Cite this: New J. Chem., 2012, 36, 933-940

Synthesis of mono(guanidinate) rare earth metal bis(amide) complexes and their performance in the ring-opening polymerization of L-lactide and *rac*-lactide[†]

Yibin Wang,^{ab} Yunjie Luo,^{*a} Jue Chen,^a Hanming Xue^a and Hongze Liang^b

Received (in Victoria, Australia) 2nd November 2011, Accepted 5th January 2012 DOI: 10.1039/c2nj20925j

One-pot salt metathesis reaction of anhydrous LnCl₃ with one equivalent of guanidinate lithium $[(SiMe_3)_2NC(NCy)_2]Li$ (Cy = cyclohexyl), following the introduction of two equivalents of NaN(SiMe_3)_2 or LiN(SiHMe_2)_2 in THF at room temperature, afforded a family of mono(guanidinate) rare earth metal bis(amide) complexes $[(SiMe_3)_2NC(NCy)_2]Ln[N(SiRMe_2)_2]_2(THF)_n$ (R = Me, n = 0, Ln = Nd (1), Lu (2), Y (3); R = H, n = 1, Ln = Y (4)) in 62–79% isolated yields. These complexes were characterized by elemental analysis, NMR spectroscopy (except for 1 for its strong paramagnetic property of Nd³⁺), FT-IR spectroscopy, and X-ray single crystal diffraction. Single crystal structural determination revealed that the central metals in 1–3 are four-coordinated with a distorted tetrahedral geometry, while that in 4 is five-coordinated with a distorted trigonal bipyramidal geometry. These complexes could serve as highly active initiators for L-lactide polymerization in toluene at 50 °C. In addition, they also showed high activity towards *rac*-lactide polymerization in THF at room temperature, affording a moderate level of heterotactic polymers ($P_r > 0.70$). Employing 4 as an initiator, a controllable polymerization fashion was observed both in L-lactide polymerization and *rac*-lactide polymerization proceeded *via* a coordination–insertion mechanism verified experimentally by end group analysis of the oligomer.

Introduction

Non-Cp ancillary ligands have received intense interest in the field of coordination and organometallic chemistry in recent years, and guanidinate anions $[R_2NC(NR')_2]^-$ are assumed to be one of the ideal isoelectronic alternatives to Cp anions because their steric and electronic properties can be easily tailed by tuning the organic substituents on nitrogen atoms.¹ Compared to the application of guanidinate frameworks in main group and d-block transition metals, the employment of such monoanionic bidentate ligands in rare earth metals was only introduced very recently.^{1a} Most of the guanidinate-ligated rare earth metal complexes reported so far are homoleptic² and bis-guanidinate-ligated rare earth metal complexes are still rather scarce.^{3b,j,4} This may be

attributed to synthesis difficulty and ligand redistribution. To date, only one example of mono(guanidinate) rare earth metal bis(amide) complex [(SiMe₃)₂NC(NCy)₂]La[N(SiMe₃)₂]₂ prepared through insertion of La–N σ bonds of La[N(SiMe₃)₂]₃ into a Cy–N=C=N-Cy molecule has ever been reported.^{3/} However, as far as the catalytic behavior of the guanidinate rare earth metal bis(amide) complexes is concerned, their performance in polymerization still remains unexplored to the best of our knowledge.

On the other hand, polylactide (PLA) is a biodegradable and biocompatible synthetic macromolecule owing to its mechanical and physical properties suitable for a variety of applications such as sutures, product packaging, and artificial tissues.⁵ The most effective method to prepare PLA is the ringopening polymerization (ROP) of lactides using metal-based initiators.⁶ Some rare earth metal complexes were found to be active for lactide polymerization.⁷ However, the application of rare earth metal complexes with the formula $LLnR_2$ (L = monoanionic ancillary ligand, R = alkyl, amide, *etc.*), which are considered to possess much open coordination spheres around rare earth metals and are expected to display unique characters for polymerization,⁸ in lactide polymerization is relatively limited, ^{3j,9} and the examples of lactide polymerization initiated solely by rare earth metal bis(amide) complexes are rather scarce.^{9a,b,f,g} It is also noteworthy that in the reported lactide polymerization cases, the initial feed

^a Organometallic Chemistry Laboratory, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, P. R. China. E-mail: lyj@nit.zju.edu.cn; Fax: +86-574-88130130;

Tel: +86-574-88130085

^b School of Materials Science & Chemical Engineering,

Ningbo University, Ningbo, Zhejiang 315211, P. R. China

[†] Electronic supplementary information (ESI) available: ¹H NMR spectrum of **4**, plot of the degree of L-LA polymerization vs. [L-LA]/[**4**], and ¹H NMR spectrum of an L-lactide oligomer using **4**/[/]PrOH as an initiator. CCDC reference numbers 803565–803567 and 816943. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2nj20925j

molar ratio of $[LA]_0/[Ln]_0$ promoted by rare earth metal complexes was always less than a few thousands.^{5a}

In our continuous study on the lactide polymerization initiated by rare earth metal complexes, we found that ligand scaffolds at the rare earth metals affected dramatically their reactivity.^{7b,d,9c,10} Herein we would like to report the synthesis and characterization of a family of neutral and mononuclear rare earth metal bis(amide) complexes bearing N,N'-dicyclohexyl-N''-bis(trimethylsilyl) guanidinate ligand [(SiMe₃)₂NC(NCy)₂]⁻. These structural discrete complexes could act as single-component initiators for L-lactide and *rac*-lactide polymerization with high activity, and under some conditions, in a controllable polymerization fashion.

