



Mono(amidinate) rare earth metal bis(alkyl) complexes: Synthesis, structure and their activity for L-lactide polymerization

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ARTICLE INFO

Article history:

Received 23 September 2008

Received in revised form 1 December 2008

Accepted 4 December 2008

Available online 16 December 2008

Keywords:

Amidinate ligands

Organo rare earth metal bis(alkyl)

complexes

Synthesis

Crystal structure

L-Lactide polymerization

ABSTRACT

Alkane elimination reaction between $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ ($\text{Ln} = \text{Y}, \text{Lu}$) with one equivalent of the amidines with different steric demanding **HL** ($[\text{CyC}(\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{H}$ (**HL**₁), $[\text{CyC}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2]\text{H}$ (**HL**₂), $[\text{PhC}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2]\text{H}$ (**HL**₃)) in THF afforded a series of mono(amidinate) rare earth metal bis(alkyl) complexes $[\text{CyC}(\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ ($\text{Ln} = \text{Y}$ (**1**), Lu (**3**)), $[\text{CyC}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2]\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ ($\text{Ln} = \text{Y}$ (**4**), Lu (**6**)), and $[\text{PhC}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (**7**) in 75–89% isolated yields. For the early lanthanide metal Nd, THF slurry of NdCl_3 was stirred with three equiv of $\text{LiCH}_2\text{SiMe}_3$ in THF, followed by addition of one equiv of the amidines **HL**₁ or **HL**₂ gave an “ate” complex $[\text{CyC}(\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Nd}(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (**2**) in 48% yield and a neutral $[\text{CyC}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2]\text{Nd}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (**5**) in 52% yield, respectively. They were characterized by elemental analysis, FT-IR, NMR spectroscopy (except for **2** and **5** for their strong paramagnetic property). Complexes **2**, **3**, **4** and **5** were subjected to X-ray single crystal structure determination. These neutral mono(amidinate) rare earth metal bis(alkyl) complexes showed activity towards L-lactide polymerization to give high molecular weight and narrow molecular weight distribution polymers.

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1. Introduction

Organo rare earth metal complexes supported by ancillary ligands other than cyclopentadienyl and its derivatives have attracted much attention and made spectacular progress in recent years [1–4]. Among these non-metallocene rare earth metal complexes, rare earth metal complexes bearing amidinate ligands, on which the steric and electronic characters are easy to be tuned, have found application in organic transformation and polymerization [5–39]. Although a library of tris(amidinate) and bis(amidinate) rare earth metal complexes have been prepared and their reactivity has been explored [5–30], to our knowledge, mono(amidinate) rare earth metal bis(alkyl) complexes are still quite limited [31–39]. The significant difficulty to obtain rare earth metal bis(alkyl) complexes is how to prevent the formation of “ate” complexes and the ligand redistribution problem. Very recently, however, pioneering and attractive works contributed independently from Hessen’s group and Hou’s group demonstrated that neutral mono(amidinate) rare earth metal bis(alkyl)/bis(benzyl) complexes, which could be further employed as precursors for

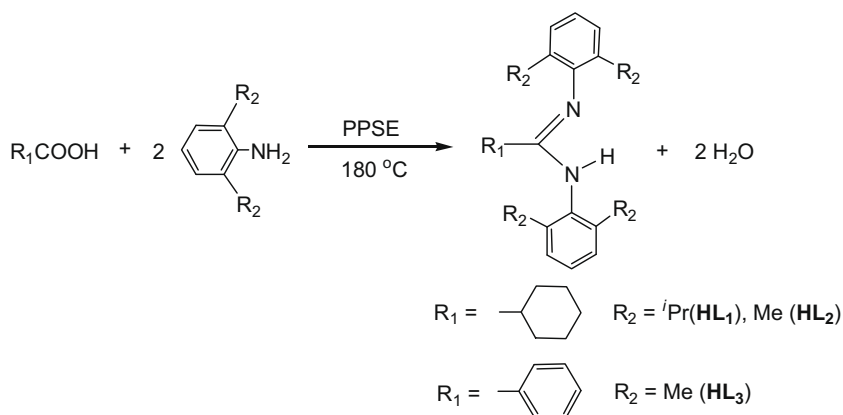
cationic catalysts with remarkable reactivity, can be achieved by alkane elimination between tris(alkyl)/tris(benzyl) rare earth metal complexes and the corresponding amidines [32–39]. Then, in most cases, especially to gain a full range of such species, these complexes are supported by the sterically bulky framework $\text{N,N}'\text{-bis}(2,6\text{-diisopropylphenyl})\text{benzamidinate}$ $[\text{PhC}(\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]^-$. In addition, the application of mono(amidinate) rare earth metal bis(alkyl) for the polymerization of polar monomers, such as lactide, has not been reported to date. Herein, we would like to report a series of mono(amidinate) rare earth metal bis(alkyl) complexes bearing different amidinate ancillary ligands. Their reactivity towards L-lactide polymerization was also described.

2. Results and discussion

2.1. Synthesis and characterization of the amidinate ligands HL ($[\text{CyC}(\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{H}$ (**HL**₁), $[\text{CyC}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2]\text{H}$ (**HL**₂), and $[\text{PhC}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2]\text{H}$ (**HL**₃))

The amidines **HL** employed in this paper can be synthesized according to the method developed by Kakimoto and co-workers [40]. Carboxylic acids reacted with two equivalents of amines in the presence of polyphosphoric acid trimethylsilyl ester (PPSE) at 180 °C for 8 h could afford the amidines **HL**₁–**HL**₃ in good isolated yields (Scheme 1). These amidines were characterized by NMR spectroscopy, HRMS, FT-IR spectroscopy, and elemental analysis.

