹H and ¹³C NMR spectra were found to match the published data.

NMR spectra were recorded on Bruker AMX-400 instrument. Deuterated solvents (toluene-d8, CD₂Cl₂, CDCl₃) were degassed by freeze—thaw—vacuum cycles and stored over 3 Å molecular sieves. Chemical shifts are reported in ppm *vs*. SiMe₄ and were determined by reference to the residual solvent peaks. All coupling constants are given in Hertz.

IR spectra were recorded on a Magna-IR 750 spectrophotometer. Elemental analysis was performed by the microanalytical laboratory at A. N. Nesmeyanov Institute of Organoelement Compounds.

Gel permeation chromatography (GPC) of polymer samples was carried out in 1,2,4-trichlorobenzene at 135 °C on a Waters GPCV-2000 chromatograph with the use of a PLgel 5 μ m MIXED-C column. Molecular masses were estimated using the universal calibration curve plotted relative to polystyrene standards.

The thermogravimetric analysis of samples was performed on a NETZSCHSTA-Jupiter449 C instrument. Measurements were carried out in a flow of argon (100 ml/min) in the temperature range 40-300 °C. The heating rate was 5 °C/min.

4.1. 2,4-Di-tert-buthyl-6-(2,2,2-trifluoro-1-hydroxyethyl)-phenol (6)

An excess of NaBH₄ was added to a stirred solution of 2.2 g (7.2 mmol) of **5** in 10 mL of methanol, after which the reaction was monitored by TLC. Upon completion of the reaction, water was added and the product was extracted by methylene chloride. The combined organic phase was washed with water, and dried over MgSO₄, after which the solvent was removed under reduced pressure. The crude product was recrystallized from toluene – hexane to give 1.62 g (73%) of a white solid. Anal. Calcd for C₁₆H₂₃F₃O₂ (304.35): C, 63.14; H, 7.62; F 18.73. Found: C, 62.98; H, 7.56; F 18.61. ¹H NMR (400 MHz, CDCl₃, δ): 7.52 (1H, s), 7.05 (1H, s), 5.21 (2H, q, 7.2 Hz), 3.25 (1H, br), 1.44 (9H, s), 1.33 (9H, s). ¹⁹F NMR (400 MHz, CDCl₃, δ): 152.54, 141.62, 136.88, 125.98, 124.50, 116.78, 35.12, 34.33, 31.27, 29.56.

4.2. 2,4-Di-tert-butyl-6-(1,1,1-trifluoro-2-hydroxy-propan-2-yl)-phenol (7)

To a solution of MeMgI (10 mmol) in Et₂O, prepared from magnesium (0.29 g, 12 mmol) and MeI (0.62 ml,10 mmol) was added dropwise an ethereal solution of 1-(2,4-di-*tert*-buthylphenyl)-2,2,2-trifluoromethylethanone-1 (1.08 g; 3.6 mmol) at 0°C. The reaction mixture allowed to slowly warm to room temperature, stirred overnight, quenched with HCl (1 M, 5 ml) and then and the product was extracted by diethyl ether. The combined organic phase was dried over Na₂SO₄, and the solvent was removed under reduced pressure. Recrystallization of the crude product from hexane gave 0.8 g (70%) of a colorless solid. ¹H NMR (CDCl₃, 25 °C) 1.28 (s, 9H), 1.42 (s, 9H), 1.90 (s, 3H), 3.09 (s, 1H) 7.00–7.04 (m, 1H), 7.34 (d, 1H, *J* = 2.3 Hz) 8.56 (s, 1H). ¹⁹F NMR (CDCl₃, 25 °C) 3.54 (s). Anal. Calcd for C₁₇H₂₅F₃O₂ (318.38): C, 64.13; H, 7.91; F, 17.90. Found: C, 64.86; H, 8.23; F, 17.24.

