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# Journal of Organometallic Chemistry

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

# Synthesis and structure of amine-bridged bis(phenolate) lanthanide complexes and their application in the polymerization of $\epsilon$ -caprolactone

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#### ARTICLE INFO

Article history: Received 25 September 2013 Received in revised form 15 October 2013 Accepted 18 October 2013

Keywords: Structure Amine-bridged bis(phenolate) lanthanide complexes Polymerization

## ABSTRACT

A series of lanthanide complexes **1–8** were afforded by the amine elimination reactions of aminebridged bis(phenols)  $H_2L_{1-3} [L_{1-3} = Et_2NCH_2CH_2N\{CH_2-(2-O-C_6H_2-R_2-3-R_1-5)_2, R_1 = {}^{t}Bu, R_2 = {}^{t}Bu$ (L<sub>1</sub>);  $R_1 = Me, R_2 = {}^{t}Bu$  (L<sub>2</sub>);  $R_1 = Me, R_2 = Me$  (L<sub>3</sub>)] and  $H_2L_{4-6} [L_{4-6} = CH_3CH_2CH_2N\{CH_2-(2-O-C_6H_2-R_2-3-R_1-5)\}_2, R_1 = {}^{t}Bu, R_2 = {}^{t}Bu$  (L<sub>4</sub>);  $R_1 = Me, R_2 = {}^{t}Bu$  (L<sub>5</sub>);  $R_1 = Me, R_2 = Me$  (L<sub>6</sub>)] with Ln [N(SiMe\_3)\_2]\_3 (Ln = La, Gd). The bis(phenolate) lanthanide amides  $L_{1-6}La[N(SiMe_3)_2]$  (1–6) were given by the reactions of La[N(SiMe\_3)\_2]\_3 with  $H_2L_{1-6}$  in 1:1 M ration in THF. The bis(phenolate) lanthanide complexes  $Ln_2[L_6]_3$  (Ln = La (7), Ln = Gd (8)) were given by the reactions of Ln[N(SiMe\_3)\_2]\_3(Ln = La, Ga) with  $H_2L_6$  in 2:3 M ratio in THF. Complexes 3 and 8 have been characterized by X-ray crystal structural analysis. The structure of complexes 3 reveals that it has unsolvated centrosymmetric dimer, built around a central, planar La<sub>2</sub>O<sub>2</sub> ring. Complex 8 possesses a THF-solvated unsymmetric dimer. The coordination geometry in complexes 3 and 8 around each of the lanthanide metal atoms can be described as a distorted octahedron. The catalytic properties of complexes 1–6 on the ring-opening polymerization of  $\varepsilon$ -caprolactone have been studied. The results show that lanthanide amides complexes 1–6 are efficient catalysts for the ring-opening polymerization of  $\varepsilon$ -caprolactone.

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# 1. Introduction

Aliphatic polyesters are an important class of polymers because of their biodegradability, biocompatibility and permeability [1,2]. Organometallic catalytic polymerization reactions have commonly been employed in the preparation of polylactide and polylactones [3]. Numerous of catalysts like alkali metals [4], alkaline earth metals [5–7], transition metals [8–11], and rare earth metals [12–16] have been explored for the ring-opening polymerization (ROP) of lactones. Among them, organolanthanide catalysts have got a great interest due to their high activities and capabilities of preparing polymers with high molecular weights in narrow polydispersity.

Amine-bridged bis(phenolate) lanthanide derivatives showed high activity for the polymerization of cyclic esters. Shen and coworkers have demonstrated that bridged bis(phenolate) lanthanide amides can serve as catalysts for the ROP of lactide [17,18] and lactones [19,20]. In the literature, they paid attention to the tetradentate amine-bis(phenolate) ligands: a type of  $[ONXO]^{2-}$  (X = N, O).

In order to generate more reactive catalysts, yet still maintain the robust nature of the catalyst precursor, we turned our attention to related amine-bis(phenolate) ligands: three tetra-dentate H<sub>2</sub>[ONNO] ligands  $H_2L_1-H_2L_3$  and three tridentate H<sub>2</sub>[ONO] ligands  $H_2L_4-H_2L_6$ . Herein, we report the synthesis and structure of a series of lanthanide complexes (1–8) supported by aminebridged bis(phenolate) ligands via the convenient protonolysis reaction. The catalytic properties of the complexes (1–6) have also been studied in the polymerization of  $\varepsilon$ -caprolactone under mild conditions. Compounds were fully characterized by nuclear magnetic resonance (NMR) spectroscopy, elemental analysis (EA), and X-ray single crystal diffraction analysis.