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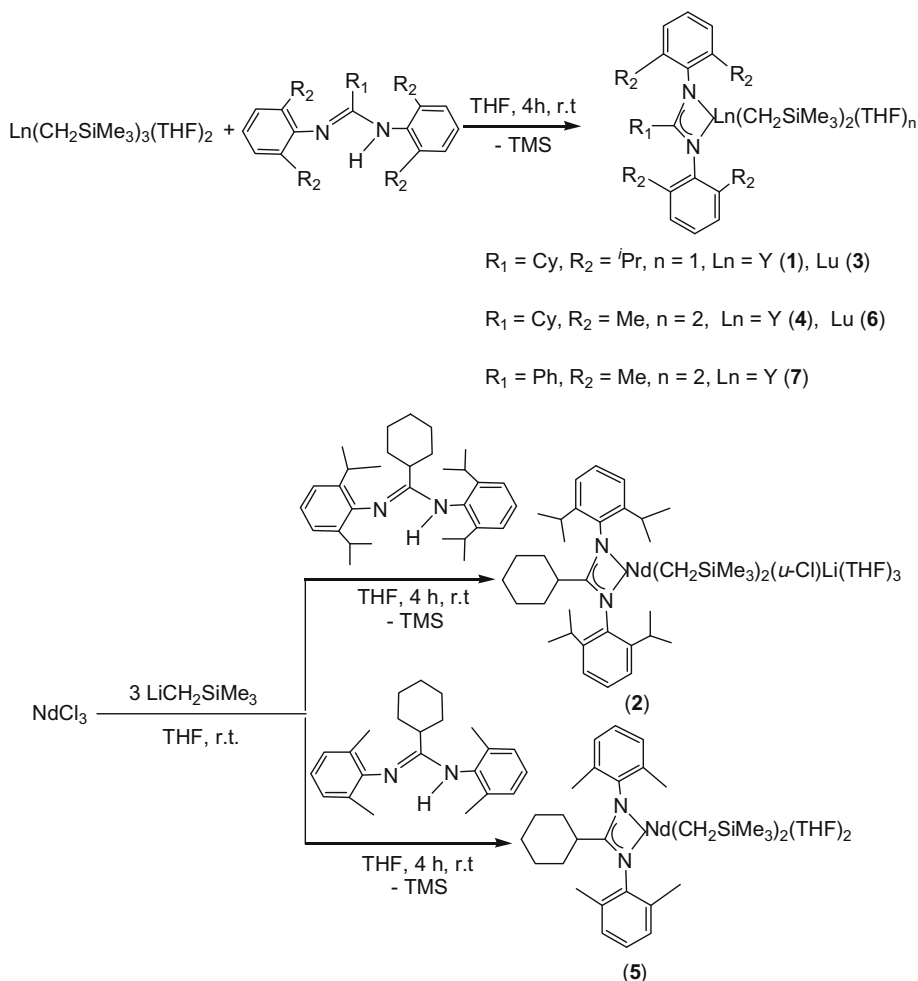


Scheme 1.

2.2. Synthesis and characterization of $[\text{CyC(N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]$
 $\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ ($\text{Ln} = \text{Y}$ (**1**), Lu (**3**)), $[\text{CyC(N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]$
 $\text{Nd}(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (**2**), $[\text{CyC(N-2,6-Me}_2\text{C}_6\text{H}_3)_2]$
 $\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ ($\text{Ln} = \text{Y}$ (**4**), Nd (**5**), Lu (**6**)), and
 $[\text{PhC(N-2,6-Me}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (**7**)

It is well known that an appropriate metal/ligand combination is rather critical to obtain neutral rare earth metal bis(alkyl) complexes. Using the strategy of protonolysis, Hessen et al. and Hou et al. prepared a series of mono(amidinate) rare earth metal

bis(alkyl)/bis(benzyl) complexes [32–39]. However, these species are supported mainly by steric demanding $\text{N,N}'$ -bis(2,6-diisopropylphenyl)benzamidinate $[\text{PhC(N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]^-$. Despite **HL**₂ and **HL**₃ are sterically less bulky than $[\text{PhC(N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]^-$, our approach to amidinate rare earth metal bis(alkyl) complexes with **HL**₁–**HL**₃ as ancillary ligands also involved alkane elimination. Treatment of $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ ($\text{Ln} = \text{Y, Lu}$) with one equivalent of the amidines **HL** in THF at room temperature for several hours, after workup, complexes **1**, **3**, **4**, **6**, and **7** could be successfully obtained in 75–89% isolated yields (Scheme 2). For the early lantha-



Scheme 2.

nide metal Nd, because its quite difficult to obtain pure and isolable Nd tris(alkyl) complex, one-pot synthetic route was adopted. Thus, THF slurry of NdCl_3 was stirred with three equiv of $\text{LiCH}_2\text{SiMe}_3$ in THF at room temperature for several hours, followed by addition of one equiv of the amidinate ligands (**HL**₁ and **HL**₂), after crystallization from hexane, complex **2** was isolated as an “ate” complex in 48% yield and complex **5** as a neutral one in 52% yield (Scheme 2). No ligand redistribution was observed in all these cases.

Complexes **1–7** are all air- and moisture-sensitive, they are soluble in THF and toluene. They were characterized by elemental analysis, FT-IR spectroscopy, NMR spectroscopy (except for **2** and **5** for their strong paramagnetic property). Complexes **2–5** were also subjected to X-ray single crystal structure determination.

Room-temperature ^1H NMR spectra of **1**, **4** and **7** in C_6D_6 show an AB spin for the methylene resonances of $\text{Y-CH}_2\text{SiMe}_3$. The methylene resonances for **1** were found at $\delta -0.23$ ppm (^1H , d, $J_{\text{Y-H}} = 3.4$ Hz) and $\delta 44.2$ ppm (^{13}C NMR), the latter is slightly up-field-shifted relative to the equivalent resonance in the related amidinate complex $[\text{PhC}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ (39.5 ppm) [32]. Restricted rotation about the N-C_{aryl} bonds gives rise to two separate doublets for the isopropyl methyl groups. In **4** and **7**, the main difference is the substituents at the carbon atom of ligating NCN moiety (cyclohexyl group for **4** and phenyl group for **7**), however, both methylene resonances of $\text{Y-CH}_2\text{SiMe}_3$ appear around $\delta 38$ ppm in ^{13}C NMR spectra, suggesting a similar electronic yttrium environment. In cases of lutetium complexes **3** and **6**, the methylene protons of $\text{Lu-CH}_2\text{SiMe}_3$ display singlet resonances at -0.47 and -0.48 ppm in ^1H NMR spectra, respectively.

Single crystals of complexes **2**, **3**, **4**, and **5** suitable for X-ray diffraction were grown from hexane at -30 °C. Their molecular structures are shown in Figs. 1–4, and crystallographic data are summarized in Table 1. With the same amidinate ligand **L**₁, **3** is a neutral bis(alkyl) complex, while **2** is an “ate” complex containing one equiv of $\text{LiCl}(\text{THF})_3$, which came from Nd tris(alkyl) complex formed *in situ* between the reaction of NdCl_3 and $\text{LiCH}_2\text{SiMe}_3$ in THF. In **3**, the bidentate amidinate ligand is bonded to Lu through nitrogen atoms, the lutetium is five-coordinated by two nitrogen atoms, two alkyls and one THF molecule to form an

