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Carbon-Bridged Bis(phenolato)lanthanide Alkoxides: Syntheses, Structures, and Their Application in the Controlled Polymerization of ϵ-Caprolactone

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A convenient method for the synthesis of lanthanide alkoxo complexes supported by a carbon-bridged bis(phenolate) ligand 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxo) ($MBMP^{2-}$) is described. The reaction of $(C_5H_5)_3Nd$ with $MBMPH_2$ in a 1:1 molar ratio in THF gave the bis(phenolato)lanthanide complex $(C_5H_5)Nd(MBMP)(THF)_2$ (**1**) in a nearly quantitative yield. Complex **1** further reacted with 1 equiv of 2-propanol in THF to yield the bis(phenolato)lanthanide isopropoxide $[(MBMP)_2Nd(\mu\text{-}OPr^i)(THF)_2]_2$ (**2**) in high yield. Complex **2** can also be synthesized by the direct reaction of $(C_5H_5)_3Nd$ with $MBMPH_2$ in a 1:1 molar ratio and then with 1 equiv of 2-propanol in situ in THF. Thus, the analogue bis(phenolato)lanthanide alkoxides $[(MBMP)_2Ln(\mu\text{-}OR)(THF)_2]_2$ [R = Pr^i, Ln = Yb (**3**); R = Me, Ln = Nd (**4**), Yb (**5**); R = CH_2Ph, Ln = Nd (**6**), Yb (**7**)] were obtained by the reactions of $(C_5H_5)_3Ln$ (Ln = Nd, Yb) with $MBMPH_2$ and then with 2-propanol, methanol, or benzyl alcohol, respectively. The ytterbium complex $\{[(MBMP)_2Yb(THF)_2]_2(\mu\text{-}OCH_2Ph)(\mu\text{-}OH)\}$ (**8**) was also isolated as a byproduct. The single-crystal structural analyses of complexes **1**–**3** and **8** revealed that the coordination geometry around lanthanide metal can be best described as a distorted tetrahedron in complex **1** and as a distorted octahedron in complexes **2**, **3**, and **8**. A O–H···Yb agostic interaction was observed in complex **8**. Complexes **2**–**7** were shown to be efficient catalysts for the controlled polymerization of ϵ-caprolactone.

Introduction

In recent years, the application of bridged bis(phenols) as ancillary ligands in main group and transition metal coordination chemistry has received considerable attention.[1,2] This is because bridged bis(phenols), as dianionic ligands, have the advantage of avoiding ligand redistribution reactions and providing a stereochemically rigid framework for the metal center that could affect stereospecific transformations. Furthermore, some of these complexes have shown interesting catalytic activity. For example, the bridged bis(phenolato)-aluminum complexes can catalyze effectively the controlled polymerization of lactide,[1a,b] propylene oxide,[1e] and ϵ-caprolactone[1d,f−h] and the corresponding group IV metal complexes can catalyze the polymerization of α-olefins and the specific polymerization of styrene in the presence of cocatalysts,[2a−k] as well as the living anionic polymerization of ϵ-caprolactone.[2l] However, the application of bridged bis(phenolates) in lanthanide chemistry has been quite limited, although some of these complexes have been found to be efficient initiators

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for the ring-opening polymerization of ϵ-caprolactone and lactide.[3]

Recently, we became interested in studying the synthesis and reactivity of lanthanide complexes that are supported by the bulky bridged bis(phenolate) ligands. In our earlier work, the new divalent lanthanide complexes based on carbon-bridged bis(phenolate ligands), 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxo) ($MBMP^{2-}$) and 2,2′-ethylidenebis-(4,6-di-*tert*-butylphenoxo) ($EDBP^{2-}$), were synthesized and found to be active for the ring-opening polymerization (ROP) of ϵ-caprolactone and cyclic carbonate. However, these complexes showed poor solubility even in THF, as a result of which the polymerizations were not well-controlled.[3i] As is well-known for systems with divalent complexes as the precatalyst, the real active species are the trivalent lanthanide complexes, which are formed from the single-electron redox reaction of divalent lanthanide complexes with monomer in situ.[4] If the formation of the central species is rate-limiting, the polymerization will not be well-controlled. Hence, we tried to synthesize the corresponding trivalent bis(phenolato)-lanthanide alkoxides and examined their catalytic behavior in the ROP of ϵ-caprolactone. We now report that the new trivalent alkoxolanthanide complexes based on the carbon-bridged bis(phenolate) ligand $MBMP^{2-}$ can be synthesized by a proton exchange reaction using $(C_5H_5)_3Ln$ as starting materials and these complexes can efficiently initiate the controlled polymerization of ϵ-caprolactone.

Experimental Section

General Procedures. All manipulations were performed under argon, using the standard Schlenk techniques. THF and toluene were distilled from sodium benzophenone ketyl before use. $(C_5H_5)_3Ln$ was prepared according to a literature procedure.[5] ϵ-Caprolactone was purchased from Acros, dried over CaH_2 for 48 h, and distilled under reduced pressure. 2-Propanol, methanol, and benzoic alcohol were dried with small amount of sodium and distilled before use. $MBMPH_2$ was commercially available. Lanthanide analyses were performed by EDTA titration with an xylenol orange indicator and a hexamine buffer.[6] Carbon and hydrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FT-IR spectrometer as KBr pellets. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges. Molecular weights and molecular weight distributions were determined against polystyrene standards by gel permeation chromatography (GPC) at 30 °C with a Water 1515 apparatus with three HR columns (HR-1, HR-2, and HR-4) using THF as the eluent.

