

Synthesis, structural characterization, and reactivity of organolanthanides derived from a new chiral ligand (*S*)-2-(pyrrol-2-ylmethyleneamino)-2'-hydroxy-1,1'-binaphthyl

Qiuwen Wang, Li Xiang, Guofu Zi *

Department of Chemistry, Beijing Normal University, Beijing 100875, China

Received 8 August 2007; received in revised form 10 October 2007; accepted 16 October 2007

Available online 22 October 2007

Abstract

Condensation of (*S*)-2-amino-2'-hydroxy-1,1'-binaphthyl with 1 equiv. of pyrrole-2-carboxaldehyde in toluene in the presence of molecular sieves at 70 °C gives (*S*)-2-(pyrrol-2-ylmethyleneamino)-2'-hydroxy-1,1'-binaphthyl (**1H₂**) in 90% yield. Deprotonation of **1H₂** with NaH in THF, followed by reaction with LnCl₃ in THF gives, after recrystallization from a toluene or benzene solution, dinuclear complexes (**1**)₃Y₂(thf)₂ · 3C₇H₈ (**3** · 3C₇H₈) and (**1**)₃Yb₂(thf)₂ · 3C₆H₆ (**4** · 3C₆H₆), respectively, in good yields. Treatment of **1H₂** with Ln[N(SiMe₃)₂]₃ in toluene under reflux, followed by recrystallization from a benzene solution gives the dimeric amido complexes {**1**-LnN(SiMe₃)₂}₂ · 2C₆H₆ (Ln = Y (**5** · 2C₆H₆), Yb (**6** · 2C₆H₆)) in good yields. All compounds have been characterized by various spectroscopic techniques, elemental analyses and X-ray diffraction analyses. Complexes **5** and **6** are active catalysts for the polymerization of methyl methacrylate (MMA) in toluene, affording syn-rich poly-(MMA)s.

© 2007 Elsevier B.V. All rights reserved.

Keywords: (*S*)-2-Amino-2'-hydroxy-1,1'-binaphthyl; Chiral organolanthanides; Synthesis; Crystal structure; Reactivity

1. Introduction

Ligand modifications have played a key role in developing new catalyst precursors for optimizing polymerization activity as well as polymer properties such as stereoregularity, molecular weight, bulky and polar comonomer incorporation, and microstructure [1]. To meet the requirements of different purposes, a large number of ancillary ligands have been developed. One of the most extensively developed families is cyclopentadienyl (Cp) and its derivatives [2]. Recently, research efforts have been directed towards non-Cp ligands by virtue of their exceptional and tunable steric and electronic features required for compensating coordinative unsaturation of metal centers [3]. The lability of lanthanide element-ligand bonds and the flexibility of their coordination geometries make these elements highly suit-

able for use in catalysis, however, the lanthanide complexes supported by non-Cp ligands usually encounter 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 [4]. Thus, chiral multidentate ligands have attracted considerable interest, which can provide proper sterics and electronics for the lanthanide metal center to prevent the side-reactions mentioned above via varying the size and electron donor of the substituents.

Although many lanthanide catalysts based on non-Cp ligands have been reported [4,5], the development of new chiral lanthanide catalysts is a desirable and challenging goal. In recent years, we have developed a series of chiral non-Cp multidentate ligands, and they have been shown that their Ir(I), Rh(I), Ti(IV), Ag(I), Zn(II) and lanthanide complexes are useful catalysts for a range of transformations [6]. In our attempt to further explore the chiral non-Cp ligand system and their application in lanthanide chemistry, we

* Corresponding author. Tel.: +86 10 5880 2237; fax: +86 10 5880 2075.
E-mail address: gzi@bnu.edu.cn (G. Zi).

have recently studied a new chiral tridentate ligand, (*S*)-2-(pyrrol-2-ylmethyleneamino)-2'-hydroxy-1,1'-binaphthyl (**1H₂**), and found it useful to stabilize the amido lanthanide complexes, which are potential catalysts for the polymerization of the olefins. We report herein the synthesis and property of this new chiral ligand, (*S*)-2-(pyrrol-2-ylmethyleneamino)-2'-hydroxy-1,1'-binaphthyl (**1H₂**), its use in lanthanide chemistry, and the application of the resulting complexes as catalysts for the polymerization of methyl methacrylate (MMA).