Results and discussion

Synthesis and characterization of mono(guanidinate) rare earth metal bis(amide) complexes

Different from the procedure adopted by Arnold and co-workers to prepare the first mono(guanidinate) rare earth metal bis(amide) complex $[(SiMe_3)_2NC(NCy)_2]La[N(SiMe_3)_2]_2$,³ we managed to employ a salt metathesis strategy to generate the aimed mono(guanidinate) rare earth metal bis(amide) complexes. One-pot salt metathesis reaction of anhydrous LnCl₃ with one equivalent of guanidinate lithium $[(SiMe_3)_2NC(NCy)_2]Li$ (formed *in situ* by treatment of Cy–N=C=N–Cy with one equivalent of (SiMe_3)_2NLi in hexane at room temperature), following addition of two equivalents of NaN(SiMe_3)_2 or LiN(SiHMe_2)_2 in THF at room temperature, after workup, afforded the corresponding mono(guanidinate) rare earth metal bis(amide) complexes $[(SiMe_3)_2NC(NCy)_2]Ln[N(SiRMe_2)_2]_2(THF)_n$ (R = Me, n = 0, Ln = Nd (1), Lu (2), Y (3); R = H, n = 1, Ln = Y (4)) in 62–79% isolated yields, as shown in Scheme 1.

Although 1–4 were prepared from salt metathetical reaction, they were isolated as neutral and mononuclear species. These complexes were thermally stable at ambient temperature in a glovebox. They were soluble in THF, toluene, diethyl ether, and even in aliphatic solvents such as hexane and pentane. The formulation of these complexes was supported by elemental analysis and FT-IR spectroscopy. The delocalized double bond of the N–C–N linkage was confirmed by the stretching of C–N bonds at approximately 1630 cm⁻¹. Room-temperature ¹H and ¹³C NMR spectra of **2–3** in C₆D₆ (except for **1** for its strong paramagnetic property of Nd³⁺) showed two singlets for the two types of SiMe₃ groups, suggesting a high symmetry of the molecules as observed in [(SiMe₃)₂NC(NCy)₂]La[N(SiMe₃)₂]₂.^{3/} In the case of **4**, a doublet resonance at 0.41 ppm (J = 3.2 Hz) in an ¹H NMR spectrum should correspond to the methyl protons of N(SiHMe₂)₂ groups, while the signal of an SiH proton appeared at 5.12 ppm.

Single crystals of 1–4 suitable for X-ray diffraction were grown from a mixture solution of hexane and toluene at -30 °C. Since 1, 2 and 3 are isomorphous, only the molecular structures of 1 and 4 are shown in Fig. 1 and 2, respectively. The crystallographic data are summarized in Table 1, and the selected bond distances and angles are listed in Table 2. The central metal Ln³⁺ in 1–3 is four-coordinated by one bidentate guanidinate ligand through two nitrogen atoms and two nitrogen atoms from two amide groups, forming a distorted



Fig. 1 Molecular structure of **1** with thermal ellipsoids at 10% probability. Hydrogen atoms have been omitted for clarity.



Scheme 1 Preparation of the mono(guanidinate) rare earth metal bis(amide) complexes.



Fig. 2 Molecular structure of **4** with thermal ellipsoids at 20% probability. Hydrogen atoms (except for Si–H) have been omitted for clarity.

tetrahedral geometry. In comparison, owing to sterically less demanding N(SiHMe₂)₂ group, the central metal Ln³⁺ **4** is fivecoordinated by one guanidinate ligand through two nitrogen atoms, two nitrogen atoms from two amide groups, and one oxygen atom from a THF molecule to adopt a distorted trigonal bipyramidal geometry. Since the structural features of these complexes are similar, only the structure of **4** is discussed in detail herein. It is found that the plane formed by Si1N3Si2 of an N(SiMe₃)₂ group on the central carbon atom of the NCN moiety and the plane of N2C1N1Y1 are not co-planar (the dihedral angle is 85.62° (for **1**, 78.78°; for **2**, 75.04°; for **3**, 76.74°)), this militates against the π -overlap between these two moieties. The dihedral angle of the plane of N1C1N2Y1 and the plane formed by N4Y1N5 is 79.59° (for **1**, 65.41°;

 Table 1
 Details of the crystallographic data and refinements for 1–4

Table 2 Selected bond distances and bond angles for
--

	1	2	3	4
Bond distance	es/Å			
N1-C1	1.342(6)	1.339(5)	1.328(7)	1.344(5)
N2C1	1.337(6)	1.334(5)	1.332(7)	1.339(5)
Ln–N1	2.413(4)	2.274(3)	2.314(4)	2.356(4)
Ln-N2	2.423(4)	2.271(3)	2.313(5)	2.328(3)
Ln–N4	2.314(4)	2.189(3)	2.225(5)	2.241(4)
Ln–N5	2.322(4)	2.199(3)	2.237(5)	2.278(4)
Bond angles/°				
N1-C1-N2	113.8(4)	114.2(4)	114.1(5)	114.3(4)
N1-Ln-N2	55.29(14)	59.18(12)	57.70(17)	57.54(12)
N4–Ln–N5	119.13(16)	117.91(14)	118.44(18)	119.47(14)

for **2**, 68.78°; for **3**, 66.75°). This orientation minimizes the interaction between the SiHMe₂ groups and the cyclohexyl group of the guanidinate ligand. The Y–N(SiHMe₂)₂ distances and the Y–N(guanidinate) distances range from 2.241(4) to 2.278(4) Å and from 2.356(4) to 2.328(3) Å, respectively. These values are identical to those of [(SiMe₃)₂NC(NCy)₂]La[N(SiMe₃)₂]₂,^{3j} if the difference of the effective ionic radii is considered.¹¹ The bite angle of N1–Y–N2 in **4** (57.54(12)°) is much larger than that in [(SiMe₃)₂NC(NCy)₂]La[N(SiMe₃)₂]₂ (53.86(9)°),^{3j} whilst the bond angle of N4–Y–N5 (119.47(14)°) is close to that in [(SiMe₃)₂NC(NCy)₂]La[N(SiMe₃)₂]₂ (120.2(1)°).^{3j}

