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Synthesis and Characterization of Lanthanide Amides Bearing Aminophenoxy Ligands and Their Catalytic Activity for the Polymerization of Lactides

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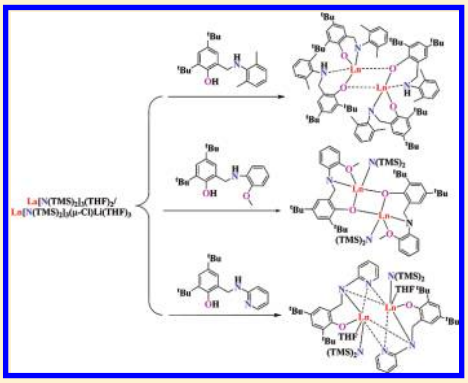
Supporting Information

ABSTRACT: A series of neutral lanthanide complexes supported by aminophenoxy ligands were synthesized, and their catalytic behavior in the polymerization of L-lactide and *rac*-lactide was explored. The amine elimination reactions of equimolar amounts of $Ln[N(TMS)_2]_3(\mu\text{-}Cl)Li(THF)_3$ and aminophenol [HONH]^1 {[HONH]^1 = 2,6-Me_2-$C_6H_4NHCH_2$(3,5-^{t}Bu$_2$-C_6H_2-2-OH)} in toluene gave the dimeric lanthanide complexes {[ON]^{1}Ln[ONH]^1}$_2$ (Ln = La (**1**), Nd (**2**)), whereas the similar reactions of $La[N(TMS)_2]_3(THF)_2$ or $Ln[N(TMS)_2]_3(\mu\text{-}Cl)Li(THF)_3$ (Ln = Nd, Sm) with the aminophenols [HONH]^2 {[HONH]^2 = (*o*-OCH_3-C_6H_4)$NHCH_2$(3,5-^{t}Bu$_2$-C_6H_2-2-OH} and [HONH]^3 {[HONH]^3 = (NC_5H_4)$NHCH_2$(3,5-^{t}Bu$_2$-C_6H_2-2-OH)} generated the neutral aminophenoxy lanthanide amides {[ON]^{2}Ln[N(TMS)$_2$]}$_2$ [Ln = La (**3**), Nd (**4**), Sm (**5**)] and {[ON]^{3}Ln[N(TMS)$_2$](THF)}$_2$ [Ln = La (**6**), Nd (**7**), Sm (**8**)], respectively, in high isolated yields. These complexes have been fully characterized. X-ray structural determination revealed that complexes **1** and **2** have unsolvated centrosymmetric dimeric structures, in which one hydrogen atom belonging to the amino group of the ligand is reserved. Complexes **3**−**5** are isostructural and have an unsolvated dimeric structure. The coordination geometry around each of the lanthanide metal atoms can be described as a distorted trigonal bipyramid. Complexes **6** and **7** have a solvated dimeric structure, and the lanthanide metal centers have distorted capped trigonal-prismatic geometries. It was found that complexes **3**−**8** are highly efficient initiators for the ring-opening polymerization of L-lactide and *rac*-lactide, affording polymers with high molecular weights.



INTRODUCTION

Throughout the past decade, significant effort has been invested in the development of alternative ligands to replace the traditional set of bis(cyclopentadienyl) ancillary ligands often used in organolanthanide chemistry,[1] because the reactivity of organolanthanide metal complexes depends mainly on the coordination environment around the metal centers. Lanthanide metals are considered to be hard acids and have an oxophilic nature, which leads to a preference for hard oxygen- or nitrogen-based ligands. On the other hand, it has been demonstrated that bridged dianionic ligands are efficient ancillary ligands for the stabilization of single-site catalysts based on trivalent lanthanide metals. Thus, the utilization of bridged bis(phenolato) and bis(amido) ligands in the design of organolanthanide metal catalysts has attracted significant attention, and some of these lanthanide metal complexes have shown high levels of activity in polymerization reactions and organic transformations.[2,3]

The aminophenoxy group is a type of dianionic N,O-chelate ligand, which combines the properties of oxygen- and nitrogen-based ligands. Aminophenol pro-ligands can be easily accessed by the reduction of the corresponding Schiff bases, which can be prepared from inexpensive and readily available starting materials. These ligand systems have been utilized in main group and transition-metal coordination chemistry, and some of these metal complexes show good activity in homogeneous catalysis.[4] The utilization of such ligands in organolanthanide chemistry, however, has not been studied to any significant degree.[5] Furthermore, most of the reported aminophenoxy lanthanide metal complexes are isolated as unexpected products from the reactions of organolanthanide complexes with Schiff bases and not from aminophenols.[5] Recently, we reported the first examples of lanthanide metal amides bearing dianionic aminophenoxy ligands synthesized from aminophenol starting materials and found that these aminophenoxy lanthanide metal complexes could initiate the ring-opening polymerization of lactide.[6] These results indicated that the dianionic N,O-chelate ligands have great potential for the design and synthesis of organolanthanide metal catalysts for homogeneous catalysis.

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However, the aminophenoxy lanthanide amide complexes obtained were anionic species $[ON]_2Ln[N(TMS)_2][Li(THF)]_2$ {$[ON]^{2-}$ = $[p\text{-}CH_3C_6H_4NCH_2(3,5\text{-}{}^tBu_2C_6H_2\text{-}2\text{-}O)]^{2-}$}, in which two aminophenoxy groups and one amido group were found to be coordinated to the central metal. The crowded coordination environments around the lanthanide metals could potentially decrease their catalytic activity because steric hindrance can have a significant impact on the catalytic activity of lanthanide complexes. Thus, we synthesized neutral aminophenoxy lanthanide amides to improve their catalytic performance. In this paper, three aminophenoxy ligands (Figure 1) were introduced to organolanthanide chemistry,

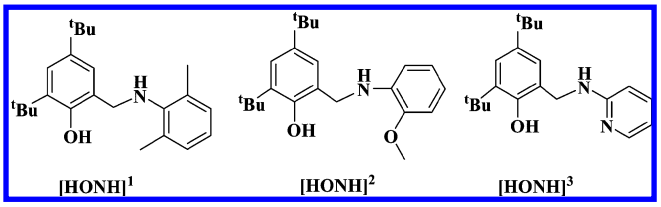

Figure 1. Aminophenoxy ligands.

and a series of aminophenoxy lanthanide complexes were synthesized and subsequently characterized. As anticipated, the neutral organolanthanide amido complexes showed high activity in the ring-opening polymerization of L-lactide and *rac*-lactide.

EXPERIMENTAL SECTION

General Procedures. The complexes described below are sensitive to air and moisture. Therefore, all manipulations were performed under pure argon with rigorous exclusion of air and moisture using Schlenk techniques. Solvents were dried and freed of oxygen by refluxing over sodium/benzophenone ketyl and distilled prior to use. $HN(TMS)_2$, L-lactide, *rac*-lactide, and ^{n}BuLi are commercially available. $HN(TMS)_2$ was dried over CaH_2 for 3 days and distilled before use. Aminophenol $[HONH]^1$ {$[HONH]^1$ = (2,6-$Me_2C_6H_4$)$NHCH_2$(3,5-^{t}Bu$_2$-C_6H_2-2-OH)},[7] $La[N(TMS)_2]_3(THF)_2$,[8] and $Ln[N(TMS)_2]_3(\mu\text{-Cl})Li(THF)_3$ (Ln = La, Nd, Sm)[9] were prepared according to the literature. Rare-earth metal analyses were performed by ethylenediaminetetraacetic acid titration with a xylenol orange indicator and a hexamine buffer.[10] 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 ^{1}H and ^{13}C NMR spectra were recorded in a d_8-THF/C_6D_6 solution for complexes **1**, **3**, **5**, **6**, and **8** with a Unity Varian spectrometer. Because of their paramagnetism, no resolvable NMR spectrum for the neodymium complexes 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 standard by gel permeation chromatography (GPC) on a PL 50 apparatus, and THF was used as an eluent at a flow rate of 1.0 mL/min at 40 °C.

