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ARTICLE TYPE

characterization of rare-earth **Synthesis** and metal complexes supported by a new pentadentate Schiff base and their application in the heteroselective polymerization of rac-lactide

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A series of neutral rare-earth metal aryloxides and amides supported by a new pentadentate (N₂O₃) Salen ligand were synthesized, and their catalytic behaviors for the ring-opening polymerization of rac-lactide (rac-LA) were explored. The protolysis reactions of N,N'-bis(3,5-di-tert-butylsalicylidene)-2,2'diaminodiphenyl ether (LH₂) with (ArO)₃Ln(THF) (ArO = $2,6-Bu_{2}^{t}-4-MeC_{6}H_{2}O$) and Ln[N(SiMe₃)₂]₃ in $_{20}$ a 1:1 molar ratio in THF gave the neutral rare-earth metal aryloxides LLn(OAr)(THF)_n [n = 0, Ln = Sc (1), Yb (2); n = 1, Ln = Y (3), Sm (4), Nd (5)] and rare-earth metal amides LLnN(SiMe₃)₂ [Ln = Yb (6), Y (7)], respectively. X-ray structural determination showed that complexes 1, 2, 6 and 7 have a monomeric structure, in which the coordination geometry around the rare-earth metal atom can be best described as a distorted trigonal prism. Complexes 3 and 5 are a THF-solvated monomer and each of 25 rare-earth metal atoms is seven-coordinated to form a distorted capped trigonal prism. It was found that all of these complexes can efficiently initiate the ring-opening polymerization (ROP) of rac-LA to give heterotactic-rich polylactides (PLAs). The highly heterotactic PLA (P_r up to 0.93) was obtained using complex 2 as the initiator at the polymerization temperature of 0 $^{\circ}$ C. The observed activity-increasing order of $1 \le 2 \le 3 \le 4 \approx 5$ is in agreement with the order of their ionic radii, whereas the order for 30 stereoselectivity is in the reverse order. The rare-earth metal Salen amides can initiate rac-LA polymerization in a controlled manner, while rare-earth metal Salen aryloxides are less controlled at room temperature.

Introduction

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Polylactides (PLAs) as biodegradable, biocompatible and 35 renewable materials have attracted intensive attention over the past two decades because of their potentially wide-ranging applications such as packing, fibers, composites and medical devices.¹ The most ₅₅ widely used in various of metal-catalyzed organic convenient method of synthesizing PLAs is the ring opening polymerization (ROP) of lactide (LA) initiated by metal-based 40 complexes,² due to the advantages of well-controlled molecular weight and narrow molecular weight distribution. Therefore, a number of main group,³⁻⁶ transition metal,⁷ and rare-earth metal complexes⁸⁻¹⁰ incorporating a variant of ligands have been synthesized for this purpose. Among the variety of initiators, 45 organo-rare-earth metal complexes have got a great interest due to their high activity, controllability and stereoselectivity. In particular, rare-earth metal complexes bearing tetradentate 65 rare-earth metal phosphasalen (an iminophosphorane derivative of heteroatom-bridged bisphenolate ligands are extremely efficient initiators for the controlled ROP of rac-LA to give highly

50 heterotactic PLAs.8

Tetradentate Salen ligands, which are generally obtained by the condensation of salicylaldehydes with diverse diamines, are one of the popular ligands in coordination chemistry of transition and rare-earth metals,^{11, 12} and the corresponding metal complexes are transformations¹³ and polymerizations.¹⁴ In particular, aluminum complexes bearing chiral and achiral Salen-type ligands can promote the ROP of rac-LA to give highly isotactic stereoblock PLAs by an enantiomorphic site control or a chain-end control ⁵⁰ mechanism.³ However, most of the rare-earth metal complexes bearing the same ligands did not affect stereoselectivity in the polymerization of rac-LA.^{3c,3d} Exceptions are yttrium complexes bearing rac-binaphthyl-bridged Salen, which generate heterorich PLAs with P_r up to 0.91.¹⁵ Recently, Williams et al. reported that the Salen ligand) complexes are high iso-selective or heteroselective initiators for rac-LA polymerization by changing the

structure of phosphasalen ligand or the metal size.¹⁰ Furthermore, pellet, cm⁻¹): 3413 (w), 2956 (s), 2906 (w), 2868 (w), 1615 (s), the catalytic activities of phosphasalen rare-earth metal complexes 1589 (s), 1532 (s), 1505 (s), 1487 (s), 1461 (w), 1431 (s), 1385 (s), are higher than those of analogous Salen rare-earth metal₆₀ 1360 (w), 1312 (w), 1256 (s), 1200 (s), 1163 (s), 1107 (w), 1026 complexes, ^{10, 3c, 16} because phosphasalen ligands are expected to be (w), 983 (w), 928 (w), 871 (s), 833 (s), 791 (s), 750 (s), 628 (w), ⁵ more electron-donating than their Salen counterparts. These results 519 (s). imply that the increased activity of rare-earth metal Salen

- substituent on the backbone of the Salen ligand. Therefore, a news preligand LH₂ (0.95 g, 1.50 mmol) in THF (20 mL). The mixture pentadentate (N₂O₃) Salen, N,N'-bis(3,5-di-tert-butylsalicylidene)- was stirred at room temperature for 12 h, and then THF was 10 2,2'-diaminodiphenyl ether, was introduced to organo-rare-earth
- metal chemistry, and a series of rare-earth metal aryloxo and bis(trimethysily)amido complexes were prepared and wellcharacterized. Furthermore, the catalytic performances of these 70 room temperature to afford complex 1 as yellow crystals (0.97 g, rare-earth metal Salen complexes in the heteroselective ROP of 72%). Anal. Calcd. for C₅₇H₇₃N₂O₄Sc: C, 76.48; H, 8.22; N, 3.13; 15 rac-LA were also explored.

Experimental Section

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General Methods. 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 20 Schlenk techniques. Solvents were dried and freed of oxygen by refluxing over sodium/benzophenone ketyl and distilled prior to $_{80}$ C(CH₃)₃), 1.33 (m, 9H, C(CH₃)₃), 1.24 (m, 2.6H, CH₂, *n*-hexane), use 3.5-Di-tert-butyl-2-hydroxybenzaldehyde. 2.2'diaminodiphenyl ether and rac-lactide (rac-LA) are commercially available. rac-LA was recrystallized twice from dry toluene and 25 then was sublimed under vacuum at 50 °C. Ln(ArO)₃(THF)¹⁷ (ArO = 2,6-Bu^t₂-4-MeC₆H₂O) and Ln[N(SiMe₃)₂]₃¹⁸ were prepared $_{85}$ 119.9, 114.8 (Ar–C), 68.1 (α -CH₂, THF), 35.9, 35.8, 35.2, 34.7, according to the procedures. 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-₃₀ 550 FTIR spectrometer as KBr pellets. The ¹H and ¹³C NMR spectra were recorded in a C_6D_6 solution for complexes 1, 3 and 7_{90} 1387 (w), 1359 (w), 1256 (s), 1200 (s), 1163 (s), 860 (w), 835 (s), with a Unity Varian spectrometer. Because of their paramagnetism, no resolvable NMR spectrum for the other complexes was obtained. The microstructures of PLAs were measured by homodecoupling ³⁵ ¹H NMR spectroscopy at 20 °C in CDCl₃ on a Unity Varian AC-400 spectrometer. 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 40 °C.

hydroxybenzaldehyde (11.7 g, 50 mmol) in methanol (30 mL) was added to a solution of 2,2'-diaminodiphenyl ether (5.0 g, 25 mmol) in methanol (60 mL). The mixture was stirred at 90 °C for 5 h and 45 then was cooled. The precipitate was filtered and washed with methanol to give the orange product (14.55 g, 92%). Anal. Calcd for C42H52N2O3: C, 79.71; H, 8.28; N, 4.43. Found: C, 80.23; H, 8.24; N, 4.45. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 13.52 (s, 2H, ArOH), 8.72 (s, 2H, N=CH), 7.38 (d, 2H, $J_{H-H} = 2.4$ Hz, ArH), 50 7.27 (s, 1H, overlap with residual signal of CDCl₃, ArH), 7.25 (d, 1H, $J_{\text{H-H}} = 2.2$ Hz, ArH), 7.18 (d, 1H, $J_{\text{H-H}} = 2.0$ Hz, ArH), 7.16 (d, Ar), 7.19 (s, 1H, Ar), 7.05 (m, 3H, Ar), 7.01 (d, 1H, $J_{\text{H-H}} = 7.2$ Hz, 2H, $J_{H-H} = 2.12$ Hz, ArH), 7.14 (d, 1H, $J_{H-H} = 2.4$ Hz, ArH), 7.11 (m, 2H, Ar*H*), 6.98 (d, 1H, J_{H-H} = 1.88 Hz, Ar*H*), 6.96 (d, 1H, J_{H-H} = 2.12 Hz, ArH), 1.39 (s, 18H, $C(CH_3)_3$), 1.25 (s, 18H, $C(CH_3)_3$).

