Synthesis, structure, and catalytic activity of new aluminum and titanium complexes based on aminobisphenolate ligands containing bulky substituents

E. A. Kuchuk,[a] K. V. Zaitsev,[a]★ F. A. Mamedova,[b] A. V. Churakov,[c] G. S. Zaitseva,[a] D. A. Lemenovsky,[a] and S. S. Karlov[a]★

[a]*M. V. Lomonosov Moscow State University, Department of Chemistry, Build. 3, 1 Leninskie Gory, 119991 Moscow, Russian Federation. Fax: +7 (495) 932 8846. E-mail: sergej@org.chem.msu.ru*
[b]*M. V. Lomonosov Moscow State University, Baku Branch, 1 ul. Universitetskaya, AZ1144 Baku, pos. Khodzhasan, Azerbaidzhan*
[c]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation*

A reaction of aminobisphenols $EtN\{CH_2[(4\text{-}Alk)(6\text{-}Bu^t)(2\text{-}HO)C_6H_2]\}_2$, Alk = Me (**1**); Bu^t (**2**) containing alkyl substituents in the phenol groups with trimethylaluminum and tetra(*tert*-butoxy)titanium gave two new aluminum derivatives with the Me—Al bond: $EtN\{CH_2[(2\text{-}Alk)\text{-}(4\text{-}Bu^t)C_6H_2(2\text{-}O—)]\}_2Al—Me$, Alk = Me (**3**); Bu^t (**4**), and two new titanium derivatives with the $Bu^tO—Ti$ bond: $EtN\{CH_2[(2\text{-}Alk)(4\text{-}Bu^t)C_6H_2(2\text{-}O—)]\}_2Ti(O—Bu^t)_2$, Alk = Me (**5**); Bu^t (**6**). The structures of new compounds were confirmed by NMR spectroscopy and elemental analysis. The structures of complexes **3** and **6** were studied by X-ray crystallography. Complexes **3** and **6** are monomeric in the solid phase: a coordination number of Al atom is 4, that of Ti atom is 5, in addition to the M—O bonds the M←N interactions are also present. Complexes **3**—**6** were studied as initiators of the ring-opening polymerization of ε-caprolactone. The resulting polymers are characterized by relatively high values of number average molecular weight, with the polydispersity being relatively low.

Key words: aluminum, titanium, complexes, polymerization, biodegradable polymers, X-ray diffraction analysis, tridentate ligands.

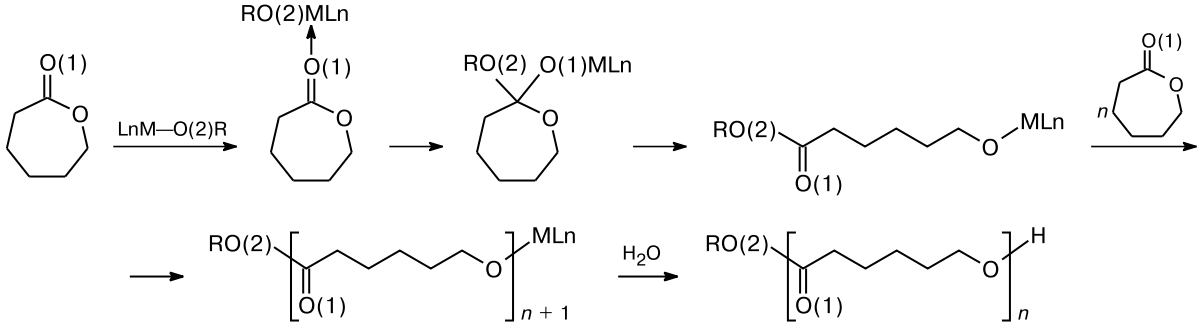
One of the most important problems working on by "green chemistry" consists in the improvement of chemical processes in order to minimize negative effects of chemical production and new materials on the environment. One of the successful examples of implementation of these principles is the use of biodegradable and biocompatible synthetic polymers instead of classic ones, for example, polyolefins. Nowadays, synthetic biodegradable polymers most frequently are obtained based on polylactide, polyglycolide, and polycaprolactone. In this case, most methods used in production of materials from standard plastic are applicable for their industrial synthesis and processing. Biodegradable polymers are used in traditional sectors of application of high-molecular-weight compounds, displacing polyolefins, first of all, for production of food packaging, and in new fields, for example, in medicine and pharmacology (drug delivery systems, matrices for production of biological tissues).

The synthesis of biodegradable polymers of the indicated type are carried out by ring-opening polymerization (ROP) of cyclic esters.[1] The most successful process of this type is the so-called coordination polymerization, which makes it possible to obtain materials with required structure, stereochemistry, and molecular mass distribution.[1,2] According to the generally accepted coordination mechainism of ROP, in the first step the metal (Lewis acid) coordinates to the carbonyl oxygen atom (O(1)=C) of the ester function. Then, one of the alkoxy substituents (RO(2)) of the starting complex is transferred from the metal atom to the electrophilic carbon atom of the ester function, with the coordination metal—oxygen bond in the fragment M←O(1)=C becoming covalent: M—O(1)—C(OR) (Scheme 1).

