Half-sandwich complexes of lanthanides with tridentate ligands $[RCH_2CH(O)CH_2OBu^n]^{2-}$ (R = C_5H_4, 1-C_9H_6): synthesis, structures, and properties. The crystal structure of the complex $\{[(\eta^5\text{-}C_5H_4)CH_2CH(\mu^2{:}\eta^1\text{-}O)CH_2OBu^n]LaN(SiMe_3)_2\}_2$

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The oxirane-ring opening of butyl glycidyl ether with cyclopentadienylsodium or indenylsodium afforded cyclopentadienyl- and indenyl-substituted alcohols $RHCH_2CH(OH)CH_2OBu^n$ (R = C_5H_4 (**1**) or 3-C_9H_6 (**2**), respectively), which were used as tridentate ligands. The reactions of these compounds with $Ln[N(SiMe_3)_2]_3$ produced the lanthanide complexes $\{[(\eta^5\text{-}R)CH_2CH(\mu^2{:}\eta^1\text{-}O)CH_2OBu^n]LnN(SiMe_3)_2\}_2$ (R = C_5H_4, Ln = La (**3**), Pr (**4**), Er (**5**), Lu (**6**); or R = 1-C_9H_6, Ln = La (**7**)). The coordination spheres of the metal atoms in these complexes involve simultaneously the η^5-cyclopentadienyl (indenyl), bridging alkoxide, and terminal amide ligands. The complexes were characterized by microanalysis, IR and NMR spectroscopy, and magnetochemistry. The crystal and molecular structure of complex **3** was established by single-crystal X-ray diffraction analysis.

Key words: lanthanides, complexes, 1-cyclopentadienyl-3-butoxypropan-2-ol, 1-indenyl-3-butoxypropan-2-ol, trimethylsilylamide ligands, synthesis, structures.

Half-sandwich complexes of d- and f-transition metals are promising catalysts of various transformations of unsaturated substrates due to their higher electron deficiency and better accessibility of the coordination spheres as compared to derivatives of the bis(cyclopentadienyl) series. Among organolanthanide complexes, sandwich complexes have received the most study, whereas the known monocyclopentadienyl compounds are few in number.[1] The latter fact is associated primarily with the ready transfer of the η^5-bonded cyclopentadienyl ligands between two metal centers[2—4] along with the known tendency of mixed ligand complexes of lanthanides to disproportionation and formation of homoligand derivatives.[5] Only a few examples of monocyclopentadienyl complexes of trivalent lanthanides containing two different σ-coordinated ligands are known.[6—7] One of the possible ways of preventing disproportionation in heteroligand lanthanide complexes consists in the use of polydentate cyclopentadienyl-substituted ligands containing several functional groups, which can form bonds with a metal center. The cyclopentadienylamide ligand was proposed as an alternative to the traditional bis(cyclopentadienyl) coordination environment.[8] It was found that alkyl complexes of rare-earth metals coordinated by this ligand exhibit high activity in catalytic polymerization,[8—11] hydrosilylation,[12] and hydroamination[13] of olefins. Until recently, cyclopentadienylalkoxy ligands, which are more readily accessible and hydrolytically more stable, were little used in the chemistry of transition metals and the data on their application refer only to titanium and zirconium complexes.[14,15]

Recently, we have prepared new cyclopentadienylalkoxy ligands and synthesized their derivatives both with di- and trivalent lanthanides.[16—19] Polydentate ligands with a side chain bearing an additional donor group, which can be coordinated to the metal atom, are of particular interest because they extend the possibilities for the construction of the coordination sphere of the

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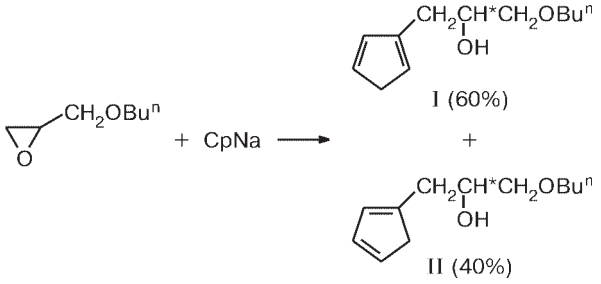
metal atom and stabilization of the resulting metal complexes.

Taking into account that both amides and alkoxides of lanthanides can catalyze various chemical transformations,[20—22] it was of interest to combine the η^5-bonded carbocyclic ligand with amide or alkoxy groups in one half-sandwich complex. For this purpose, we synthesized cyclopentadienyl- and indenyl-substituted alcohols bearing the ether substituent, *viz.*, $RCH_2CH(OH)CH_2OBu^n$ (R = C_5H_5, 3-C_9H_7), studied their reactions with silylamide derivatives of trivalent lanthanides $Ln[N(SiMe_3)_2]_3$, established the structures of the resulting complexes, and examined their reactivities.

