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# Synthesis and structural diversity of lanthanide amidate complexes and their catalytic activities for the ring-opening polymerization of *rac*-lactide

Xiaolin Hu<sup>a</sup>, Chengrong Lu<sup>a</sup>, Bing Wu<sup>a</sup>, Hao Ding<sup>a</sup>, Bei Zhao<sup>a,\*</sup>, Yingming Yao<sup>a,\*\*</sup>, Qi Shen<sup>a,b</sup>

<sup>a</sup> Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China <sup>b</sup> State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, PR China

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### ABSTRACT

Anionic lanthanide amidate complexes, Li(THF)Ln[C<sub>6</sub>H<sub>5</sub>C(O)NC<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>]<sub>4</sub>(THF)<sub>n</sub>·(sol)<sub>m</sub> (Ln = La (1), Nd (2), Sm (3), Yb (4), Y (5), n = 0 or 1; sol = THF or *n*-Hex), were synthesized for the first time by direct protonolysis reaction of LiLn(N<sup>i</sup>Pr<sub>2</sub>)<sub>4</sub>(THF) with benzamide proligand, C<sub>6</sub>H<sub>5</sub>CONHC<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub> (HL). It was confirmed by their characterization data that complexes 1–5 presented rich and varied structures with changeable coordination modes of the amidate ligands. On the other hand, similar reactions of HL with neutral homoleptic lanthanide amides, Ln[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, Cleanly yielded the neutral lanthanide amidate complexes, {PhC(O)NC<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>}<sub>2</sub>Ln{OC(Ph)(C<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>)N-H-N(C<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>)<sub>2</sub>C(Ph)O](THF)<sub>2</sub> (Ln = La (6), Nd (7), Sm (8)). Single-crystal X-ray structural determination revealed that complexes **6**–**8** featured an unprecedented N–H–N bond between two of the amidate ligands, making it the most notable difference from normal neutral analogs. Complexes **1–8** were characterized by elemental analysis and IR spectroscopy, with additional <sup>1</sup>H NMR spectroscopy in the case of complexes **1, 5** and **6**. Furthermore, both the anionic and neutral lanthanide amidate complexes proved to be efficient catalysts for the ring-opening polymerization of *rac*-lactide, affording heterotactic-rich polylactides. The anionic lanthanide amidate complexes exhibited significantly higher activities than their neutral counterparts due to the cooperative effect.

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### 1. Introduction

The use of readily accessible classes of organic compounds as ancillary ligands is a key facet of organometallic and coordination chemistry. In the past two decades, a very simple group of *N*,O-chelating molecules, namely deprotonated organic amides (amidates), has received considerable attention in organotransition metal chemistry because of such attractive features as ease of preparation and tunability of steric and electronic properties [1]. Furthermore, some of these transition metal amidate complexes have shown great potential applications in catalytic transformations, such as hydroamination and hydroamination/cyclization [2],  $\alpha$ -alkylation [2c], allylic etherification [3], olefin oxidation [4], Strecker reaction [5], asymmetric intermolecular boron Heck-type reactions [6], oxygen activation and intramolecular C–H bond activation [7], and polymerization [8,9].

The amidate group possesses two different donor atoms, namely N and O, in its scaffold, and can adopt a variety of coordination

modes when bound to a metal center [2a,10]. A survey of the literature reveals that most characterized transition metal amidate complexes fall into one of the following three categories: i) monodentate: O-bound or N-bound, ii) bridging and iii) chelating (see Fig. 1). It is well-known that the lanthanide metals display more varied coordination numbers compared to the transition metals in their complexes. Hence, the amidate group may give rise to additional coordination modes in organolanthanide chemistry. However, to date, studies on the synthesis and reactivity of the lanthanide amidate complexes remain rather limited, and only a few papers have been published in this field to our best knowledge [11]. There are different methods reported for the synthesis of lanthanide amidate complexes, including the insertion of isocyanate into Ln-C bonds [12], the insertion of CO into organolanthanide azobenzene derivative [13], the one-electron reduction and coupling reaction using bisaryloxo samarium(II) complex and phenyl isocyanate [14], and the disruptive acylation of dianionic guanidiate ligand using PhCOCI [15]. Nevertheless, the most direct method to access lanthanide amidate complexes involves the reaction of amide proligands with organolanthanide precursors [11].

Encouraged by these results, we began to get interested in the design and synthesis of lanthanide amidate complexes. What we

<sup>\*</sup> Corresponding author. Fax: +86 512 65880305.

<sup>\*\*</sup> Corresponding author.

E-mail addresses: xlhu@suda.edu.cn (X. Hu), zhaobei@suda.edu.cn (B. Zhao).

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Fig. 1. Several possible coordination modes of amidate ligands.

focused on were as below: Would there be different coordination modes in lanthanide amidate complexes? And what kinds of structure—reactivity relationships exist in the lanthanide amidate complexes?

As for their application on the ring-opening polymerization (ROP), Zi et al. [11e,f] obtained isotactic-rich polylactides with low *Pm* using amidate lanthanide amides as catalysts, while the stereo-control ability of bridged bis(phenolate) lanthanide complexes was far better [16]. Since ancillary ligand plays a crucial rule on the stereoselectivity, we are eager to investigate into the characteristics, including both activity and stereocontrol ability, of organolanthanide amidate complexes acting as catalysts for ROP of *rac*-lactide.

Herein, we report the synthesis of two new series of lanthanide amidate complexes via the convenient protonolysis reactions. Structural characterization revealed that the amidate ligands indeed exhibit diverse coordination modes, and the presence of an N–H–N bond between two amidate ligands was also observed for the first time. All the lanthanide amidates were proved to be efficient catalysts for the ring-opening polymerization of *rac*-lactide, affording heterotactic-rich polylactides. Here we report these results.

#### 2. Experimental

#### 2.1. General procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. Metal analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. Melting points were determined in sealed Ar-filled capillary tubes and are uncorrected. The IR spectra were recorded on a Magna-IR 550 spectrometer. Molecular weight and molecular weight distributions were determined against a polystyrene standard by gel permeation chromatography (GPC) on a waters 1515 apparatus with three HR columns (HR-1, HR-2, and HR-4); THF was used as an eluent at 30 °C. <sup>1</sup>H NMR spectra were measured on a Unity Inova-400 spectrometer in C<sub>6</sub>D<sub>6</sub> or CDCl<sub>3</sub>.