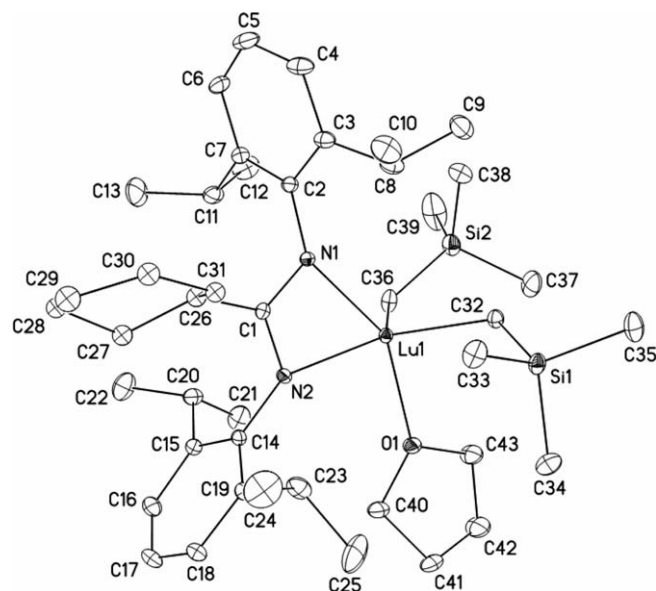


Fig. 2. Molecular structure of $[\text{CyC}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ (**3**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å) and angles (°): $\text{Lu}(1)\text{-N}(1) = 2.317(3)$, $\text{Lu}(1)\text{-N}(2) = 2.308(3)$, $\text{Lu}(1)\text{-O}(1) = 2.315(3)$, $\text{Lu}(1)\text{-C}(32) = 2.328(4)$, $\text{Lu}(1)\text{-C}(36) = 2.327(4)$, $\text{N}(1)\text{-C}(1) = 1.341(5)$, $\text{N}(2)\text{-C}(1) = 1.340(5)$, $\text{N}(2)\text{-Lu}(1)\text{-N}(1) = 57.98(11)$, $\text{C}(36)\text{-Lu}(1)\text{-C}(32) = 110.98(17)$, $\text{N}(1)\text{-C}(1)\text{-N}(2) = 113.5(3)$.

edge-bridged tetrahedral geometry [41]. The THF molecule occupies a position roughly in the plane defined by the lutetium atom and the NCN moiety of the amidinate ligand (dihedral angles of NCNLu and the plane formed by $\text{N}(2)\text{Lu}(1)\text{O}(1)$ is 178.67°). The alkyl groups are oriented above and below the NCNLu plane to minimize interaction with 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$ groups (dihedral angles of NCNLu and the plane formed by $\text{C}(32)\text{Lu}(1)\text{C}(36)$ is 89.65°). The

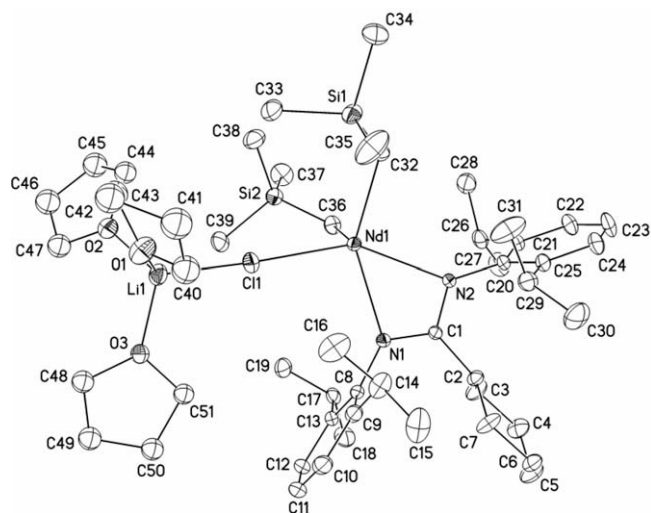


Fig. 1. Molecular structure of $[\text{CyC}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Nd}(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-Cl})\text{Li}(\text{THF})_3$ (**2**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å) and angles (°): $\text{Nd}(1)\text{-N}(1) = 2.476(3)$, $\text{Nd}(1)\text{-N}(2) = 2.498(3)$, $\text{Nd}(1)\text{-C}(36) = 2.456(6)$, $\text{Nd}(1)\text{-C}(32) = 2.476(5)$, $\text{Nd}(1)\text{-Cl}(1) = 2.7154(15)$, $\text{Nd}(1)\text{-C}(1) = 2.941(4)$, $\text{Cl}(1)\text{-Li}(1) = 2.321(10)$, $\text{N}(1)\text{-C}(1) = 1.319(5)$, $\text{N}(2)\text{-C}(1) = 1.334(5)$, $\text{C}(36)\text{-Nd}(1)\text{-C}(32) = 105.0(2)$, $\text{N}(1)\text{-Nd}(1)\text{-N}(2) = 53.08(11)$, $\text{N}(1)\text{-C}(1)\text{-N}(2) = 113.8(4)$, $\text{Li}(1)\text{-Cl}(1)\text{-Nd}(1) = 177.2(3)$.

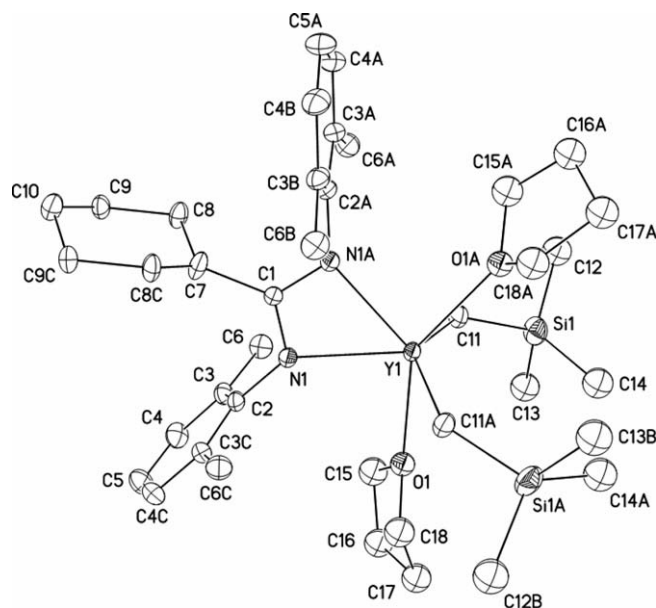


Fig. 3. Molecular structure of $[\text{CyC}(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (**4**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å) and angles (°): $\text{Y}(1)\text{-N}(1) = 2.375(7)$, $\text{Y}(1)\text{-N}(1\text{A}) = 2.375(7)$, $\text{Y}(1)\text{-C}(11) = 2.429(11)$, $\text{Y}(1)\text{-C}(11\text{A}) = 2.429(11)$, $\text{Y}(1)\text{-O}(1) = 2.463(8)$, $\text{Y}(1)\text{-O}(1\text{A}) = 2.463(8)$, $\text{N}(1)\text{-C}(1) = 1.320(9)$, $\text{C}(1)\text{-N}(1\text{A}) = 1.320(9)$, $\text{C}(11)\text{-Y}(1)\text{-C}(11\text{A}) = 140.9(5)$, $\text{N}(1)\text{-Y}(1)\text{-N}(1\text{A}) = 55.8(3)$, $\text{N}(1)\text{-C}(1)\text{-N}(1\text{A}) = 114.8(10)$.

