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Synthesis and crystal structure of binuclear diindenyllanthanide alkoxides, X-ray crystal structure of $[(C_9H_7)_2Nd(\mu,\eta^2\text{-}OCH_2\underbrace{CHCH_2CH_2CH_2}_{O})]_2$

Wei-Wen Ma,[a] Zhong-Zhi Wu,[a] Rui-Fang Cai,[a] Zu-En Huang[a]* and Jie Sun[b]

[a] Department of Chemistry, Fudan University, Shanghai 200433, P.R. China

[b] The Open Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai 200032, P.R. China

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Abstract—The reaction of triindenyllanthanide complexes $(C_9H_7)_3Ln\cdot THF$ (Ln = Nd, Pr) with equimolar 2-tetrahydrofurfuryl methanol in THF solution at room temperature forms two new binuclear diindenyllanthanide alkoxides, namely $[(C_9H_7)_2Ln(\mu,\eta^2\text{-}OCH_2\underbrace{CHCH_2CH_2CH_2}_{O})]_2$ [Ln = Nd (**1**) and Pr (**2**)]. These two new complexes have been characterized by IR, MS spectra and metal analysis, indicating they are oxygen-bridging dimers. Complex **1** has also been studied by X-ray crystallography. The crystal structure of Nd complex revealed that the oxygen atoms of tetrahydrofurfuryl methoxide ligand act as both a bridging and a chelate donating group in the title complexes. The Nd atom is coordinated by two η^5-C_9H_7 ring centroids, two oxygen atoms of tetrahydrofurfuryl methoxide ligands and an oxygen atom of tetrahydrofuran ring, indicating a nine coordination number. The Nd–C (η^5-C_9H_7) distances range from 2.79(2) to 2.92(2) Å, averaging 2.81(2) Å. The Nd–O(1) (μ-OR′) bond distances are 2.30(1) and 2.31(1) Å, averaging 2.305(1) Å. In the intramolecular five-membered chelating ring, the Nd–O(2) distance is 2.51(1) Å. © 1997 Elsevier Science Ltd

Keywords: neodymium; praseodymium; indenyl; tetrahydrofurfuryl methoxide; crystal structure.

It is well known that lanthanide metals are quite oxophilic and the oxygen-stabilized organolanthanide complexes are tractable for exploring their physical and chemical properties. The alkoxide group is a suitable co-ligand for synthesis of stable organolanthanide complexes. Therefore, the chemistry of mixed-ligand organolanthanides involving cyclopentadienyl and alkoxide ligands has attracted much attention [1–11]. But only a few indenyl alkoxide complexes of the rare earth elements are known [9,12]. Obviously, this area still remains to be explored. Given the physical properties of rare earth, the steric factors are important in organometallic chemistry and can affect the structures as well as the stability of organolanthanide complexes. Owing to 'lanthanide contraction', 'light' lanthanides, whose ionic radii are large, tend to have higher coordination numbers than 'heavy' lanthanides. Therefore, the ligand redistribution reactions are easier to occur to the lighter lanthanide complexes [13]. The larger steric bulk of ligand and chelating ligand can enhance the stability of the lighter organolanthanide complexes [14,15,16]. In order to obtain the stable binuclear lighter diindenyl lanthanide alkoxides, we herein report the synthesis and crystal structure of two new binuclear diindenyllanthanide alkoxides $[(C_9H_7)_2Nd(\mu,\eta^2\text{-}OCH_2R)]_2$, R = $\underbrace{CHCH_2CH_2CH_2}_{O}$, Ln = Nd (**1**), Pr (**2**), by using the chelating ligand 2-tetrahydrofurfuryl methoxide ligand as bridging group.

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* Author to whom correspondence should be addressed.