Results and Discussion

Cyclopentadienyl- and indenyl-substituted ether alcohols $RCH_2CH(OH)CH_2OBu^n$ (R = C_5H_5 or 3-C_9H_7) were prepared according to a procedure reported previously for related compounds[23] by the nucleophilic opening of the oxirane ring of *n*-butyl glycidyl ether under the action of cyclopentadienyl- or indenylsodium, respectively, in DME. The former reaction was carried out at 60 °C (the ratio $CH_2CHCH_2OBu^n$ (O): CpNa = 1 : 5), and racemic 3-cyclopentadienyl-1-butoxy-2-propanol (**1**) was isolated by vacuum distillation as a mixture of two positional isomers I and II in a ratio of 3 : 2 (^{1}H NMR data) in 34% yield (Scheme 1).

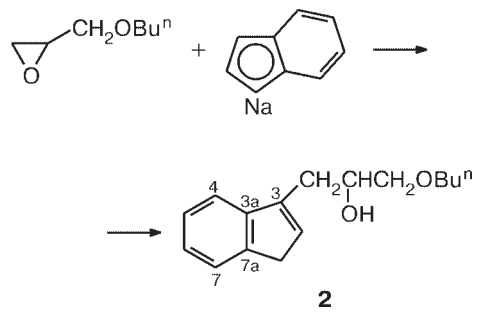
Scheme 1



The ring opening of *n*-butyl glycidyl ether with indenylsodium at room temperature (the ratio $CH_2CHCH_2OBu^n$ (O): IndNa = 1 : 1) was accompanied by the formation of a new carbon—carbon bond at position 3 of the five-membered ring of indene to give the only isomer of 1-butoxy-3-(inden-3′-yl)-2-propanol (**2**) in 39% yield (Scheme 2).

Compounds **1** and **2** were prepared as pale-yellow oils and characterized by the data from ^{1}H and ^{13}C NMR and IR spectroscopy, HPLC, and microanalysis.

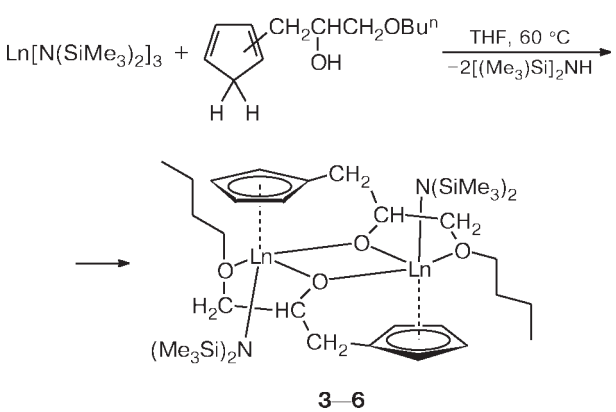
Scheme 2



It should be noted that elimination of hexamethyldisilazane from lanthanide amides under the action of stronger C—H- or E—H-acids has been successfully used for the preparation of lanthanide derivatives both in the oxidation states +2 [24] and +3.[13] It was of interest to use this reaction for the synthesis of trivalent lanthanide complexes containing simultaneously the cyclopentadienyl, alkoxide, and amide ligands.

It was found that the reactions of alcohol **1** with $Ln[N(SiMe_3)_2]_3$ (Ln = La, Pr, Er, or Lu) in THF at 60 °C were accompanied by elimination of two equivalents of hexamethyldisilazane and were completed in 24 h. The complexes $\{[(\eta^5\text{-}C_5H_4)CH_2CH(\mu^2{:}\eta^1\text{-}O)CH_2OBu^n]LnN(SiMe_3)_2\}_2$ (Ln = La (**3**), Pr (**4**), Er (**5**), or Lu (**6**)) were obtained in moderate yields by recrystallization from hexane (Scheme 3).

Scheme 3



Ln = La (**3**), 48%; Pr (**4**), 53%; Er (**5**), 32%; Lu (**6**), 28%

Complexes **3** and **6** were obtained as colorless crystalline compounds. Complexes **4** and **5** were pale-green and pale-pink finely crystalline powders, respectively. All these complexes are very sensitive to atmospheric moisture and oxygen, readily

soluble in THF, DME, and toluene, and poorly soluble in hexane.

The IR spectra of complexes **3**—**6** have absorption bands characteristic of the cyclopentadienyl anion (at 3030 and 760 cm^{-1}), the bis(trimethylsilylamide) ligands (at 830—850 and 1240—1250 cm^{-1} for $SiMe_3$ and at 925 cm^{-1} for Si—N), and the C—O groups of the ether fragments of the side chain (at 860 and 1000—1030 cm^{-1}). The absorption bands of the hydroxy groups of the starting ligand are absent.