### 2.2. Synthesis of $C_6H_5CONHC_6H_3(^iPr)_2$ (HL)

A 250 mL round-bottomed flask was charged with a solution of 2,6-diisopropylaniline (6.66 g, 37.5 mmol) and K<sub>2</sub>CO<sub>3</sub> (5.53 g, 40 mmol) in anhydrous ether (50 mL). The mixture was cooled to 0 °C, and a ether solution (20 mL) of benzoyl chloride (5.27 g, 37.5 mmol) was added dropwise. The resulting off-white suspension was left to stir at room temperature for 2 h. After filtration and washed by water, a white solid was obtained. The solid was recrystallized from hot ethanol. Yield: 7.04 g (67%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  9.75 (s, 1H, NH), 8.00 (d, *J* = 8 Hz, 2H, aryl H), 7.60 (t, *J* = 8 Hz, 1H, aryl H), 7.54 (t, *J* = 8 Hz, 2H, aryl H), 7.30 (t, *J* = 8 Hz, 2H, aryl H), 7.20 (d, *J* = 8 Hz, 2H, aryl H), 3.08 (septet, *J* = 8 Hz, 2H,

CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (d, J = 8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.10 (d, J = 8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>19</sub>H<sub>23</sub>NO: C, 81.10; H, 8.24; N, 4.98. Found C, 81.07; H, 8.28; N, 4.93. IR (KBr pellet, cm<sup>-1</sup>): 3305 (m), 3062 (w), 2962 (m), 1643 (s), 1520 (s), 1489 (s), 1385 (w), 1292 (m), 798 (w), 744 (w), 698 (m).

### 2.3. Synthesis of Li(THF)La[ $C_6H_5C(O)NC_6H_3(^iPr)_2$ ]<sub>4</sub>(THF)·(THF)<sub>1.5</sub> (1)

To a THF solution of HL (2.25 g, 8.00 mmol), LiLa(N<sup>i</sup>Pr<sub>2</sub>)<sub>4</sub>(THF) (1.24 g, 2.00 mmol) in 20 mL THF was slowly added. The mixture was stirred at room temperature for 4 h. After the reaction, the volatile solvent was pumped off, and the residue was recrystallized from a mixture solution of THF and hexane at room temperature to give 1 as colorless crystals. Yield: 2.40 g (79%). Mp. 267.3-267.9 °C (dec.). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  7.73 (d, J = 7.2 Hz, 6H, aryl H), 7.25 (t, J = 8 Hz, 4H, aryl H), 7.14 (t, J = 10 Hz, 10H, aryl H), 7.07 (t, *J* = 7.6 Hz, 8H, aryl H), 6.86 (br s, 4H, aryl H), 3.55 (s, 14H, OCH<sub>2</sub>CH<sub>2</sub>), 3.16 (septet, J = 6.8 Hz, 8H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (s, 14H, OCH<sub>2</sub>CH<sub>2</sub>), 1.20  $(d, J = 6.4 \text{ Hz}, 48\text{H}, \text{CH}(\text{CH}_3)_2)$ .<sup>T3</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  166.4 (C= O), 147.3, 135.4, 129.0, 127.9, 124.2 (aryl C), 68.3 (OCH<sub>2</sub>CH<sub>2</sub>), 39.9 (OCH<sub>2</sub>CH<sub>2</sub>), 29.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.4 (CH(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>180</sub>H<sub>232</sub>Li<sub>2</sub>N<sub>8</sub>O<sub>15</sub>La<sub>2</sub> (3039.44): C 71.13, H 7.69, N 3.69, La 9.14. Found: C 71.08, H 7.50, N 3.79, La 9.30. IR (KBr pellet, cm<sup>-1</sup>): 3064 (w), 2963 (m), 2868 (w), 1560 (w), 1522 (s), 1488 (s), 1384 (w), 1290 (m), 924 (w), 797 (m), 745 (m), 695 (m).

### 2.4. Synthesis of $Li(THF)Nd[C_6H_5C(O)NC_6H_3(^{1}Pr)_2]_4(THF) \cdot (THF)_{1.5}$ (2)

Following the method described for complex **1**, using HL (2.25 g, 8.00 mmol) and LiNd(N<sup>i</sup>Pr<sub>2</sub>)<sub>4</sub> (1.25 g, 2.00 mmol), afforded **2** as blue crystals. Yield: 2.17 g (71%). Mp. 214.9–215.6 °C (dec.). Anal. Calcd for  $C_{180}H_{232}Li_2N_8O_{15}Nd_2$  (3050.10): C 70.88, H 7.67, N 3.67, Nd 9.46. Found: C 70.78, H 7.50, N 3.94, Nd 9.73. IR (KBr pellet, cm<sup>-1</sup>): 3064 (w), 2963 (m), 2869 (w), 1580 (w), 1522 (m), 1488 (m), 1389 (w), 1291 (w), 925 (w), 797 (m), 745 (m), 695 (m).

### 2.5. Synthesis of $Li(THF)Sm[C_6H_5C(O)NC_6H_3(^iPr)_2]_4 \cdot (n-Hex)$ (3)

Following the method described for complex **1**, using HL (2.53 g, 9.00 mmol) and LiSm(N<sup>i</sup>Pr<sub>2</sub>)<sub>4</sub> (1.42 g, 2.25 mmol), afforded **3** as colorless crystals. Yield: 2.30 g (71%). Mp. 213.7–215.0 °C (dec.). Anal. Calcd for  $C_{86}H_{110}LiN_4O_5Sm$  (1437.07): C 71.88, H 7.72, N 3.90, Sm 10.46. Found: C 71.53, H 7.66, N 4.11, Sm 10.44. IR (KBr pellet, cm<sup>-1</sup>): 3064 (w), 2964 (m), 2868 (w), 1580 (w), 1522 (s), 1488 (s), 1290 (m), 797 (m), 745 (m), 695 (m).

### 2.6. Synthesis of Li(THF)Yb[C<sub>6</sub>H<sub>5</sub>C(O)NC<sub>6</sub>H<sub>3</sub>( $^{i}Pr$ )<sub>2</sub>]<sub>4</sub>·(n-Hex) (**4**)

Following the method described for complex **1**, using HL (2.25 g, 8.00 mmol) and LiYb(N<sup>i</sup>Pr<sub>2</sub>)<sub>4</sub> (1.31 g, 2.00 mmol), afforded **4** as colorless crystals. Yield: 2.20 g (75%). Mp. 217.3–218.5 °C (dec.). Anal. Calcd for C<sub>86</sub>H<sub>110</sub>LiN<sub>4</sub>O<sub>5</sub>Yb (1459.76): C 70.76, H 7.60, N 3.84, Yb 11.85. Found: C 70.67, H 7.30, N 3.97, Yb 11.72. IR (KBr pellet, cm<sup>-1</sup>): 3064 (w), 2963 (m), 2868 (w), 1580 (w), 1522 (s), 1488 (s), 1291 (w), 923 (w), 797 (m), 745 (m), 708 (m).