2. Experimental

2.1. General methods

All experiments were performed under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Methyl methacrylate (MMA) was freshly distilled from CaH₂ immediately prior to use. (*S*)-2-amino-2'-hydroxy-1,1'-binaphthyl [7] and Ln[N(SiMe₃)₂]₃ [8] were prepared according to the literature methods. All chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. Molecular weights of the polymer were estimated by gel permeation chromatography (GPC) using a PL-GPC 50 apparatus. ¹H and ¹³C NMR spectra were recorded on a Bruker AV 500 spectrometer at 500 and 125 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

2.2. Preparation of (*S*)-2-(pyrrol-2-ylmethyleneamino)-2'-hydroxy-1,1'-binaphthyl (**1H₂**)

Pyrrole-2-carboxaldehyde (0.95 g, 10.0 mmol) was mixed with (*S*)-2-amino-2'-hydroxy-1,1'-binaphthyl (2.85 g, 10.0 mmol) in dry toluene (50 mL). A few 4 Å molecular sieves were added, and the solution was warmed up to 70 °C and kept for one day at this temperature. The solution was filtered and the solvent was removed under reduced pressure. The resulting brown solid was recrystallized from mixed solvents (20 mL) of benzene and *n*-hexane (1:1) to give **1H₂** as yellow crystals. Yield: 3.26 g (90%). M.p.: 178–180 °C. ¹H NMR (C₆D₆): δ 9.10 (br, s, 1H), 8.09 (s, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.91 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.37–7.14 (m, 7H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.68 (s, 1H), 6.49 (d, *J* = 3.3 Hz, 1H), 6.12 (d, *J* = 2.5 Hz, 1H); proton of OH was not observed. ¹³C NMR (C₆D₆): δ 152.0, 150.3, 148.7, 134.5, 133.5, 132.3, 130.3, 130.0, 129.8, 129.5, 128.3, 127.4, 127.0, 126.5, 126.4,

125.4, 125.3, 123.7, 123.3, 123.0, 120.2, 119.2, 118.0, 117.6, 109.9. IR (KBr, cm⁻¹): ν 3432 (s), 3299 (s), 3049 (w), 2954 (w), 1621 (vs), 1608 (vs), 1586 (vs), 1503 (s), 1414 (s), 1340 (s), 1273 (s), 1139 (s), 1036 (s), 957 (s), 813 (s), 746 (s). Anal. Calc. for C₂₅H₁₈N₂O: C, 82.85; H, 5.01; N, 7.73. Found: C, 82.62; H, 4.79; N, 7.63%.

2.3. Preparation of (I)₃Y₂(thf)₂ · 3C₇H₈ (**3** · 3C₇H₈)

A solution of **1H₂** (0.36 g, 1.0 mmol) in THF (20 mL) was stirred with NaH (0.5 g, 20.8 mmol) at room temperature for 2 h and then filtered, the filtrate was added to a suspension of YCl₃ (0.19 g, 1.0 mmol) in THF (10 mL). The mixture was stirred at room temperature overnight, and the solvent was removed under vacuum. The resulting oily residue was extracted with toluene (10 mL × 2), and the toluene solutions were combined and concentrated to about 5 mL. **3** · 3 C₇H₈ was isolated as orange-red crystals after this solution stood at room temperature for three days. Yield: 0.42 g (75%). M.p.: 280–282 °C (dec.). ¹H NMR (C₆D₆): δ 8.13–6.37 (m, 61H), 5.91 (m, 1H), 5.22 (m, 1H), 2.94 (m, 4H, THF), 2.70 (m, 2H, THF), 2.40 (m, 2H, THF), 2.23 (s, 9H, C₆H₅CH₃), 0.77 (m, 2H, THF), 0.66 (m, 2H, THF), 0.56 (m, 2H, THF), 0.33 (m, 2H, THF); Note: protons (46H) of three ligand anions **1** were overlapped with protons (15H) of three toluene molecules as a multiple resonance ranged from 8.13 to 6.37 ppm. ¹³C NMR (C₆D₆): δ 160.4, 159.2, 157.3, 157.2, 155.4, 150.3, 148.4, 146.8, 146.3, 139.8, 139.2, 137.6, 137.2, 136.1, 135.2, 134.7, 134.6, 134.1, 132.6, 131.7, 130.7, 129.1, 128.8, 128.4, 128.3, 128.1, 127.3, 127.2, 126.6, 126.4, 126.3, 126.2, 126.1, 125.6, 125.5, 125.3, 124.6, 124.2, 124.1, 122.8, 122.3, 121.9, 120.4, 119.8, 118.7, 117.7, 113.3, 112.9, 112.2, 67.4 (THF), 25.3 (THF), 21.2; other carbon resonances overlapped. IR (KBr, cm⁻¹): ν 3048 (w), 2956 (w), 2887 (w), 1619 (w), 1614 (w), 1572 (s), 1552 (s), 1503 (s), 1389 (s), 1292 (s), 1259 (s), 1035 (s), 807 (s). Anal. Calc. for C₁₀₄H₈₈N₆O₅Y₂: C, 74.37; H, 5.28; N, 5.00. Found: C, 74.09; H, 5.06; N, 5.13%.