4.3. 2,4-Di-tert-buthyl-6-(2,2,2-trifluoro-1-hydroxy-1-phenylethyl)-phenol (8)

To a stirred solution of PhMgBr (25 mmol) in ether (50 mL) was added dropwise a solution of 1-(2,4-di-*tert*-buthylphenyl)-2,2,2-

trifluoromethylethanone-1 (2.17 g, 7.2 mmol) in ether (25 mL) at 0 °C in 1 h. After completion of the addition, the mixture was allowed to stand at room temperature overnight. The resulting mixture was poured into an aqueous NH₄Cl solution and extracted with ether. The organic layer was removed, dried (Na₂SO₄) and evaporated under reduced pressure. Recrystallization of the crude product from hexane gave 2.21 g (81%) of a colorless solid. ¹H NMR (CDCl₃, δ) 1.26 (s, 9H), 1.37 (s, 9H), 3.49 (s, 1H) 7.03–7.10 (m, 1H), 7.31–7.43 (m, 4H) 7.44–7.56 (m, 3H). ¹⁹F NMR (CDCl₃, δ), 3.00 (s). Anal. Calcd for C₂₂H₂₇F₃O₂ (380.44): C, 69.46; H, 7.15; F, 14.98. Found: C, 69.85; H, 7.41; F, 14.57.

4.4. 2,4-Di-tert-buthyl-6-(2,2,2-trifluoro-1-hydroxy-1-pentafluorophenyl-ethyl)-phenol (9)

A solution of 1.0 ml (8.1 mmol) of C₆F₅Br in 20 mL of Et₂O was cooled to -78 °C, and 3.24 mL of ⁿBuLi (2.5 M solution in hexane, 8.1 mmol) was added dropwise. The reaction mixture was stirred at -78 °C for 30 min, and then a solution of 1-(2,4-di-tert-buthylphenyl)-2,2,2-trifluoromethylethanone-1 (1.1 g, 3.64 mmol) in diethyl ether was added dropwise. The resultant solution was stirred overnight at room temperature, cooled to 0 °C, and then quenched with an aqueous NH₄Cl solution (50 mL) and extracted with ether. The combined organic phase was dried over Na₂SO₄, and the solvent was removed under reduced pressure. Recrystallization of the crude product from hexane gave 2.99 g (82%) of a colorless solid; mp 149–150 °C. ¹H NMR (300 MHz, CDCl₃): 1.30 (s, 9H), 1.37 (s, 9H), 4.43 (t, 1H, J = 4.2 Hz), 6.76 (s, 1H), 7.22-7.28 (m, 1H), 7.38 (d, 1H, I = 2.2 Hz). ¹⁹F NMR (CDCl₃) 1.39 (br. s, 3F), -59.84-60.05 (m, 2F), -73.21 to -73.26 (m, 1F), -82.96-83.13 (m, 2F). Anal. Calcd for C₂₂H₂₂F₈O₂ (470.41): C, 56.17; H, 4.71; F, 32.31. Found: C, 56.72; H, 4.95; F, 31.67.

4.5. 2,4-Di-tert-buthyl-6-(1-hydroxy-1-methyl-ethyl)-phenol (10)

A solution of 2-bromo-4,6-di-tert-butylphenol (2.86 g, 10 mmol) in Et₂O (20 ml) was added dropwise to a solution of nBuLi (20 mmol) in Et₂O (20 ml) at -78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The solution was cooled to -78 °C, and a solution of acetone (1.47 ml, 20 mmol) in Et₂O (10 ml) was added dropwise. The reaction mixture was stirred overnight at room temperature and then quenched with 30 ml of saturated NH₄Cl (aq). The organic layer was separated, dried over Na₂SO₄, filtered, and concentrated by distillation under reduced pressure. Pure product (1.48 g, 56%) was obtained by column chromatography over silica (hexanes) as white solid. Anal. Calcd for C₁₇H₂₈O₂ (264.40): C, 77.22; H, 10.67; O, 12.10. Found: C, 77.13; H, 10.51. ¹H NMR (300 MHz, CDCl₃): 1.35 (s, 9H), 1.42 (s, 9H), 1.87 (s, 6H), 5.70 (s, 2H), 7.28 (s, 1H), 7.43(s, 1H).