$(C_5H_5)Nd(MBMP)(THF)_2$ (1). A THF solution (25 mL) containing $MBMPH_2$ (1.12 g, 3.30 mmol) was slowly added to a THF solution of $(C_5H_5)_3Nd$ (40 mL, 3.30 mmol). The reaction mixture was stirred for 1 h at 40 °C, and the solvent was removed under vacuum. Toluene (80 mL) was added to extract the product, and pale-blue microcrystals were obtained in a nearly quantitative yield (2.15 g) from 10 mL of toluene at −10 °C. Mp: 188−190 °C (dec). Anal. Calcd for $C_{36}H_{51}O_4Nd$: C, 62.48; H, 7.43; Nd, 20.84. Found: C, 62.04; H, 7.38; Nd, 20.58. IR (KBr, cm^{-1}): 2955 (s), 2916 (s), 2870 (s), 1605 (m), 1458 (vs), 1389 (s), 1362 (s), 1250 (s), 1204 (s), 1130 (m), 1045 (m), 914 (w), 864 (m), 729 (m). The crystals suitable for an X-ray diffraction analysis were obtained from the concentrated THF solution.

$[(MBMP)Nd(\mu\text{-}OPr^{i}{}_2)(THF)_2]_2$ (2). Method A. To a THF solution (35 mL) of complex **1** (1.51 g, 2.18 mmol) was added 2-propanol (0.16 mL, 2.18 mmol) by syringe. The reaction mixture was stirred overnight at room temperature, and the solvent was removed under vacuum. THF (60 mL) was added to extract the product, and pale-blue microcrystals were obtained from the concentrated THF solution (20 mL) at room temperature (1.28 g, 86% based on Nd). Mp: 166−168 °C (dec). Anal. Calcd for $C_{68}H_{106}O_{10}Nd_2$: C, 59.53; H, 7.79; Nd, 21.02. Found: C, 59.12; H, 7.53; Nd, 20.47. IR (KBr, cm^{-1}): 2955 (s), 2917 (m), 2870 (m), 1605 (w), 1462 (s), 1435 (s), 1385 (m), 1253 (s), 1138 (w), 1049 (w), 860 (w), 790 (w). The crystals suitable for an X-ray diffraction analysis were obtained by slow cooling of a hot toluene solution.

Method B. A THF solution (25 mL) of $MBMPH_2$ (1.19 g, 3.45 mmol) was slowly added to a THF solution of $(C_5H_5)_3Nd$ (42 mL, 3.45 mmol) at 40 °C. After the solution was stirred for 1 h at 40 °C, 2-propanol (0.26 mL) was added by syringe. The mixture was stirred overnight, and then the solvent was evaporated under reduced pressure. THF was added to extract the product, and pale-blue microcrystals were obtained from the concentrated THF solution (1.94 g, 82%).

$[(MBMP)Yb(\mu\text{-}OPr^{i}{}_2)(THF)_2]_2$ (3). The synthesis of complex **3** was carried out in the same way as that described for complex **2** (method B), but $(C_5H_5)_3Yb$ (3.05 mmol) was used instead of $(C_5H_5)_3Nd$. A 1.77 g amount of orange-yellow microcrystals was obtained from a concentrated THF solution (12 mL) (81% based on Yb). Mp: 109−111 °C (dec). Anal. Calcd for $C_{68}H_{106}O_{10}Yb_2$: C, 57.13; H, 7.47; Yb, 24.21. Found: C, 57.43; H, 7.13; Yb, 23.83. IR (KBr, cm^{-1}): 2955 (s), 2915 (s), 2871 (s), 1605 (w), 1468 (s), 1441 (s), 1389 (m), 1232 (m), 1132 (w), 861 (m), 769 (w). The crystals suitable for an X-ray diffraction analysis were obtained by slowly cooling the hot THF solution.

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Table 1. Crystallographic Data for Complexes **1**−**3** and **8**

param	**1**·THF	**2**·2THF	**3**·2THF	**8**·2THF
formula	$C_{40}H_{59}NdO_5$	$C_{76}H_{122}Nd_2O_{12}$	$C_{76}H_{122}O_{12}Yb_2$	$C_{77}H_{116}O_{12}Yb_2$
fw	764.11	1516.27	1573.82	1579.78
T (K)	193(2)	193(2)	193(2)	193(2)
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
unit cell				
a (Å)	8.7082(3)	13.723(5)	13.335(1)	14.4866(3)
b (Å)	25.238(1)	17.247(6)	17.830(1)	15.2484(7)
c (Å)	35.48(6)	16.279(6)	15.772(1)	20.279(1)
α (deg)	90	90	90	87.215(5)
β (deg)	90.755(1)	93.800(4)	92.996(4)	70.035(4)
γ (deg)	90	90	90	66.052(4)
V (Å^3)	7798.2(5)	3844(2)	3744.7(5)	3826.6(3)
Z	8	2	2	2
D_{calcd} (g cm^{-3})	1.302	1.310	1.396	1.371
μ (mm^{-1})	1.371	1.390	2.539	2.485
F(000)	3192	1588	1628	1628
cryst size (mm)	0.48 × 0.34 × 0.25	0.51 × 0.25 × 0.20	0.55 × 0.50 × 0.25	0.40 × 0.38 × 0.15
$\theta_{\max}$ (deg)	25.35	27.48	27.48	25.35
collcd reflcns	66 315	30 774	36 833	38 052
unique reflcns	14 215	8784	8538	13 950
obsd reflcns [$I \geq 2.0\sigma(I)$]	12 919	5931	8170	11 453
no. of variables	846	442	391	791
GOF	1.148	1.004	1223	1.112
R	0.0436	0.0660	0.0414	0.0443
wR	0.0914	0.1340	0.0899	0.0907