2.4. Preparation of (I)₃Yb₂(thf)₂ · 3C₆H₆ (**4** · 3C₆H₆)

This compound was prepared as red crystals from the reaction of **1H₂** (0.36 g, 1.0 mmol), NaH (0.5 g, 20.8 mmol) and YbCl₃ (0.28 g, 1.0 mmol) in THF (30 mL) and recrystallization from benzene according to a similar procedure as outlined in the synthesis of **3** · 3 C₇H₈. Yield: 0.57 g (70%). M.p.: 255–257 °C (dec.). IR (KBr, cm⁻¹): ν 3044 (w), 2964 (w), 1617 (w), 1581 (w), 1571 (s), 1559 (s), 1500 (w), 1388 (w), 1290 (s), 1259 (s), 1034 (s), 806 (s). Anal. Calc. for C₁₀₁H₈₂N₆O₅Yb₂: C, 67.18; H, 4.58; N, 4.65. Found: C, 67.03; H, 4.49; N, 4.97%.

2.5. Preparation of {I-YN(SiMe₃)₂}₂ · 2C₆H₆ (**5** · 2C₆H₆)

A toluene solution (10 mL) of **1H₂** (0.36 g, 1.0 mmol) was slowly added to a toluene solution (10 mL) of

$\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ (0.57 g, 1.0 mmol) with stirring at room temperature. The resulting solution was refluxed overnight to give a yellow solution. The solvent was removed under vacuum, and the resulting oily residue was extracted with benzene (10 mL \times 2). The benzene solutions were combined and concentrated to about 2 mL. $\mathbf{5} \cdot 2 \text{C}_6\text{H}_6$ was isolated as yellow crystals after this solution stood at room temperature for five days. Yield: 0.55 g (80%). M.p.: 285–287 °C (dec.). ^1H NMR (C_6D_6): δ 8.00 (d, $J = 8.9$ Hz, 1H), 7.77 (d, $J = 8.9$ Hz, 1H), 7.57 (d, $J = 8.2$ Hz, 1H), 7.54 (s, 1H), 7.48 (d, $J = 8.1$ Hz, 1H), 7.43 (d, $J = 8.8$ Hz, 1H), 7.17 (s, 6H, C_6H_6), 7.10–6.80 (m, 7H), 6.38 (d, $J = 3.5$ Hz, 1H), 6.10 (s, 1H), 5.65 (m, $J = 1.45$ Hz, 1H), 0.56 (s, 6H), 0.32 (s, 3H), -0.56 (s, 9H). ^{13}C NMR (C_6D_6): δ 158.3, 149.5, 145.8, 140.3, 137.3, 135.3, 133.9, 131.9, 131.2, 130.8, 130.3, 128.9, 128.3, 127.0, 126.8, 126.7, 126.6, 126.3, 124.9, 124.2, 123.6, 123.4, 123.1, 119.9, 114.4, 128.1 (C_6H_6), 5.8, 4.1, 1.7. IR (KBr, cm^{-1}): ν 3051 (w), 2960 (s), 2919 (w), 1620 (w), 1610 (s), 1571 (s), 1500 (s), 1458 (w), 1260 (s), 1092 (s), 1032 (s), 1018 (s), 801 (s). Anal. Calc. for $\text{C}_{74}\text{H}_{80}\text{N}_6\text{O}_2\text{Si}_4\text{Y}_2$: C, 64.61; H, 5.86; N, 6.11. Found: C, 64.73; H, 5.96; N, 6.02%.