In the following step, the ring undergoes opening with the formation of the ester function C(=O(1))O(2)R. As a result of this process, the metal atom remains covalently bonded to the oxygen atom of the new alkoxy group, and it is removed after completion of polymerization by hydrolysis, which not always can be performed completely. At the present time, toxic tin bis(2-ethylhexanoate) is used as initiator in the industrial synthesis of polymers based on aliphatic esters, therefore, the synthesis of new nontoxic initiators of polymerization seems very relevant.[1] Besides the low toxicity of metal, initiators of polymerization

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1743—1749, July, 2016.

Scheme 1



should meet the following requirements: the metal should be stable to the oxidation state changes, the complex should be stable enough to β-cleavage.[2] Apart form that, the structure of the ligand should interfere with the aggregation of the complex, at the same time, the presence of very bulky groups in the ligand in close proximity of the metal atom can complicate polymerization, hindering the attack by a nucleophile on the electrophilic metal center.

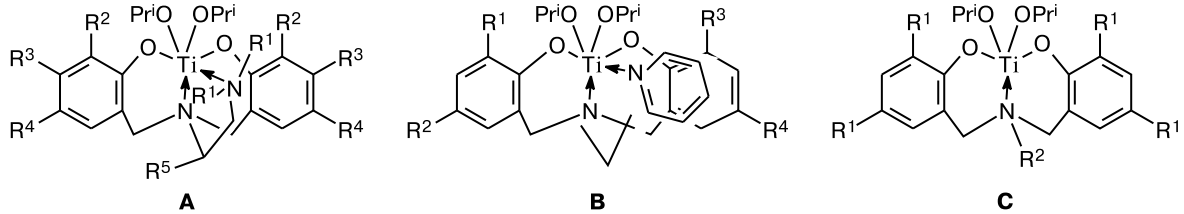
The purpose of the present work is the synthesis of new titanium and aluminum complexes potentially applicable as initiators of ROP, studies of their structures, investigation of a possibility of using of new complexes in polymerization of e-caprolactone.

Results and Discussion

The design of the ligand system plays a key role in the development of catalyst systems capable of efficient initiation of ROP, giving rise to polymers with desired characteristics. One of the most promising types of ligand systems for titanium and aluminum are the tridentate sterically bulky ligands of the $N\{O^-\}_2$-type. In continuation of our studies on the synthesis of the $N\{O^-\}_2$-type derivatives of main subgroup elements and titanium, we synthesized new earlier unknown complexes based on aminobisphenols **1** and **2**.[3–8]

Aminobisphenols are one of the most frequently used types of ligands for obtaining complexes active as initiators of ROP.[9–22] The structures of known by the present time such titanium compounds containing two alkoxy groups (**A**—**D**) and aluminum compounds containing a methyl group (**E**) are given below.

Note that the ligands used can be divided into two types: tridentate ligands and tetradentate ligands containing an additional donor group in the molecule. A comparison of characteristics of these compounds as initiators of



Compound	R^1	R^2	R^3	R^4	R^5
A	Me	H	Me	Me	H
	Me	Me	H	Me	H
	Me	Bu^t	H	Bu^t	H
	Et	Me	H	Me	H
	Me	Bu^t	H	Me	H
	Me	Cl	H	Me	H
	Me	Bu^t	H	Me	H
	Me	Bu^t	H	Bu^t	(*R*)-Me
B	Me	Me	Me	Me	—
	Bu^t	Bu^t	Bu^t	Bu^t	—
	H	H	$C(Me)_2Ph$	$C(Me)_2Ph$	—

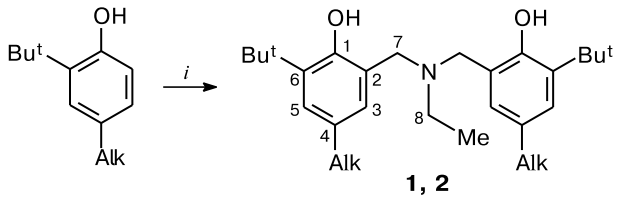
Compound	R^1	R^2
C	Bu^t	Pr^i
	Bu^t	Bu^t
	Bu^t	Pr
	Bu^t	Bn
	Bu^t	Me
	Bu^t	α-$CH_{2naphthyl}$

Compound	R^1	R^2	R^3
E	Bu^t	Bu^t	Pr^i
	Bu^t	Bu^t	Pr
	Bu^t	Bu^t	Bu^t
	Bu^t	Me	$(CH_2)_2NMe_2$
	Bu^t	Bu^t	$(CH_2)_2NMe_2$
	Bu^t	Bu^t	CH_2Py
	Bu^t	Bu^t	Me
	Me	Me	$(CH_2)_2NMe_2$
	Pr^i	Pr^i	$(CH_2)_2NMe_2$
	Cl	Cl	$(CH_2)_2NMe_2$

polymerization evidences in favor of the use of compounds based on the tridentate ligands as more active initiators, that is obviously related to the higher Lewis acidity of the metal center in these derivatives.[12] Apart form that, even insignificant variation in the structure of initiator can lead to a considerable change in its catalytic properties.[1,2] Therefore, an actual problem is the synthesis of new derivatives of the indicated type and establishing influence of the structure of obtained compounds on polymerization activity.