The ^1H NMR spectrum of complex **3** in pyridine-d_5 at 20 °C has two singlets at δ 0.31 and 0.34 with the intensity ratio of 2 : 1 belonging to the protons of the bis(trimethylsilylamide) ligand and a triplet at δ 0.98 (J = 7.6 Hz) assigned to the methyl group of the butoxy fragment. The signals of all other groups are broadened and are observed as nonresolved multiplets. The signals for the protons of the methylene group at the cyclopentadienyl ring are diastereotopic and are observed at δ_H 2.76 and 3.14. Four protons of the substituted cyclopentadienyl ring of the ligand give three broadened singlets with the intensity ratio of 2 : 1 : 1. An increase in the temperature to 70 °C led to a slight narrowing of the signals. However, attempts to obtain spectra with well-resolved signals failed. In the NMR spectrum measured in toluene-d_8 at 20 °C, the protons of the Me_3Si fragment of the amide ligand are observed already as a singlet at δ_H 0.32. Unlike the spectrum in pyridine-d_5, the latter spectrum has a set of three broadened multiplets for the protons of the methylene substituent of the cyclopentadienyl ring at δ_H 2.22, 2.31, and 2.58 with the intensity ratio of 1 : 0.5 : 0.5 and two multiplets at δ_H 3.27 and 3.76 with equal intensities corresponding to the protons of the CH_2O group. The cyclopentadienyl protons give three broadened singlets at δ_H 6.02 (2 H), 6.14 (1 H), and 6.68 (1 H). A decrease in the temperature to −20 °C gave rise to decoalescence of most of the signals. At −60 °C, three signals correspond to the Me_3Si group, the methine proton of the CHO group gives two multiplets with approximately equal intensities, and the protons of the cyclopentadienyl fragment give seven signals, the intensity of one of these signals being doubled as compared to other signals due to overlapping of two signals. Apparently, broadening of the signals and the observed temperature dependence result from dynamic processes occurring in solutions of complex **3**. In the ^1H NMR spectra (in toluene-d_8 and pyridine-d_5) of lutetium analog **6**, the signals are also substantially broadened at room temperature. However, the spectral pattern is, on the whole, similar to that observed for **3**.

The magnetic moments of compounds **4** and **5** (3.3 and 9.4 μB, respectively, at room temperature) are close