EXPERIMENTAL

Materials and instrumentation

All manipulations were carried out on a Schlenk vacuum line or in a glove box filled with a moisture- and oxygen- free nitrogen atmosphere. THF solvent was refluxed and distilled over sodium benzophenone ketyl immediately before use. The 2-tetrahydrofurfuryl methanol was of analytically pure grade and redistilled prior to use. Anhydrous $LnCl_3$ [17] and $(C_9H_7)_3Ln \cdot THF$ (Ln = Nd, Pr) [18] were prepared according to the literature methods. Metal analyses for lanthanides were accomplished using complexation titration with disodium EDTA [19]. Infrared spectra were recorded on a Nicolet FT-IR-50-X spectrometer in Nujol and Fluorolube mulls. Mass spectra were obtained on a HP5989A mass spectrometer with EI (70 ev) mode. The samples were rapidly introduced by the direct inlet techniques. The data of m/z are referred to the isotopes of ^1H, ^{12}C, ^{16}O, ^{144}Nd, and ^{141}Pr.

Preparation of complexes **1** *and* **2**

The complex **1** $[(C_9H_7)_2Nd(\mu,\eta^2\text{-}OCH_2\underbrace{CHCH_2CH_2CH_2}_{O})]_2$ was obtained by reaction of $(C_9H_7)_3Nd \cdot THF$ (0.40 g, 0.71 mmol) with equimolar 2-tetrahydrofurfuryl methanol in 20 cm^3 THF at room temperature for 12 h and purified by recrystallization from n-hexane/THF in yield 33.1%. Then, an appropriate amount of product was redissolved in THF. The solution was concentrated by reduced pressure to give a saturated THF solution, which was cooled to −10°C to give a number of blue, prismatic crystals suitable for X-ray analysis. IR (cm^{-1}): 3067 w, 2925 w, 2856 w, 1462 w, 1113 s, 1061 s, 1019 s, 919 m, 877 w, 813 m, 766 s, 721 s. MS data (70 ev): m/z [fragment, relative intensity %] = 320 [Nd_2O_2, 0.07], 304 [Nd_2O, 0.07], 289 [$(C_9H_7)NdOCH_2$, 0.08], 275 [$(C_9H_7)NdO$, 0.12], 259 [$(C_9H_7)Nd$, 0.08], 245 [$NdOCH_2R$, 0.11], RCH_2OOCH_2R [202, 0.38], 176 [NdO_2, 0.24], 160 [NdO, 0.20], 144 [Nd, 0.69], 117 [C_9H_7+2, 9.83], 116 [C_9H_7+1, 74.46], 115 [C_9H_7, 80.51], 102 [$HOCH_2R$, 1.96], 101 [OCH_2R, 0.83], 71 [R, 100.00], R = tetrahydrofurfuryl ring. Anal. Calc. for $C_{46}H_{46}O_4Nd_2$: Nd, 30.3%. Found: Nd, 30.1%.

The procedure for the preparation of the Pr complex (**2**) was identical to that for the Nd complex (**1**). A brown product was obtained (yield 26.6%). IR (cm^{-1}): 3064 w, 2923 m, 2857 w, 1461 m, 1113 s, 1063 s, 1019 s, 916 m, 874 w, 813 m, 766 s, 719 s. MS data (70 ev): m/z [assignment, relative identity %] = 531 [$(C_9H_7)_2PrOCH_2R+O_2C_2H_4-1$, 5.94], 375 [$(C_9H_7)Pr+O_2C_2H_4-1$, 8.91], 314 [$Pr_2O_2$, 0.99], 282 [$(C_9H_7)PrOCH_2-2$, 2.97], 272 [$(C_9H_7)PrO$, 0.99], 256 [$(C_9H_7)Pr$, 0.99], 242 [$PrOCH_2R$, 0.99], 202 [$RCH_2OOCH_2R$, 1.98], 189 [$PrO_2$, 1.98], 157 [PrO, 3.96], 141 [Pr, 9.90], 117 [C_9H_7+2, 9.90], 116 [C_9H_7+1, 49.50], 115 [C_9H_7, 54.46], 102 [$HOCH_2R$, 2.97], 101 [OCH_2R, 2.97], 71 [R, 100.00], R = tetrahydrofurfuryl ring. Anal. Calc. for $C_{46}H_{46}O_4Pr_2$: Pr, 29.8%. Found: 30.0%.