2.6. Preparation of $\{\mathbf{1}\text{-YbN}(\text{SiMe}_3)_2\}_2 \cdot 2\text{C}_6\text{H}_6$ ($\mathbf{6} \cdot 2\text{C}_6\text{H}_6$)

This compound was prepared as orange crystals from the reaction of $\mathbf{1H}_2$ (0.36 g, 1.0 mmol) with $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_3$ (0.65 g, 1.0 mmol) in toluene (20 mL) and recrystallization from benzene by a similar procedure as in the synthesis of $\mathbf{5} \cdot 2\text{C}_6\text{H}_6$. Yield: 0.63 g (82%). M.p.: 294–296 °C (dec.). IR (KBr, cm^{-1}): ν 3053 (w), 2961 (s), 2921 (w), 1616 (w), 1605 (w), 1571 (s), 1560 (s), 1500 (s), 1458 (s), 1291 (w), 1259 (s), 1089 (s), 1018 (s), 801 (s). Anal. Calc. for $\text{C}_{74}\text{H}_{80}\text{N}_6\text{O}_2$ -

Si_4Yb_2 : C, 57.57; H, 5.22; N, 5.44. Found: C, 57.78; H, 5.43; N, 5.16%.

2.7. Reaction of $\mathbf{6}$ with Me_3SiCl

A benzene (5 mL) solution of Me_3SiCl (32 mg, 0.3 mmol) was added to a benzene (10 mL) solution of $\{\mathbf{1}\text{-YbN}(\text{SiMe}_3)_2\}_2 \cdot 2\text{C}_6\text{H}_6$ ($\mathbf{6} \cdot 2\text{C}_6\text{H}_6$; 232 mg, 0.15 mmol) with stirring at room temperature. This mixture was kept at 60 °C overnight with stirring and filtered. The filtrate was concentrated to about 1 mL, and three drops of THF was added. Red crystals were isolated after this solution stood at room temperature for two weeks, which were identified as $(\mathbf{1})_3\text{Yb}_2(\text{thf})_2 \cdot 3\text{C}_6\text{H}_6$ ($\mathbf{4} \cdot 3\text{C}_6\text{H}_6$) by X-ray diffraction analysis. Yield: 0.81 mg (45%).

2.8. General procedure for polymerization of MMA

A toluene (2 mL) solution of $\mathbf{5} \cdot 2\text{C}_6\text{H}_6$ (0.025 g, 0.037 mmol) was adjusted to a constant temperature using an external bath. Into the well-stirred solution was syringed 2.0 mL (1.86 g, 18.6 mmol) of methyl methacrylate, and the reaction mixture was vigorously stirred for 3 h at that temperature. The polymerization was quenched by the addition of acidified methanol. The resulting precipitated poly-(MMA) was collected, washed with methanol several times, and dried in vacuum at 50 °C overnight.

2.9. X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Rigaku Saturn CCD diffractometer at 113(2) K using graphite monochromated Mo $\text{K}\alpha$ radiation

Table 1
Crystal data and experimental parameters for compounds $\mathbf{1H}_2$ and $\mathbf{3-6}$

