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Synthesis and Characterization of Salalen Lanthanide Complexes and Their Application in the Polymerization of *rac*-Lactide

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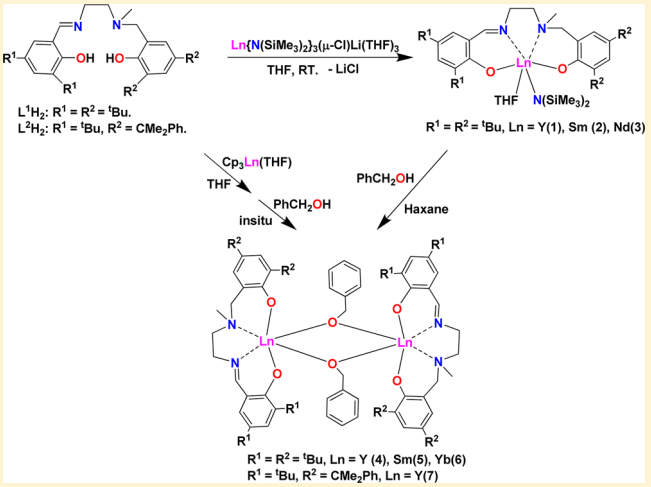
Supporting Information

ABSTRACT: A series of neutral lanthanide complexes supported by ONNO Salalen-type ligands were synthesized, and their catalytic activity for the polymerization of *rac*-lactide (*rac*-LA) was explored. The amine elimination reactions of $Ln[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3$ with the ONNO Salalen-type ligand L^1H_2 (L^1 = (2-O-C_6H_2-Bu^t_2-3,5)CH=$NCH_2CH_2N(Me)CH_2$(2-O-C_6H_2-Bu^t_2-3,5)) in a 1:1 molar ratio in tetrahydrofuran (THF) gave the neutral lanthanide amides $L^1Ln[N(SiMe_3)_2](THF)$ (Ln = Y (**1**), Sm (**2**), Nd (**3**)). Reaction of the lanthanide amides with benzyl alcohol produces the dimeric lanthanide alkoxo complex $(L^1LnOCH_2Ph)_2$ (Ln = Y (**4**), Sm (**5**)) in high isolated yield. $Y[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3$ reacted with the Salalen-type ligand L^2H_2 (L^2 = (2-O-C_6H_2-Bu^t_2-3,5)CH=$NCH_2CH_2N(Me)CH_2${2-O-C_6H_2-$(CPhMe_2)_2$-3,5}) in a 1:l molar ratio in THF also gave the desired yttrium amide, but this complex could not be separated because of its very good solubility even in *n*-pentane. The proton exchange reactions of L^1H_2 and L^2H_2 with $(C_5H_5)_3Ln(THF)$ in a 1:1 molar ratio in THF and then with 1 equiv of benzyl alcohol gave the desired lanthanide alkoxides $[L^1Ln(OCH_2Ph)]_2$ (Ln = Y (**4**), Sm (**5**), Yb (**6**)) and $[L^2Y(OCH_2Ph)]_2$ (**7**), respectively. Complexes **1**−**7** were well characterized by elemental analyses, IR spectra, X-ray single-crystal structure determination, and NMR spectroscopy in the case of complexes **1**, **4**, and **7**. Complexes **1**−**3** are isostructural and have a solvated monomeric structure. The coordination geometry around the lanthanide atom can be best described as a distorted trigonal bipyramid. Complexes **4**−**7** are dimeric species in the solid state. They all contain a Ln_2O_2 core bridging through the oxygen atoms of the two OCH_2Ph groups. Each of the lanthanide atoms is also six-coordinated to form a distorted octahedron. It was found that all the complexes are efficient initiators for the ring-opening polymerization of *rac*-LA, giving PLA with good heterotacticity (P_r up to 0.85). The observed order of increase in activity is in agreement with the order of the ionic radii, whereas the stereoselectivity is in reverse order. The steric bulkiness of the substituents on the phenol ring has no obvious impact on the rate and stereocontrolability of the polymerizations. The Ln−O species resulted in more controllable polymerization than the corresponding Ln−N species, and complex **4** can initiate *rac*-LA polymerization in a controlled manner.



INTRODUCTION

Poly(lactides) (PLA) are among the most important synthetic biodegradable polymers investigated for biomedical and pharmaceutical applications, such as controlled drug delivery, resorbable sutures, medical implants, and scaffolds for tissue engineering.[1] The most efficient synthesis, and the commercial route to PLA, involves the ring-opening polymerization (ROP) of lactide.[1d,g] Because the chain stereochemistry of the monomeric units in the polymer chains plays a decisive role in the mechanical, physical, and degradation properties of PLA materials, the design and synthesis of catalysts to prepare different stereospecific PLA architectures is a major topic.

Throughout the past decade, significant effort has been invested in the development of discrete, well-characterized metal complexes to initiate the stereocontrolled ROP of lactides.[2] In most cases, the catalytic efficiency and the degree of chain stereocontrol of the resulting polymers is strongly influenced by the nature of the ancillary ligands and the metal center. Subtle modifications in the ligand framework may have a major effect on the ROP of *rac*-lactide (*rac*-LA). It has been found that the lanthanide derivatives stabilized by bridged bis(phenolate) ligands are efficient catalysts for the ROP of

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lactides; especially, the lanthanide complexes supported by amine-bridged bis(phenolate) groups can initiate the highly stereoselective ROP of *rac*-LA to give PLAs with heterotacticity up to 0.99.[3] To further understand the effect of the backbone of the bis(phenolate) ligands on the stereoselectivity of *rac*-LA polymerization, the design and synthesis of lanthanide initiators with different bis(phenolate) ancillary ligands are still meaningful.

Salen and Salan are two types of popular ligands in transition-metal chemistry, and the corresponding metal complexes are now widely used as catalysts in a variety of metal-catalyzed organic transformations and polymerizations.[3,4] Salalen ligands, which are half-Salan/half-Salen hybrid ligands, have received little attention. Just like Salen and Salan, Salalen ligands can be easily synthesized via simple condensation of primary amine with 1 equiv of a substituted salicylaldehyde to form the "half-Salen" part, followed by a Mannich condensation of the secondary amine with 1 equiv of formaldehyde and 1 equiv of a substituted phenol to complete the "half-Salan" part. Accordingly, it is relatively easy to evaluate the steric and electronic effects of Salalen ligands, which is advantageous for fine tuning of the structures of the corresponding Salalen metal complexes and for systematically exploiting their catalytic behaviors. Recently, Salalen ligands have been used to stabilize metal-based catalysts, which can catalyze a number of transformations, such as asymmetric oxidations,[5] hydrophosphonylation of aldehydes and aldimines,[6] hydrosilylation of organic carbonyl compounds,[7] copolymerization of epoxide and CO_2,[8] and polymerization of olefins[9] and lactide.[10] However, all of these catalysts focused on Al(III), Zn(II), Cr(III), and group 4 elements. To our knowledge, there has been no report concerning the application of Salalen ligands to rare-earth organometallic chemistry.

In this paper, the Salalen ligand was introduced to organolanthanide chemistry for the first time, and a series of lanthanide bis(trimethylsilyl)amido and alkoxo complexes supported by unsymmetrical Salalen ligands (amine/imine bis(phenolate)) were prepared and well-characterized, using $Ln[N(SiMe_3)_2]_3(\mu\text{-Cl})Li(THF)_3$ and $(C_5H_5)_3Ln(THF)$ as the precursors. It was found that these lanthanide Salalen complexes are efficient initiators for the ROP of *rac*-LA to give PLAs with good heterotacticity, and the lanthanide alkoxides can initiate *rac*-LA polymerization in a controlled manner. Herein we report these results.

