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Article

Synthesis of Rare-Earth Metal Amides Bearing an Imidazolidine-Bridged Bis(phenolato) Ligand and Their Application in the Polymerization of L-Lactide

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A series of neutral rare-earth metal amides supported by an imidazolidine-bridged bis(phenolato) ligand were synthesized, and their catalytic activity for the polymerization of L-lactide was explored. The amine elimination reactions of Ln[N(TMS)$_2$]$_3$(μ-Cl)Li(THF)$_3$ with H$_2$[ONNO] {H$_2$[ONNO] = 1,4-bis(2-hydroxy-3,5-di-*tert*-butyl-benzyl)-imidazolidine} in a 1:1 molar ratio in tetrahydrofuran (THF) gave the neutral rare-earth metal amides [ONNO]Ln[N(TMS)$_2$](THF) [Ln = La (**1**), Pr (**2**), Nd (**3**), Sm (**4**), Yb (**5**), and Y (**6**)] in high isolated yields. All of these complexes are fully characterized. X-ray structural determination revealed that complexes **1**−**6** are isostructural and have a solvated monomeric structure. The coordination geometry around each of the rare-earth metal atoms can be best described as a distorted trigonal bipyramid. It was found that complexes **1**−**6** are efficient initiators for the ring-opening polymerization of L-lactide, and the ionic radii of the central metals have a significant effect on the catalytic activity. A further study revealed that these rare-earth metal amides can initiate L-lactide polymerization in a controlled manner in the presence of 1 equiv of isopropyl alcohol.

Introduction

In recent years, the utilization of bridged bis(phenolate) ligands in organolanthanide or organolanthanoid chemistry has attracted considerable attention, because some of these bridged bis(phenolate) lanthanide complexes have shown great potential application in homogeneous catalysis. These ligand systems have attractive features, such as being easily available, tunable, and even potentially recyclable, which allows the possibility for a systematic study on the effect of the steric and electronic properties of the bisphenolic portion on the reactivity of the corresponding lanthanide complexes.[1−3]

It was found that the presence of heteroatom(s) on the bridged bis(phenolate) ligands has a significant influence on the reactivity of the corresponding lanthanide complexes, because the coordination of the electron-donating heteroatom(s) to the lanthanide atom led to an increase of the electron density around the metal center, which improves their reactivity in some cases. For example, the divalent ytterbium complex stabilized by a diamino bis(phenolate) ligand shows distinctively high activity for ε-caprolactone polymerization in comparison with other divalent ytterbium

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Chart 1
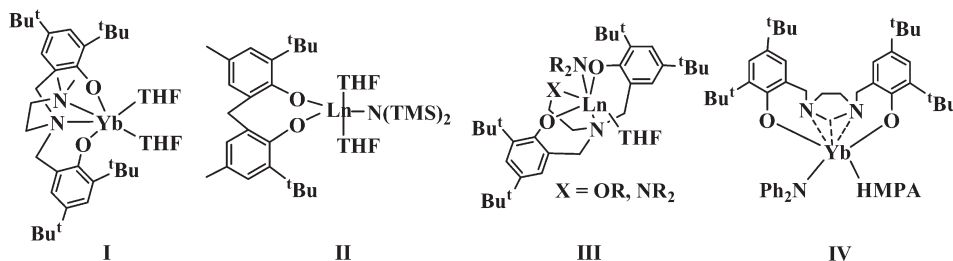
species, and its reactivity toward PhNCO and PhC≡CH as a single electron transfer reagent is similar to those of divalent samarium complexes (Chart 1, I).[11] The number of hetero-atom(s) of the bridged bis(phenolate) ligands has been found to show a profound effect on the reaction outcome for the amine elimination reactions of divalent samarium systems;[1n] the trivalent amine bridged bis(phenolate) lanthanide complexes showed higher catalytic activities for ε-caprolactone polymerization (Chart 1, III) than the methylene-linked ones (Chart 1, II).[1e,2d] To systematically investigate the effect of the structures of the ancillary ligands on the reactivity of the corresponding lanthanide complexes, a series of ytterbium derivatives supported by a new imidazolidine-bridged bis(phenolate) ligand was synthesized by a direct salt metathe-sis reaction (Chart 1, IV). However, all of these ytterbium complexes showed low or no activity toward ε-caprolactone or lactide polymerization.[1m] These unexpected results should be attributed mainly to the coordination of hexamethylphos-phoric triamide (HMPA) at the ytterbium center, which was introduced to improve the solubility of the imidazolidine-bridged bis(phenolate) ytterbium chloride. Therefore, it is expected that the imidazolidine-bridged bis(phenolate) lanthanide derivatives without a coordinated HMPA mole-cule should have high activity.

The amine elimination reaction is a straightforward meth-od for the synthesis of lanthanide amides, and the standard precursors are the bulky bis(trimethylsilyl)amido lanthanide complexes $Ln[N(TMS)_2]_3$ or $Ln[N(TMS)_2]_3(\mu\text{-Cl})Li(THF)_3$ (TMS = $SiMe_3$; THF = tetrahydrofuran).[4] However, these kinds of precursors seem to be problematic in the bridged bis (phenolate) systems.[5] The popular precursors used in these cases are the sterically less demanding bis(dimethylsilyl)ami-do lanthanide complexes $Ln[N(SiHMe_2)_2]_3(THF)_2$.[1b,1c,1i,1j,3] Moreover, Mountford et al. recently reported that the amine elimination reaction of $Sm[N(TMS)_2]_3$ with amine bridged bis(phenols) gave the unexpected zwitterionic amine bridged bis(phenolate) samarium complexes instead of the desired samarium amides (Scheme 1).[1q] However, it was found that the bulky bis(trimethylsilyl)amido rare-earth metal com-plexes $Ln[N(TMS)_2]_3(\mu\text{-Cl})Li(THF)_3$ are suitable starting materials for the synthesis of rare-earth metal amido com-plexes in our case. In this contribution, a series of neutral rare-earth metal bis(trimethylsilyl)amido complexes bearing an

Scheme 1
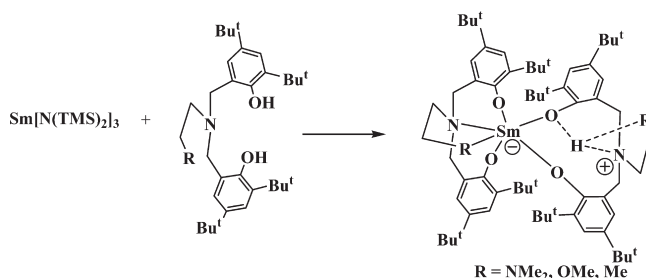
imidazolidine-bridged bis(phenolato) ligand were synthesized by amine elimination reactions. Moreover, these rare-earth metal amides are indeed efficient initiators for the ring-open-ing polymerization of L-lactide, and a further study revealed that these lanthanide amides can initiate L-lactide polymer-ization in a controlled manner in the presence of isopropyl alcohol. Here, we report these results.