Lactide polymerization

In order to assess the polymerization behavior of these neutral mono(guanidinate) rare earth metal bis(amide) complexes, 1–4 were employed firstly as initiators for the ring-opening polymerization of L-lactide. As illustrated in Table 3, all these neutral complexes alone could serve as single-component initiators for L-lactide polymerization in toluene at 50 °C, with an activity trend of 4 > 3 > 2 > 1. Remarkably, these complexes displayed high activity. For instance, using 4 as an initiator, the conversion could reach up to 93% in two minutes

	1	2	3	4
Formula	C31H76N5NdSi6	C31H76LuN5Si6	C ₃₁ H ₇₆ N ₅ Si ₆ Y	C31H76N5OSi6Y
FW	831.75	862.48	776.42	792.42
T/K	293(2)	293(2)	293(2)	223(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\overline{1}$
a/Å	9.5611(10)	9.6391(14)	9.5883(16)	12.0258(13)
$b/\text{\AA}$	24.392(3)	24.143(4)	24.230(4)	19.1155(19)
c/Å	20.327(2)	20.157(3)	20.194(3)	20.642(2)
$\alpha/^{\circ}$	90	90	90	75.965(5)
$\beta/^{\circ}$	91.353(3)	91.219(3)	91.177(5)	87.006(6)
$\gamma/^{\circ}$	90	90	90	85.555(6)
$V/Å^3$	4739.3(8)	4689.8(11)	4690.7(13)	4587.0(8)
Z	4	4	4	4
$D_{\rm calc}/{\rm g\cdot cm^{-3}}$	1.166	1.222	1.099	1.147
μ/mm^{-1}	1.271	2.283	1.421	1.456
F (000)	1764	1808	1680	1712
Crystal size/mm	$0.80 \times 0.60 \times 0.40$	$0.80 \times 0.50 \times 0.30$	$0.60 \times 0.60 \times 0.50$	$0.80 \times 0.50 \times 0.20$
Reflections collected	32 618	43 812	44 680	39 101
Independent reflections	8530	8565	8574	16946
No. of variables	407	407	407	854
GOF on F^2	1.120	1.173	1.272	1.141
$R[I > 2\sigma(I)]$	0.0543	0.0419	0.1070	0.0753
wR	0.1071	0.0843	0.1692	0.1266



Run	Initiator	[M]/ [Ln]	t/ min	Conv. ^b (%)	$\begin{array}{l} TOF\times \\ 10^{-4}\!/h^{-1} \end{array}$	$M_{ m n,calcd}^c \times 10^{-4}$	${M_{ m n,obsd}}^d_{ m imes 10^{-4}}$	$M_{\mathrm{w}/}$ $M_{\mathrm{n}}^{\prime\prime}$
1	1	4000	2	79	9.5	22.75	14.84	1.67
2	2	4000	2	100	12.0	28.80	17.62	1.62
3	2	6000	2	93	16.7	40.20	14.07	1.71
4	2	10 000	2	72	21.6	51.80	12.91	1.76
5	3	4000	2	100	12.0	28.80	13.87	1.52
6	3	6000	2	96	17.3	41.47	19.83	1.66
7	3	10 000	2	82	24.6	59.04	13.13	1.72
8	4	500	2	100	1.5	3.60	4.13	1.65
9	4	1000	2	100	3.0	7.20	7.94	1.55
10	4	1500	2	100	4.5	10.80	11.43	1.58
11	4	2000	2	100	6.0	14.40	13.86	1.61
12	4	3000	2	100	9.0	21.60	11.41	1.70
13	4	4000	2	100	12.0	28.80	16.28	1.58
14	4	6000	2	100	18.0	43.20	19.40	1.63
15	4	10000	2	93	27.9	66.96	17.51	1.62
an					1 10			

^{*a*} Polymerization conditions: [M] = 1.0 M, in toluene, 50 °C. ^{*b*} Conv. = conversion. ^{*c*} M_n of PLA calculated from $M_{n,calcd}$ = 144 × ([LA]/2[Ln]) × Conv. (LA). ^{*d*} Determined by GPC at 40 °C in THF relative to polystyrene standards; corrected by the Mark– Houwink equation [$M_{n,obsd}$ = 0.58 M_n (GPC)].

even when the molar ratio of $[LA]_0/[Y]_0$ was increased up to 10 000. This represents the first example that displays such high activity in lactide polymerization promoted by rare earth metal-based initiators, and its activity can compete with the most active metal-based initiator reported so far.¹² It is also noteworthy that, a controllable polymerization fashion was

Table 4 rac-Lactide polymerization by $1-4^a$

observed in the molar ratio range of $[LA]_0/[Y]_0$ from 500 to 2000 with **4** as the initiator, as the molecular weights of the resulting polymers increased almost linearly with the increase in the molar ratio of monomer-to-initiator while the molecular weight distributions kept nearly constant (Table 3, runs 8–11).