Both complex **1** and **2** have no melting points and decomposition occur at around 100°C. They are soluble in THF but sparingly soluble in toluene and insoluble in hexane. The complexes are extremely sensitive to air and moisture. They decompose into white powders within 2 min when exposed to air (10°C, relative humidity 50%).

X-ray structure determination

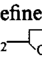
A blue prismatic crystal was sealed in a thin-wall glass capillary under dried and oxygen-free nitrogen atmosphere for X-ray analysis. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K_α ($\lambda = 0.71069$ Å) radiation and a 12 kW rotating anode generator at room temperature (20.0°C). The unit-cell parameters were determined by least-squares refinement of the setting angles of 20° carefully centered reflections in the range $18.59 < 2\theta < 21.74°$. The intensities of three representative reflections were measured after every 200 reflections. Over the course of data collection, the standards decreased by 1.8%. A linear correction factor was applied to the data to account for this phenomenon. The data were also corrected for Lorentz and polarization effects and empirical absorption. A summary of crystallographic data and data collection parameters is given in Table 1.

The structure was solved by direct methods [20] and expanded using Fourier techniques [21]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The positions of the hydrogen atoms were calculated using a C—H bond length of 0.95 Å and ideal angles. Neutral atom scattering factors were taken from Cromer and Waber [22]. All calculations were performed on a Micro VAX3100 computer using the teXsan crystallographic software package of Molecular Structure Corporation (1985 & 1992). Lists of final atomic coordination and thermal parameters, full bond lengths and angles, together with F_o/F_c values have been deposited as supplementary data with the editor. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Center.

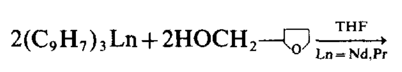
RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization of complexes

Both complex **1** and complex **2** were synthesized by reaction of $(C_9H_7)_3Ln \cdot THF$ with equimolar 2-tetrahydrofurfuryl methanol in THF at room temperature. The reaction equation is as follows:

Table 1. Crystallographic data and refinement parameters for $[(C_9H_7)_2Ln(\mu,\eta^2—OCH_2—$$)]_2$

Formula	$C_{46}H_{46}O_4Nd_2$
Fw	951.35
Crystal dimensions (mm)	0.20 × 0.20 × 0.30
Crystal system	monoclinic
Space group	$P2_1/n$ (#14)
Lattice Parameters	
a (Å)	11.245(2)
b (Å)	14.712(3)
c (Å)	11.823(2)
β (°)	94.43(2)
V (Å^3)	1950.0(7)
Z	2
D_c (g cm^{-3})	1.620
F(000)	948.00
Radiation (Å)	Mo-K$_\alpha$ (λ = 0.71069)
μ_c (cm^{-1})	26.74
T (K)	293
Scan type	ω–2θ
Scan rate (°/min)	16.0
Scan width (°)	$1.63 \pm 0.3 \tan\theta$
$2\theta_{max}$	45.0
No. of reflections measured	2821
No. of observations ($I > 3.00\sigma(I)$)	1393
No. of variables	235
R	0.047
R_w	0.049
GOF	1.66
Weight scheme ω	$1/\sigma^2(F_o)$
p-factor	0.02
Max shift/error	0.07
ρ_{max} (e Å^{-3})	0.55



$$2(C_9H_7)_3Ln + 2HOCH_2— \xrightarrow[Ln = Nd,Pr]{THF} [(C_9H_7)_2Ln(\mu,\eta^2—OCH_2—)]_2 + 2C_9H_8$$