4.6. $\{2-[\alpha-trifluoromethyl-methanolato]-4,6-di-tert-butyl-phenolato\}dichlorodi(propan-2-ol)titanium (12)$

To a stirred solution of **6** (0.304 g, 1 mmol) in 10 ml of dried toluene a solution of Ti(O-iPr)₂Cl₂ (0.237 g, 1 mmol) in 10 ml of toluene was added dropwise over 5 min. After the formation of a dark purple precipitate, the mixture was heated to homogenization. On cooling, the dark purple crystals that formed were filtered off and washed with cold toluene. Yield – 0.188 Γ (36%). Anal. Calcd for C₂₂H₃₇Cl₂F₃O₄Ti (541.29): C, 48.82; H, 6.89; Cl, 13.10; F, 10.53; Ti, 8.84. Found: C, 48.65; H, 6.73; Cl, 12.87; F, 10.35; Ti, 8.92. ¹H NMR (CDCl₃, 25 °C) 1.40 (s, 9H), 1.52 (s, 9H), 1.98 (s, 12H), 3.12 (s, 2H), 3.89 (br.s, 2H), 5.05 (m, 1H), 7.20 (s, 1H), 7.38 (s, 1H). ¹⁹F NMR (CDCl₃, 25 °C) 3.98 (s).

Complexes 13-18 were prepared via a procedure similar to that

for **12**:

4.7. $\{2-[\alpha-methy]-\alpha-trifluoromethy]-methanolato]-4,6-di-tert$ $butyl-phenolato}dichlorodi(propan-2-ol)titanium (13)$

Yield – 0.8 g (70%). Anal. Calcd for $C_{23}H_{39}Cl_2F_3O_4Ti$ (555.32): C, 49.75; H, 7.08; Cl, 12.77; F, 10.26; Ti, 8.62. Found: C, 49.59; H, 6.87; Cl, 12.64; F, 10.11; Ti, 8.76. ¹H NMR (CDCl₃): 1.28 (s, 9H), 1.42 (s, 9H), 1.67 (s, 9H), 1.99 (s, 12H), 3.09 (s, 2H), 4.12 (br.s, 2H), 7.00–7.04 (m, 1H), 7.34 (d, 1H, J = 2.3 Hz). ¹⁹F NMR (CDCl₃): - 3.76 (s).

4.8. $\{2-[\alpha-pheny]-\alpha-trifluoromethy]-methanolato]-4,6-di-tert$ $butyl-phenolato}dichlorodi(propan-2-ol)titanium (14)$

Yield - 0.13 r (42%). Anal. Calcd for $C_{28}H_{41}Cl_2F_3O_4Ti$ (617.39): C, 54.47; H, 6.69; Cl, 11.48; F, 9.23; Ti, 7.75. Found: C, 54.29; H, 6.56; Cl, 11.37; F, 9.12; Ti, 7.43. ¹H NMR (toluene-d⁸, 25 °C): 0.96 (br. s, 9H), 1.17 (s, 9H), 1.67 (s, 12H), 3.42 (br. s, 2H), 4.20 (s, 2H), 6.95-7.08 (m, 5H), 7.26 (s, 1H), 7.50 (d, 1H, J = 2.3 Hz). ¹⁹F NMR (toluene-d⁸, 25 °C): - 71.96 (s).

4.9. $\{2-[\alpha-pentafluoropheny]-\alpha-trifluoromethy]-methanolato]-4,6$ $di-tert-buty]-phenolato}dichlorodi(propan-2-ol)titanium (15)$

Yield – 2.18 g (62%). Anal. Calcd for $C_{28}H_{36}Cl_2F_8O_4Ti$ (707.34): C, 47.54; H, 5.13; Cl, 10.02; F, 21.49; Ti, 6.77. Found: C, 47.31; H, 4.97; Cl, 9.95; Ti, 6.54. ¹H NMR (CD₂Cl₂): 1.21 (s, 9H), 1.35 (d, *J* = 6.2 Hz, 12H), 1.50 (s, 9H), 3.60 (br. s, 2H), 6.93 (s, 1H), 7.40 (d, *J* = 1H, 2.3 Hz). ¹⁹F NMR (CD₂Cl₂): -75.15 (s, 3F), - 134.10 (br.s, 2F), - 152.58–152.68 (m, 1F), -161.42–161.64 (m, 2F).