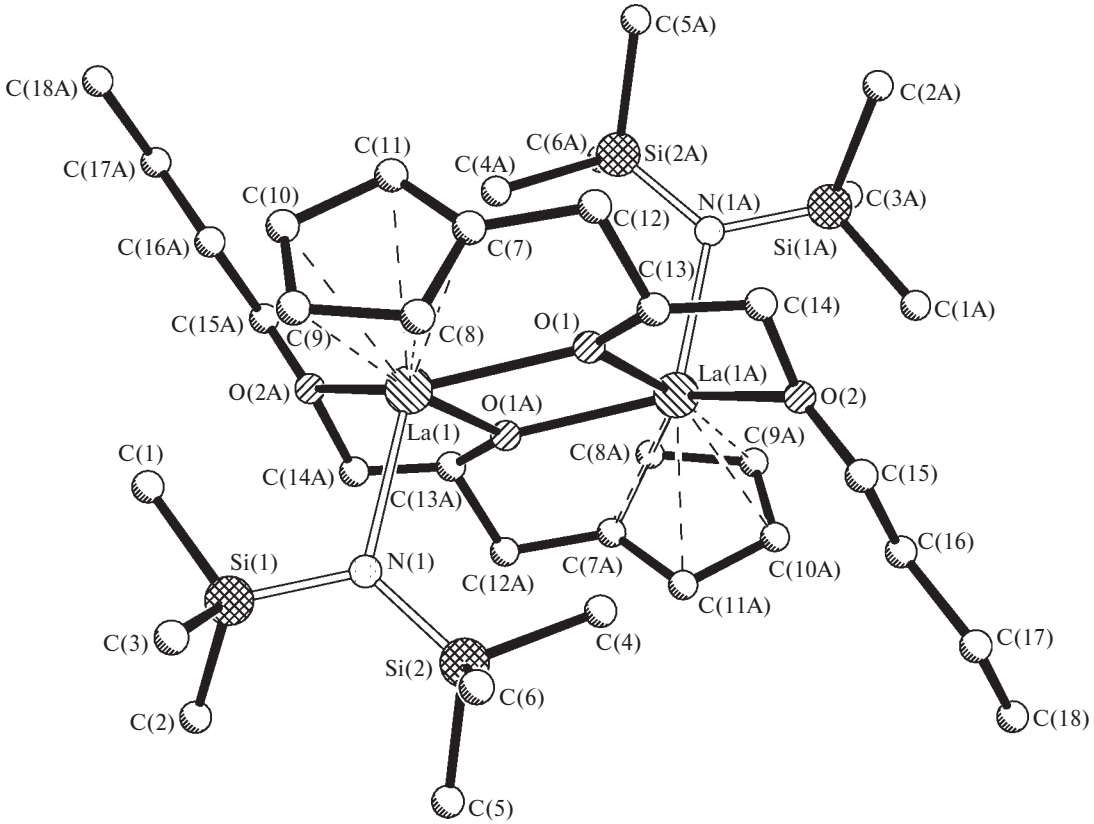


Fig. 1. Molecular structure of complex **3**.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **3**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
La(1)—O(1)	2.348(6)	O(1)—La(1)—N(1)	114.2(2)	O(1)—La(1)—O(1A)	66.3(2)
La(1)—O(1A)	2.429(6)	N(1)—La(1)—O(1A)	98.1(2)	O(1)—La(1)—O(2)	123.0(2)
La(1)—C(7)	2.841(8)	N(1)—La(1)—O(2)	99.4(2)	O(1A)—La(1)—O(2)	64.4(2)
La(1)—C(9)	2.898(9)	O(1)—La(1)—C(7)	63.3(2)	N(1)—La(1)—C(7)	116.9(2)
La(1)—C(11)	2.857(8)	O(1A)—La(1)—C(7)	126.8(2)	O(2)—La(1)—C(7)	136.9(2)
Si(1)—N(1)	1.708(7)	O(1)—La(1)—La(1A)	33.76(13)	N(1)—La(1)—La(1A)	109.02(17)
O(1)—C(13)	1.425(10)	O(1A)—La(1)—La(1A)	32.49(13)	O(2)—La(1)—La(1A)	93.28(15)
O(2)—C(14)	1.463(12)	C(7)—La(1)—La(1A)	95.75(19)	N(1)—Si(1)—C(3)	112.9(4)
C(12)—C(13)	1.510(13)	N(1)—Si(2)—C(5)	112.8(5)	Si(1)—N(1)—Si(2)	121.6(4)
C(15)—C(16)	1.509(13)	Si(1)—N(1)—La(1)	116.5(3)	Si(2)—N(1)—La(1)	121.7(3)
C(17)—C(18)	1.509(18)	C(13)—O(1)—La(1)	125.5(6)	C(13)—O(1)—La(1A)	119.9(6)
La(1)—N(1)	2.395(6)	La(1)—O(1)—La(1A)	113.7(2)	C(15)—O(2)—C(14)	117.7(8)
La(1)—O(2)	2.627(6)	C(15)—O(2)—La(1)	135.2(5)	C(14)—O(2)—La(1)	102.8(6)
La(1)—C(8)	2.857(8)	C(11)—C(7)—La(1)	76.4(5)	C(12)—C(7)—La(1)	110.1(5)
La(1)—C(10)	2.874(9)	C(7)—C(12)—C(13)	111.2(8)	O(1)—C(13)—C(12)	109.9(8)
La(1)—La(1A)	4.0012(19)	O(2)—C(15)—C(16)	110.0(8)	C(15)—C(16)—C(17)	113.5(9)
Si(2)—N(1)	1.713(7)	C(18)—C(17)—C(16)	112.5(11)		
O(2)—C(15)	1.417(11)				
C(7)—C(12)	1.512(13)				
C(13)—C(14)	1.370(15)				
C(16)—C(17)	1.523(13)				

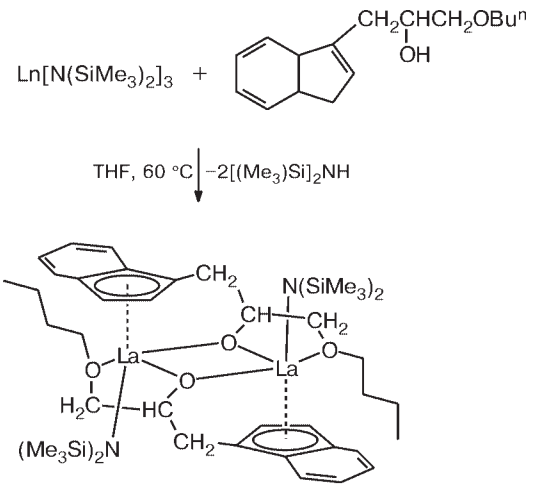
to the average values observed for organometallic compounds of these elements.[25]

According to the results of X-ray diffraction analysis, two lanthanum atoms in complex **3** (Fig. 1, Table 1) are located at a nonbonded distance (4.001 Å) and are linked *via* two bridging oxygen atoms (La—O, 2.348(6) and 2.429(6) Å) of two 1-butoxy-3-cyclopentadienylpropan-2-yl oxide ligands. The cyclopentadienyl rings of these ligands are η^5-coordinated to the metal atoms (La—C, 2.841(8)—2.898(9) Å). The remaining vertices of the coordination polyhedra of all metal atoms are occupied by the nitrogen atom of the terminal amide group $N(SiMe_3)_2$ (La—N 2.395(6) Å) and the oxygen atom of the butoxy fragment of the ligand to form formally the chelate five-membered LaOCCO metallocycle (La—O, 2.627(6) Å). As a result, the coordination number of each lanthanum(+3) atom is equal to 7.