EXPERIMENTAL SECTION

General Procedures. All of the manipulations were performed under a purified argon atmosphere using standard Schlenk techniques. The solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. $HN(SiMe_3)_2$ and *n*-BuLi are commercially available. $HN(SiMe_3)_2$ was dried over CaH_2 for 4 days and distilled before use. $Ln[N(SiMe_3)_2]_3(\mu\text{-Cl})Li(THF)_3$ (Ln = Y, Sm, Nd),[11a−c] $(C_5H_5)_3Ln(THF)$,[11d] and the ligand L^1H_2 (L^1 = (2-O-C_6H_2-Bu^t_2-3,5)CH═$NCH_2CH_2N(Me)CH_2$(2-O-C_6H_2-Bu^t_2-3,5))[12] were prepared according to the procedures reported in the literature. Benzyl alcohol was dried over 4 Å molecular sieves for 1 week and then distilled before use. *rac*-LA was recrystallized twice from dry toluene and then was sublimed under vacuum at 50 °C. Lanthanide analyses were performed by EDTA titration with a xylenol orange indicator and a hexamine buffer.[13] 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**, **4**, and **7** with a Unity Varian spectrometer. Because of their paramagnetism, no resolvable NMR spectra for the other complexes were obtained. Molecular weights and molecular weight distributions (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. The microstructures of PLAs were measured by homodecoupling ^1H NMR spectroscopy at 20 °C in $CDCl_3$ on a Unity Varian AC-400 spectrometer. MALDI-TOF mass spectra were recorded using a Bruker Reflex II mass spectrometer (Bremen, Germany).

Synthesis of Ligand Precursor L^2H_2. A solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (4.68 g, 20 mmol) was added to *N*-methylethylenediamine (1.8 mL, 20 mmol) in methanol (30 mL). The mixture was stirred to give a clear yellow solution at room temperature, and then a solution of 2,4-bis(α,α-dimethylbenzyl)-phenol (8.25 g, 25 mmol) and paraformaldehyde (0.90 g, 30 mmol) in methanol was added. The mixture was refluxed for 24 h and then was cooled. The precipitate was filtered and washed with ice-cold methanol to give the yellow product (9.01 g, 71%). Anal. Calcd for $C_{43}H_{56}N_2O_2$: C, 81.60; H, 8.92; N, 4.43. Found: C, 81.78; H, 8.74; N, 4.66. MS: *m*/*z* calcd for $C_{43}H_{57}N_2O_2$ 633.4420, found 633.4407. ^1H NMR (400 MHz, $DCCl_3$, 25 °C): δ 8.12 (s, 1H, N═CHAr), 7.37 (s, 1H, ArH), 7.20−7.06 (m, 12H, ArH), 6.72 (s, 1H, ArH), 3.61 (s, 2H, $ArCH_2N$), 3.45 (s, 2H, NCH_2), 2.63 (s, 2H, NCH_2), 2.25 (s, 3H, NCH_3), 1.68 (s, 6H, $C(CH_3)_2Ph$), 1.64 (s, 6H, $C(CH_3)_2Ph$), 1.43 (s, 9H, $C(CH_3)_3$), 1.32 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $DCCl_3$, 25 °C): δ 167.31 (N═CHAr), 158.09, 153.90, 151.92, 151.60, 140.10, 136.76, 136.18, 135.29, 128.05, 127.88, 126.99, 126.68, 125.75, 125.03, 124.47, 121.42, 117.89, 109.85 (Ar−C), 62.20 ($ArCH_2N$), 57.62 (NCH_2), 56.41 (NCH_2), 42.62 (NCH_3), 42.15 ($C(CH_3)_2Ph$), 35.15 ($C(CH_3)_3$), 34.27 ($C(CH_3)_3$), 31.66 ($C(CH_3)_3$), 31.24 ($C(CH_3)_2Ph$), 29.57 ($C(CH_3)_3$). IR (KBr pellet, cm^{-1}): 2956 s, 1617 m, 1465 s, 1374 m, 1245 m, 1214 m, 1023 w, 872 w, 767 m, 693 s.

Synthesis of $L^1Y[N(SiMe_3)_2](THF)$ (1). To a THF solution of $Y[N(SiMe_3)_2](\mu\text{-Cl})Li(THF)_3$ (10 mL, 2.89 mmol) was added a THF solution of L^1H_2 (10 mL, 1.47 g, 2.89 mmol). The mixture was stirred for 2 h at room temperature, and then THF was evaporated completely under reduced pressure. Hexane (10 mL) was added to extract the residue twice, and the precipitate formed was removed by centrifugation. The solvent was concentrated to about 8 mL, and colorless crystals were obtained at room temperature in several days (1.91 g, 80%). 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, 62.09; H, 9.43; N, 5.25; Y, 10.98. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 7.71 (d, *J* = 2.5 Hz, 1H, ArH), 7.50 (d, *J* = 2.5 Hz, 1H, ArH), 7.26 (s, 1H, N═CHAr), 6.96 (d, *J* = 2.4 Hz, 1H, ArH), 6.89 (d, *J* = 2.4 Hz, 1H, ArH), 4.37 (d, *J* = 12.8 Hz, 1H, $ArCH_2N$), 3.58 (br, 4H, α-CH_2 THF), 3.21 (m, 1H, NCH_2), 2.75 (d, *J* = 12.8 Hz, 1H, $ArCH_2N$), 2.56 (m, 1H, NCH_2), 2.24 (s, 3H, NCH_3), 2.10 (m, 1H, NCH_2), 1.77 (s, 9H, $C(CH_3)_3$), 1.51 (s, 9H, $C(CH_3)_3$), 1.41 (s, 9H, $C(CH_3)_3$), 1.40 (br, 4H, β-CH_2 THF), 1.31 (s, 9H, $C(CH_3)_3$), 1.27 (m, 1H, NCH_2), 0.38 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ 171.2 (N═CHAr), 163.9, 160.2, 139.7, 137.6, 137.3, 130.7, 129.8, 125.7, 124.9, 122.8, 121.3 (Ar−C), 68.09 (α-CH_2, THF), 65.1 ($ArCH_2N$), 57.2 (NCH_2), 54.0 (NCH_2), 43.9 (NCH_3), 35.8 ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 34.1 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 30.2 ($C(CH_3)_3$), 25.8 (β-CH_2, THF), 5.01 ($SiMe_3$). IR (KBr pellet, cm^{-1}): 2960 s, 2900 s, 2869 s, 1620 s, 1540 m, 1470 s, 1440 s, 1410 m, 1360 m, 1310 m, 1250 m, 1200 w, 1160 m, 933 m, 881 m, 835 s, 742 w, 652 w.

Synthesis of $L^1Sm[N(SiMe_3)_2](THF)$ (2). The synthesis of complex **2** was carried out in the same way as that described for complex **1**, but $Sm[N(SiMe_3)_2](\mu\text{-Cl})Li(THF)_3$ (10 mL, 2.82 mmol) was used instead of $Y[N(SiMe_3)_2](\mu\text{-Cl})Li(THF)_3$. Yellow crystals were obtained in a hexane (7 mL)/THF (1 mL) solution (1.86 g, 74%). 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, 58.36; H, 8.80; N, 4.07; Sm, 16.79. IR (KBr pellet, cm^{-1}): 2960 s, 2900 s, 2869 s, 1620 s, 1540 m, 1470 s, 1440 s, 1410 m, 1360 m, 1310 m, 1250 m, 1200 w, 1160 m, 928 m, 877 m, 839 s, 742 w, 617 w.

Synthesis of $L^1Nd[N(SiMe_3)_2](THF)$ (3). The synthesis of complex **3** was carried out in the same way as that described for

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complex **1**, but Nd[N(SiMe$_3$)$_2$](μ-Cl)Li(THF)$_3$ (12 mL, 2.95 mmol) was used instead of Y[N(SiMe$_3$)$_2$](μ-Cl)Li(THF)$_3$. Green crystals were obtained in a hexane (9 mL)/THF (1 mL) solution (2.01 g, 77%). 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, 58.66; H, 8.41; N, 4.93; Nd, 16.45. IR (KBr pellet, cm^{-1}): 2960 s, 2910 s, 2869 s, 1620 s, 1530 m, 1470 s, 1440 s, 1410 m, 1360 m, 1310 m, 1250 m, 1200 w, 1160 m, 933 m, 876 m, 835 s, 741 w, 611 w.