4.10. $\{2-[\alpha,\alpha-diphenylmethanolato]-4,6-di-tert-butyl-phenolato\}$ dichlorodi(propan-2-ol)titanium **(16)**

Anal. Calcd for $C_{33}H_{46}Cl_2O_4Ti$ (625.49): C, 63.37; H, 7.41; Cl, 11.34; Ti, 7.65. Found: C, 63.19; H, 7.20; Cl, 11.19; Ti, 7.83. ¹H NMR (CD₂Cl₂, δ , *J*/Hz): 1.14 (s, 9H) 1.34 (d, *J* = 5.9 Hz, 12H), 1.47 (s, 9H), 3.78 (s, 2H), 4.55 (br.s, 2H), 4.67 (s, 2H), 6.76 (s, 1H), 7.39–7.16 (m, 11H). ¹³C NMR (CD₂Cl₂, δ): 24.23, 30.07, 31.02, 34.40, 35.48, 70.64, 122.69, 126.21, 127.62, 128.52, 129.09, 131.86, 134.29, 144.51, 146.25.

4.11. $\{2-[\alpha,\alpha-dimethylmethanolato]-4,6-di-tert-butyl-phenolato\}$ dichlorodi(propan-2-ol)titanium (17)

Anal. Calcd for $C_{23}H_{42}Cl_2O_4Ti$ (501.35): C, 55.10; H, 8.44; Cl, 14.14; Ti, 9.55. Found: C, 54.87; H, 8.29; Cl, 14.02; Ti, 9.38. ¹H NMR (CDCl₃): 1.41 (s, 9H), 1.46 (s, 9H), 1.85 (s, 12H), 1.99 (s, 6H), 3.09 (s, 2H), 7.34 (m, 1H), 7.64 (s, 1H).

4.12. {2-[methanolato]-4,6-di-tert-butyl-phenolato} dichlorodi(propan-2-ol)titanium (18)

Anal. Calcd for $C_{21}H_{38}Cl_2O_4Ti$ (473.30): C, 53.29; H, 8.09; Cl, 14.98; Ti, 10.11. Found: C, 53.04; H, 7.91; Cl, 14.73; Ti, 10.00. ¹H NMR (CDCl₃): 1.76 (s, 9H), 1.85 (s, 9H), 1.97 (s, 12H), 3.09 (s, 2H), 4.26 (br.s, 2H), 4.58 (m, 2H), 7.76 (s, 1H), 7.96 (s, 1H).

4.13. *L*₂*TiLi*(*OⁱPr*)*thf* (19)

To a stirred solution of 2,4-Di-*tert*-butyl-6-(1,1,1,3,3,3-hexafluoro-2-hydroxypropan-2-yl)phenol (0.372 g, 1 mmol) in 10 ml of dried THF a solution of TiLi($O^{-i}Pr$)₅ (0.35 g, 1 mmol) in 10 ml of THF was added dropwise over 5 min. After the formation of a white precipitate, the mixture was heated to homogenization. On cooling, the crystals were filtered off, washed with cold toluene and

recrystallized from dichloromethane to give crystals suitable for X-ray analysis. Yield - 0.111 g (24%). Anal. Calcd for $C_{41}H_{55}F_{12}LiO_6Ti$ (926.66): C, 53.14; H, 5.98; F, 24.60; Li, 0.75; Ti, 5.17. Found: C, 52.89; H, 5.77; F, 24.47. 1 H NMR (CDCl₃): 1.70 (s, 18H), 1.82 (s, 18H), 1.88 (s, 6H), 2.78 (s, 1H), 4.20 (br.s, 1H), 4.62–4.69 (m, 8H), 7.25–7.64 (m, 4H).

4.14. X-ray structure analysis

X-ray diffraction data for the single crystals of **15** were collected using a "Bruker SMART APEX DUO" CCD diffractometer, for the single crystals of **19** - using "Bruker SMART APEX II" diffractometer. The resulting images were integrated [26]. Precise unit cell dimensions and errors were determined. Absorption correction was applied semiempirically using the SADABS program [27]. Details of X-ray data collection and subsequent refinement are listed in Table 1. Initially spherical atom refinements were undertaken with SHELXTL PLUS 5.0 using the full-matrix least-squares method [28]. All non-hydrogen atoms were allowed to have an anisotropic thermal motion. Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC 993410, 993411).

Acknowledgment

Financial support from the Russian Foundation of Basic Researches (Project Nos. 13-03-12181, 14-03-31260 and 14-03-00904) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.08.017.