# 2. Experimental

# 2.1. General procedures

The complexes described below are sensitive to air and moisture. Therefore, all manipulations were performed under pure







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<sup>0022-328</sup>X/\$ - see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jorganchem.2013.10.031

nitrogen with rigorous exclusion of air and moisture using Schlenk techniques and glovebox. THF, toluene, and hexane were distilled from sodium benzophenone ketyl before use. HN(TMS)<sub>2</sub>, ε-Caprolactone, and <sup>n</sup>BuLi are commercially available. HN(TMS)<sub>2</sub> and ε-Caprolactone was dried over CaH<sub>2</sub> for 3 days and distilled before use. The starting complexes La[N(TMS)<sub>2</sub>]<sub>3</sub>/Gd[N(TMS)<sub>2</sub>]<sub>3</sub> [21] and  $H_2L_1 \sim H_2L_6$  [22] were synthesized according to published methods. Lanthanide analyses were performed by EDTA titration with a xylenol orange indicator and hexamine buffer. Elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. NMR spectra were recorded on a Bruker Advance 400 spectrometer at resonant frequencies of 400 MHz for <sup>1</sup>H and 101 MHz for <sup>13</sup>C nuclei using  $C_6D_6$  or  $d_6$ -DMSO as the solvent. Melting points were observed in sealed capillaries and were uncorrected. The weight average molecular weight  $(M_w)$  and the number average molecular weight  $(M_n)$  were determined by GPC on a Water GPC system equipped with four Waters Ultrastyragel columns ( $300 \times 7.5$  mm, guarded and packed with  $1 \times 10^5$ ,  $1 \times 10^4$ ,  $1 \times 10^3$ , and 500 A gels) in series. Tetrahydrofuran (THF, 1 mL min<sup>-1</sup>) was used as the eluent and the signal was monitored by a differential refractive index detector. Monodispersed polystyrene was used as the molecular weight standard.

# 2.1.1. Syntheses of $[Et_2NCH_2CH_2N\{CH_2-(2-0-C_6H_2-3,5^{-t}Bu_2)\}_2]La [N(TMS)_2], L_1La[N(TMS)_2] (1)$

La[N(TMS)<sub>2</sub>]<sub>3</sub> (1.30 g, 2.09 mmol) dissolved in 10 mL of THF was added to  $H_2L_1$  (1.16 g, 2.09 mmol) dissolved in 10 mL THF. The reaction mixture was stirred for 3 h at 60 °C, and then the solvent was removed under oil pump vacuum. The residue was extracted with mixture of THF and hexane, and recrystallized to afford a pale yellow solid (1.25 g, 70%). M.p.: 245 °C–248 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.59 (s, ArH, 2H), 7.12 (s, ArH, 2H), 3.76 (s, ArCH<sub>2</sub>, 4H), 2.82 (s, NCH<sub>2</sub>, 2H), 2.12 (s, NCH<sub>2</sub>, 2H), 1.66 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.40 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.28 (s, NCH<sub>2</sub>CH<sub>3</sub>, 4H), 0.74 (s, 6H), 0.51 (s, Si(CH<sub>3</sub>)<sub>3</sub>, 18H). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 162.1 (Ar), 137.2 (Ar), 135.7 (Ar), 126.3 (Ar), 124.3 (Ar), 124.3 (Ar), 69.6 (ArCH<sub>2</sub>), 60.7 (NCH2), 51.7 (NCH2), 47.4 (NCH2), 35.5 (C(CH<sub>3</sub>)<sub>3</sub>), 34.25 (C(CH<sub>3</sub>)<sub>3</sub>), 32.2 (C(CH<sub>3</sub>)<sub>3</sub>), 30.7 (C(CH<sub>3</sub>)<sub>3</sub>), 25.4 (CH<sub>2</sub>CH<sub>3</sub>), 5.8 (Si(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>42</sub>H<sub>76</sub>LaN<sub>3</sub>O<sub>2</sub>Si<sub>2</sub>: C, 59.28; H, 8.94; N, 4.94; La, 16.34. Found: C, 59.04; H, 9.07; N, 4.79; La, 16.11.

## 2.1.2. Syntheses of [Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-(2-O-C<sub>6</sub>H<sub>2</sub>-<sup>t</sup>Bu-3-Me-5)]<sub>2</sub>]La[N(TMS)<sub>2</sub>](THF), L<sub>2</sub>La[N(TMS)<sub>2</sub>](THF) (2)

The synthesis of **2** was carried out by the same way as that for the synthesis of **1**, but  $H_2L_2$  (0.59 g, 1.26 mmol) and  $La[N(TMS)_2]_3$ (0.78 g, 1.26 mmol) was used and subsequent work to afford **2** as a yellow power (0.82 g, 85%). M.p.: 211 °C-213 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.29 (s, ArH, 2H), 6.76 (s, ArH, 2H), 3.72 (s, ArCH<sub>2</sub>, 4H, THF, 4H), 2.88 (d, *J* = 2.8 Hz, NCH<sub>2</sub>, 4H), 2.35 (s, ArCH<sub>3</sub>, 6H), 1.62 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.36 (s, NCH<sub>2</sub>, 4H, THF, 4H), 0.78 (t, *J* = 6.6 Hz, CH<sub>2</sub>CH<sub>3</sub>, 6H), 0.51 (s, Si(CH<sub>3</sub>)<sub>3</sub>, 18H). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 162.3 (Ar), 136.2 (Ar), 130.3 (Ar), 129.3 (Ar), 124.8 (Ar), 123.5 (Ar), 68.8 (THF– CH<sub>2</sub>), 60.1 (ArCH<sub>2</sub>), 51.6 (NCH<sub>2</sub>), 47.3 (NCH<sub>2</sub>), 35.1 (C(CH<sub>3</sub>)<sub>3</sub>), 30.6 (C(CH<sub>3</sub>)<sub>3</sub>), 25.6 (ArCH<sub>3</sub>), 21.0 (CH<sub>2</sub>CH<sub>3</sub>), 5.9 (Si(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>40</sub>H<sub>72</sub>LaN<sub>3</sub>O<sub>3</sub>Si<sub>2</sub>: C, 57.27; H, 8.59; N, 5.01; La, 16.57. Found: C, 57.01; H, 8.63; N, 4.89; La, 16.42.