[(MBMP)Nd(μ-OMe)(THF)$_2$]$_2$ (4). To a THF solution of $(C_5H_5)_3Nd$ (31 mL, 2.54 mmol) was slowly added at 40 °C a THF solution (20 mL) of $MBMPH_2$ (0.86 g, 2.54 mmol). After the solution was stirred for 1 h at 40 °C, methanol (0.10 mL) was added by syringe. The mixture was stirred overnight at room temperature, and then centrifugation was used to remove the solution. Complex **4** was obtained as pale-blue microcrystals. The second crop was isolated from the concentrated THF solution (25 mL) (1.55 g, 93% based on Nd). Mp: 182−184 °C (dec). Anal. Calcd for $C_{64}H_{98}O_{10}Nd_2$: C, 58.41; H, 7.51; Nd, 21.92. Found: C, 58.29; H, 7.23; Nd, 21.72. IR (KBr, cm^{-1}): 2955 (s), 2916 (s), 1628 (w), 1466 (s), 1435 (s), 1385 (m), 1254 (m), 1049 (m), 860 (m).

[(MBMP)Yb(μ-OMe)(THF)$_2$]$_2$ (5). The synthesis of complex **5** was carried out in the same way as that described for complex **4**, but $(C_5H_5)_3Yb$ was used instead of $(C_5H_5)_3Nd$. A 1.82 g amount of orange-yellow microcrystals was obtained from the concentrated THF solution (20 mL) (85% based on Yb). Mp: 128−130 °C (dec). Anal. Calcd for $C_{64}H_{98}O_{10}Yb_2$: C, 55.96; H, 7.19; Yb, 25.20. Found: C, 55.46; H, 6.98; Yb, 24.83. IR (KBr, cm^{-1}): 2956 (s), 2916 (s), 1627 (w), 1466 (s), 1434 (s), 1385 (m), 1252 (m), 1050 (m), 861 (m).

[(MBMP)Nd(μ-OCH$_2$Ph)(THF)$_2$]$_2$ (6). The synthesis of complex **6** was carried out in the same way as that described for complex **2**, but benzyl alcohol was used instead of 2-propanol. A 1.42 g amount of pale-blue microcrystals was obtained from the concentrated THF solution (18 mL) (83% based on Nd). Mp: 165−167 °C (dec). Anal. Calcd for $C_{76}H_{106}O_{10}Nd_2$: C, 62.18; H, 7.28; Nd, 19.65. Found: C, 61.74; H, 6.96; Nd, 19.82. IR (KBr, cm^{-1}): 2954 (s), 1616 (m), 1476 (s), 1444 (s), 1379 (m), 1269 (s), 1033 (s), 879 (m).

[(MBMP)Yb(μ-OCH$_2$Ph)(THF)$_2$]$_2$ (7). The synthesis of complex **7** was carried out in the same way as that described for complex **3**, but benzyl alcohol was used instead of 2-propanol. A 1.38 g amount of orange-yellow microcrystals was obtained from the concentrated THF solution (15 mL) (80% based on Yb). Mp: 133−135 °C (dec). Anal. Calcd for $C_{76}H_{106}O_{10}Yb_2$: C, 59.83; H, 7.00; Yb, 22.68. Found: C, 59.53; H, 6.77; Yb, 22.35. IR (KBr, cm^{-1}): 2954 (s), 1615 (w), 1476 (s), 1443 (s), 1378 (m), 1269 (s), 1032 (s), 879 (m).

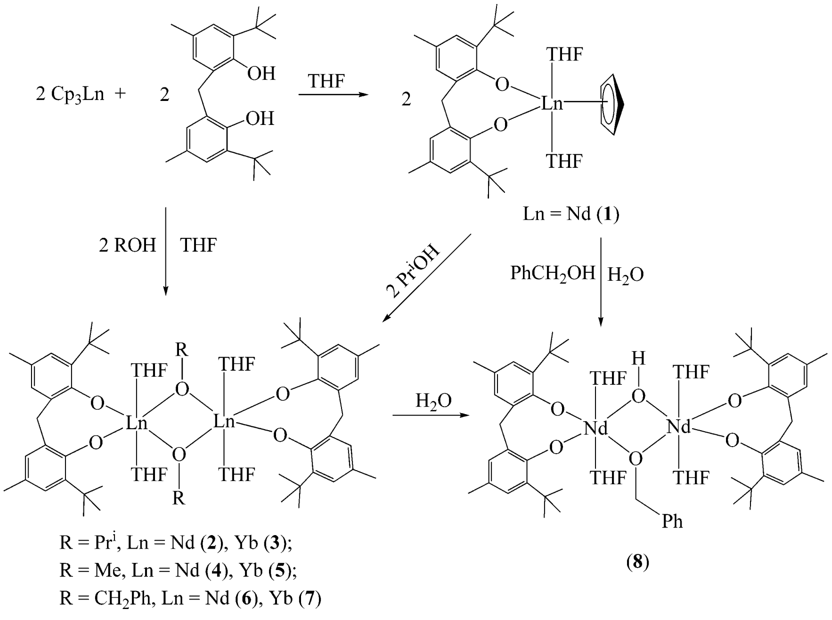
{[(MBMP)Yb(THF)$_2$]$_2$(μ-OCH$_2$Ph)(μ-OH)} (8). During synthesis of complex **7**, a small amount of orange crystals (complex **8**) was isolated before the THF was removed. IR (KBr, cm^{-1}): 3383 (s), 2955 (s), 1620 (m), 1435 (s), 1385 (m), 1270 (s), 1165 (m), 1035 (s), 887 (m), 698 (m).