Synthesis of (o-$OCH_3C_6H_4$)$NHCH_2$(3,5-^{t}Bu$_2$-C_6H_2-2-OH) {[HONH]^2}. *o*-Anisidine (11.3 mL, 100 mmol) was added under vigorous stirring to a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (23.4 g, 100 mmol) in refluxing absolute ethanol (250 mL), which was allowed to react for 48 h. The crystalline orange solid was filtered and washed with cold absolute ethanol. The precipitate (28.9 g, 85 mmol) was added under vigorous stirring to a suspension of $NaBH_4$ (4.0 g, 100 mmol) in ethanol (200 mL). The reaction mixture was stirred for 12 h, resulting in a white suspension, and then the solvent was completely removed under reduced pressure. The solid residue was extracted into $CHCl_3$. The organic layer was dried with Na_2SO_4 and filtered. After removal of the solvent under reduced pressure, the residue was crystallized in hexane, and a solid was isolated (23.9 g, 70%). Anal. Calcd for $C_{22}H_{31}NO_2$: C, 77.38; H, 9.15; N, 4.10. Found: C, 77.53; H, 9.32; N, 3.86. ^{1}H NMR (400 MHz, $CDCl_3$): 8.67 (s, 1H, Ph-OH), 7.32 (s, 1H, Ph), 7.04 (s, 1H, Ph), 6.98−6.78 (m, 4H, Ph), 4.53 (s, 1H, NH), 4.37 (s, 2H, CH_2), 3.84 (s, 3H, Me), 1.45 (s, 9H, ^{t}Bu), 1.33 (s, 9H, ^{t}Bu). ^{13}C NMR (100 MHz, $CDCl_3$): 157.00(Ph), 152.87(Ph), 145.59(Ph), 141.41(Ph), 138.17(Ph), 137.91(Ph), 126.62(Ph), 125.48(Ph), 123.84(Ph), 112.69(Ph), 110.23(CH_2), 42.55(OMe), 35.37($C(CH_3)_3$), 34.32($C(CH_3)_3$), 31.83($C(CH_3)_3$), 29.93($C(CH_3)_3$).

Synthesis of (NC_5H_4)$NHCH_2$(3,5-^{t}Bu$_2$-C_6H_2-2-OH) {[HONH]^3}. A procedure similar to that described for $[HONH]^2$ was used, but with 2-pyridinamine (9.4 g, 100 mmol) instead of *o*-anisidine. A solid was isolated (20.3 g, 65%). Anal. Calcd for $C_{20}H_{28}N_2O$: C, 76.89; H, 9.03; N, 8.96. Found: C, 76.61; H, 8.89; N, 8.75. ^{1}H NMR (400 MHz, $CDCl_3$): 11.76 (s, 1H, Ph-OH), 8.06 (d, J = 5.1 Hz, 1H, Ph), 7.40−7.32 (m, 1H, Ph), 7.29 (d, J = 2.4 Hz, 1H, Ph), 7.09 (d, J = 2.4 Hz, 1H, Ph), 6.59−6.52 (m, 1H, Ph), 6.41 (d, J = 8.5 Hz, 1H), 5.09 (s, 1H, NH), 4.46 (d, J = 6.6 Hz, 2H, CH_2), 1.45 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 157.31(Ph), 153.19(Ph), 145.91(Ph), 141.73(Ph), 138.49(Ph), 138.22(Ph), 137.51(Ph), 126.93(Ph), 125.80(Ph), 124.16(Ph), 113.01(Ph), 110.55(CH_2), 35.68($C(CH_3)_3$), 34.64($C(CH_3)_3$), 32.14($C(CH_3)_3$), 30.25($C(CH_3)_3$).

Synthesis of {[ON]^{1}La[ONH]^1]}$_2$ (1). To a stirred toluene solution of $La[N(TMS)_2]_3(\mu\text{-Cl})Li(THF)_3$ (20 mL, 1.76 g, 2.00 mmol) was added a toluene solution of $[HONH]^1$ (20 mL, 0.68 g, 2.00 mmol). The mixture was stirred for 2 h at 90 °C, and then the precipitate formed (LiCl) was separated by centrifugation. Toluene was evaporated to about 15 mL under reduced pressure. Colorless block microcrystals were obtained from a concentrated toluene solution in a few days (1.39 g, 85%). Mp: 315−317 °C. Anal. Calcd for $C_{92}H_{126}N_4La_2O_4$: C, 67.80; H, 7.79; N, 3.44; La, 17.04. Found: C, 67.58; H, 7.83; N, 3.69; La, 17.31. ^{1}H NMR for **1**·2toluene (400 MHz, d_8-THF+C_6D_6): 7.38−7.27 (m, 4H, Ph−CH_3), 7.22−7.11 (m, 8H, Ph), 6.87−7.03 (m, 6H, Ph−CH_3), 6.64−6.84 (m, 6.3 Hz, 8H, Ph), 6.34−6.52 (m, 4H, Ph), 4.21 (s, 4H, CH_2), 3.99 (d, J = 25.4 Hz, 4H, CH_2), 3.76 (s, 2H, NH), 2.31 (s, 6H, CH_3−Ph), 2.14−1.96 (m, 24H, Me), 1.46 (s, 36H, ^{t}Bu), 1.17−1.08 (s, 36H, ^{t}Bu). ^{13}C{^{1}H} NMR (100 MHz, d_8-THF+C_6D_6): 163.37(Ph), 147.24(Ph), 145.74(Ph), 137.53(Ph), 135.94(Ph), 135.78(Ph), 131.04(Ph), 129.51(Ph), 129.32(Ph), 128.55(Ph), 126.90(Ph), 125.68(Ph), 125.00(Ph), 124.64(Ph), 123.91(Ph), 123.72(Ph), 57.11(CH_2Ar), 55.47(CH_2Ar), 35.68($C(CH_3)_3$), 34.13($C(CH_3)_3$), 32.01($C(CH_3)_3$), 30.58($C(CH_3)_3$), 23.08(CH_3), 21.38(CH_3), 18.92(CH_3), 14.32(CH_3). IR (KBr, cm^{-1}): 3036(s), 2881(s), 2375(s), 1816(s), 1639(m), 1685(m), 1457(s), 1389(s), 1249(s), 998(s), 844(m), 748(m), 601(w), 532(s).

Synthesis of {[ON]^{1}Nd[ONH]^1]}$_2$ (2). The synthesis of complex **2** was carried out in the same way as that described for complex **1**, but $Nd[N(TMS)_2]_3(\mu\text{-Cl})Li(THF)_3$ (1.77 g, 2.00 mmol) was used instead of $La[N(TMS)_2]_3(\mu\text{-Cl})Li(THF)_3$. Blue crystals were obtained at room temperature in several days (1.25 g, 76%). Mp: 279−281 °C. Anal. Calcd for $C_{92}H_{126}N_4Nd_2O_4$: C, 67.36; H, 7.74; N, 3.41; Nd, 17.58. Found: C, 67.77; H, 7.84; N, 3.07; Nd, 17.81. IR (KBr, cm^{-1}): 3063(s), 2858(s), 2446(s), 2350(s), 1635(s), 1492(m), 1442(m), 1238(s), 1130(w), 1083(s), 1000(m), 836(s), 709(w), 597(s), 532(s).

Synthesis of {[ON]^{2}La[N(TMS)$_2$]}$_2$ (3). To a stirred toluene solution of $La[N(TMS)_2]_3(THF)_2$ (20 mL, 1.53 g, 2.00 mmol) was added a toluene solution of $[HONH]^2$ (20 mL, 0.68 g, 2.00 mmol). The mixture was stirred for 2 h at 90 °C, and then the toluene solution was concentrated to about 30 mL under reduced pressure. Colorless crystals were obtained at room temperature in several days (2.63 g, 90%). Mp: 274−276 °C. Anal. Calcd for $C_{56}H_{94}La_2N_4O_4Si_4$: C, 52.65; H, 7.42; N, 4.38; La, 21.75. Found: C, 52.51; H, 7.58; N, 3.98; La, 21.46. ^{1}H NMR for **3**·2toluene (400 MHz, d_8-THF): 7.05−7.20 (m, 4H, Ar-CH_3), 7.02−7.04 (m, 8H, Ar), 6.63−6.76 (m, 6H, Ar-CH_3), 6.44 (d, J = 7.8 Hz, 2H, Ar), 6.04 (t, J = 7.5 Hz, 2H, Ar), 4.19 (s, 4H, CH_2), 4.11 (s, 6H, MeO), 2.30 (s, 6H, Ar-CH_3), 1.45 (s, 18H, ^{t}Bu-Ar), 1.25 (s, 18H, ^{t}Bu-Ar), 0.03 (s, 36H, $N(TMS)_2$). ^{13}C{^{1}H} NMR (100 MHz, d_8-THF): 163.12(Ph), 150.60(Ph), 148.26(Ph), 138.50(Ph), 136.26(Ph), 134.27(Ph), 130.57(Ph), 129.77(Ph), 129.01(Ph),