Ligands **1** and **2** were synthesized by Mannich reaction upon reflux of aqueous methanol solution of ethylamine, formaldehyde, and the corresponding phenol (Scheme 2). The target ligands were isolated in satisfactory yields. Compound **1** is new, compound **2** was obtained earlier according to a similar scheme.[23]

Scheme 2

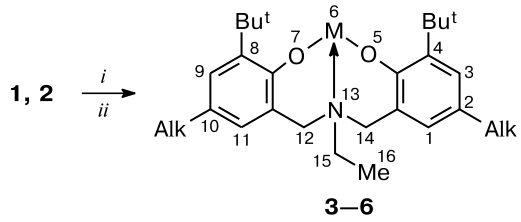


Alk = Me (**1**), Bu^t (**2**)

Reagents and conditions: *i.* $EtNH_2$, CH_2=O, $MeOH/H_2O$, Δ.

The reaction of ligands **1** and **2** with 1 equivalent of trimethylaluminum or tetra(*tert*-butoxy)titanium furnished four earlier unknown target complexes **3**—**6** (Scheme 3). The yields in all the reactions were high (see Experimental section). It should be noted that the titanium complexes based on aminobisphenolate ligands containing *tert*-butoxy groups were obtained for the first time and, therefore, for the first time were tested as initiators of ROP.

Scheme 3



M = AlMe: Alk = Me (**3**), Bu^t (**4**)
M = $Ti(OBu^t)_2$: Alk = Me (**5**), Bu^t (**6**)

Reagents and conditions: *i.* $AlMe_3$, PhMe, 20 °C or *ii.* $Ti(OBu^t)_4$, PhMe, 20 °C.

The structures of compounds **3**—**6** in solution of $CDCl_3$ were determined from the multinuclear NMR spectroscopy data. The ^1H and ^{13}C NMR spectra of aluminum methyl derivatives **3** and **4** and titanium di-*tert*-butoxy derivatives **5** and **6** are characterized by the presence of one set of signals, that unambiguously indicates a monomeric structure of these compounds (since a dimeric compound in this case should be formed by the reaction of the oxygen atoms and aluminum or oxygen and titanium and this leads to nonequivalence of two symmetric "halves" of the ligand or nonequivalence of *tert*-butoxy groups). At the same time, it should be noted that a general pattern of the spectra of titanium derivatives (broad signals, one set of signals for two nonequivalent *tert*-butoxy group, see below the X-ray diffraction data) indicates proceeding dynamic processes in these complexes at room temperature.

The structures of complexes **3** and **6** were confirmed by X-ray diffraction analysis (Figs 1 and 2). The main bond distances and bond angles are given in Tables 1 and 2, respectively.

Complex **3** according to the X-ray diffraction data is monomeric in the solid phase. A coordination number of the aluminum atom in complex **3** is four, whereas a coor-

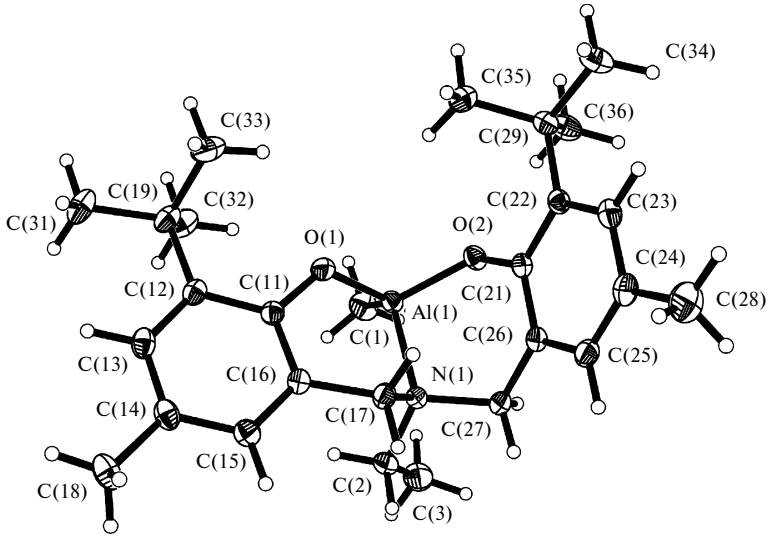


Fig. 1. Molecular structure of compound **3**. Thermal ellipsoids are given with 50% probability.

Table 1. Main interatomic distances (*d*) in the structures **3** and **6**

Bond	*d*/Å	
	3	**6**
M—O_{Phen}	1.7459(7)	1.8823(17)
	1.7493(7)	1.8890(17)
Al—C	1.9465(11)	—
Ti—O(Bu^t)	—	1.7779(17)
	—	1.7847(18)
M—N	2.0101(8)	2.2973(19)

Table 2. Main bond angles (ω) in the structures **3** and **6**

Angle	ω/deg	
	3	**6**
O_{Phen}—M—O_{Phen}	112.43(3)	138.24(8)
O_{Phen}—M—N	98.22(3)	80.54(7)
	98.96(3)	79.38(7)
C—Al—N	117.89(4)	—
(Bu^t)O—Ti—N	—	90.50(8)
	—	163.75(8)
O_{Phen}—Al—C	113.85(4)	—
	113.75(4)	—
(Bu^t)O—Ti—O_{Phen}	—	94.92(8)
	—	107.13(8)
	—	94.32(8)
	—	109.27(8)
(Bu^t)O—Ti—O(Bu^t)	—	105.74(9)

Note. Phen is the phenolate.

dination polyhedron of the central atom is a distorted trigonal monopyramide, in which the nitrogen atom occupies an apical position. It is known that complexes with such coordination geometry are the most efficient in the initiation of polymerization, since they retain a possibility for the nucleophilic agent to access the metal atom.[24] The Al—O, Al—N, and Al—C bond distances in complex **3** are close to those found earlier[9,25] for related bisphenolate complexes containing a $C(O)_2Al\leftarrow N$ coordination unit.