Typical Procedure for the Polymerization Reaction. The procedures for the polymerization of ϵ-caprolactone initiated by complexes **2**−**7** were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with a solution of initiator in toluene. To this solution was added desired amount of ϵ-caprolactone by syringe. The contents of the flask were then stirred vigorously at 50 °C for desired time, during which time an increase in viscosity was observed. The reaction mixture was quenched by the addition of 1 M HCl−ethanol solution and then poured into methanol to precipitate the polymer, which was dried under vacuum and weighed.

X-ray Crystallography. Suitable single crystals of complexes **1**−**3** and **8** were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo Kα radiation ($\lambda = 0.710\ 70$ Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. The hydrogen atom on the hydroxyl group (H(6)) in complex **8** was located according to the difference Fourier map and was refined isotropically. The other hydrogen atoms in these complexes were all generated geometrically (C−H bond lengths fixed at 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELEXL-97 (for complexes **1**, **3**, and **7**) and CRYSTALS (for complex **2**) programs.

Scheme 1



Results and Discussion

Synthesis and Characterization of Carbon-Bridged Bis(phenolato)lanthanide Complexes. Since the mono-bis(phenolato)lanthanide chlorides (MBMP)LnCl(THF)$_x$, the potential precursors for the synthesis of bis(phenolato)lanthanide derivatives, cannot be prepared by the general salt metathesis reaction of anhydrous $LnCl_3$ with $MBMPNa_2$ in a 1:1 molar ratio,[7] we tried to synthesize the neutral bis(phenolato)lanthanide complexes by a proton exchange reaction. $MBMPH_2$ in THF was added to the THF solution of $(C_5H_5)_3Nd$ in a 1:1 molar ratio at 40 °C. The color of the solution changed immediately from purple-blue to yellow-green. After workup, blue microcrystals were obtained from the toluene solution. The composition of complex **1** was established as $(C_5H_5)Nd(MBMP)(THF)_2$ by elemental analyses (C, H, and Nd) and single-crystal structure determination (Scheme 1). Complex **1** reacted with 1 equiv of 2-propanol in THF to give complex **2**, after workup, as pale-blue crystals (Scheme 1). Furthermore, complex **2** can also be synthesized by the direct reaction of $(C_5H_5)_3Nd$ with $MBMPH_2$ in a 1:1 molar ratio and then with 1 equiv of 2-propanol in situ. Therefore, the carbon-bridged bis(phenolato)lanthanide alkoxo complexes $[(MBMP)Ln(\mu\text{-}OR)_2(THF)_2]$ (R = Pr^i, Ln = Yb (**3**); R = Me, Ln = Nd (**4**), Yb (**5**); R = CH_2Ph, Ln = Nd (**6**), Yb (**7**)) can be conveniently prepared by a proton exchange reaction using $(C_5H_5)_3Ln$ as starting materials (Scheme 1). During the synthesis of complex **7**, a small amount of $\{[(MBMP)Yb(THF)_2]_2(\mu\text{-}OCH_2Ph)(\mu\text{-}OH)\}$ (**8**) was concomitantly isolated as orange crystals as a byproduct. The formation of complex **8** contributed to the presence of trace water in the reaction mixture (Scheme 1). Complexes **2**, **3**, **6**, and **7** are moderately soluble in THF and slightly soluble in toluene, while complexes **4** and **5** are slightly soluble in THF. Due to their limited solubility in THF, complexes **4** and **5** precipitated immediately from THF solution when methanol was added to the reaction systems. Among these complexes, the solubility of the ytterbium compounds is larger than that of the corresponding neodymium species. These complexes gave satisfactory elemental analyses (C, H, and Ln), and their IR spectra showed the characteristic absorptions of the aryloxo group. However, these complexes did not provide any resolvable ^1H NMR spectra, due to the strong paramagnetism of the central metal ions. The definitive structures of complexes **1**−**3** and **8** were determined by single-crystal structure analysis (see below). We proposed that complexes **4**−**7** exist as a dimer in the solid state according to the structures of the analogous complexes **2** and **3**. Attempts to determine their definitive structures were unsuccessful due to solvent loss and the deterioration in crystal quality.

Crystal Structure Analyses. Crystals of complex **1** suitable for an X-ray structure determination were obtained from the concentrated THF solution. Complex **1** crystallizes with two crystallographically independent but chemically similar molecules (**1a**,**b**) in the unit cell; the selected bond lengths and angles of **1a** are provided in Table 2. An ORTEP of molecule **1a** is depicted in Figure 1. Complex **1** has a monomeric structure; neodymium atom is coordinated by a cyclopentadienyl group, two oxygen atoms from one MBMP group, and two oxygen atoms from two THF molecules. The coordination number of the central metal is 7, and the coordination geometry at the neodymium atom can be best described as a distorted trigonal bipyramid if the cyclopentadienyl group is considered to occupy one coordination site.