Compound	$\mathbf{1H}_2$	$\mathbf{3} \cdot 3\text{C}_7\text{H}_8$	$\mathbf{4} \cdot 3\text{C}_6\text{H}_6$	$\mathbf{5} \cdot 2\text{C}_6\text{H}_6$	$\mathbf{6} \cdot 2\text{C}_6\text{H}_6$
Formula	$\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}$	$\text{C}_{104}\text{H}_{88}\text{N}_6\text{O}_5\text{Y}_2$	$\text{C}_{101}\text{H}_{82}\text{N}_6\text{O}_5\text{Yb}_2$	$\text{C}_{74}\text{H}_{80}\text{N}_6\text{O}_2\text{Si}_4\text{Y}_2$	$\text{C}_{74}\text{H}_{80}\text{N}_6\text{O}_2\text{Si}_4\text{Yb}_2$
Formula weight	362.41	1679.62	1805.81	1375.62	1543.88
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P12_11$	$P12_11$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	10.505(2)	11.827(2)	11.800(6)	11.592(1)	11.617(1)
b (Å)	8.547(2)	18.450(3)	18.404(9)	15.410(1)	15.488(1)
c (Å)	11.379(2)	19.377(3)	18.721(9)	38.373(2)	38.410(1)
β (°)	107.694(3)	95.299(8)	93.226(7)	90	90
V (Å ³)	973.3(3)	4210.0(11)	4059(3)	6854.2(5)	6911.2(3)
Z	2	2	2	4	4
D_{calc} (g/cm ³)	1.237	1.325	1.477	1.333	1.484
$\mu(\text{Mo K}\alpha)_{\text{calc}}$ (mm ⁻¹)	0.076	1.431	2.350	1.805	2.808
Size (mm)	0.28 \times 0.24 \times 0.20	0.22 \times 0.16 \times 0.14	0.16 \times 0.14 \times 0.10	0.20 \times 0.18 \times 0.16	0.22 \times 0.18 \times 0.16
$F(000)$	380	1744	1820	2864	3112
2θ Range (°)	3.76–52.98	3.06–50.00	3.10–52.00	3.68–55.72	3.66–55.78
Number of reflections, collected	5697	31 863	33 166	63 829	62 741
Number of unique reflections [R_{int}]	2148 [0.020]	14 124 [0.131]	15 808 [0.053]	16 280 [0.068]	16 473 [0.050]
Number of observed reflections	2148	14 124	15 808	16 280	16 473
Absorption correction (T_{max} , T_{min})	0.98, 0.97	0.82, 0.74	0.80, 0.70	0.76, 0.71	0.66, 0.58
R	0.033	0.092	0.055	0.044	0.027
R_w	0.080	0.163	0.105	0.083	0.050
R_{all}	0.040	0.151	0.061	0.062	0.028
Goodness-of-fit	1.08	1.06	1.13	1.03	1.01

($\lambda = 0.71070 \text{ \AA}$). An empirical absorption correction was applied using the SADABS program [9]. All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package [10]. All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **1H₂** and **3–6** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 2
Selected bond distances (Å) and bond angles (°) for **1H₂** and **3–6**