Satisfactory lanthanide analysis of two complexes has been obtained. The IR spectra of two new complexes are very similar. They all exhibit the characteristic absorption for the η^5-C_9H_7 group near 3067–3064, 1462–1461, 1019, 877–874, 766, 721–719 cm^{-1} [23]. The absorption peaks appearing at 1062 and 916 cm^{-1} may be attributed to the $\nu^{as}_{C–O–C}$ and $\nu^{s}_{C–O–C}$ mode, indicating the presence of tetrahydrofurfuryl group. The remaining absorption for the 2-tetrahydrofurfuryl methoxide ligand display characteristically at 2925–2923, 2857–2856, 813 cm^{-1} [24]. The mass spectra clearly show the main peaks value of two ligands, indenyl and 2-tetrahydrofurfuryl methoxide, of the two new complexes. The presence of $[Ln_2O_2]^+$ and $[Ln_2O]^+$ ions in the spectra evidently indicates the oxygen-bridging structure of the complexes. But the spectra do not show the molecular ions peaks and their relevant large fragments of $[Ln(\mu\text{-}OR)_2Ln]$ unit complexes, which show in the mass spectra of the corresponding binuclear bis(cyclopentadienyl) alkoxides [11,16]. This feature shows that the thermal stability of the title complexes is inferior to that of the corresponding cyclopentadienyl complexes. In fact, their decomposition temperature is much lower than those of cycopentadienyl complexes [7,11,16]. In view of the mass spectra data, there are the peaks of $[(C_9H_7)Ln]^+$, $[(C_9H_7)LnOCH_2]^+$, $[(C_9H_7)LnO]^+$ and $[LnO_2]^+$. This feature may suggest that dimeric $[(C_9H_7)_2Ln(\mu\text{-}OCH_2R)]_2$ complexes, in the vapor state, are easier to dissociate into monomeric structure than $[(Cp_2Ln(\mu\text{-}OR)]_2$ complex [11,16].

Description of the X-ray crystal structure of complex 1

The molecular structure of $[(C_9H_7)_2Nd(\mu,\eta^2—OCH_2R)]_2$ is shown in Fig. 1. There is a typical oxygen-bridging dimeric structure, which is similar to binuclear bis(cyclopentadienyl) lanthanide alkoxides [6,7,8,11], and two intramolecular five-membered chelate rings formed by coordination of tetrahydrofuran