### 2.7. Synthesis of Li(THF)Y[C<sub>6</sub>H<sub>5</sub>C(O)NC<sub>6</sub>H<sub>3</sub>( $^{i}$ Pr)<sub>2</sub>]<sub>4</sub>(THF)·(THF) (**5**)

Following the method described for complex **1**, using HL (2.25 g, 8.00 mmol) and LiY(N<sup>i</sup>Pr<sub>2</sub>)<sub>4</sub> (1.14 g, 2.00 mmol), afforded **5** as colorless crystals. Yield: 2.09 g (73%). Mp. 227.7–228.3 °C (dec.). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.75 (br m, 6H, aryl H), 7.13 (br s, 14H, aryl H), 6.92–6.68 (br m, 12H, aryl H), 3.66 (br s, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.48 (s, 2H,

C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>, 12H, OC<u>H</u><sub>2</sub>CH<sub>2</sub>), 1.29 (s, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>, 12H, OCH<sub>2</sub>C<u>H</u><sub>2</sub>), 1.20 (s, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 0.98 (br s, 24H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  176.4 (C=O), 147.4, 140.5, 135.8, 130.6, 125.2, 124.3, 68.7 (OCH<sub>2</sub>CH<sub>2</sub>), 32.3 (OCH<sub>2</sub>C<u>H</u><sub>2</sub>), 29.6 (C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 28.9 (C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 26.0 (CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 24.3 (CH(C<u>H</u><sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>88</sub>H<sub>112</sub>LiN<sub>4</sub>O<sub>7</sub>Y (1437.07): C 73.72, H 7.87, N 3.91, Y 6.20. Found: C 73.82, H 7.80, N 4.12, Y 6.17. IR (KBr pellet, cm<sup>-1</sup>): 3064 (w), 2963 (m), 2869 (w), 1580 (w), 1522 (m), 1488 (m), 1290 (w), 797 (m), 745 (m), 695 (m).

## 2.8. Synthesis of $\{PhC(O)NC_{6}H_{3}(^{i}Pr)_{2}\}_{2}La\{OC(Ph)(C_{6}H_{3}(^{i}Pr)_{2})N-H-N(C_{6}H_{3}(^{i}Pr)_{2})C(Ph)O\}(THF)_{2}$ (**6**)

A Schlenk flask was charged with HL (1.69 g, 6.00 mmol), THF (10 mL), and a stir bar.  $La[N(SiMe_3)_2]_3$  (2.00 mmol, 15 mL of THF) was then added slowly, and the color of the solution gradually changed to light yellow. After stirring overnight at room temperature, the solvent was removed under vacuo. The residue was extracted by hexane to remove extra La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, then the solid left was dissolved in THF/hexane, and crystallized at room temperature to give **6** as colorless crystals. Yield: 1.20 g (57%, based on HL). Mp. 259.7–261.3 °C (dec.). <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>): δ 8.92 (s, 1H, NH), 7.91 (d, J = 8 Hz, 2H, aryl H), 7.52 (br s, 6H, aryl H), 7.39 (t, J = 7.2 Hz, 1H, aryl H), 7.32 (t, J = 7.2 Hz, 2H, aryl H), 7.19 (t, J = 7.2 Hz, 2H, 2Hz)*J* = 8 Hz, 1H, aryl H), 7.10 (m, 4H, aryl H), 7.02 (m, 6H, aryl H), 6.90 (m, 7H, aryl H), 6.86 (m, 3H, aryl H), 3.27 (m, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.17  $(\text{septet}, J = 6.8 \text{ Hz}, 2\text{H}, C\text{H}(C\text{H}_3)_2), 1.11 (d, J = 6.8 \text{ Hz}, 12\text{H}, C\text{H}(C\text{H}_3)_2),$ 0.90 (br s, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.63 (br s, 18H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, THF-*d*<sub>8</sub>): δ 166.8 (C=O), 147.5, 140.3, 136.1, 133.8, 131.8, 130.6, 129.9, 129.0, 128.5, 128.3, 127.9, 123.8, 123.7, 123.2 (aryl C), 29.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.1 (CH(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>84</sub>H<sub>105</sub>N<sub>4</sub>O<sub>6</sub>La (1405.63): C 71.78, H 7.53, N 3.99, La 9.88. Found: C 71.73, H 7.32, N 3.90, La 10.00. IR (KBr pellet, cm<sup>-1</sup>): 3295 (m), 3064 (w), 2964 (m), 2868 (w), 1642 (s), 1522 (m), 1488 (s), 1290 (m), 797 (w), 745 (w), 695 (w).

### 2.9. Synthesis of $\{PhC(O)NC_{6}H_{3}(^{i}Pr)_{2}\}_{2}Nd\{OC(Ph)(C_{6}H_{3}(^{i}Pr)_{2})N-H-N(C_{6}H_{3}(^{i}Pr)_{2})C(Ph)O\}(THF)_{2}$ (**7**)

Following the method described for complex **6**, using HL (1.69 g, 6.00 mmol) and Nd[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (2.00 mmol, 15 mL of THF),

#### Table 1

afforded **7** blue crystals. Yield: 1.27 g (60%, based on HL). Mp. 270.3–271.8 °C (dec.). Anal. Calcd for  $C_{84}H_{105}N_4O_6Nd$  (1410.96): C 71.50, H 7.50, N 3.97, Nd 10.22. Found: C 71.38, H 7.32, N 3.94, Nd 10.20. IR (KBr pellet, cm<sup>-1</sup>): 3299 (m), 3063 (w), 2963 (m), 2868 (w), 1642 (s), 1522 (m), 1488 (s), 1290 (m), 797 (w), 745 (w), 695 (w).

## 2.10. Synthesis of $\{PhC(O)NC_{6}H_{3}({}^{i}Pr)_{2}\}_{2}Sm\{OC(Ph)(C_{6}H_{3}({}^{i}Pr)_{2})N-H-N(C_{6}H_{3}({}^{i}Pr)_{2})C(Ph)O\}(THF)_{2} (\mathbf{8})$

Following the method described for complex **6**, using HL (2.53 g, 9.00 mmol) and Sm[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (3.00 mmol, 20 mL of THF), afforded **7** as colorless crystals. Yield: 2.05 g (64%, based on HL). Mp. 264.4–265.3 °C (dec.). Anal. Calcd for  $C_{84}H_{105}N_4O_6Sm$  (1417.07): C 71.20, H 7.47, N 3.95, Sm 10.61. Found: C 71.39, H 7.48, N 4.03, Sm 10.59. IR (KBr pellet, cm<sup>-1</sup>): 3298 (m), 3064 (w), 2964 (m), 2868 (w), 1642 (s), 1522 (m), 1488 (m), 1290 (w), 797 (w), 745 (w), 600 (w).