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Table 1. Crystallographic Data for Complexes 1−7

	1·2toluene	**2**·2toluene	**3**·2toluene	**4**·2toluene	**5**·2toluene	**6**·2toluene	**7**·2toluene
formula	$C_{106}H_{142}N_4La_2O_4$	$C_{106}H_{142}N_4Nd_2O_4$	$C_{70}H_{110}La_2N_4O_4Si_4$	$C_{70}H_{110}N_4Nd_2O_4Si_4$	$C_{70}H_{110}N_4Sm_2O_4Si_4$	$C_{74}H_{120}La_2N_6O_4Si_4$	$C_{74}H_{120}N_6Nd_2O_4Si_4$
fw	1814.06	1824.72	1461.80	1472.46	1484.68	1547.94	1558.60
T (K)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
cryst size	0.30 × 0.20 × 0.08	0.25 × 0.20 × 0.14	0.40 × 0.30 × 0.20	0.38 × 0.22 × 0.22	0.26 × 0.24 × 0.23	0.30 × 0.25 × 0.20	1.00 × 0.35 × 0.30
a (Å)	11.9940(9)	11.974(1)	12.4370(7)	12.3331(9)	12.306(1)	10.094(2)	10.100(1)
b (Å)	13.134(1)	13.123(1)	20.853(1)	20.850(1)	20.852(2)	14.244(3)	14.162(2)
c (Å)	15.517(1)	15.379(1)	15.5541(9)	15.592(1)	15.601(1)	15.441(3)	15.343(2)
α (deg)	88.399(4)	88.044(5)				108.887(3)	108.345(2)
β (deg)	82.988(4)	82.648(5)	110.397(1)	110.702(2)	110.752(2)	92.534(3)	92.086(2)
γ (deg)	87.902(5)	88.124(5)				101.661(3)	102.169(2)
V (Å^3)	2423.9(3)	2394.4(4)	3781.0(4)	3750.6(5)	3743.6(6)	2042.7(6)	2023.9(5)
Z	1	1	2	2	2	1	1
D_{calcd} (g cm^{-3})	1.243	1.265	1.284	1.304	1.317	1.258	1.279
μ (mm^{-1})	0.921	1.124	1.223	1.478	1.663	1.136	1.374
F(000)	952	958	1520	1532	1540	808	814
θ_{max} (deg)	25.50	25.50	25.50	25.50	25.50	27.5	27.50
reflns collected	21 004	19 745	18 923	19 096	20 704	17 267	18 306
unique reflns	8978	8858	7004	6932	6921	7523	9072
final R [$I > 2.0\sigma(I)$]	0.0883	0.0637	0.0576	0.0449	0.0532	0.0476	0.0403
R(int)	0.0633	0.0478	0.039	0.0327	0.0437	0.0438	0.0302
wR	0.1928	0.1416	0.1346	0.1015	0.1117	0.1197	0.1011
GOF on F^2	1.055	1.080	1.109	1.118	1.145	1.071	1.074

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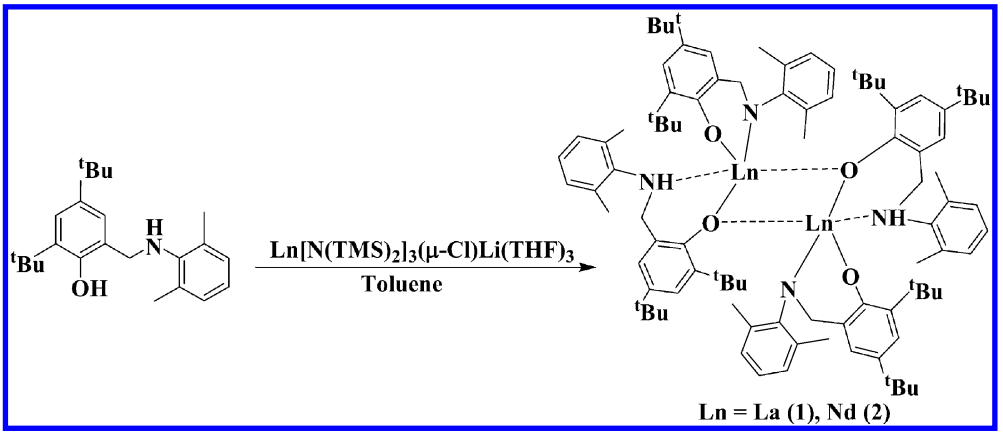
Scheme 1. Synthesis of Complexes 1 and 2



124.86(Ph), 124.26(Ph), 121.83(Ph), 109.84(Ph), 109.19(Ph), 108.86(Ph), 107.61(Ph), 58.02(CH_2Ar), 50.69(OCH_3), 35.82(C-(CH_3)$_3$), 34.59(C(CH_3)$_3$), 32.60(C(CH_3)$_3$), 31.24(C(CH_3)$_3$), 21.65-(CH_3), 4.79(Si(CH_3)$_3$). IR (KBr, cm^{-1}): 3635(s), 2945(s), 2336(m), 1604(s), 1535(s), 1458(m), 1358(m), 1290(w), 1200(s), 1150(w), 1086(s), 1083(m), 860(w), 836(s), 745(s), 553(m).

Synthesis of {[ON]^{2}Nd[N(TMS)$_2$]}$_2$ (4). The synthesis of complex **4** was carried out in the same way as that described for complex **2**, but [HONH]^2 (20 mL, 0.68 g, 2.00 mmol) was used instead of [HONH]^1. Blue crystals were obtained at room temperature in several days (2.59 g, 88%). Mp: 195−197 °C. Anal. Calcd for $C_{56}H_{94}N_4Nd_2O_4Si_4$: C, 52.21; H, 7.35; N, 4.34; Nd, 22.39. Found: C, 52.10; H, 7.53; N, 3.90; Nd, 22.59. IR (KBr, cm^{-1}): 3650(s), 2958(s), 2466(s), 1640(s), 1508(s), 1458(s), 1419(m), 1358(m), 1300(w), 1245(s), 1172(w), 1122(s), 1022(m), 883(w), 836(s), 748(s), 532(m).

Synthesis of {[ON]^{2}Sm[N(TMS)$_2$]}$_2$ (5). The synthesis of complex **5** was carried out in the same way as that described for complex **4**, but Sm[N(TMS)$_2$]$_3$(μ-Cl)Li(THF)$_3$ (1.78 g, 2.00 mmol) was used instead of Nd[N(TMS)$_2$]$_3$(μ-Cl)Li(THF)$_3$. Red block microcrystals were obtained from a concentrated toluene solution in a few days (2.55 g, 86%). Mp: 246−248 °C. Anal. Calcd for $C_{56}H_{94}N_4O_4Sm_2Si_4$: C, 51.72; H, 7.29; N, 4.31; Sm, 23.13. Found: C, 51.43; H, 7.47; N, 4.67; Sm, 23.25. ^{1}H NMR for **5**·2toluene (400 MHz, d_8-THF + C_6D_6): 8.57 (s, 2H, Ar), 7.79 (d, J = 7.6 Hz, 2H, Ar), 7.15 (d, J = 24.4 Hz, 2H, Ar), 6.30 (m, 4H, Ar), 6.18 (m, 10H, Ar-CH_3), 5.93 (m, 2H, Ar), 5.07(s, 2H, CH_2), 4.32 (s, 2H, CH_2), 3.47 (s, 6H, MeO), 1.33 (s, 6H, Ar-CH_3), 1.07 (s, 18H, ^{t}Bu-Ar), 0.28 (s, 18H, ^{t}Bu-Ar), −2.24 (s, 36H, N(TMS)$_2$). IR (KBr, cm^{-1}): 3700(s), 2954(s), 2450(s), 1600(s), 1477(s), 1358(m), 1230(m), 1246(s), 1169(w), 1122(s), 984(m), 933(s), 836(s), 744(s), 602(s), 521(m).

