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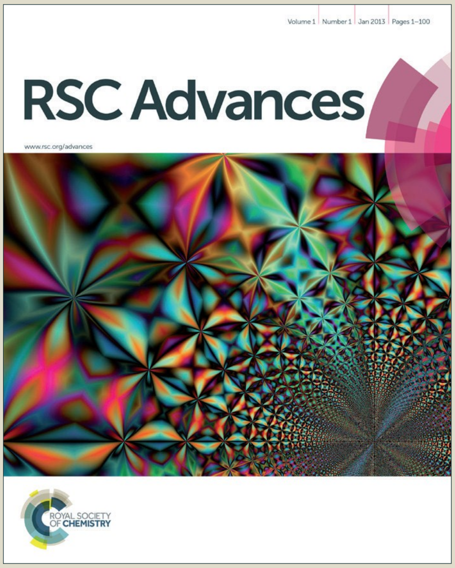

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ARTICLE

Heteroleptic lanthanide amides complexes bearing carbon-bridged bis(phenolate) ligands: synthesis, structure and their application in the polymerization of ε-caprolactone

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A convenient method for the synthesis of anionic lanthanide amides complexes bearing carbon-bridged bis(phenolate) ligands H_2L [L = (*o*-CH_3)PhCH(C_6H_2-3-^{t}Bu-5-R-2-O)$_2$, R = Me, L = L_1; R = ^{t}Bu, L = L_2] is described. The bis(phenolato)lanthanide complexes LLnN($SiMe_3$) [L = L_1, Ln = La (**1**); Ln = Gd (**2**); L = L_2, Ln = La (**3**); Ln = Gd (**4**)] were synthesized by the reaction of Ln[N($SiMe_3$)$_2$]$_3$ (Ln = La, Gd) with $\mathbf{H_2L}$ in a 1:1 molar ratio in THF at 60 °C in nearly quantitative yields. The bis(phenolato)lanthanide pyrazolato complexes LLnPzMe_2·(THF)$_3$ [L = L_1, Ln = La (**5**); Ln = Gd (**6**); L = L_2, Ln = La (**7**); Ln = Gd (**8**)] was obtained by using LLnN($SiMe_3$) obtained further reacting with another 1 equiv of 3,5-dimethylpyrazole (Me_2PzH) in high yields. Meanwhile, the complexes LLnPzMe_2 can also be synthesized by the direct reaction of Ln[N($SiMe_3$)$_2$]$_3$ with H_2L and Me_2PzH in 1:1:1 molar ratio in situ in THF. Complexes **5 - 8** have been characterized by X-ray crystal structural analysis. The central lanthanide metal atom is seven-coordinated by one bis(phenolate) ligand, one pyrazole ligand and three THF molecules in a distorted pentagonal bipyramid. The catalyst activity of compounds **1 - 8** to the ring-opening polymerization of ε-caprolactone was studied. The catalyst mechanism was studied and discussed as well.

Introduction

Aliphatic polyesters are a prefered choice for potential commodity plastic of environmentally-friendly because of their biodegradability, biocompatibility and potential availability from renewable resources.[1-3] The polymerization mechanism could be defined as enzymatic polymerization,[4-6] polycondenzation,[7] anionic polymerization,[8,9] cationic polymerization,[10,11] or coordination/insertion polymerization.[12,13] Ring opening polymerization of cyclic esters, however, is currently a topical research field with metal complex-induced coordination/insertion type polymerization. A wide range of metals have been explored for the ring-opening (ROP) polymerization of lactones through the coordination/insertion mechanism; typically alkali metals,[14] alkaline earth metals,[15-17] transition metals,[18-20] and rare earth metals.[21-23] Among them, organolanthanide based system seems to be active and suitable in preparing the well-defined polymers with high molecular weights in narrow polydispersity due to their high activities and capabilities.[24,25] Recently, bulky carbon-bridged bis(phenolate) ligands have attracted increasing attention in organolanthanide chemistry.[26-28] Not only have they attractive features, such as being easily available and tunable, but it can also provide O,O-bidentate chelating to stabilize the metal center to realize the single active site complex and limit back-biting side reaction during polymerization. Carbon-bridged bis(phenolate) lanthanide derivatives showed higher activity for the polymerization of cyclic esters. Shen and co-workers have demonstrated that bridged bis(phenolate) lanthanide complexes can serve as catalysts for the ROP of lactide[29] and lactones.[30] However, most of them paid attention to bis(phenolate)lanthanide alkoxides.[31,32] Meanwhile, The structural chemistry of anionic five-membered nitrogen heterocyclic ligands, especially pyrazolate and 1,2,4-triazolate ligands, has received much attention because of the structural diversity and variety of the coordination modes of these compounds.**[33]** Pyrazolate ligands are among the most versatile of ligands, with 20 different coordination modes identified so far.**[34-36]** To the best of our knowledge, the application of the heteroleptic pyrazolato lanthanide complexes bearing carbon-bridged bis(phenolate) ligands in ring-opening polymerization has not been reported.

In order to develop the new lanthanide containing organometallic complexes which could be used as catalyst in the polymerization of polyesters, we turned our attention to related carbon-bis(phenolate) ligands with two O,O-bidentate ligands (H_2L_1 - H_2L_2). We report here the synthesis a series of bis(phenolato)lanthanide complexes (**1** – **4**) and heteroleptic pyrazolato lanthanide complexes (**5** - **8**) bearing carbon-bridged bis(phenolate) ligands for the first time. The complexes obtained were characterized by nuclear magnetic resonance (NMR) spectroscopy and elemental analysis, respectively. The single crystals of complexes **5** - **8** have been determined by X-ray diffraction. The catalytic properties of the complexes (**1** - **8**) have also been studied in the polymerization of ε-caprolactone under mild conditions.

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Results and discussion

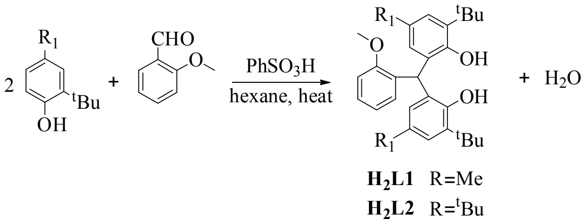
Synthesis and Characterization of Lanthanide Complexes 1 – 8.