Experimental Section

General Procedures. All of the manipulations were performed under an argon atmosphere, using the standard Schlenk tech-niques. $HN(TMS)_2$, L-lactide, and n-BuLi are commercially available. $HN(TMS)_2$ was dried over CaH_2 for 4 days and distilled before use. THF, toluene, and hexane were dried and freed of oxygen by refluxing over sodium/benzophenone ketyl and distilled prior to use. $[ONNO]H_2$ {$H_2[ONNO]$ = 1,4-bis-(2-hydroxy-3,5-di-*tert*-butyl-benzyl)-imidazolidine},[1m] LiN-$(TMS)_2$,[6] and $Ln[N(TMS)_2]_3(\mu\text{-Cl})Li(THF)_3$ (Ln = La, Pr, Nd, Sm, Yb, and Y)[7] were prepared according to the published procedures. Rare-earth metal analyses were performed by ethylenediaminetetraacetic acid titration with a xylenol orange indicator and a hexamine buffer.[8] Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. The ^1H and ^{13}C NMR spectra were recorded in a C_6D_6 solution for complexes **1** and **6** with a Unity Varian spectrometer. Because of their paramagnetism, no resolvable NMR spectrum for complexes **2−5** was obtained. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges. Molecular weight and molecular weight distribution (PDI) were determined against a polystyrene stan-dard by gel permeation chromatography (GPC) on a PL 50

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apparatus, and THF was used as an eluent at a flow rate of 1.0 mL/min at 40 °C.

Synthesis of [ONNO]La[N(TMS)₂](THF) (1). To a THF solution of La[N(TMS)₂]₃(μ-Cl)Li(THF)₃ (2.42 g, 2.76 mmol) was added a THF solution of [ONNO]H₂ (10 mL, 1.40 g, 2.76 mmol). The mixture was stirred overnight at 50 °C, and then THF was evaporated completely under reduced pressure. Toluene (20 mL) was added to the residue, and the mixture was stirred at 80 °C for about 0.5 h. The precipitate formed was removed by centrifugation, and then the solvent was evaporated completely under reduced pressure again. Hexane (30 mL) was added to precipitate the product. The powder obtained was dissolved in a hexane/THF solution, and colorless crystals were obtained from a concentrated solution (about 15 mL) at −5 °C over several days (2.03 g, 84%). Mp: 220−222 °C. Anal. calcd for $C_{43}H_{76}N_3O_3Si_2La$: C, 58.81; H, 8.72; N, 4.79; La, 15.82. Found: C, 58.76; H, 8.60; N, 4.64. La, 15.65. ¹H NMR (400 MHz, C_6D_6): 7.46 (d, ^4J(H, H) = 2.4 Hz, 2H, ArH), 6.83 (d, ^4J(H, H) = 2.4 Hz, 2H, ArH), 4.18 (d, ^2J(H, H) = 14.0 Hz, 2H, ArCH₂; overlap with THF signal), 4.10 (br, s, 4H, α-CH₂ THF), 3.48 (m, 2H, NCH₂CH₂N imidazolidine ring), 3.42 (d, ^2J(H, H) = 7.9 Hz, 1H, NCH₂N imidazolidine ring), 2.88 (d, ^2J(H, H) = 14.0 Hz, 2H, ArCH₂), 1.97 (m, 2H, NCH₂CH₂N imidazolidine ring), 1.85 (d, ^2J(H, H) = 7.6 Hz, 1H, NCH₂N imidazolidine ring), 1.55 (s, 18H, C(CH₃)₃), 1.48 (br, s, 4H, β-CH₂ THF), 1.42 (s, 18H, C(CH₃)₃), 0.35 (s, 18H, TMS). ¹³C {1H} NMR (400 MHz, C_6D_6): 122.01 (Ph), 161.41 (Ph), 136.23 (Ph), 123.95 (Ph), 136.28 (Ph), 124.83 (Ph), 71.35 (NCH₂N imidazolidine ring), 67.89 (α-CH₂ THF), 57.22 (N(CH₂)₂N imidazolidine), 51.11 (CH₂Ar), 35.50 (C(CH₃)₃), 34.13 (C-(CH₃)₃), 32.19 (C(CH₃)₃), 30.55 (C(CH₃)₃), 25.40 (β-CH₂ THF), 5.58 (TMS). IR (KBr, cm⁻¹): 2955(s), 2905(s), 2869(s), 1605(m), 1477(s), 1440(s), 1413(s), 1361(s), 1301(s), 1237(s), 1202(m), 1165(m), 1133(m), 1025(w), 933(s), 881(s), 834(s), 741(m). The crystals suitable for an X-ray diffraction analysis were obtained by slow cooling of the hot hexane/THF solution.

Synthesis of [ONNO]Pr[N(TMS)₂](THF) (2). The synthesis of complex **2** was carried out in the same way as that described for complex **1**, but Pr[N(TMS)₂]₃(μ-Cl)Li(THF)₃ (3.29 g, 3.74 mmol) was used instead of La[N(TMS)₂]₃(μ-Cl)Li(THF)₃. Colorless crystals were obtained from a concentrated THF/hexane solution (about 15 mL) at −5 °C over a few days (2.66 g, 81%). Mp: 241−243 °C. Anal. calcd for $C_{43}H_{76}N_3O_3Si_2Pr$: C, 58.68; H, 8.70; N, 4.77; Pr, 16.01. Found: C, 58.62; H, 8.63; N, 4.58; Pr, 15.86. IR (KBr, cm⁻¹): 2956(s), 2905(s), 2869(s), 1605(m), 1477 (s), 1441(s), 1413(s), 1361(s), 1301(s), 1237(s), 1201(m), 1165(m), 1133(m), 1019(w), 933(s), 882(s), 834(s), 741(m). The crystals suitable for an X-ray diffraction analysis were obtained from the concentrated hexane/THF solution.

Synthesis of [ONNO]Nd[N(TMS)₂](THF) (3). The synthesis of complex **3** was carried out in the same way as that described for complex **1**, but Nd[N(TMS)₂]₃(μ-Cl)Li(THF)₃ (2.59 g, 2.94 mmol) was used instead of La[N(TMS)₂]₃(μ-Cl)Li-(THF)₃. Blue microcrystals were obtained from a concentrated hexane/THF solution (about 10 mL) over a few days (2.17 g, 84%). Mp: 248−250 °C. Anal. calcd for $C_{43}H_{76}N_3O_3Si_2Nd$: C, 58.46; H, 8.67; N, 4.76; Nd, 16.33. Found: C, 58.40; H, 8.68; N, 4.52; Nd, 16.07. IR (KBr, cm⁻¹): 2957(s), 2906(s), 2869(s), 1606-(m), 1477(s), 1441(s), 1413(s), 1361(s), 1300(s), 1237(s), 1202(m), 1164(m), 1133(m), 879(s), 835(s). The crystals suitable for an X-ray diffraction analysis were obtained in the toluene solution at room temperature.

Synthesis of [ONNO]Sm[N(TMS)₂](THF) (4). The synthesis of complex **4** was carried out in the same way as that described for complex **1**, but Sm[N(TMS)₂]₃(μ-Cl)Li(THF)₃ (2.78 g, 3.12 mmol) was used instead of La[N(TMS)₂]₃(μ-Cl)Li(THF)₃. Colorless microcrystals were obtained from a concentrated hexane/THF solution over a few days (2.22 g, 80%). Mp: 225−227 °C. Anal. calcd for $C_{43}H_{76}N_3O_3Si_2Sm$: C, 58.05; H, 8.61; N, 4.72;

Sm, 16.90. Found: C, 58.11; H, 8.58; N, 4.55; Nd, 16.73. IR (KBr, cm⁻¹): 2958(s), 2906(s), 2870(s), 1606(m), 1477(s), 1441 (s), 1412(s), 1361(s), 1301(s), 1237(s), 1202(m), 1165(m), 1133 (m), 1025(w), 933(s), 881(s), 834(s). The crystals suitable for an X-ray diffraction analysis were obtained in the hexane/THF solution at room temperature.