#### 2.11. X-ray structure determination of complexes 1-8

Owing to air and moisture sensitivity, suitable single crystals of complexes **1–8** were each sealed in thin-walled glass capillaries. Intensity data were collected on a Rigaku Mercury CCD equipped with graphite-monochromatized Mo K $\alpha$  ( $\lambda = 0.71070$  Å) radiation. Details of the intensity data collection and crystal data are given in Tables 1 and 3. The crystal structures of these complexes were solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares analysis on  $F^2$ . All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically with assigned appropriate isotropic thermal parameters. The structures were solved and refined by using the SHELXL-97 program [17].

### 2.12. A typical polymerization procedure

The procedures for the polymerization of *rac*-lactide initiated by complexes **1–8** were similar, and a typical polymerization procedure is given below. A 30 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with the desired amount of *rac*-

	<b>1</b> · 1.5THF	<b>2</b> · 1.5THF	<b>3</b> ·hexane	<b>4</b> hexane	5 · THF
Formula	C <sub>90</sub> H <sub>116</sub> LiN <sub>4</sub> O <sub>7.5</sub> La	C <sub>90</sub> H <sub>116</sub> LiN <sub>4</sub> O <sub>7.5</sub> Nd	C <sub>86</sub> H <sub>110</sub> LiN <sub>4</sub> O <sub>5</sub> Sm	C <sub>86</sub> H <sub>110</sub> LiN <sub>4</sub> O <sub>5</sub> Yb	C88H112LiN4O2A
Fw	1519.72	1525.05	1437.07	1459.76	1433.67
T (K)	223(2)	223(2)	223(2)	223(2)	223(2)
Cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Crystal size (mm <sup>3</sup> )	$0.50\times0.50\times0.25$	$0.50\times0.20\times0.20$	$0.45 \times 0.40 \times 0.40$	$0.44 \times 0.36 \times 0.20$	$0.70\times0.45\times0.20$
a (Å)	14.2651(11)	14.2222(10)	14.3040(6)	14.1723(9)	13.5155(9)
b (Å)	27.5870(20)	27.6355(18)	25.7255(11)	25.8143(17)	24.4574(17)
<i>c</i> (Å)	21.6884(14)	21.6369(16)	21.8575(9)	21.8163(15)	25.0322(18)
β (°)	99.849(3)	99.713(2)	93.6180(10)	92.640(2)	93.166(2)
<i>V</i> (Å <sup>3</sup> )	8409.1(11)	8382.2(10)	8027.0(6)	7973.0(9)	8261.9(10)
Ζ	4	4	4	4	4
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	1.200	1.208	1.189	1.216	1.153
$\mu$ (mm <sup>-1</sup> )	0.563	0.674	0.782	1.224	0.760
F (000)	3216	3228	3036	3068	3064
$\theta$ range (°)	3.07-27.50	3.08-25.50	3.02-27.50	3.02-27.49	3.01-25.50
Collected	76,077	43,096	45,947	44,303	41,995
Unique reflns	19,203	15,523	18,181	18,131	15,304
R	0.0718	0.0955	0.0689	0.0654	0.0859
wR	0.1463	0.1759	0.1361	0.1229	0.1786
R <sub>int</sub>	0.0611	0.0864	0.0542	0.0542	0.0635
GOF	1.230	1.218	1.177	1.167	1.122
Peak/hole (e/Å <sup>3</sup> )	1.026, -0.780	0.655, -0.923	0.693, -0.858	0.811, -1.078	0.637, -0.517

 Table 2

 Selective bond lengths (Å) and bond angles (°) for complexes 1–4.

	1	2	3	4
Ln-µ-O(1)	2.317(3)	2.262(5)	2.256(3)	2.175(3)
Ln-κ-O(4)	2.457(3)	2.385(5)	2.371(3)	2.265(3)
Ln–O(av. in $\mu$ -O: $\kappa^2$ -L)	2.550(3)	2.475(4)	2.436(3)	2.328(3)
Ln-O(6)	2.603(3)	2.551(5)	_	_
Ln—N(av. in μ-O:κ <sup>2</sup> -L)	2.669(3)	2.617(5)	2.485(3)	2.406(4)
$Ln-\kappa-N(4)$	2.728(3)	2.694(5)	2.455(3)	2.362(4)
C-O (av.)	1.295(5)	1.308(8)	1.306(5)	1.305(5)
C—N (av.)	1.302(5)	1.307(8)	1.304(5)	1.308(6)
O(4) - Ln - N(4)	50.24(9)	51.70(16)	54.33(11)	56.80(13)
C(58)-O(4)-Ln	100.3(2)	101.4(4)	97.2(3)	96.8(3)
O(4) - C(58) - N(4)	117.7(3)	116.8(6)	115.8(4)	114.8(4)
C(58)-N(4)-Ln	87.7(2)	86.7(4)	92.7(3)	91.6(3)

lactide and toluene. Then a solution of the initiator in toluene was added to this solution by syringe. The mixture was stirred vigorously at room temperature for the desired time, during which time an increasing viscosity was observed. The reaction mixture was quenched by the addition of methanol and then poured into ethanol to precipitate the polymer, which was dried under vacuum and weighed.

### 3. Results and discussion

### 3.1. Synthesis and characterization of anionic and neutral rare earth metal amidate complexes **1–8**

The amide proligand, *N*-2,6-diisopropylphenylbenzamide,  $C_6H_5C(O)NHC_6H_3(^iPr)_2$  (HL), was synthesized through the reaction of 2,6-diisopropylaniline and benzoyl chloride. Reaction of 4 equiv of HL with anionic lanthanide amido complexes, LiLn(- $N^iPr_2$ )<sub>4</sub>(THF) (Ln = La, Nd, Sm, Yb and Y), in THF at room temperature, gave the final products as crystalline samples from THF/ hexane mixed solvent in good isolated yields, after routine workup. Disappearance of the amido N–H signal ( $\delta$  9.75) in the <sup>1</sup>H NMR spectrum of the lanthanum complex confirms the occurrence of protonolysis. The chemical shifts of the aryl hydrogens moved upfield, from 8.00–7.20 ppm to 7.73–6.86 ppm, which is an

 Table 3

 Selected crystal data and experimental parameters for complexes 6–8.