Ligands (H_2L_1 and H_2L_2) were prepared according to the literature procedure (scheme 1).[37] A series of lanthanide complexes can be synthesized by amine elimination reaction. Bis(phenolato)lanthanide complexes (**1** – **4**) could be prepared by the reaction of $Ln[N(SiMe_3)_2]_3$ (Ln = La, Gd) with H_2L (H_2L_1 and H_2L_2) in a 1:1 molar ratio in THF at 60 °C in nearly quantitative yields. Complexes **5** – **8** ($LLnPzMe_2(THF)_3$ [L = L_1, Ln = La (**5**); Ln = Gd (**6**); L = L_2, Ln = La (**7**); Ln = Gd (**8**)] could be synthesized by using complex **1** - **4** further reacting with 1 equiv of Me_2PzH in THF in high yields (Scheme 2). Complexes **5** - **8** can also be synthesized by the direct reaction of $Ln[N(SiMe_3)_2]_3$ with H_2L_1/H_2L_2 and Me_2PzH in a 1:1:1 molar ratio in situ in THF. (Scheme 2)

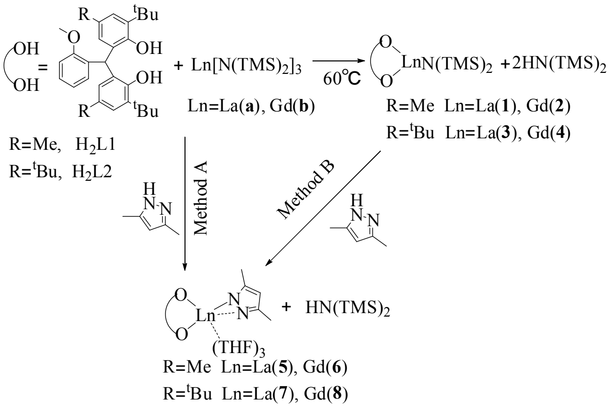
Meanwhile，we had tried another way for synthesis of complexes **5** - **8**. First of all, $Ln[N(SiMe_3)_2]_3$ reacted with Me_2PzH in a 1 : 1 molar ratio in THF to produce complexes **$Me_2PzLn[N(TMS)_2]_2(THF)_2$**, which can be used as a precursor to synthesize the corresponding heteroleptic pyrazolato lanthanide complexes **5** - **8** by a further reaction with 1 equiv of H_2Ln (n = 1, 2). (Scheme 3)

Due to the strong paramagnetism of the central metal ions (Gd), complexes **2**, **4**, **6** and **8** did not provide any resolvable ^1H NMR spectra. In the ^1H NMR spectrum of complex **1** and **3**, except for the resonances of the L^{2-} groups, $Si(CH_3)^-$ group and THF molecules，no resonance of the hydroxyl proton of the bridged bis(phenol) was observed, indicating that the phenolate lanthanide amides was formed. Disappearance of the $Si(CH_3)^-$ group signal (δ = 0.4 ~ 0.5) in the ^1H NMR spectra of lanthanide complexes **5** and **7**, indicating that the substitution reaction had been achieved. In the FT-IR pectrogram, we find the absorption peak of complexes **1** - **8** are very similar to the corresponding ligands ,and the absorption of active hydrogen of ligands H_2L and Me_2PzH are disappeared，which can also indicate that the substitution reaction had indeed occurred.

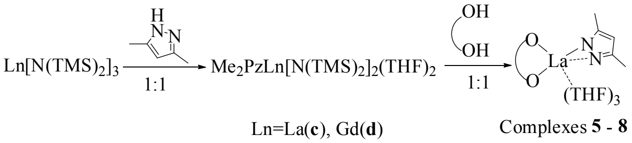
It was unsuccessful to determine definitive structures of complexes **1** – **4**, due to solvent loss and the deterioration in crystal quality. By single-crystal structure analysis, the definitive structures of complexes **5** - **8** were determined (see below). The definitive molecular structures determined by X-ray crystal structural analysis are consistent with the ^1H NMR results.



Scheme 1. Synthesis of the ligands.



Scheme 2. Synthesis of the complexes **1** – **8**



Scheme 3. Synthesis of the complexes **5** and **7** (Method C)

Crystal structures

Crystals suitable for X-ray structure determination of complexes **5** - **8** were obtained from a hexane/THF mixed solution at room temperature. The crystallographic data and experimental details of the data collection, as well as the structure refinement are given in table 1. The molecular structures of molecules **5** and **6** are depicted in Fig. 1 and Fig. 2.

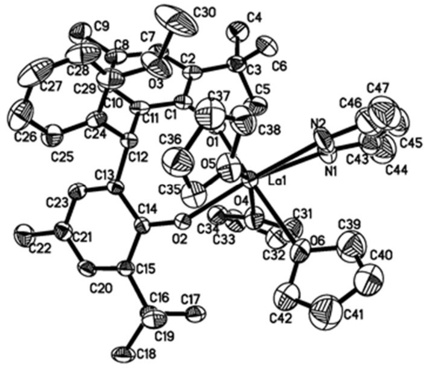


Figure 1. Molecular structure of complex 5 showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Crystallographic data for **5** - **8**.