# 2.1.3. Syntheses of { $[Et_2NCH_2CH_2N\{CH_2-(2-O-C_6H_2-3,5-Me_2)\}_2]La [N(TMS)_2]\}_2$ , { $L_3La[N(TMS)_2]\}_2$ (3)

La[N(TMS)<sub>2</sub>]<sub>3</sub> (1.17 g, 1.89 mmol) dissolved in 10 mL THF was added to  $H_2L_3$  (0.73 g, 1.89 mmol) dissolved in 10 mL THF. The reaction mixture was stirred for 3 h at 60 °C, and then the solvent was removed under oil pump vacuum to afford a pale yellow solid (1.04, 82%). The residue was extracted with mixture of THF and hexane (1:3), from which **3** was obtained as colorless crystals in several

days. Complex **3** was soluble in THF, little soluble in toluene and hexane. M.p.: 309 °C–311 °C. <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO):  $\delta = 6.90$  (s, ArH, 1H), 6.79–6.61 (m, ArH, 4H), 6.59 (s, ArH, 2H), 6.44 (s, ArH, 1H), 3.31 (s, ArCH<sub>2</sub>, 4H), 2.36 (s, NCH<sub>2</sub>, 2H), 2.09–1.96 (m, ArCH<sub>3</sub>, NCH<sub>2</sub>, 30H), 0.79 (s, CH<sub>2</sub>CH<sub>3</sub>, 6H), 0.64 (t, J = 6.7 Hz, CH<sub>2</sub>CH<sub>3</sub>, 6H), 0.01 (s, Si(CH<sub>3</sub>)<sub>3</sub>, 36H). <sup>13</sup>C NMR (101 MHz,  $d_6$ -DMSO)  $\delta$  164.1 (Ar), 129.2 (Ar), 128.8 (Ar), 125.8 (Ar), 123.9 (Ar), 118.2 (Ar), 67.49 (ArCH<sub>2</sub>), 31.42 (NCH<sub>2</sub>), 31.15 (NCH<sub>2</sub>), 25.60 (NCH<sub>2</sub>), 22.53 (ArCH<sub>3</sub>), 18.14 (ArCH<sub>3</sub>), 12.73 (CH<sub>2</sub>CH<sub>3</sub>), 3.16 (Si(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>60</sub>H<sub>104</sub>La<sub>2</sub>N<sub>6</sub>O<sub>4</sub>Si<sub>4</sub>: C, 52.80; H, 7.63; N, 6.16; La, 20.37. Found: C, 52.71; H, 7.83; N, 6.04; La, 20.18.

# 2.1.4. Syntheses of $[CH_3CH_2CH_2N\{CH_2-(2-O-C_6H_2-3,5^{-t}Bu_2)\}_2]La [N(TMS)_2](THF), L_4La[N(TMS)_2](THF)_2 (4)$

The synthesis of **4** was carried out by the same way as that for the synthesis of **1**, but  $H_2L_4$  (0.78 g, 1.58 mmol) and  $La[N(TMS)_2]_3$ (0.98 g, 1.58 mmol) was used and subsequent work to afford **4** as a yellow power (1.15 g, 78%). M.p.: 213 °C-215 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 7.57$  (s, ArH, 2H), 7.14 (s, ArH, 2H), 3.65 (s, THF, 8H), 3.55 (d, J = 5.2 Hz, ArCH<sub>2</sub>, 4H), 2.52 (d, J = 6.9 Hz, NCH<sub>2</sub>CH<sub>2</sub>, 2H), 1.69 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.41 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.35 (s, NCH<sub>2</sub>CH<sub>2</sub>, 2H), 1.30 (s, THF, 8H), 0.61 (t, J = 6.6 Hz, CH<sub>2</sub>CH<sub>3</sub>, 3H), 0.35 (s, Si(CH<sub>3</sub>)<sub>3</sub>, 18H). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 161.8$  (Ar), 137.5 (Ar), 135.4 (Ar), 126.4 (Ar), 124.3 (Ar), 124.1 (Ar), 69.3 (THF-C), 59.4 (ArCH<sub>2</sub>), 52.1 (NCH<sub>2</sub>), 35.5 (C(CH<sub>3</sub>)<sub>3</sub>), 34.3 (C(CH<sub>3</sub>)<sub>3</sub>), 32.2 (C(CH<sub>3</sub>)<sub>3</sub>), 30.7 (C(CH<sub>3</sub>)<sub>3</sub>), 25.5 (THF-C), 15.3 (CH<sub>3</sub>CH<sub>2</sub>), 11.7 (CH<sub>2</sub>CH<sub>3</sub>), 4.9 (Si(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>47</sub>H<sub>85</sub>LaN<sub>2</sub>O<sub>4</sub>Si<sub>2</sub>: C, 60.17; H, 9.07; N, 2.99; La, 14.82. Found: C, 60.05; H, 9.17; N, 2.86; La, 14.68.