Synthesis of [L^{1}Y(OCH$_2$Ph)]$_2$ (4). *Method A.* To a hexane solution of complex **1** (1.87 g, 2.26 mmol) was added a hexane solution of benzyl alcohol (0.23 mL, 2.26 mmol), and a white powder formed immediately. The reaction mixture was stirred for 1 h at room temperature, and then the precipitate that formed was collected by centrifugation. Benzene (10 mL) and THF (1 mL) were added to extract the residue. Colorless crystals were obtained at 5 °C in several days (1.35 g, 85%). Anal. Calcd for $C_{80}H_{114}N_4O_6Y_2$: C, 68.36; H, 8.18; N, 3.99; Y, 12.65. Found: C, 68.79; H, 8.77; N, 3.68; Y, 12.84. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.82 (d, J = 2.4 Hz, 2H, ArH), 7.41 (m, 6H, ArH), 7.32 (s, 2H, N=CHAr), 7.00 (m, 8H, ArH), 6.88 (d, J = 2.4 Hz, 2H, ArH), 5.30 (d, J = 12.5 Hz, 2H, OCH$_2$Ph), 5.14 (d, J = 12.5 Hz, 2H, OCH$_2$Ph), 3.94 (d, J = 12.8 Hz, 2H, ArCH$_2$N), 2.99 (m, 2H, NCH$_2$), 2.80 (d, J = 12.8 Hz, 2H, ArCH$_2$N), 2.68 (s, 6H, NCH$_3$), 2.54 (m, 2H, NCH$_2$), 2.12 (m, 2H, NCH$_2$), 1.94 (s, 18H, C(CH$_3$)$_3$), 1.44 (s, 18H, C(CH$_3$)$_3$), 1.43 (s, 18H, C(CH$_3$)$_3$), 1.37 (s, 18H, C(CH$_3$)$_3$), 1.34 (m, 2H, NCH$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 170.2 (N=CHAr), 164.1, 160.9, 138.7, 136.8, 130.5, 129.8, 127.1, 125.3, 124.2, 123.5, 122.4 (Ar−C), 69.2 (OCH$_2$Ph), 65.2 (ArCH$_2$N), 58.2 (NCH$_2$), 54.5 (NCH$_2$), 45.3 (NCH$_3$), 36.1 (C(CH$_3$)$_3$), 35.4 (C(CH$_3$)$_3$), 34.2 (C(CH$_3$)$_3$), 32.3 (C(CH$_3$)$_3$), 31.8 (C(CH$_3$)$_3$), 30.7 (C(CH$_3$)$_3$), 30.0 (C(CH$_3$)$_3$). IR (KBr pellet, cm^{-1}): 2950 s, 2900 s, 2860 s, 1620 s, 1530 m, 1470 s, 1440 s, 1410 s, 1360 m, 1310 m, 1230 m, 1200 m, 1160 m, 1010 m, 879 w, 839 w, 744 w, 696 w, 650 w.

Method B. To a THF solution of (C$_5$H$_5$)$_3$Y(THF) (1.00 g, 2.81 mmol) was added a THF solution of L^{1}H$_2$ (1.44 g, 2.81 mmol). The reaction mixture was stirred for 1 h at room temperature, and then benzyl alcohol (0.29 mL, 2.81 mmol) was added by a syringe. The mixture was stirred for 24 h, and then THF was evaporated completely under vacuum. Toluene (10 mL) and THF (1 mL) were added to extract the residue. Colorless crystals were obtained at 5 °C in several days (1.58 g, 80%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.81 (s, 2H, ArH), 7.45 (m, 6H, ArH), 7.32 (s, 2H, N=CHAr), 6.94 (m, 8H, ArH), 6.88 (s, 2H, ArH), 5.30 (d, J = 12.6 Hz, 2H, OCH$_2$Ph), 5.13 (d, J = 12.3 Hz, 2H, OCH$_2$Ph), 3.94 (d, J = 12.9 Hz, 2H, ArCH$_2$N), 2.99 (m, 2H, NCH$_2$), 2.80 (d, J = 12.8 Hz, 2H, ArCH$_2$N), 2.68 (s, 6H, NCH$_3$), 2.59 (m, 2H, NCH$_2$), 2.07 (m, 2H, NCH$_2$), 1.94 (s, 18H, C(CH$_3$)$_3$), 1.45(m, 36H, C(CH$_3$)$_3$), 1.37 (s, 18H, C(CH$_3$)$_3$), 1.31 (m, 2H, NCH$_2$).

Synthesis of [L^{1}Sm(OCH$_2$Ph)]$_2$ (5). The synthesis of complex **5** was carried out in the same way as that described for complex **4** (method A), but complex **2** (2.14 g, 2.40 mmol) was used instead of complex **1**. Yellow crystals were obtained in a hexane (10 mL)/THF (3 mL) solution (1.40 g, 76%). Anal. Calcd for $C_{80}H_{114}N_4O_6Sm_2$: C, 62.86; H, 7.52; N, 3.67; Sm, 19.67. Found: C, 62.55; H, 7.69; N, 3.81; Sm, 19.54. IR (KBr pellet, cm^{-1}): 2950 s, 2901 s, 2860 s, 1620 s, 1530 m, 1470 s, 1440 s, 1410 s, 1360 m, 1310 m, 1230 m, 1200 m, 1160 m, 1010 m, 879 w, 841 w, 744 w, 695 w, 650 w.

Synthesis of [L^{1}Yb(OCH$_2$Ph)]$_2$ (6). The synthesis of complex **6** was carried out in the same way as that described for complex **4** (method B), but (C$_5$H$_5$)$_3$Yb(THF) (1.23 g, 2.80 mmol) was used instead of (C$_5$H$_5$)$_3$Y(THF). Yellow crystals were obtained in a hexane (12 mL)/THF (2 mL) solution (1.70 g, 77%). Anal. Calcd for $C_{80}H_{114}N_4O_6Yb_2$: C, 61.05; H, 7.30; N, 3.56; Yb, 21.99. Found: C, 61.32; H, 7.68; N, 3.24; Yb, 22.25. IR (KBr pellet, cm^{-1}): 2950 s, 2900 s, 2860 s, 1620 s, 1530 m, 1470 s, 1440 s, 1410 s, 1360 m, 1310 m, 1230 m, 1200 m, 1160 m, 1010 m, 879 w, 841 w, 744 w, 695 w, 650 w.

Synthesis of [L^{2}Y(OCH$_2$Ph)]$_2$ (7). The synthesis of complex **7** was carried out in the same way as that described for complex **4** (method B), but L^{2}H$_2$ (1.74 g, 2.75 mmol) was used instead of L^{1}H$_2$. Colorless crystals were obtained in a hexane (9 mL)/THF (5 mL) solution (1.89 g, 83%). Anal. Calcd for $C_{100}H_{122}N_4O_6Y_2$: C, 72.62; H, 7.44; N, 3.39; Y, 10.75. Found: C, 72.82; H, 7.77; N, 3.21; Y, 11.08. IR (KBr pellet, cm^{-1}): 2952 s, 2900 s, 2866 s, 1620 s, 1530 m, 1470 s, 1440 s, 1410 s, 1360 m, 1310 m, 1230 m, 1208 m, 1160 m, 1015 m, 879 w, 839 w, 744 w, 696 w, 643 w. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.80 (d, J = 2.3 Hz, 2H, ArH), 7.35 (m, 8H, ArH), 7.30 (d, J = 2.3 Hz, 2H, ArH), 7.22 (s, 2H, N=CHAr), 7.14 (s, 2H, ArH), 7.02 (m, 10H, ArH), 6.93 (d, J = 2.3 Hz, 2H, ArH), 6.85 (m, 10H, ArH), 6.75 (d, J = 2.3 Hz, 2H, ArH), 4.76 (d, J = 12.4 Hz, 2H, OCH$_2$Ph), 4.54 (d, J = 12.4 Hz, 2H, OCH$_2$Ph), 3.68 (d, J = 13.2 Hz, 2H, ArCH$_2$N), 2.93 (m, 2H, NCH$_2$), 2.58 (d, J = 13.2 Hz, 2H, ArCH$_2$N), 2.52 (s, 6H, NCH$_3$), 2.09 (m, 2H, NCH$_2$), 1.87 (s, 18H, C(CH$_3$)$_3$), 1.78 (m, 2H, NCH$_2$), 1.67 (m, 12H, C(CH$_3$)$_2$Ph), 1.58 (s, 6H, C(CH$_3$)$_2$Ph), 1.43 (s, 18H, C(CH$_3$)$_3$), 1.41 (m, 6H, C(CH$_3$)$_2$Ph), 1.29 (m, 2H, NCH$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 170.2 (N=CHAr), 164.0, 160.6, 152.4, 143.7, 138.6, 136.8, 136.2, 135.8, 130.7, 129.8, 128.6, 128.6, 127.5, 127.3, 126.9, 125.6, 124.7, 124.0, 122.5 (Ar−C), 68.7 (OCH$_2$Ph), 64.9 (ArCH$_2$N), 58.2 (NCH$_2$), 54.5 (NCH$_2$), 45.1 (NCH$_3$), 42.9 (C(CH$_3$)$_2$Ph), 42.6(C(CH$_3$)$_2$Ph), 36.1 (C(CH$_3$)$_3$), 34.2 (C(CH$_3$)$_3$), 31.9 (C(CH$_3$)$_3$), 31.6 (C(CH$_3$)$_2$Ph), 31.0 ((C(CH$_3$)$_2$Ph)).