	5	**6**	**7**	**8**
formula	$C_{47}H_{67}LaN_2O_6$	$C_{47}H_{67}GdN_2O_6$	$C_{53}H_{79}LaN_2O_6$	$C_{53}H_{79}GdN_2O_6$
formula weight	894.94	913.28	979.09	997.43
crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	$P2_1/c$	$P2_1/c$
a/Å	13.336 (2)	13.348 (2)	13.629 (3)	13.740 (2)
b/Å	14.166 (3)	14.064 (3)	19.851 (4)	20.389 (4)
c/Å	16.340 (3)	16.293 (3)	19.143 (4)	18.914 (3)
α/deg	75.288 (2)	75.129 (2)	90	90
β/deg	70.091 (2)	69.752 (2)	96.50 (3)	97.246 (2)
γ/deg	63.392 (2)	62.759 (2)	90	90
V/Å^3	2576.1 (8)	2533.6 (8)	5145.8 (19)	5256.2 (15)
Z	2	2	4	4
Dc/Mg m^{-3}	1.154	1.197	1.264	1.260
F(000)	936	950	2064	2092
μ/mm^{-1}	0.87	1.35	0.88	1.31
Cryst size (mm)	0.20×0.20× 0.20	0.20×0.20× 0.20	0.20×0.20× 0.20	0.20×0.20× 0.20
temp/K	296	296	173	296
ϑ range (°)	1.3-25	1.3-25	3.2-25	1.5-25
reflections	8990	8764	9034	9257
R1	0.064	0.059	0.030	0.031
wR2	0.221	0.205	0.076	0.080
Δρmin, max/e Å^{-3}	−0.59，1.82	−1.19，1.89	−0.39, 0.60	−0.40, 0.54
goodness of fit	1.12	1.05	1.05	1.03

$^{a)}$ $R_1 = \sum(||F_o|-|F_c||)/\sum|F_o|$; $wR_2 = [\sum(w(F_o^2-F_c^2)^2)/\sum(wF_o^4)]^{1/2}$.

$^{b)}$ $w_5 = 1 / [\sigma^2(F_o^2) + (0.159\ P)^2]$, $P = (F_o^2+2F_c^2)/3$.

$w_6 = 1 / [\sigma^2(F_o^2) + (0.1414\ P)^2]$, $P = (F_o^2+2F_c^2)/3$.

$w_7 = 1 / [\sigma^2(F_o^2) + (0.0351P)^2]$, $P = (F_o^2+2F_c^2)/3$.

$w_8 = 1 / [\sigma^2(F_o^2) + (0.0405P)^2 + 1.2726P]$, $P = (F_o^2+2F_c^2)/3$.

$^{c)}$ $S = [\sum w(F_o^2-F_c^2)^2]/(n-p)^{1/2}$, n = number of reflections, p = parameters used.

Complex **5** and **6** are isostructural, they have a monomeric structure; the lanthanide atom are seven-coordinated by two nitrogen atoms from pyrazolato group, two oxygen atoms from one L1^{2-} group, and three oxygen atoms from three THF molecules. The coordination geometry at the lanthanide atom can be best described as a distorted pentagonal bipyramid. The average La-O(Ar) bond lengths of **5** (2.272 (6) Å) is comparable with Gd-O(Ar) bond lengths of **6** (2.18 (3) Å) taking into account the difference in ionic radii is considered. The average La-O(Ar) bond lengths (for **5**) is comparable with those in $(C_5H_5)La(MBMP)(THF)_3$ (2.256 Å) (MBMP^{2-} = 2,2-methylene-bis(6-tert-butyl-4-methyl-phenoxo))[38] and [ONNO]LaCp (2.291 Å) [ONNO = $Me_2NCH_2CH_2N\{CH_2$-(2-O- C_6H_2)-tBu-3-Me-5)}$_2$],[39] but slightly longer than those in [(MBMP)La(μ-OCH_2Ph)$(THF)_2]_2$ (2.226 Å)[40] and $L'_2La(TMS)_2$ (2.227 Å) (L' = 3,5-But$_2$-2-(O)-C_6H_2CH=N-2,6-Pr$^i_2$-C_6H_3).[13] The average C-O bond lengths of the phenolate ligands in complexes **5** and **6** are 1.335(7) Å and 1.351(8) Å, respectively, which are apparently shorter than the single C-O bond length, reflecting substantial electron delocalization from the oxygen into the aromatic rings.

In complexes **5** and **6**, the two nitrogen atoms of pyrazolato group are also coordinated to the lanthanide atom, the Ln-N (1) bond lengths is comparable with Ln-N (2) bond lengths. The average La-N bond lengths of **5** (2.512(6) Å) is comparable with Gd-N bond lengths of **6** (2.415 (7) Å) when the difference in ionic radii is considered.

Compared with the neutral pyrazole, the C-C bond lengths and C-N bond lengths of the anionic pyrazole have some obvious difference. In $[La(Ph_2Pz)_3(Ph_2PzH)_2]$,[41] the C-C bond lengths of the neutral pyrazole are 1.372 Å and 1.410 Å, the C-N bond lengths are 1.343 Å and 1.354 Å, respectively. While in complex **5**, the C-C bond lengths of the anionic pyrazole are 1.368 Å and 1. 374 Å, the C-N bond lengths are 1.333 Å and 1.339 Å, respectively. So, it's very difficult to distinguish between C-C single bond and C=C double bond from the bond length, as also is unable to distinguish between C-N single bond and C=N double bond. The chemical shift of C-H protons for neutral pyrazole ligand Me_2PzH is 5.73 ppm, however the chemical shift of C-H protons for anionic pyrazole ligand Me_2Pz-（complexes **5** and **7**）is 5.76 ppm，it is clearly that there is a slight difference between neutral and anionic pyrazole ligand，which could be attributed to the anionic pyrazole ligand undergo delocalization.

The molecular structures of **7** and **8** are depicted in Fig. 3 and Fig. 4, with their selected bond lengths and bond angles listed in Table 2. Complexes **7** and **8** are isostructural, they have a monomeric structure; the central metal atom is seven-coordinated by one bis(phenolate) ligand, one pyrazole groups, and three THF molecules in a distorted pentagonal bipyramid. The average La-O(Ar) bond lengths of **7** (2.304 (17) Å) is comparable with Gd-O(Ar) bond lengths of **8** (2.195 (2) Å) considering the difference in ionic radii. The molecular structure analysis of complexes **7** and **8** are consistent with the complex **5** and **6**.

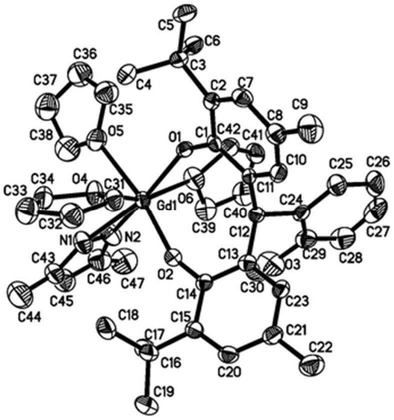


Figure 2. Molecular structure of complex **6** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity.