## 2.1.5. Syntheses of $[CH_3CH_2CH_2N\{CH_2-(2-O-C_6H_2-^tBu-3-Me-5)\}_2]$ $La[N(TMS)_2](THF), L_5La[N(TMS)_2](THF) (5)$

The synthesis of **5** was carried out by the same way as that for the synthesis of **1**, but **H<sub>2</sub>L<sub>5</sub>** (0.56 g, 1.37 mmol) and La[N(TMS)<sub>2</sub>]<sub>3</sub> (0.85 g, 1.37 mmol) was used and subsequent work to afford **5** as a yellow power (0.75 g, 75%). M.p.: 209 °C–211 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.27 (s, ArH, 2H), 6.82 (s, ArH, 2H), 3.76 (s, THF, 4H), 3.48 (s, ArCH<sub>2</sub>, 4H), 2.54 (d, *J* = 6.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>, 2H), 2.33 (s, ArCH<sub>3</sub>, 6H), 1.65 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18 H, THF, 4H), 1.28 (s, NCH<sub>2</sub>CH<sub>2</sub>, 2H), 0.57 (t, *J* = 6.7 Hz, CH<sub>2</sub>CH<sub>3</sub>, 3H), 0.36 (s, Si(CH<sub>3</sub>)<sub>3</sub>, 18H). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 161.9 (Ar), 135.9 (Ar), 130.3 (Ar), 124.8 (Ar), 124.1 (Ar), 59.1 (ArCH<sub>2</sub>), 35.1 (C(CH<sub>3</sub>)<sub>3</sub>), 30.6 (C(CH<sub>3</sub>)<sub>3</sub>), 25.1 (NCH<sub>2</sub>CH<sub>2</sub>), 23.1 (NCH<sub>2</sub>CH<sub>2</sub>), 21.1 (ArCH<sub>3</sub>), 11.7 (CH<sub>2</sub>CH<sub>3</sub>), 4.9 (Si(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>37</sub>H<sub>65</sub>LaN<sub>2</sub>O<sub>3</sub>Si<sub>2</sub>: C, 56.85; H, 8.32; N, 3.59; La, 17.78. Found: C, 56.73; H, 8.16; N, 3.45; La, 17.70.

# 2.1.6. Syntheses of $[CH_3CH_2CH_2N\{CH_2-(2-0-C_6H_2-3,5-Me_2)\}_2]La$ $[N(TMS)_2], L_6La[N(TMS)_2]$ (6)

The synthesis of **6** was carried out by the same way as that for the synthesis of **1**, but **H<sub>2</sub>L<sub>6</sub>** (0.48 g, 1.45 mmol) and La[N(TMS)<sub>2</sub>]<sub>3</sub> (0.90 g, 1.45 mmol) was used and subsequent work to afford **6** as a yellow power (0.74 g, 82%). M.p.: 260 °C–262 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 6.90 (s, ArH, 2H), 6.72 (s, ArH, 2H), 3.57 (s, ArCH<sub>2</sub>, 4H), 2.44 (s, NCH<sub>2</sub>, 2H), 2.31 (s, CH<sub>2</sub>CH<sub>3</sub>, 2H), 2.21 (s, ArCH<sub>3</sub>, 6H), 1.38 (s, ArCH<sub>3</sub>, 6H), 0.46 (t, *J* = 6.5 Hz, CH<sub>2</sub>CH<sub>3</sub>, 3H), 0.20 (s, Si(CH<sub>3</sub>)<sub>3</sub>, 18H). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 161.6 (Ar), 133.1 (Ar), 129.3 (Ar), 128.6 (Ar), 127.4 (Ar), 125.7 (Ar), 68.03 (ArCH<sub>2</sub>), 31.9 (NCH<sub>2</sub>), 25.7 (NCH<sub>2</sub>), 23.1 (ArCH<sub>3</sub>), 20.7 (ArCH<sub>3</sub>), 14.4 (CH<sub>2</sub>CH<sub>3</sub>), 11.6 (CH<sub>2</sub>CH<sub>3</sub>), 4.5 (Si(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>27</sub>H<sub>4</sub>5LaN<sub>2</sub>O<sub>2</sub>Si<sub>2</sub>: C, 51.86; H, 7.20; N, 4.48; La, 22.23. Found: C, 51.73; H, 7.36; N, 4.41; La, 22.31.