Synthesis of [ONNO]Yb[N(TMS)₂](THF) (5). The synthesis of complex **5** was carried out in the same way as that described for complex **1**, but Yb[N(TMS)₂]₃(μ-Cl)Li(THF)₃ (1.40 g, 1.53 mmol) was used instead of La[N(TMS)₂]₃(μ-Cl)Li(THF)₃. Pale-yellow microcrystals (1.26 g, 90%) were isolated from a concentrated toluene solution. Mp: 217−219 °C. Anal. calcd for $C_{43}H_{76}N_3O_3Si_2Yb$: C, 56.61; H, 8.40; N, 4.61; Yb, 18.97. Found: C, 56.53; H, 8.38; N, 4.39; Yb, 18.64. IR (KBr, cm⁻¹): 2956(s), 2906(s), 2870(s), 1605(m), 1477(s), 1440(s), 1413(s), 1364(s), 1303(s), 1238(s), 1202(m), 1167(m), 1134(m), 1025(w), 933(s), 883(s), 834(s). The crystals suitable for an X-ray diffraction analysis were obtained in the toluene solution at room temperature.

Synthesis of [ONNO]Y[N(TMS)₂](THF) (6). The synthesis of complex **6** was carried out in the same way as that described for complex **1**, but Y[N(TMS)₂]₃(μ-Cl)Li(THF)₃ (1.94 g, 2.34 mmol) was used instead of La[N(TMS)₂]₃(μ-Cl)Li-(THF)₃. Colorless crystals were obtained from a concentrated hexane/THF solution (about 10 mL) after 1 day (1.51 g, 78%). Mp: 219−221 °C. Anal. calcd for $C_{43}H_{76}N_3O_3Si_2Y$: C, 62.36; H, 9.25; N, 5.07; Y, 10.74. Found: C, 62.18; H, 9.13; N, 4.94; Y, 10.61. ¹H NMR (300 MHz, C_6D_6): 7.44 (s, 2H, ArH), 6.80 (s, 2H, ArH), 4.29 (br, s, 4H, α-CH₂ THF), 4.23 (d, ^2J(H, H) = 14.1 Hz, 2H, ArCH₂), 3.61 (d, ^2J(H, H) = 7.5 Hz, 1H, NCH₂N imidazolidine ring), 3.54 (br, m, 2H, NCH₂CH₂N imidazolidine ring), 2.85 (d, ^2J(H, H) = 14.1 Hz, 2H, ArCH₂) 2.10 (d, ^2J(H, H) = 7.4 Hz, 1H, NCH₂N imidazolidine ring 1.90 (br, m, 2H, NCH₂CH₂N imidazolidine ring), 1.56 (s, 18H, C(CH₃)₃), 1.41 (s, 18H, C(CH₃)₃), 1.22 (br, s, 4H, β-CH₂ THF), 0.35(s, 18H, TMS). ¹³C{1H} NMR (300 MHz, C_6D_6): 121.76 (Ph), 160.58 (Ph), 136.68 (Ph), 123.88 (Ph), 137.18 (Ph), 124.32 (Ph), 71.25 (NCH₂N imidazolidine ring), 68.99 (α-CH₂ THF), 56.91 (N-(CH₂)₂N imidazolidine), 51.81 (CH₂Ar), 35.62 (C(CH₃)₃), 34.09 (C(CH₃)₃), 32.11 (C(CH₃)₃), 30.84 (C(CH₃)₃), 25.23 (β-CH₂ THF), 6.10 (TMS). IR (KBr, cm⁻¹): 2956 (s), 2904 (s), 2868 (s), 1606 (m), 1478 (s), 1441 (s), 1413 (s), 1361 (s), 1300 (s), 1238 (s), 1202 (m), 1165 (m), 1133 (m), 933 (m), 881 (s), 834 (s).

Method B. To a hexane solution of Y[N(TMS)₂]₃ (1.16 g, 2.03 mmol) was added a hot hexane solution of [ONNO]H₂ (20 mL, 1.03 g, 2.03 mmol). The mixture was stirred overnight at 50 °C. THF (2 mL) was added, and colorless microcrystals were obtained from a concentrated hexane/THF solution (about 15 mL) overnight at room temperature (1.28 g, 76%). ¹H NMR (300 MHz, C_6D_6): 7.46 (s, 2H, ArH), 6.82 (s, 2H, ArH), 4.31 (br, s, 4H, α-CH₂ THF), 4.22 (d, ^2J(H, H) = 14.0 Hz, 2H, ArCH₂), 3.63 (d, ^2J(H, H) = 7.5 Hz, 1H, NCH₂N imidazolidine ring), 3.55 (br, m, 2H, NCH₂CH₂N imidazolidine ring), 2.87 (d, ^2J(H, H) = 14.0 Hz, 2H, ArCH₂) 2.10 (d, ^2J(H, H) = 7.4 Hz, 1H, NCH₂N imidazolidine ring 1.91 (br, m, 2H, NCH₂CH₂N imidazolidine ring), 1.56 (s, 18H, C(CH₃)₃), 1.41 (s, 18H, C-(CH₃)₃), 1.24 (br, s, 4H, β-CH₂ THF), 0.35 (s, 18H, TMS).

Typical Procedure for the Polymerization Reaction. The procedures for the polymerization of L-lactide initiated by complexes **1−6** were similar, and a typical polymerization procedure is given here. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with the desired amount of L-lactide and toluene. The contents of the flask were then stirred at 70 °C until L-lactide was dissolved, and then a solution of the initiator in toluene was added to this solution using a syringe. The mixture was stirred vigorously at 70 °C for the desired time, during which an increase in the viscosity was observed. The reaction mixture was quenched by the addition of methanol and then poured into methanol to

Table 1. Crystallographic Data for Complexes **1**−**3**

compound	**1**	**2**	**3·toluene**
formula	$C_{43}H_{76}N_3$-O_3Si_2La	$C_{43}H_{76}N_3$-O_3Si_2Pr	$C_{50}H_{84}N_3$-O_3Si_2Nd
fw	878.16	880.16	975.62
T (K)	293(2)	223(2)	293(2)
cryst syst	monoclinic	monoclinic	monoclinic
cryst size (mm^3)	0.60 × 0.35 × 0.30	0.35 × 0.27 × 0.20	0.63 × 0.29 × 0.20
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	10.384(1)	10.3377(9)	14.906(2)
b (Å)	20.663(2)	20.537(2)	32.608(3)
c (Å)	22.752(3)	22.632(2)	12.321(2)
β (deg)	100.223(3)	100.196(2)	112.249(3)
V (Å^3)	4804.1(9)	4729.2(7)	5542.6(11)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.214	1.236	1.169
μ (mm^{-1})	0.976	1.118	1.018
$F(000)$	1856	1864	2068
θ_{max} (deg)	25.35	25.35	25.35
collected reflns	22563	45766	51669
unique reflns	8754	8647	10110
obsd reflns [$I > 2.0\sigma(I)$]	5679	7199	7848
no. of variables	480	478	520
GOF	1.110	1.153	1.152
R	0.0961	0.0639	0.0874
wR	0.2097	0.1159	0.1625
largest diff peak, hole (e Å^{-3})	1.025, −2.351	1.352, −0.845	0.797, −0.659

Table 2. Crystallographic Data for Complexes **4**−**6**

compound	**4**	**5·toluene**	**6**
formula	$C_{43}H_{76}N_3$-O_3Si_2Sm	$C_{50}H_{84}N_3$-O_3Si_2Yb	$C_{43}H_{76}N_3$-O_3Si_2Y
fw	889.60	1004.42	828.16
T (K)	223(2)	223(2)	293(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
cryst size (mm^3)	0.30 × 0.30 × 0.27	0.41 × 0.40 × 0.20	0.80 × 0.50 × 0.30
a (Å)	10.311(1)	14.509(2)	12.525(2)
b (Å)	20.498(2)	32.814(4)	10.578(1)
c (Å)	22.631(2)	12.059(2)	35.864(5)
β (deg)	100.160(2)	111.367(2)	90.665(4)
V (Å^3)	4707.8(8)	5346.5(11)	4751.2(10)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.255	1.248	1.158
μ (mm^{-1})	1.336	1.833	1.315
$F(000)$	1876	2108	1784
θ_{max} (deg)	25.35	25.34	25.35
collected reflns	39410	46446	22329
unique reflns	8481	9757	8665
obsd reflns [$I > 2.0\sigma(I)$]	7247	8374	5688
no. of variables	480	511	449
GOF	1.161	1.181	1.145
R	0.0453	0.0563	0.1034
wR	0.0896	0.1053	0.1846
largest diff peak, hole (e Å^{-3})	1.279, −0.753	1.609, −0.728	0.602, −0.661

precipitate the polymer, which was dried under a vacuum and weighed.