Synthesis of {[ON]^{3}La[N(TMS)$_2$](THF)}$_2$ (6). The synthesis of complex **6** was carried out in the same way as that described for complex **3**, but [HNOH]^3 (0.62 g, 2.00 mmol) was used instead of [HONH]^2. Colorless block microcrystals were obtained from a concentrated toluene solution in a few days (1.42 g, 92%). Mp: 303−305 °C. Anal. Calcd for $C_{60}H_{104}La_2N_6O_4Si_4$: C, 52.85; H, 7.69; N, 6.16; La, 20.37. Found: C, 52.42; H, 7.81; N, 6.43; La, 19.95. ^{1}H NMR (400 MHz, d_8-THF): 7.48−7.29 (m, 4H, Ph), 7.28−7.00 (m, 8H, pyridine ring), 4.19−4.36 (m, 4H, CH_2), 3.75 (s, α-CH_2 THF), 1.90 (s, β-CH_2 THF), 1.41 (s, 36H, ^{t}Bu), 0.21(s, 36H, N(TMS)$_2$). ^{13}C{^{1}H} NMR (100 MHz, d_8-THF): 163.10(Ph), 161.76(Ph), 152.00(pyridine ring), 141.80(pyridine ring), 136.10(pyridine ring), 135.46(Ph), 129.48(Ph), 125.85(pyridine ring), 123.12(pyridine ring), 121.51(Ph), 111.83(Ph), 111.22(CH_2), 67.21(α-CH_2, THF), 32.33-(C(CH_3)$_3$), 30.55(C(CH_3)$_3$), 26.17(C(CH_3)$_3$), 25.10(β-CH_2, THF), 23.34(C(CH_3)$_3$), 14.33(C(CH_3)$_3$), 5.11(Si(CH_3)$_3$), 4.41(Si(CH_3)$_3$), 2.58(Si(CH_3)$_3$). IR (KBr, cm^{-1}): 3410(s), 2956(s), 2906(m), 2868(m), 2588(m), 1990(m), 1910(m), 1614(s), 1572(m), 1512(s), 1478(m), 1440(m), 1361(s), 1252(m), 1201(w), 1162(m), 1066(s), 932(s), 881(s), 837(s), 770(s), 736(m), 682(w), 523(w).

Synthesis of {[ON]^{3}Nd[N(TMS)$_2$](THF)}$_2$ (7). The synthesis of complex **7** was carried out in the same way as that described for complex **4**, but [HONH]^3 (0.62 g, 2.00 mmol) was used instead of [HONH]^2. Blue block microcrystals were obtained from a concentrated toluene solution in a few days (1.39 g, 89%). Mp: 284−286 °C. Anal. Calcd for $C_{60}H_{104}N_6Nd_2O_4Si_4$: C, 52.44; H, 7.63; N, 6.11; Nd, 20.99. Found: C, 52.18; H, 7.76; N, 5.89; Nd, 20.63. IR (KBr, cm^{-1}): 3427(s), 2956(s), 2905(m), 2866(m), 2596(m), 1970(m), 1812(m), 1616(s), 1570(m), 1512(s), 1483(w), 1439(s), 1389(m), 1361(m), 1299(m), 1236(m), 1201(w), 1068(m), 932(m), 884(m), 840(s), 769(s), 735(m), 525(w).

Synthesis of {[ON]^{3}Sm[N(TMS)$_2$](THF)}$_2$ (8). The synthesis of complex **8** was carried out in the same way as that described for complex **5**, but [HONH]^3 (0.62 g, 2.00 mmol) was used instead of [HONH]^2. Yellow block microcrystals were obtained from a concentrated toluene solution in a few days (1.39 g, 89%). Mp: 238−240 °C. Anal. Calcd for $C_{60}H_{104}N_6Sm_2O_4Si_4$: C, 51.97; H, 7.56; N, 6.06; Sm, 21.69. Found: C, 51.60; H, 7.72; N, 6.39; Sm, 22.08. ^{1}H NMR (400 MHz, C_6D_6): 8.19 (b, 2H, Ar), 7.56 (b, 2H, Ar), 5.93 (b, 4H, Py), 5.38(b, 4H, Py), 4.70 (b, 2H, CH_2), 4.31 (b, 2H, CH_2), 2.53 (b, 8H, THF), 1.89 (s, 18H, ^{t}Bu-Ar), 1.77 (s, 18H, ^{t}Bu-Ar), 1.22 (b, 8H, THF), 0.08 (b, 36H, N(TMS)$_2$). IR (KBr, cm^{-1}): 3406s, 2957s, 2904m, 2867m, 2585m, 1933m, 1613s, 1512m, 1476m, 1440s, 1361s, 1300m, 1254m, 1201s, 1156s, 1131m, 1067s, 932s, 881s, 839s, 770s, 736m, 646m, 524m.

Typical Procedure for the Polymerization Reaction. The procedures for the polymerization of L-lactide or *rac*-lactide initiated by complexes **3**−**8** were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with the desired amount of L-lactide and toluene under argon. The contents of the flask were maintained at the desired temperature until the lactide was dissolved, and then a solution of the initiator in toluene was added to this solution by syringe. The mixture was stirred vigorously for the desired time, during which time an increase in the viscosity was observed. The reaction mixture was quenched by the addition of methanol and then poured into methanol to precipitate the polymer, which was dried under vacuum and weighed.

X-ray Crystallography. Suitable single crystals of complexes **1**−**7** 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 ω scan mode using Mo Kα radiation (λ = 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 Table 1.

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

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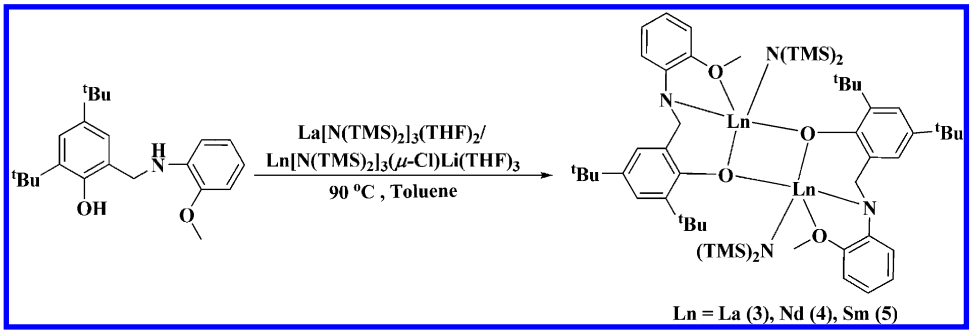
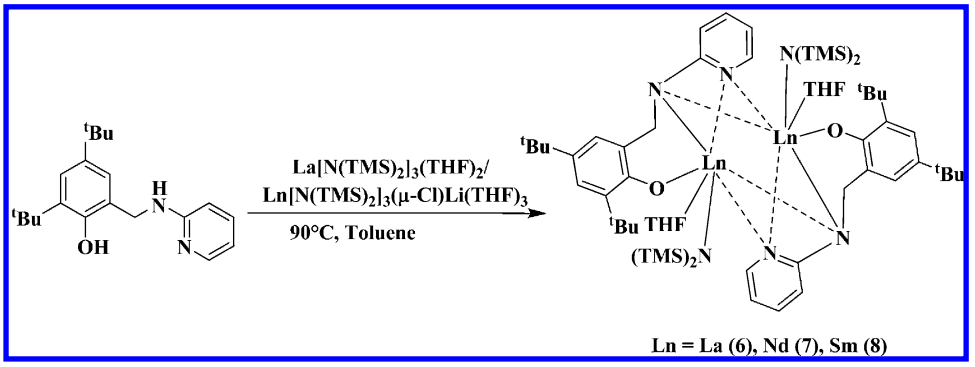
Scheme 2. Synthesis of Complexes 3−5



Scheme 3. Synthesis of Complexes 6−8



included in the structure factor calculation in the final stage of full-matrix least-squares refinement.