Typical Procedure for the Polymerization Reaction. The procedures for the polymerization of *rac*-LA initiated by the complexes **1**−**7** were similar, and a typical polymerization procedure is given below. A 20 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with the desired amount of monomer and solvent. After the monomer was dissolved, a solution of the initiator was added to this solution by syringe. The mixture was immediately 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 ethanol and then poured into ethanol to precipitate the polymer, which was dried under vacuum and weighed.

Oligomer Preparation. The oligomerization of *rac*-LA was carried out with complex **4** as the initiator in THF and toluene, respectively, at 25 °C under the condition of a [monomer]/[initiator] molar ratio of of 20. The reaction mixture was stirred for 0.5 h and then quenched by adding *n*-hexane and 1 drop of water. The precipitated oligomers were collected, dried under vacuum, and used for ^{1}H NMR, ^{13}C NMR, and MALDI-TOF measurement.

X-ray Crystallographic Structure Determination. 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 S1 (Supporting Information).

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. The hydrogen atoms in these complexes were 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 calculations in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELXL-97 programs.

RESULTS AND DISCUSSION

Synthesis and Characterization of Salalen Lanthanide Complexes. An amine elimination reaction is a straightforward method for the synthesis of lanthanide amides, and the standard precursors are Ln[N(SiMe$_3$)$_2$]$_3$ and Ln[N(SiMe$_3$)$_2$]$_3$(μ-Cl)Li(THF)$_3$. However, for the Salen ligands, the popular precursor used is the sterically less demanding but valuable bis(dimethylsilyl)amido lanthanide complex Ln[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$. The cheaper Ln[N(SiMe$_3$)$_2$]$_3$ reacted with the ligand precursor SalenH$_2$ to form generally an oligomeric, THF-insoluble product.[14] When the Salalen ligand precursors were prepared, we wanted to know whether

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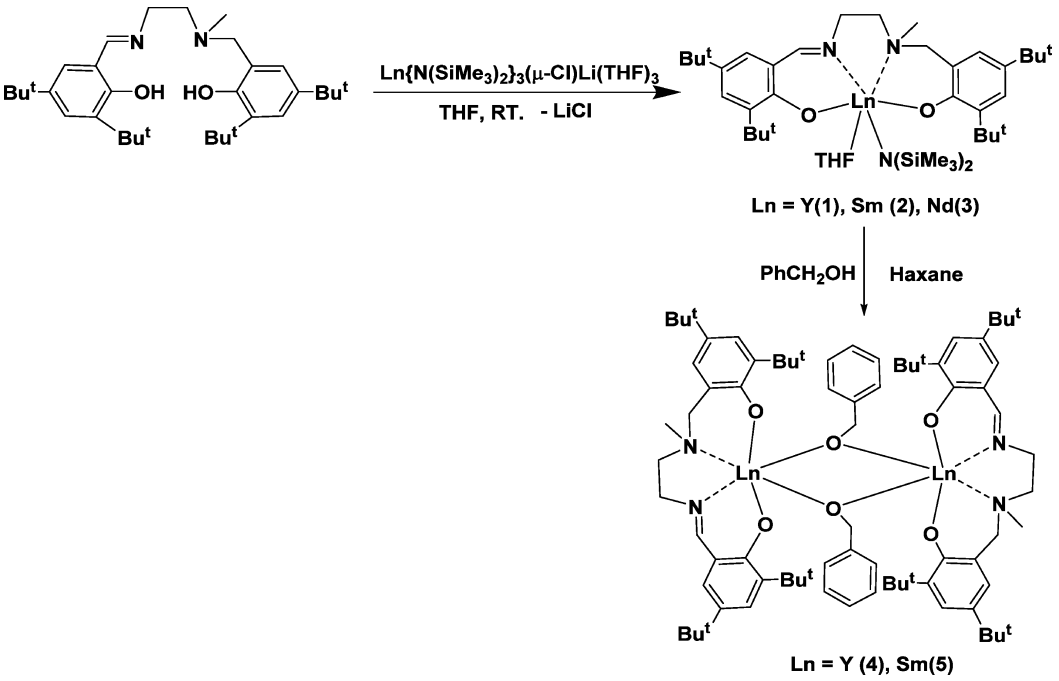
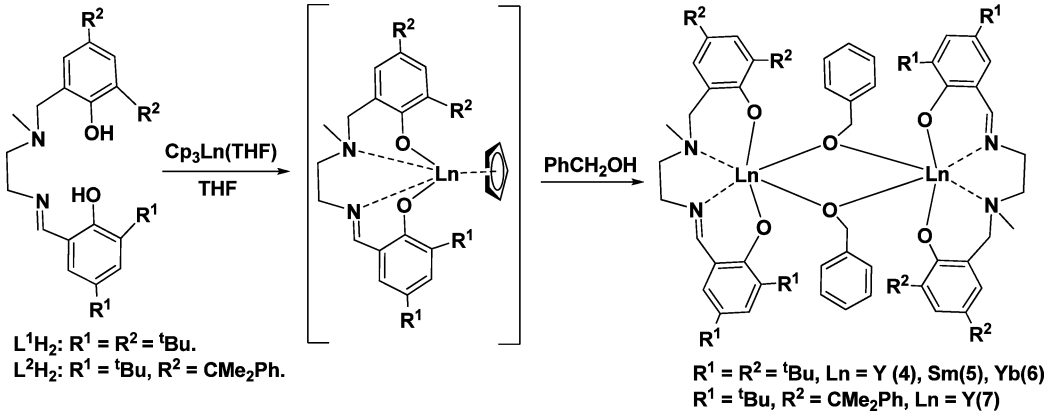
Scheme 1



Scheme 2



$Ln[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3$ could be used as the precursor to synthesize the Salalen lanthanide amido complexes. Thus, an NMR-scale reaction was conducted first. When $Y[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3$ was added to a C_6D_6 solution of 1 equiv of L^1H_2, the yellow solution turned slightly muddy, indicating that LiCl might be formed. The ^1H NMR spectrum showed that the O*H* signals of the ligand precursor at 13.92 and 10.92 ppm disappeared, and single sharp resonances at 0.10 ppm for $HN(SiMe_3)_2$ and at 0.38 ppm for $LY\text{-}N(SiMe_3)_2$ arose, which demonstrated that the Salalen yttrium amide was formed. On a preparative scale, $Y[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3$ reacted with L^1H_2 in THF in a 1:1 molar ratio for 2 h at room temperature; after workup, the desired neutral yttrium amido complex $L^1Y[N(SiMe_3)_2](THF)$ (**1**) was isolated from a concentrated hexane solution as colorless microcrystals in high yield (80%). This method can also be used to synthesize the Salalen lanthanide amides with larger ionic radii, and $L^1Ln[N(SiMe_3)_2](THF)$ (Ln = Sm (**2**), Nd (**3**)) were also obtained, as shown in Scheme 1. These results proved that the cheap $Ln[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3$ is a useful starting material for preparing Salalen lanthanide amides.

An NMR monitoring reaction revealed that $Y[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3$ reacted with the Salalen ligand precursor L^2H_2 (L^2 = (2-O-C_6H_2-Bu^t_2-3,5)CH═$NCH_2CH_2NMeCH_2${2-O-C_6H_2-$(CPhMe_2)_2$-3,5}), possessing larger substituents on the phenol ring, to give also the yttrium amide $L^2Y[N(SiMe_3)_2]$-(THF). However, this compound could not be isolated because of its very good solubility even in *n*-pentane.