	6	7	8
Formula	C <sub>84</sub> H <sub>105</sub> N <sub>4</sub> O <sub>6</sub> La	C <sub>84</sub> H <sub>105</sub> N <sub>4</sub> O <sub>6</sub> Nd	C <sub>84</sub> H <sub>105</sub> N <sub>4</sub> O <sub>6</sub> Sm
Fw	1405.63	1410.96	1417.07
T (K)	223(2)	223(2)	223(2)
Cryst syst	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c
Crystal size	$\textbf{0.80} \times \textbf{0.40}$	0.90  imes 0.40	$\textbf{0.40} \times \textbf{0.30}$
(mm <sup>3</sup> )	× 0.40	× 0.40	× 0.25
a (Å)	24.038(4)	23.866(4)	23.850(3)
b (Å)	16.233(2)	16.167(2)	16.1262(13)
<i>c</i> (Å)	23.040(4)	23.070(3)	23.317(2)
β(°)	120.317(3)	120.447(3)	121.417(2)
V (Å <sup>3</sup> )	7761(2)	7673.9(19)	7653.0(13)
Ζ	4	4	4
D <sub>calc</sub> (g/cm <sup>3</sup> )	1.203	1.221	1.230
$\mu$ (mm <sup>-1</sup> )	0.603	0.730	0.821
F (000)	2968	2980	2988
$\theta$ range (°)	3.03-27.50	3.04-27.50	3.05-27.48
Collected	21687	21649	21773
Unique reflns	8715	8756	8688
R	0.0509	0.0448	0.0714
wR	0.0986	0.0851	0.1174
R <sub>int</sub>	0.0473	0.0472	0.0718
GOF	1.159	1.106	1.226
Peak/hole (e/ Å <sup>3</sup> )	0.611, -0.897	0.481, -0.851	0.517, -0.949

indication of the increase in electron density, as a result of coordination to the metal center. The septet at 3.15 ppm is assigned to the methine proton in the isopropyl group, while the corresponding methyl protons appear at 1.20 ppm as a doublet. The signals observed for the coordinated THF methylene protons are at 1.38 and 3.55 ppm respectively, which are close to typical residual THF solvent signals (1.40 and 3.57 ppm) [18]. Elemental analyses revealed that these complexes consist of four amidate ligands in the solid state. Definitive molecular structure determination revealed that these are anionic lanthanide-lithium amidate complexes, Li(THF)Ln[C<sub>6</sub>H<sub>5</sub>C(O)NC<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>]<sub>4</sub>(THF)<sub>n</sub> · (sol)<sub>m</sub> (Ln = La (1), Nd (2), Sm (3), Yb (4) and Y (5), n = 0 or 1; sol = THF or n-Hex), as shown in Scheme 1. All the complexes are air and moisture sensitive. They are soluble in THF, toluene, and slightly soluble in hexane.

Crystals of complexes **1–5** suitable for X-ray diffraction were obtained from hexane/THF mixed solvent at room temperature. Since complexes **1** and **2** are isostructural, and so are complexes **3** and **4**, hence, only the representative molecular structures of complexes **1**, **3** and **5** are shown in Figs. 2–4, respectively. Details of their crystallographic data are summarized in Table 1, and the corresponding selected bond lengths and angles are provided in Table 2.

Complexes 1 and 2 are isomorphous, and so are complexes 3 and 4. Their structures have much in common except for a tetrahydrofuran molecule coordinated to the lanthanide metal. Four amidate groups are bound to lanthanide and lithium atoms: one bridges the two atoms (namely,  $\mu$ -N: $\mu$ -O-amidate); the other chelates the lanthanide (namely,  $\kappa^2$ -amidate); another two chelate the lanthanide and also act as bridges between metals (namely,  $\mu$ -O: $\kappa^2$ amidate), as those observed in the known complexes,  $[(C_5H_5)_2Ln(\mu \eta^{1}:\eta^{2}-OC(N=C(NMe_{2})_{2})NPh)]_{2}$  (Ln = Gd, Er) [19], [Cp<sub>2</sub>Dy(OC(Ph))]\_{2} NCy]<sub>2</sub> [15] and [Y(<sup>t</sup>Bu[O,N](CH<sub>3</sub>)<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> [11c]. The lanthanide metal is eight coordinated in complexes 1 and 2, seven for 3 and 4. The lanthanide metallocycles defined by rare earth metals and the chelating amidate groups are essentially planar, since the sum of the bond angles are about 360° (see Table 2). This is similar to those reported in a related monoamidate yttrium complex (MeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Y(THF)(N(<sup>i</sup>Pr)<sub>2</sub>[O,N]Ph) [20], and a homoleptic tris(amidate) complex  $[(THF)Y(Nap[O,N](^{i}Pr)_{2}Ph)_{3}]_{2}$  [11c].

In complex **1**, the La– $\mu$ -O bond distance is 2.317(3) Å, and 2.457(3) Å for the La– $\kappa$ -O bond. For the  $\mu$ -O: $\kappa^2$ -bonding amidate group, the average length of the La–O bond is 2.550(3) Å, which is significantly longer than either the La– $\mu$ -O or La– $\kappa$ -O bonds. Meanwhile, the average distance of La–N in the  $\mu$ -O: $\kappa^2$ -bonding mode is 2.669(3) Å, which is slightly shorter than that of the pure chelating ligand (2.728(3) Å). These data indicate that when the amidate group adopts the  $\mu$ -O: $\kappa^2$ -coordination mode, the interaction between La and O atoms is weakened to a certain extent, while that between La and N atoms is somewhat strengthened. The average C–O and C–N bond lengths in the  $\kappa^2$ -amidate backbone are very close (1.295(5) and 1.302(5) Å), suggesting significant electron delocalization. The bond parameters in complex **2** are similar to the corresponding values in complex **1**, taking into account the difference in ionic radii.

For complex **3**, the average Sm–O ( $\mu$ -O: $\kappa^2$ -amidate) bond length is 2.436(3) Å, which is also longer than those for Sm– $\mu$ -O (2.256(3) Å) and Sm– $\kappa$ -O (2.371(3) Å). All these bond lengths are significantly shorter than that for Sm– $\kappa$ -O (2.515(6) Å) in the reported complex, ( $\sigma$ OMe: $\kappa$ O: $\kappa$ N-**1**)<sub>2</sub>SmN(SiMe<sub>3</sub>)<sub>2</sub> (**1** = (*R*)-2-(mesitoylamino)-2'-methoxy-6,6'-dimethyl-1,1'-biphenyl) [11e]. The Sm–N bond distance is 2.455(3) Å in  $\kappa^2$ -bonding mode, which is consistent with the corresponding value (2.448(8) Å) in ( $\sigma$ OMe:- $\kappa$ O: $\kappa$ N-**1**)<sub>2</sub>SmN(SiMe<sub>3</sub>)<sub>2</sub>. The electron delocalization through the  $\kappa^2$ -amidate backbone in complex **3** is confirmed by the average C–O and C–N distances (1.306(5) and 1.304(5) Å, respectively).