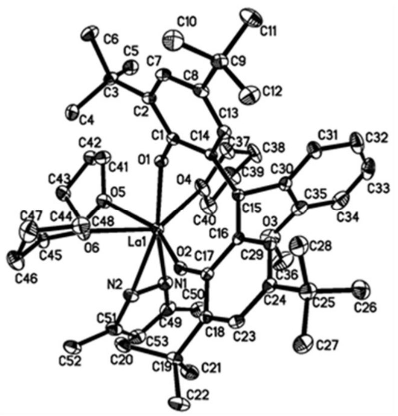


Figure 3. Molecular structure of complex **7** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity.

Catalytic activity studies

Their performance of complexes **1** - **8** as catalysts for the ROP of ε-CL was examined in a toluene solution at 20 °C, and the preliminary results are listed in table 2. It can be seen that all complexes are efficient initiators of the polymerization of ε-CL in toluene. All polymerizations proceeded fast and completed within 1 h to give polymers with relatively narrow molecular weight distributions (PDIs) (≤1.53). These initiators showed high activity (even for $[M]_0/[I_{1-4}]_0$ = 750), the polymerization still can proceed smoothly) and produced PCL with a molecular weight of 8.73×10^4 and a PDI of 1.18. In comparison with carbon-bridged Bis(phenolato)lanthanide alkoxides reported by Yao and co-workers (time of polymerization 1 h, temperature 17 °C, yield 31–100%, Mn 0.68×10^4- 4.56×10^4, PDI 1.14–1.29),[42] complexes **1** - **4** exhibit higher catalytic activity.

The ionic radii of the lanthanide metals have a profound effect on the polymerization activity of the corresponding lanthanide complexes.[36] However, these lanthanum amides showed similar

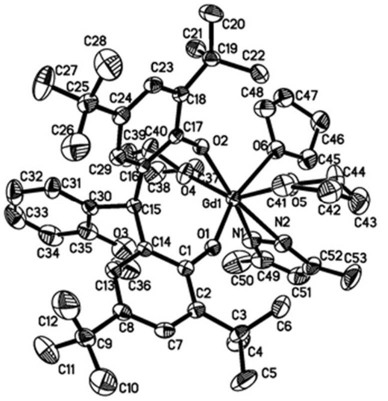
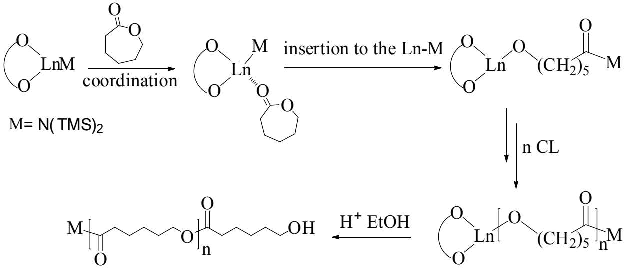


Figure 4. Molecular structure of complex **8** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

activity for the polymerization in comparison with the corresponding gadolinium amides complexes. For example, using complex **1** as the initiator, the yield reaches 95% (Mn: 6.43×10^4)and 77% (Mn: 8.73×10^4) when the molar ratio of monomer to initiator are respectively 100 and 500 (Entry 1, 3); whereas the yield is 92% (Mn: 7.85×10^4) and 83% (Mn: 5.84×10^4) using the complex **2** as the initiator (Entry 5, 7), which isn't consistent with the active trend for the polymerization of cyclic esters initiated by the lanthanide-based complexes.[43,44] All of the same kind of amido lanthanide complexes show a similar catalytic behavior.

The amides groups has a significant effect on the polymerization. Complexes **1** - **4** showed higher activity for polymerization than the complexes **5** - **8**. Using **1** as the initiator, the yield reaches 95% in 1 min at room temperature when the molar ratio of monomer to initiator ($[M_0]/[I_0]$) is 250, whereas the yield is 81% in 30 min using **5** as the initiator under the same polymerization conditions (Entries 1, 17). Using **1** - **4** as the initiator, even for $[M]_0/[I]_0$ = 750, the polymerization still can proceed, while it wasn't completed after several days when using complexes **5** – **8** as the initiator under the same polymerization conditions， which was attributed to the different molecular structures of the lanthanide amides, the bulky –$PzMe_2$ groups may have a bad effect on the polymerization. However, the effect of the bis(phenolato) groups in these complexes on the polymerization was not observed.

The microstructure of PCL was determined by ^1H NMR experiments using initiator **1** and a 10 :1 monomer to initiator ratio, as shown in Figure 5.



Scheme 4. Possible Mechanism for the ROP of ε-CL.

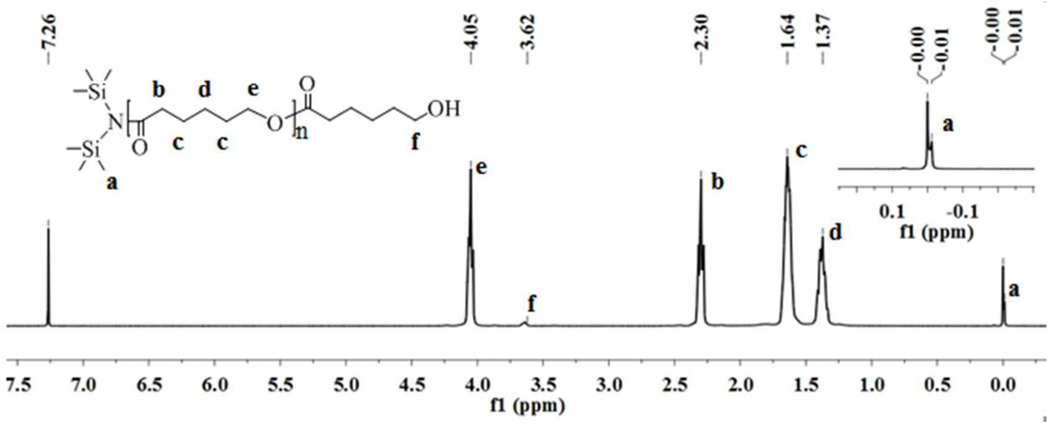


Figure 5. ^{1}H NMR spectrum of PCL ($CDCl_3$)