A further NMR-tube reaction revealed that these Salalen lanthanide complexes can be transferred to the corresponding Salalen lanthanide alkoxides. When equimolar $PhCH_2OH$ was added to a C_6D_6 solution of complex **1**, the peak at 0.38 ppm disappeared and two doublet peaks at 5.30 and 5.14 ppm appeared, which can be attributed to the resonances of the $PhCH_2O$ group of the target yttrium alkoxide. Thus, reactions of the Salalen lanthanide amides with benzyl alcohol produced the dimeric Salalen lanthanide alkoxo complexes $[L^1Ln\text{-}(OCH_2Ph)]_2$ (Ln = Y (**4**), Sm (**5**)) in high isolated yields, as shown in Scheme 1.

We recently found that the easily available $Cp_3Ln(THF)$ is a useful precursor for preparing bridged bis(phenolate) lanthanide alkoxo complexes.[3c,d] Thus, we tried to synthesize the

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lanthanide alkoxo complex stabilized by L^2 using $Cp_3Y(THF)$ as the precursor. A ^1H NMR monitoring reaction revealed that the reaction did not occur immediately when $Cp_3Y(THF)$ was added to a C_6D_6 solution of 1 equiv of L^2H_2, because of the insolubility of $Cp_3Y(THF)$ in C_6D_6. However, when the mixture was heated slightly, the precipitate of $Cp_3Y(THF)$ disappeared, and the solution changed from yellow to brilliant yellow, indicating that the reaction took place. In the ^1H NMR spectrum, the signals of O*H* of the ligand precursor disappeared and a single sharp resonance at 6.33 ppm for the cyclopentadienyl group appeared. In addition, the splitting peaks for the eliminated cyclopentadiene were also observed at 6.49, 6.30, and 2.69 ppm. These results indicated the formation of a Salalen yttrium cyclopentadienyl complex. After equimolar $PhCH_2OH$ was added, the brilliant yellow solution turned slightly muddy immediately, the single sharp resonance at 6.33 ppm almost disappeared, and two doublet peaks at 4.76 and 4.54 ppm of the $PhCH_2O$ group appeared, which indicated the transformation of the Salalen yttrium cyclopentadienyl complex to a Salalen yttrium alkoxo complex. On a preparative scale, the expected Salalen yttrium alkoxo complex $[L^2Y(OCH_2Ph)]_2$ (**7**) was obtained in high isolated yield. A further study revealed that complexes **4**–**6** can also be synthesized via the proton exchange reactions of $(C_5H_5)_3Ln(THF)$ with L^1H_2 in a 1:l molar ratio in THF for 1 h and then with 1 equiv of benzyl alcohol, as shown in Scheme 2.

The compositions of complexes **1**–**7** were confirmed by elemental analysis and NMR spectroscopy in the cases of complexes **1**, **4**, and **7**. The definitive molecular structures were determined by single-crystal structure analysis. Complexes **1**–**7** 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 they were stored under argon. Complexes **1**–**3** are freely soluble in hexane, while compounds **4**–**7** are freely soluble in THF and toluene and slightly soluble in hexane.

Crystal Structures. Crystals suitable for an X-ray structure determination of complexes **1**–**3** were obtained from a hexane solution at room temperature, whereas the crystals of complex **4** were obtained from a benzene solution and complexes **5**–**7** were obtained from a hexane/THF solution. The selected bond lengths and angles for these complexes are provided in Tables 1 and 2.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 1–3

	1	2	3
	Bond Lengths		
Ln1–O1	2.131(5)	2.186(4)	2.234(5)
Ln1–O2	2.152(5)	2.199(4)	2.201(4)
Ln1–O3	2.410(6)	2.497(4)	2.554(5)
Ln1–N1	2.419(8)	2.498(5)	2.552(5)
Ln1–N2	2.617(6)	2.684(4)	2.773(6)
Ln1–N3	2.330(6)	2.374(5)	2.397(5)
	Bond Angles		
O3–Ln1–N1	161.53(16)	159.31(16)	155.82(18)
O1–Ln1–O2	96.0(2)	95.81(15)	100.03(18)
O2–Ln1–N2	72.5(2)	70.93(14)	70.05(16)
N2–Ln1–N3	93.5(2)	93.75(15)	92.80(18)
N3–Ln1–O1	105.3(2)	107.14(15)	114.05(18)

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 4–7

	4	5	6	7
	Bond Lengths			
Ln1–O1	2.139(6)	2.196(4)	2.133(5)	2.150(4)
Ln1–O2	2.108(6)	2.183(4)	2.106(5)	2.129(4)
Ln1–O3	2.261(6)	2.342(4)	2.237(6)	2.273(3)
Ln1–O3A	2.265(5)	2.318(4)	2.222(5)	2.281(3)
Ln1–N1	2.427(7)	2.504(5)	2.393(7)	2.438(5)
Ln1–N2	2.551(7)	2.611(5)	2.488(7)	2.522(4)
	Bond Angles			
O1–Ln1–N2	144.2(2)	141.20(2)	147.8(2)	144.69(14)
N1–Ln1–O2	91.7(2)	88.00(16)	92.1(2)	92.25(15)
O2–Ln1–O3	97.3(2)	160.03(16)	96.3(2)	92.31(13)
O3–Ln1–O3A	72.5(2)	72.31(16)	73.4(2)	73.07(13)
O3A–Ln1–N1	96.3(2)	171.13(14)	96.4(2)	99.43(14)
N1–Ln1–O3	167.0(2)	99.31(15)	167.8(2)	163.42(15)
O2–Ln1–O3A	162.2(2)	99.02(15)	164.1(2)	162.84(14)

X-ray diffraction analyses displayed that complexes **1**–**3** are isostructural and have solvated monomeric structures. Thus, only the ORTEP diagram of complex **1** is shown in Figure 1.

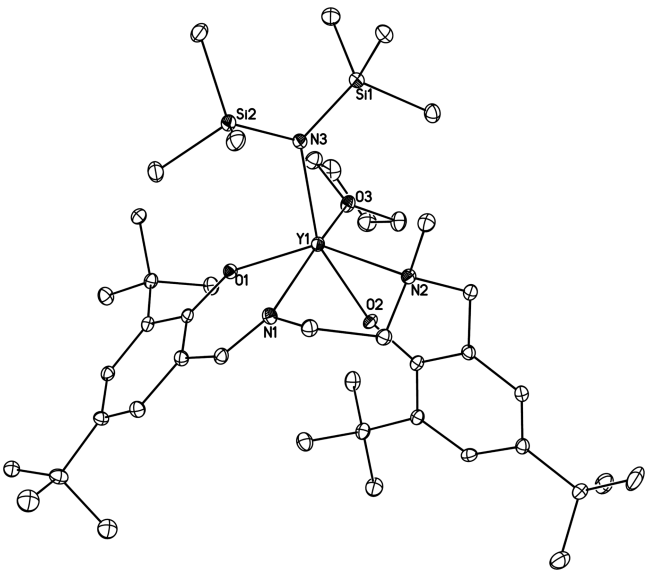

Figure 1. ORTEP diagram of complex **1** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level, and hydrogen atoms are omitted for clarity. Complexes **2** and **3** are isomorphous with complex **1**.

Just as for Salan and Salen lanthanide complexes,[4b,14] the two nitrogen atoms of the imine and amine bridges were found to bind to the metal center in the solid state. The lanthanide ion is six-coordinated by two oxygen atoms and two nitrogen atoms from the dianionic Salalen ligand, one nitrogen atom from the amido group, and one oxygen atom from one THF molecule. The coordination geometry around the metal center can be best described as a slightly distorted octahedron, in which O(1), O(2), N(2), and N(3) occupy equatorial positions and O(3) and N(1) occupy axial positions. In complexes **1**–**3**, the average Ln–O(Ar) bond lengths are 2.142(5), 2.193(4), and 2.218(5) Å, respectively. The increasing trend Y < Sm < Nd reflects the usual lanthanide contraction from Nd^{3+} to Y^{3+}. Similar consequences are also observed from the Ln–N bond

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lengths in these complexes. As expected, the Ln−N(imine) bond length is considerably shorter than the Ln−N(amine) bond length.