⁵⁵ ¹³C{¹H} NMR (100 MHz, CDCl₃, 25 °C): δ 165.1 (CH=N), 158.7, 149.9, 140.4, 139.9, 137.1, 128.1, 127.4, 127.0, 124.4, 121.2, 119.5 0.89 (t, 3H, CH_3 , *n*-hexane). ¹³C{¹H} NMR (100 MHz, C_6D_6 , 118.6(Ar-C), 35.3, 34.3 (C(CH₃)₃), 31.7, 29.6 (C(CH₃)₃). IR (KBr

Synthesis of LSc(OAr) (1). A solution of Sc(OAr)₃ (10 mL, complexes might be expected upon introducing electron-donating 0.15 M, 1.50 mmol) in THF was injected quickly to a solution of evaporated completely under reduced pressure. The resultant vellow solid was washed with hexane about three times, and crystallized from a mixture of THF (2 ml) and *n*-hexane (4 ml) at Found: C, 77.09; H, 8.02; N, 3.05. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 8.28 (s, 1H, CH=N), 8.11 (s, 1H, CH=N), 7.78 (d, 1H, $J_{\text{H-H}} = 2.6$ Hz, ArH), 7.60 (d, 1H, $J_{\text{H-H}} = 2.56$ Hz, ArH), 7.19 (m, 75 2H, ArH), 7.10 (m, 1H, ArH), 7.05 (m, 1H, ArH), 6.97 (m, 3H, ArH), 6.91 (m, 1H, ArH), 6.71(m, 2H, ArH), 6.64 (m, 1H, ArH), 6.55 (m, 1H, ArH), 3.57 (m, 3H, α-CH₂, solvate THF), 2.33 (s, 3H, CH_3), 1.45 (s, 27H, overlap with THF signal, $C(CH_3)_3$), 1.43 (m, 3H, overlap with Bu^t signal, β -CH₂, solvate THF), 1.38(s, 9H, 1.19 (s, 9H, C(CH₃)₃), 0.89 (t, 2H, CH₃, *n*-hexane). ${}^{13}C{}^{1}H{}$ NMR (100 MHz, C₆D₆, 25 °C): δ 167.9, 165.0 (CH=N), 161.5, 152.2, 148.5, 144.9, 141.0, 140.5, 139.8, 138.5, 137.8, 133.0, 131.8, 130.0, 129.7, 129.4, 127.1, 126.5, 125.9, 125.4, 124.3, 122.4, 121.9, 121.6, 34.5, 34.4 (C(CH₃)₃), 32.3 (CH₂, *n*-hexane), 32.8, 32.0, 31.9, 31.8, 30.6, 30.3 (C(CH₃)₃), 26.2 (β-CH₂ THF), 23.4 (CH₂, *n*-hexane), 22.0 (CH₃), 14.7 (CH₃, *n*-hexane). IR (KBr pellet, cm⁻¹): 2955 (s), 2903 (w), 2867 (w), 1616 (s), 1589 (s), 1541 (s), 1488 (s), 1407 (s), 745 (s), 699 (w).

Synthesis of LYb(OAr) (2). The synthesis of complex 2 was carried out in the same way as that described for complex 1, but Yb(OAr)₃(THF) (10.5 mL, 0.143 M, 1.50 mmol) was used instead of Sc(OAr)₃. Yellow crystals were obtained in a THF/toluene/nhexane (1:1:2) solution (1.04 g, 68%). Anal. Calcd. for C₅₇H₇₃N₂O₄Yb: C, 66.91; H, 7.19; N, 2.14. Found: C, 67.36; H, 7.11; N, 2.17. IR (KBr pellet, cm⁻¹): 2953 (s), 2905 (w), 2867 (w), 1614 (s), 1588 (s), 1531 (s), 1486 (s), 1427 (s), 1387 (s), 1359 (w), Synthesis of LH₂. A solution of 3,5-di-*tert*-butyl-2- $_{100}$ 1332 (w), 1229 (s), 1163 (s), 1107 (w), 928 (w), 835 (s), 791 (w), 744 (s), 675 (w).

> Synthesis of LY(OAr)(THF) (3). The synthesis of complex 3 was carried out in the same way as that described for complex 1, but Y(OAr)₃(THF) (6.4 mL, 0.235 M, 1.50 mmol) was used instead solution of THF (3 mL) and n-hexane (3 mL) (1.13 g, 69%). Anal. Calcd. for C₆₁H₈₁N₂O₅Y: C, 72.45; H, 8.07; N, 2.77. Found: C, 72.66; H, 7.51; N, 2.82. ¹H NMR (400 MHz, C₆D₆, 25 °C) : δ 8.32 (s, 1H, CH=N), 8.14 (s, 1H, CH=N), 7.76 (s, 1H, Ar), 7.68 (s, 1H, Ar), 6.85 (m, 3H, Ar), 6.68 (m, 4H, Ar), 3.51 (m, 8H, α-CH₂, THF), 2.27 (s, 3H, CH_3), 1.60 (s, 18H, $C(CH_3)_3$), 1.50 (s, 9H, $C(CH_3)_3$), 1.39 (s, 9H, C(CH₃)₃), 1.38 (m, 8H, β-CH₂, THF), 1.35 (m, 9H, C(CH₃)₃), 1.27 (s, 9H, C(CH₃)₃), 1.24 (m, 4H, CH₂, *n*-hexane),

141.2, 140.4, 138.1, 137.7, 137.3, 136.4, 132.6, 132.1, 130.7, 130.4₆₀ stirring bar, was charged with *rac*-LA (0.50 g, 3.47 mmol) and 126.8, 126.2, 125.4, 124.2, 123.3, 122.6, 121.4, 120.4, 113.3 (Ar- THF (2.78 mL). After the monomer was dissolved, a THF solution C), 68.2 (a-CH₂, THF), 36.2, 34.9, 34.7, 34.5 (C(CH₃)₃), 32.3, 32.0, of complex 2 (0.69 mL, 0.0069 mmol) was added by syringe. The $_{\rm 5}$ 30.8, 30.6 (C(CH₃)₃), 31.9 (CH₂, *n*-hexane), 26.0 (β -CH₂, THF), mixture was immediately stirred vigorously for 10 minutes at 23.4 (CH₂, n-hexane), 22.0 (CH₃), 14.7 (CH₃, n-hexane). IR (KBr 25 °C, during which time an increase in the viscosity was observed. pellet, cm⁻¹): 2955 (s), 2904 (w), 2866 (w), 1616 (s), 1588 (s), 154265 The reaction mixture was quenched by the addition of 1.0 mL of (s), 1486 (s), 1474 (s), 1407 (s), 1399 (w), 1255 (s), 1200 (s), 1163 HCl/CH₃OH (0.05/10 v/v) and then poured into ethanol to (s), 860 (w), 835 (s), 746 (s), 675 (s).

Synthesis of LSm(OAr)(THF) (4). The synthesis of complex 4 was carried out in the same way as that described for complex 1, but Sm(OAr)₃(THF) (16.3 mL, 0.092 M, 1.50 mmol) was used₇₀ out with complex 2 and 7 in THF at 25 °C in a molar ratio of instead of Sc(OAr)₃. Yellow crystals were obtained in a THF/toluene/n-hexane (1:1:1) solution (1.04 g, 65%). Anal. Calcd.

¹⁵ for C₆₁H₈₁N₂O₅Sm: C, 68.30; H, 7.61; N, 2.61. Found: C, 68.64; H, 7.80; N, 2.61. IR (KBr pellet, cm⁻¹): 2956 (s), 2905 (w), 2867 (w), 1699 (s), 1617 (s), 1588 (s), 1538 (s), 1486 (s), 1387 (s), 1359 (w), 75 1229 (s), 1163 (s), 1107 (w), 835 (s), 744 (s), 680 (s).

