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Synthesis, structure, and catalytic activity of organoyttrium complexes with chiral binaphthyl-based amidate ligands

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ABSTRACT

Two new chiral organoyttrium amidate complexes $1-Y[N(SiMe_3)_2]_2$ (**3**) and $2-Y[N(SiMe_3)_2]_2 \cdot C_6H_{12}$ ($4 \cdot C_6H_{12}$) have been readily prepared in good yields by silylamine elimination reaction between Y[N (SiMe_3)_2]_3 and chiral binaphthyl-based amidate ligands, (R)-2,2'-bis(mesitoylamino)-1,1'-binaphthyl (**1**) and (S)-2-(mesitoylamino)-2'-(dimethylamino)-1,1'-binaphthyl (**2**), respectively. Complexes **2** and **3** have been characterized by various spectroscopic techniques, elemental analyses, and X-ray diffraction analyses. Complexes **3** and **4** are active catalysts for the polymerization of *rac*-lactide, leading to the isotactic-rich polylactides.

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Chiral rare earth metal complexes based on non-Cp ligands have attracted increasing attention in the past decades [1–6]. This interest is spurred by the lability of rare earth metal element-ligand bonds and the flexibility of their coordination geometries. These features make them highly suitable for use in catalysis. However, the rare earth metal complexes supported by non-Cp ligands usually suffer from salt addition, dimerization or ligand redistribution, and these factors also make it difficult to generate well-defined chiral architectures that will lead to efficient enantioselective reactions [1]. Thus, the development of new chiral rare earth catalysts is a desirable and challenging goal. In recent years, we have developed a series of chiral non-Cp multidentate ligands, and their early transition metal complexes are useful catalysts for a wide range of transformations [7–15]. For example, group 4 metal complexes with chiral binaphthylamidate ligands (R)-2,2'-bis(mesitoylamino)-1,1'-binaphthyl (1) [12] and (S)-2-(mesitoylamino)-2'-(dimethylamino)-1,1'-binaphthyl (2) [11] are useful chiral catalysts for the hydroamination/cyclization, in which good enantioselectivities (up to 86% ee) with excellent conversions (up to 100%) have been obtained [16]. Encouraged by the attractive features of the amidate ligand system, and to our knowledge, no chiral rare earth metal amidate catalyst has been reported. We have recently started exploring ligands 1 and 2 in rare earth chemistry.

It has been documented that rare earth metal amidate complexes can be efficiently prepared via silylamine elimination reaction between $Ln[N(SiMe_3)_2]_3$ and protic amidate ligands [17,18]. It is rational to propose that the acidic protons in the chiral amidate ligands 1 and 2 would allow the similar silylamine elimination to occur between **1** or **2** and metal amides. In fact, treatment of **1** or **2** with 1 equiv of $Y[N(SiMe_3)_2]_3$ in toluene gives, after recrystallization from a toluene or cyclohexane solution, the amidate yttrium complexes $1-Y[N(SiMe_3)_2]_2$ (**3**) and $2-Y[N(SiMe_3)_2]_2 \cdot C_6H_{12}$ ($4 \cdot C_6H_{12}$), respectively, in good yields (Schemes 1 and 2) [19]. Complexes **3** and **4** are stable in dry nitrogen atmosphere, while they are very sensitive to moisture. Complexes **3** and **4** are soluble in organic solvents such as THF, DME, pyridine, toluene, and benzene, but only slightly soluble in *n*-hexane. Complexes **3** and **4** have been characterized by various spectroscopic techniques, elemental analyses, and X-ray diffraction analyses [19,20].

The solid-state structure of **3** shows that the Y³⁺ is σ -bound to one nitrogen atom and two oxygen atoms from ligand **1** and two nitrogen atoms from two amido N(SiMe₃)₂ groups in a distorted-trigonalbipyramidal geometry (Fig. 1) with the average distance of Y-N (2.330 (3) Å), and the average distance of Y-O (2.254(2) Å), respectively. The potentially tetradentate amidate ligand adopts a tridentate binding mode. The solution NMR characterization data are also consistent with this *C*₁ symmetric binding mode, as the ¹³C NMR spectra show two signals at about 181.5 ppm and 172.0 ppm for the carbonyl group, attributable to a bidentate (κO , κN) binding and a monodentate (κO) binding, respectively [12]. The distances of Y-N(SiMe₃)₂ are 2.272(3) and 2.286(3) Å, which are slightly longer than that found in [(S)-2-Me₂N-C₂₀H₁₂-2'-(NCHC₄H₃N)]₂YN(SiMe₃)₂ (2.258(2) Å) [7]. The twisting between two naphthyl rings of torsion angle is 85.9(1)°, indicating that they are almost perpendicular to each other.