In complex **1**, the Y−O(Ar) bond length of 2.142(5) Å is in accord with the values in bridged bis(phenolate) yttrium complexes, such as (Salen)Y[N(SiHMe$_2$)$_2$](THF) (2.16 Å; Salen = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-ethylenediamine]),[14a] [NNOO]Y(OC$_6$H$_4$-4-CH$_3$)(THF) (2.152(4) Å; NNOO = Me$_2$NCH$_2$CH$_2$N{CH$_2$-(2-O-C$_6$H$_2$-Bu$^t_2$-3,5)}$_2$),[3c] [NNOO]Y(OCH$_2$CF$_3$)(THF) (2.158(3) Å),[3d] and [ONOO]Y[N(SiHMe$_2$)$_2$](THF) (2.151(2) Å; ONOO = MeOCH$_2$CH$_2$N{CH$_2$-(2-O-C$_6$H$_2$-^{t}Bu$_2$-3,5)}$_2$).[15]

Complexes **4**−**6** are isostructural and have unsolvated dimeric structures. The ORTEP diagram of complex **4** is shown in Figure 2. Complexes **4**−**6** contain a Ln$_2$O$_2$ core

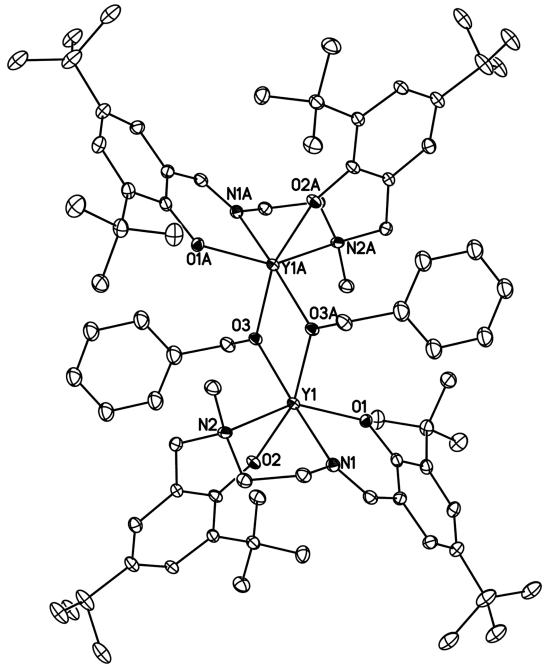

Figure 2. ORTEP diagram of complex **4** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level, and hydrogen atoms are omitted for clarity. Complexes **5** and **6** are isomorphous with complex **4**.

bridging through the oxygen atoms of the two OCH$_2$Ph groups. Each of the lanthanide atoms is six-coordinated by two oxygen atoms and two nitrogen atoms from the dianionic Salalen ligand and two oxygen atoms from the two OCH$_2$Ph groups. The average Y−O(Ar) bond length of 2.124(6) Å in complex **4** is comparable with the corresponding value in complex **1**. The average Y−O(CH$_2$Ph) bond length (2.263(5) Å) is in accord with the values in [(Salan)Y(OPr^i)]$_2$ (2.276(2) Å; Salan = MeN(CH$_2$)$_2$MeN{CH$_2$-(2-O-C$_6$H$_2$-Bu$^t_2$-3,5)}$_2$).[4b] Complex **7** also has an unsolvated dimeric structure, and the ORTEP diagram is shown in Figure 3. The coordination environment around yttrium atom in complex **7** is identical with those in complexes **4**−**6**. The Y−O(Ar) and Y−O(CH$_2$Ph) bond lengths are 2.140(4) and 2.277(3) Å, respectively, which are consistent with the corresponding bond lengths in complex **4**.

Ring-Opening Polymerization of *rac*-LA by Complexes 1−7. To understand the relationship of the structures of these Salalen lanthanide complexes on the polymerization activity, controllability, and stereoselectivity, the catalytic

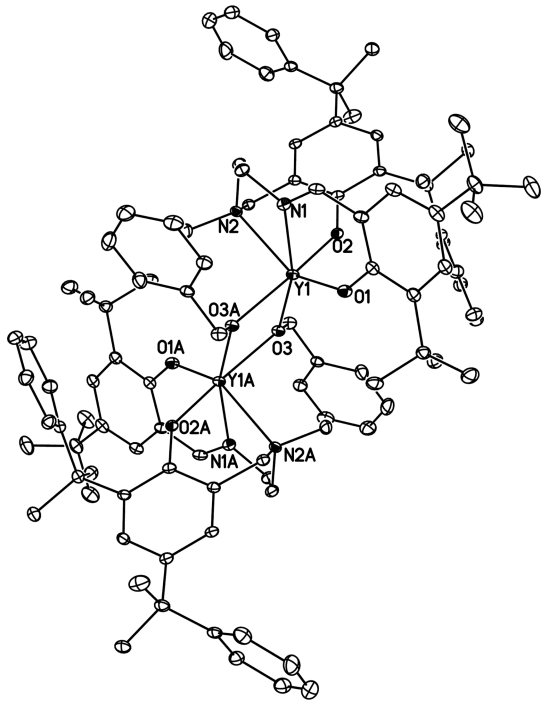

Figure 3. ORTEP diagram of complex **7** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level, and hydrogen atoms are omitted for clarity.

behaviors of complexes **1**−**7** for the ROP of *rac*-*β*-butyrolactone and *rac*-LA were examined. To our surprise, these Salalen lanthanide complexes are inert for *rac*-*β*-butyrolactone polymerization. It has reported that the lanthanide amido and alkoxo complexes stabilized by Salan and amine bridged bis(phenolate) ligands showed good activity and stereoselectivity for *rac*-*β*-butyrolactone.[3,4b] These results indicated that the backbone of the ancillary ligands has a crucial influence on the catalytic property of the corresponding lanthanide derivatives for *rac*-*β*-butyrolactone polymerization. It was found that these Salalen lanthanide complexes are active for *rac*-LA polymerization, and the representative polymerization data are summarized in Table 3.

It can be seen that all of the lanthanide amido complexes can initiate the ROP of *rac*-LA to give the PLAs with high molecular weights. Polymerization media play a key role not only in polymerization activity but also in stereoselectivity. For example, using complex **1** as the initiator, the yield is 99% and P_r is 0.84 (P_r = probability of racemic enchainment) in THF, when the molar ratio of monomer to initiator is 400 (Table 3, entry 2), whereas the yield is only 85% and P_r is 0.60 in toluene even when the reaction time is extended to 5 h under the same polymerization conditions (Table 3, entry 5).

The ionic radii of the lanthanide metals have an obvious effect on the catalytic activity and stereoselectivity for *rac*-LA polymerization. Using neodymium complex **3** as the initiator, the yield is 90% when the molar ratio of monomer to initiator is 2000 in 1 h (Table 3, entry 9), whereas the yield is 68% using yttrium complex **1** as the initiator (Table 3, entry 4). The decreasing activity order Nd > Sm > Y is in agreement with the order of their ionic radii, which is also consistent with the active trend observed in the other lanthanide initiator systems for *rac*-LA polymerization.[3d,16] This may be attributed to the larger ionic radii resulting in a greater opening of the metal

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Table 3. Polymerization of *rac*-LA Initiated by Complexes 1−6[a]

cntry	cat.	$[M]_0/[I]_0$	t	yield (%)[b]	M_c[c] ($\times 10^4$)	M_n[d] ($\times 10^4$)	PDI[d]	P_r[e]
1	**1**	400	30 min	90	5.18	4.66	1.44	0.85
2	**1**	400	1 h	99	5.70	4.47	1.51	0.84
3	**1**	1000	1 h	90	12.96	12.02	1.47	0.85
4	**1**	2000	1 h	68	19.58	9.23	1.47	0.85
5[f]	**1**	400	5 h	85	4.90	5.73	1.58	0.60
6	**2**	1000	1 h	92	13.25	11.70	1.57	0.72
7	**2**	2000	1 h	82	23.62	10.44	1.66	0.72
8	**3**	1000	1 h	95	13.68	11.33	1.40	0.69
9	**3**	2000	1 h	90	25.92	13.06	1.51	0.69
10	**4**	100	2 h	90	1.30	1.51	1.30	0.85
11	**4**	200	2 h	94	2.71	3.40	1.33	0.85
12	**4**	400	1 h	77	4.44	3.92	1.23	0.84
13	**4**	400	2 h	94	5.41	4.67	1.17	0.85
14	**4**	600	2 h	90	7.78	7.22	1.27	0.85
15	**4**	800	2 h	87	10.02	10.57	1.22	0.83
16	**5**	800	2 h	95	10.94	11.24	1.25	0.73
17	**6**	400	3 h	85	4.90	5.45	1.18	0.76
18	**7**	400	2 h	96	5.53	5.79	1.29	0.85
19	**7**	600	2 h	91	7.86	8.16	1.14	0.83