Table 2. Polymerization of ε-CL initiated by **1 – 8**^{a}

entry	initiator	$[M]_0/[I]_0$	Time (min)	Yield^b （%）	M_n^{c} (10^4)	PDI^c
1	**1**	100	1	95	6.43	1.47
2	**1**	250	1	93	6.78	1.39
3	**1**	500	10	77	8.73	1.18
4	**1**	750	60	46	5.63	1.42
5	**2**	100	1	92	7.85	1.41
6	**2**	250	1	90	6.73	1.53
7	**2**	500	10	83	5.84	1.30
8	**2**	750	60	50	5.36	1.28
9	**3**	100	1	97	6.21	1.37
10	**3**	250	1	100	5.83	1.21
11	**3**	500	10	80	6.81	1.45
12	**3**	750	60	54	5.72	1.33
13	**4**	100	1	88	6.29	1.27
14	**4**	250	1	96	7.34	1.29
15	**4**	500	10	83	5.47	1.18
16	**4**	750	60	44	4.85	1.23
17	**5**	100	10	81	3.42	1.41
18	**5**	250	30	82	3.53	1.39
19	**6**	100	10	83	3.31	1.34
20	**6**	250	30	77	3.78	1.37
21	**7**	100	10	82	4.32	1.28
22	**7**	250	30	87	4.68	1.31
23	**8**	100	10	88	3.67	1.26
24	**8**	250	30	79	4.57	1.39
25	**a**	100	1	86	5.61	2.03
26	**a**	250	10	98	6.42	2.24
27	**b**	100	1	89	6.70	2.15
28	**b**	250	10	96	5.84	2.38

[a] General polymerization conditions: $[M]_0/[I]_0$: the ratio of monomer to Ln (Gd or La), solvent = toluene, T = 20 °C.

[b] Yield: weight of polymer obtained/weight of monomer used.

[c] Measured by GPC in THF calibrated with polystyrene standard.

The ^{1}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 a-position to terminal hydroxy group. One possible polymerization mechanism is via the coordination/insertion (shown in Scheme 4), which is similar to the literature.[45,46]

Experimental section

$HN(TMS)_2$ (TMS=$SiMe_3$), ε-Caprolactone, and ^{n}BuLi are commercially available. All manipulations were performed under pure 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. ε-Caprolactone was dried over CaH_2 for 3 days， and distilled under reduced pressure. $HN(TMS)_2$ was dried with small amount of sodium and distilled before use. The starting complexes $La[N(TMS)_2]_3$/$Gd[N(TMS)_2]_3$,[47] H_2L_1~H_2L_2[38] and Me_2PzH[48] were synthesized according to published procedures. Lanthanide analysis were performed by EDTA titration with a xylenol orange indicator and hexamine buffer. NMR spectra were recorded on a Bruker Advance 400 spectrometer at resonant frequencies of 400 MHz for ^{1}H and 101 MHz for ^{13}C nuclei using C_6D_6 or d_6-DMSO as the solvent. Elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. 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 (300×7.5 mm, guarded and packed with 1×10^5, 1×10^4, 1×10^3, and 500 A gels) in series. Tetrahydrofuran (THF, 1 mL min^{-1}) 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.

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 ω scan mode using MoKα radiation (λ = 0.71073 Å) at 223(2) K. All measured independent reflections (I > 2σ(I)) were used in the structural analysis and semi-empirical absorption corrections were applied using SADABS.[49] The structure was solved and refined using SHELXL-97.[50] All hydrogen atoms were positioned geometrically and refined using a riding model. The non-hydrogen atoms were refined with anisotropic thermal parameters.

Ring-Opening Polymerization for ε-Caprolactone

The procedures for the ring-opening polymerization of ε-Caprolactone initiated by complexes **1** - **8** 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. To this solution was added desired amount of ε-Caprolactone by syringe. The mixture was stirred vigorously for the desired time. Then，a couple drops of 1 M HCl - ethanol solution were added to fully quench and the polymer was precipitated, which was dried under vacuum and weighed.

General procedure

Synthesis of [(*o*-OCH$_3$)PhCH(C$_6$H$_2$-3-^{t}Bu-5-Me-2-O)$_2$]La[N(TMS)$_2$], [L$_1$La[N(TMS)$_2$] (1). H$_2$L1 (0.92 g, 2.06 mmol) dissolved in 15 mL of THF was slowly added to La[N(TMS)$_2$]$_3$ (1.28 g, 2.06 mmol) dissolved in 25 mL of THF. The reaction mixture was stirred for 3 h at 60 °C, and all volatiles were removed under oil pump vacuum. 10 mL of toluene was added to extract the product, and orange-yellow microcrystals were obtained in a nearly quantitative yield by cooling the toluene solution (1.41 g, 92 % based on La). mp. 236-238 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25°C): δ = 7.21 (s, Ar*H*, 2 H), 7.13 (s, Ar*H*, 2 H), 7.01 (d, J = 7.4 Hz, Ar*H*, 2 H), 6.74 (d, J = 7.9 Hz, Ar*H*, 1 H), 6.56 (d, J = 2.0 Hz, Ar*H*, 1 H), 5.84 (s, C*H*, 1 H), 3.00 (s, OC*H*$_3$, 3 H), 2.20 (s, C*H*$_3$, 6 H), 1.29 (s, C(C*H*$_3$)$_3$, 18 H), 0.48 (s, Si(C*H*$_3$)$_3$, 18 H). ^{13}C NMR (101 MHz, C$_6$D$_6$, 25°C): δ = 158.7 (Ar), 158.1 (Ar), 136.8 (Ar), 132.5 (Ar), 130.2 (Ar), 129.4 (Ar), 129.3 (Ar), 127.3 (Ar), 125.8 (Ar), 124.1 (Ar), 121.5 (Ar), 113.1 (Ar), 55.9 (O*C*H$_3$), 41.7 (*C*H), 35.5 (*C*(CH$_3$)$_3$), 30.7 (*C*(CH$_3$)$_3$), 25.5 (*C*H$_3$), 5.4 (Si(CH$_3$)$_3$). Anal. Calcd for C$_{36}$H$_{54}$LaNO$_3$Si$_2$: C, 58.12; H, 7.32; N, 1.88; La, 18.67. Found: C, 57.94; H, 7.54; N, 1.72; La, 18.51. IR (KBr, cm^{-1}): 2961 (s), 2899 (m), 2871 (m), 1601 (w), 1460 (m), 1437 (m), 1362 (m), 1248 (w), 1024 (w), 833 (w), 752 (w).