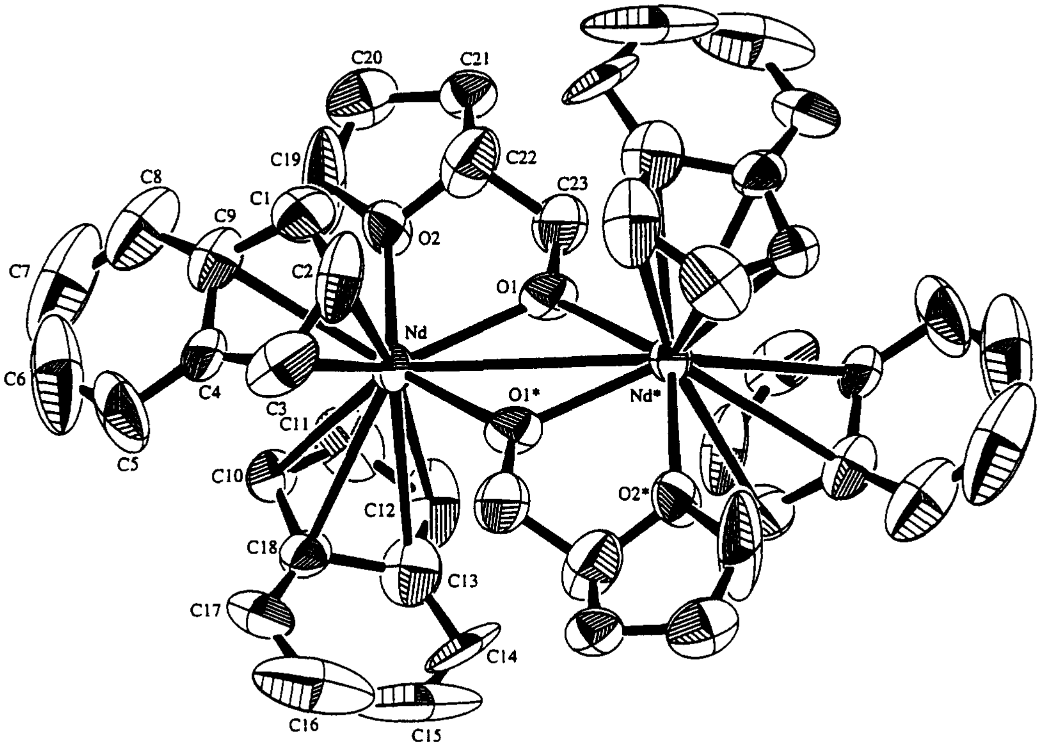


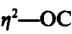
Fig. 1. The molecular structure of $[(C_9H_7)_2Ln(\mu,\eta^2\text{—}OCH_2\text{—}$⟨O⟩$)]_2$ with the hydrogen atom omitted for clarity.

rings in the molecular of complex Nd. The Nd atom is coordinated by two η^5-C_9H_7 ring centroids, two oxygen atoms of tetrahydrofurfuryl methoxide group and an oxygen atom of tetrahydrofuran ring of OCH_2R ligands, giving the central metal a coordination number of nine if the five-membered ring of η^5-C_9H_7 group is viewed as occupying three coordination sites. The coplanar bridging unit Nd_2O_2 is composed of two Nd atoms and two oxygen atoms of 2-tetrahydrofurfuryl methoxides. The oxygen atom of tetrahydrofuran ring, bridging oxygen, Nd atom and two C atoms of 2-tetrahydrofurfuryl methoxides ligands form a five-membered chelating ring, which is planar.

Selected bond distances and angles are listed in Table 2. The Nd—C (η^5-C_9H_7) distances are unexceptional, ranging from 2.71(2)–2.92(2) Å and average 2.81(2) Å, which is close to those of reported indenyl lanthanide complexes, $(C_9H_7)_3Nd \cdot THF$ [25], 2.81 Å $[Na(THF)_6]\{[(C_9H_7)_3Nd]_2(\mu\text{-}Cl)\}$ [23], 2.85 Å and $(C_9H_7)_3Gd \cdot THF$ [25], 2.80 Å. The Nd—O(1) (μ-OR′) bond distances are 2.30(1) and 2.31(1) Å, averaging 2.305(1) Å. Only a few indenyl alkoxide lanthanide complexes are known [9,12,26], and only the X-ray crystallographic characterization of dimeric $[(C_9H_7)Y(\mu\text{-}O^tBu)(O^tBu)]_2$ has been published [9,12]. Therefore, we compare some bonding parameters between the complex **1** and the related known dinuclear cyclopentadienyl alkoxide lanthanide complexes in Table 3. In view of data in Table 3, it is revealed that the length of the bridging Ln—O(1) of both diindenyl lanthanide alkoxide complex and biscyclopentadienyl lanthanide complexes are similar, ranging from 2.30–2.35 Å, when the difference in metallic ionic radii was taken into account [27,28].

In the bridging unit Nd_2O_2, the angles of Nd—O—Nd and O—Nd—O are 114.1(5) and 65.9(5)°, respectively, which are very different from the corresponding values (106 and 74°) [8,11,29] in analogous cyclopentadienyl lanthanides. We suppose that this variation in angles may be attributed to the chelating coordination bond Ln ← O(2) affection and the larger steric repulsion of 2-tetrahydrofurfuryl methoxide ligand, because the angles of Y—O—Y and O—Y—O in indenyl complex $[(C_9H_7)Y(\mu\text{-}O^tBu)(O^tBu)]_2$ is also 75.8 and 104.2° [9]. The angle of Cp—Ln—Cp is 129.96, which is close to the corresponding cyclopentadienyl complexes, ranging from 126 to 127° [8,11,29].