# 2.1.7. Syntheses of $[CH_3CH_2CH_2N\{CH_2-(2-0-C_6H_2-3,5-Me_2)\}_2]_3La_2(THF)$ , (**L**<sub>6</sub>)<sub>3</sub>La<sub>2</sub>(**THF**) (**7**)

To a THF solution of  $La[N(TMS)_2]_3$  (0.88 g, 1.42 mmol) was added a THF solution of  $H_2L_6$  (0.70 g, 2.13 mmol). The reaction mixture was stirred for 3 h at 60 °C, and then the solvent was removed

#### Table 1

Crystal and data collection parameters of complexes 3 and 8

	3	$\pmb{8}{\cdot}0.5C_6H_{14}$
Formula	C <sub>60</sub> H <sub>104</sub> La <sub>2</sub> N <sub>6</sub> O <sub>4</sub> Si <sub>4</sub>	C <sub>70</sub> H <sub>96</sub> Gd <sub>2</sub> N <sub>3</sub> O <sub>7</sub>
Formula weight	1363.67	1406.00
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
a/Å	12.1448(9)	13.2206(3)
b/Å	16.2868(10)	14.3852(5)
c/Å	17.5273(15)	20.4636(6)
$\alpha / ^{\circ}$	90	85.527(2)
$\beta  ^{\circ}$	101.064(8)	72.852(2)
$\gamma l^{\circ}$	90	66.446(3)
V/Å <sup>3</sup>	3402.5(5)	3405.42(17)
Z	2	2
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	1.331	1.371
F(000)	1416	1442
$\mu/\text{mm}^{-1}$	1.35	1.98
Cryst size (mm)	$0.22 \times 0.20 \times 0.18$	$0.22\times0.20\times0.18$
Temp/K	223	223
$\theta$ range (°)	3.1-24.0	3.2-28.3
Reflections	4161	14,185
R1 <sup>a</sup>	0.047	0.033
wR2 <sup>b</sup>	0.097	0.071
$\Delta  ho_{ m min}$ , max/e Å $^{-3}$	-0.53, 1.07	-0.67, 1.27
Goodness of fit <sup>c</sup>	1.032	1.04

<sup>a</sup>  $R_1 = \sum (||F_0| - |F_c||) / \sum |F_0|; wR_2 = [\sum (w(F_0^2 - F_c^2)^2) / \sum (wF_0^4)]^{1/2}.$ 

 $\begin{array}{l} w_1 = \sum_{i=1}^{n} |1/[\sigma^2(F_0^2) + (0.0318P)^2], P = (F_0^2 + 2F_c^2)/3, w_8 = 1/[\sigma^2(F_0^2) + (0.0209P)^2 + 1.5203P], P = (F_0^2 + 2F_c^2)/3, \\ c S = [\sum w(F_0^2 - F_c^2)^2]/(n - p)^{1/2}, n = \text{number of reflections}, p = \text{parameters used}. \end{array}$ 

under vacuum to afford a pale yellow solid (0.80, 91%). M.p.: 290 °C-294 °C. <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO)  $\delta = 6.68$  (s, ArH, 2H), 6.62 (s, ArH, 4H), 6.54 (s, ArH, 6H), 3.60 (t, J = 5.8 Hz, ArCH<sub>2</sub>, 4H, THF, 4H), 3.33 (s, ArCH<sub>2</sub>, 2H), 3.25 (s, ArCH<sub>2</sub>, 2H), 2.11 (s, ArCH<sub>3</sub>, 6H), 2.08 (s, ArCH<sub>3</sub>, 6H), 2.06 (s, ArCH<sub>3</sub>, 12H), 2.02 (s, ArCH<sub>3</sub>, 12H), 1.76 (t, I = 5.9 Hz, THF, 4H), 1.61–1.48 (m, CH<sub>2</sub>CH<sub>3</sub>, 2H), 1.40 (dd, I = 14.4, 7.0 Hz,  $CH_2CH_3$ , 4H), 0.63 (t, I = 7.1 Hz,  $CH_2CH_3$ , 3H), 0.43 (t, I = 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>, 6H). <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta = 163.1$  (Ar), 161.7 (Ar), 130.1 (Ar), 130.0 (Ar), 129.8 (Ar), 128.9 (Ar), 128.7 (Ar), 124.0 (Ar), 123.9 (Ar), 123.6 (Ar), 123.5 (Ar), 119.2 (Ar), 117.7 (Ar), 67.00 (THF), 57.2 (ArCH<sub>2</sub>), 57.0 (ArCH<sub>2</sub>), 54.3 (ArCH<sub>2</sub>), 49.6 (NCH<sub>2</sub>),

25.1 (ArCH<sub>3</sub>), 20.3 (ArCH<sub>3</sub>), 20.3 (ArCH<sub>3</sub>), 17.3 (ArCH<sub>3</sub>), 17.2 (ArCH<sub>3</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>), 13.4 (CH<sub>2</sub>CH<sub>3</sub>), 12.0(CH<sub>2</sub>CH<sub>3</sub>), 11.7 (CH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>67</sub>H<sub>89</sub>La<sub>2</sub>N<sub>3</sub>O<sub>7</sub>: C, 60.62; H, 6.71; N, 3.17; La, 20.95. Found: C, 60.57; H, 6.84; N, 3.26; La, 21.02.