It was found that the reaction of ligand **2** with $[(Me_3Si)_2N]_3La$ in THF at 60 °C was also accompanied by the replacement of two bis(trimethylsilyl) groups to give the complex $\{[(\eta^5\text{-}1\text{-}C_9H_6)CH_2CH(\mu^2{:}\eta^1\text{-}O)CH_2OBu^n]LaN(SiMe_3)_2\}_2$ (**7**), which was isolated after recrystallization from cyclohexane as a colorless finely crystalline powder in 64% yield (Scheme 4). Unfortunately, we failed to obtain single crystals suitable for X-ray diffraction study. However, by analogy with cyclopentadienyl derivatives, it was assumed that complex **7** occurs as a dimer.

The studies of the reactivities of complexes **3**—**7** demonstrated that complex **3** exhibited moderate activity in

Scheme 4



7

catalysis of styrene polymerization (after one day, the conversion at room temperature was 25%). Compounds **3**—**7** proved to be inactive as catalysts of hydrosilylation of 1-decene with phenylsilane and hydroamination of 1-decene with *tert*-butylamine.

Experimental

The synthesis was carried out under conditions precluding exposure to atmospheric oxygen and moisture using the stan-

dard Schlenk technique. Hexane, toluene, and THF were dried over sodium benzophenone ketyl, thoroughly degassed, and condensed *in vacuo* into a reaction tube immediately before use. The IR spectra were recorded on a Specord M 80 instrument as films or Nujol mulls. The ^{1}H and ^{13}C NMR spectra were measured on Bruker DPX 200 and Bruker DPX 400 instruments. The chemical shifts are given in the δ scale relative to the known shifts of the residual protons of deuterated solvents. Analysis of volatile organic products was performed on a Tsvet-530 instrument (katharometer as the detector; steel 2 m × 3 mm-column packed with 5% SE-30 on Chromaton N-AW; helium as the carrier gas). Lanthanide amides were prepared according to known procedures.[26] The magnetic measurements were carried out according to a procedure described previously.[27]

1-Butoxy-3-(cyclopenta-1,4-dienyl)propan-2-ol and 1-butoxy-3-(cyclopenta-1,3-dienyl)propan-2-ol (a mixture of two isomers) (1). A solution of *n*-butyl glycidyl ether (5.8 g, 45 mmol) in DME (20 mL) was slowly added to a solution of CpNa (20.0 g, 227 mmol) in DME (125 mL). The reaction mixture was stirred at 60 °C for 5 h and hydrolyzed with a 20% NH_4Cl solution (25 mL). Then H_2O (200 mL) was added and the mixture was extracted with diethyl ether (2×100 mL). The ethereal layer was separated and dried over $CaCl_2$. Volatile compounds were removed *in vacuo*. The pale-yellow oil that obtained was distilled *in vacuo* (130—132 °C/15 Torr). Compound **3** was obtained in a yield of 3.0 g (34%). Found (%): C, 73.86; H, 10.32. $C_{12}H_{20}O_2$. Calculated (%): C, 73.62; H, 10.02. 1-Butoxy-3-(cyclopenta-1,4-dienyl)propan-2-ol. ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 0.92 (t, 3 H, Me, J = 7.2 Hz); 1.36 (m, 2 H, γ-CH_2, Bu); 1.55 (m, 2 H, β-CH_2, Bu); 2.55 (d, 2 H, C$\underline{H}_2$C$_5$H$_5$, J = 6 Hz); 2.69 (s, 1 H, OH), 2.97 (m, 2 H, CH_2, C_5H_5); 3.25—3.50 (m, 2 H, CH_2O); 3.45 (t, 2 H, α-CH_2, Bu, J = 6.8 Hz); 4.00 (m, 1 H, CHO); 6.12, 6.25, and 6.43 (all m, 3 H each, C_5H_5). ^{13}C NMR ($CDCl_3$, 50 MHz), δ: 13.9 (Me); 19.2 (β-CH_2, Bu); 31.6 (γ-CH_2, Bu); 33.97 (C$\underline{H}_2$C$_5$H$_5$); 41.4 (CH_2, C_5H_5); 69.6 (CHOH); 71.1 (α-CH_2, Bu); 74.4 (CH_2O); 128.6, 128.8, 134.1 (CH, C_5H_5); 142.9 (C, C_5H_5). 1-Butoxy-3-(cyclopenta-1,3-dienyl)propan-2-ol. ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 0.92 (t, 3 H, Me, J = 7.2 Hz); 1.37 (m, 2 H, γ-CH_2, Bu); 1.55 (m, 2 H, β-CH_2, Bu); 2.59 (d, 2 H, C$\underline{H}_2$C$_5$H$_5$, J = 6 Hz); 2.69 (s, 1 H, OH); 2.95 (m, 2 H, CH_2, C_5H_5); 3.25—3.50 (m, 2 H, CH_2O); 3.45 (t, 2 H, α-CH_2, Bu, J = 6.8 Hz); 3.94 (m, 1 H, CHO); 6.29, 6.43, and 6.47 (all m, 3 H each, C_5H_5). ^{13}C NMR ($CDCl_3$, 50 MHz): 13.9 (Me); 19.3 (β-CH_2, Bu); 31.7 (γ-CH_2, Bu); 34.8 (C$\underline{H}_2$C$_5$H$_5$); 43.9 (CH_2, C_5H_5), 70.2 (CHOH); 71.2 (α-CH_2, Bu); 74.6 (CH_2O); 128.9, 132.3, 134.7 (CH, C_5H_5); 145.1 (C, C_5H_5). IR (KBr), ν/cm^{-1}: 3420 (OH); 3160 (C=CH); 2900 (Me); 1600 (C=C); 1480 (Me); 1380 (Me); 1120 (C—O); 900 (C—O); 810 (CH); 790 (CH); 750 ($(CH_2)_n$); 600 (RHC=CHR′).