RESULTS AND DISCUSSION

Synthesis of the Aminophenoxy Lanthanide Complexes. We previously reported that the amine elimination reaction of aminophenol [HONH] {[HONH] = [*p*-$CH_3C_6H_4NHCH_2$(3,5-$^tBu_2C_6H_2$-2-OH)]} with lanthanide amide gave the anionic aminophenoxy lanthanide amides.[6] We postulated that the ligand used was not sterically imposing enough to stabilize the neutral aminophenoxy lanthanide amide. In order to understand the effect of the steric bulk of the aminophenoxy group on the synthesis of aminophenoxy lanthanide complexes, a new aminophenol, [HONH]^1, was synthesized. It was found that the reactions of an equimolar mixture of [HONH]^1 and Ln[N($SiMe_3$)$_2$]$_3$(μ-Cl)Li(THF)$_3$ in toluene at room temperature did not afford the desired neutral aminophenoxy lanthanide amido complexes or the similar anionic lanthanide amido complexes reported previously,[6] but instead gave the aminophenoxy lanthanide complexes {[ON]^{1}Ln[ONH]^1}$_2$ (Ln = La (**1**), Nd (**2**)), as shown in Scheme 1. These results indicated that the steric bulk of the aminophenoxy ligand has a profound effect on the outcome of the amine elimination reaction of aminophenol with lanthanide amide. Reaction temperatures of 0 and 90 °C were investigated and found to have no effect on the outcome of these reactions, both providing only the homoleptic aminophenoxy lanthanide

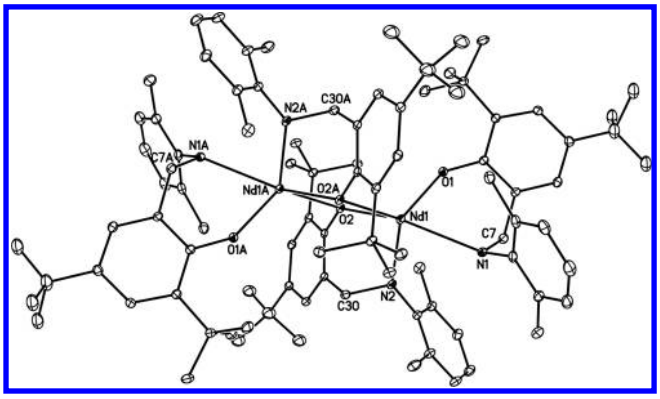


Figure 2. Molecular structure of complex **2** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Disordered carbon atoms of *tert*-butyl groups and hydrogen atoms are omitted for clarity. Complex **1** is isomorphous with complex **2**.

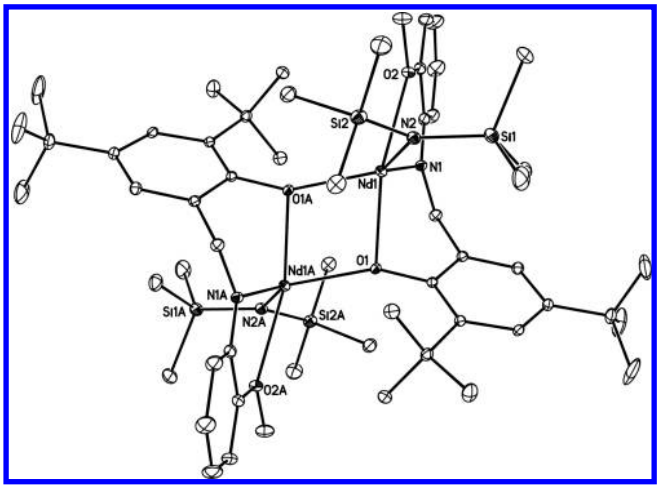


Figure 3. Molecular structure of complex **4** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Disordered carbon atoms of *tert*-butyl groups and hydrogen atoms are omitted for clarity. Complexes **3** and **5** are isomorphous with complex **4**.

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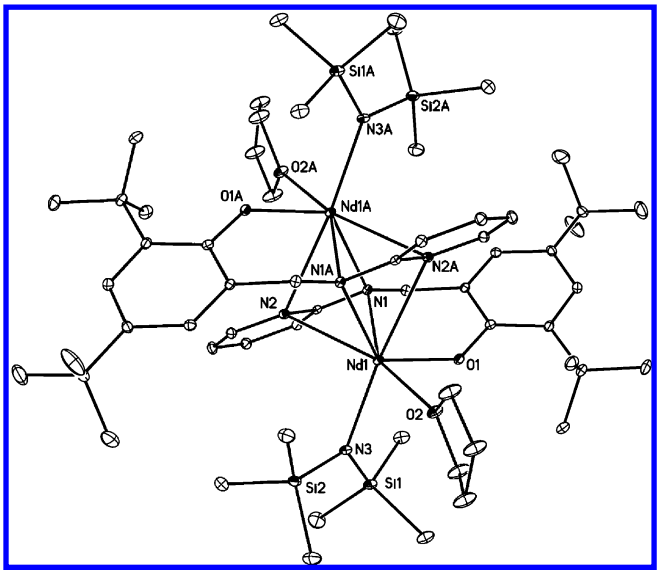

Figure 4. Molecular structure of complex **7** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Disordered carbon atoms of *tert*-butyl groups and hydrogen atoms are omitted for clarity. Complex **6** is isomorphous with complex **7**.

Table 2. Polymerization L-Lactide by Complexes 3−8[a]

entry	initiator	$[M]_0/[I]_0$	T (°C)	t (min)	yield (%)[b]	M_n[c] (×10⁴)	PDI[c]
1	**3**	3000	70	10	93	11.19	1.61
2	**3**	4000	70	60	23	2.70	2.19
3	**4**	500	25	30	83	12.74	1.69
4	**4**	500	50	30	92	7.45	2.36
5	**4**	500	70	5	98	6.96	1.68
6[d]	**4**	500	25	30	30	2.98	1.25
7[d]	**4**	500	50	15	75	8.33	1.44
8[e]	**4**	500	25	5	69	11.92	2.29
9	**4**	2000	70	10	94	19.21	1.52
10	**4**	2500	70	10	82	18.64	1.54
11	**5**	1500	70	10	97	19.46	1.50
12	**5**	2000	70	30	92	20.48	1.51
13	**5**	2500	70	30	80	18.90	1.53
14	**6**	3000	70	10	100	18.72	1.59
15	**6**	4000	70	60	94	13.89	1.57
16	**7**	3000	70	60	96	17.98	1.47
17	**7**	4000	70	60	90	18.62	1.51
18	**8**	2000	70	30	95	10.18	1.44
19	**8**	2500	70	30	93	12.25	1.49

[a]General polymerization conditions: toluene as the solvent, [L-LA] = 1 mol/L. [b]Yield: weight of polymer obtained/weight of monomer used. [c]Measured by GPC calibrated with standard polystyrene samples. [d]In THF. [e]in CH_2Cl_2.

complexes. In the ^{1}H NMR spectrum of complex **1**, a singlet resonance at δ 3.76 ppm corresponding to the N−H proton was observed, which was similar to the N−H resonance of the aminophenol ligand reported in the literature.[7b] This result indicated that a hydrogen atom was bonded to a nitrogen atom. In accordance with the presence of an N−H proton, doublet resonances at δ 3.99 ppm for one CH_2(Ar) group with J = 25.4 Hz were observed because of the coupling interaction with N−H, whereas a singlet resonance at δ 4.21 ppm for another CH_2(Ar) group was observed. The compositions of complexes

Table 3. Polymerization *rac*-Lactide by Complexes 3 −8[a]

entry	initiator	$[M]_0/[I]_0$	T (°C)	t (min)	yield (%)[b]	M_n[c] (×10⁴)	PDI[c]	P_r[d]
1	**3**	3000	25	20	88	33.00	1.53	0.80
2	**3**	4000	25	20	82	36.41	1.43	0.70
3	**4**	4000	25	20	78	38.71	1.50	0.74
4	**4**	4000	25	1 h	95	43.70	1.49	0.71
5	**4**	5000	25	1 h	85	42.38	1.54	0.72
6	**5**	2000	25	2 h	82	23.33	1.30	0.71
7	**5**	3000	25	2 h	81	15.93	1.53	0.70
8	**6**	2000	25	12	94	13.42	1.54	0.66
9	**6**	3000	25	12	73	10.02	1.60	0.67
10	**7**	500	25	12	91	11.95	1.47	0.70
11	**7**	1000	25	12	87	14.62	1.59	0.69
12	**7**	2000	25	12	79	6.56	1.51	0.63
13	**8**	1000	25	6	58	8.35	1.47	0.63
14	**8**	1000	25	12	80	11.52	1.60	0.65
15	**8**	2000	25	6	38	10.94	1.48	0.68
16	**8**	2000	25	12	74	21.31	1.68	0.71

[a]General polymerization conditions: THF as the solvent, [*rac*-LA] = 1 mol/L. [b]Yield: weight of polymer obtained/weight of monomer used. [c]Measured by GPC calibrated with standard polystyrene samples. [d]P_r is the probability of racemic linkages between monomer units determined from the methane region of the homonuclear decoupled ^{1}H NMR spectrum.