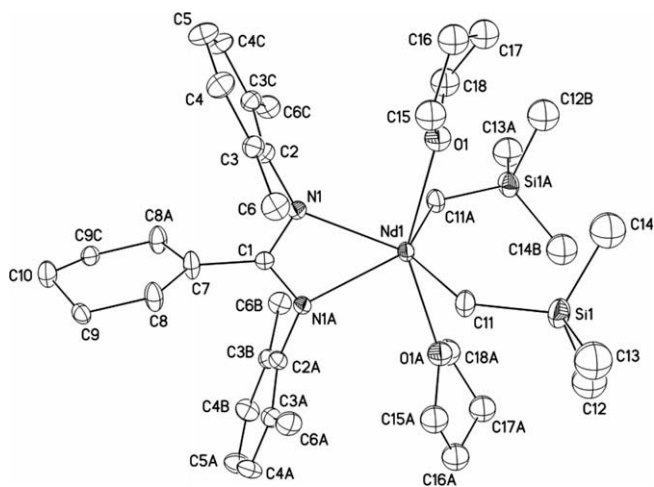


Fig. 4. Molecular structure of $[\text{CpC}(\text{N-2,6-Me}_2\text{C}_6\text{H}_3)_2]\text{Nd}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (**5**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 10% probability level. Selected bond lengths (Å) and angles ($^\circ$): $\text{Nd}(1)-\text{N}(1) = 2.453(7)$, $\text{Nd}(1)-\text{N}(1\text{A}) = 2.453(7)$, $\text{Nd}(1)-\text{C}(11) = 2.546(15)$, $\text{Nd}(1)-\text{C}(11\text{A}) = 2.546(15)$, $\text{Nd}(1)-\text{O}(1) = 2.593(11)$, $\text{Nd}(1)-\text{O}(1\text{A}) = 2.593(11)$, $\text{N}(1)-\text{C}(1) = 1.322(10)$, $\text{C}(1)-\text{N}(1\text{A}) = 1.322(10)$, $\text{C}(11)-\text{Nd}(1)-\text{C}(11\text{A}) = 138.6(6)$, $\text{N}(1)-\text{Nd}(1)-\text{N}(1\text{A}) = 53.6(4)$, $\text{C}(1)-\text{Nd}(1)-\text{O}(1) = 105.2(3)$, $\text{C}(1)-\text{Nd}(1)-\text{O}(1\text{A}) = 105.2(3)$, $\text{N}(1)-\text{C}(1)-\text{N}(1\text{A}) = 113.6(12)$.

$\text{Lu}-\text{CH}_2\text{SiMe}_3$ distances are 2.328(4) and 2.327(4) Å, which are almost identical to the $\text{Y}-\text{CH}_2\text{SiMe}_3$ distances in $[\text{PhC}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ (2.374(4) and 2.384(4) Å) [32], if the ionic radius is considered [42]. The distances between lutetium and the ligating nitrogen atoms ($\text{Lu}-\text{N} = 2.308(3)$ and 2.317(3) Å) are also consistent with those found in $[\text{PhC}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ (2.339(3) and 2.369(2) Å) [32]. The bite angle of $\text{N}(2)-\text{Lu}(1)-\text{N}(1) = 57.98(11)^\circ$ is comparable with that in $[\text{PhC}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ ($\text{N}(1)-\text{Y}-\text{N}(2) = 57.27(9)^\circ$). In **2**, the central metal Nd is five-coordinated by two alkyl groups, two nitrogen atoms and one chlorine to form a distorted pyramidal geometry. The amidinate Nd bis(alkyl) moiety is linked with $\text{Li}(\text{THF})_3^+$ moiety by chlorine anion. The bond angle of $\text{Nd}(1)-\text{Cl}(1)-\text{Li}(1)$ ($177.2(3)^\circ$) is close to straight angle, this deposi-

tion reduces the steric repulsion between the amidinate Nd bis(alkyl) moiety and $\text{Li}(\text{THF})_3^+$ moiety. For **4** and **5**, X-ray diffraction revealed that they are isostructural, and both are neutral bis(alkyl) bis(THF)-adduct complexes. Therefore, only the structure of **4** is discussed here. As shown in Figs. 3, **4** is a C_2 symmetric molecule. The yttrium atom is six-coordinated by two nitrogen atoms, two alkyl groups, and two THF molecules. The alkyl groups occupy axial positions relative to the NCNY plane (dihedral angles of NCNY and the plane formed by $\text{C}(11)\text{YC}(11\text{A})$ is 90.00°), while the THF molecules lie exactly in the NCNY plane (dihedral angles of NCNY and the plane formed by $\text{O}(1)\text{YO}(1\text{A})$ is 0°). In **4**, both $\text{Y}-\text{CH}_2\text{SiMe}_3$ bond distances are 2.437(14) Å, which are nearly identical to those in $[\text{PhC}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (2.427(2) and 2.433(2) Å) [32]. The Y–N distances are 2.371(8) Å, which are slightly shorter than those in $[\text{PhC}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (2.395(1) and 2.397(1) Å) [32], indicating the steric congestion around the coordination sphere of the yttrium ion in **4** is reduced with sterically less hindered amidinate ligand L_2^- .

2.3. Polymerization of *l*-lactide

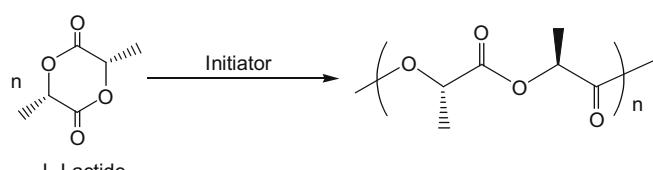
Poly(lactides) (PLAs) are the promising biodegradable and biocompatible synthetic macromolecules, and have been widely applied in medicine, pharmaceuticals, as well as in tissue engineering [43,44]. The most effective method to prepare PLAs is the ring-opening polymerization (ROP) of lactides by metal-based catalysts/initiators, and it has been proven that metal alkoxides usually possess the highest efficiency [45–46]. Some rare earth metal complexes also exhibited good performance for lactide polymerization [47–53]. In order to understand the polymerization behavior of mono(amidinate) rare earth metal bis(alkyl) complexes, the neutral complexes **1**, **3–7** were tested for the ring-opening polymerization of *l*-lactide, $[\text{PhC}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ was also employed in this experiment for comparison. The preliminary polymerization results are listed in Table 2.

All of these neutral complexes are active for *l*-lactide polymerization, and the conversions are all greater than 84% at 70°C for 30 min in toluene in case of $[M]/[I] = 100$ (molar ratio). The influence of central metal on the polymerization activity is obvious. For example, among these complexes, the lutetium complexes

Table 1
Details of the crystallographic data and refinements for **2–5**.