Oligomer for End Group Analysis. The oligomerization of L-lactide was carried out with complex **3** in toluene at 70 °C under the condition of a molar ratio of [monomer]/[initiator] of 5. The reaction was terminated by adding 1 mL of 5% HCl/MeOH after 0.5 h. The oligomer was precipitated from methanol. The product was dissolved in THF, followed by precipitation in methanol. After filtration, the white product was dried under vacuum conditions.

X-Ray Crystallography. Suitable single crystals of complexes **1**−**6** were sealed in a thin-walled glass capillary for determination of the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in the ω scan mode using Mo Kα radiation ($\lambda = 0.71070$ Å). 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 Tables 1 and 2.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of 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 the SHELEXL-97 programs.

Results and Discussion

Synthesis and Characterization of the Rare-Earth Metal Amides. Attempts to synthesize the imidazolidine-bridged bis(phenolate) rare-earth metal amido complexes in the absence of HMPA via a salt metathesis reaction were unsuccessful until now.[1m] Thus, the amine elimination reaction was used to synthesize these complexes.[3] The bis(trimethylsilyl)amido rare-earth metal complexes Ln[N(TMS)$_2$]$_3$(μ-Cl)Li(THF)$_3$ reacted with H$_2$[ONNO] in THF in a 1:1 molar ratio at 50 °C; after workup, the

desired neutral rare-earth metal amido complexes [ONNO]Ln[N(TMS)$_2$](THF) [Ln = La (**1**), Pr (**2**), Nd (**3**), Sm (**4**), Yb (**5**), Y (**6**)] were isolated from a concentrated hexane/THF or toluene solution as microcrystals in high yields (78−90%), as shown in Scheme 2. The compositions of complexes **1**−**6** were confirmed by elemental analysis and NMR spectroscopy in the case of complexes **1** and **6**, and their definitive molecular structures were determined by single-crystal structure analysis. Complexes **1**−**6** are extremely sensitive to air and moisture. The crystals decompose in a few minutes when they are exposed to air, but neither the crystals nor the solution showed any sign of decomposition after several months when stored under argon. All of the rare-earth metal amido complexes are freely soluble in THF and toluene and slightly soluble in hexane.

The outcome in our case is quite different from those of the protolytic ligand exchange reactions of Sm[N-(TMS)$_2$]$_3$ with the amine bis(phenols) H$_2$O$_2$NR [H$_2$O$_2$-NR = XCH$_2$CH$_2$N(2-HO-3,5-C$_6$H$_2$^{t}Bu$_2$)$_2$; X = OMe, NMe$_2$, or Me], which gave exclusively the zwitterions Sm(O$_2$NR)(HO$_2$NR).[1q] To exclude the effect of the starting materials, the reaction of Y[N(TMS)$_2$]$_3$ with the imidazolidine-bridged bis(phenols) was carried out. ^{1}H NMR revealed that the final product is complex **6**. The difference among these amine bis(phenolate) ligands is the structures of their bridges. These results reveal that the structure of the bridge has a profound influence on the reactivity of bridged bis(phenols) with the bis(trimethylsilyl)amido rare-earth metal complexes.

The definitive molecular structures of complexes **1**−**6** were determined by X-ray structure analysis. All of these complexes are isostructural and have a solvated monomeric structure crystallized in the monoclinic system. Only the ORTEP diagram of complex **1** is shown in Figure 1. Selected bond lengths and bond angles are provided in Table 3. Like those found in other amine or

Scheme 2
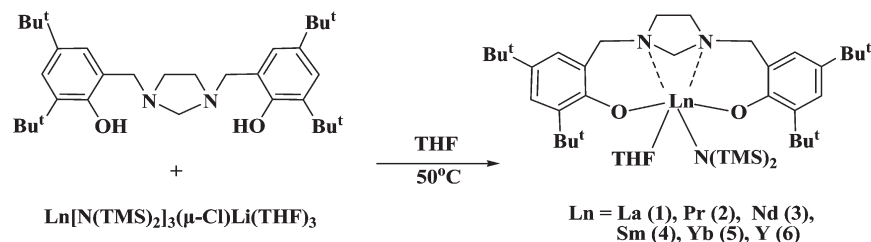
N-heterocycle bridged bis(phenolate) metal complexes,[9] two nitrogen atoms from the imidazolidine ring were found to bind to the metal center in the solid state. The central rare-earth metal atom is six-coordinated by two oxygen atoms, two nitrogen atoms from the bis(phenolate) ligands, one nitrogen atom from the amido group, and one oxygen atom from the THF molecule. The coordination geometry at the central metal can be best described as a distorted trigonal bipyramid if the imidazolidine ring is considered to occupy one coordination site, in which O1, O2, and N6 are considered to occupy the equatorial plane.

The average Ln−O(Ar) bond lengths range from 2.258(6) (for La) to 2.130(4) Å (for Yb, see Table 3), which reflected the usual lanthanide contraction from La^{3+} to Yb^{3+}.[10] Similar consequences of the decrease of the ionic radii of the Ln^{3+} ions from La^{3+} to Yb^{3+} are also observed from the Ln−O(THF) and the average Ln−N-(amine) bond lengths in these complexes. However, the influence of the lanthanide contraction on the bite angle of O1−Ln1−O2 is not obvious, and the corresponding bond angles are about 108°. The Ln−C14 bond lengths [2.954(9), 2.927(5), 2.889(7), 2.874(4), 2.771(6), and 2.852(6) Å in complexes **1**−**6**, respectively] are comparable with those observed in some neutral arene lanthanide complexes, such as $Pr(\eta^6\text{-}1,3\text{-}Me_2C_6H_4)(AlCl_4)_3$ [2.95(2) Å],[11] $Nd(\eta^6\text{-}C_6H_6)(AlCl_4)_3$ [2.93(2) Å],[12] $Sm(\eta^6\text{-}C_6Me_6)(AlCl_4)_3$ [2.89(5) Å],[13] and $Yb(\eta^6\text{-}C_6Me_6)(AlCl_4)_3$ [2.87(4) Å],[14] but are apparently larger than the values reported for related Ln−C(carbene) bonds in lanthanide carbene complexes, such as $NdL^1[N(SiMe_3)_2]_2$ ($L^1 = {}^tBuNCH_2CH_2[C\{{}^tBuN(CHCH)N\}]$) [2.609(3) Å],[15a] $SmL^1[(NSiMe_3)_2]_2$ [2.588(2) Å],[15b] $YL^1[N(SiMe_3)_2]_2$ [2.501(5) Å],[15b] and $[O\text{-}4,6\text{-di-}^tBu\text{-}C_6H_2\text{-}2\text{-}CH_2\text{-}[C\{RN(CHCH)N^iPr\}]_2YbN(^iPr)_2$ (R = ^iPr, Me) [2.535(7), 2.487(4) Å].[15c] The bond angles around C14 in complexes **1**−**6** are comparable with the corresponding bond angles in $\{[ONNO]Na_2(THF)_2\}_2$.[1m] Furthermore, ^{13}C NMR spectra revealed that the signals of C14 are singlet in complexes **1** and **6**, and the chemical shifts are similar to that of the free ligand. These results indicate

that there is an absence of agostic interaction of C14 with the rare-earth metal in these complexes.