**Scheme 1.** Synthesis of anionic rare earth metal amidate complexes 1–5.

In complex **5**, the coordination modes for three of the four amidate ligands are identical to those observed in complexes **1–4**, with the fourth amidate ligand adopting a monodentate coordination mode (namely,  $\eta^1$ -amidate). This difference may have arisen as a result of the coordination of THF molecule and steric hindrance about the yttrium atom, in view of the relatively small ionic radius of yttrium. Such bonding mode was also observed in earlier work

Fig. 2. ORTEP diagram of complex 1 with the probability ellipsoids drawn at the 20% level, and hydrogen atoms are omitted for clarity. Complex 2 is isomorphous with complex 1.

published by Schafer [11c]. The geometry around the yttrium atom can be described as a pentagonal-bipyramid, with O(1) and O(6) at the two apical positions (O(1)–Y–O(6) 165.93(11)°), and O(2), O(3), O(4), N(2) and N(3) almost coplanar with the yttrium atom (the sum of the central angles is 360.55°). The Y– $\eta^1$ -O(4) bond distance is 2.132(3) Å, which is slightly shorter than that for the Y– $\mu$ -O(1) (2.169(3) Å). Nevertheless, both Y–O bonds are apparently shorter than that of the  $\mu$ -O: $\kappa^2$ -amidate (2.370(3) Å on average). The average Y–N bond length is 2.494(3) Å, which is slightly longer than that reported in the literature [11c].



**Fig. 3.** ORTEP diagram of complex **3** with the probability ellipsoids drawn at the 20% level, and hydrogen atoms are omitted for clarity. Complex **4** is isomorphous with complex **3**.



**Fig. 4.** ORTEP diagram of complex **5** with the probability ellipsoids drawn at the 20% level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (o):  $Y - \mu - O(1) 2.169(3)$ ,  $Y - \eta^1 - O(4) 2.132(3)$ , Y - O (av. in  $\mu - O:\kappa^2 - L) 2.370(3)$ , Y - O(6) 2.369(3), Y - N (av. in  $\mu - O:\kappa^2 - L) 2.494(3)$ , C - O (av.) 1.306(5), C - N (av.) 1.292(5); O(1) - Y - O(6) 165.93(11), O(3) - Y(1) - O(2) 67.95(10), O(2) - Y(1) - N(2) 53.70(10), O(4) - Y(1) - N(2) 93.99(11), O(4) - Y(1) - N(3) 90.50(11), O(3) - Y(1) - N(3) 54.41(11).

In order to obtain neutral lanthanide amidate complexes, the neutral lanthanide amido complex, Ln[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, was used as starting material instead of LiLn(N<sup>i</sup>Pr<sub>2</sub>)<sub>4</sub>(THF). The protonolysis reaction of  $Ln[N(SiMe_3)_2]_3$  (Ln = La, Nd, Sm) with the proligand HL in a 1:3 molar ratio in THF at room temperature, followed by crystallization from a mixture of hexane and THF, afforded three lanthanide amidate complexes in good isolated yields. Elemental analyses revealed that there are also four amidate ligands in each of these complexes. In the IR spectra, the N-H stretching vibrations were observed as broad peaks at about 3295–3299 cm<sup>-1</sup>. For the lanthanum complex 6, a singlet resonance at 8.92 ppm was observed in the <sup>1</sup>H NMR spectrum, which can be attributed to the amido N-H proton (upfield shift from 9.75 ppm of the free amide). More comprehensive analysis showed that one amidate ligand might coordinate to the lanthanum metal as a monodentate neutral molecule in the THF- $d_8$  solution, while the others adopt chelating modes, since there were three groups of peaks assigned to the protons of methyl groups in the isopropyl, which could be divided into two classes according to the splitting and peak areas. However, definitive single-crystal X-ray structural determination revealed that complexes 6-8 in solid-state are the isomorphous neutral lanthanide amidate complexes containing N-H-N bonding,



**Fig. 5.** ORTEP diagram of complex **6** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level, and partial hydrogen atoms are omitted for clarity. Complexes **7** and **8** are isomorphous with complex **6**.

{PhC(O)NC<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>}<sub>2</sub>Ln{OC(Ph)(C<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>)N-H-N(C<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>) C(Ph)O}(THF)<sub>2</sub> (Ln = La (**6**), Nd (**7**) and Sm (**8**)), which was kind of different from the structure determined by the NMR spectrum of complex **6** in solution (Scheme 2). Further progresses to get a homoleptic neutral complex bearing three (not four) amidate ligands failed, neither at high temperature nor in toluene. Complexes **6–8** are also air and moisture sensitive. Their solubilities in organic solvents are higher in comparison with the anionic ones.

Crystals of complexes **6–8** suitable for X-ray diffraction were obtained from hexane/THF mixed solvent at room temperature. Since complexes **6–8** are isomorphous, only the molecular structure of complex **6** is depicted in Fig. 5 as a representation. Details of the crystallographic data of complexes **6–8** are given in Table 3 and selected bond lengths and angles are listed in Table 4.

Complex **6** crystallizes in the monoclinic crystal system, *C*2/*c* space group, and has *C*<sub>2</sub>-symmetric structure and a coordination number of eight. As shown in Fig. 5, the lanthanum atom is coordinated to two THF molecules and four amidate groups, where there are two types of amidates: two of the amidates are bound to the central metal in a chelating manner and the other two coordinate in a monodentate fashion. The La– $\eta^1$ -O(2) bond length is 2.387(2) Å, while the La– $\kappa$ -O(1) bond is 2.468(2) Å, which are both longer than those in anionic complex **1**, but shorter than those found in [(THF)Y(Nap[O,N](<sup>i</sup>Pr)<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub> (2.284 Å on average) [11c],



Ln = La (6, 57 %), Nd (7, 60 %), Sm (8, 64 %)

Scheme 2. Synthesis of neutral lanthanide amidate complexes 6-8.

Table 4
Selected bond distances (Å) and bond angles (°) for complexes $6-8$ .