	2	3	4	5
Formula	$\text{C}_{51}\text{H}_{91}\text{ClLiN}_2\text{NdO}_3\text{Si}_2$	$\text{C}_{43}\text{H}_{75}\text{LuN}_2\text{OSi}_2$	$\text{C}_{39}\text{H}_{67}\text{N}_2\text{O}_2\text{Si}_2\text{Y}$	$\text{C}_{39}\text{H}_{67}\text{N}_2\text{NdO}_2\text{Si}_2$
FW	1023.07	867.20	741.04	796.37
<i>T</i> (K)	293(2)	293(2)	213(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 21/ <i>n</i>	<i>P</i> 21/ <i>n</i>	<i>C</i> mcm	<i>C</i> mcm
<i>a</i> (Å)	14.9502(14)	12.1257(11)	16.612(3)	16.590(4)
<i>b</i> (Å)	18.7717(18)	20.166(2)	19.550(4)	19.922(5)
<i>c</i> (Å)	21.408(2)	18.9893(18)	13.443(3)	13.358(3)
α ($^\circ$)	90.00	90.00	90	90
β ($^\circ$)	93.444(2)	92.505(2)	90	90
γ ($^\circ$)	90.00	90.00	90	90
<i>V</i> (Å ³)	5979.0(10)	4639.0(8)	4365.9(15)	4414.9(19)
<i>Z</i>	4	4	4	4
<i>D</i> _{calc} (g cm ^{−3})	1.133	1.242	1.127	1.198
μ (mm ^{−1})	0.986	2.210	1.421	1.261
<i>F</i> (000)	2172	1816	1592	1676
Crystal size (mm)	0.78 × 0.74 × 0.40	0.80 × 0.60 × 0.40	0.42 × 0.30 × 0.21	0.80 × 0.55 × 0.30
θ_{max} ($^\circ$)	25.35	25.35	25.00	25.34
Reflections collected	57489	43030	19835	20997
Independent reflections	10962	8456	1983	2184
No. of variables	550	442	127	116
GOF on <i>F</i> ²	1.147	1.107	1.198	1.156
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0576	0.0369	0.0995	0.0803
<i>wR</i>	0.1260	0.0836	0.2374	0.2084

Table 2
L-lactide polymerization with mono(amidinate) rare earth bis(alkyl) complexes^a



Run	Initiator	Yield ^b (%)	$M_{n,calcd}^c \times 10^{-4}$	$M_{n,obsd}^d \times 10^{-4}$	M_w/M_n^d	Efficiency ^e (%)
1	1	91	0.66	3.36	1.20	20
2	3	100	0.72	4.71	1.25	15
3	4	93	0.70	2.52	1.29	28
4	5	84	0.61	2.97	1.32	21
5	6	100	0.72	3.64	1.21	20
6	7	90	0.65	3.37	1.23	19
7	[PhC(N-2,6- <i>i</i> -Pr ₂ C ₆ H ₃) ₂]Y(CH ₂ SiMe ₃) ₂ (THF)	89	0.64	2.33	1.26	27

^a Polymerization conditions: [L-LA]/[Ln] = 100, [L-LA] = 0.5 M, in toluene, t = 30 min, 70 °C.

^b Isolated yields of PLA.

^c M_n of PLA calculated from $M_{n,calcd} = 144 \times ([LA]/2[Ln]) \times \text{yield (LA)}$.

^d Determined by GPC at 40 °C in THF relative to polystyrene standards; corrected by the Mark-Houwink equation [$M_{n,obsd} = 0.58M_n$ (GPC)] [57].

^e Initiation efficiency = $M_{n,calcd}/M_{n,obsd}$.

exhibited the highest activity (Table 2, runs 2 and 5), the activity order is **6** > **4** > **5**, which is strongly against the order of the effective ionic radii Nd³⁺ (1.123 Å) > Y³⁺ (1.040 Å) > Lu³⁺ (1.001 Å) [42]. GPC curves of the resulting polymers were all unimodal with quite narrow molecular weight distributions ($M_w/M_n < 1.32$), indicative of single-catalyst behavior as observed in other rare earth metal bis(alkyl) catalyst systems [51,54]. However, these amidinate rare earth metal alkyl complexes showed rather low initiation efficiency (15–28%). Under the present polymerization conditions, the steric congestion around the central metal has little effect on the polymerization activity (runs 1, 3, 6 and 7).

3. Conclusions

Alkane elimination reaction between Ln(CH₂SiMe₃)₃(THF)₂ (Ln = Y, Lu) with one equivalent of the amidines with different steric demanding **HL** ([CyC(N-2,6-*i*-Pr₂C₆H₃)₂]H (**HL**₁), [CyC(N-2,6-Me₂C₆H₃)₂]H (**HL**₂), and [PhC(N-2,6-Me₂C₆H₃)₂]H (**HL**₃)) in THF afforded a series of mono(amidinate) rare earth metal bis(alkyl) complexes [CyC(N-2,6-*i*-Pr₂C₆H₃)₂]Ln(CH₂SiMe₃)₂(THF) (Ln = Y (**1**), Lu (**3**)), [CyC(N-2,6-Me₂C₆H₃)₂]Ln(CH₂SiMe₃)₂(THF)₂ (Ln = Y (**4**), Lu (**6**)), and [PhC(N-2,6-Me₂C₆H₃)₂]Y(CH₂SiMe₃)₂(THF)₂ (**7**). Treatment of Nd tris(alkyl) complexes, which was formed *in situ* from the reaction of THF slurry of NdCl₃ with LiCH₂SiMe₃, with 1 equiv. of the amidines **HL**₁ or **HL**₂ gave an “ate” complex [CyC(N-2,6-*i*-Pr₂C₆H₃)₂]Nd(CH₂SiMe₃)₂(μ-Cl)Li(THF)₃ (**2**) and a neutral [CyC(N-2,6-Me₂C₆H₃)₂]Nd(CH₂SiMe₃)₂(THF)₂ (**5**), respectively. Ligand redistribution was not observed during the preparation of these mono(amidinate) rare earth metal bis(alkyl) complexes, even using sterically less demanding **HL**₂ and **HL**₃. These neutral mono(amidinate) rare earth metal bis(alkyl) complexes showed activity towards L-lactide polymerization to give high molecular weight and quite narrow molecular weight distribution polymers. The polymerization activity is strongly dependent upon the central metals with the activity order Lu > Y > Nd.

4. Experimental

4.1. Materials and procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and 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 the glovebox. Dichloromethane was dried by stirring with CaH₂, and distilled before use. Anhydrous LnCl₃ were purchased from STREM. LiCH₂SiMe₃ (1 M solution in pentane) was obtained from Aldrich, dried under vacuum before use. P₂O₅ was purchased from Sinopharm Chemical Reagent Co. Ltd. Hexamethyldisiloxane, 2,6-diisopropylaniline, 2,6-dimethylaniline, and cyclohexanecarboxylic acid were purchased from Acros, and used as received. L-Lactide was purchased from TCI, and was recrystallized from hot toluene. Deuterated solvents (CDCl₃ and C₆D₆) were obtained from CIL. Ln(CH₂SiMe₃)₃(THF)₂ (Ln = Y, Lu) [55,56] polyphosphoric acid trimethylsilyl ester (PPSE) [40], and [PhC(N-2,6-*i*-Pr₂C₆H₃)₂]Y(CH₂SiMe₃)₂(THF) [32] were prepared according to the literature.