Synthesis of LNd(OAr)(THF) (5). The synthesis of complex 5 ²⁰ was carried out in the same way as that described for complex 1, but Nd(OAr)₃(THF) (12.5 mL, 0.12 M, 1.50 mmol) was used instead of Sc(OAr)₃. Green crystals were obtained in a THF/*n*-so 0.71073 Å and $\lambda = 0.71075$ Å). The diffracted intensities were hexane solution (1.09 g, 68%). Anal. Calcd. for C₆₁H₈₁N₂O₅Nd: C, 68.69; H, 7.65; N, 2.63. Found: C, 68.65; H, 7.62; N, 2.56. IR (KBr 25 pellet, cm⁻¹): 2953 (s), 2905 (w), 2867 (w), 1614 (s), 1588 (s), 1532 (s), 1486 (s), 1459 (s), 1420 (s), 1387 (w), 1332 (w), 1229 (s), 1163 (s), 1126 (w), 835 (s), 791 (w), 744 (s), 689 (s).

of $LYb[N(SiMe_3)_2]$ (6). Synthesis А solution of Yb[N(SiMe₃)₂]₃ (9.7 mL, 0.154 M, 1.50 mmol) in THF was ³⁰ injected quickly to a solution of preligand LH₂ (0.95 g, 1.50 mmol) in THF (20 mL). The mixture was stirred overnight at room temperature, and then THF was evaporated completely under⁹⁰ final stage of full-matrix least-squares refinement. The structures reduced pressure. The resultant yellow solid was crystallized from a mixture of THF and *n*-hexane at room temperature to afford 35 yellow crystals of 6 after several days (0.94 g, 65%). Anal. Calcd. for C₄₈H₆₈N₃O₃Si₂Yb: C, 59.79; H, 7.11; N, 4.36; Found: C, 59.79; H, 7.13; N, 4.35.

Synthesis of LY[N(SiMe₃)₂] (7). The synthesis of complex 7 was carried out in the same way as that described for complex 6^{95} 40 but Y[N(SiMe₃)₂]₃ (7.4 mL, 0.203 M, 1.50 mmol) was used instead of Yb[N(SiMe₃)₂]₃. Yellow crystals were obtained in a THF/nhexane solution (0.88 g, 67%). Anal. Calcd. for C₅₂H₇₆N₃O₄Si₂Y (7·THF): C, 65.59; H, 8.04; N, 4.41. Found: C, 65.54; H, 8.00; N, 4.33. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 8.16 (s, 1H, CH=N),¹⁰⁰

- 45 8.03 (s, 1H, CH=N), 7.84 (s, 1H, Ar), 7.64(s, 1H, ArH), 6.98 (m, 5H, ArH), 6.79 (m, 1H, ArH), 6.59 (m, 4H, ArH), 3.54 (m, 6H, a-CH₂, THF), 1.91 (s, 9H, C(CH₃)₃), 1.63 (s, 9H, C(CH₃)₃), 1.37 (m, 6H, overlap with Bu^t signal, β -CH₂, THF), 1.36 (s, 9H, overlap with THF signal, C(CH₃)₃), 1.27 (s, 9H, C(CH₃)₃), 0.18 (s,18H,¹⁰⁵
- ⁵⁰ Si(CH₃)₃). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ 168.0, 166.7 (CH=N), 148.4, 141.2, 136.5, 136.2, 131.5, 130.8, 130.5, 126.6, 126.4, 126.0, 125.4, 123.1, 122.3, 120.6, 120.5, 114.9 (Ar-C), 69.0 (α-CH₂, THF), 36.6, 36.4, 34.5 (C(CH₃)₃), 32.3 (CH₂, n-hexane), 32.1, 30.9, 30.7 (C(CH₃)₃), 25.7 (β -CH₂, THF), 23.4 (CH₂, n^{-10} 55 hexane), 14.7 (CH₃, *n*-hexane), 3.8, 3.0, 2.4 (Si(CH₃)₃).

Typical Procedure for the Polymerization Reaction. The procedures for the polymerization of rac-LA initiated by the complexes 1-7 were similar. A typical polymerization procedure is

25 °C) : 168.9, 168.4 (CH=N), 160.9, 151.3, 146.4, 144.0, 141.0, as follows: A 20 mL reaction flask, equipped with a magnetic precipitate the polymer. The polymeric product was filtered and dried at 50°C for 12 h in vacuum, and weighed (0.48 g, 95%).

> Oligomer Preparation. Oligomerization of rac-LA was carried monomer/initiator of 20. The reaction was stirred for 5 min and then quenched by adding wet *n*-hexane. The precipitated oligomers were collected, dried under vacuum, and used for ¹H NMR and MALDI-TOF mass spectra measurement.

> X-Ray Crystallographic Structure Determination. Suitable single crystals of complexes 1-3 and 5-7 were sealed in a thinwalled 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-K α radiation (λ = corrected for Lorentz/polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table S1.

The structures were solved by direct methods and refined by s 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 calculation in the were solved and refined using SHELEXL-97 programs.

Results and discussion

Synthesis and Structure of Rare-earth Metal Aryloxides 1-5. The new pentadentate (N₂O₃) Salen, N,N'-bis(3,5-di-tertbutylsalicylidene)-2,2'-diaminodiphenyl ether (LH₂), was synthesized by the condensation reaction of 3,5-di-tert-butyl-2hydroxybenzaldehyde with 2,2'-diaminodiphenyl ether in 2:1 molar ratio in refluxing methanol, and isolated in 92% yield as orange powder. It was fully characterized by ¹H, ¹³C{¹H} NMR spectroscopy and elemental analysis.

Previous works have shown that the protolysis reaction between homoleptic rare-earth metal aryloxides and preligands is a useful method for the synthesis of salt-free rare-earth metal aryloxo derivarives¹⁹. Therefore, this method was also used to synthesize the desired heteroleptic rare-earth metal aryloxides in present case. Reactions of $(ArO)_3Ln(THF)$ (ArO = 2,6-Bu^t₂-4-MeC₆H₂O) with the Salen precursor (LH₂) in a 1:1 molar ratio in THF, after workup, gave the desired rare-earth metal aryloxides $LLn(OAr)(THF)_n$ [n = 0, Ln = Sc (1), Yb (2); n = 1, Ln = Y (3), Sm (4), Nd (5)] as microcrystals in high isolated yields (65-72%) from a mixture solution of THF and n-hexane, as shown in Scheme 1. Complexes 1-5 are fully characterized by element analysis, IR and NMR spectroscopy in the case of complexes 1 and 3. The IR spectra of complexes 1-5 exhibited two strong absorption bands ¹¹⁵ near 1616 and 1588 cm⁻¹, which were characteristic bands of the group. All of these complexes are soluble in THF and toluene, but₅₅ bridged insoluble in *n*-hexane.



The definitive molecular structures of complexes 1-5 were 10 further confirmed by single-crystal structure determination. All of bond lengths and bond angles are provided in Table 1. The bond parameters for complex 4 were not provided due to the poor quality of the crystal data.²⁰ It was found that the ionic radii of the rare-15 earth metals can influence the solid state structure of the rare-earth metal Salen complexes. In complexes 1 and 2, there is no THF molecule to coordinate to the scandium and ytterbium ions, 75 Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for whereas there is one THF molecule to coordinate to the larger yttrium, samarium and neodymium ions in complexes 3-5. 20 Complexes 1 and 2 are isomorphous and only the molecular