References

- [1] D. Takeuchi, Dalton Trans. 39 (2010) 311.
- [2] M. Bochmann, Organometallics 29 (2010) 4711.
- [3] S. Budagumpi, K.-H. Kim, I. Kim, Coord. Chem. Rev. 255 (2011) 2785.
- [4] M. Delferro, T.J. Marks, Chem. Rev. 111 (2011) 2450.
- [5] C. Redshaw, Y. Tang, Chem. Soc. Rev. 41 (2012) 4484.
- [6] H. Makio, H. Terao, A. Iwashita, T. Fujita, Chem. Rev. 111 (2011) 2363.
- [7] N. Nakata, T. Toda, A. Ishii, Polym. Chem. 2 (2011) 1597.
- [8] T.-Q. Xu, W. Gao, Y. Mu, L. Ye, Polyhedron 26 (2007) 3357.
 [9] M.V. Solov'ev, S.Ch. Gagieva, V.A. Tuskaev, N.M. Bravaya, O.E. Gadalova,
- V.N. Khrustalev, A.O. Borissova, B.M. Bulychev, Russ. Chem. Bull. 60 (2011) 2227.
- [10] H. Makio, T. Fujita, Acc. Chem. Res. 42 (2009) 1532.
- [11] S.Ch. Gagieva, T.A. Sukhova, D.V. Savinov, V.A. Optov, N.M. Bravaya, Y.N. Belokon', B.M. Bulychev, Russ. Chem. Bull. 52 (2003) 1693.
- [12] L.A. Rishina, N.M. Galashina, S.C. Gagieva, V.A. Tuskaev, Y.V. Kissin, Eur. Polym. J. 49 (2013) 147.
- [13] V.A. Tuskaev, S.C. Gagieva, V.I. Maleev, A.O. Borissova, M.V. Solov'ev, Z.A. Starikova, B.M. Bulychev, Polymer 54 (2013) 4455.
- [14] Y.N. Belokon', S.Ch. Gagieva, T.A. Sukhova, A.B. Dmitriev, K.A. Lyssenko, N.M. Bravaya, B.M. Bulychev, D. Seebach, Russ. Chem. Bull. 54 (2005) 2348.
- [15] L.A. Rishina, N.M. Galashina, S.Ch. Gagieva, V.A. Tuskaev, B.M. Bulychev, Y.N. Belokon', Polym. Sci. Ser. A 50 (2008) 110.
- [16] L.A. Rishina, S.S. Lalayan, S.Ch. Gagieva, V.A. Tuskaev, E.O. Perepelitsyna, Y.V. Kissin, Polymer 54 (2013) 6526.
- [17] V.A. Tuskaev, S.Ch. Gagieva, D.A. Kurmaev, N.A. Kolosov, I.V. Fedyanin, B.M. Bulychev, Inorg. Chim. Acta 425 (2015) 275.
- [18] Y.V. Kissin, T.E. Nowlin, R.I. Mink, A.J. Brandolini, Macromolecules 33 (2000) 4599.
- [19] Y.V. Kissin, R.I. Mink, A.J. Brandolini, T.E. Nowlin, J. Polym, Sci. Part A Polym. Chem. 47 (2009) 3271.
- [20] L.I. Tarutina, F.O. Pozdnyakova, Spektral/nyi Analiz Polimerov [Spectroscopic Analysis of Polymers], Khimiya, Leningrad, 1986 (in Russian).
- [21] G.B. Galland, L.F. Da Silva, A. Nicolini, J. Polym, Sci. Part A Polym. Chem. 43 (2005) 4744.
- [22] J.A. Ewen, J. Am, Chem. Soc. 106 (1984) 6355.
- [23] K. Mikami, M. Terada, T. Nakai, J. Am, Chem. Soc. 112 (1990) 3949.
 - [24] M.J. Hampden-Smith, D.S. Williams, A.L. Rheingold, Inorg. Chem. 29 (1990) 4076.
 - [25] J.M. Mayer, I.J. Rhile, J. Am, Chem. Soc. 126 (2004) 12718.
 - [26] Bruker, Saint-Plus, USA: Bruker AXS Inc, Madison, Wisconsin, 2001.
 - [27] G.M. Sheldrick, SADABS, Bruker/Siemens Area Detector Absorption Correction Program, V. 2.03, Bruker AXS, Madison, Wisconsin, 2003.
 - [28] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.