Furthermore, all these rare earth metal bis(amide) complexes were also found to be active for the ring-opening polymerization of rac-lactide at room temperature in various organic solvents, as shown in Table 4. Again, 4 demonstrated the highest activity (Table 4, runs 1-4). Microstructural analysis of the resulting polymers by homonuclear decoupled ¹H NMR spectroscopy revealed that all these complexes exerted a moderate level of heterotacticity ($P_r > 0.70$).¹³ Polymerization solvent affected not only the polymerization activity, but also the level of stereo-selectivity. For example, using 4 as the initiator in THF, 1000 equiv. of rac-lactide could be consumed completely in one hour to produce polymer with $P_r = 0.73$ (Table 4, run 5). In comparison, when the polymerization was performed in toluene, only 90% yield of the polymer with $P_r = 0.60$ was obtained even when the polymerization was prolonged to 9 hours (Table 4, run 9). Notably, a controllable polymerization of rac-lactide was also observed with 4 when the molar ratio of $[LA]_0/[Y]_0$ was in the range from 500 to 4000 (Table 4, runs 4–7).

Despite the two amide groups bonded to each rare earth metal in these complexes, GPC curves of the resulting polymers were all unimodal, indicative of an equivalent polymerization behavior of the two amide groups (see Fig. S2 in ESI†). To gain some insights into the polymerization mechanism with these rare earth metal bis(amide) complexes, oligomerization of L-lactide by **4** at $[LA]_0/[Y]_0 = 7$ in toluene at room temperature was carried out. No signal for the guanidinate ligand was observed in the ¹H NMR spectrum of the resulting oligomer, suggesting that the ancillary ligand was not engaged in the initiation stage (Fig. 3). However, analysis of the oligomer revealed that,



Run	Initiator	[M]/[Ln]	Solvent	t/h	Conv. ^{<i>b</i>} (%)	$TOF/h^{-1} \\$	$M_{ m n,calcd}{}^c imes 10^{-4}$	$M_{\rm n,obsd}^{d} \times 10^{-4}$	$M_{ m w}/{M_{ m n}}^d$	$P_{\rm r}^{\ e}$
1	1	500	THF	1	90	450	3.24	5.33	1.54	0.72
2	2	500	THF	1	58	290	2.09	15.26	1.69	0.77
3	3	500	THF	1	51	255	1.84	12.15	1.80	0.78
4	4	500	THF	1	100	500	3.60	4.13	1.65	0.76
5	4	1000	THF	1	100	1000	7.20	6.86	1.65	0.73
6	4	2000	THF	1	100	2000	14.40	13.91	1.70	n.d. ^g
7	4	4000	THF	1	88	3520	25.34	24.72	1.72	n.d. ^g
8 ^f	4	1000	THF	0.25	100	4000	7.20	5.66	1.91	0.63
9	4	1000	Toluene	9	90	100	6.48	4.89	1.39	0.60
10	4	1000	CH_2Cl_2	1	84	840	6.05	13.97	1.86	0.58

^{*a*} Polymerization conditions: $[M] = 1.0 \text{ mol } L^{-1}$, 25 °C. ^{*b*} Conv. = conversion. ^{*c*} M_n of PLA calculated from $M_{n,calcd} = 144 \times ([LA]/2[Ln]) \times Conv.$ (LA). ^{*d*} Determined by GPC at 40 °C in THF relative to polystyrene standards; corrected by the Mark–Houwink equation $[M_{n,obsd} = 0.58M_n \text{ (GPC)}]$. ^{*e*} P_r is the probability of racemic linkages between monomer units determined from the methine region of the homonuclear decoupled ¹H NMR spectrum at 20 °C in CDCl₃. ^{*f*} Performed in THF at 60 °C. ^{*g*} n.d.: not determined.



Fig. 3 ¹H NMR spectrum (400 MHz, CDCl₃) of an L-lactide oligomer using **4** as an initiator after quenching with ethanol (*, ethanol and monomer signals). Polymerization conditions: $[LA]_0/[Y]_0 = 7$, in toluene, 20 min, 20 °C.

besides the resonances at 4.35, 2.69, and 1.49 ppm for the end group of HOCH(CH₃)CO–, a set of signals in the region of 0.3-0.1 ppm and a multiplet signal at 4.55 ppm could be assigned to the N(SiHMe₂)₂ group. However, these signals disappeared when the oligomerization was carried out in the presence of 2-propanol (see Fig. S3 in ESI†). In the MALDI-TOF mass spectrum (Fig. 4), oligomers with the N(SiHMe₂)₂ end cap could also be found. These results showed that the

silylamido groups acted as the initiating group in the ringopening polymerization of L-lactide with these rare earth metal bis(amide) complexes, as illustrated in Scheme 2. Remarkably, the MALDI-TOF mass spectrum also showed that the intramolecular transesterification took place extensively to afford cyclic oligomers. The small amount of oligomers with the carboxylic acid end might stem from the hydrolysis of $H-[OCH(CH_3)CO]_n-N(SiHMe_2)_2$.







Scheme 2 Proposed mechanism scenario of L-lactide polymerization initiated by mono(guanidinate) rare earth metal bis(amide) complexes.