	6	7	8
Ln-κ-O(1)	2.468(2)	2.4123(18)	2.385(3)
$Ln-\eta^1-O(2)$	2.387(2)	2.3335(19)	2.303(3)
Ln-O(3)	2.589(2)	2.5374(18)	2.517(3)
Ln-κ-N(1)	2.621(2)	2.571(2)	2.538(3)
O(1) - C(1)	1.286(3)	1.285(3)	1.288(5)
O(2)-C(20)	1.282(3)	1.276(3)	1.282(5)
N(1) - C(1)	1.306(4)	1.307(3)	1.318(5)
N(2)-C(20)	1.301(4)	1.314(4)	1.317(6)
N(2)-H(2)	0.8700	0.8700	0.8700
C(1)-O(1)-Ln	99.1(2)	98.7(2)	98.8(2)
O(1)-C(1)-N(1)	117.6(3)	117.7(2)	116.7(4)
C(1)-N(1)-Ln	91.50(17)	90.76(16)	91.0(3)
O(1)-Ln-N(1)	51.57(7)	52.75(6)	53.5(1)

taking into consideration the difference in the ionic radii. The La-N bond length is 2.621(2) Å, which is apparently shorter than the La-N(κ<sup>2</sup>-L) (2.728(3) Å) in complex **1**. The C–O (1.286(3) Å) and C–N (1.306(4) Å) bond lengths are indicative of electron delocalization through the  $\kappa^2$ -amidate backbone in complex **6**. The sum of the four angles in the chelating amidate metallacycle in complex 6 is 359.8°, implying that the lanthanide metal center and the  $\kappa^2$ -amidate backbone are exactly in the same plane (see Table 4), which is similar to the earlier examples above. It is noteworthy that there is a special bonding situation in complex **6**, where the two nitrogen atoms of the two monodentate amidate ligands share one hydrogen atom to form an N–H–N bridge. This result is guite different from that in  $[(Nap[O,NH](^{i}Pr)_{2}Ph)Y(Nap[O,N](^{i}Pr)_{2}Ph)_{3}]$  [11c], for which the fourth amide coordinates to the yttrium atom in its neutral form. This is the first time such kind of bonding is observed in amidate coordination chemistry.

### 3.2. Catalytic activity of complexes **1–8** for the polymerization of rac-lactide

Biodegradable polymers, such as  $poly(\epsilon$ -caprolactone) (PCL) and poly(lactide) (PLA), have recently attracted significant attention as replacements for conventional synthetic materials because of their biodegradability, biocompatibility and permeability. Ring-opening polymerization of cyclic esters initiated by organometallic complexes is a convenient method for the synthesis of these high molecular weight polymers. Zi and co-workers have demonstrated that unbridged bis(amidate) lanthanide amides can serve as catalysts for the ROP of *rac*-lactide, affording isotactic-rich polylactides [11e,f]. With complexes **1–8** in hand, their performance as catalysts for the ROP of *rac*-lactide was examined (Scheme 3), and the results are listed in Table 5. It can be seen that both the anionic and neutral lanthanide amidate complexes can initiate the polymerization of rac-lactide in high activity under mild polymerization conditions, to give the polylactides (PLAs) with high molecular weights and relatively narrow molecular weight distributions (PDI = 1.22-1.62). It was found that the nature of the initiators has a profound

 Table 5

 Polymerization of *rac*-lactide initiated by lanthanide amidate complexes.<sup>a</sup>

Entry         Cat.         [M]/[I]         t (min)         Yield (%) $M_n (\times 10^4)$ PDl <sup>b</sup> Ph           1         1 (La)         2500:1         30         >99         21.30         1.56         0.           2         1 (La)         3000:1         40         97         25.25         1.49         0.           3         2 (Nd)         2500:1         40         96         12.52         1.40         0.           4         2 (Nd)         3000:1         40         80         18.57         1.32         0.								
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Entry	t. [N	[M]/[I] t (	(min)	Yield (%)	$M_{ m n}~( imes 10^4)$	PDI <sup>b</sup>	Pr <sup>c</sup>
2         1 (La)         3000:1         40         97         25.25         1.49         0.           3         2 (Nd)         2500:1         40         96         12.52         1.40         0.           4         2 (Nd)         3000:1         40         80         18.57         1.32         0.           5         - 0.00:1         - 0.00:1         - 0.00:1         10.41         0.	1	La) 25	2500:1	30 ;	>99	21.30	1.56	0.59
3         2 (Nd)         2500:1         40         96         12.52         1.40         0.           4         2 (Nd)         3000:1         40         80         18.57         1.32         0.           5         900:0:1         60         10.41         10.01         144         0.02	2	La) 30	3000:1 4	40	97	25.25	1.49	0.57
4 2 (Nd) 3000:1 40 80 18.57 1.32 0.	3	Nd) 25	2500:1 4	40	96	12.52	1.40	0.64
5 <b>3</b> (C) 2000-1 CO 00 10.40 1.44 0	4	Nd) 30	3000:1 4	40	80	18.57	1.32	0.61
5 <b>3</b> (Sm) 2000:1 60 98 10.49 1.44 0.	5	Sm) 20	2000:1 0	60	98	10.49	1.44	0.59
6 <b>3</b> (Sm) 2500:1 60 94 6.63 1.45 0.	6	Sm) 25	2500:1 0	60	94	6.63	1.45	0.62
7 <b>4</b> (Yb) 300:1 60 99 3.67 1.22 0.	7	Yb) 3	300:1 0	60	99	3.67	1.22	0.58
8 <b>4</b> (Yb) 1000:1 110 81 8.33 1.23 0.	8	Yb) 10	1000:1 11	10	81	8.33	1.23	0.58
9 <b>5</b> (Y) 1000:1 60 96 8.02 1.25 0.	9	Y) 10	1000:1 (	60	96	8.02	1.25	0.58
10 <b>5</b> (Y) 1500:1 140 86 12.21 1.26 0.	10	Y) 15	1500:1 14	40	86	12.21	1.26	0.60
11 <b>6</b> (La) 250:1 60 83 2.32 1.49 0.	11	La) 2	250:1 0	60	83	2.32	1.49	0.57
12 <b>6</b> (La) 300:1 120 80 3.53 1.50 0.	12	La) 3	300:1 12	20	80	3.53	1.50	0.62
13 <b>7</b> (Nd) 500:1 50 97 9.03 1.44 0.	13	Nd) !	500:1 5	50	97	9.03	1.44	0.57
14 <b>7</b> (Nd) 1000:1 60 73 10.13 1.45 0.	14	Nd) 10	1000:1 (	60	73	10.13	1.45	0.54
15 <b>8</b> (Sm) 2000:1 60 94 8.11 1.62 0.	15	Sm) 20	2000:1 0	60	94	8.11	1.62	0.59
16 <b>8</b> (Sm) 2500:1 60 27 3.57 1.62 0.	16	Sm) 25	2500:1 (	60	27	3.57	1.62	0.63

<sup>a</sup> Conditions: 20 °C, [LA] = 1.0 mol/L, toluene.

<sup>b</sup> Measured by GPC (using polystyrene standards in THF).

 $^{\rm c}$  Pr is the probability of racemic enchainment of monomer units calculated according to the methine region of the homonuclear decoupled  $^{1}{\rm H}$  NMR spectrum in CDCl<sub>3</sub> at 25 °C.

influence on the catalytic activity. The anionic lanthanide amidate complexes exhibited significantly higher activities than their neutral counterparts as expected. For example, the conversion reached 96% in the case of [M]/[I] = 2500 within 40 min using anionic neodymium complex **2** as the initiator, whereas the polymerization initiated by the neutral neodymium complex **7** only afforded 73% yield in 1 h, even upon decreasing the molar ratio of [M]/[I] to 1000/1 (entries 3 and 14). Similar phenomenon was also observed for  $\varepsilon$ -caprolactone polymerization initiated by organolanthanide complexes [21].