In the intramolecular five-membered chelating ring, the Nd—O(2) distance is 2.51(1) Å, which is slightly longer than the lengths of Nd—O(1) (bridging),

Table 2. Selected bond distances (Å) and angles (°) for $[(C_9H_7)_2Ln(\mu,\eta^2\text{—}OCH_2$$)]_2$

Distances (Å)			
Nd—Nd[a]	3.872(2)	Nd—O(1)	2.31(1)
Nd—O(1)[a]	2.30(1)	Nd—O(2)	2.51(1)
Nd—C(1)	2.77(2)	Nd—C(2)	2.77(2)
Nd—C(3)	2.75(2)	Nd—C(4)	2.91(2)
Nd—C(9)	2.90(2)	Nd—C(10)	2.72(2)
Nd—C(11)	2.71(2)	Nd—C(12)	2.81(2)
Nd—C(13)	2.92(2)	Nd—C(18)	2.84(2)
O(1)—C(23)	1.46(2)	O(2)—C(19)	1.39(2)
O(2)—C(22)	1.42(2)	C(1)—C(2)	1.37(3)
O(1)—C(9)	1.44(3)	C(2)—C(3)	1.39(3)
C(3)—C(4)	1.36(3)	C(4)—C(5)	1.35(3)
C(4)—C(9)	1.42(3)	C(5)—C(6)	1.33(4)
C(6)—C(7)	1.39(5)	C(7)—C(8)	1.31(4)
C(8)—C(9)	1.37(3)	C(10)—C(11)	1.37(3)
C(10)—C(18)	1.43(2)	C(11)—C(12)	1.42(3)
C(12)—C(13)	1.40(3)	C(13)—C(14)	1.37(3)
C(13)—C(18)	1.45(3)	C(14)—C(15)	1.28(5)
C(15)—C(16)	1.46(6)	C(16)—C(17)	1.34(4)
C(17)—C(18)	1.43(3)	C(19)—C(20)	1.36(3)
C(20)—C(21)	1.47(3)	C(21)—C(22)	1.56(3)
C(22)—C(23)	1.47(3)		
$C_9H_7(1)$[b]—Nd	2.550	$C_9H_7(2)$[b]—Nd	2.512
ring 3[b]—Nd	0.000		
Nd—O(1)—Nd[a]	114.1(5)	O(1)—Nd—O(1)[a]	65.9(5)
O(1)—Nd—O(2)	68.4(4)	O(1)[a]—Nd—O(2)	134.1(4)
Nd—O(1)—C(23)	117(1)	Nd[a]—O(1)—C(23)	128(1)
Nd—O(2)—C(19)	142(1)	Nd—O(2)—C(22)	112(1)
C(19)—O(2)—C(22)	104(1)		
O(2)—C(22)—C(21)	106(1)	O(2)—C(22)—C(23)	107(1)
O(1)—C(23)—C(22)	112(1)	C(21)—C(22)—C(23)	116(1)
C(2)—C(1)—C(9)	108(1)	C(2)—C(1)—C(3)	106(2)
C(2)—C(3)—C(4)	111(2)	C(3)—C(4)—C(9)	106(1)
C(1)—C(9)—C(4)	106(1)		
C(5)—C(4)—C(9)	120(2)	C(4)—C(5)—C(6)	114(3)
C(5)—C(6)—C(7)	128(4)	C(6)—C(7)—C(8)	115(4)
C(7)—C(8)—C(9)	121(3)	C(4)—C(9)—C(8)	119(2)
$C_9H_7(1)$—Nd—$C_9H_7(2)$	126.96	$C_9H_7(2)$—Nd—ring 3	25.18
$C_9H_7(1)$—Nd—ring 3	154.84	ring 3—ring 4[b]	11.35

[a] Represents atoms which are marked by asterisks in Fig. 1.