Samples of organo rare earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. NMR (¹H and 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. X-ray structural determinations were carried out on a Rigaku Mercury diffractometer. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer. TOF HRMS spectra were obtained from a Micromass OR-TOF spectrometer. Melting points were not calibrated. Molecular weight and molecular weight distribution of the polymers were measured by PL GPC 50 at 40 °C using THF as eluent against polystyrene standards.

4.2. Synthesis of [CyC(N-2,6-*i*-Pr₂C₆H₃)₂]H (**HL**₁)

In a Schlenk flask, P₂O₅ (9.0 g, 63.4 mmol), hexamethyldisiloxane (20 mL, 93.7 mmol), and dry dichloromethane (20 mL) were refluxed for 30 min. Then the volatiles were removed under vacuum to afford a viscous syrup PPSE. Cyclohexanecarboxylic acid (0.96 g, 7.50 mmol) and 2,6-diisopropylaniline (3.0 mL, 15.0 mmol) were added to this viscous syrup, and the mixture was reacted at 180 °C for 8 h. The resulting mixture was poured into 1 M NaOH solution (150 mL) to produce an oil that could solidify overnight. The solid was washed with water and was recrystallized from ethyl alcohol to give the title compound as colorless crystals (2.0 g, 60%). ¹H NMR (400 MHz, CDCl₃): δ 0.97 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.19 (d, J = 6.0 Hz, 6H, CH(CH₃)₂), 1.25 (d, 12H, CH(CH₃)₂), 1.61 (d, 1H,

CH₂), 1.70, 1.73, 1.81, 2.10 (m, 11H, Cy-H), 3.13 (m, 2H, CH(CH₃)₂), 3.20 (m, 2H, CH(CH₃)₂), 5.20 (s, 1H, N-H), 7.02, 7.12 (m, 6H, Ar-H). ¹³C NMR (100 MHz, CDCl₃): δ 22.6, 23.0, 24.2, 25.6 (CH(CH₃)₂), 26.0, 26.3 (Cy-CH₂), 28.2, 28.5 (CH(CH₃)₂), 31.1 (Cy-CH₂), 39.3 (Cy-CH), 122.8, 123.1, 123.7, 128.1, 133.3, 139.2, 144.5, 147.3 (Ar-C), 159.1 (NCN). Anal. Calc. for C₃₁H₄₆N₂: C, 83.35; H, 10.38; N, 6.27. Found: C, 83.23; H, 10.41; N, 6.35%.

4.3. Synthesis of [CyC(N-2,6-Me₂C₆H₃)₂]H (HL₂)

Following the procedure as that for HL₁. Using cyclohexanecarboxylic acid (0.96 g, 7.50 mmol) and 2,6-dimethylaniline (1.85 mL, 15.0 mmol) to produce the title compound as colorless crystals after recrystallization from ethyl alcohol. Yield: 1.70 g (68%). ¹H NMR (400 MHz, CDCl₃): δ 1.05, 1.21, 1.60, 1.73, 1.91, 2.05 (m, 11H, Cy-H), 2.23 (d, 12H, CH₃), 5.27 (br, 1H, N-H), 6.85, 7.04 (m, 6H, Ar-H). ¹³C NMR (100 MHz, CDCl₃): δ 17.9 (CH₃), 18.9 (CH₃), 25.8, 26.1, 31.2 (Cy-CH₂), 39.7 (Cy-CH), 122.4 (Ar ipso-C), 127.1, 128.2, 128.4, 129.0, 136.2, 136.5, 146.0 (Ar-C), 159.8 (NCN). FT-IR (KBr, cm⁻¹): 3422 (m), 3344 (m), 2927 (s), 2853 (m), 1641 (s), 1589 (m), 1472 (m), 1449 (m), 1390 (m), 1336 (m), 1275 (m), 782 (m), 760 (m). Anal. Calc. for C₂₃H₃₀N₂: C, 82.59; H, 9.04; N, 8.37. Found: C, 82.63; H, 9.11; N, 8.27%. HRMS [C₂₃H₃₀N₂]⁺: calcd 334.2409, found 334.2408. M.p. 132.4 °C.

4.4. Synthesis of [PhC(N-2,6-Me₂C₆H₃)₂]H (HL₃)

Following the procedure as that for HL₁. Using benzoic acid (0.92 g, 7.50 mmol) and 2,6-dimethylaniline (1.85 mL, 15.0 mmol) to produce the title compound as off-white crystals after recrystallization from ethyl alcohol. Yield: 2.12 g (86%). ¹H NMR (400 MHz, CDCl₃): δ 2.13 (s, 6H, CH₃), 2.36 (s, 6H, CH₃), 5.73 (s, 1H, N-H), 6.93, 7.11, 7.18, 7.29, 7.46 (m, 11H, Ar-H). ¹³C NMR (100 MHz, CDCl₃): δ 18.0 (CH₃), 19.1 (CH₃), 123.0, 126.6, 127.2, 127.8, 128.3, 128.5, 129.0, 129.5, 134.9, 135.3, 137.1, 145.9 (Ar-C), 153.9 (NCN). FT-IR (KBr, cm⁻¹): 3441 (m), 2961 (s), 2867 (w), 1644 (s), 1588 (w), 1464 (m), 1439 (w), 1376 (m), 1279 (m), 1226 (m), 1167 (s), 1100 (w), 779 (m), 768 (m). Anal. Calc. for C₂₃H₂₄N₂: C, 84.11; H, 7.37; N, 8.53. Found: C, 83.75; H, 7.68; N, 8.58%. HRMS [C₂₃H₂₄N₂]⁺: calcd 328.1939, found 328.1939. M.p. 124.5 °C.