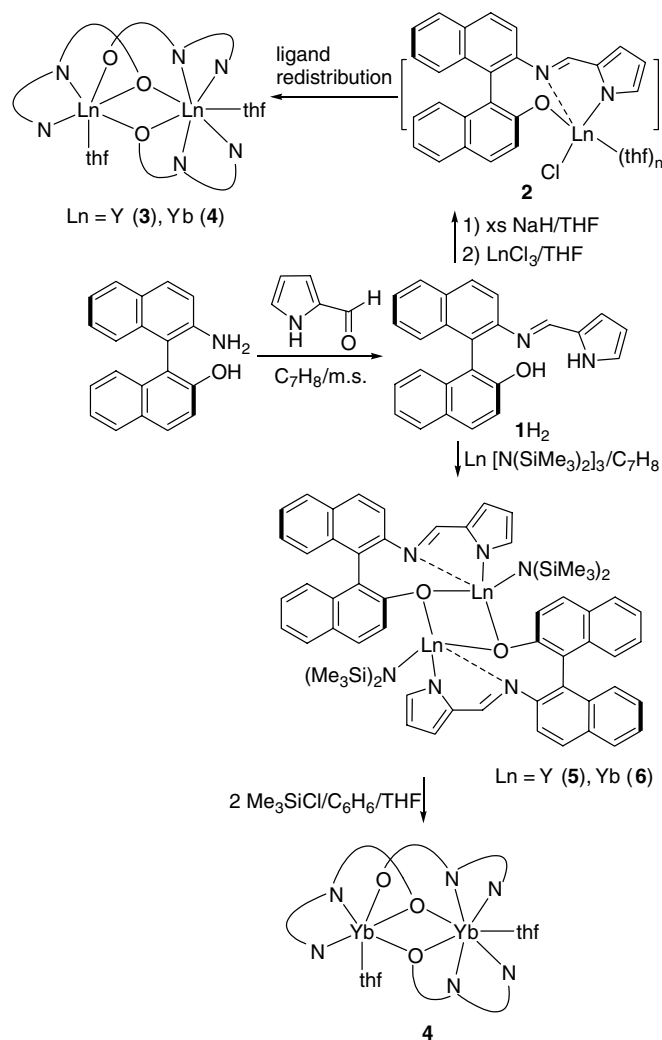
Compound 1H₂			
N(1)–C(21)	1.273(3)	Torsion (pyrrolyl–imine)	0.7(2)
Torsion (aryl–imine)	51.7(2)	Torsion (aryl–aryl)	81.1(2)
Compound 3 · 3C ₇ H ₈			
Y(1)–O(1)	2.328(6)	Y(1)–O(2)	2.300(6)
Y(1)–O(4)	2.386(6)	Y(1)–N(1)	2.467(9)
Y(1)–N(2)	2.413(8)	Y(1)–N(5)	2.469(8)
Y(1)–N(6)	2.393(9)	Y(2)–O(1)	2.292(6)
Y(2)–O(2)	2.315(6)	Y(2)–O(3)	2.104(6)
Y(2)–O(5)	2.390(7)	Y(2)–N(3)	2.438(9)
Y(2)–N(4)	2.356(9)	Y(1)···Y(2)	3.660(6)
Y(1)–O(1)–Y(2)	104.8(3)	Y(1)–O(2)–Y(2)	104.9(2)
Torsion (aryl–imine)	30.9(3)	Torsion (aryl–aryl)	65.2(3)
	60.1(3)		65.8(3)
	57.9(3)		64.9(3)
Compound 4 · 3C ₆ H ₆			
Yb(1)–O(1)	2.315(5)	Yb(1)–O(2)	2.256(5)
Yb(1)–O(4)	2.368(5)	Yb(1)–N(1)	2.428(7)
Yb(1)–N(2)	2.349(7)	Yb(1)–N(5)	2.453(7)
Yb(1)–N(6)	2.351(6)	Yb(2)–O(1)	2.226(6)
Yb(2)–O(2)	2.284(5)	Yb(2)–O(3)	2.060(6)
Yb(2)–O(5)	2.378(8)	Yb(2)–N(3)	2.370(7)
Yb(2)–N(4)	2.325(8)	Yb(1)···Yb(2)	3.594(2)
Yb(1)–O(1)–Yb(2)	104.6(2)	Yb(1)–O(2)–Yb(2)	104.7(2)
Torsion (aryl–imine)	61.7(2)	Torsion (aryl–aryl)	62.8(2)
	29.6(2)		66.5(2)
	69.4(2)		65.3(2)
Compound 5 · 2C ₆ H ₆			
Y(1)–O(1)	2.329(2)	Y(1)–O(2)	2.167(2)
Y(1)–N(1)	2.438(3)	Y(1)–N(2)	2.311(3)
Y(1)–N(5)	2.218(3)	Y(2)–O(1)	2.166(2)
Y(2)–O(2)	2.340(2)	Y(2)–N(3)	2.456(3)
Y(2)–N(4)	2.293(3)	Y(2)–N(6)	2.213(3)
Y(1)···Y(2)	3.571(1)	Y(1)–O(1)–Y(2)	105.1(1)
Y(1)–O(2)–Y(2)	104.7(1)	Torsion (aryl–imine)	31.7(1)
			32.4(1)
Torsion (aryl–aryl)	66.7(1)		
	72.8(1)		
Compound 6 · 2C ₆ H ₆			
Yb(1)–O(1)	2.304(2)	Yb(1)–O(2)	2.157(2)
Yb(1)–N(1)	2.425(3)	Yb(1)–N(2)	2.265(3)
Yb(1)–N(5)	2.170(3)	Yb(2)–O(1)	2.162(2)
Yb(2)–O(2)	2.297(2)	Yb(2)–N(3)	2.420(3)
Yb(2)–N(4)	2.279(3)	Yb(2)–N(6)	2.183(3)
Yb(1)···Yb(2)	3.525(1)	Yb(1)–O(1)–Yb(2)	104.2(1)
Yb(1)–O(2)–Yb(2)	104.6(1)	Torsion (aryl–imine)	33.7(1)
			31.8(1)
Torsion (aryl–aryl)	71.6(1)		
	64.7(1)		

3. Results and discussion

3.1. Synthesis and characterization of ligand

The C₁-symmetric pyrrole imine ligand, (*S*)-2-(pyrrol-2-ylmethyleneamino)-2'-hydroxy-1,1'-binaphthyl (**1H₂**), is readily prepared by condensation of (*S*)-2-amino-2'-hydroxy-1,1'-binaphthyl with 1 equiv. of pyrrole-2-carboxaldehyde in the presence of molecular sieves in toluene at 70 °C (Scheme 1). The product is isolated in 90% yield after recrystallization from benzene and *n*-hexane (1:1).