Synthesis of [(o-OCH$_3$)PhCH(C$_6$H$_2$-3-^{t}Bu-5-Me-2-O)$_2$]Gd[N(TMS)$_2$], [L$_1$Gd[N(TMS)$_2$] (**2**)**.** The synthesis of complex **2** was carried out in the same way as the described for the synthesis of complex **1**, but Gd[N(TMS)$_2$]$_3$ (1.32 g, 2.07mmol) was used instead of La[N(TMS)$_2$]$_3$. Orange-yellow microcrystals were obtained from subsequent work (1.47 g, 93 % based on Gd). mp. 242-245 °C. Anal. Calcd for C$_{36}$H$_{54}$GdNO$_3$Si$_2$: C, 56.73; H, 7.14; N, 1.84; Gd, 20.63. Found: C, 56.58; H, 7.37; N, 1.75; Gd, 20.49. IR (KBr, cm^{-1}): 2960 (s), 2902 (m), 2870 (m), 1599 (w), 1460 (m), 1439 (m), 1361 (m), 1245 (w), 1018 (w), 834 (w), 750 (w).

Synthesis of [(o-OCH$_3$)PhCH(C$_6$H$_2$-3,5-^{t}Bu$_2$-2-O)$_2$]La[N(TMS)$_2$], [L$_2$La[N(TMS)$_2$] (**3**). The synthesis of complex **3** was carried out in the same way as the described for the synthesis of complex **1**, but H$_2$L2 (0.99 g, 1.86 mmol) was used instead of H$_2$L1. The following procedure is similar to that described for complex **1**, and complex **3** was isolated as orange-yellow crystals (1.45 g, 92 %). mp. 241-243 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25°C): δ = 7.43 (d, J = 7.6 Hz, Ar*H*, 2 H), 7.40 (d, J = 2.0 Hz, Ar*H*, 2 H), 7.12 (d, J = 7.9 Hz, Ar*H*, 1 H), 6.76 (t, J = 7.4 Hz, Ar*H*, 1 H), 6.59 (d, J = 2.4 Hz, Ar*H*, 1 H), 5.79 (s, C*H*, 1 H), 3.00 (s, OC*H*3, 3 H), 2.20 (s, C*H*3, 6 H), 1.36 (s, C(C*H*$_3$)$_3$, 18 H), 1.29 (s, C(C*H*$_3$)$_3$, 18 H), 0.47 (s, Si(C*H*$_3$)$_3$, 18 H). ^{13}C NMR (101 MHz, C$_6$D$_6$, 25°C): δ = 158.6 (Ar), 158.3 (Ar), 137.8 (Ar), 137.3 (Ar), 135.9 (Ar), 132.1 (Ar), 129.8 (Ar), 127.2 (Ar), 126.0 (Ar), 121.6 (Ar), 121.1 (Ar), 113.5 (Ar), 56.3 (O*C*H$_3$), 42.1 (*C*H), 35.8 (*C*(CH$_3$)$_3$), 34.4 (*C*(CH$_3$)$_3$), 32.1 (C(*C*H$_3$)$_3$), 30.7 (C(*C*H$_3$)$_3$), 5.4 (Si(*C*H$_3$)$_3$). Anal. Calcd for C$_{42}$H$_{66}$LaNO$_3$Si$_2$: C, 60.92; H, 8.03; N, 1.69; La, 16.77. Found: C, 60.98; H, 8.14; N, 1.52; La, 16.84. IR (KBr, cm^{-1}): 2957 (s), 2905 (m), 2871(m), 1595 (w), 1462 (m), 1440 (m), 1359 (m), 1246 (w), 1022 (w), 831 (w), 751 (w).

Synthesis of [(o-OCH$_3$)PhCH(C$_6$H$_2$-3,5-^{t}Bu$_2$-2-O)$_2$]Gd[N(TMS)$_2$], [L$_2$Gd[N(TMS)$_2$] (4). Synthesis of complex **4** was carried out in the same way as that described for complex **1**, but H$_2$L2 (0.99 g, 1.86 mmol) and Gd[N(TMS)$_2$]$_3$ (1.19 g, 1.86 mmol) was used and subsequent work to afford **4** as orange-yellow microcrystals (1.46 g, 93 % based on Gd). mp. 248-251 °C. Anal. Calcd for C$_{42}$H$_{66}$GdNO$_3$Si$_2$: C, 59.60; H, 7.86; N, 1.65; Gd, 18.58. Found: C, 59.54; H, 7.94; N, 1.53; Gd, 18.64. IR (KBr, cm^{-1}): 2960 (s), 2895 (m), 2868 (m), 1603 (w), 1458 (m), 1442 (m), 1360 (m), 1251 (w), 1025 (w), 829 (w), 754 (w).