The solid-state structure of $4 \cdot C_6 H_{12}$ shows there is one **4** molecule and one solvated cyclohexane molecule in the lattice. In the molecule **4**, the Y³⁺ is σ -bound to two nitrogen atoms and one oxygen atom from ligand **2** and two nitrogen atoms from two amido N(SiMe₃)₂ groups in a distorted-trigonal-bipyramidal geometry (Fig. 2) with the

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Scheme 1. Synthesis of complex 3.

average distance of Y-N 2.388(5) Å, and the distance of Y-O 2.294(4) Å, respectively. The distances of Y-N(SiMe₃)₂ are 2.265(5) and 2.244 (5) Å, which are slightly longer than those found in {[$2,6^{-i}Pr_2C_6H_3NC$ (O)]-1-C₁₀H₇}Y[N(SiMe₃)₂]₂(THF) (2.214(2) and 2.231(2) Å) [18]. The twisting between two naphthyl rings of torsion angle is 67.9(2)°, which is comparable to those found in (**2**)₂Ti(NMe₂)₂ (70.4(2) and 69.9(4)°) and (**2**)₂Zr(NMe₂)₂ (71.6(5) and 69.2(5)°) [11].

The polymerization data show that the complexes **3** and **4** can initiate the ring opening polymerization (ROP) of racemic-lactide (rac-LA) [21] under mild conditions (Table 1). It allows the complete conversion of 1000 equiv of lactide within 2 h at room temperature in toluene at $[rac-LA] = 1.0 \text{ mol } L^{-1}$ (Table 1, entries 1 and 2). However, polymerizations with these yttrium initiators/catalysts proceed much more slowly in THF (Table 1, entries 5 and 6), presumably due to the competitive coordination between the monomer and this donor solvent [22]. This difference in activity between toluene and THF solvent is observed more clearly at a lower temperature (Table 1, entries 1, 2, 5 and 6) than at higher temperature (Table 1, entries 3, 4, 7 and 8). The microstructure of polymers, as determined by homodecoupled ¹H NMR experiments in the region of 5.30–5.00 ppm [23– 26], shows the resulting polylactides are all isotactic-rich (riched in the region of 5.16-5.11 ppm) under our conditions examined. Molecular weights and polydispersities of the polymers produced ranged from 65.4 to 71.3 kg mol⁻¹ and 1.21 to 1.34, respectively. Our results show that the catalytic activities of **3** and **4** resemble that of [2- $(2.6^{-i}Pr_2C_6H_3N CH)C_4H_3N]_2Y(CH_2SiMe_3)(THF)_2$ [27], while the microstructure of the resulting polylactides are similar to those initiated by [(S)-2-MeO-C₂₀H₁₂-2'-(NCHC₄H₃N)]₂LnN(SiMe₃)₂}₂ [10].

In conclusion, two new chiral rare earth metal amidate complexes have been readily prepared *via* silylamine elimination reaction between Y[N(SiMe₃)₂]₃ and chiral binaphthyl-based amidate ligands **1** and **2**. Both complexes are active catalysts for the polymerization of *rac*-lactide, leading to the isotactic-rich polylactides.

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Scheme 2. Synthesis of complex 4.



Fig. 1. Molecular structure of 3. Selected bond lengths (Å) and bond angles (deg): Y(1)-O(1) 2.340(2), Y(1)-O(2) 2.168(2), Y(1)-N(1) 2.433(2), Y(1)-N(3) 2.272(3), Y(1)-N(4) 2.286(3), Y(1)-C(21) 2.801(3), O(1)-Y(1)-O(2) 141.68(9), O(1)-Y(1)-N(1) 54.68(7), O(1)-Y(1)-N(3) 107.96(9), O(1)-Y(1)-N(4) 87.71(9), O(2)-Y(1)-N(1) 87.91(8), O(2)-Y(1)-N(3) 101.49(9), O(2)-Y(1)-N(4) 101.14(10), N(1)-Y(1)-N(3) 127.72(9), N(1)-Y(1)-N(4) 115.86(11), torsion (aryl-aryl) 85.9(1).