3-(1-Butoxy-3′-indenyl)propan-2-ol (2). A solution of *n*-butyl glycidyl ether (6.4 g, 49.5 mmol) in DME (30 mL) was slowly added to a solution of C_9H_7Na(THF) (10.4 g, 49.5 mmol) in DME (150 mL) at ~20 °C. The resulting mixture was refluxed for 5 h and treated as described for compound **1**. After vacuum distillation, compound **2** was obtained in a yield of 4.8 g (39%) as a yellow oil (b.p. 140—142 °C (10^{-2} Torr)). Found (%): C, 78.14; H, 9.21. $C_{16}H_{22}O_2$. Calculated (%): C, 78.00; H, 8.99. IR (KBr), ν/cm^{-1}: 3390 (OH); 3010 (C=CH); 2890 (Me); 1590 (C=C); 1440 (CH); 1380 (CH); 1100 (C—O); 900 (C—O); 780, 760, 710 (C—H arom.). ^{1}H NMR (20 °C, $CDCl_3$), δ: 0.92 (t, 3 H, Me, J = 7.2 Hz); 1.37 (m, 2 H, γ-CH_2); 1.56 (m, 2 H, β-CH_2); 2.58 (d, 1 H, OH, J = 3.4 Hz); 2.76 (m, 2 H, Ind-C$\underline{H}_2$); 3.31—3.52 (m, 4 H, C$\underline{H}_2$—O—C$\underline{H}_2$); 3.34 (m, 2 H, CH_2, C_9H_7); 4.16 (m, 1 H, C$\underline{H}$(OH)); 6.23 (m, 1 H, 2-CH, C_9H_7); 7.15—7.50 (m, 4 H, 4,5,6,7-CH, C_9H_7). ^{13}C NMR (20 °C, $CDCl_3$), δ: 13.9 (Me); 19.4 (γ-CH_2); 31.8 (β-CH_2); 32.0 (Ind-C$\underline{H}_2$); 38.0 (1-CH_2, C_9H_7); 69.1 (CH); 71.3 (OCH_2); 79.5 (CH_2O); 119.1 (4-CH, C_9H_7); 123.8 (7-CH, C_9H_7); 124.7 (6-CH, C_9H_7); 126.1 (5-CH, C_9H_7); 130.5 (2-CH, C_9H_7); 140.6 (3-CH, C_9H_7); 144.4 (7-C, C_9H_7); 145.2 (8-C, C_9H_7).