## 2.1.8. Syntheses of [CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>N{CH<sub>2</sub>-(2-0-C<sub>6</sub>H<sub>2</sub>-3,5- $Me_2$ ) $_{2}Gd_2(THF), (L_6)_3Gd_2(THF) (8)$

To a THF solution of Gd[N(TMS)<sub>2</sub>]<sub>3</sub> (1.31 g, 2.05 mmol) was added a THF solution of H<sub>2</sub>L<sub>6</sub> (1.01 g, 6.76 mmol). The reaction mixture was stirred for 3 h at 60 °C, and then the solvent was removed under vacuum to afford a pale yellow solid (1.17, 89%). The residue was extracted with mixture of THF and hexane, from which 8 was obtained as colorless crystals in several days. M.p.: 319 °C-321 °C. Anal. Calcd for C<sub>67</sub>H<sub>89</sub>Gd<sub>2</sub>N<sub>3</sub>O<sub>7</sub>: C, 58.99; H, 6.53; N, 3.08; Gd, 23.07. Found: C, 59.04; H, 6.71; N, 3.16; Gd, 23.13.

#### 2.2. Experimental for $\varepsilon$ -caprolactone ring-opening polymerization

The procedures for the ring-opening polymerization of  $\varepsilon$ -caprolactone initiated by complexes **1–6** were similar, and a typical polymerization procedure is given below.

In the glovebox, a 100 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with a solution of initiator in toluene. Then the desired  $\varepsilon$ -caprolactone was added to this solution by syringe. The mixture was stirred vigorously for the desired time and then exposed to air. A couple drops of 1 M HCl and ethanol solution were added to fully quench and the polymer was precipitated, which was dried under vacuum and weighed.

For product analyses, 0.0300 g of poly(CL) was dissolved in 4 mL of THF overnight. After centrifugation, the clear solution was measured by GPC with THF (1 mL min<sup>-1</sup>) as the eluent. The weights of poly(CL) were calculated with monodispersed polystyrene as the molecular weight standard.

#### 2.3. X-ray data collection and refinement of crystal structure

The crystals of the complexes were mounted on a glass fiber for X-ray measurement. Diffraction data were collected on a Rigaku Mercury CCD area detector in the  $\omega$  scan mode using MoK $\alpha$ 



Scheme 1. Synthesis of the ligands.



Scheme 2. Synthesis of the complexes 1–3.



Scheme 3. Synthesis of the complexes 4–6.

radiation ( $\lambda = 0.71073$  Å) at 223(2) K. All measured independent reflections ( $I > 2\sigma(I)$ ) were used in the structural analyses and semiempirical absorption corrections were applied using SADABS [23]. The structure was solved and refined using SHELXL-97 [24]. All hydrogen atoms were positioned geometrically and refined using a riding model. The non-hydrogen atoms were refined with aniso-tropic thermal parameters. In complex 3, the disorder ethyl and silicon methyl were split into C21C22/C25C27 and C21'C22'/ C25'C27' with occupancies of 31.9 (7) and 68.1(7)%, respectively. In complex 8, the disorder carbon atom C17 and THF were split into C17/C64C65C66C67 and C17'/C64'C65'C66'C67' with occupancies of 79.7(23) and 20.3(23)\%, respectively. The disorder *n*-hexane solvent was split into C68C69C70 and C68'C69'C70' with occupancies of 82.6(11) and 17.4(11)\%, respectively. The crystallographic data and experimental details of the data collection, as well as the structure refinement are given in Table 1. Diagrams were made



Scheme 4. Synthesis of the complexes 7 and 8.



**Fig. 1.** Molecular structure of complex **3** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.



Fig. 2. ORTEP drawing of the molecular core of 3.

with SHELXL-97 as well and all calculations were performed on a Pentium 4 computer.

# 3. Results and discussion

# 3.1. Synthesis and characterization of lanthanide complexes 1–8

The ligand  $H_2L_1-H_2L_6$  was prepared according to the literature procedure in Scheme 1 [22]. An amine elimination reaction was used to synthesize the lanthanide complexes here. Slow addition of a THF solution of  $H_2L$  into the THF solution of  $Ln[N(TMS)_2]_3$ (Ln = La, Gd) at room temperature, stirred for 3 h at 60 °C. After workup, the desired complexes **1–8** were isolated from a concentrated mixture of THF and hexane, as shown in Schemes 2–4.

Disappearance of the phenolate O–H signal ( $\delta$  = 13–14) in the <sup>1</sup>H NMR spectra of lanthanide complexes confirms the occurrence of protonolysis. The chemical shifts of the **L**<sub>n</sub>La–N(SiC**H**<sub>3</sub>)<sub>2</sub> in the

(0) C

Table 2	
Selected bond lengths (Å) and bond angle	S



**Fig. 3.** Molecular structure of complex **8** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.



Fig. 4. ORTEP drawing of the molecular core of 8.

complexes (1–6), given by the reaction of the  $Ln[N(TMS)_2]_3$  with  $H_2L_n$  (n = 1-6) in 1:1 M ratio, demonstrated that the phenolate lanthanide amides was formed.