4.5. Synthesis of [CyC(N-2,6-ⁱPr₂C₆H₃)₂]Y(CH₂SiMe₃)₂(THF) (1)

To a 30 mL of colorless THF solution of Y(CH₂SiMe₃)₃(THF)₂ (0.990 g, 2.00 mmol), HL₁ (0.893 g, 2.00 mmol) in 20 mL THF was added dropwisely at room temperature. The mixture was stirred at room temperature for 4 h. Then the solvent was removed under reduced pressure to afford an off-white powder. The powder was extracted with 30 mL of hexane and filtered. The filtrate was concentrated and cooled at -30 °C overnight to give [CyC(N-2,6-ⁱPr₂C₆H₃)₂]Y(CH₂SiMe₃)₂(THF)₂ as colorless crystals in two crops. Yield: 1.4 g (89%). ¹H NMR (500 MHz, C₆D₆) δ: -0.23 (d, J = 3.0 Hz, 4H, CH₂SiMe₃), 0.28 (s, 18H, SiMe₃), 0.64 (m, 4H, Cy-CH₂), 1.10 (b, 4H, β-THF), 1.20 (m, 4H, Cy-CH₂), 1.33 (d, J = 7.0 Hz, 12H, CH(CH₃)₂), 1.38 (d, J = 7.0 Hz, 12H, CH(CH₃)₂), 1.82 (d, 2H, Cy-CH₂), 2.47 (m, 1H, Cy-CH), 3.4 (b, 4H, α-THF), 3.60 (m, 4H, CH(CH₃)₂), 7.07–7.16 (6H, Ar-H). ¹³C NMR (100 MHz, C₆D₆) δ: 4.3 (TMS), 23.7 (CH(CH₃)₂), 24.7 (Cy-CH₂), 25.9 (β-THF), 26.4 (Cy-CH₂), 26.6 (CH(CH₃)₂), 28.5 (Cy-CH₂), 30.2 (Cy-CH), 38.9, 39.3 (CH(CH₃)₂), 44.2 (CH₂TMS), 70.0 (α-THF), 123.9, 125.0, 143.1 (Ar-C), 180.6 (NCN). FT-IR (KBr, cm⁻¹): 2959 (s), 2928 (s), 2866 (m), 1636 (s), 1460 (s), 1434 (s), 1393 (m), 1323 (m), 1247 (m), 862 (m), 762 (m). Anal. Calcd for C₄₄H₇₇N₂O₂Si₂Y: C, 66.46; H, 9.76; N, 3.52. Found: C, 66.59; H, 9.88; N, 3.46%.

4.6. Synthesis of [CyC(N-2,6-ⁱPr₂C₆H₃)₂]Nd(CH₂SiMe₃)₂(μ-Cl)Li(THF)₃ (2)

To a 20 mL of THF slurry of NdCl₃ (0.376 g, 1.5 mmol), LiCH₂-SiMe₃ (0.424 g, 4.50 mmol) in 20 mL of THF was added dropwisely at room temperature. The resulting clear green solution was allowed to stir at room temperature for half an hour. Then HL₁ (0.670 g, 1.5 mmol) in 20 mL of THF was added slowly at room temperature. The mixture was stirred at room temperature for 4 h. Then the solvent was removed under reduced pressure to afford a green powder. The powder was extracted with hexane (3 × 10 mL) and filtered. The filtrate was concentrated and cooled at -30 °C overnight to give [CyC(N-2,6-ⁱPr₂C₆H₃)₂]Nd(CH₂SiMe₃)₂(μ-Cl)Li(THF)₃ as green crystals. Yield: (0.65 g, 48%). Anal. Calc. for C₅₁H₉₁ClLiN₂NdO₃Si₂: C, 59.87; H, 8.98; N, 2.74. Found: C, 59.68; H, 8.75; N, 2.81%.

4.7. Synthesis of [CyC(N-2,6-ⁱPr₂C₆H₃)₂]Lu(CH₂SiMe₃)₂(THF) (3)

To a 20 mL of colorless THF solution of Lu(CH₂SiMe₃)₃(THF)₂ (0.58 g, 1.0 mmol), HL₁ (0.447 g, 1.0 mmol) in 20 mL THF was added dropwisely at room temperature. The mixture was stirred at room temperature for 4 h. Then the solvent was removed under reduced pressure to afford a off-white powder. The powder was extracted with 30 mL of hexane and filtered. The filtrate was concentrated and cooled at -30 °C overnight to give [CyC(N-2,6-ⁱPr₂C₆H₃)₂]Lu(CH₂SiMe₃)₂(THF)₂ as colorless crystals. Yield: 0.71 (76%). ¹H NMR (500 MHz, C₆D₆) δ: -0.47 (s, 4H, CH₂SiMe₃), 0.26 (s, 18H, SiMe₃), 0.63 (m, 4H, Cy-CH₂), 1.12 (m, 4H, β-THF), 1.18 (m, 4H, Cy-CH₂), 1.32 (d, J = 6.5 Hz, 12H, CH(CH₃)₂), 1.38 (d, J = 6.5 Hz, 12H, CH(CH₃)₂), 1.81 (d, 2H, Cy-CH₂), 2.45 (m, 1H, Cy-CH), 3.54 (m, 4H, α-THF), 3.62 (m, 4H, CH(CH₃)₂), 7.06–7.16 (6H, Ar-H). ¹³C NMR (125 MHz, C₆D₆) δ: 4.2 (TMS), 23.7 (CH(CH₃)₂), 24.3 (β-THF), 25.7 (Cy-CH₂), 26.1 (Cy-CH₂), 26.4 (CH(CH₃)₂), 28.1 (Cy-CH₂), 29.9 (CH(CH₃)₂), 44.2 (Cy-CH), 45.3 (CH₂TMS), 70.5 (α-THF), 123.7, 124.9, 142.7, 143.1 (Ar-CH), 180.2 (NCN). FT-IR (KBr, cm⁻¹): 2961 (s), 2866 (s), 1634 (s), 1459 (s), 1384 (m), 1354 (m), 1315 (s), 1238 (s), 859 (s), 804 (m). Anal. Calc. for C₄₄H₇₇LuN₂O₂Si₂: C, 59.97; H, 8.81; N, 3.18. Found: C, 59.94; H, 8.58; N, 3.32%.

4.8. Synthesis of [CyC(N-2,6-Me₂C₆H₃)₂]Y(CH₂SiMe₃)₂(THF)₂ (4)

To a 20 mL of colorless THF solution of Y(CH₂SiMe₃)₃(THF)₂ (0.930 g, 1.88 mmol), HL₂ (0.628 g, 1.88 mmol) in 20 mL THF was added dropwisely at room temperature. The mixture was stirred at room temperature for 4 h. Then the solvent was removed under reduced pressure to afford an off-white powder. The powder was washed with hexane and dried. Yield: 1.2 g (86%). ¹H NMR (400 MHz, C₆D₆) δ: -0.30 (d, J = 2.8 Hz, 4H, CH₂TMS), 0.31 (s, 18H, CH₂TMS), 0.52–0.67 (m, 4H, Cy-CH₂), 1.09 (d, 2H, Cy-CH₂), 1.17 (br s, 8H, β-THF), 1.27 (d, 2H, Cy-CH₂), 1.81 (d, 2H, Cy-CH₂), 2.24 (m, 1H, Cy-CH), 2.40 (s, 12H, Ph-Me), 3.57 (br s, 8H, α-THF), 6.91, 7.01 (6H, Ar-H). ¹³C NMR (100 MHz, C₆D₆) δ: 4.5 (SiTMS), 20.2 (Ph-Me), 25.1 (β-THF), 25.9, 26.7, 29.3 (Cy-CH₂), 36.9, 37.2 (CH₂TMS), 44.1 (Cy-CH), 69.6 (α-THF), 123.8, 132.8, 146.5 (Ar-C), 179.8 (NCN). FT-IR (KBr, cm⁻¹): 2933 (s), 2853 (s), 1637 (s), 1589 (m), 1478 (s), 1375 (m), 1355 (m), 1309 (m), 1250 (m), 1035 (m), 959 (m), 861 (m), 763 (s). Anal. Calc. for C₄₀H₆₈N₂O₂Si₂Y: C, 63.71; H, 9.09; N, 3.72. Found: C, 63.98; H, 8.86; N, 3.79%.