Complex **6** according to the X-ray diffraction data is also monomeric in the solid phase. A coordination number of the titanium atom in complex **6** is five, whereas a coordination polyhedron of the central atom is a distorted trigonal bipyramide, in which the nitrogen atom and one of two *tert*-butoxy groups occupy apical positions, whereas

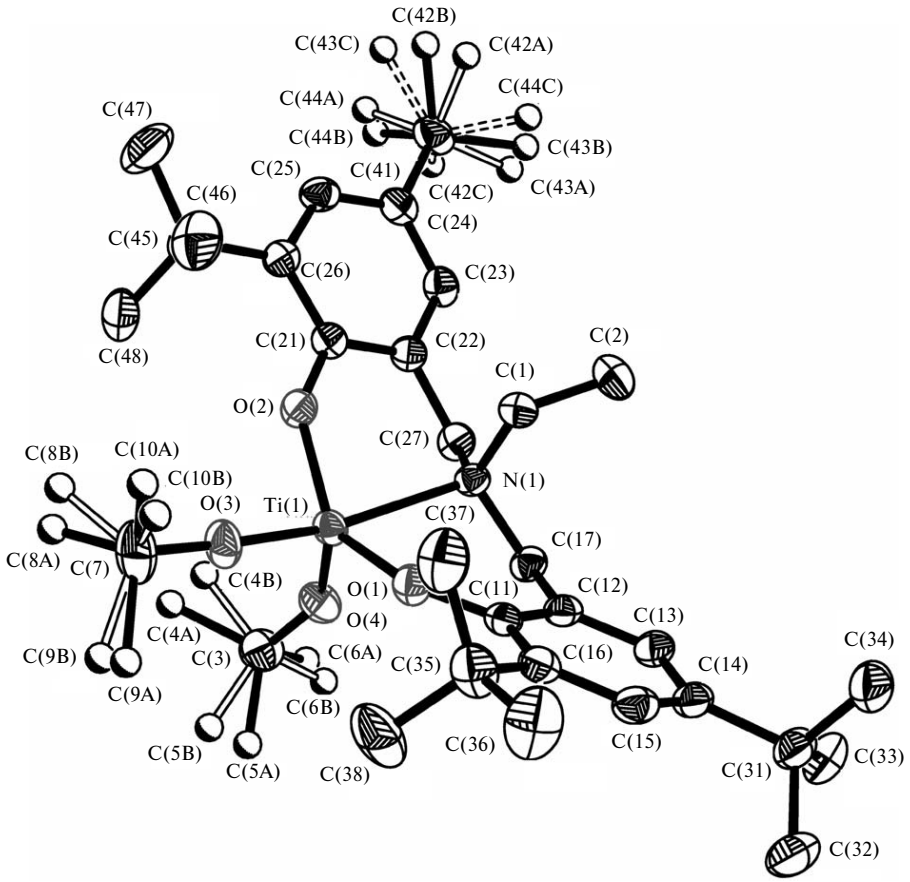


Fig. 2. Molecular structure of compound **6**. Thermal ellipsoids are given with 50% probability. Hydrogen atoms are omitted. Minor components of disordering are shown in empty and dashed lines.

Table 3. Polymerization with ε-caprolactone ring-opening initiated by complexes **3**—**6**

Entry	Initiator	[Complex]/[BnOH]	*t*/h	C (%)	M_n/g mol^{-1}		M_w/M_n
					GPC[a]	Calculated[b]	
1[c]	**3**	1 : 1	0.5	99	21325	34008	1.11
2[c]	**4**	1 : 1	0.5	99	19953	34008	1.12
3[d]	**5**	—	1	63	18481	21647	1.36
4[d]	**6**	—	1	38	15386	13086	1.32
5[c]	**6**	—	0.5	4	—	—	—

[a] Determined by gel-permeation chromatography with the correction factor of 0.56.
[b] M_n(theor) = 114.14 ([caprolactone]/[catalyst]) conversion + M(BnO or Bu^{t}O).
[c] Polymerization in solution of toluene ([caprolactone] = 2 mol L^{-1}), 50 °C, [caprolactone]/[catalyst] = 300:1.
[d] Polymerization in bulk: 100 °C, [caprolactone]/[catalyst] = 300 : 1.

the second *tert*-butoxy group and both phenolate oxygen atoms occupy equatorial positions. The Ti—O and Ti—N bond distances in complex **6** are close to those found earlier[10] for related di-isopropoxy bisphenolate complex containing a $(O)_4Ti\leftarrow N$ coordination unit (see Tables 1 and 2).

The activity of complexes **3**—**6** as initiators of polymerization was studied on a model reaction with ε-caprolactone (Table 3). For complexes **3** and **4** with methyl substituents on aluminum, the polymerization was carried out in solution (in the presence of benzyl alcohol (BnOH) as an external nucleophile), in the case of complexes **5** and **6** with *tert*-butoxy substituents on titanium it was carried out in the melt of the monomer.