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- diagram of complex 1 is shown in Fig. 1. In complexes 1 and 2, each of the rare-earth metal atoms is six-coordinated with three I oxygen atoms and two nitrogen atoms from the pentadentate (N_2O_3) Salen ligand, and one oxygen atom from the aryloxo group. I 25 The coordination geometry around the metal center can be best described as a distorted trigonal prism, in which the dihedral angles between the two triangular faces defined by O1, O4, N1 and O2, T O3, N2, respectively, are 8.13° for 1 and 11.6° for 2. The Sc-O(Salen) distances of 1.984(2) and 2.022(2) Å and the Sc-N(Salen) I 30 bond lengths of 2.348(2) and 2.270(2) Å in complex 1 are comparable with the corresponding bond lengths in F
- [(Salen')Sc(THF)₂][BPh₄] (av. 1.970(2) Å and 2.228(3) Å, Salen' N,N'-bis(3,5-di-tert-butylsalicylidene)ethane-1,2-diamine),12d (Salcyc)ScCl(THF) (av. 1.975(5) Å and 2.234(6) Å, Salcyc = (35 (1R,2R)-(-)-1,2-cyclohexanediyl)bis(nitrilomethylidyne)bis(2,4-di-
- *tert*-butyl)phenol)^{12e} and other six-coordinate scandium hydroxo complexes with Salen ligands (1.977-2.028 Å and 2.248-2.321 Å)^{12e}. It is noteworthy that the Sc-O(ether) distance of 2.578(2) Å is much longer than the Sc-O(THF) bond lengths in C
- 40 [(Salen')Sc(THF)2][BPh4] (2.177(2) and 2.154(2) Å)^{12d} and (Salcyc)ScCl(THF) (2.287(5) and 2.284(2) Å), 12e reflecting that C the interaction between the scandium atom and the oxygen atom of the diphenyl ether group is very weak. The Sc-O(Ar) distance of 1.955(2) Å is slightly shorter than the Sc-O(Salen) distances, but
- 45 comparable to the Sc-O(phenolate) bond lengths (1.947(2)-1.969(1) Å) in scandium amino-bridged bis(phenolate) complexes.⁸¹ In complex 2, the Yb-O(Salen) distances of 2.104(2) and 2.132(2) Å, the Yb-N(Salen) bond lengths of 2.432(3) and 2.389(3) Å, and the Yb-O(ether) bond length of 2.514(2) Å 50 compare well with those in complex 1 when the difference in the
- ionic radii between Yb and Sc is considered.²¹ The Yb-O(Ar) distance of 2.070(3) Å is consistent with the corresponding bond

C=N group.^{12d} The ¹H NMR spectra of complexes 1 and 3 clearly lengths in ethylene-bridged bis(β -ketoiminato) ytterbium aryloxide showed the peaks of the pentadentate Salen ligand and the aryloxo $[CH_3NC(Me)CHCOPh]_2Yb(OAr)(THF)] (2.090(3) Å)^{22}$ and amine bis(phenolate) ytterbium arvloxide complex $[Me_2NCH_2CH_2N\{CH_2-(2-O-C_6H_2-Bu_2^t-3,5)\}_2]Yb(OC_6H_3-2,6 Pr_{2}^{i}$ (THF) (2.084(6) Å).^{8h}

Complexes 3 and 5 are isomorphous and only the molecular diagram of complex 3 is shown in Fig. 2. Each of the metal centers 60 in complexes 3 and 5 is seven-coordinated by one aryloxy group, one THF and the pentadentate (N2O3) Salen ligand. The coordination geometry around the metal center can be best described as a distorted capped trigonal prismatic environment, in which O2, O4, N1 and O3, O5, N2 can be considered to constitute 65 the two triangular faces of the prism with the dihedral angle of 6.12° for 3 and 7.36° for 5, and O1 to occupy the capping position. The dihedral angles between the two phenolate groups in complexes 3 and 5 are 129.3° and 130.7°, respectively, which are bigger than those in complexes 1 and 2 (101.0° for 1 and 104.3° for these complexes have monomeric structures, and their selected $_{70}$ 2), probably due to the low coordination number in the later. The Ln-O(Salen), Ln-N(Salen), Ln-O(Ar) and Ln-O(ether) bond lengths in complexes 3 and 5 are comparable to the corresponding values in complexes 1 and 2 when the difference in metal sizes is taken in consideration.²¹

Complexes 1-3 and 5								
Bond lengths	1	2	3	5				
_n1-O1	2.578(2)	2.514(2)	2.529(2)	2.587(2)				
.n1-O2	1.984(2)	2.104(2)	2.171(2)	2.235(2)				
_n1- O3	2.022(2)	2.132(2)	2.207(2)	2.272(2)				
_n1- O4	1.955(5)	2.070(3)	2.129(3)	2.207(2)				
_n1-N1	2.348(2)	2.432(3)	2.523(3)	2.615(3)				
_n1-N2	2.270(2)	2.389(3)	2.519(3)	2.619(3)				
Bond angles	1	2	3	5				
01-Ln1-N1	63.94(7)	64.46(9)	62.13(9)	61.18(8)				
01-Ln1-N2	64.26(7)	64.40(9)	62.18(9)	61.00(8)				
01-Ln1-O4	89.35(7)	90.06(9)	87.80(9)	89.23(8)				
N1-Ln1-N2	108.19(8)	110.38(10)	118.24(10)	116.10(9)				
02-Ln1-O3	91.34(8)	91.22(10)	91.80(9)	96.67(8)				
04-Ln1-O5	-	-	168.76(10)	169.83(9)				

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Fig. 1 Molecular structure of complex 1 showing the atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms and free solvent molecules are omitted for clarity. Complex 2 is isomorphous 5 with complex 1.



 Fig. 2 Molecular structure of complex 3 showing the atom numbering scheme.
 (Salen')Y[N(SiHMe_2)](THF)

 10 Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms₆₀ (Salcyc)Y[N(SiHMe_2)](THF)

 and free solvent molecules are omitted for clarity. Complex 5 is isomorphous
 (Salpren)Y[N(SiHMe_2)](THF)

 with complex 3.
 (Minethylpropandiyl)bis(nitrilow)

Synthesis and Structure of Ytterbium and Yttrium Amides 6 ¹⁵ and 7. In order to compare the catalytic behavior of the rare-earth metal Salen aryloxides and amides in the ROP of *rac*-LA, the ytterbium and yttrium amides supported by the pentadentate (N_2O_3) Salen ligand were prepared. Generally, amine elimination reaction is a straightforward method for the synthesis of rare-earth ²⁰ metal amides using Ln[N(SiMe_3)_2]_3 as the precursor.^{12a, c-e} This synthetic approach did succeed in our case, although the reaction of $Y[N(SiMe_3)_2]_3$ with the Salen N,N'-bis(3,5-di-tertbutylsalicylidene)ethylenediamine did not afford the desired

yttrium amide.^{12a} Treatment of Ln[N(SiMe₃)₂]₃ with H₂L in a 1:1 ²⁵ molar ratio in THF for 12 h at room temperature conveniently afforded the expected ytterbium and yttrium amide LLnN(SiMe₃)₂ [Ln = Yb (**6**), Y (**7**)] as light yellow crystals in good yields (65% for complex **6**, 67% for complex **7**) upon crystallization from a mixture solution of THF and *n*-hexane (Scheme 2). Complexes **6** ³⁰ and **7** were characterized by element analysis and NMR spectroscopy in the case of complex **7**, and their molecular structures were determined by single-crystal structure analysis. Both complexes are extremely sensitive to air and moisture, but they are stable in dry argon atmosphere. Complexes **6** and **7** are ³⁵ freely soluble in THF and toluene, but insoluble in *n*-hexane.





Complexes 6 and 7 are isomorphous and only the molecular diagram of complex 6 is shown in Fig. 3. The selected bond lengths and angles for complexes 6 and 7 are listed in Table 2. In complexes 6 and 7, each of the metal centers is six-coordinated by one amido group and the pentadentate (N_2O_3) Schiff base. The 45 coordinate geometry around the metal center can be best described as a distorted trigonal prism, which is similar to those in complexes 1 and 2. The dihedral angles of the planes of the trigonal faces are 16.0° for 6 and 16.8° for 7. The Ln-O(Salen) and Ln-N(Salen) bond lengths in complexes 6 and 7 are comparable to the corresponding 50 values in complexes 1 and 2 when the difference in metal sizes is taken in consideration.²¹ However, the Yb-O(ether) and Y-O(ether) distances of 2.694(4) Å and 2.663(2) Å, respectively, are obviously longer than the Yb-O(ether) bond length in complex 2, reflecting the strong influence of the bulky amido group $[N(SiMe_3)_2]$ to the 55 metal center. The Ln-N(amide) distances in complexes 6 and 7 are 2.202(5) and 2.245(2) Å, respectively, which are comparable to the corresponding bond lengths in β -ketoiminato ytterbium amides (2.222-2.230 Å)²²⁻²³ and yttrium Salen amides, such as Å),^{12a} (Salen')Y[N(SiHMe₂)](THF) (2.27)Å)²⁴ (2.303(2))and (Salpren)Y[N(SiHMe₂)](THF) [2.309 Å, Salpren = (2, 2 dimethylpropandiyl)bis(nitrilomethylidyne)bis(2,4-di-tertbutyl)phenol].12d



Fig. 3 Molecular structure of complex 6 showing the atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms and free solvent molecules are omitted for clarity. Complex 7 is isomorphous 5 with complex 6.