4.9. Synthesis of [CyC(N-2,6-Me₂C₆H₃)₂]Nd(CH₂SiMe₃)₂(THF)₂ (5)

To a 20 mL of THF slurry of NdCl₃ (0.376 g, 1.5 mmol), LiCH₂-SiMe₃ (0.424 g, 4.50 mmol) in 20 mL of THF was added dropwisely at room temperature. The resulting clear green solution was allowed to stir at room temperature for half an hour. Then HL₂

(0.424 g, 1.50 mmol) in 20 mL of THF was added slowly at room temperature. The mixture was stirred at room temperature for 4 h. Then the solvent was removed under reduced pressure to afford a green powder. Yield: 0.62 g (52%). FT-IR (KBr, cm^{-1}): 2930 (s), 2852 (s), 1638 (s), 1589 (m), 1471 (s), 1354 (m), 1308 (m), 1227 (s), 1094 (m), 862 (m), 763 (s). Anal. Calc. for $\text{C}_{40}\text{H}_{68}\text{N}_2\text{NdO}_2\text{Si}_2$: C, 59.36; H, 8.47; N, 3.46. Found: C, 59.53; H, 8.42; N, 3.39%.

4.10. Synthesis of $[\text{CyC}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2]\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (**6**)

To a 20 mL of colorless THF solution of $\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (0.581 g, 1.00 mmol), HL_2 (0.334 g, 1.00 mmol) in 20 mL THF was added dropwisely at room temperature. The mixture was stirred at room temperature for 4 h. Then the solvent was removed under reduced pressure to afford an off-white powder. The powder was washed with hexane and dried. Yield: 0.71 g (83.4%). ^1H NMR (500 MHz, C_6D_6) δ : -0.48 (s, 4H, CH_2SiMe_3), 0.29 (s, 18H, SiMe_3), 0.60 (m, 4H, CH_2), 1.12 (m, 4H, CH_2), 1.24 (m, 8H, β -THF), 1.81 (d, 2H, CH_2), 2.25 (m, 1H, CH), 2.42 (s, 12H, Ph-Me), 6.91, 7.02 (6H, Ar-H). ^{13}C NMR (125 MHz, C_6D_6) δ : 4.3 (TMS), 19.9 (Ph-Me), 20.5 (Cy- CH_2), 25.1 (Ph-Me), 25.6 (β -THF), 26.4, 29.4 (Cy- CH_2), 44.1 (Cy-CH), 45.5 (CH_2TMS), 68.7 (α -THF), 123.9, 132.7, 133.2, 145.8 (Ar-CH), 179.1 (NCN). FT-IR (KBr, cm^{-1}): 2938 (s), 2853 (s), 1638 (m), 1590 (w), 1472 (s), 1373 (m), 1355 (m), 1309 (m), 1236 (s), 1196 (w), 1044 (m), 858 (s), 763 (s). Anal. Calc. for $\text{C}_{40}\text{H}_{68}\text{LuN}_2\text{O}_2\text{Si}_2$: C, 57.19; H, 8.16; N, 3.33. Found: C, 57.28; H, 8.15; N, 3.42%.

4.11. Synthesis of $[\text{PhC}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (**7**)

To a 20 mL of colorless THF solution of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (0.754 g, 1.52 mmol), HL_3 (0.50 g, 1.52 mmol) in 20 mL THF was added dropwisely at room temperature. The mixture was stirred at room temperature for 4 h. Then the solvent was removed under reduced pressure to afford an off-white powder. The powder was extracted with hexane (3×10 mL) and filtered. The filtrate was concentrated and cooled at -30°C overnight to give $[\text{PhC}(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ as colorless crystals. Yield: 0.83 g (75%). ^1H NMR (400 MHz, C_6D_6) δ : -0.18 (d, $J = 2.9$ Hz, 4H, CH_2TMS), 0.32 (s, 18H, CH_2TMS), 1.20 (br s, 8H, β -THF), 2.37 (s, 12H, Ph-Me), 3.60 (br s, 8H, α -THF), 6.62, 6.78, 6.85, 7.03 (11H, Ph-H). ^{13}C NMR (100 MHz, C_6D_6) δ : 4.6 (SiTMS), 20.1 (Ph-Me), 25.1 (β -THF), 37.9, 38.3 (CH_2TMS), 69.7 (α -THF), 123.3, 123.7, 126.9, 127.2, 128.5, 132.2, 132.5, 146.5, 147.2 (Ar-C), 174.7 (NCN). FT-IR (KBr, cm^{-1}): 3341 (m), 2955 (s), 1628 (s), 1589 (w), 1466 (s), 1435 (s), 1366 (s), 1250 (s), 1204 (m), 1034 (m), 987 (s), 833 (s), 764 (s), 694 (s). Anal. Calc. for $\text{C}_{39}\text{H}_{60}\text{N}_2\text{O}_2\text{Si}_2\text{Y}$: C, 63.82; H, 8.24; N, 3.82. Found: C, 63.85; H, 8.13; N, 3.89%.

4.12. Polymerization of *l*-lactide

A typical procedure for *l*-Lactide polymerization was described (Table 2, run 1). In a 20 mL Schleck flask, complex **1** (20 mg, 26 μmol), *l*-lactide (368 mg, 2.6 mmol), and toluene (5.2 mL) were stirred at 70°C for 30 min. The resulting viscous solution was quenched by an excess amount of ethanol, filtered, and then dried at 60°C *in vacuo* to constant weight (335 mg, 91%).

4.13. X-ray crystallographic study

Suitable single crystals of complexes were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo $K\alpha$ radiation ($\lambda = 0.71070 \text{ \AA}$). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1. The struc-

tures 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. All the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELXL-97 program.

5. Supplementary material

CCDC 698451, 698452, 698453 and 698454 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.

Acknowledgements

This work was partly financial supported by the National Natural Science Foundation of China (20604023), Zhejiang Provincial Natural Science Foundation (Y406301), Ningbo Municipal Natural Science Foundation (2008A610056), and Key Laboratory Foundation of Ningbo (2007A22011).

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