All the tested compounds were found to be active in the ring-opening polymerization of e-caprolactone and demonstrated high conversion of the monomer both in solution (aluminum compounds) and in the melt (titanium compounds), with the polymers being formed with relatively small values of polydispersity. It is necessary to note that compound **6** is low active in the polymerization in solution in contrast to relative diisopropoxy derivatives studied earlier, that is obviously due to the increase in the steric bulkiness of the alkoxy group.

In conclusion, in the course of this study we synthesized and structurally characterized new aluminum and titanium complexes based on sterically bulky aminobisphenolate ligands, which possess catalytic activity in the ring-opening polymerization of cyclic esters.

Experimental

All the manipulations with aluminum and titanium derivatives were carried out under dry argon, using standard Schlenk technique. ^{1}H and ^{13}C NMR spectra were recorded at room (25 °C) temperature on Bruker Avance 400 or Agilent 400 MR spectrometers (400 and 100 MHz, respectively), using $CDCl_3$ as a solvent and a reference (residual protons of the deuterosolvent); chemical shifts are given relative to Me_4Si. Elemental analysis was performed in the Organic Microanalysis Laboratory of Department of Chemistry of MSU. Compound **4** turned out to be extremely hydrolytically unstable, which complicated obtaining satisfactory elemental analysis data for these compound (see the experimental data). Gel-permeation chromatography was carried out on an HPLC chromatograph (a Phenogel 10^4 Å column, a refractometric detector), the solvent was THF, the flow rate was 1 mL min^{-1}, the concentration of the sample was 1%, the amount of the sample was 200 μL, calibration with polystyrene standards. Solvents were purified according to the standard procedures. Toluene and hexane were refluxed and distilled over metallic sodium. ε-Caprolactone was purified by distillation over CaH_2. 2-*tert*-Butyl-4-methylphenol (Aldrich), $Ti(OBu^t)_4$ (Aldrich), and $AlMe_3$ (2 *M* solution in toluene) (Aldrich) were used without additional purification. Compound **2** was obtained according to the procedure described earlier[23] (however, no ^{13}C NMR and elemental analysis data were reported in the work[23]).

2,2′-[(Ethylimino)dimethanediyl]bis(6-*tert*-butyl-4-methylphenol) (1). 2-*tert*-Butyl-4-methylphenol (3.97 g, 24.2 mmol), 36% aqueous solution of formaldehyde (1.62 mL, 19.4 mmol), 70% aqueous solution of $EtNH_2$ (0.78 mL, 12.1 mmol), and methanol (10 mL) were placed into a flask. The solution was refluxed for 23 h, then the solvent was evaporated *in vacuo*. The resulting orange oil was dissolved in light petroleum ether and left for slow evaporation of the solvent for three days. The crystals formed were thoroughly washed with cold light petroleum ether and dried *in vacuo*. This compound can be also recrystallized from light petroleum ether for further purification. M.p. 109—110 °C. The yield was 2.28 g (47%). ^{1}H NMR ($CDCl_3$), δ: 1.16 (t, 3 H, C(8)H_2Me, *J* = 7.1 Hz); 1.40 (s, 18 H, 2 C(6)Bu^t); 2.25 (s, 6 H, 2 C(4)Me); 2.63 (q, 2 H, C(8)H_2, *J* = 7.1 Hz); 3.65 (s, 4 H, 2 NC(7)H_2); 6.75 (m, 2 H, 2 C(3)H); 7.02 (m, 2 H, 2 C(5)H). ^{13}C NMR ($CDCl_3$), δ: 11.00 (C(8)H_2Me); 20.77 (2 C(4)Me); 29.63 (C(6)CMe_3); 34.56 (C(6)CMe_3); 46.99 (C(8)H_2); 56.20 (2 NC(7)H_2); 122.35, 127.25, 128.08, 128.81, 136.78, 152.53 (carbon atoms of the aromatic rings). Found (%): C, 78.53; H, 9.61; N, 3.79. $C_{26}H_{39}NO_2$. Calculated (%): C, 78.54; H, 9.89; N, 3.52.

2,2′-[(Ethylimino)dimethanediyl]bis(4,6-di-*tert*-butylphenol) (2). Aminobisphenol **2** was obtained similarly from 2,4-di-*tert*-butylphenol with the same molar ratios of reagents in 52% yield.

^{13}C NMR ($CDCl_3$, δ: 11.11 (C(8)H_2Me); 29.70, 31.64 (2 C(6)CMe_3); 34.16, 34.86 (2 C(6)CMe_3); 47.18 (C(8)H_2); 56.56 (2 NC(7)H_2); 121.63, 123.49, 125.00, 136.03, 141.49, 152.44 (Ar). Found (%): C, 79.62; H, 10.38; N, 3.02. $C_{32}H_{51}NO_2$. Calculated (%): C, 79.78; H, 10.67; N, 2.91.