1 and **2** were confirmed by elemental analysis, and definitive molecule structures were provided by an X-ray diffraction study.

To further explore the effect of ligand structure on the outcome of the amine elimination reaction, an aminophenol containing an additional coordination site, $[HONH]^2$, was synthesized and used to synthesize organolanthanide complexes. A ^{1}H NMR monitoring reaction of La[N(TMS)$_2$]$_3$(μ-Cl)Li(THF)$_3$ with the aminophenol $[HONH]^2$ was carried out. Treatment of La[N(TMS)$_2$]$_3$(μ-Cl)Li(THF)$_3$ with one equivalent of $[HONH]^2$ in C_6D_6 at room temperature revealed that a rapid reaction was taking place, and precipitation of solid material was noted in the tube. The precipitate disappeared when 0.5 mL of THF-d_8 was added. The ^{1}H NMR analysis revealed that a lanthanum amido complex, $[ON]^2$La[N(TMS)$_2$](THF)$_x$, had formed, with the elimination of HN(TMS)$_2$. On a preparative scale, attempts were made to simplify the synthetic procedure by separating the lanthanum amido complex from LiCl using hot toluene. Thus, the reaction of an equimolar mixture of La[N(TMS)$_2$]$_3$(μ-Cl)Li(THF)$_3$ with $[HONH]^2$ in toluene at 90 °C was investigated. The reaction still gave a large amount of precipitate, which indicated the poor solubility of $[ON]^2$La[N(TMS)$_2$](THF)$_x$ in hot toluene. When the neutral lanthanum amide La[N(TMS)$_2$]$_3$(THF)$_2$ was used to replace La[N(TMS)$_2$]$_3$(μ-Cl)Li(THF)$_3$, the desired neutral aminophenoxy lanthanum amido complex {$[ON]^2$La[N(TMS)$_2$]}$_2$ (**3**) was isolated in high yield from a concentrated toluene solution as block crystals, as shown in Scheme 2. Therefore, the neutral lanthanum amide La[N(TMS)$_2$]$_3$(THF)$_2$ was used to synthesize aminophenoxy lanthanum complexes. In contrast, the reaction of an equimolar mixture of $[HONH]^2$ with Ln[N(TMS)$_2$]$_3$(μ-Cl)Li(THF)$_3$ (Ln = Nd, Sm) in toluene at 90 °C conveniently afforded the final products {$[ON]^2$Ln[N(TMS)$_2$]}$_2$ [Ln = Nd (**4**), Sm (**5**)] in yields of up to 88%, as shown in Scheme 2. These results indicated that the presence of an additional coordination site in the amino-

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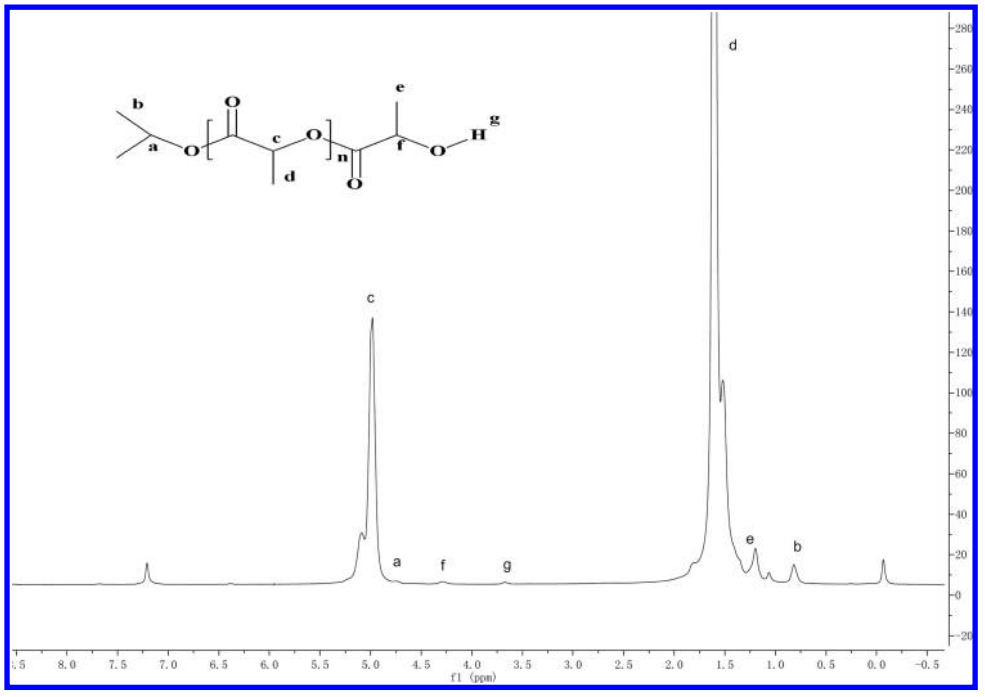

Figure 5. ^{1}H NMR spectrum of the oligomer of L-lactide initiated by complex **8** in 25 °C in $CDCl_3$.

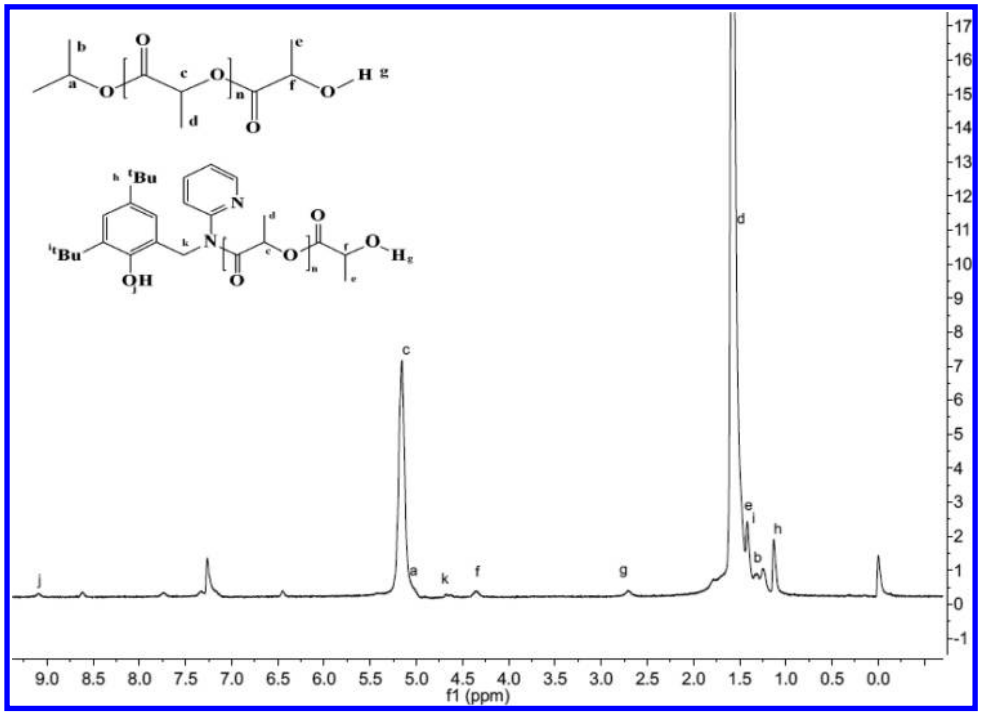

Figure 6. ^{1}H NMR spectrum of the oligomer of L-lactide initiated by complex **8** in 70 °C in $CDCl_3$.

phenoxy ligand plays a crucial role in the stabilization of neutral aminophenoxy lanthanide amido complexes. The compositions of complexes **3**−**5** were confirmed by elemental analysis and IR spectroscopy, as well as by NMR spectroscopy in the case of complexes **3**, and **5**. The definitive molecular structures of these complexes were confirmed by single-crystal structure analysis. Complex **3** is soluble in THF, but insoluble in toluene, whereas complexes **4** and **5** are soluble in THF and toluene, but insoluble in hexane.