The Nd−C(Cp) bond lengths range from 2.738(5) to 2.822(5) Å, giving an average of 2.784(6) Å, which is comparable well with that in $(C_5H_5)NdCl_2(THF)_3$.[8] The Nd−O(Ar) bond lengths of 2.165(3) and 2.181(3) Å are comparable with those in $[(ArO)_3Nd(THF)]$ (ArO = 2,6-di-*tert*-butyl-4-methylphenolate) (2.176 Å),[9] $[Nd(Odpp)_3(DME)]$

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[7] Xu, X. P.; Ma, M. T.; Yao, Y. M.; Zhang, Y.; Shen, Q. *Eur. J. Inorg. Chem.* **2005**, 676.

Table 2. Selected Bond Lengths and Bond Angles in Complexes **1**, **2**, **3**, and **8**

	1a	**2**	**3**	**8**
Ln(1)−O(1)	2.165(3)	2.228(5)	2.131(3)	2.109(3)
Ln(1)−O(2)	2.181(3)	2.203(5)	2.108(3)	2.091(3)
Ln(1)−O(3)	2.476(3)	2.329(5)	2.226(3)	2.332(4)
Ln(1)−O(3A)		2.392(4)	2.262(3)	
Ln(1)−O(4)	2.525(3)	2.582(5)	2.422(3)	2.360(4)
Ln(1)−O(5)		2.556(5)	2.435(3)	2.268(3)
Ln(1)−O(6)				2.211(4)
Ln(1)−C(24A)		3.101(7)	3.080(4)	
Ln(1)−H(6)				2.71(6)
C(1)−O(1)	1.330(5)	1.342(8)	1.349(5)	1.351(6)
C(7)−O(2)	1.332(5)	1.347(8)	1.348(5)	1.335(6)
O(1)−Ln(1)−O(2)	85.92(12)	96.1(2)	99.82(10)	96.34(14)
O(3)−Ln(1)−O(4)	75.40(12)	96.8(2)	98.00(10)	171.99(13)
O(4)−Ln(1)−O(5)		76.592)	75.17(10)	94.95(13)
O(5)−Ln(1)−O(6)				69.97(14)
Ln(1)−O(1)−C(1)	151.9(3)	141.8(4)	141.0(2)	151.7(3)
Ln(1)−O(2)−C(7)	151.7(3)	154.9(4)	151.6(2)	151.9(3)

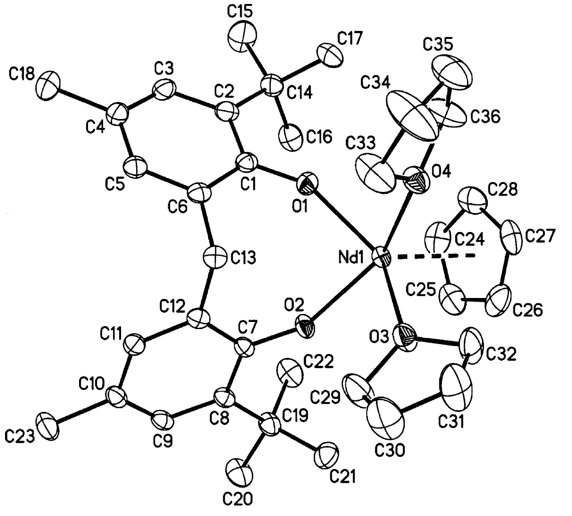

Figure 1. ORTEP diagram of complex **1** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

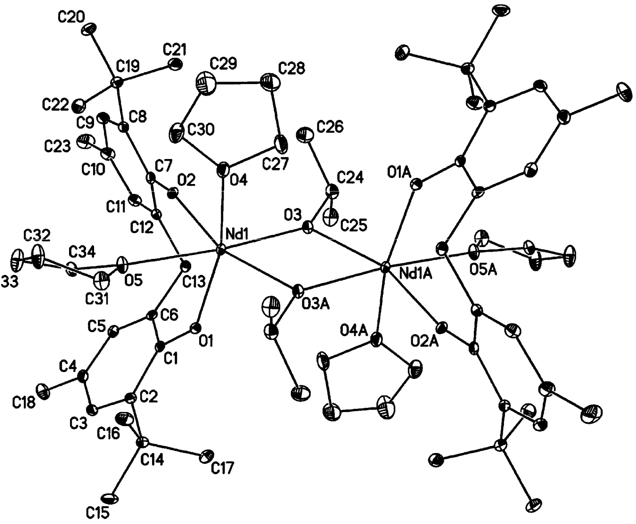

Figure 2. ORTEP diagram of complex **2** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity.