Synthesis of [(o-OCH$_3$)PhCH(C$_6$H$_2$-3-^{t}Bu-5-Me-2-O)2]La(PzMe$_2$)(THF)$_3$, [L1Gd(Me$_2$Pz)(THF)$_3$] (5). Method A. Complex 1 (1.16 g, 1.56 mmol) dissolved in 10 mL of THF was added to Me$_2$PzH (0.15 g, 1.56 mmol) dissolved in 10 mL of THF. The reaction mixture was stirred for 6 h at 60 °C, and then the all volatiles was removed under oil pump vacuum. Toluene was added to extract the product, and pale-blue microcrystals were obtained from the concentrated toluene solution at -30 °C (1.20 g, 86 % base on La). mp. 256-258 °C. ^{1}H NMR (400 MHz, d$_6$-DMSO, 25°C): δ = 7.25 (t, J = 7.5 Hz, Ar*H*, 1 H), 7.16 (s, Ar*H*, 1 H), 7.08 (m, Ar*H*, 1 H), 6.77 (d, J = 7.9 Hz, Ar*H*, 1 H), 6.60 (s, Ar*H*, 2 H), 6.51 (s, Ar*H*, 2 H), 6.39 (s, C*H*, 1 H), 5.75 (s, Pz*H*, 1 H), 3.60 (t, J = 5.8 Hz, THF, 12 H), 3.34 (s, OC*H*$_3$, 3 H), 2.12 (s, Pz(C*H*$_3$)$_2$, 6 H), 2.02 (s, ArC*H*$_3$, 6 H), 1.76 (t, J = 5.9 Hz , THF, 12 H), 1.37 (s, C(C*H*$_3$)$_3$, 18 H). ^{13}C NMR (101 MHz, d$_6$-DMSO, 25°C): δ = 162.7 (Ar), 161.2 (Ar), 157.9 (C(Pz), 137.1 (Ar), 134.2 (Ar), 133.9 (Ar), 129.7 (Ar), 128.2 (Ar), 127.3 (Ar), 125.3 (Ar), 122.8 (Ar), 121.5 (Ar), 112.2 (Ar), 103.1 (C(Pz)), 67.5 (THF), 56.4 (OCH$_3$), 55.5 (CH), 35.0 (C(CH$_3$)$_3$), 31.4 (C(CH$_3$)$_3$), 31.2 (ArCH$_3$), 25.6 (THF), 21.5 (CH$_3$). Anal. Calcd for C$_{47}$H$_{67}$LaN$_2$O$_6$: C, 63.08; H, 7.55; N, 3.13; La, 15.22. Found: C, 62.92; H, 7.67; N, 3.04; La, 15.13. IR (KBr, cm^{-1}): 2960 (s), 2920 (m), 2868 (m), 1590 (w), 1465 (m), 1442 (m), 1397 (w), 1285 (w), 1250 (m), 1178 (w), 1034 (w), 864 (w), 754 (m), 692 (w).

Method B. H$_2$L$_1$ (0.92 g, 2.06 mmol) dissolved in 15 mL of THF was slowly added to La[N(TMS)$_2$]$_3$ (1.28 g, 2.06 mmol) dissolved in 25 mL of THF at 60 °C. After the solution was stirred for 3 h at 60 °C, Me_2PzH (0.20 g, 2.06 mmol) was added. The reaction mixture was stirred for 6 h at 60 °C, and then the all volatiles were removed under oil pump vacuum. Toluene was added to extract the product, and pale-blue microcrystals were obtained by cooling the toluene solution (1.56 g, 85% base on La).

Method C. Me_2PzH (0.84 g, 1.35 mmol) dissolved in 15 mL of THF was slowly added to La[N(TMS)$_2$]$_3$ (0.13 g, 1.35 mmol) dissolved in 25 mL of THF at -30 °C. After the solution was stirred for 12 h at 60 °C, H_2L1 (0.60 g, 1.35 mmol) was added. The reaction mixture was stirred for 6 h at 60 °C, and then the all volatiles were removed under oil pump vacuum. Toluene was added to extract the product, and pale-blue microcrystals were obtained by cooling the toluene solution (0.86 g, 85% base on La).

Complex **c**｛**Me_2PzLa[N(TMS)$_2$]$_2$(THF)$_2$**｝： mp. 187-189 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 6.17 (s, 1H, Pz-H), 3.68 (m, 8H, THF), 2.29 (s, 6H, CH_3), 1.34 (m, 8H, THF), 0.34 (s, 36H, $SiMe_3$). ^{13}C NMR (101 MHz, C_6D_6): δ 145.2(C=N), 109.4(C=C), 68.5(THF), 24.9(THF), 13.0(CH3), 3.6(Si(CH_3)$_3$). Anal. calcd. for $C_{25}H_{57}LaN_4O_2Si_4$: La, 19.93; C, 43.08; H, 8.24; N, 8.04. Found: La, 19.73; C, 43.24; H, 8.02; N, 8.19.

Complex **d**｛**Me_2PzGd[N(TMS)$_2$]$_2$(THF)$_2$**｝： mp. 194-196 °C. Anal. calcd. for $C_{25}H_{57}GdN_4O_2Si_4$: Gd, 21.92; C, 41.86; H, 8.29; N, 7.81. Found: La, 21.71; C, 42.03; H, 8.13; N, 8.02.

Synthesis of [(o-OCH$_3$)PhCH(C_6H_2-3-^{t}Bu-5-Me-2-O)$_2$]Gd(PzMe$_2$)(THF)$_3$, [L1Gd(Me$_2$Pz)(THF)$_3$] (6). The synthesis of complex **6** was carried out in the samilar way as that described for complex **5** (method B), but Gd[N(TMS)$_2$]$_3$ (1.12 g, 1.75 mmol) was used instead of La[N(TMS)$_2$]$_3$. Amount of pale-blue microcrystals were obtained from the concentrated tolune solution (1.39 g, 87 %, base on Gd). mp. 267-269 °C. Anal. Calcd for $C_{47}H_{67}GdN_2O_6$: C, 61.81; H, 7.39; N, 3.07; Gd, 17.22. Found: C, 61.72; H, 7.51; N, 3.14; Gd, 17.11. IR (KBr, cm^{-1}): 2958 (s), 2919 (m), 2871 (m), 1587 (w), 1467 (m), 1442 (m), 1394 (w), 1288 (w), 1246 (m), 1180 (w), 1030 (w), 866 (w), 756 (m), 691 (w).