[a]General polymerization conditions: THF as the solvent, [*rac*-LA] = 1 mol/L, at 25 °C. [b]Yield: (weight of polymer obtained)/(weight of monomer used). [c]$M_c = 144.13 \times [M]_0/[I]_0 \times$ (polymer yield) (%). [d]Measured by GPC calibrated with standard polystyrene samples. [e]Measured by homodecoupling ^{1}H NMR spectroscopy at 25 °C. [f]In toluene.

coordination sphere in the vicinity of the σ ligand, which makes the insertion of *rac*-LA into Ln−N bonds easier. These Salalen lanthanide amido complexes polymerize *rac*-LA to give PLAs with moderate to good heterotacticity. The increasing order in heterotacticity Nd (P_r = 0.69) < Sm (P_r = 0.72) < Y (P_r = 0.84−0.85) follows the decreasing order of ionic radii of the central metal, which indicated that a crowded coordination environment around the metal center is essential for higher stereoselectivity for *rac*-LA polymerization. The influence of the ionic radii of the metal center in this system is in agreement with the observations reported in the amine-bridged bis(phenolate)−lanthanide systems.[3a,d,17] It has been reported that the aluminum methyl complex of the same Salalen ligand showed isotactic selectivity for *rac*-LA polymerization (P_m = 0.61),[10c] whereas the Ti(IV) counterpart complex showed atactic selectivity (P_r = 0.50).[10b] However, the heterotactic selectivity can reach P_r = 0.85 in our cases. These results indicated that the stereoselectivity of a metal complex for the ROP of *rac*-LA is affected by the Lewis acidity of the central metal.

Generally, the polymerization initiated by lanthanide amides was not well-controlled, because the silylamide group is less nucleophilic than alkoxide, which caused a relatively slow initiation.[3a,18] To explore the difference in the initiation of the polymerization between the amide and the alkoxide groups in our system, the catalytic behavior of the lanthanide alkoxides **4**−**6** toward the polymerization of *rac*-LA was also examined. As anticipated, the polymerization was more slowly initiated by complexes **4**−**6** in comparison with complexes **1**−**3**. For example, using the amido complex **1** as the initiator, the polymerization was complete in 1 h when the molar ratio of monomer to initiator was 400 (Table 3, entry 1). However, the yield was 77% when the polymerization was initiated by complex **4** under the same polymerization conditions (Table 3, entry 12). A similar phenomenon was also observed in the dithiaalkanediyl-bridged lanthanide amide systems.[18] This difference might also be attributed to the fact that the Salalen lanthaide alkoxides have dimeric structures, and the cleavage of the dimeric structure by the monomer is slow.

The property of the initiating groups has an obvious effect not only on the catalytic activity but also on the controllability for *rac*-LA polymerization. The Salalen lanthanide alkoxides showed better controllability for *rac*-LA polymerization than the lanthanide amides, to give polymers with narrow molecular weight distributions (1.17−1.33). 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 as shown in Figure 4 (Table 3, entries 10, 11, and 13−15).

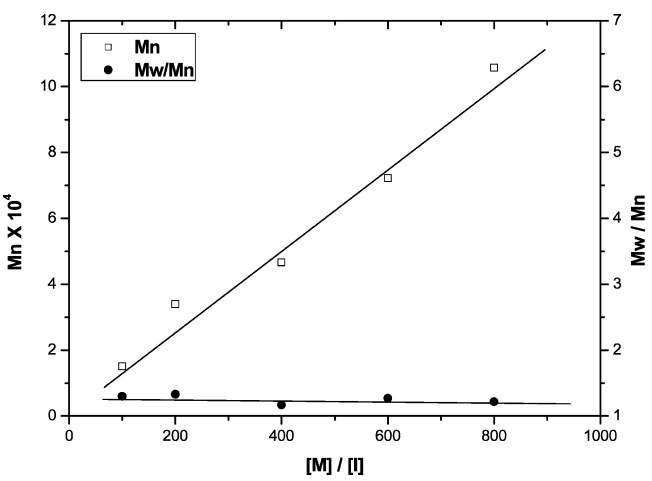

Figure 4. Polymerization of *rac*-LA initiated by complex **4** in THF at 25 °C: relationship between the number-average molecular weight (M_n) and the molar ratio of monomer to initiator.

When the molar ratio of monomer to initiator increased, the molecular weights of the resultant polymers increased linearly, whereas the molecular weight distributions were kept almost unchanged, indicating that the polymerization process is controlled.

The initiation groups had no obvious effect on the stereoselectivity. These Salalen lanthanide akoxo complexes showed similar stereoselectivities for *rac*-LA polymerization in comparison with the corresponding lanthanide amides. These results are consistent with those observed in the literature.[3a,18] To elucidate the influence of the bulkiness of the substituent on the phenol ring on the polymerization stereoselectivity, the polymerization behavior of $[L^2Y(OCH_2Ph)]_2$ (**7**) for the ROP of *rac*-LA was further examined. It was found that the steric bulkiness of the substituent group on the phenol ring has no obvious effect on the stereoselectivity in our system. The P_r value of the PLA initiated by complex **7** is almost the same as that of the PLA initiated by complex **4**. A similar phenomenon was also found by Okuda's group in the dithiaalkanediyl-bridged lanthanide amide systems.[18] However, Carpentier and co-workers found that bulky and conformationally flexible *ortho* substituents enhanced the heteroselectivity in the amine bridged bis(phenolate) lanthanide systems.[3a,19]

The initiation mechanism was elucidated by end group analysis of the oligomer of *rac*-LA, which was prepared by the

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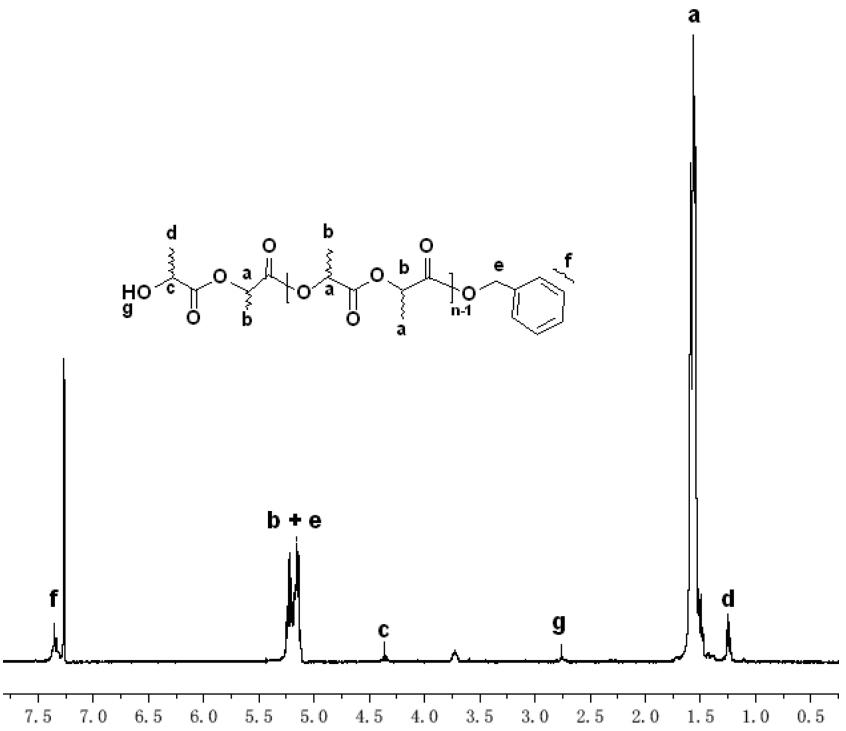

Figure 5. ^{1}H NMR spectrum of *rac*-LA oligomer initiated by complex **4** in $CDCl_3$ ([*rac*-LA]$_0$/**4** = 20:1, 25 °C).