4,8-Di(*tert*-butyl)-13-ethyl-2,6,10-trimethyl-13,14-dihydro-12*H*-5,7-dioxa-13-aza-6-aluminadibenzo[*a*,*f*]cyclodecadiene (3). Trimethylaluminum (1.02 mL, 2.04 mmol, 2 *M* solution in toluene) was added dropwise to a solution of ligand **1** (0.75 g, 1.89 mmol) in toluene (20 mL) $AlMe_3$ at room temperature. Evolution of CH_4 was observed. The resulting solution was stirred for 24 h. Then, the solvent was evaporated *in vacuo*. The residue was diluted with hexane (5 mL), stirred for 20 min, and filtered to obtain the compound (0.68 g, 82%) as a white powder. ^{1}H NMR ($CDCl_3$), δ: –0.62 (s, 3 H, AlMe); 1.21 (t, 3 H, $C\underline{H}_3C(15)H_2$, J = 7.3 Hz); 1.38 (s, 18 H, C(8)Bu^t, C(4)Bu^t); 2.22 (s, 6 H, C(2)Me, C(10)Me); 2.89 (q, 2 H, $C(15)\underline{H}_2$, J = 7.3 Hz); 3.65 (d, 2 H, $NC(12/14)\underline{H}_2$, J = 13.1 Hz); 3.76 (d, 2 H, $NC(14/12)\underline{H}_2$, J = 13.4 Hz); 6.68 (m, 2 H, C(1)H, C(11)H); 7.05 (d, 2 H, C(3)H, C(9)H, J = 2.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 6.30 ($\underline{Me}C(15)H_2$); 20.73 (C(2)$\underline{Me}$, C(10)$\underline{Me}$); 29.47 (C(4)$C\underline{Me}_3$, C(8)$C\underline{Me}_3$); 34.72 (C(4)$\underline{C}Me_3$, C(8)$\underline{C}Me_3$); 47.54 ($C(15)H_2$); 54.96 ($NC(12)H_2$, $NC(14)H_2$); 121.20, 126.24, 128.06, 128.42, 138.97, 155.20 (carbon atoms of the aromatic rings), the signal for AlMe was not found. Found (%): C, 74.37; H, 9.44; N, 3.42. $C_{27}H_{40}AlNO_2$. Calculated (%):C, 74.11; H, 9.21; N, 3.20.

2,4,8,10-Tetra(*tert*-butyl)-13-ethyl-6-methyl-13,14-dihydro-12*H*-5,7-dioxa-13-aza-6-aluminadibenzo[*a*,*f*]cyclodecadiene (4) was obtained similarly to complex **3** starting from ligand **2** (0.24 g, 0.5 mmol) and $AlMe_3$ (0.26 mL, 0.52 mmol). After treatment with hexane (2 mL) and drying *in vacuo*, complex **4** (0.22 g, 84%) was obtained as a white powder. ^{1}H NMR ($CDCl_3$), δ: –0.63 (s, 3 H, AlMe); 1.22 (t, 3 H, $\underline{Me}C(15)H_2$, J = 7.4 Hz); 1.24 (s, 18 H, C(2)Bu^t, C(10)Bu^t); 1.38 (s, 18 H, C(4)Bu^t, C(8)Bu^t); 2.91 (q, 2 H, $C(15)\underline{H}_2$, J = 7.4 Hz); 3.65, 3.76 (both d, 4 H, $NC(12/14)\underline{H}_2$, J = 13.3 Hz); 6.85 (d, 2 H, C(1)$\underline{H}$, C(11)$\underline{H}$, J = 2.4 Hz); 7.25 (d, 2 H, C(3)$\underline{H}$, C(9)$\underline{H}$, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$)), δ: 6.42 ($\underline{Me}C(15)H_2$); 29.54 (C(2)$C\underline{Me}_3$, C(10)$C\underline{Me}_3$); 31.69 (C(4)$C\underline{Me}_3$, C(8)$C\underline{Me}_3$); 34.09 (C(2)$\underline{C}Me_3$, C(10)$\underline{C}Me_3$); 35.04 (C(4)$\underline{C}Me_3$, C(8)$\underline{C}Me_3$); 47.67 ($\underline{C}(15)H_2$); 55.50 ($N\underline{C}(12)H_2$, $N\underline{C}(14)H_2$); 120.54, 124.20, 124.70, 138.27, 139.76, 155.05 (carbon atoms of the aromatic rings), the signal for AlMe was not found. Found (%): C, 72.45; H, 9.53; N, 2.58. $C_{33}H_{52}AlNO_2$. Calculated (%): C, 75.97; H, 10.05; N, 2.68.

6,6-Di(*tert*-butoxy)-4,8-di(*tert*-butyl)-13-ethyl-2,10-dimethyl-13,14-dihydro-12*H*-5,7-dioxa-13-aza-6-titanadibenzo[*a*,*f*]-cyclodecadiene (5). A solution of ligand **1** (0.33 g, 0.82 mmol) in toluene (5 mL) was slowly added to $Ti(OBu^t)_4$ (0.28 g, 0.82 mmol). The resulting yellow solution was stirred for 24 h, then, the solvent was evaporated at reduced pressure. The target compound was thoroughly dried *in vacuo* to obtain the product (0.47 g, 97%) as a light yellow powder. ^{1}H NMR ($CDCl_3$), δ: 0.8 (t, 3 H, $\underline{Me}C(15)H_2$, J = 7.0 Hz); 1.42 (s, 9 H, TiOBu^t); 1.44 (s, 9 H, TiOBu^t); 1.46 (s, 18 H, C(4)Bu^t, C(8)Bu^t); 2.24 (s, 6 H, C(2)$\underline{Me}$, C(10)$\underline{Me}$); 2.74 (q, 2 H, $C(15)\underline{H}_2$, J = 7.0 Hz); 3.55 (br.s, 2 H, $NC(12)\underline{H}_2$); 4.04 (d, $NC(14)\underline{H}_2$, J = 12.5 Hz); 6.72 (m, 2 H, C(1)H, C(11)H); 6.99 (d, 2 H, C(3)H, C(9)H, J = 2.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 5.73 ($\underline{Me}C(15)H_2$); 20.82 (C(2)$\underline{Me}$, C(10)$\underline{Me}$); 29.74 (C(4)$C\underline{Me}_3$, C(8)$C\underline{Me}_3$); 32.06, 32.27 (TiOC$\underline{Me}_3$);