Bis[(1-butoxy-3-cyclopentadienylpropan-2-olato)bis(trimethylsilyl)amidolanthanum], {[(η^5-C_5H_4)CH_2CH(μ^2:η^1-O)CH_2OBu^n]LaN($SiMe_3$)$_2$}$_2$ (3). A solution of ligand **1** (0.63 g, 3.24 mmol) was added to a solution of $[(Me_3Si)_2N]_3La$ (2.01 g, 3.24 mmol) in THF (50 mL). The reaction mixture was heated at 60—65 °C for 24 h. Volatile products were removed with vacuum condensation (80 °C, 0.01 Torr) and two portions of hot toluene (10 mL) were added to the residue. The solvent and volatile products were distilled off with vacuum condensation (80 °C, 0.01 Torr). The GLC analysis of the condensate revealed hexamethyldisilazane in a yield of 0.76 g (73%). The solid residue was extracted with hot hexane (20 mL) at 50 °C. Cooling of the extract to ~20 °C afforded colorless crystals of **3** in a yield of 0.72 g (48%). Found (%): C, 43.32; H, 7.02; La, 28.45. $C_{36}H_{72}La_2N_2O_4Si_4$. Calculated (%): C, 43.83; H, 7.29; La, 28.15. IR, ν/cm $^{-1}$: 3030 (Cp); 1240 (Me_3Si); 1000 (C—O); 928 (Si—N); 860 (C—O); 830 (Me_3Si); 760 (Cp). ^{1}H NMR (20 °C, pyridine-d_5), δ: 0.31 and 0.34 (both s,~2 : 1, overall 36 H, $SiMe_3$); 0.98 (t, 6 H, Me, J = 7.6 Hz); 1.31 (m, 4 H, γ-CH_2, Bu); 1.78 (m, 4 H, β-CH_2, Bu); 2.76 and 3.14 (both m, 2 H each, CpC$\underline{H}_2$); 3.70 (m, 4 H, OC$\underline{H}_2$); 3.84 (m, 2 H, C$\underline{H}$O); 4.02 (m, 4 H, C$\underline{H}_2$O); 6.35 (br.s, 4 H, Cp); 6.39 (br.s, 2 H, Cp); 6.48 (br.s, 2 H, Cp). ^{13}C NMR (20 °C, benzene-d_6), δ: 4.9, 5.3, and 5.6 ($(Me)_3Si$); 13.9 and 14.3 (Me); 18.8, 25.7, and 27.2 (γ-CH_2); 29.4, 30.2, and 31.9 (β-CH_2); 34.9 (Cp$\underline{C}H_2$); 67.8 (CHO); 74.0 (OCH_2); 78.9 (CH_2O); 103.4 (Cp); 105.1 (Cp); 109.7 (Cp); 110.9 (Cp); 128.6 (Cp at CH_2).

Bis[(1-butoxy-3-cyclopentadienylpropan-2-olato)bis(trimethylsilyl)amidopraseodymium], {[(η^5-C_5H_4)CH_2CH(μ^2:η^1-O)CH_2OBu^n]PrN($SiMe_3$)$_2$}$_2$ (4). The reaction was conducted and the product was isolated as described above with the use of $[(Me_3Si)_2N]_3Pr$ (1.20 g, 1.93 mmol) and compound **1** (0.38 g, 1.93 mmol). The GLC analysis of the condensate revealed hexamethyldisilazane in a yield of 0.45 g (72%). Complex **4** was obtained in a yield of 0.51 g (53.7%) as a pale-green finely crystalline powder. Found (%): C, 43.17; H, 6.88; Pr, 27.93. $C_{36}H_{72}N_2O_4Pr_2Si4$. Calculated (%): C, 43.65; H, 7.26; Pr, 28.44. IR (Nujol mulls, KBr), ν/cm $^{-1}$: 3030 (Cp); 1260 (Me_3Si); 1050 (C—O); 930 (Si—N); 860 (C—O); 820 (Me_3Si); 760 (Cp).

Bis[(1-butoxy-3-cyclopentadienylpropan-2-olato)bis(trimethylsilyl)amidoerbium], {[(η^5-C_5H_4)CH_2CH(μ^2:η^1-O)CH_2OBu^n]ErN($SiMe_3$)$_2$}$_2$ (5). The reaction was carried out and the product was isolated as described above with the use of $[(Me_3Si)_2N]_3Er$ (2.53 g, 3.90 mmol) and compound **1** (0.76 g, 3.90 mmol). The GLC analysis of the condensate revealed hexamethyldisilazane in a yield of 1.08 g (86%). Complex **4**

was obtained in a yield of 0.87 g (42.5%) as a pale-pink finely crystalline powder. Found (%): C, 41.01; H, 6.39; Pr, 32.54. $C_{36}H_{72}Er_2N_2O_4Si_4$. Calculated (%): C, 41.44; H 6.90; Er, 32.06. IR (Nujol mulls, KBr), ν/cm $^{-1}$: 3050 (Cp); 1240 (Me_3Si); 1040 (C—O); 925 (Si—N); 860 (C—O); 820 (Me_3Si); 770 (Cp).