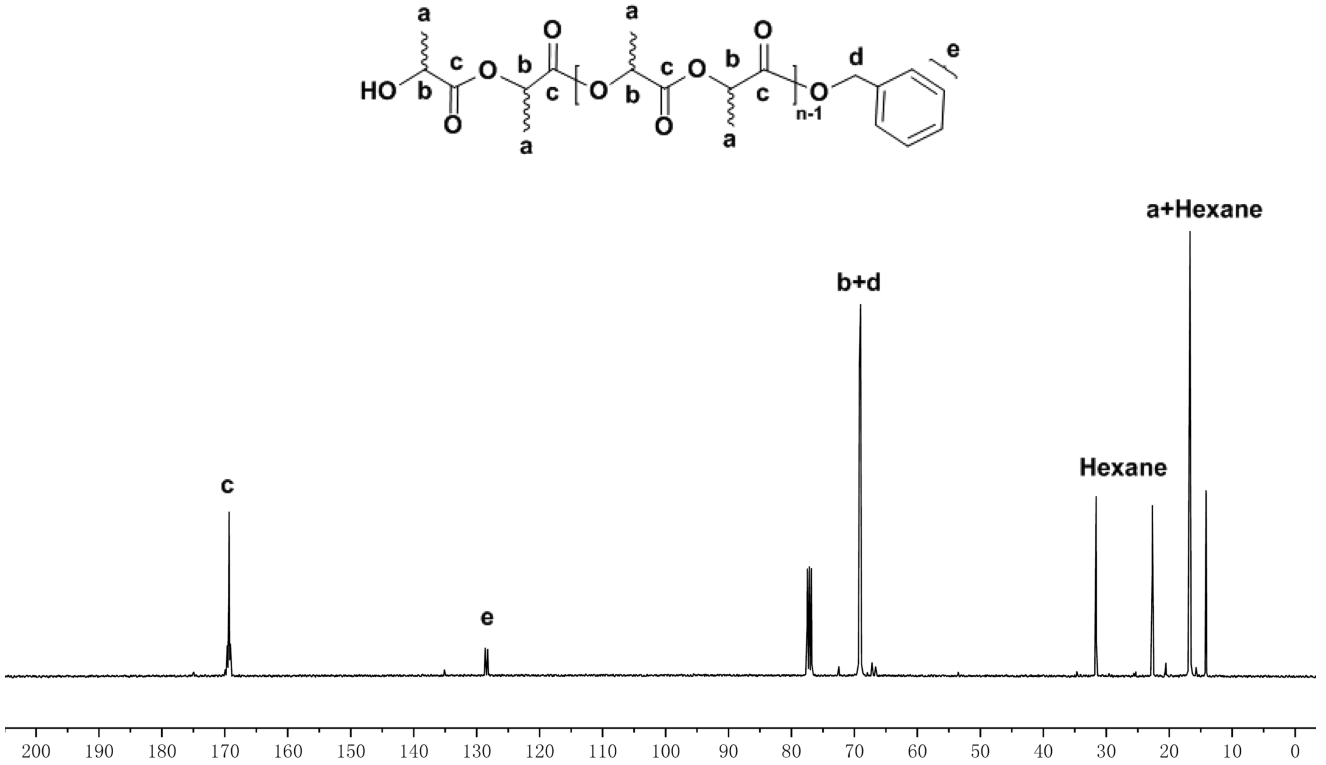

Figure 6. ^{13}C NMR spectrum of *rac*-LA oligomer initiated by complex **4** in $CDCl_3$ ([*rac*-LA]$_0$/**4** = 20:1, 25 °C).

reaction of complex **4** with *rac*-LA in a 1:20 molar ratio. End-group analysis by ^{1}H NMR spectroscopy showed clearly the existence of a benzyloxy group and a $HOCH(CH_3)CO-$ group according to the resonances at about 7.35 ppm for the former and at 1.26, 2.75, and 4.34 ppm for the latter, as shown in Figure 5. Meanwhile, no proton resonance of the Salalen ligand was observed in the ^{1}H NMR spectrum of the oligomer, which revealed that the Salalen group was not involved in the polymerization process. The existence of a benzyloxy group was also confirmed by ^{13}C NMR spectroscopy, according to the resonance at about 128.6 ppm (Figure 6). A MALDI-TOF mass spectrum further revealed that only oligomers with $PhCH_2O-$ end groups were formed (Figure 7), and it also indicated that there is a small degree of transesterification side

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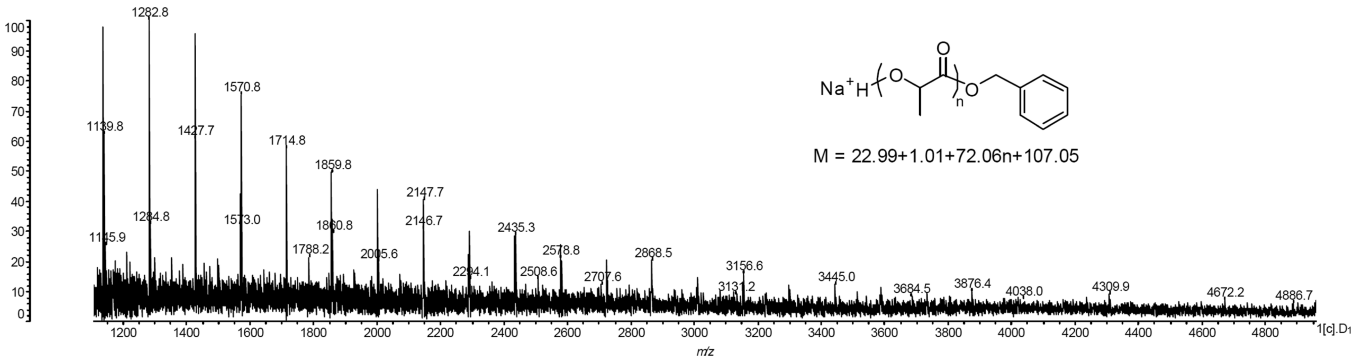

Figure 7. MALDI-TOF mass spectrum of *rac*-LA oligomer initiated by complex **4** ($[rac\text{-LA}]_0/\mathbf{4}$ = 20:1, in THF, 25 °C; doped with NaI).

reactions during the lactide polymerization initiated by the Salalen yttrium alkoxide, giving rise to series of chains separated by the mass of a lactide unit (144) rather than that of a lactic acid (72). Thus, the polymerization proceeds via a common "coordination−insertion" mechanism.

CONCLUSION

In summary, a Salalen-type ligand was introduced in organolanthanide chemistry for the first time, and a series of neutral lanthanide amido and alkoxo complexes were synthesized via amine elimination reactions and proton exchange reactions using the readily available $Ln[N(SiMe_3)_2]_3(\mu\text{-}Cl)Li(THF)_3$ and $Cp_3Ln(THF)$ as the precursors, respectively. Their structural features have been provided by an X-ray diffraction study. It was found that these lanthanide complexes are efficient initiators for the ROP of *rac*-LA, displaying good activity and stereoselectivity, to give PLAs with moderate to good heterotacticity. The nature of the initiating groups has a significant effect on the activity and the controllability but has no obvious effect on the stereoselectivity. The observed increasing order of activity is in agreement with the order of the ionic radii, but the heterotacticity follows the opposite sequence. The steric bulkiness of the substituent group on the phenol ring has no obvious effect on the stereocontrollability of *rac*-LA polymerization. However, these Salalen lanthanide complexes are inert for *rac*-β-butyrolactone, indicating that the backbone of the ancillary ligands has a crucial influence on the catalytic property of the corresponding lanthanide derivatives for *rac*-β-butyrolactone polymerization.

ASSOCIATED CONTENT

Supporting Information

CIF files and a table giving X-ray crystallographic data for **1**−**7** and figures giving additional characterization data. 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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