The central metal also has a great influence on the polymerization activity. For instance, using the anionic lanthanide amidate complexes as the initiators, complete polymerization of 2500 equiv of the monomer was achieved in only 30 min for complex 1 (entry 1), whereas for complexes 2 and 3, attaining similar yields with the same catalyst loading required 40 min (entry 3) and 60 min (entry 6), respectively. However, high yield of 96% is obtainable in 60 min using yttrium complex 5, even when the catalyst loading was decreased to 1000/1 (entry 9). The observed decreasing order of activity, La > Nd > Sm > Y > Yb, is consistent with the trend in ionic radii (La (1.16 Å) > Nd (1.11 Å) > Sm (1.02 Å) > Y (0.96 Å) > Yb (0.93 Å)). This decreasing order of activity is generally seen for cyclic polymerizations initiated by organolanthanide complexes [22]. To our surprise, in contrast to the anionic series, the trend in activity for the neutral lanthanide amidate complexes is La < Nd < Sm (entries 11–16), which is opposite to the ionic radii. A similar activity order has been reported previously by Shen et al. for methyl methacrylate polymerization [23], but the reason is still not well understood.

The microstructures of the polymers obtained were determined from the homonuclear decoupled <sup>1</sup>H NMR spectra in CDCl<sub>3</sub>. The present polymerization systems yielded heterotactic-rich



Scheme 3. Catalytic reaction of complexes 1-8 for the polymerization of rac-lactide.

a. Cat. = anionic lanthanide amidate complexes

 $Li(THF)Ln[C_{6}H_{5}C(O)NC_{6}H_{3}(^{i}Pr)_{2}]_{4}(THF)_{n} \xrightarrow{LA} Li(LA)Ln[C_{6}H_{5}C(O)NC_{6}H_{3}(^{i}Pr)_{2}]_{4}(THF)_{n} \xrightarrow{a_{1}} Li(LA)Ln[C_{6}H_$ 



b. Cat. = neutral lanthanide amidate complexes

{PhC(O)NC<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>}<sub>2</sub>Ln{OC(Ph)(C<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>)N---H---N(C<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>)C(Ph)O}(THF)<sub>2</sub>

Sol. → {PhC(O)NC<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>}<sub>3</sub>Ln{PhC(O)NHC<sub>6</sub>H<sub>3</sub>(<sup>i</sup>Pr)<sub>2</sub>}(THF)<sub>2</sub>  $b_1$ 



Scheme 4. Proposed catalytic mechanisms for the ROP of rac-lactide.

polylactides, and the Pr ranges from 0.54 to 0.64. These results are quite different from those initiated by the chiral lanthanide amidate amido complexes, which gave isotactic-rich polylactides [11e,f], suggesting that the coordination environment around the metal center may be a major deciding factor for the stereoselectivity during polymerization [11e]. However, there is no distinct difference in stereoselectivity between the anionic and the neutral lanthanide amidate complexes. Further investigation of the ligand architecture for this transformation is in progress.

To figure out the active species and mechanism for the catalytic process, we conducted end group analysis of the oligomers of *rac*lactide, which were synthesized by the reaction of complex **1** or **8** with *rac*-lactide in a 1:15 molar ratio. End group analysis by <sup>1</sup>H NMR spectroscopy (Fig. 6) showed clearly the existence of one

amidate ligand according to the resonances between 7 and 8 ppm for the aromatic rings, at about 3.11 and 1.19 ppm for the isopropyl groups as well. Thus, the polymerization proceeds by a common "coordination—insertion" mechanism, as shown in Scheme 4.

When using anionic lanthanide amidate complexes as catalysts, it is believed that the cooperative effect plays an important role in the catalytic reaction [21a], contributing to much higher activities. First, *rac*-lactide (represented by "LA" in Scheme 4) is supposed to replace THF that originally coordinated to lithium to form **a**<sub>1</sub> species. Second, *rac*-lactide can coordinate to both Ln and Li metals concomitantly through its carbonyl group and ester group, respectively, and then insert into the Ln–N (chelating amidate group) bond, and the second *rac*-lactide can coordinate to Ln and Li, forming the corresponding active species **a**<sub>2</sub>. The process repeats to



Fig. 6. <sup>1</sup>H NMR spectrum of the oligomer of *rac*-lactide initiated by complex 1 in CDCl<sub>3</sub>.

yield the polymer. In the case of neutral lanthanide amidate complexes, their structures firstly alter to form  $\mathbf{b_1}$  when dissolved in solvent. Then, *rac*-lactide is coordinated to the metal center and a sequential nucleophilic attack on the carbonyl carbon of the lactide by one of the amidate groups forms new metal—alkoxo species  $\mathbf{b_2}$ . The propagation step is the continued monomer coordination and insertion into the active metal—alkoxo bond just like that of anionic catalysts.

### 4. Conclusions

In summary, two series of anionic and neutral lanthanide amidate complexes were successfully synthesized and wellcharacterized. In these complexes, the amidate group shows great diversity in terms of the bonding mode. The amidate ligands in complexes 1–4 adopt  $\kappa^2$ -N,O-;  $\mu$ -O: $\kappa^2$ -N,O-; and  $\mu$ -N: $\mu$ -O-modes, while in yttrium complex **5**, one amidate is  $\eta^1$ -bound to the central Y though the carbonyl oxygen. Furthermore, in the neutral complexes 6-8, two amidate groups are bound to the central metal via  $\eta^1$  mode using the carbonyl oxygen, and linked to one another by an N–H–N bridge, which was confirmed by <sup>1</sup>H NMR, IR spectrum and structural determination. To the best of our knowledge, this is the first observation of such bonding mode in lanthanide amidate complexes, providing a full landscape of the rich characteristics of amidate as ligand in organolanthanide chemistry. Subsequent study revealed that these lanthanide amidate complexes can serve as efficient initiators for the ring-opening polymerization of raclactide and yielded heterotactic-rich polymers with high molecular weights and relatively narrow molecular weight distributions. The anionic lanthanide amidate complexes exhibited significantly higher activities than their neutral counterparts due to the cooperative effect.

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#### **Appendix A. Supplementary material**

CCDC-850238 (for 1), CCDC-850239 (for 2), CCDC-850240 (for 3), CCDC-852822 (for 4), CCDC-852821 (for 5), CCDC-850237 (for 6), CCDC-850241 (for 7), and CCDC-850242 (for 8) 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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