Complexes 6 and 7

Bond	6	7	Bond angles	6	7
lengths	Ū	,	Donu angres	Ū	
Ln1-O1	2.694(4)	2.663(2)	O1-Ln1-N1	61.38(15)	61.66(6) ⁵⁵
Ln1-O2	2.101(4)	2.168(2)	O1-Ln1-N2	61.54(16)	61.31(6)
Ln1-O3	2.141(4)	2.135(2)	O1-Ln1-N3	97.36(17)	97.76(7)
Ln1-N1	2.471(5)	2.459(2)	N1-Ln1-O3	165.96(16)	106.50(7)
Ln1-N2	2.419(5)	2.502(2)	N1-Ln1-N2	104.07(17)	104.92(7)
Ln1-N3	2.202(5)	2.245(2)	O2-Ln1-O3	93.47(17)	93.94(6) 65

ROP of rac-LA Initiated by Rare-earth Metal Salen Complexes 1-7. The catalytic behavior of complexes 1-7 for the ring-opening₇₀ is beneficial for stereoselectivity.^{8b,ik,9a} polymerization of rac-LA was examined and the representative results are listed in Table 3. It was found that all of these rare-earth 15 metal Salen complexes can effectively initiate the ROP of rac-LA in THF to give the polymers with high molecular weights and 1.46). These rare-earth metal Salen complexes displayed a relatively higher activity in comparison with those reported rare-20 earth metal Salen complexes.^{3c,m,15,16} For example, using yttrium aryloxide 3 as the initiator, polymerization was almost complete in $_{25}$ took about 14 h for [(Salbinap)YOCH₂CH₂NMe₂]₂^{3c} [SalbinapH₂ = conversion and the molecular weight distribution (PDI) of the butyl-2-hydroxybenzylideneamino)-1,1'-binaphthyl] to reach living fashion at 0 °C. complete conversion when the molar ratios of monomer to initiator

30 were 100 and 300, respectively. The high activity of the pentadentate Salen rare-earth metal complexes might be ascribed to the existence of an additional donor group on the backbone of the Salen ligand, which is consistent with that found by Williams et al. in the phosphasalen rare-earth metal alkoxide systems.¹⁰

As shown in Table 3, polymerization media has a great impact 35 on the catalytic activity, but has no obvious effect on the stereoselectivity for rac-LA polymerization. Overall, THF is a good solvent. For instance, using yttrium aryloxide 3 as the initiator, a yield of 96% can be reached within 10 min in THF at ⁴⁰ room temperature when the molar ratio of monomer to initiator is 500, and P_r value of the resulted PLA is 0.81 (P_r = probability of racemic enchainment; Table 3, entry 9; Fig. S1); whereas the yield is 90% and P_r is 0.79 in toluene under the same polymerization conditions (Table 3, entry 10). Furthermore, polymerization 45 performed in CH₂Cl₂ led to a dramatic decrease in activity, but the heterotacticity of the resultant PLA dropped slightly ($P_r = 0.78$, Table 3, entry 11). The solvent effect on the stereoselectivity in our cases is quite different from those observed in the amine-bridged bis(phenolate) rare-earth metal systems.8b,i-k,9a In the latter, the Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for⁵⁰ polymerizations in THF gave apparently higher selectivity than those in toluene and in CH₂Cl₂.

The ionic radii of the rare-earth metals also affected the catalytic activity and stereoselectivity for rac-LA polymerization. The samarium (4) and neodymium (5) complexes showed the highest activity among these rare-earth metal Salen aryloxides and the yields exceeded 85% within 5 min when the molar ratio of monomer to initiator was 500 (Table 3, entries 13 and 16), whereas the yield was only 71% using the scandium complex (1) as the initiators even if the molar ratio of monomer to initiator decreased to 100 and the reaction time was extended to 100 min (Table 3, entry 1). The increasing order of activity $Sc \ll Yb \ll Y \ll Sm \approx Nd$ is in agreement with the order of their ionic radii of the central metals. In contrast, the increasing order in stereoselectivity follows the decreasing order of the ionic radii, e.g. Nd $(P_r = 0.76) < \text{Sm} (P_r)$ $= 0.78) < Y (P_r = 0.81) < Yb (P_r = 0.85) \approx Sc (P_r = 0.85)$ (Table 3, entries 1, 2, 8, 13 and 16). The influence of the ionic radii on the polymerization of rac-LA in this system is in agreement with the

previous observations: a crowded coordination environment around the metal center is disadvantageous for polymerization activity, but

In order to understand the influence of polymerization temperature on the heterotacticity of the resultant polymer, the polymerization of rac-LA at different temperature was conducted using ytterbium aryloxide 2 as the initiator (Table 4, entries 3, 5, 6 moderate to narrow molecular weight distributions (PDI = 1.02-75 and 7). The results show that lowering the polymerization temperature from 25 to 0 °C resulted in an increase in Pr from 0.85 to 0.93, and a decrease in PDI from 1.30 to 1.06 (Table 3, entries 3 and 7; Fig. S2). A similar phenomenon was also observed in zincbased polymerization system.²⁵ This change might be attributed to 15 min at room temperature when the molar ratio of monomer to₈₀ the depression of transesterification reactions during the rac-LA initiator was 1000 (Table 3, entry 12). However, using the polymerization at 0 $^{\circ}$ C. The measured molecular weights (M_n) of binaphthyl-bridged yttrium Salen complexes as the initiators, it the resulting polymers increased linearly with the monomer 2,2'-bis(2-hydroxybenzylideneamino)-1,1'-binaphthyl] and 3 h for polymers kept almost unchange (1.02-1.09) (Fig. 4), indicating the $(Salbinap')Y[N(SiHMe_2)](THF)^{15}$ [Salnap'H₂ = 2,2'-bis(3-tert-₈₅ polymerization of rac-LA initiated by complex 2 proceeds in a

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				Yield	$M_{ m c}{}^c$	$M_{\rm n}{}^d$		
Entry	Cat.	$[M]_0/[I]_0$	<i>t</i> /min	$(\%)^{b}$	(×10 ⁴)	(×10 ⁴)	PDI^d	$P_{\rm r}^{\ e}$
1	1	100	100	71	1.02	1.31	1.07	0.85
2	2	500	5	70	5.05	5.95	1.21	0.85
3	2	500	10	95	6.85	6.24	1.30	0.85
4	2	1000	15	87	12.54	11.82	1.23	0.85
5 ^f	2	500	60	99	7.13	6.91	1.13	0.88
6 ^g	2	250	60	91	3.28	3.78	1.02	0.94
7^g	2	250	75	96	3.46	4.33	1.06	0.93
8	3	500	5	77	5.55	5.06	1.28	0.81
9	3	500	10	96	6.92	7.21	1.38	0.81
10^{h}	3	500	10	90	6.49	6.05	1.35	0.79
11 ^{<i>i</i>}	3	500	10	51	3.68	4.28	1.56	0.78
12	3	1000	15	92	13.26	13.29	1.28	0.81
13	4	500	5	86	6.20	6.96	1.34	0.78
14	4	500	10	98	7.06	7.55	1.44	0.78
15	4	1000	15	96	13.84	14.55	1.33	0.79
16	5	500	5	85	6.13	6.59	1.38	0.76
17	5	500	10	98	7.07	8.21	1.46	0.76
18	5	1000	15	98	13.56	14.21	1.39	0.78
19	6	500	5	90	6.49	10.81	1.19	0.89
20	6	1000	12	88	12.68	12.02	1.16	0.90
21	6	2000	60	95	27.39	21.33	1.22	0.89
22	7	500	5	92	6.63	9.22	1.23	0.89
23	7	1000	12	94	13.55	13.47	1.20	0.88
24	7	1500	20	85	18.38	20.39	1.21	0.88
25	7	2000	60	96	27.67	25.29	1.24	0.86
26	7	3000	60	90	38.91	33.67	1 19	0.85

^{*a*} General polymerization conditions: THF as the solvent, $[rac-LA]_0 = 1 \text{ mol/L}$, at 25 °C. ^{*b*} Yield: weight of polymer obtained/weight of monomer used. ^{*c*} Mc = (144.14) × $[M]_0/[I]_0$ × (polymer yield) (%). ^{*d*} Measured by GPC calibrated with standard polystyrene samples. ^{*e*} Pr is the probability of racemic linkages between 5 monomer units determined from the methane region of the homonuclear decoupled ¹H NMR spectrum at 25 °C. ^{*f*} At 10 °C. ^{*g*} At 0 °C. ^{*h*} In Toluene .^{*i*} In CH₂Cl₂.