The average Ln−O(Ar) bond lengths in complexes **1**−**6** (Table 3) are comparable with the corresponding bond lengths in bridged bis(phenolate) lanthanide complexes $[ONOO]La[N(SiMe_2H)_2](THF)$ $[ONOO = MeOCH_2CH_2N\{CH_2\text{-}(2\text{-}O\text{-}C_6H_2\text{-}^tBu_2\text{-}3,5)\}_2]$ [2.272(3) Å],[1c] $(MBMP)La(THF)(\mu\text{-}MBMP)_2La(THF)_2$ $[MBMP = 2,2'\text{-}CH_2\text{-}(1\text{-}O\text{-}C_6H_2\text{-}Me\text{-}4\text{-}^tBu\text{-}6)\}_2]$ [2.286(4) Å],[2e] $(MBMP)Nd[N(TMS)_2](THF)_2$ [2.200(2) Å], [Li(THF)_4][(MBMP)Nd\{N(TMS)_2\}_2] [2.195(3) Å],[2d] [ONNO]Yb(NPh_2)(HMPA) [2.127(4) Å],[1m] and $[ONOO]Y\text{-}[N(SiMe_2H)_2](THF)$ [2.154(2) Å][1b] but are slightly larger than that in $[Li(THF)_4][(MBMP)Yb\{N(TMS)_2\}_2]$ [2.087(3) Å],[2d] when the difference in ionic radii is considered. The Yb−N(ring) bond lengths of 2.499(4) and 2.507(4) Å are comparable with the corresponding values observed in [ONNO]Yb(NPh_2)(HMPA) [2.497(4) and 2.504(4) Å][1m] and other amine bridged bis(phenolate) lanthanide complexes.[1] The Ln−N(TMS)_2 bond lengths are also in accordance with those of the bis(phenolate) rare-earth metal amido complexes mentioned above, when the difference in ionic radii is considered.[1b−1e,2f]

Ring-Opening Polymerization of L-Lactide by Complexes 1−6. Biodegradable polymers have recently gained great attention as a replacement for conventional synthetic materials.[16] Among the biodegradable polymers that have been developed during the past few decades, poly(ε-caprolactone) and poly(lactide) (PLA) are of particular interest because of their biodegradable, biocompatible, and permeable properties.[17] The major method for the synthesis of these polymers is the ring-opening polymerization of lactones/lactides and functionally related compounds. Many kinds of structurally well-defined organometallic and coordination complexes have been reported to be efficient initiators for the ring-opening polymerization of lactones/lactides, and all of these systems give polymers with high molecular weights. To understand the effect of bis(phenolate) ligands on

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polymerization activity and controllability, the catalytic behavior of complexes **1**−**6** for the ring-opening polymerization of L-lactide was examined.
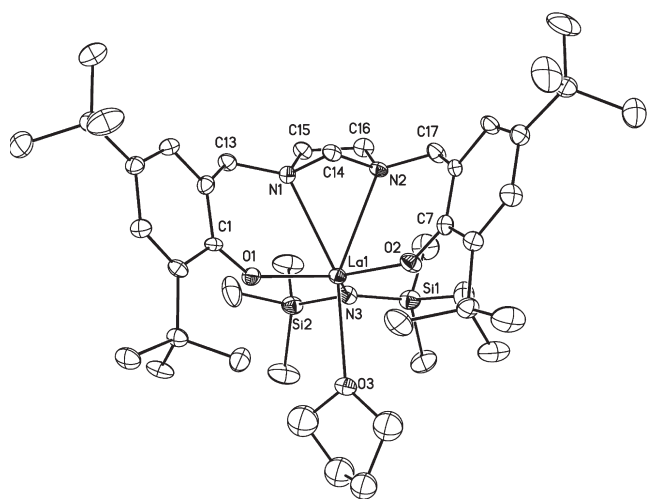
Figure 1. ORTEP diagram of complex **1** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms are omitted for clarity.

As expected, the imidazolidine-bridged bis(phenolato) rare-earth amido complexes without coordinated HMPA are efficient initiators for the ring-opening polymerization of L-lactide.[1m,2a] The representative L-lactide polymerization data are summarized in Table 4. It can be seen that all of these rare-earth amido complexes can initiate effectively L-lactide polymerization in toluene, giving the resultant polymers with high molecular weights and relatively broad molecular weight distributions (M_w/M_n = 1.34−1.89). These initiators showed high activity; even for $[M]_0/[1]_0$ = 700, the polymerization still can proceed in 70% yield in 2 h (entry 6) and produce a PLA with a molecular weight of 9.56×10^4 and a PDI of 1.65. The polymerization temperature could affect the polymerization. The higher the temperature was, the faster the polymerization proceeded. For instance, using complex **3** as the initiator, an almost complete yield could be reached at 70 °C at 30 min when the molar ratio of monomer to initiator ([M]/[I]) is 600 (entry 14), whereas the yield was 32% at 50 °C in 2 h (entry 13) under the same polymerization conditions. Therefore, all of the polymerization reactions in toluene were preferably conducted at 70 °C.

The ionic radii of the rare-earth metals have a significant effect on the catalytic activity for L-lactide polymerization.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg)

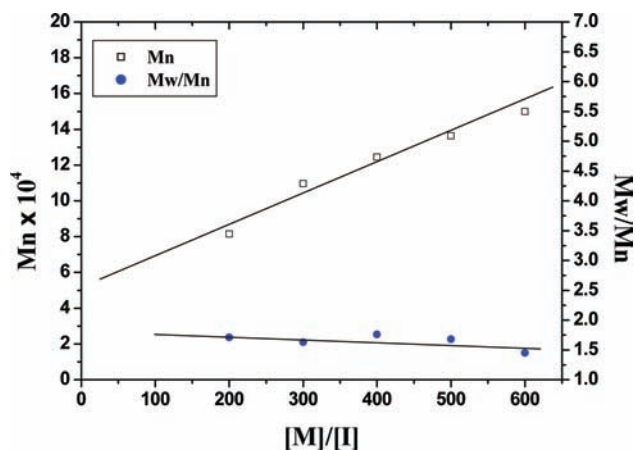|	**1**	**2**	**3**	**4**	**5**	**6**
Ln1−O1	2.268(6)	2.249(4)	2.226(5)	2.209(3)	2.135(4)	2.125(4)
Ln1−O2	2.248(6)	2.232(4)	2.232(5)	2.195(3)	2.125(4)	2.145(4)
Ln−O(av)	2.258(6)	2.240(5)	2.229(5)	2.202(3)	2.130(4)	2.135(4)
Ln1−O3	2.619(7)	2.575(4)	2.548(5)	2.521(3)	2.391(4)	2.429(5)
Ln1−N1	2.699(7)	2.664(4)	2.626(6)	2.620(3)	2.507(4)	2.549(5)
Ln1−N2	2.721(6)	2.657(4)	2.628(5)	2.608(3)	2.499(4)	2.542(5)
Ln1−N3	2.422(7)	2.391(4)	2.365(6)	2.354(3)	2.245(5)	2.305(5)
Ln1−C14	2.954(9)	2.927(5)	2.889(7)	2.874(4)	2.771(6)	2.852(6)
O1−Ln1−O2	109.8(2)	108.4(1)	111.1(2)	108.9(1)	108.4(2)	104.1(2)
O1−Ln1−N3	124.4(2)	124.9(2)	122.1(2)	124.5(1)	125.8(2)	116.6(2)
O2−Ln1−N3	125.6(3)	126.0(2)	125.8(2)	125.4(1)	123.2(2)	137.9(2)
N1−Ln1−O3	157.8(2)	156.4(1)	156.1(2)	155.8(1)	154.3(2)	162.4(2)
N2−Ln1−O3	154.4(2)	154.4(1)	154.3(2)	154.3(1)	154.1(2)	146.6(2)
C14−Ln1−O3	159.0(2)	158.8(2)	159.3(2)	158.9(1)	160.5(2)	157.5(2)