## 3.2. Crystal structures

Crystals suitable for an X-ray structure determination of complexes **3** and **8** were obtained from a hexane/THF mixed (3:1) solution at room temperature. The molecular structure diagrams of complex **3**, which is unsolvated and centrosymmetric, are shown in

Bond lengths (Å)					
La(1)-O(1)	2.495(3)	La(1)-O2)	2.240(3)	La(1)-O(1A)	2.488(3)
La(1)-N(1)	2.784(3)	La(1)-N2)	2.972(4)	La(1)-N(3)	2.428 (4)
Bond angles (°)					
O(1)-La(1)-N(1)	75.36(10)	O(1)-La(1)-N(3)	99.94(11)	O(1)-La(1)-O(2)	138.91(10)
O(1)-La(1)-O(1A)	65.70(11)	O(1A-La(1)-N(2))	162.94(10)	O(2)-La(1)-N(1)	72.78(11)
N(1)-La(1)-N(2)	63.28 (11)	N(1)-La(1)-N(3)	159.85(12)	N(2)-La(1)-N(3)	96.91(12)
La(1) - O(2) - C(3)	145.1(3)	La(1)-O(1)-La(1A)	114.30(11)	La(1)-N(1)-C(19)	116.3 (3)
La(1)-N(2)-C(20)	102.6 (3)	N(1)-C(19)-C(20)	113.4 (4)	N(2)-C(20)-C(19)	113.1 (4)

Table 3		
Selected bond lengths	(Å) and bond angles (°	) for 8.

0 ()	8 ()				
Bond lengths (Å)					
Gd(1)-O(1)	2.332(2)	Gd(1)-O(2)	2.139(2)	Gd(1-O(3)	2.130(2)
Gd(1)-O(4)	2.348(2)	Gd(1)-N(1)	2.576(3)	Gd(1-N(2)	2.584(3)
Gd(2)-O(1)	2.284(2)	Gd(2)-O(4)	2.277(2)	Gd(2-O(5)	2.172(2)
Gd(2)–O(6)	2.159(2)	Gd(2)-O(7)	2.413(2)	Gd(2-N(3)	2.597(3)
Bond angles (°)					
N(1)-Gd(1)-O(1)	78.73 (8)	N(1)-Gd(1)-O(2)	76.32 (9)	N(2)-Gd(1)-O(1)	106.41(8)
N(2)-Gd(1)-O(2)	101.17 (8)	N(2)-Gd(1)-O(3)	76.54 (9)	O(1) - Gd(1) - O(2)	144.63(8)
O(1)-Gd(1)-O(3)	93.42 (9)	O(2)-Gd(1)-O(3)	114.46(10)	O(3)-Gd(1)-O(4)	147.15(8)
Gd(1) - O(1) - Gd(2)	106.85 (9)	O(1)-Gd(2)-O(4)	74.23 (8)	O(1)-Gd(2)-O(5)	101.44(8)
O(1)-Gd(2)-O(6)	103.91 (8)	O(1)-Gd(2)-O(7)	85.26 (9)	O(1)-Gd(2)-N(3)	176.48(8)
O(5)-Gd(2)-O(6)	153.36 (9)	O(5)-Gd(2)-O(7)	87.18 (9)	O(6)-Gd(2)-N(3)	77.36(8)

Table 4

Polymerization of ε-CL initiated by 1–6<sup>a</sup>.

Entry	Initiator	$[M]_0/[I]_0$	Time (min)	Yield <sup>b</sup> (%)	$M_{\rm n}^{\ \rm c}(10^4)$	PDI <sup>c</sup>
1	1	100	1	62	2.5	1.39
2	1	250	1	53	1.8	1.65
3	2	100	1	57	3.7	1.15
4	2	250	1	66	2.7	1.02
5	3	100	1	35	0.85	1.48
6	3	250	1	20	0.63	1.63
7	4	100	1	60	5.4	1.20
8	4	250	1	70	2.0	1.67
9	5	100	1	73	1.2	1.57
10	5	250	1	97	1.3	1.61
11	6	100	1	100	0.81	1.35
12	6	250	1	74	0.72	1.53

<sup>&</sup>lt;sup>a</sup> General polymerization conditions:  $[M]_0 = 0.5$  M, solvent = toluene, T = 20 °C.

<sup>b</sup> Yield: weight of polymer obtained/weight of monomer used.
 <sup>c</sup> Measured by GPC relative to monodispersed polystyrene.