Conclusions

In summary, a family of neutral and mononuclear mono(guanidinate) rare earth metal bis(amide) complexes $[(SiMe_3)_2NC(NCy)_2]Ln[N(SiRMe_2)_2]_2(THF)_n$ (R = Me, n = 0, Ln = Nd(1), Lu(2), Y(3); R = H, n = 1, Ln = Y(4)) was prepared by one-pot salt metathesis reaction of anhydrous LnCl₃, guanidinate lithium [(SiMe₃)₂NC(NCy)₂]Li, and NaN(SiMe₃)₂ or $LiN(SiHMe_2)_2$ in 1:1:2 molar ratio in THF at room temperature. No ligand redistribution and "ate" complexes were observed in the preparation process. All these mono(guanidinate) rare earth metal bis(amide) complexes alone showed high activity towards L-lactide polymerization. The polymerization could complete in few minutes in toluene at 50 °C even when the molar ratio of [LA]₀/[Ln]₀ reached up to 10000, and afforded polymers with unimodal molecular weight distributions. Furthermore, these complexes were also active for rac-lactide polymerization to produce polymers with a moderate level of heterotacticity. Employing 4 as an initiator, a controllable polymerization fashion was observed both in L-lactide polymerization and rac-lactide polymerization under certain conditions. End group analysis of the oligomer revealed that the ring-opening polymerization proceeded via a coordination-insertion mechanism.

Experimental part

Materials and procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using the standard Schlenk techniques and argon-filled glovebox. Solvents (toluene, hexane, and THF) were distilled from sodium/ benzophenone ketyl, degassed by the freeze-pump-thaw method, and dried over fresh Na chips in a glovebox. Anhydrous $LnCl_3$ was purchased from STREM. *n*-BuLi (1.0 M in hexane solution), HN(SiMe₃)₂, HN(SiHMe₂)₂, and carbodiimide (Cy-N=C=N-Cy) were purchased from Acros, and used as received. L-Lactide and *rac*-lactide (99.5%) were obtained from Shenzhen Brightchina Industrial Co., Ltd. and were recrystallized from hot toluene. Deuterated solvents (CDCl₃, C_6D_6) were obtained from CIL.

Samples of organo rare earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. NMR (¹H, ¹³C) spectra were recorded on a Bruker AVANCE III spectrometer at 25 °C. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument, quoted data are the average of at least two independent determinations. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer. Molecular weight and molecular weight distribution of the polymers were measured by PL GPC 50 with two mixed-B columns at 40 °C using THF as an eluent against polystyrene standards, flow rate: 1 mL min⁻¹, sample concentration: 1 mg mL⁻¹.

Synthesis of [(SiMe₃)₂NC(NCy)₂]Nd[N(SiMe₃)₂]₂ (1)

All reactions were carried out at room temperature. *n*-BuLi (1.0 mL, 1.0 mmol, 1.0 M in hexane) was added drop by drop to a hexane solution (30 mL) of HN(SiMe₃)₂ (0.161 g, 1.0 mmol). After 20 min, the resulting solution (containing LiN(SiMe₃)₂ formed *in situ*) was added slowly to a hexane solution of Cy–N=C=N–Cy (0.206 g, 1.0 mmol). The reaction mixture was stirred for 0.5 h, and then was added slowly to a THF slurry

of NdCl₃ (0.251 g, 1.0 mmol). After the resulting clear blue solution was stirred for 15 min, NaN(SiMe₃)₂ (1.2 mL, 2.0 mmol, 1.67 M in THF solution) was added *via* a pipette, and the reaction mixture was kept for 24 h. Removal of the volatiles under the reduced pressure gave a blue residue, which was washed by hexane, and was extracted by toluene (2 × 10 mL). Drying up the solvents afforded the aimed product as a blue powder (0.66 g, 79%). Recrystallization from a mixture solution of hexane and toluene gave 1 as blue crystals. FT-IR (KBr, cm⁻¹): 2930 (s), 2854 (s), 1634 (s), 1451 (m), 1252 (m), 842 (s). Anal. calcd for C₃₁H₇₆N₅NdSi₆: C, 44.76; H, 9.21; N, 8.42. Found: C, 44.65; H, 9.07; N, 8.63%.

Synthesis of [(SiMe₃)₂NC(NCy)₂]Lu[N(SiMe₃)₂]₂ (2)

2 was prepared by a procedure similar to that of **1**. Using *n*-BuLi (1.0 mL, 1.0 mmol, 1.0 M in hexane), HN(SiMe₃)₂ (0.161 g, 1.0 mmol), Cy–N=C=N-Cy (0.206 g, 1.0 mmol), LuCl₃ (0.281 g, 1.0 mmol) and NaN(SiMe₃)₂ (1.2 mL, 2.0 mmol, 1.67 M in THF solution), **2** was isolated as a white powder (0.53 g, 62%). Recrystallization from a mixture solution of hexane and toluene gave **2** as colorless crystals. ¹H NMR (400 MHz, C₆D₆): δ 0.23 (s, 18H, CNSi*Me*₃), 0.46 (s, 36H, YNSi*Me*₃), 1.16 (m, 6H, Cy-C*H*₂), 1.59 (m, 6H, Cy-C*H*₂), 1.76 (d, 4H, Cy-C*H*₂), 1.89 (d, 4H, Cy-C*H*₂), 3.48 (m, 2H, Cy-C*H*). ¹³C NMR (100 MHz, C₆D₆): δ 2.8 (CNSi*Me*₃), 5.5 (YNSi*Me*₃), 26.2, 26.3, 37.9 (Cy-CH₂), 55.5 (Cy-CH), 169.4 (NCN). FT-IR (KBr, cm⁻¹): 2929 (s), 2853 (s), 1635 (s), 1451 (m), 1252 (s), 955 (s), 841 (s). Anal. calcd for C₃₁H₇₆LuN₅Si₆: C, 43.17; H, 8.88; N, 8.12. Found: C, 43.05; H, 8.62; N, 8.53%.