Table 4. Polymerization of L-Lactide Initiated by Complexes **1**−**6**[a]

entry	initiator	$[M]_0/[I]_0$	T (°C)	t	yield (%)[b]	M_c^c($\times 10^4$)	M_n^d ($\times 10^4$)	PDI[d]
1	**1**	200	70	30 min	98	2.82	8.15	1.71
2	**1**	300	70	30 min	97	4.19	10.96	1.63
3	**1**	400	70	30 min	97	5.59	12.45	1.76
4	**1**	500	70	30 min	95	6.84	13.64	1.68
5	**1**	600	70	30 min	98	8.47	14.99	1.45
6	**1**	700	70	2 h	70	7.06	9.56	1.65
7	**2**	600	70	30 min	96	8.29	15.42	1.58
8	**2**	700	70	2 h	46	4.64	6.75	1.76
9	**3**	200	50	5 min	92	2.65	11.71	1.64
10[e]	**3**	200	50	5 min	60	1.73	3.88	1.46
11[e]	**3**	200	50	80 min	89	2.56	5.95	1.53
12	**3**	300	70	30 min	100	4.32	9.72	1.63
13	**3**	600	50	2 h	32	2.76	6.57	1.52
14	**3**	600	70	30 min	96	8.29	15.69	1.58
15	**3**	700	70	2 h	42	4.23	6.99	1.69
16	**4**	400	70	30 min	89	5.13	7.51	1.57
17	**4**	600	70	30 min	68	5.88	9.88	1.34
18	**5**	200	70	30 min	96	2.76	13.68	1.69
19	**5**	400	70	1 h	40	2.30	5.23	1.63
20	**6**	200	70	30 min	95	2.74	13.01	1.64
21	**6**	400	70	1 h	60	3.46	10.94	1.89

[a] General polymerization conditions: toluene as the solvent, [L-LA] = 1 mol/L. [b] Yield: weight of polymer obtained/weight of monomer used. [c] M_c = (144.13) × $[M]_0/[I]_0$ × (polymer yield) (%). [d] Measured by GPC calibrated with standard polystyrene samples. [e] In THF.

Figure 2. Polymerization of L-lactide initiated by complex **1** in toluene at 70 °C. Relationship between the number-averaged molecular weight (M_n) and the molar ratio of monomer to initiator.

Upon a decrease of the ionic radii, the catalytic activity apparently decreased. Using lanthanum complex **1** as the initiator, the yield was 98% when the molar ratio of monomer to initiator wass 600 at 30 min (entry 5), whereas it was 40% using ytterbium complex **5** for the polymerization at 1 h, even when the molar ratio of monomer to initiator decreased to 400 under the same polymerization temperature (entry 19). The observed activity decreasing order, La > Pr > Nd > Sm > Y > Yb, is in agreement with the order of ionic radii, which is consistent with the active trend observed in the methylene-linked bis(phenolate) lanthanide systems for the polymerization of ε-caprolactone[2b−2d] and the bis(allyl) diketiminatolanthanide complexes for lactide polymerization.[18] This may be attributed to the larger ionic radii resulting in a greater opening of the metal coordination sphere in the vicinity of the σ ligand, which makes the insertion of L-lactide into Ln−N bonds easier. In comparison with the alkoxy-amino-bis(phenolate) rare-earth metal amido complexes,[1j] complexes **1−6** are less active. The alkoxy-amino-bis(phenolate) yttrium amide can initiate the complete polymerization of L-lactide when the molar ratio of monomer to initiator is as high as 500 within 1 h. However, the yield was 60% using the imidazolidine-bridged bis(phenolate) yttrium amide (**6**) as the initiator at 70 °C over 1 h, even when the molar ratio of monomer to initiator ([M]/[I]) decreased to 400 (entry 21). These results reveal that the structure of the bridge of the bis(phenolate) group has a significant effect on the catalytic activity of the corresponding rare-earth metal amido complexes for L-lactide polymerization.

The polymerization medium played an important role in influencing the catalytic activity and the molecular weight of the resultant polymers. The complexes show higher activity in toluene than in THF. When complex **3** was used as the initiator, the polymerization yield in toluene at 50 °C reached 92% in less than 5 min and gave a polymer with a high molecular weight when the $[M]_0/[I]_0$ was 200 (entry 9), whereas the yield of the polymer is 60% in THF under the same polymerization conditions and has an apparently low molecular weight (entry 10). The

solvent effect in our case is in contrast to those observed in the dithiaalkanediyl-bridged bis(phenolate)[3b] and the alkoxy-amino bridged bis(phenolate) rare-earth metal amido systems.[1j]

As shown in Figure 2, the molecular weight of the resultant polymers increased linearly with the increase of the ratio of monomer to initiator using complex **1** as the initiator. However, the molecular weight distributions were relatively broad, which indicates that the polymerization is not well-controlled. Normally, the broader molecular weight distribution may mainly contribute to the transesterification reaction during the polymerization process or to the relatively slow initiation.[19] To obtain some insights into the initiation mechanism, we intend to observe the end group of the lactide oligomers formed by complex **3** at $[LA]_0/[Nd]_0 = 5$. However, the attempts were unsuccessful, and no obvious signals for N(TMS)$_2$ were observed, which is consistent with those initiated by other rare-earth metal amido complexes.[1c,20]

Ring-Opening Polymerization of L-Lactide in the Presence of 2-Propanol. Generally, the polymerization initiated by rare-earth metal amides was not well-controlled, giving a broadly distributed polymer, because the silylamide group is less nucleophilic than alkoxide, which caused a relatively slow initiation.[3c] To understand the difference between the initiation by the amide and the alkoxide groups in our system, the L-lactide polymerization was conducted with complexes **1−6** in the presence of 2-propanol. The NMR tube reactions of complex **6** with isopropanol in 1:1, 1:2, and 1:3 ratios afforded nearly the same signal pattern, along with the release of free amine HN(TMS)$_2$ ($\delta = 0.091$ ppm), indicating the formation of the expected bis(phenolate) rare-earth metal alkoxides. Furthermore, the multiplets for methine protons of the O^{i}Pr group at 4.64 ppm (1:1) shifted to 4.26 ppm (1:2) and 4.05 ppm (1:3) and were broadened, which can be attributed to an exchange process of the isopropyl group with free isopropanol.[3b] Similar to the polymerization of lactide initiated by the in situ generated rare-earth metal alkoxides in the literature,[1i−1k,3] the polymerizations of L-lactide initiated by complexes **1−6**/2-propanol are well-controlled, and the results are provided in Table 5. It can be seen that the polymerizations of L-lactide with complexes **1−6** in the presence of 1 equiv of 2-propanol gave the polymers with narrow molecular weight distributions ($M_w/M_n = 1.26−1.39$). Meanwhile, the number-average molecular weights of the resultant PLAs decreased significantly, and in most cases, the measured molecular weights of M_n are close to the calculated ones of M_c, which indicate that the polymerization is controlled. To further elucidate the controlled character of the polymerization, the relationship between the number-average molecular weight (M_n) and the molar ratio of monomer to initiator ($[M]_0/[I]_0$) was measured in toluene at 70 °C, initiated by complex **4** in the presence of 1 equiv of 2-propanol, as depicted in Figure 3. When the monomer/initiator ratio was increased, the molecular weight of the resultant polymer