(2.191 Å) (Odpp = 2,6-diphenylphenolate),[10] $[Nd(Odpp)_3(THF)_2]$ (2.190 Å),[11] $[Nd(Odpp)_3(THF)]$ (2.193 Å),[11] and $Nd(Odpp)_3$ (2.169 Å)[11] but slightly shorter than those in $[Na(THF)_6][Nd(ArO)_4]$ (2.230 Å)[9] and $K[Nd(OC_6H_3Pr^i{}_2\text{-}2,6)$ (2.211 Å).[12] The C−O distances of the phenolate ligands of 1.330(5) and 1.332(5) Å, respectively, are apparently shorter than the single bond length, reflecting substantial electron delocalization from the oxygen into the aromatic rings. The bite angle O(1)−Nd−O(2) of 85.9(1)° for the bis(phenolate) ligand is comparable with those found in $[La\{1,1'\text{-}(2\text{-}OC_6H_2\text{-}t\text{Bu}_2\text{-}3,5)_2\}\{CH(SiMe_3)_2\}(THF)_3]$ (88.1(3)°)[3a] and $[Ln(1,1'\text{-}(2\text{-}OC_6H\text{-}t\text{Bu-}3\text{-}Me_2\text{-}5,6)_2)\{N(SiHMe_2)_2\}(THF)]_2$ (Ln = Y (88.79(6)°), La (88.83(7)°)).[3b] The Nd(1)−O(1)−C(1) and Nd(1)−O(2)−C(7) bond angles are 151.9(3) and 151.7(3)°, respectively, which are similar to the corresponding bond angles in $K[Nd(OC_6H_3\text{-}i\text{Pr}_2\text{-}2,6)_4]$.[12]

Crystals of complexes **2** and **3** suitable for an X-ray structure determination were obtained by slow cooling of the hot toluene solution. Their molecular structural diagrams, which are centrosymmetric, are shown in Figures 2 and 3 with their selected bond lengths and bond angles listed in Table 2. Complexes **2** and **3** are isostructural. The structure shows a dimeric feature containing a Ln_2O_2 core bridging through the oxygen atoms of the isopropoxy groups. The two bridging oxygen atoms and two lanthanide atoms are exactly coplanar as required by the crystallographic symmetry. The central metal atom is six-coordinated by one bis(phenolate) ligand, two isopropoxy groups, and two THF molecules in a distorted octahedron. O(1) and O(3)−O(5) can be considered to occupy equatorial positions within the octahedron about the lanthanide center with ΣO−Ln−O = 360.0° for complex **2** and 359.5° for complex **3**. O(2) and O(3A) occupy axial positions, and the O(2)−Ln−O(3A) angle is distorted away from the idealized 180° to 162.4(2)° for complex **2** and 164.4(1)° for complex **3**.

In complexes **2** and **3**, the average Nd−O(Ar) and Yb−O(Ar) bond lengths of 2.215(6) and 2.119(3) Å, respectively, are in accordance with the corresponding bond lengths observed in complex **1** and those (aryloxo)lanthanide complexes mentioned above when the difference in ionic radii is considered. Two isopropoxy groups are unsymmetrically coordinated to the central metal atoms with the deviation of 0.063 Å for complex **2** and 0.036 Å for complex **3**, respectively. The $Ln-O(Pr^i)$ bond lengths in complexes **2** and **3** are comparable with the bond lengths of the bridging Ln−O(R) bonds reported in $[(C_5H_5)_2Lu(\mu\text{-}OCH_2CH_2CH_2CH_2Ph)]_2$,[13] $[(Me_3CC_5H_4)_2Ce(\mu\text{-}OPr^i)]_2$,[14] and $[(C_5H_5)_2Yb(\mu\text{-}OPr)]_2$,[15] when the difference in metallic ion radii is

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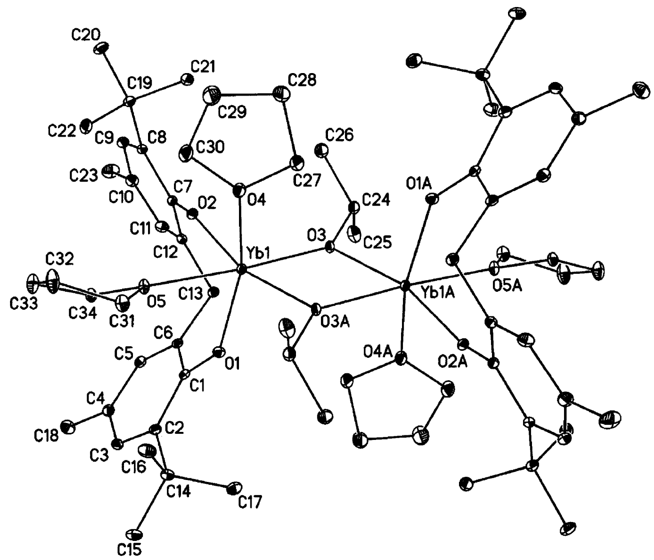

Figure 3. ORTEP diagram of complex **3** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity.

considered. It is worth noting that there is an electostatic interaction of the α-carbon atom of one isopropoxy group with the central metal atom. The Ln$-$C(24A) bond lengths are 3.101(7) Å for complex **2** and 3.080(4) Å for complex **3**, respectively, which are comparable to those of 3.067(5) Å for η^3-diketiminate bonding in (CH$_3$C$_5$H$_4$)[(DIPPh)$_2$-nacnac]YbCl ((DIPPh)$_2$nacnac = *N*,*N*-diisopropylphenyl-2,4-pentanediimine anion),[16] 2.986(6) and 3.180(9) Å for bridging η^2-C$_5$H$_5$ bonding in (C$_5$Me$_5$)$_2$Sm(μ-C$_5$H$_5$)Sm(C$_5$Me$_5$)$_2$,[17] and 2.814(4) to 3.148(6) Å for chelating η^6-,η^1-Ph-Yb bonding in [Yb(Odpp)$_3$]$_2$ (Odpp = 2,6-diphenylphenolate),[18] respectively. The bite angles for O(1)$-$Ln$-$O(2) (96.1(2)° for complex **2**, 99.8(1)° for complex **3**) are slightly larger than those found in [Ln(1,1′-(2-OC$_6$H-*t*Bu-3-Me$_2$-5,6)$_2$)-{N(SiHMe$_2$)$_2$}(THF)]$_2$[3b] and [La{1,1′-(2-OC$_6$H$_2$-*t*Bu$_2$-3,5)$_2$}-{CH(SiMe$_3$)$_2$}(THF)$_3$].[3a] The Ln(1)$-$O(2)$-$C(7) bond angles are slightly larger than the Ln(1)$-$O(1)$-$C(1) angle but compare well with those in complex **1**. The more acute Ln(1)$-$O(1)$-$C(1) bond angle can be attributed to the existence of Ln$-$C(24A) electrostatic interaction.