Synthesis of [(SiMe₃)₂NC(NCy)₂]Y[N(SiMe₃)₂]₂ (3)

3 was prepared by a procedure similar to that of **1**. Using *n*-BuLi (1.0 mL, 1.0 mmol, 1.0 M in hexane), HN(SiMe₃)₂ (0.161 g, 1.0 mmol), Cy–N=C=N-Cy (0.206 g, 1.0 mmol), YCl₃ (0.195 g, 1.0 mmol) and NaN(SiMe₃)₂ (1.2 mL, 2.0 mmol, 1.67 M in THF solution), **3** was isolated as a white powder (0.54 g, 70%). Recrystallization from a mixture solution of hexane and toluene gave **3** as colorless crystals. ¹H NMR (400 MHz, C₆D₆): δ 0.24 (s, 18H, CNSi*Me*₃), 0.43 (s, 36H, YNSi*Me*₃), 1.20 (m, 6H, Cy-C*H*₂), 1.53 (m, 6H, Cy-C*H*₂), 1.77 (d, 4H, Cy-C*H*₂), 1.89 (d, 4H, Cy-C*H*₂), 3.34 (m, 2H, Cy-C*H*). ¹³C NMR (100 MHz, C₆D₆): δ 2.8 (CNSi*Me*₃), 5.2 (YNSi*Me*₃), 26.2, 26.3, 38.2 (Cy-CH₂), 55.3 (Cy-CH), 169.6 (NCN). FT-IR (KBr, cm⁻¹): 2930 (s), 2854 (s), 1634 (s), 1451 (m), 1252 (s), 955 (m), 842 (s). Anal. calcd for C₃₁H₇₆N₅Si₆Y: C, 47.95; H, 9.87; N, 9.02. Found: C, 47.74; H, 9.58; N, 9.47%.

Synthesis of [(SiMe₃)₂NC(NCy)₂]Y[N(SiHMe₂)₂]₂(THF) (4)

4 was prepared by a procedure similar to that of **1**. Using *n*-BuLi (1.0 mL, 1.0 mmol, 1.0 M in hexane), HN(SiMe₃)₂ (0.161 g, 1.0 mmol), Cy–N=C=N–Cy (0.206 g, 1.0 mmol), YCl₃ (0.195 g, 1.0 mmol) and LiN(SiHMe₂)₂ (0.276 g, 2.0 mmol, prepared from *n*-BuLi and HN(SiHMe₂)₂ in hexane in 1:1 molar ratio), **4** was isolated as a white powder. Recrystallization from a solution of hexane gave **4** as colorless crystals (0.54 g, 68%). ¹H NMR (400 MHz, C₆D₆): δ 0.30 (s, 18H, N(SiMe₃)₂), 0.41 (d, J = 3.2 Hz, 24H, N(SiHMe₂)₂), 1.23 (m, 6H, Cy-CH₂), 1.38 (m, 4H, THF- β -CH₂), 1.62 (m, 6H, Cy-CH₂),

1.83 (d, J = 13.2 Hz, 4H, Cy-CH₂), 1.93 (d, J = 11.6 Hz, 4H, Cy-CH₂), 3.39 (m, 2H, Cy-H), 4.01 (m, 4H, THF-α-CH₂), 5.12 (m, 4H, N(SiHMe₂)₂). ¹³C NMR (100 MHz, C₆D₆): δ 2.7 (CNSiMe₃), 3.9 (YNSiHMe₂), 25.5 (THF-β-CH₂), 26.4, 26.5, 37.5 (Cy-CH₂), 54.9 (Cy-CH), 71.2 (THF-α-CH₂), 167.9 (NCN). FT-IR (KBr, cm⁻¹): 2932 (s), 2852 (s), 1634 (m), 1451 (s), 1345 (m), 1252 (s), 1194 (m), 1139 (m), 1049 (s), 944 (s). Anal. calcd for C₃₁H₇₆N₅OSi₆Y: C, 47.00; H, 9.67; N, 8.84. Found: C, 46.81; H, 9.49; N, 9.02%.

Typical procedure for the polymerization of L-lactide

The procedures for polymerization initiated by these complexes were similar, and a typical polymerization procedure is given below. In a glovebox, the desired amount of toluene and L-lactide was mixed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. The flask was taken out from the glovebox and attached to a well-purged argon Schlenk line. The flask was placed in an oil bath with a temperature of 50 °C. After L-lactide was dissolved, toluene solution of the rare earth metal bis(amide) complex was quickly injected into the flask *via* a syringe. The mixture was stirred vigorously at 50 °C for the predetermined time, during which an increase in viscosity was observed. The polymerization was terminated by addition of ethanol, and then a large amount of ethanol was poured into the flask to precipitate the polymer. The resulting polymer was dried under vacuum at 60 °C overnight and weighted.

Typical procedure for the polymerization of rac-lactide

The procedures for polymerization initiated by these complexes were similar, and a typical polymerization procedure is given below. In a glovebox, the desired amount of solvent and D,L-lactide was mixed in a 50 mL Schlenk flask equipped with a magnetic stirring bar. After D,L-lactide was completely dissolved, toluene solution of the rare earth metal bis(amide) complex was quickly added into the flask *via* a pipette. The mixture was stirred vigorously at ambient temperature for the predetermined time, during which an increase in viscosity was observed. The polymerization was terminated by addition of ethanol, and then a large amount of ethanol was poured into the flask to precipitate the polymer. The resulting polymer was dried under vacuum at 60 °C overnight and weighted.