Table 4. Details of X-ray diffraction studies of compounds **3** and **6**

Compound	**3**	**6**
Molecular formula	$C_{27}H_{40}Al_1N_1O_2$	$C_{40}H_{67}N_1O_4Ti_1$
M	437.58	673.85
Crystal dimensions/mm	0.30×0.20×0.20	0.22×0.10×0.01
Crystal system	Triclinic	Triclinic
T/K	150	183
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.2225(8)	9.8752(12)
b/Å	11.2115(9)	12.1154(15)
c/Å	12.4730(10)	18.070(2)
α/deg	97.2090(11)	95.897(2)
β/deg	112.1535(10)	101.755(2)
γ/deg	102.3804(10)	99.499(2)
V/Å^3	1259.12(17)	2066.6(4)
Z	2	2
d_{cald}/g cm^{-3}	1.154	1.083
μ/mm^{-1}	0.103	0.243
F(000)	476	736
θ Range of scanning θ	2.24—29.00	2.15—26.00
Number of reflections		
measured	14070	18353
independent	6669	8109
(R_{int})	(0.0137)	(0.0264)
with $I \geq 2\sigma(I)$	6043	6253
Number of refined parameters	440	461
R_1 [$I \geq 2\sigma(I)$]	0.0344	0.0531
wR_2 (for all reflections)	0.1002	0.1460
Reliability on F^2	1.023	1.027
Residual electron density (max/min)/e Å^{-3}	0.396/–0.200	0.713/–0.594

34.81 (C(8)$\underline{C}Me_3$, C(4)$\underline{C}Me_3$); 43.79 (br, $\underline{C}(15)H_2$); 55.52 (br, $NC(12)H_2$, $NC(14)H_2$), 81.69, 82.14 ($TiO\underline{C}Me_3$), 124.45, 126.69, 127.07, 127.96, 135.90, 159.28 (carbon atoms of the aromatic rings). Found (%): C, 69.21; H, 9.28; N, 2.58. $C_{34}H_{55}TiNO_4$. Calculated (%): C, 69.25; H, 9.40; N, 2.38.

6,6-Di(*tert*-butoxy)-2,4,8,10-tetra(*tert*-butyl)-13-ethyl-13,14-dihydro-12*H*-5,7-dioxa-13-aza-6-titanadibenzo[*a*,*f*]cyclodecadiene (6) was obtained similarly to complex **5** starting from ligand **2** (0.23 g, 0.48 mmol) and $Ti(OBu^t)_4$ (0.16 g, 0.48 mmol). Complex **6** (0.30 g, 96%) was obtained as a yellow powder. ^1H NMR ($CDCl_3$), δ: 0.80—0.90 (m, 3 H, $\underline{Me}C(15)H_2$); 1.28 (s, 18 H, $C(2)Bu^t$, $C(10)Bu^t$); 1.39 (s, 9 H, $TiOBu^t$); 1.47 (s, 27 H, $TiOBu^t$ and $C(4)Bu^t$, $C(8)Bu^t$, overlap of two signals); 2.71—2.85 (m, 2 H, $C(15)H_2$); 3.63 (br.s, 2 H, $NC(12/14)H_2$); 3.93 (d, 2 H, $NC(14/12)H_2$, J = 11.7 Hz); 6.91 (s, 2 H, C(1)H, C(11)H); 7.20 (s, 2 H, C(3)H, C(9)H). ^{13}C NMR ($CDCl_3$), δ: 5.80 ($\underline{Me}C(15)H_2$); 29.82 ($C(2)C\underline{Me}_3$, $C(10)C\underline{Me}_3$); 31.71 ($TiOC\underline{Me}_3$, $C(4)C\underline{Me}_3$, $C(8)C\underline{Me}_3$, overlap of two signals); 32.18 ($TiOC\underline{Me}_3$); 34.19, 35.10 ($C(4)C\underline{Me}_3$ $C(8)C\underline{Me}_3$); 45.29 (br, $\underline{C}(15)H_2$); 54.96 (br, $N\underline{C}(12)H_2$, $N\underline{C}(14)H_2$); 82.98, 84.10 ($O\underline{C}Me_3$); 122.88, 123.93, 124.32, 135.03, 140.43, 159.21 (carbon atoms of the aromatic rings). Found (%): C, 71.72; H, 9.96; N, 2.04. $C_{40}H_{67}TiNO_4$. Calculated (%):C, 71.30; H, 10.02; N, 2.08.

X-ray diffraction study of compounds **3** and **6** was performed on a Bruker SMART APEX II automated diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator, ω-scan technique). Correction for adsorption was introduced based on the measurements of intensities of equivalent reflections.[26] The structures were solved by direct method; all the nonhydrogen atoms (except of disordered Bu^t groups in **6**) were refined by the full-matrix anisotropic least squares method on F^2 (*SHELXTL*[27]). In compound **6**, the *tert*-butyl groups containing the atoms C(3) and C(7) are rotationally disordered over two positions with the occupancy ratios of 0.66/0.34 and 0.54/0.46, while the group, containing the atom C(41) is disordered similarly, but over three positions (0.46/0.32/0.22). All three groups were refined with the imposition of restrictions on the C—Me and Me···Me distances (SADI). In the structure **3**, all the hydrogen atoms were found from the difference Fourier synthesis and refined isotropically, whereas in the structure **6** all the hydrogen atoms were placed in the calculated position and refined using a riding scheme. The experimental details are given in Table 4.