The molecular structural diagram of complex **8** is shown in Figure 4, and its selected bond lengths and bond angles are listed in Table 2. Complex **8** is a dinuclear complex with both ytterbium atoms coordinated by a MBMP^{2-} group and two THF molecules and bridged by one benzyloxy and one hydroxyl group. Each ytterbium atom is six-coordinated in a distorted octahedron, with two oxygen atoms from bis(phenolate) and two bridging oxygen atoms forming the equatorial plane and the two oxygen atoms from the THF molecules occupying the axial positions. Unlike those in complexes **2** and **3**, the benzyloxy group and the hydroxyl group are symmetrically coordinated to the ytterbium atoms with a maximum deviation of 0.01 Å.

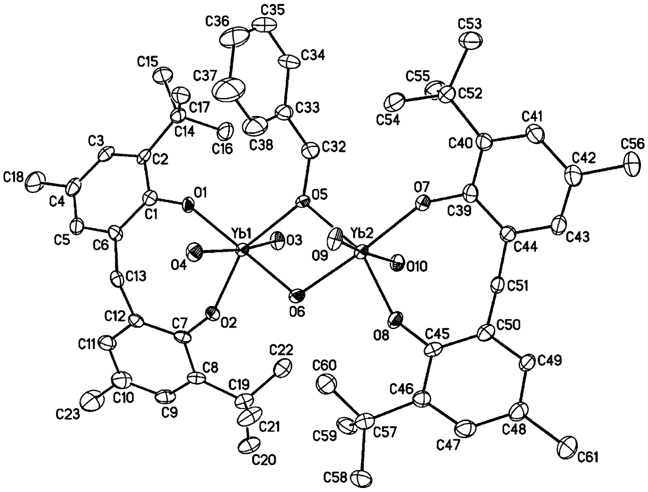

Figure 4. ORTEP diagram of complex **8** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Carbon atoms of THF molecules (O3, O4, O9, and O10) and hydrogen atoms are omitted for clarity.

The averaged Yb$-$O(Ar) and Yb$-$O(Bn) bond length of 2.100(3) and 2.268(3) Å are similar to the corresponding bond lengths in complex **3**. The Yb$-$O(H) bond length of 2.211(4) Å is in accordance with that found in other organolanthanide hydroxides.[19] The most remarkable feature of the structure of complex **8** is that there is remote O$-$H$\cdots$Yb interaction involving the hydroxide hydrogen atom. This Yb(1)$-$H(6) bond length of 2.71(6) Å is significantly longer than the Ln$-$H bond length in most of the organolanthanide hydrides,[20-23] but it accords with the Lu(1)$-$H(2) of 2.70(5) Å in [(C$_5$Me$_4$SiMe$_3$)LuH$_2$]$_4$,[23] Y(1)$-$H(16e) of 2.935(6) Å in (C$_5$Me$_5$)Y(OC$_6$H$_3{}^t$Bu$_2$)CH(SiMe$_3$)$_2$,[24] Lu$-$H(191) of 2.74(9) Å in [Me$_2$Si(C$_5$H$_4$)(C$_5$Me$_4$)]LuCH(SiMe$_3$)$_2$,[25] and Lu(1)$-$H(2) of 2.66(2) Å in *rac*-[Me$_2$Si(2-Me-Benz-Ind)$_2$]LuN(SiHMe$_2$),[26] in which the C(Si)$-$H$\cdots$Ln agostic interaction was considered indubitably to exist.

Controlled Polymerization of ϵ-Caprolactone Catalyzed by Complexes 2−7. The aliphatic polyesters, such as poly(ϵ-caprolactone) (PCL) and poly(lactide) (PLA), and their copolymers have received wide application in the medical field as biodegradable surgical sutures or as a delivery medium for controlled release of drugs due to their biodegradable, biocompatible, and permeable properties.[27] The

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Scheme 2

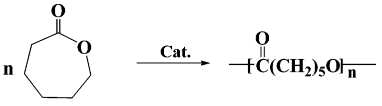

Table 3. Polymerization of e-Caprolactone Initiated by Complexes **2**−**7**[a]

run	initiator	$[M]_0/[I]_0$ (molar ratio)	*t* (h)	conversn (%)	M_n (10^{-4}) calcd[b]	M_n (10^{-4}) obsd[c]	PDI
1	**2**	400	1	100	4.56	3.65	1.26
2	**2**	600	1	100	6.84	5.23	1.14
3	**3**	400	1	15	0.68	0.65	1.19
4	**3**	400	2	31	1.41	1.19	1.13
5	**3**	400	4	51	2.32	1.76	1.23
6	**3**	400	7.5	88	4.01	2.95	1.16
7	**3**	400	14	97	4.42	3.19	1.27
8	**3**	400	26	100	4.56	3.77	1.29
9[d]	**3**	400	73.5	50	2.28	1.61	1.18
10	**4**	400	1	100	4.56	5.75	1.25
11	**4**	600	1	100	6.84	6.94	1.29
12	**5**	400	4	53	2.42	1.89	1.17
13	**5**	400	8	83	3.78	2.56	1.25
14	**6**	400	1	100	4.56	4.71	1.16
15	**6**	600	1	100	6.84	6.40	1.25
16	**7**	400	4	49	2.23	1.71	1.18
17	**7**	400	8	78	3.56	2.21	1.22