Procedure for the oligomerization of L-lactide by 4

In a glovebox, 50 mg of L-lactide and 40 mg of **4** were dissolved in 1 mL of toluene at 20 °C. The mixture was stirred vigorously for 20 min, and was quenched by the addition of ethanol containing 5% of HCl. The resulting white powder was washed with a large amount of ethanol, and dried under vacuum at 60 °C overnight (20 mg).

Crystal structural determination

Suitable single crystals of the complexes were sealed in a thinwalled glass capillary for structural determination. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo K_{α} radiation ($\lambda = 0.71070$ Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. The structures were solved and refined using SHELEXL-97 program. CCDC 803565–803567, and 816943 contains the supplementary crystallographic data for **1–4**, respectively.

Acknowledgements

This work was partly financially supported by the National Natural Science Foundation of China (21172195), Science and Technology Department of Zhejiang Province (2010R10020), and State Key Laboratory of Rare Earth Resource Utilization (RERU2011020). The authors are grateful to Mr. Yong Zhang of Suzhou University for help with X-ray analysis.

References

- For recent reviews, see (a) A. A. Trifonov, Coord. Chem. Rev., 2010, 254, 1327; (b) F. T. Edelmann, Chem. Soc. Rev., 2009, 38, 2253; (c) M. P. Coles, Dalton Trans., 2006, 985; (d) W. E. Piers and D. J. H. Emslie, Coord. Chem. Rev., 2002, 233, 131; (e) F. T. Edelmann, D. M. M. Freckmann and H. Schumann, Chem. Rev., 2002, 102, 1851; (f) P. J. Bailey and S. Pace, Coord. Chem. Rev., 2001, 214, 91.
- (a) C. W. Qian, X. M. Zhang, J. M. Li, F. Xu, Y. Zhang and Q. Shen, Organometallics, 2009, 28, 3856; (b) G. G. Skvortsov, D. M. Lyubov, M. V. Yakovenko, G. K. Fukin, A. V. Cherkasov and A. A. Trifonov, Russ. Chem. Bull., 2009, 58, 1126; (c) D. Heitmann, C. Jones, P. C. Junk, K. Lippert and A. Stasch, Dalton Trans., 2007, 187; (d) L. Y. Zhou, H. M. Sun, J. L. Chen, Y. M. Yao and Q. Shen, J. Polym. Sci., Part A: Polym. Chem., 2005, 43, 1778; (e) L. Y. Zhou, Y. M. Yao, Y. Zhang, M. Q. Xue, J. L. Chen and Q. Shen, Eur. J. Inorg. Chem., 2004, 2167; (f) J. L. Chen, Y. M. Yao, Y. J. Luo, L. Y. Zhou, Y. Zhang and Q. Shen, J. Organomet. Chem., 2004, 689, 1019; (g) J. Zhang, R. F. Cai, L. H. Weng and X. G. Zhou, Organometallics, 2004, 23, 3303.
- 3 (a) G. G. Skvortsov, M. V. Yakovenko, P. M. Castro, G. K. Fukin, A. V. Cherkasov, J.-F. Carpentier and A. A. Trifonov, Eur. J. Inorg. Chem., 2007, 3260; (b) A. A. Trifonov, D. M. Lyubov, G. K. Fukin, E. V. Baranov and Y. A. Kurskii, Organometallics, 2006, 25, 3935; (c) A. A. Trifonov, D. M. Lyubov, E. A. Fedorova, G. K. Fukin, H. Schumann, S. Mühle, M. Hummert and M. N. Bochkarev, Eur. J. Inorg. Chem., 2006, 747; (d) F. G. Yuan, Y. Zhu and L. F. Xiong, J. Organomet. Chem., 2006, 691, 3377; (e) A. A. Trifonov, G. G. Skvortsov, D. M. Lyubov, N. A. Skorodumova, G. K. Fukin, E. V. Baranov and V. N. Glushakova, Chem.-Eur. J., 2006, 12, 5320; (f) A. A. Trifonov, E. A. Fedorova, G. K. Fukin and M. N. Bochkarev, Eur. J. Inorg. Chem., 2004, 4396; (g) Y. M. Yao, Y. J. Luo, J. L. Chen, Z. Q. Zhang, Y. Zhang and Q. Shen, J. Organomet. Chem., 2003, 679, 229; (h) Y. J. Luo, Y. M. Yao, Q. Shen, K. B. Yu and L. H. Weng, Eur. J. Inorg. Chem., 2003, 318; (i) Y. J. Luo, Y. M. Yao and Q. Shen, Macromolecules, 2002, 35, 8670; (j) G. R. Giesbrecht, G. D. Whitener and J. Arnold, J. Chem. Soc., Dalton Trans., 2001, 923; (k) Z. P. Lu, G. P. A. Yap and D. S. Richeson, Organometallics, 2001, 20, 706; (1) Y. L. Zhou, G. P. A. Yap and D. S. Richeson, Organometallics, 1998, 17, 4387.
- 4 (a) Y. Cao, Z. Du, W. B. Li, J. M. Li, Y. Zhang, F. Xu and Q. Shen, *Inorg. Chem.*, 2011, **50**, 3729; (b) P. Cui, Y. F. Chen, G. Y. Li and W. Xia, *Angew. Chem.*, *Int. Ed.*, 2008, **47**, 9944;

(c) S. Z. Ge, A. Meetsma and B. Hessen, Organometallics, 2008, 27, 3131; (d) D. M. Lyubov, G. K. Fukin and A. A. Trifonov, Inorg. Chem., 2007, 46, 11450; (e) G. G. Skvortsov, M. V. Yakovenko, G. K. Fukin, A. V. Cherkasov and A. A. Trifonov, Russ. Chem. Bull., 2007, 56, 1742; (f) J. Zhang, X. G. Zhou, R. F. Cai and L. H. Weng, Inorg. Chem., 2005, 44, 716; (g) A. A. Trifonov, G. G. Skvortsov, D. M. Lyubov, G. K. Fukin, E. A. Fedorova and M. N. Bochkarev, Russ. Chem. Bull., 2005, 54, 2511.