Fig. 4 Plots of M_n and M_w/M_n vs conversion for ROP of *rac*-LA initiated by complex **2**. Conditions: THF as solvent, $[M]_0/[I]_0 = 250$, $[M]_0 = 1.0$ M, T = 0 ¹⁰ °C.

The influence of the structure of initiating group on the catalytic behavior was also investigated. In comparison with rare-

earth metal aryloxides, rare-earth metal amides showed higher 15 activity for rac-LA polymerization (Table 3, entries 2, 8, 19, 22). For example, using ytterbium amide 6 as the initiator, a 90% yield was achieved in 5 min at room temperature when the molar ratio of monomer to initiator is 500 (Table 3, entry 19), whereas the yield was 70% using ytterbium aryloxide 2 as the initiator 20 (Table 3, entry 2). These results are consistent with those observed in the salalen rare-earth metal amide systems^{9a,i}. Generally, the organo-rare-earth metal amides showed worse controllability for rac-LA polymerization than the rare-earth metal alkoxides due to the lower nucleophilicity of the silvlamide 25 group.^{8b,9a,i} However, rare-earth metal amides 6 and 7 displayed good controllability. The number average molecular weights (M_n) of the resulting polymers increased with the molar ratio of monomer to initiator $([M]_0/[I]_0)$ (Table 3, entries 19-26), whereas the molecular weight distributions (PDI) kept almost unchanged $_{30}$ (1.16-1.24). Furthermore, a linear increase in M_n with monomer conversion recorded with yttrium amide 7 as initiator, while the PDIs kept in the range of 1.19-1.24, as shown in Fig. 5. The MALDI-TOF mass spectrum of the oligomer obtained from the oligomerization of rac-LA with complex 7 and quenching with 35 benzyl alcohol (Fig. S3), revealed that almost no

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transesterification side reactions occurred during the polymerization because the peaks accounting for oligomers with a nonintegral lactide repeat unit are relatively small in comparison with those of oligomers with a integral lactide repeat ⁵ unit. These results displayed that the rare-earth metal amide stabilized by pentadentate Salen group can initiate *rac*-LA polymerization in a controlled manner.



¹⁰ Fig. 5 Plots of M_n and M_w/M_n vs conversion for ROP of *rac*-LA initiated by complex 7. Conditions: THF as solvent, [M]₀/[I]₀ = 2000, [M]₀ = 1.0M, T = 25°C.



¹⁵ Fig. 6 Kinetics of the rac-LA polymerization using complex 2 as initiator in THF at 25 °C, [M]₀ = 1 M. (•) [M]₀/[I]₀ = 1000, $k_{app} = 0.2495 \pm 0.0067 \text{ min}^{-1}$ (linear fit, R² = 0.998); (Δ) [M]₀/[I]₀ = 1500, $k_{app} = 0.1489 \pm 0.0038 \text{ min}^{-1}$ (linear fit, R² = 0.999); (•) [M]₀/[I]₀ = 2000, $k_{app} = 0.11914 \pm 0.00057 \text{ min}^{-1}$ (linear fit, R² = 0.997); (•) [M]₀/[I]₀ = 2500, $k_{app} = 0.10434 \pm 0.0037 \text{ min}^{-1}$ 20 (linear fit, R² = 0.998).



25 Fig. 7 k_{app} versus the concentration of complex 2 for the *rac*-LA polymerization at 25°C in THF ($k_p = 243.7 \pm 1.29$ L•mol⁻¹ min⁻¹, linear fit, $R^2 = 0.996$).

To further elucidate the polymerization behavior, the 30 polymerization kinetics of *rac*-LA initiated by complex 2 was measured with different molar ratios of monomer/initiator at 25 °C in THF. In each case, the conversion increases as the prolongation of the polymerization time, and a first order kinetics dependence on the concentration of rac-LA with a momentary 35 induction time was observed as shown in Fig. 6. This induction period may be related to the much bulky aryloxide group. To determine the order in initiator, k_{app} (the apparent polymerization rate constant) was plotted versus the concentration of complex 2 (Fig. 7). From this plot, k_{app} increased linearly with the initiator 40 concentration, manifesting that the order of initiator is first-order as well. Therefore, the polymerization of rac-LA using 2 followed a kinetic equation of the form $-d[M]/dt = k_{app}[M] =$ $k_{\rm p}$ [M][I], where $k_{\rm p}$ is the propagation rate constant. To gain some insights into the ROP mechanism of rac-LA with these rare-earth 45 metal Salen complexes, oligomerization of rac-LA by complex 2 in a 1:20 molar ratio at room temperature was carried out. Endgroup analysis of the oligomer by ¹H NMR spectroscopy clearly showed the existence of an aryloxide group (ArO-) according to the resonances at about 1.56, 2.07, 7.43 ppm, as 50 shown in Fig. S4. Meanwhile, no proton resonance of the Salen ligand was observed in the ¹H NMR spectrum of the oligomer, which revealed that the pentadentate (N₂O₃) Salen group was not involved in the polymerization process. A MALDI-TOF mass spectrum of the oligomer further revealed that only oligomers 55 with OAr end cap were formed (Fig. 8). These results indicated that the aryloxide group in complex 2 acted as the initiating group in the ROP of rac-LA and the polymerization proceeds via a common "coordination -insertion" mechanism. Remarkably, peaks accounting for linear oligomers with a nonintegral lactide 60 repeat unit also could be found in the MALDI-TOF mass spectrum, which indicating that there are intermolecular transesterfication reactions during the rac-LA polymerization and the polymerization of rac-LA initiated by the rare-earth metal aryloxides at room temperature is not well controlled.

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Fig. 8 MALDI-TOF mass spectrum of *rac*-LA oligomer initiated by complex **2** ([M]₀/[I]₀ =20:1, in THF, 25 °C; doped with CF₃CO₂Na).

Conclusions

⁵ In summary, a new pentadentate (N₂O₃) Salen group was first introduced into organo-rare-earth metal chemistry, and a series of neutral rare-earth metal amido and aryloxo complexes stabilized by this ligand were synthesized via protolysis reactions using (ArO)₃Ln(THF) and Ln[N(SiMe₃)₂]₃ as the precursors,
¹⁰ respectively, and their structural features have been provided by an X-ray diffraction study. It was found that all of these rare-earth metal Salen complexes are efficient initiators for the ROP of *rac*-LA and display good activity and hetereoselectivity. The observed activity-increasing order Sc << Yb < Y < Sm ≈ Nd is in
¹⁵ agreement with the order of the ionic radii, but the heterotacticity follows the opposite sequence. Lowering the polymerization temperature caused an increase in heterotacticity. The results presented here indicated that the Salen ligand systems have great potential application in designing highly active polymerization

20 initiators.

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References

- (a) R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, **12**, 1841; (b) C.-S. Ha, Jr. and J. A. Gardella, *Chem. Rev.*, 2005, **10**;
- 2 (a) B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, J. Chem. Soc., Dalton Trans. 2001, 2215; (b) O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, Chem. Rev., 2004, 104, 6147; (c) R. H. Platel, L.
- M. Hodgson and C. K. Williams, *Polym. Rev.*, 2008, 48, 11; (d) N. Ajellal, J.-F. Carpentier, C. Guillaume, S. M. Guillaume, M. Helou, V. Poirier, Y. Sarazin and A. Trifonov, *Dalton Trans.*, 2010, 39, 8363; (e) M. Kakuta, M. Hirata, Y. Kimura, *Polym. Rev.*, 2009, 49, 107; (f) C. M. Thomas, *Chem. Soc. Rev.*, 2010, 39, 165; (g) M. J.