[a] Polymerization conditions: toluene as solvent, $V_{sol.}/V_{[M]} = 4:1$, $T = 50$ °C. [b] M_n(calcd) × (M_w of ε-CL) × [ε-CL]$_0$/[Ln] × (polymer yield). [c] Determined by GPC analysis in THF calibrated with standard poly(styrene). [d] $T = 17$ °C.

major method that is used to synthesize these polymers is the ring-opening polymerization (ROP) of lactones/lactides and functionally related compounds (Scheme 2). Many kinds of organometallic and coordination complexes have been reported to be efficient initiators for the ROP of lactones/lactides, giving polymers with both high molecular weights and high yields.[28,29] Among them, the controlled polymerization systems are especially interesting, since they afford the possibility of tailoring the composition and the structure of the polymer obtained.[28a]

The catalytic behavior of complexes **2**−**7** for the ROP of ε-caprolactone was examined. The preliminary results are summarized in Table 3. It can be seen that all the complexes are efficient initiators of the controlled polymerization of ε-caprolactone in toluene. All the polymers obtained with these initiators have narrow molecular weight distributions (PDIs) (<1.30). These initiators showed high activity (even for $[M]_0/[\mathbf{2}]_0 = 600$, the polymerization still can proceed smoothly) and produced PCL with a molecular weight of 5.23×10^4 and a PDI of 1.14. The central metal ion has significant effect on the polymerization. Using neodymium alkoxo complexes as initiators, the polymerization completed in 1 h at $[M]_0/[I]_0 = 400$, while it was completed after 14 h when using ytterbium alkoxo complexes as the initiator under the same polymerization conditions. The active trend is consistent with the increasing order of their ionic radii. The effect of the alkoxo groups in these complexes on the polymerization was not observed. All of these alkoxo lanthanide complexes show a similar catalytic behavior. The polymerization temperature affects the reaction rate but not the molecular weight and PDIs of the result polymers at same conversion. The polymerizations at higher temperature (runs 3−7) were faster than that at room temperature (run 9) using complex **3** as the initiator, whereas the molecular weight and PDI of the polymer obtained were almost the same as those of the polymer that was obtained at 17 °C under the same conversions (runs 5 and 9). The main feature for the present initiators is that polymerization with them can proceed at a broad range of reaction temperatures from 17 to 50 °C in a controlled fashion, compared with the systems using lanthanocene alkyls or alkoxides as initiators.[30]

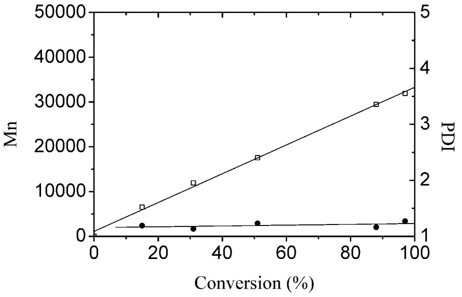

Figure 5. Polymerization of ε-caprolactone initiated by complex **3** in toluene at 50 °C. The relationship between the number-averaged molecular weight (M_n) and the conversion is shown.

To elucidate the controlled character of the polymerization, the relationship between the number-averaged molecular weight (M_n) and the conversion of the polymerization in toluene at 50 °C using complex **3** as the initiator was measured as shown in Figure 5. A linear relationship between M_n and conversion exists, while the PDIs remained unchanged (runs 3−7). These results indicated that obviously all of the polymerization processes are controlled.

Conclusion

We have shown that lanthanide alkoxo complexes supported by carbon-bridged bis(phenolate) ligand MBMP^{2-} can be conveniently synthesized using $(C_5H_5)_3Ln$ as starting materials by a proton exchange reaction. $(C_5H_5)_3Ln$ reacted with MBMPH$_2$ in a 1:1 molar ratio to give the mixed-ligand complex $(C_5H_5)Ln(MBMP)$ in an almost quantitatively yield, which can be used as a precursor to synthesize the corresponding alkoxolanthanide complexes by a further reaction with 1 equiv of alcohol. These alkoxolanthanide complexes are well-characterized, and three of them are structurally characterized. The coordination geometries around the central metals in these alkoxolanthanide complexes are similar. It

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is interesting to note that the O−H···Yb agostic interaction was observed in complex **8**. Furthermore, it was found that these alkoxolanthanide complexes can catalyze the controlled polymerization of ϵ-caprolactone. Controlled polymerization that is catalyzed by structurally well-defined metal complexes is especially interesting, because they afford the possibility of understanding the catalyst structure/reactivity relationships. Studies on the synthesis and reactivity of other carbon-bridged bis(phenolato)lanthanide complexes, such as aryloxides, amides, and alkyls, are in process in our laboratory.

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Supporting Information Available: Tables of X-ray diffraction data for complexes **1**−**3** and **8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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