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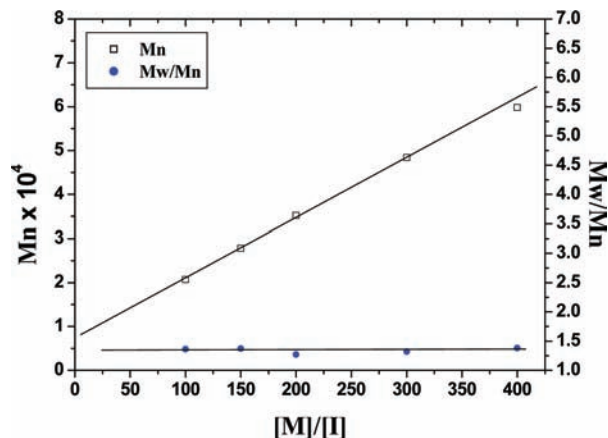
Table 5. Polymerization of L-Lactide Initiated by Complexes **1**−**6** in the Presence of 2-Propanol[a]

entry	initiator	$[M]_0/[I]_0/[^iPrOH]$	t	yield (%)[b]	M_c[c] (× 10^4)	M_n[d] (× 10^4)	PDI[d]
1	**1**	300/1/1	2 h	95	4.10	5.59	1.28
2	**1**	400/1/1	2 h	96	5.53	6.54	1.39
3	**1**	500/1/1	2 h	94	6.77	7.62	1.35
4	**1**	600/1/1	2 h	94	8.12	8.46	1.37
5	**1**	700/1/1	4 h	75	7.56	7.62	1.34
6	**2**	400/1/1	2 h	96	5.53	7.02	1.32
7	**2**	600/1/1	2 h	91	7.86	8.62	1.36
8	**3**	300/1/1	30 min	100	4.32	6.14	1.35
9	**3**	400/1/1	30 min	75	4.32	4.46	1.34
10	**3**	400/1/1	2 h	100	5.76	6.70	1.27
11	**3**	600/1/1	30 min	46	3.97	4.26	1.38
12	**3**	600/1/1	2 h	92	7.95	8.56	1.33
13	**4**	100/1/1	30 min	92	1.32	2.07	1.36
14	**4**	150/1/1	30 min	95	2.05	2.78	1.37
15	**4**	200/1/1	30 min	94	2.71	3.52	1.27
16	**4**	300/1/1	2 h	98	4.23	4.84	1.32
17	**4**	400/1/1	2 h	93	5.36	5.93	1.38
18	**5**	200/1/1	30 min	42	1.21	1.72	1.26
19	**5**	200/1/1	2 h	94	2.71	3.92	1.37
20	**5**	300/1/1	2 h	32	1.38	1.98	1.30
21	**6**	200/1/1	30 min	72	2.07	2.87	1.36
22	**6**	200/1/1	1 h	92	2.65	4.12	1.39
23	**6**	300/1/1	2 h	99	4.27	5.29	1.37
24	**6**	400/1/1	1 h	76	4.38	5.74	1.38
25	**6**	400/1/1	2 h	96	7.61	5.53	1.34
26	**6**	400/1/2	30 min	92	4.32	2.65	1.28
27	**6**	400/1/3	30 min	94	3.87	2.38	1.16
28	**6**	500/1/1	1 h	62	6.00	4.46	1.36
29	**6**	500/1/2	30 min	94	4.87	3.38	1.29
30[e]	**6**	500/1/1	20 min	91	6.55	7.04	1.44

[a] General polymerization conditions: toluene as the solvent, [L-LA] = 1 mol/L, Tp = 70 °C. [b] Yield: weight of polymer obtained/weight of monomer used. [c] M_c = (144.13) × $[M]_0/[I]_0/[^iPrOH]$ × (polymer yield) (%). [d] Measured by GPC calibrated with standard polystyrene samples. [e] Polymerization in the presence of 0.1 mL THF.

increased linearly, while molecular weight distributions were kept almost unchanged, indicating obviously that the polymerization process is a controllable/controlled one.

The polymerization of L-lactide in the presence of 2-propanol is slower. For example, using the amido complex **3** as the initiator, the polymerization proceeded almost completely in 30 min when the molar ratio of monomer to initiator was 600 (Table 4, entry 14). However, the yield was 46% when initiated by complex **3**/2-propanol under the same polymerization conditions (Table 5, entry 11), and the yield can reach 92% after 2 h (Table 5, entry 12). A similar phenomenon was also observed by Okuda et al. in the dithiaalkanediyl-bridged bis(phenolate) rare-earth metal amide systems, and it was attributed to the rare-earth metal alkoxides generated in situ having dimeric structures via the bridging alkoxo groups. Also, the cleavage of the dimeric structure by the monomer is slow.[3b] For our cases, the formation of the dimeric rare-earth metal alkoxo species is also possible, because we recently found that the lanthanide amides stabilized by a methylene-bridged bis(phenolate) group have monomeric structures, whereas the corresponding lanthanide alkoxides have dimeric structures.[2b−2d] Further experiments revealed that the polymerization is apparently faster in the presence of 2 or 3 equiv of 2-propanol (Table 5, entries 24−29). The yield is 76% initiated by complex **6**/2-propanol (1:1) over 1 h when the molar ratio of monomer to initiator is 400 (Table 5, entry 24), whereas the yields are over 90% over 30 min as the amount of 2-propanol increases under the same
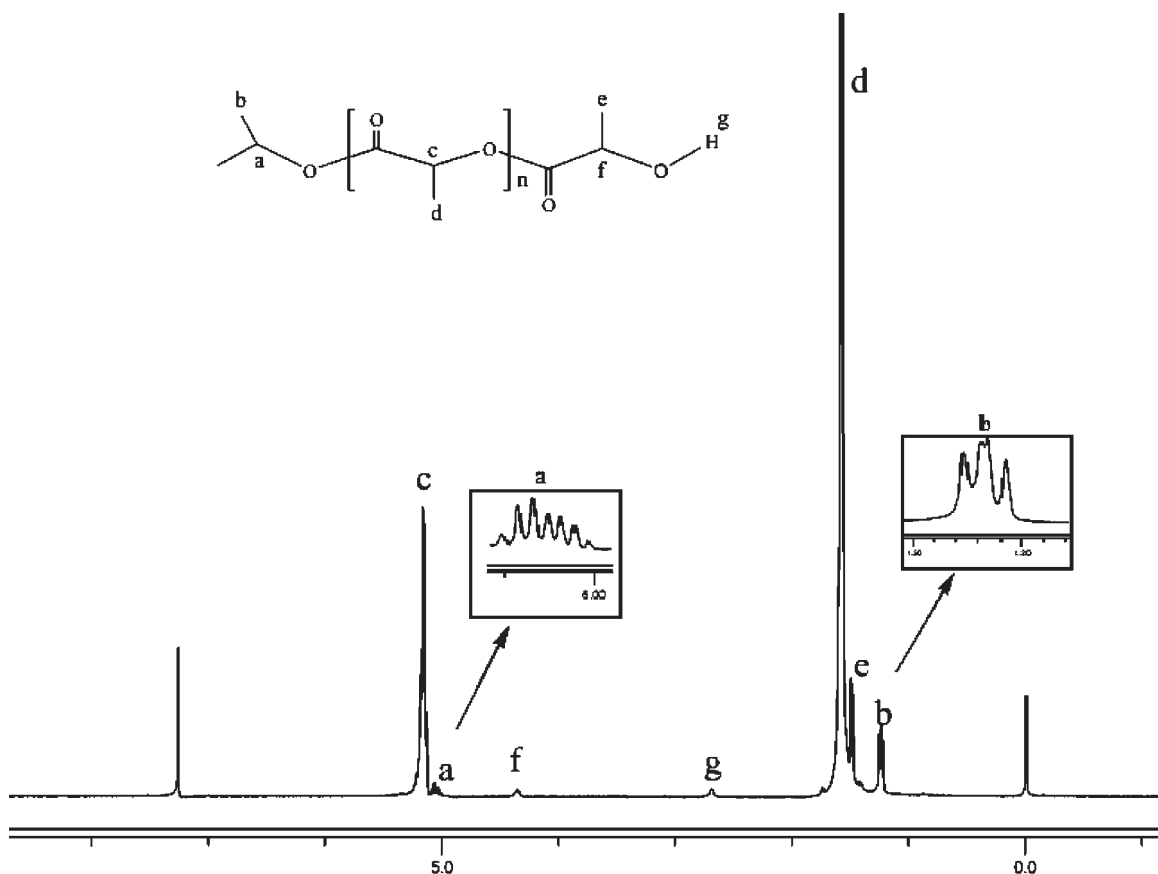