- Stanford and A. P. Dove, *Chem. Soc. Rev.*, 2010, **39**, 486; (h) P. J.
 Dijkstra, H. Du and J. Feijen, *Polym. Chem.*, 2011, **2**, 520; (i) J.-C.
 Buffet and J. Okuda, *Polym. Chem.*, 2011, **2**, 2758.
- (a) N. Spassky, M. Wisniewski, C. Pluta and A. Le Borgne, 3 Macromol. Chem. Phys., 1996, 197, 2627; (b) M. Wisniewski, A. Le Borgne and N. Spassky, Macromol. Chem. Phys., 1997, 198, 1227; (c) T. M. Ovitt and G. W. Coates, J. Am. Chem. Soc., 1999, 121, 4072; (d) T. M. Ovitt and G. W. Coates, J. Am. Chem. Soc., 2002, 124, 1316; (e) N. Nomura, R. Ishii, M. Akakura and K. Aoi, J. Am. Chem. Soc., 2002, 124, 5938; (f) Z. Zhong, P. J.Dijkstra and J. Feijen, Angew. Chem. Int. Ed., 2002, 41, 4510; (g) Z. Zhong, P. J.Dijkstra and J. Feijen, J. Am. Chem. Soc., 2003, 125, 11291. (h) K. Majerska and A. Duda, J. Am. Chem. Soc., 2004, 126, 1026; (i) N. Nomura, R. Ishii, Y. Yamamoto and T. Kondo, Chem.-Eur. J., 2007, 13, 4433; (j) M. H. Chisholm, J. C. Gallucci, K. T. Quisenberry and Z. Zhou, Inorg. Chem., 2008, 47, 2613; (k) E. D. Cross, L. E. N. Allan, A. Decken and M. P. J.Shaver, Polym. Sci. Part A: Polym. Chem., 2013, 51, 1137; (I) X. Pang, R. Duan, X. Li and X. Chen, Polym. Chem., 2014, 5, 3894; (m) A. Alaaeddine, C. M. Thomas, T. Roisnel and J.-F. Carpentier, Organometallics , 2009, 28, 1469.
- (a) D. J. Darensbourg, O. Karroonnirun and S. J.Wilson, Inorg. Chem., 2011, 50, 6775; (b) E. L. Whitelaw, G. Loraine, M. F.;Mahon and M. D. Jones, Dalton Trans., 2011, 40, 11469; (c) C. Bakewell, R. H. Platel, S. K. Cary, S. M. Hubbard, J. M. Roaf, A. C. Levine, A. J. P. White, N. J. Long, M. Haaf and C. K. Williams, Organometallics, 2012, 31, 4729; (d) K. Matsubara, C. Terata, H.
- Sekine, K. Yamatani, T. Harada, K. Eda, M. Dan, Y. Koga and M. Yasuniwa, J. Polym. Sci. Part A: Polym. Chem., 2012, 50, 957; (e)
 S. L. Hancock, M. F. Mahon, M. D. Jones, Dalton Trans., 2013, 42, 9279; (f) M. Normand, V. Dorcet, E. Kirillov and J.-F.Carpentier, Organometallics, 2013, 32, 1694; (g) B. Gao, R. Duan, X. Pang, X. Li, Z. Qu, Z. Tang, X. Zhuang and X. Chen, Organometallics, 2013,
- 32, 5435; (h) P. Sumrit and P. Hormnirun, *Macromol. Chem. Phys.*, 2013, 214, 1845; (i) K. V. Zaitsev, Y. A. Piskun, Y. F. Oprunenko, S. S. Karlov, G. S. Zaitseva, I. V. Vasilenko, A. V. Churakov and S. V. Kostjuk, *J. Polym. Sci. Part A: Polym. Chem.*, 2014, 52, 1237; (j)
- J. S. Klitzke, T. Roisnel, E. Kirillov, O. Casagrande and J.-F. Carpentier, *Organometallics*, 2014, **33**, 5693; (k) J. S. Klitzke, T. Roisnel, E. Kirillov, O. Casagrande and J.-F. Carpentier, *Organometallics*, 2014, **33**, 309.
- ⁸⁰ 5 (a) A. F. Douglas, B. O. Patrick and P. Mehrkhodavandi, *Angew. Chem. Int. Ed.*, 2008, **47**, 2290; (b) A. Pietrangelo, S. C. Knight, A. K. Gupta, L. J. Yao, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2010, **132**, 11649; (c) M. Normand, E. Kirillov, T. Roisnel and J.-F. Carpentier, *Organometallics*, 2012, **31**, 1448; (d)
- D. C. Aluthge, B. O. Patrick and P. Mehrkhodavandi, *Chem. Commun.*, 2013, **49**, 4295; (e) A. Kapelski and J. Okuda, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, **51**, 4983; (f) C. Bakewell, A. J. P. White, N. J. Long and C. K. Williams, *Inorg. Chem.*, 2013, **52**, 12561.
- 90 6 (a) M. G. Cushion and P. Mountford, *Chem. Commun.*, 2011, 47, 2276; (b) W. Yi and H. Ma, *Inorg. Chem.*, 2013, 52, 11821; (c) Y. Gao, Z. Dai, J. Zhang, X. Ma, N. Tang and J. Wu, *Inorg. Chem.*, 2014, 53, 716; (d) H.-J. Chuang, H.-L. Chen, J.-L. Ye, Z.-Y. Chen, P.-L. Huang, T.-T. Liao, T.-E. Tsai and C.-C. Lin, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, 51, 696; (e) H. Xie, Z. Mou, B. Liu, P. Li, W. Rong, S. Li and D. Cui, *Organometallics*, 2014, 33, 722.
- 7 (a) E. L. Whitelaw, M. G. Davidson and M. D. Jones, Chem. Commun., 2011, 47, 10004; (b) A. Stopper, J. Okuda and M. Kol, Macromolecules, 2012, 45, 698; (c) C. A. Wheaton and P. G. Hayes, Catal. Sci. Technol., 2012, 2, 125; (d) H. Wang and H. Ma, Chem. 100 Commun., 2013, 49, 8686; (e) M. Honrado, A. Otero, J. Fernández-Baeza, L. F. Sánchez-Barba, A. Lara-Sánchez, J. Tejeda, M. P. Carrión, J. Martínez-Ferrer, A. Garcés and A. M. Rodríguez, Organometallics, 2013, 32, 3437; (f) S. Abbina and G. Du, ACS Macro Lett., 2014, 3, 689; (g) M. Honrado, A. Otero, J. Fernández-105 Baeza, L. F. Sánchez-Barba, A. Garcés, A. Lara-Sánchez and A. M. Rodríguez, Organometallics, 2014, 33, 1859; (h) A. Stopper, K. Press, J. Okuda, I. Goldberg and M. Kol, Inorg. Chem., 2014, 53, 9140
- 110 8 (a) C.-X. Cai, A. Amgoune, C. W. Lehmann and J.-F. Carpentier, *Chem. Commun.*, 2004, **40**, 330; (b) A. Amgoune, C. M. Thomas, T. Roisnel and J.-F. Carpentier, *Chem.-Eur. J.*, 2006, **12**, 169; (c) A.

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Amgoune, C. M. Thomas and J.-F. Carpentier, *Macromol. Rapid Commun.*, 2007, **28**, 693; (d) X. Liu, X. Shang, T. Tang, N. Hu, F. Pei, D. Cui, X. Chen and X. Jing, *Organometallics*, 2007, **26**, 2747; (e) L. Clark, M. G. Cushion, H. E. Dyer, A. D. Schwarz, R. Duchateau and P. Mountford, *Chem. Commun.*, 2010, **46**, 273; (f) M. Bouyahyi, N. Ajellal, E. Kirillov, C. M. Thomas and J.-F. Carpentier, *Chem.-Eur. J.*, 2011, **17**, 1872; (g) W. Zhao, D. Cui, X. Liu and X. Chen, *Macromolecules*, 2010, **43**, 6678; (h) K. Nie, X. Gu, Y. Yao, Y. Zhang and Q. Shen, *Dalton Trans.*, 2010, **39**, 6832;