Figs. 1 and 2, with selected bond distances and angles listed in Table 2. The structure shows a dimeric feature containing an  $Ln_2O_2$  core bridging through the oxygen atoms of the two OAr 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 three oxygen atoms and two nitrogen atoms from a dianionic bis(phenolate) ligand (L<sub>3</sub>), and one nitrogen atom from  $-N(TMS)_2$  group. One oxygen atom in this bis(phenolate) ligand (L<sub>3</sub>) is monodentate to lanthanide and another is as a  $\mu_2$ -O-bridge between metals. The coordination geometry around the metal center can be best described as a slightly distorted octahedron, in which O(1), O(2), N(1), and N(3) occupied equatorial positions and O(1A) and N(2) occupied axial positions. The La(1)–O(2) bond length (2.240(3) Å) is shorter than those in [ONNO]LaCp (2.291(2) Å) [ONNO=Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N{CH<sub>2</sub>-(2-O- $C_6H_2-^{t}Bu-3-Me-5)_{2}$  [25]. The La(1)-O-µ<sub>2</sub> bond length of 2.495(3) Å and 2.488 Å, respectively, and the average 2.491(3) Å, are closed to those in [La(OAr)<sub>3</sub>(THF)<sub>3</sub>]<sub>2</sub>·5THF (2.494 Å) [26]. The La-N(TMS)<sub>2</sub> bond length (2.428(4) Å) is longer than those in {[ON]La  $[N(TMS)_2]_2$  (2.392(9) Å)  $[ON = 3,5^{-t}Bu_2-2-(OH)-C_6H_2CH_2NHC_6H_4$ o-OCH3] [27]. The La-Namine bond (2.784(3) Å and 2.972(4) Å) were longer comparable to the literature [25]. The bite angle O(1)-La(1)-O(2) of 138.91(10)" for the bis(pheno1ate) ligands is apparently smaller than the corresponding angles found in aminebis(pheno1ate) lanthanide alkane [28] and amides [29].

Single-crystal X-ray diffraction shows that complex **8** possess a THF-solvated dimeric structure with half a hexane in a unit cell (Figs. 3 and 4). The structure contains an  $Ln_2O_2$  core bridging



Fig. 5. <sup>1</sup>H NMR spectrum of PCL.



Scheme 5. Possible Mechanism for the ROP of *e*-CL.

through the oxygen atoms of the two OAr groups, adopting a twisted octahedral geometry. The selected bond distances and angles are listed in Table 3. Each of the Gd atoms is six-coordinated but their bonding environment are different, and there are two different coordination modes in the bis(phenolate) ligand (**L**<sub>6</sub>). The Gd1 atom is coordinated to two single coordinate oxygen atoms (O2 and O3), two  $\mu_2$ -bridge oxygen atoms (O1 and O4) and two nitrogen atoms(N1 and N2). The Gd2 atom is coordinated to one oxygen atom (O7) from THF, two single coordinate oxygen atoms (O5, O6), two  $\mu_2$ -bridge oxygen atoms (O1 and O4) and one nitrogen atom(N3). The Gd–O(Ar) bond length is comparable to that formed in the Gd<sub>4</sub>(Cat)<sub>6</sub>(THF)<sub>6</sub> (Cat = 3,5-di-*tert*-butyl-catecholate) [30]. The O1–Gd1–O2, O3–Gd1–O4 and O5–Gd2–O6 bond angles are 144.63(8)°, 147.15(8)° and 153.36(9)°, respectively.

#### 3.3. Catalytic activity studies

Their performance of complexes **1–6** as catalysts for the ROP of  $\varepsilon$ -CL was examined in a toluene solution at 20 °C, and the preliminary results are listed in Table 4. It can be seen that all complexes are efficient initiators of the polymerization of  $\varepsilon$ -CL in toluene. All polymerizations proceeded fast and completed within 1 min to give polymers with relatively narrow molecular weight distributions (PDIs) (1.02–1.63).

For the complexes **1–6**, the influence of the substituent groups, located ortho- and para-position to the binding oxygen atoms, and the presence of side arm donor were studied. The data shows that the polymerization yields of complex **4–6** with tridentate [ONO] ligands are higher than those of complexes **1–3** with an extra side arm nitrogen donor (average yields: 56.5 (for **1**) < 65 (for **4**), 61.5 (for **2**) < 85 (for **5**), 27.5 (for **3**) < 87 (for **6**)). The bulky *t*-Bu substituents may have a good effect on the polymerization, with a higher molecular weight ( $M_n$  (10<sup>4</sup>): 2.5 for **1**, 3.7 for **2**, 0.85 for **3**).

The microstructure of PCL was determined by <sup>1</sup>H NMR experiments using initiator **2** and a 15:1 monomer to initiator ratio, as shown in Fig. 5. The <sup>1</sup>H NMR spectrum of the polymer clearly shown that only the  $-N(SiMe_3)_2$  group was observed, according to the resonance at -0.01 ppm. No resonance signal was observed for the phenolate ligand. The signal at 3.64 ppm can be assigned to the methylene protons at  $\alpha$ -position to terminal hydroxy group. One possible polymerization mechanism is via the coordination/insertion (shown in Scheme 5), which is similar to the literature [27,31,32].

## 4. Conclusion

In summary, a series of lanthanide (La/Gd) complexes stabilized by amine-bridged bis(phenolate) ligands were synthesized via amine elimination reactions, and the structural features of complexes (**3** and **8**) were determined by X-ray diffraction study. It was found that the bis(phenolate) lanthanide amides (**1**–**6**) were efficient initiators for the ring-opening polymerization of  $\varepsilon$ -CL. NMR spectrum of PCL revealed that the ring-opening polymerization of  $\varepsilon$ -CL proceeded via a coordination-insertion mechanism.

#### Acknowledgment

This work was supported by National Science and Technology of Major Project (2009ZX02039-002), and State Key Laboratory of ASIC & System, Fudan University (12KF007).

#### Appendix A. Supplementary material

CCDC 941929 and 941930 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data\_request/cif.

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