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Appendix A. Supplementary material

CCDC 791749, and 791750 contain the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the



Fig. 2. Molecular structure of 4. Selected bond lengths (Å) and bond angles (deg): Y(1)-N(1) 2.367(4), Y(1)-N(2) 2.674(5), Y(1)-N(3) 2.265(5), Y(1)-N(4) 2.244(5), Y(1)-O(1) 2.294(4), Y(1)-C(21) 2.736(6), N(1)-Y(1)-N(2) 76.7(2), N(1)-Y(1)-N(3) 126.8(2), N(1)-Y(1)-N(4) 113.6(2), N(2)-Y(1)-N(3) 95.6(2), N(2)-Y(1)-N(4) 109.8(2), N(3)-Y(1)-N(4) 118.8(2), O(1)-Y(1)-N(1) 56.9(2), O(1)-Y(1)-N(2) 133.08(13), O(1)-Y(1)-N(3) 105.9(2), O(1)-Y(1)-N(4) 95.66(17), torsion (aryl-aryl) 67.9(2).

Table 1

Polymerization of *rac*-lactide (LA) catalyzed by complex **3** and **4**^a.



rac-Lactide

Isotactic Polvlactide

| Entry | Precatalyst | T (°C) | Solvent | Conv. (%) | M_n^b (kg/mol) | $M_{\rm w}/M_{\rm n}^{\rm b}$ | <i>P</i> _m ^c (%) |
|-------|-------------|--------|---------|------------------|------------------|-------------------------------|--|
| 1 | 3 | 20 | Toluene | 100 | 70.3 | 1.28 | 68 |
| 2 | 4 | 20 | Toluene | 100 | 69.5 | 1.34 | 59 |
| 3 | 3 | 40 | Toluene | 100 ^d | 71.3 | 1.21 | 71 |
| 4 | 4 | 40 | Toluene | 100 ^d | 70.4 | 1.24 | 62 |
| 5 | 3 | 20 | THF | 85 | 65.4 | 1.32 | 68 |
| 6 | 4 | 20 | THF | 90 | 67.8 | 1.30 | 60 |
| 7 | 3 | 40 | THF | 95 ^d | 67.2 | 1.34 | 66 |
| 8 | 4 | 40 | THF | 98 ^d | 68.7 | 1.29 | 63 |

^a Conditions: precat./LA (mol/mol) = 1/1000; polymerization time, 2 h; solvent, 5 mL; [LA] = 1.0 mol/L.

Measured by GPC (using polystyrene standards in THF).

^c P_m is the probability of meso linkages between monomer units and is determined from the methine region (5.30–5.00 ppm) of the homonuclear decoupled ¹H NMR spectrum in CDCl₃ at 25 °C [23-26].

¹ Polymerization time, 0.5 h.

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary material with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.09.034.

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- [19] Preparation of 3. Under nitrogen gas, a toluene solution (10 mL) of 1 (0.29 g, 0.5 mmol) was slowly added to a toluene solution (10 mL) of Y[N(SiMe₃)₂]₃ (0.28 g, 0.5 mmol) with stirring at room temperature. The resulting solution was refluxed overnight to give a light yellow solution. The solution was filtered, and the filtrate was concentrated to about 2 mL. 3 was isolated as colorless crystals after this solution stood at room temperature for three days. Yield: 0.39 g (79%). M.p.: 218–220 °C (dec.). ¹H NMR (C_6D_6): δ 8.06 (d, J = 8.8 Hz, 1H, aryl), 7.91 (d, J = 8.8 Hz, 1H, aryl), 7.64 (d, J = 8.1 Hz, 1H, aryl), 7.51 (m, 2H, aryl), 7.43 (m, 2H, aryl), 6.83 (m, 3H, aryl), 6.65 (m, 2H, aryl), 6.55 (s, 2H, aryl), 6.46 (s, 2H, aryl), 6.36 (s, H), NI), 2.67 (s, 3H, CH₃), 2.14 (s, 6H, CH₃), 2.12 (s, 3H, CH₃), 1.80 (s, 3H, CH₃), 1.76 (s, 3H, CH₃), 0.53 (s, 9H, Si(CH₃)₃), 0.32 (s, 27H, Si(CH₃)₃). ¹³C NMR (C₆D₆): δ 181.5, 172.0, 139.8, 138.2, 137.8, 137.5, 136.5, 136.1, 134.9, 134.3, 134.2, 132.7,