The successful synthesis of complexes **3**−**5** demonstrated that the strategy of introducing an additional coordination atom in the ligand is practical for stabilizing the neutral aminophenoxy lanthanide complexes. In order to elucidate the electronic and steric effects of the ligand on the activity of the aminophenoxy lanthanide amido complexes, a ligand containing a pyridine group, $[HNOH]^3$, was synthesized and used to stabilize the expected lanthanide amido complexes. Similarly, the reaction of an equimolar mixture of $La[N(SiMe_3)_2]_3(THF)_2$ with $[HONH]^3$ in toluene gave the neutral aminophenoxy lanthanide amide $\{[ON]^2La[N(TMS)_2](THF)\}_2$ (**6**) in high isolated yield, as shown in Scheme 3. As expected, the reactions of an equimolar mixture of

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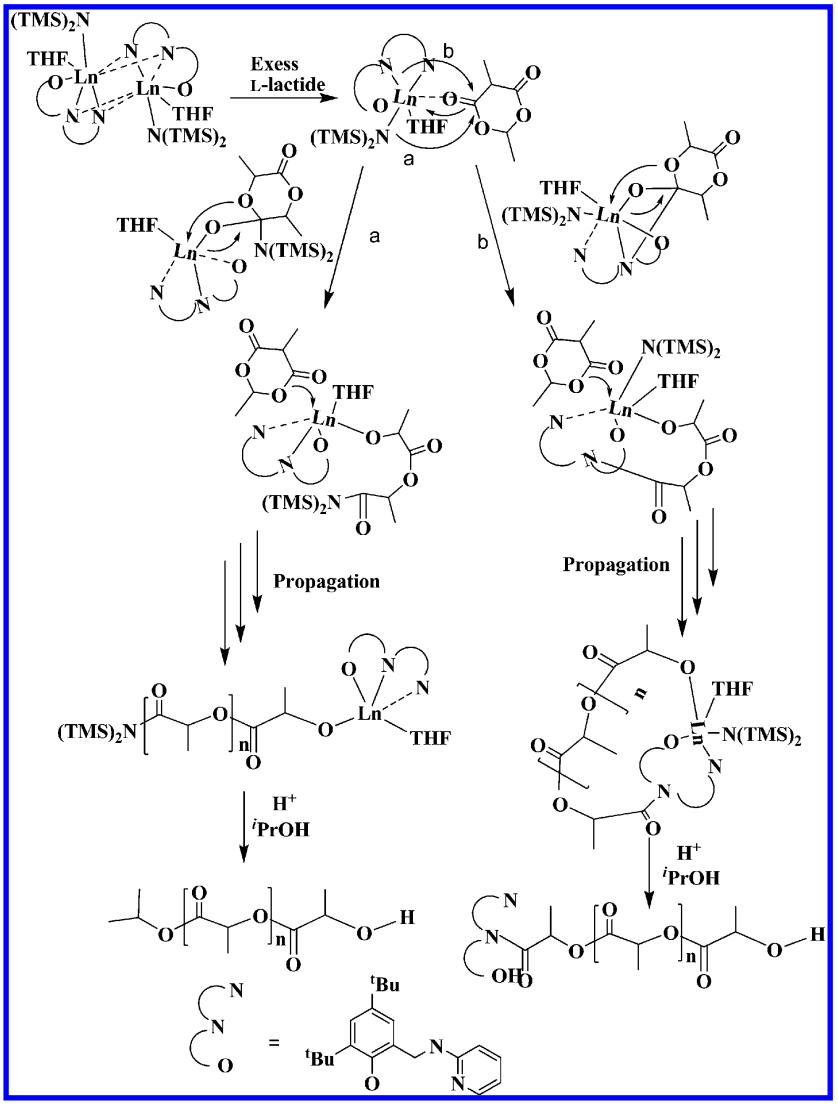
Scheme 4. Possible Mechanism for the Ring-Opening Polymerization of L-Lactide



$Ln[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3$ with $[HNOH]^3$ in toluene afforded $\{[ON]^3Ln[N(TMS)_2](THF)\}_2$ (Ln = Nd (**7**), Sm (**8**)) in high isolated yields under the same reaction conditions (Scheme 3). Complexes **6**–**8** were subsequently characterized by elemental analysis and IR spectroscopy, as well as ^1H NMR spectroscopy in the case of complexes **6**, and **8**. Complexes **6**–**8** demonstrated relatively good solubility in toluene in comparison with complexes **3**–**5**.

Complexes **1** and **2** are isostructural. The molecular diagram of complex **1** is depicted in the figure (Figure 2). Complexes **1** and **2** have unsolvated centrosymmetric dimeric structures and possess bridging aminophenoxy-O atoms. Each of the metal atoms in the complexes is coordinated to one oxygen atom and one nitrogen atom from a dianionic aminophenoxy ligand and two oxygen atoms and one nitrogen atom from two monoanionic aminophenoxy ligands. The coordination environment can be described as a distorted trigonal bipyramid with the O(1) and N(2) atoms occupying the axial positions of the bipyramid. The terminal Ln–O(Ar) bond distances in complexes **1** and **2** are 2.248(5) and 2.191(4) Å, respectively. As expected in these complexes, the Ln–N1(amino) bond lengths are longer than the Ln–N2(amido) bond lengths.

The molecular structures of complexes **3**–**5** are isomorphous. Only the ORTEP diagram of complex **4** is shown in the figure (Figure 3). Complexes **3**–**5** have unsolvated dimeric structures with two toluene molecules involved in the crystal lattice. Similarly to observations made in complexes **1** and **2**, the two central metal atoms in complexes **3**–**5** were bridged by two aryloxo-O atoms. Each of the metal atoms is five-coordinated by two oxygen atoms and one nitrogen atom from one aminophenoxy group and one oxygen atom from another aminophenoxy group, as well as one nitrogen atom from the hexamethyldisilylamide group. The coordination geometry around the metal center was distorted trigonal bipyramidal, in which the O(1) and O(2) atoms occupy the apical positions. The length of the Ln–N(CH_2Ar) bond ranged from 2.371(10) to 2.211(4) Å, which was in agreement with the contraction of ionic radii in the lanthanide metal ions. The average length of the Ln–O(Ar) bonds was in the range 2.437(6)–2.347(3) Å, which was comparable with the Ln–O(Ar) bond lengths reported in the literature.[11] The average length of the Ln–N(TMS) bonds in complexes **3**–**5** was 2.392(9), 2.337(3), and 2.307(4) Å, respectively, which was comparable with the corresponding bond lengths in {(MBMP)-

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$Ln[N(TMS)_2](THF)_2\}$[2e] when the difference in ionic radii was considered.[12]

The molecular structures of complexes **6** and **7** were determined by X-ray crystal diffraction. Complexes **6** and **7** are isomorphous. Only the ORTEP diagram of complex **7** is shown in Figure 4. Complexes **6** and **7** have solvated dimeric structures. They consist of two metal ions, two aminophenoxy groups, two $N(TMS)_2$ groups, and two THF molecules. In contrast with complexes **3**−**5**, complexes **6** and **7** possess bridging aminophenoxy-N atoms rather than dimerizing though the aminophenoxy-O atoms. Each of the lanthanide metal atoms is seven-coordinated by four nitrogen atoms and one oxygen atom from two aminophenoxy groups and one nitrogen atom from the $N(TMS)_2$ group, as well as one oxygen atom from a THF molecule. The overall coordination geometry around the lanthanide metal atoms can be considered to be a distorted capped trigonal prism with the cap position occupied by the N(2) atom.

The average length of the Ln(1)−O(1) bonds in complexes **6** and **7** was 2.234(3) and 2.187(2) Å, respectively, which was shorter than the corresponding bond lengths in complexes **3** and **4**. This difference was attributed to the formation of bridged bonds in the latter. As expected, the average length of the Ln−N(CH_2Ar) bonds was longer than the corresponding lengths in complexes **3** and **4**. The lengths of the Ln−N(TMS) bonds in complexes **6** and **7** are slightly longer than those in complexes **3** and **4**, which was attributed to the increase in the coordination number.[12]

Ring-Opening Polymerization of Lactides by Complexes 3−8. Biodegradable polymers, such as poly(ε-caprolactone) (PCL) and poly(lactide) (PLA), have recently attracted significant attention as replacements for conventional synthetic materials because of their biodegradable, biocompatible, and permeable properties.[13] Ring-opening polymerization of cyclic esters initiated by organometallic complexes is a convenient method for the synthesis of these high molecular weight polymers.[14] To further explore the relationship between the structures of the catalysts and their catalytic properties and behaviors, complexes **3**−**8** were examined in the ring-opening polymerization of L-lactide and *rac*-lactide.