Bis[(1-butoxy-3-cyclopentadienylpropan-2-olato)bis(trimethylsilyl)amidolutetium], {[(η^5-C_5H_4)CH_2CH(μ^2:η^1-O)CH_2OBu^n]LuN($SiMe_3$)$_2$}$_2$ (6). The reaction was performed and the product was isolated as described above with the use of [(Me_3Si)$_2$N]$_3$Lu (1.80 g, 2.74 mmol) and compound **1** (0.53 g, 2.74 mmol). The GLC analysis of the condensate revealed hexamethyldisilazane in a yield of 0.60 g (68%). Complex **4** was obtained in a yield of 0.65 g (45%) as a colorless finely crystalline powder. Found (%): C, 40.31; H, 6.33; Lu, 33.29. $C_{36}H_{72}Lu_2N_2O_4Si_4$. Calculated (%): C, 40.84; H, 6.80; Lu, 33.05. IR (Nujol mulls, KBr), ν/cm $^{-1}$: 3030 (Cp); 1230 (Me_3Si); 1050 (C—O); 930 (Si—N); 860 (C—O); 830 (Me_3Si); 760 (Cp). ^{1}H NMR (20 °C, benzene-d_6), δ: 0.36 and 0.62 (both s, 18 H, $SiMe_3$); 0.92 (m, 6 H, Me); 1.32—1.90 (br.m, 8 H, β- and γ-CH_2, Bu); 2.71—3.19 (br.m, 4 H, CpC$\underline{H}_2$); 3.31—4.31 (br.m, 10 H, C$\underline{H}$(O)C$\underline{H}_2$OC$\underline{H}_2$); 5.83—6.78 (br.m, 8 H, Cp).

Bis[(3-(1-butoxy)(3′-indenyl)propan-2-olato)bis(trimethylsilyl)amidolanthanum], {[(η^5-1-C_9H_6)CH_2CH(μ^2:η^1-O)CH_2OBu^n]LaN($SiMe_3$)$_2$}$_2$ (7). A solution of compound **2** (0.54 g, 2.18 mmol) in THF (20 mL) was added to a solution of [(Me_3Si)$_2$N]$_3$La (1.35 g, 2.18 mmol) in THF (20 mL). The reaction mixture was heated at 60—65 °C for 24 h. Volatile products were removed *in vacuo* and condensed into an separate flask. Hot toluene (30 mL) was added to the residue. The resulting solution was heated at 60—65 °C for 3 h. The toluene and volatile products were removed *in vacuo* on heating (80 °C, 0.01 Torr) and condensed. The GLC analysis of the condensate revealed hexamethyldisilazane in a yield of 0.57 g (82%). Recrystallization of the solid residue from cyclohexane afforded complex **7** in a yield of 0.76 g (64%) as small colorless crystals. Found (%): C, 48.32; H, 7.32; La, 24.97. $C_{44}H_{76}La_2N_2O_4Si_4$. Calculated (%): C, 48.63; H, 7.04; La, 25.56. IR (Nujol mulls, KBr), ν/cm^{-1}: 3030 (Cp); 1250 (Me_3Si); 1060 (C—O); 935 (Si—N); 870 (C—O); 830 (Me_3Si); 760, 745, 755 (C_9H_6). ^{1}H NMR (20 °C, benzene-d_6), δ: 0.2—0.6 (m, 36 H, $SiMe_3$); 0.6—1.9 (br.m, 18 H, OC$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_3$); 2.2—3.9 (m, 10 H, —C$\underline{H}_2$C$\underline{H}$(O)C$\underline{H}_2$O—); 6.1—7.9 (m, 12 H arom., C_9H_6).

X-ray diffraction analysis of complex 3. X-ray diffraction analysis was performed in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences) on a Siemens-P3/R3 diffractometer (λMo-Kα, graphite monochromator, 153 K, θ/2θ scanning technique). The crystallographic data for compounds **1** and the details of its refinement are given in Table 2. The structure was solved by direct methods using the SHELXS-86 program package[28] and refined by the least-squares method with anisotropic thermal parameters using the SHELXL-93 program package.[29] The hydrogen atoms were placed in geometrically calculated positions and refined using the riding model. The complete tables of the atomic coordinates and thermal parameters were deposited with the Cambridge Structural Database.

Table 2. Crystallographic parameters of complex **3**

Molecular formula	$C_{40}H_{80}La_2N_2O_5Si_4$
Molecular weight	1059.24
Space group	*C*2/*c*
a/Å	24.948(12)
b/Å	155.635(7)
c/Å	14.302(7)
α/deg	90
β/deg	109.29(4)
γ/deg	90
V/Å^3	5266(4)
Z	2
ρ_{calc}/g cm^{-3}	1.336
μ/cm^{-1}	17.28
θ/2θ Scan range	1.73—29.07
Number of measured reflections	7000
Number of reflections with $I > 2\sigma$	6850 (R_{int} = 0.1630)
Number of parameters in the refinement	240
R_1 ($I > 2\sigma(I)$)	0.0774
wR_2	0.1400

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