131.4, 131.0, 129.7, 128.3, 128.0, 125.7, 124.9, 124.5, 124.4, 124.3, 123.8, 122.7, 122.2, 24.4, 21.7, 4.1, 3.1. IR (KBr, cm⁻¹): v 3310 (m), 2936 (m), 1722 (s), 1471 (s), 1389 (s), 1270 (s), 1159 (s), 972 (s), 753 (s). Anal. Calcd for C₅₂H₇₁N₄O₂Si₄Y: C, 63.38; H, 7.26; N, 5.69. Found: C, 63.49; H, 7.06; N, 5.77%. Preparation of 4 · C₆H₁₂. This compound was prepared as colorless crystals from the reaction of 2 (0.23 g, 0.5 mmol) with $Y[N(SiMe_3)_2]_3$ (0.28 g, 0.5 mmol) in toluene (20 mL) and recrystallization from a cyclohexane solution by a similar procedure as in the synthesis of **3**. Yield: 0.40 g (85%). M.p.: 169–171 °C (dec.). ¹H NMR (C₆D₆): δ 7.81 (d, J=9.2 Hz, 1H, aryl), 7.63 (m, 2H, aryl), 7.44 (d, J=8.1 Hz, 1H, aryl), 7.28 (d, J=8.9 Hz, 1H, aryl), 7.14 (d, J=9.6 Hz, 1H, aryl), 7.05 (m, 2H, aryl), 6.92 (m, 2H, aryl), 6.85 (s, 1H, aryl), 6.79 (m, 1H, aryl), 6.50 (s, 2H, aryl), 2.81 (s, 3H, CH₃), 2.70 (s, 6H, NCH₃), 2.09 (s, 3H, CH₃), 1.65 (s, 3H, CH₃), 1.43 (s, 12H, C₆H₁₂), 0.66 (s, 18H, Si(CH₃)₃), 0.27 (s, 18H, Si(CH₃)₃). ¹³C NMR (C₆D₆): δ 182.0, 145.1, 141.1, 138.5, 136.3, 134.5, 134.3, 133.9, 132.7, 131.6, 130.7, 130.2, 128.9, 128.5, 128.4, 127.3, 126.8, 126.6, 126.1, 125.6, 124.6, 123.4, 119.4, 47.4, 27.0, 22.8, 20.5, 6.1, 5.4. IR (KBr, cm⁻¹): v 2961 (m), 2932 (w), 1612 (m), 1455 (s), 1417 (s), 1259 (s), 1093 (s), 1066 (s), 1014 (s), 929 (s), 797 (s). Anal. Calcd for C₅₀H₇₇N₄OSi₄Y: C, 63.12; H, 8.16; N, 5.89. Found: C, 63.23; H, 8.07; N, 5.73%.

- [20] *Crystal data for* **3**: $C_{52}H_{71}N_4O_2Si_4Y$, fw = 985.40, monoclinic, P12₁1, *a* = 12.708(2) Å, b = 19.822(3) Å, c = 17.621(2) Å, $\beta = 104.67(1)^{\circ}$, V = 4294.0(9) Å³, Z = 2, R1 = 0.046 for 14786 ($I > 2\sigma(I)$), wR2 = 0.127 (all data). Crystal data for $4 \cdot C_{e}H_{12}$: $C_{50}H_{77}N_4OSi_4Y$, fw = 951.43, triclinic, P1, a = 9.000(1) Å, b = 11.502(1) Å c = 13.067(2) Å, $\alpha = 101.60(1)$, $\beta = 95.96(1)$, $\gamma = 91.03(1)$, V = 5963.3(3) Å³, Z=1, R1 = 0.048 for 5613 ($I>2\sigma(I)$), wR2 = 0.099 (all data).
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