Figure 3. Polymerization of L-lactide initiated by complex **4** in the presence of 1 equiv of 2-propanol in toluene at 70 °C. Relationship between the number-averaged molecular weight (M_n) and the molar ratio of monomer to initiator.

polymerization conditions (Table 5, entries 26 and 27). Moreover, the polymerization of L-lactide is also faster in the presence of a small amount of THF initiated by complex **6**/2-propanol (1:1) (Table 5, entry 30). These results imply that the imidazolidine-bridged bis(phenolate) rare-earth metal alkoxides generated in situ have dimeric structures, and the coordination of excessive 2-propanol or THF can cleave the dimeric structures to produce the monomeric species.
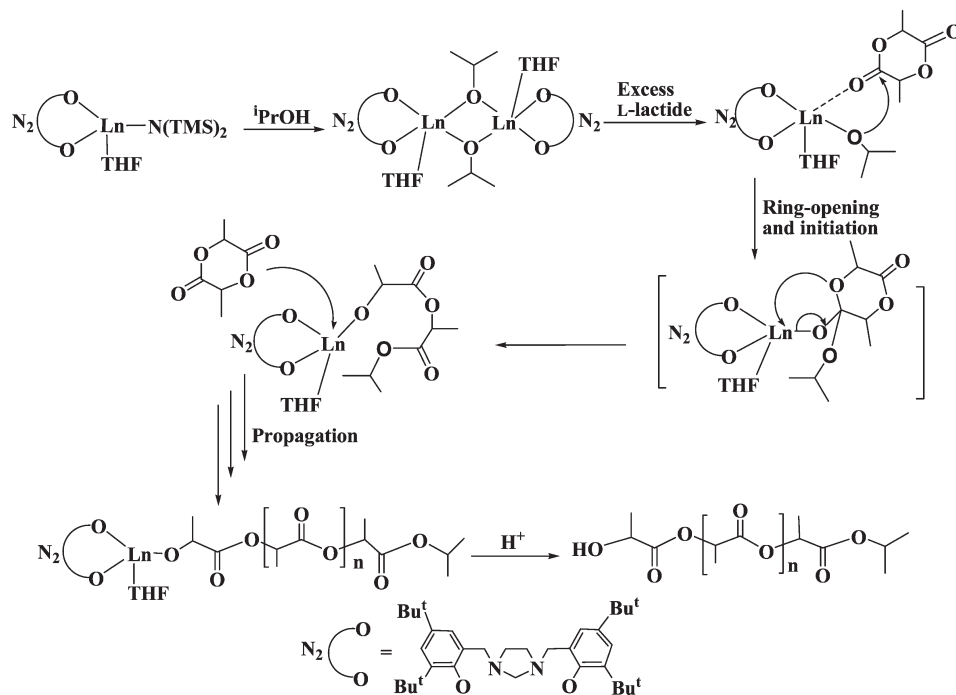
The initiation mechanism was elucidated by end-group analysis of the oligomer of L-lactide, which was

Figure 4. ^{1}H NMR spectrum of the oligomer of L-lactide initiated by the complex **3**/2-propanol system in CDCl$_3$.

Scheme 3

synthesized by the reaction of complex **3** with L-lactide in a 1:5 molar ratio. End-group analysis by ^{1}H NMR spectroscopy showed clearly the existence of an isopropoxo group and a HOCH(CH$_3$)CO— group according to the resonances at about 1.23 and 5.04 ppm for the former

and 1.48, 2.68, and 4.35 ppm for the latter, as shown in Figure 4.[3b,21] Obviously, the isopropoxo group existing in the oligomer must come from 2-propanol. Meanwhile, no

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aromatic proton resonances were observed from the ^{1}H NMR spectrum of the oligomer, which revealed that the bis(phenolate) group was not involved in the polymerization process. Moreover, the signals of the HN (TMS)$_2$ group were also not observed in the ^{1}H NMR spectrum, suggesting that the free silylamine did not further exchange with the alkoxide group. Thus, the polymerization proceeds by a common "coordination–insertion" mechanism, as shown in Scheme 3. The bridged bis(phenolate) rare-earth metal amide reacts with 2-propanol to generate in situ the corresponding alkoxide, which may exist as a dimer. Then, L-lactide is coordinated to the metal center and cleaves the dimeric structure to produce the monomeric species. A sequential nucleophilic attack on the carbonyl carbon of the coordinated lactide by the isopropoxo group forms a new metal–alkoxo group. The propagation step is the continued monomer coordination and insertion into the active metal–alkoxo bond.

Conclusion

In summary, a series of neutral imidazolidine-bridged bis(phenolate) rare-earth metal amido complexes without coordinated HMPA were successfully synthesized via an amine elimination reaction, and their structure features have been determined by an X-ray diffraction study. These complexes represent the first structurally characterized examples of bridged bis(phenolate) rare-earth metal amido complexes, which were synthesized via an amine elimination reaction using the common bulky bis(trimethylsilyl)amido rare-earth metal complexes as the precursors. These results reveal that the structure of the bridged bis(phenols) has a profound influence on the outcome of this kind of amine elimination reaction. The imidazolidine-bridged bis(phenolate) rare-earth metal amido complexes were found to be efficient initiators for the ring-opening polymerization of L-lactide, and the observed activity increasing order is in agreement with the order of ionic radii. Moreover, these amido complexes can initiate the controlled polymerization of L-lactide in the presence of 2-propanol. These results indicated that the imidazolidine-bridged bis(phenolate) ligands might have great potential in the design and synthesis of rare-earth metal catalysts for homogeneous catalysis. Further studies are in process in our laboratory.

Supporting Information Available: Crystallographic data for complexes **1**−**6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.