As expected, the aminophenoxy lanthanide amides were efficient initiators in the ring-opening polymerization of L-lactide. The representative polymerization results are shown in Table 2. It is clear that L-lactide polymerization can be initiated by all of the lanthanide complexes, affording polymers with high molecular weights. Furthermore, the catalytic activities of these neutral lanthanide amides are greater than those of the anionic aminophenoxy lanthanide amides.[6] For example, using the neodymium complex **4** as the initiator, a 94% yield was achieved in 10 min at 70 °C when the molar ratio of monomer to initiator was 2000 (Table 2, entry 12). When the anionic aminophenoxy neodymium amide was used as the initiator, however, a yield of 86% was achieved in 4 h at 70 °C, when the molar ratio of monomer to initiator was 1800.[6] The activities of these neutral lanthanide amides are also greater than those of the imidazolidine-bridged bis(phenolate) lanthanide amides.[11]

As shown in Table 2, the polymerization medium also has a profound effect on the catalytic activity and the molecular weight of the resultant polymers. It was found that the lanthanide metal amido complexes showed greater activity in toluene than in THF (Table 2, entries 3 and 6). Although a yield of 69% could be achieved in 5 min using CH_2Cl_2 as the solvent, the molecular weight distribution of the resultant polymer was relatively broad (Table 2, entry 8). As expected, the polymerization temperature affected the polymerization. At higher temperatures, the polymerization proceeded at a greater rate (Table 2, entries 4−6). Therefore, all of the polymerization procedures for L-lactide were carried out in toluene solvent at 70 °C.

The structure of the aminophenoxy lanthanide amides can also affect their catalytic behavior for L-lactide polymerization. The lanthanide amides **6**−**8** showed greater activity in comparison with complexes **3**−**5** and gave polymers with relatively narrow molecular weight distributions (PDI = 1.44−1.59) (Table 2, entries 14−19). For example, the lanthanum amide **6** can polymerize almost completely 4000 equivalents of L-lactide at 70 °C in one hour (Table 2, entry 15), whereas the lanthanum amide **3** can polymerize 4000 equivalents of L-lactide to give a yield of 23% under the same polymerization conditions (Table 2, entry 2). This difference in activity was attributed to the different molecular structures of the lanthanide amides. Although all of complexes **3**−**8** have dimeric structures, complexes **3**−**5** are unsolvated O-bridged dimers, whereas complexes **6**−**8** are solvated N-bridged dimers. This difference implied that the coordination environments around the lanthanide metals in complexes **3**−**5** were more crowded than those in complexes **6**−**8**. In noncoordination solvent, the dimeric structures are maintained. Thus, complexes **6**−**8** showed greater catalytic activity.

Stereoselective polymerization of *rac*-lactide has received significant interest in recent years from academic and industrial research groups. The polymerization is extremely sensitive to the structures of the catalysts, because the environment of the last unit of the propagating active species must be sterically proper to incorporate the configurationally opposite enantiomer.[15] To further elucidate the effect of the structures of the ancillary ligands of lanthanide-based catalysts on the polymerization stereoselectivity, the catalytic behavior of complexes **3**−**8** in the ring-opening polymerization of *rac*-lactide was also tested. The results are summarized in Table 3.

It can be seen that these lanthanide amides smoothly initiated the ring-opening polymerization of *rac*-lactide in THF at 25 °C to afford polymers with high molecular weights and relatively narrow molecular weight distributions (PDI = 1.30−1.60). The activity of these neutral aminophenoxy lanthanide complexes is greater than the anionic ones.[6] For example, using the neodymium complex **4** as the initiator at room temperature, the polymerization was complete in one hour when the molar ratio of monomer to initiator was 4000 (Table 3, entry 4). When the anionic neodymium complex was used as the initiator, however, a yield of 88% was achieved in six hours when the molar ratio of monomer to initiator was 500.[6] The ionic size of the lanthanide metal ions has an obvious effect on the catalytic activity in *rac*-lactide polymerization. The observed increasing order in activity is in agreement with the order of ionic radii, which is consistent with that observed in L-lactide polymerization. The structures of the aminophenoxy groups can also affect the catalytic activity of the corresponding lanthanide complexes in *rac*-lactide polymerization. Complexes **6**−**8** performed poorly in comparison to complexes **3**−**5** in *rac*-lactide polymerization. These results are contrary to those observed for L-lactide polymerization, as mentioned above. It is worthy to note that the activities of complexes **3**−**5** for *rac*-lactide polymerization are greater than those for L-lactide polymerization, in spite of the fact that the former polymerizations were conducted in THF at room temperature. For

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instance, complex **3** polymerized 4000 equivalents of *rac*-lactide in THF at room temperature to give an 82% yield in 20 min, whereas complex **3** polymerized L-lactide in toluene at 70 °C to give a 23% yield in one hour. We attributed these differences to the different structures of these complexes in toluene and in THF. In the coordinated THF solution, the dimeric structures of these complexes were broken, whereas in toluene solution the dimeric structure was maintained, as mentioned above.

The ionic radii have no obvious effect on the stereoselectivity, and these complexes showed stereoselectivity in *rac*-lactide polymerization, affording heterotactic-rich PLA. The P_r values of all of the polymers obtained ranged from 0.63 to 0.71. The ability of these complexes to control the steroechemical outcome of the polymerization is similar to that of the anionic aminophenoxy lanthanide complexes.[6] Cui and her co-workers reported that the coordination geometry around the metal center plays a critical role in governing the stereoselectivity of *rac*-lactide polymerization.[15a] In our experience, however, although their coordination environments around the lanthanide metals are quite different, a discernible difference in stereoselectivity was not observed when the neutral and the anionic aminophenoxy lanthanide complexes were used as initiators. The ability of these complexes to control the stereochemical outcome of the polymerization is worse than those of the amine-bridged bis(phenolate) lanthanide complexes, which can polymerize *rac*-lactide to give high heterotactic polymers with a P_r value greater than 0.95.[15a,c,f] These results revealed that the ancillary ligand plays a crucial role in controlling the stereoselectivity in *rac*-lactide polymerization.

The initiation mechanism was also elucidated by end-group analysis of the oligomer of L-lactide, which was prepared by the polymerization of L-lactide initiated by complex **8** in a 1:10 molar ratio and subsequently quenched by 2-propanol. The ^{1}H NMR spectrum of the oligomer clearly showed that only the isopropoxo group was observed, according to the resonances at 1.25 and 5.10 ppm. No resonance signal was observed for the phenoxyamido ligand at room temperature, as shown in the figure (Figure 5). However, when the oligomerization was conducted at 70 °C, the aromatic proton resonances in the range 6.50−7.75 ppm and the methyl and methylene proton resonances of the phenoxyamido group at 1.15, 1.47, and 4.75 ppm were observed as shown in Figure 6, indicating that the phenoxyamido group was involved in the polymerization. Furthermore, the presence of an isopropoxo group was indicated by resonances at 1.25 and 5.00 ppm. Obviously, the isopropoxo group existing in the oligomer must have come from 2-propanol, which was introduced by the exchange reaction of 2-propanol with the -N(TMS)$_2$ group.[6] These results revealed that the Ln-N(TMS)$_2$ group initiated the polymerization at room temperature (Scheme 4, path a), whereas both the Ln-N(TMS)$_2$ and Ln-N(amido) groups initiated the polymerization at higher temperatures (Scheme 4, paths a and b).

CONCLUSION

In summary, a series of lanthanide metal complexes supported by dianionic aminophenoxy ligands were prepared using a general amine elimination reaction of bis(trimethylsilyl)amido lanthanide metal complexes with aminophenols, and their structural features have been determined by X-ray diffraction study. It was found that the presence of an additional coordination site in the aminophenoxy ligand plays a crucial role in the stabilization of neutral aminophenoxy lanthanide amido complexes. These neutral aminophenoxy lanthanide amides are efficient initiators in L-lactide and *rac*-lactide polymerization, and their activities are greater than the corresponding anionic ones. The structures of the aminophenoxy ligands clearly affect the activity of the corresponding lanthanide amides. Furthermore, the polymerization of *rac*-lactide initiated by aminophenoxy lanthanide complexes gave heterotactic-rich polymers. These results indicated that the organolanthanide catalysts stabilized by dianionic N,O-chelate ligands have great potential in homogeneous catalysis. Further studies are under way in our laboratory.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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