X-ray diffraction studies were performed in the Multiaccess Center of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences. The structure **3** and **6** were deposited with the Cambridge Crystallographic Data Center (CCDC 1439269 and 1439270, respectively).

Organoaluminum compounds were synthesized and studied with the financial support of the Russian Science Foundation (Project No. 14-33-00017). The synthesis and studies of organotitanium compounds were financially supported by the Russian Foundation for Basic Research (Project ofi-m 13-03-12054). The studies were carried out using equipment purchased at the expense of the Development Program of the M. V. Lomonosov Moscow State University.

References

1. O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147.
2. J. Wu, T.-L. Yu, C.-T. Chen, C.-C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602.
3. K. V. Zaitsev, S. S. Karlov, A. A. Selina, Yu. F. Oprunenko, A. V. Churakov, B. Neumüller, J. A. K. Howard, G. S. Zaitseva, *Eur. J. Inorg. Chem.*, 2006, 1987.
4. K. V. Zaitsev, M. V. Bermeshev, A. A. Samsonov, Yu. F. Oprunenko, A. V. Churakov, J. A. K. Howard, S. S. Karlov, G. S. Zaitseva, *New J. Chem.*, 2008, **32**, 1415.
5. M. Huang, E. Kh. Lermontova, K. V. Zaitsev, A. V. Churakov, Yu. F. Oprunenko, J. A. K. Howard, S. S. Karlov, G. S. Zaitseva, *J. Organomet. Chem.*, 2009, **694**, 3828.
6. Yu. A. Piskun, I. V. Vasilenko, S. V. Kostjuk, K. V. Zaitsev, G. S. Zaitseva, S. S. Karlov, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1230.
7. M. Huang, M. M. Kireenko, K. V. Zaitsev, Yu. F. Oprunenko, A. V. Churakov, J. A. K. Howard, M. V. Zabalov, E. Kh. Lermontova, J. Sundermeyer, T. Linder, S. S. Karlov, G. S. Zaitseva, *J. Organomet. Chem.*, 2012, **706—707**, 66.
8. M. M. Kireenko, E. A. Kuchuk, K. V. Zaitsev, V. A. Tafeenko, Y. F. Oprunenko, A. V. Churakov, E. Kh. Lermontova, G. S. Zaitseva, S. S. Karlov, *Dalton Trans.*, 2015, **44**, 11963.
9. C.-T. Chen, C.-A. Huang, B.-H. Huang, *Macromolecules*, 2004, **37**, 7968.
10. A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, *Dalton Trans.*, 2006, 887.
11. A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, A. F. Johnson, P. Khunkamchoo, S. L. Roberts, S. S. F. Wong, *Macromolecules*, 2006, **39**, 7250.
12. C.-T. Chen, C.-A. Huang, B.-H. Huang, *Dalton Trans.*, 2003, 3799.
13. O. Wichmann, R. Sillanpää, A. Lehtonen, *Coord. Chem. Rev.*, 2012, **256**, 371.
14. L. M. Alcazar-Roman, B. J. O´Keefe, M. A. Hillmyer, W.B. Tolman, *Dalton Trans.*, 2003, 3082.
15. L.-C. Liang, S.-T. Lin, C.-C. Chien, *J. Chin. Chem. Soc.*, 2013, **60**, 710.
16. E.Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Inorg. Chem.*, 2001, **40**, 4263.
17. L.-C. Liang, S.-T. Lin, C.-C. Chien, *Inorg. Chem.*, 2013, **52**, 1780.
18. K. Phomphrai, P. Chumsaeng, P. Sangtrirutnugul, P. Kongsaeree, M. Pohmakotr, *Dalton Trans.*, 2010, **39**, 1865.
19. Z. Tang, V. C. Gibson, *Eur. Polym. J.*, 2007, **43**, 150.
20. Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey, M. Bochmann, *Dalton Trans.*, 2006, 340.
21. D. Peri, C. M. Manna, M. Shavit, E. Y. Tshuva, *Eur. J. Inorg. Chem.*, 2011, **2011**, 4896.
22. S. Barroso, P. Adro, M. T. Duarte, A. Meetsma, J. C. Pessoa, M. W. Bouwkamp, A. M. Martins, *Eur. J. Inorg. Chem.*, 2011, 4277.
23. E. Safaei, M. Rasouli, T.Weyhermüller, E. Bill, *Inorg. Chim. Acta*, 2011, **375**, 158.
24. A. R. Hutchison, A. Mitra, D. A. Atwood, *Main Group Chem.*, 2005, **4**, 187.
25. J. S. Klitzke, T. Roisnel, E. Kirillov, O. L. Casagrande, J.-F. Carpentier, *Organometallics*, 2014, **33**, 5693.
26. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.
27. G. M. Sheldrick, *SADABS*, *Program for scaling and correction of area detector data*, University of Göttingen, Germany, 1997.

Received February 4, 2016;
in revised form May 18, 2016