- Gu, Y. Yao, Y. Zhang and Q. Shen, *Datton Trans.*, 2010, **39**, 6852;
 (i) K. Nie, L. Fang, Y. Yao, Y. Zhang, Q. Shen and Y. Wang, *Inorg. Chem.* 2012, **51**, 11133; (j) S. Yang, Z. Du, Y. Zhang, and Q. Shen, *Chem. Commun.*, 2012, **48**, 9780; (k) S. Yang, K. Nie, Y. Zhang, M. Xue, Y. Yao and Q. Shen, *Inorg. Chem.*, 2014, **53**, 105; (l) Y. Chapurina, J. Klitzke, O. Casagrande, M. Awada, V. Dorcet, E. Kirillov and J.-F. Carpentier, *Dalton Trans.*, 2014, **43**, 14322.
- (a) H. Ma, T. P. Spaniol and J. Okuda, Angew. Chem. Int. Ed., 2006, 45, 7818; (b) H. Ma, T. P. Spaniol and J. Okuda, Inorg. Chem., 2008, 47, 3328; (c) P. L. Arnold, J.-C. Buffet, R. Blaudeck, S. Sujecki and C. Wilson, Chem.-Eur. J., 2009, 15, 8241; (d) P. L. Arnold, J.-C. Buffet, R. P. Blaudeck, S. Sujecki, A. J. Blake and C. 20 Wilson, Angew. Chem. Int. Ed., 2008, 47, 6033; (e) R. H. Platel, A. J. P. White and C. K. Williams, Chem. Commun., 2009, 4115; (f) R. H. Platel, A. J. P. White and C. K. Williams, Inorg. Chem., 2011, 50, 7718; (g) Z. Mou, B. Liu, X. Liu, H. Xie, W. Rong, L. Li, S. Li and D. Cui, Macromolecules, 2014, 47, 2233; (h) N. Maudoux, T. 25 Roisnel, J.-F. Carpentier and Y. Sarazin, Organometallics, 2014, 33, 5740; (i) K. Nie, W. Gu, Y. Yao, Y. Zhang and Q. Shen, Organometallicsm, 2013, 32, 2608; (j) E. Grunova, E. Kirillov, T. Roisnel and J.-F. Carpentier, Organometallics, 2008, 27, 5691.
- 30 10 (a) C. Bakewell, T.-P.-A. Cao, N. Long, X. F. L. Goff, A. Auffrant and C. K. Williams, *J. Am. Chem. Soc.*, 2012, 20577; (b) T.-P.-A. Cao, A. Buchard, X. F. L. Goff, A. Auffrant and C. K. Williams, *Inorg. Chem.*, 2012, **51**, 2157; (c) C. Bakewell, T.-P.-A. Cao, X. F. L. Goff, N. J. Long, A. Auffrant and C. K. Williams, *Organometallics*, 2013, **32**, 1475; (d) C. Bakewell, A. J. P. White, N. J. Long and C. K. Williams, *Angew. Chem. Int. Ed.*, 2014, **53**, 9226.
- (a) D. A. Atwood and M. J. Harvey, *Chem. Rev.*, 2001, **101**, 37; (b)
 M. Sakamoto, K. Manseki and K. Okawa, *Coord. Chem. Rev.*, 2001,
 219-221, 379; (c) S. Akine and T. Nabeshima, *Dalton Trans.*, 2009, 10395; (d) H. Miyasaka, A. Saitoh and S. Abe, *Coord. Chem. Rev.*, 2007, **251**, 2622; (e) K.C. Gupta and A. K. Sutar, *Coord. Chem. Rev.*, 2008, **252**, 1420; (f) M. Andruh, *Chem. Commun.*, 2011, **47**, 3025.
- 45 12 (a) O. Runte, T. Priermeier and R. Anwander, *Chem. Commun.*, 1996, 1385; (b) W. J. Evans, C. H. Fujimoto and J. W. Ziller, *Chem. Commun.*, 1999, 311; (c) C. Meermann, P. Sirsch, K. W. Törnroos and R. Anwander, *Dalton Trans.*, 2006, 1041; (d) Q. Liu, C. Meermann, H. W. Görlitzer, O. Runte, E. Herdtweck, P. Sirsch, K.
- W. Törnroos and R. Anwander, *Dalton Trans.*, 2008, 6170; (e) C. Meermann, K. W. Törnroos and R. Anwander, *Inorg. Chem.*, 2009, 48, 2561; (f) E. M. Broderick, P. S. Thuy-Boun, N. Guo, C. S. Vogel, J. Sutter, J. T. Miller, K. Meyer and P. L. Diaconescu, *Inorg. Chem.*, 2011, 50, 2870; (g) E. M. Broderick, N. Guo, C. S. Vogel,
- 55 C. Xu, J. Sutter, J. T. Miller, K. Meyer, P. Mehrkhodavandi and P. L. Diaconescu, J. Am. Chem. Soc., 2011, 133, 9278.
- (a) L. Canali and D. C. Sherrington, *Chem. Soc. Rev.*, 1999, 28, 85;
 (b) E. N. Jacobsen, *Acc. Chem. Res.*, 2000, 33, 421;
 (c) T. Katsuki, *Chem. Soc. Rev.*, 2004, 33, 437;
 (d) C. Baleizão and H. Garcia,
- 60 Chem. Rev., 2006, 106, 3987; (e) A. Zulauf, M. Mellah, X. Hong and E. Schulz, *Dalton Trans.*, 2010, 39, 6911; (f) B. Wu, J. C. Gallucci, J. R. Parquette and T. V. RajanBabu, *Chem. Sci.*, 2014, 5, 1102.
- (a) D. J. Darensbourg, R. M. Mackiewicz, A. L. Phelps and D. R.
 Billodeaux, Acc. Chem. Res., 2004, 37, 836; (b) D. J. Darensbourg, Chem. Rev., 2007, 107, 2388; (c) A. Decortes, A. M. Castilla and A. W. Kleij, Angew. Chem. Int. Ed., 2010, 49, 9822; (d) M. R. Kember, A. Buchard and C. K. Williams, Chem. Commun., 2011, 47, 141; (e)
 S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, Coord. Chem. Rev., 2011, 255, 1460; (f) A. Sauer, A. Kapelski, C. Fliedel, S. Dagorne, M. Kol and J. Okuda, Dalton Trans., 2013, 42, 9007.
- Dagone, M. Korand, S. Okuda, Daton Trans. 2013, 42, 9007.
 (g) D. Pappalardo, M. Bruno, M. Lamberti, M. Mazzeo and C. Pellecchia, J. Mol. Catal. A: Chem., 2013, 379, 303.

- 16 E. M. Broderick and P. L. Diaconescu, *Inorg. Chem.*, 2009, **48**, 4701.
 - 17 (a) L. Zhang, Y. Yao, Y. Luo, Q. Shen and J. Sun, *Polyhedron*, 2000, **19**, 2243; (b) P. B. Hitchcock, M. F. Lappert and A. Singh, *J. Chem. Soc., Chem. Commun.*, 1983, 1499; (c) G. Qi, Y. Lin, J. Hu and Q. Shen, *Polyhedron*, 1995, **14**, 413.
- 80 18 D. C. Bradley, J. S. Ghotra, F. A. Hart, J. Chem. Soc., Dalton Trans., 1973, 1021-1023.
 - (a) H. Peng, Z. Zhang, R. Qi, Y. Yao, Y. Zhang, Q. Shen and Y. Cheng, *Inorg. Chem.*, 2008, 47, 9828; (b) W. J. Evans, C. H. Fujimoto and J. W. Ziller, *Polyhedron*, 2002, 21, 1683.
- ⁸⁵ 20 There were several molecules of disordered THF in the unit cell for complex **4** which hindered an acceptable refinement of the structure. The structure was obtained in the monoclinic, space group $P_{21/c}$, a = 10.963(2) Å, b = 30.267(6) Å, c = 21.811(5) Å, V = 7146(3) Å³, $a = \gamma = 90.00^{\circ}$, $\beta = 99.072(6)^{\circ}$, Z = 4.
- 90 21 R. D. Shannon, Acta Cryst., 1976, A32, 751.
 - 22 L. Fan, Y. Wang, Y. Yao, B. Wu and Q. Shen, Z. Anorg. Allg. Chem., 2013, 639, 739.
 - (a) X. Han, L. Wu, Y. Yao, Y. Zhang and Q. Shen, *Chin. Sci. Bull.*, 2009, 54, 3795; (b) B. Xu, X. Han, Y. Yao, Y. Zhang and Q. Shen, *Chin. J. Chem.*, 2010, 28, 1013; (c) X. Gu, X. Han, Y. Yao, Y. Zhang and Q. Shen, *J. Organomet. Chem.*, 2010, 695, 2726; (d) L. Huang, X. Han, Y. Yao, Y. Zhang and Q. Shen, Y. Zhang and Q. Shen, *Appl. Organometal. Chem.*, 2011, 25, 464.
 - 24 M.-H. Lin and T. V. RajanBabu, Org. Lett., 2002, 4, 1607.
- (a) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229;
 (b) Y. Huang, W.-C. Hung, M.-Y. Liao and T.-E. Tsai, *J. Polym. Sci. Part A: Polym. Chem.*, 2009, **47**, 2318;
 (c) H.-Y. Chen, H.-Y. Tang and C.-C. Lin, *Macromolecules*, 2006, **39**, 3745.