[b] $C_9H_7(1)$: C(1), C(2), C(3), C(4), C(9) ; $C_9H_7(2)$: C(10), C(11), C(12), C(13), C(18) ; ring 3 : Nd, O(1), C(23), C(22), O(2) ; ring 4 : O(2), C(19), C(20), C(21), C(22).

2.30(1) and 2.31(1) Å and close to weak bond, Nd—O(THF), [2.557(21) Å] in $(C_9H_7)_3Nd\cdot THF$ [25]. Probably owing to this feature, the bond between the Nd atom and the oxygen atom of tetrahydrofuran ring of tetrahydrofurfuryl ligand is a weak bond and it is weaker than the bridging, σ-Ln—O(1) bond. The remaining C—O bond distances of chelating ring, 1.42(2), 1.46(2) Å are normal C—O bond distances (1.43 Å). The length of C—C bond of five-membered ring is slightly shorter than a normal single C—C bond (1.54 Å).

In the η^5-C_9H_7 ring, the distances of all 10 C—C bonds and all inner angles are similar to the $(C_9H_7)_3Nd\cdot THF$ [25].

In a short word, complex Nd (1) is dimer bridged by the oxygen atoms of tetrahydrofurfuryl methoxide ligands. The intramolecular five-membered chelate rings formed by chelating coordination of tetrahydrofuran rings of tetrahydrofurfuryl methoxide ligands exist in it.

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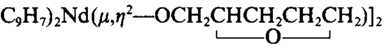
Table 3. Comparative crystallographic data in some known organolanthanide alkoxides

Complex[a]	**1**	**2**	**3**	**4**	**5**	**6**
Ln—O (Å)$_{av}$	2.305(1)	2.236(7)	2.209(11)	2.18(1)	2.197(7)	2.200(5)
Ln—C$_{av}$ (Å)	2.81(2)	2.69(3)	2.643(19)	2.59(2)	2.60(2)	2.601(16)
ΔLn^{3+} (Å)[b]	0.000	0.115	0.137	0.137	0.137	0.137
Corrected Ln—O (Å)$_{av}$	2.305(1)	2.351(5)	2.346(11)	2.317(1)	2.334(7)	2.337(5)
Corrected Ln—C$_{av}$ (Å)	2.81(2)	2.805(3)	2.780(19)	2.727(2)	2.737(2)	2.738(16)
Ln—Ln (Å)	3.872(2)	3.524(2)	3.5324(15)	3.483(3)	3.492(1)	3.581(11)
O—Ln—O (°)	65.9(5)	75.8(2)	73.7(2)	74.0(4)	74.7(3)	73.8(2)
Ln—O—Ln (°)	114.1(5)	104.2(2)	106.3(2)	106.0(4)	105.3(3)	106.2(2)
Cp—Ln—Cp[c] (°)	129.96	—	127.11(4)	127.3	126.2	126.2
Ref.	this work	[9]	[8]	[11]	[11]	[29]

[a] Complex **1**: 
$(C_9H_7)_2Nd(\mu,\eta^2\text{—}OCH_2\underbrace{CHCH_2CH_2CH_2}_{O})]_2$

Complex **2**: $[C_9H_7)Y(\mu\text{—}O^tBu)(O^tBu)]$

Complex **3**: $[Cp_2Yb(\mu\text{—}OCH_2CH{=}CHCH_3)]_2$

Complex **4**: $[Cp_2Yb(\mu\text{—}OCH_2CH_2CH_2CH_2CH_3)]_2$

Complex **5**: $[Cp_2Yb(\mu\text{—}OCH_2CH_2CH(Me)_2)]_2$

Complex **6**: $[Cp_2Yb(\mu\text{—}OCH{=}CH{=}CH_2)]_2$

[b] ΔLn^{3+} = Separation between the radii of Nd^{3+} ion and related metallic ions [27].

[c] Cp: Centroid of η^5-C_9H_7 ring.

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