Synthesis of [(o-OCH$_3$)PhCH(C_6H_2-3,5-^{t}Bu$_2$-2-O)$_2$]La(PzMe$_2$)(THF)$_3$, [L$_2$La(PzMe$_2$)(THF)$_3$] (**7**). The synthesis of complex **7** was carried out in the samilar way as that described for complex **5** (method B), but H_2L2 (1.15 g, 2.16 mmol) was used instead of H_2L1. Pale-blue microcrystals were obtained from the concentrated tolune solution (1.84 g, 87%, base on La). mp. 264-266 °C. ^{1}H NMR (400 MHz, d_6-DMSO, 25°C) : δ = 7.25 (m, Ar*H*, 1 H), 7.18 (d, J = 7.1 Hz, Ar*H*, 1 H), 7.06 (m, Ar*H*, 1 H) , 6.99 (d, J = 6.3 Hz, Ar*H*, 2 H), 6.76 (d, J = 5.8 Hz, Ar*H*, 2 H), 6.65 (m, Ar*H*, 1 H), 6.27 (s, C*H*, 1 H), 5.76 (s, Pz*H*, 1 H), 3.60 (t, J = 5.8 Hz, THF, 12 H), 3.19 (s, OCH_3, 3 H), 2.13 (s, Pz(CH_3)$_2$, 6 H), 1.76 (t, J = 5.9 Hz, THF, 12 H), 1.39 (s, C(CH_3)$_3$, 18 H), 1.13 (s, C(CH_3)$_3$, 18 H). ^{13}C NMR (101 MHz, d_6-DMSO, 25°C): δ = 162.71 (Ar), 161.9 (Ar), 159.1 (C(Pz), 139.8 (Ar), 133.6 (Ar), 133.5 (Ar), 133.0 (Ar), 132.6 (Ar), 130.4 (Ar), 129.4 (Ar), 128.7 (Ar), 124.5 (Ar), 112.9 (Ar), 103.8 (*C*(Pz)), 67.5 (THF), 56.8 (O*C*H$_3$), 54.9 (*C*H), 35.0 (C(CH$_3$)$_3$), 33.9 (*C*(CH$_3$)$_3$), 32.5 (C(*C*H$_3$)$_3$), 31.5 (C(*C*H$_3$)$_3$), 25.6 (THF), 21.5 (*C*H$_3$). Anal. Calcd for $C_{53}H_{79}LaN_2O_6$: C, 65.01; H, 8.13; N, 2.86; La, 14.19. Found: C, 64.88; H, 8.26; N, 2.77; La, 14.28. IR (KBr, cm^{-1}): 2958 (s), 2905 (m), 2870 (m), 1594 (w), 1460 (m), 1438 (m), 1360 (m), 1288 (w), 1251 (w), 1049 (w), 1030 (w), 835 (w), 756 (m), 691 (w).

Syntheses of [(o-OCH$_3$)PhCH(C_6H_2-3,5-^{t}Bu$_2$-2-O)$_2$]Gd(PzMe$_2$)(THF)$_3$, [L$_2$Gd(PzMe$_2$)(THF)$_3$] (8). The synthesis of complex 8 was carried out in the samilar way as that described for complex 5 (method B), but H_2L2 (1.04 g, 1.95 mmol) and Gd[N(TMS)2]3 (1.24 g, 1.95 mmol) was used and subsequent work to afford 8 as pale-blue microcrystals (1.64 g, 84 %, base on Gd). mp. 272-274 °C. Anal. Calcd for $C_{53}H_{79}GdN_2O_6$: C, 63.82; H, 7.98; N, 2.81; Gd, 15.77. Found: C, 63.68; H, 7.86; N, 2.97; Gd, 15.63. IR (KBr, cm^{-1}): 2960 (s), 2904 (m), 2866 (m), 1600 (w), 1461 (m), 1436 (m), 1361 (m), 1292 (w), 1254 (w), 1054 (w), 1029 (w), 833 (w), 756 (m), 692 (w).

Conclusion

In summary, a series of new heteroleptic lanthanide amides complexes bearing carbon-bridged bis(phenolate) ligands have been synthesized via simple protonolysis exchange reactions using Ln[N(TMS)$_2$]$_3$(Ln = La, Gd) as the starting material. At frist, Ln[N(TMS)$_2$]$_3$ reacted with H_2Ln (n = 1, 2) to produce complexes **1** – **4**, which can further react with 1 equiv of Me_2PzH in THF to yield heteroleptic pyrazolato lanthanide complexes **5** – **8** in high yield. Meanwhile, Ln[N(TMS)$_2$]$_3$(Ln = La, Gd) reacted with Me_2PzH to form complex Me_2PzLn[N(TMS)$_2$]$_2$(THF)$_2$, which can be used as a precursor to synthesize the corresponding heteroleptic pyrazolato lanthanide complexes by a further reaction with 1 equiv of H_2Ln (n = 1, 2). Moreover, the complexes LLnPzMe$_2$ can also be synthesized by the direct reaction of Ln[N(SiMe$_3$)$_2$]$_3$ with H_2L and Me_2PzH in 1:1:1 molar ratio in situ in THF, all of these syntheses are quite straight forward and easy to access. These aminolanthanide complexes are well-characterized, and **5** – **8** of them are structurally characterized. The coordination geometries around the central metals in these complexes are similar. Furthermore, it was found that these complexes can catalyze the controlled polymerization ε-CL via a coordination-insertion mode, and the amides groups has a significant effect on the polymerization.

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For Table of Contents Use Only

Heteroleptic lanthanide amides complexes bearing carbon-bridged bis(phenolate) ligands: synthesis, structure and their application in the polymerization of ε-caprolactone

Yan-Xu Zhou[1], Jing Zhao [1], Ling Peng[1], Yu-Long Wang[1], Xian Tao[1], Ying-Zhong Shen[1*]

The bis(phenolato)lanthanide complexes LLnN(SiMe$_3$) [L = L$_1$, Ln = La (**1**); Ln = Gd (**2**); L = L$_2$, Ln = La (**3**); Ln = Gd (**4**)] were synthesized by the reaction of Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = La, Gd) with **H$_2$L** in a 1:1 molar ratio in THF. Complexes **5** – **8** can also be synthesized by the direct reaction of Ln[N(SiMe$_3$)$_2$]$_3$ with H$_2$L and Me$_2$PzH in 1:1:1 molar ratio in situ in THF. Complexes **5 - 8** have been characterized by X-ray crystal structural analysis. The catalyst activity of compounds **1** - **8** to the ring-opening polymerization of ε-caprolactone was studied.