- R. A. Auras, L. T. Lim, S. E. M. Selke and H. Tsuji, *PolyLactic Acid: Synthesis, Structure, Properties, Processing, and Applications,* John Wiley & Sons, Inc., Hoboken, 2010; (b) A. P. Gupta and V. Kumar, *Eur. Polym. J.*, 2007, 43, 4053; (c) R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, 2004, 4, 835; (d) R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, 12, 1841; (e) P. Mainil-Varlet, B. Rahn and S. Gogolewski, *Biomaterials*, 1997, 18, 257; (f) R. Langer and J. P. Vacanti, *Science*, 1993, 260, 920.
- 6 (a) O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147; (b) B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *J. Chem. Soc., Dalton Trans.*, 2001, 2215.
- 7 (a) A. Buchard, R. H. Platel, A. Auffrant, X. F. L. Goff, P. L. Floch and C. K. Williams, Organometallics, 2010, 29, 2892; (b) Y. J. Luo, P. Xu, Y. L. Lei, Y. Zhang and Y. R. Wang, Inorg. Chim. Acta, 2010, 363, 3597; (c) J. F. Wang, Y. M. Yao, Y. Zhang and Q. Shen, Inorg. Chem., 2009, 48, 744; (d) Z. J. Zhang, X. P. Xu, W. Y. Li, Y. M. Yao, Y. Zhang, Q. Shen and Y. Luo, Inorg. Chem., 2009, 48, 5715; (e) H. Y. Ma, T. P. Spaniol and J. Okuda, Inorg. Chem., 2008, 47, 3328; (f) N. Ajellal, D. M. Lyubov, M. A. Sinenkov, G. K. Fukin, A. V. Cherkasov, C. M. Thomas, J.-F. Carpentier and A. A. Trifonov, Chem.-Eur. J., 2008, 14, 5440; (g) M. Konkol, T. P. Spaniol, M. Kondracka and J. Okuda, *Dalton Trans.*, 2007, 4095; (h) A. Amgoune, C. M. Thomas and J.-F. Carpentier, Macromol. Rapid Commun., 2007, **28**, 693; (*i*) H. Y. Ma, T. P. Spaniol and J. Okuda, *Angew. Chem., Int. Ed.*, 2006, **45**, 7818; (*j*) H. Y. Ma and J. Okuda, Macromolecules, 2005, 38, 2665; (k) H. Y. Ma, T. P. Spaniol and J. Okuda, Dalton Trans., 2003, 4770; (l) T. M. Ovitt and G. W. Coates, J. Am. Chem. Soc., 2002, 124, 1316.
- 8 (a) M. Nishiura and Z. M. Hou, *Nat. Chem.*, 2010, **2**, 257; (b) P. M. Zeimentz, S. Arndt, B. R. Elvidge and J. Okuda, *Chem. Rev.*, 2006, **106**, 2404.
- 9 (a) J. Buffet and J. Okuda, Dalton Trans., 2011, 40, 7748;
 (b) M. Lu, Y. M. Yao, Y. Zhang and Q. Shen, Dalton Trans., 2010, 39, 9530; (c) Y. J. Luo, X. L. Wang, J. Chen, C. C. Luo, Y. Zhang and Y. M. Yao, J. Organomet. Chem., 2009, 694, 1289;
 (d) X. L. Liu, X. M. Shang, T. Tang, N. H. Hu, F. K. Pei, D. M. Cui, X. S. Chen and X. B. Jing, Organometallics, 2007, 26, 2747; (e) B. Liu, D. M. Cui, J. Ma, X. S. Chen and X. B. Jing, Chem.-Eur. J., 2007, 13, 834; (f) X. M. Shang, X. L. Liu and D. M. Cui, J. Polym. Sci., Part A: Polym. Chem., 2007, 45, 5662;
 (g) I. Westmoreland and J. Arnold, Dalton Trans., 2006, 4155;
 (h) L. F. Sánchz-Barba, D. L. Hughes, S. M. Humphrey and M. Bochmann, Organometallics, 2005, 24, 3792.
- 10 Y. J. Luo, W. Y. Li, D. Lin, Y. M. Yao, Y. Zhang and Q. Shen, Organometallics, 2010, 29, 3507.
- 11 R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr., 1976, 32, 751.
- 12 L. Y. Wang and H. Y. Ma, Macromolecules, 2010, 43, 6535.
- 13 (a) M. T. Zell, B. E. Padden, A. J. Paterick, M. Thakur, R. T. Kwan, M. A. Hillmyer and E. J. Munson, *Macromolecules*, 2002, **35**, 7700; (b) K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad and E. J. Munson, *Macromolecules*, 1998, **31**, 1487; (c) K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, T. A. Lindgren, M. A. Doscotch, J. I. Siepmann and E. J. Munson, *Macromolecules*, 1997, **30**, 2422.