Ligand **1H₂** is air-stable, but sensitive to hydrolysis, and very soluble in CH₂Cl₂, CHCl₃, toluene and benzene, and only slightly soluble in *n*-hexane. It has been fully characterized by various spectroscopic techniques, elemental analyses, and single-crystal X-ray analysis. Both the ¹H and ¹³C NMR spectra of **1H₂** indicate that it is non-symmetrical on the NMR timescale, which is consistent with its C₁-symmetric structure. The IR spectrum of **1H₂** shows typical characteristic O–H, N–H and N=C absorptions at 3432, 3299 and 1621 cm^{−1}, respectively.



Scheme 1.

3.2. Synthesis and characterization of complexes

Deprotonation of the chiral ligand **1H**₂ is achieved by reaction with an excess of NaH in THF. The resulting disodium salt **1Na**₂ thus formed is reacted with 1 equiv. of LnCl₃ in THF to give, after recrystallization from a toluene or benzene solution, the dinuclear complexes (**1**)₃Y₂(thf)₂ · 3 C₇H₈ (**3** · 3C₇H₈) and (**1**)₃Yb₂(thf)₂ · 3C₆H₆ (**4** · 3C₆H₆), respectively, in good yields (Scheme 1). No organolanthanide chloride complexes of the type **1**-LnCl(thf)_{*n*} (**2**) are isolated, regardless of the size of the lanthanide ions. These complexes are stable in a dry nitrogen atmosphere, while they are very sensitive to moisture. They are soluble in organic solvents such as THF, DME, pyridine, toluene, and benzene, and slightly soluble in *n*-hexane. They have been characterized by various spectroscopic techniques, elemental analyses, and single-crystal X-ray analyses. Since the salt metathesis does not offer the desirable organolanthanide chloride complexes, an alternate method is then sought.

It has been documented that amido lanthanide complexes can be efficiently prepared via silylamine elimination reactions of Ln[N(SiMe₃)₂]₃ and protic reagents [6e,11]. It is rational to propose that two acidic protons in the ligand **1H**₂ would allow the similar silylamine elimination to occur between **1H**₂ and metal amides. In fact, treatment of **1H**₂ with 1 equiv. of Ln[N(SiMe₃)₂]₃ in toluene at reflux temperature gives, after recrystallization from a benzene solution, organolanthanide amides {**1**-LnN(SiMe₃)₂}₂ · 2C₆H₆ (Ln = Y (**5** · 2C₆H₆), Yb (**6** · 2C₆H₆)) in good yields (Scheme 1). These complexes are stable in a dry nitrogen atmosphere, while they are very sensitive to moisture. They are soluble in organic solvents such as THF, DME, pyridine, toluene, and benzene, and only slightly soluble in *n*-hexane. They have been characterized by various spectroscopic techniques, elemental analyses, and single-crystal X-ray analyses. The ¹H NMR spectrum of **5** · 2C₆H₆ supports the ratio of amino group N(SiMe₃)₂ and ligand **1** is 1:1. Their IR spectra exhibit a weak typical characteristic N=C absorption at about 1620 cm⁻¹.

3.3. Molecular structures of compounds **1H**₂, and **3–6**

The solid-state structures of **1H**₂ and **3–6** have all been confirmed by single-crystal X-ray diffraction analyses. Selected bond distances and angles are listed in Table 2 for comparison.

The molecular structure of **1H**₂ shows that it crystallizes in a C₁ symmetric distorted-tetrahedral geometry (Fig. 1). As expected, the distance (1.273(3) Å) of C=N is in agreement with a C=N double bond. The naphthalene units are twisted with the imine group (torsion angle is 51.7(2)°), and a more dramatic twisting is observed between the naphthalene rings which are almost perpendicular to each other (torsion angles is 81.1(2)°).

The solid-state structures of **3** · 3C₇H₈ and **4** · 3C₆H₆ as derived from single-crystal X-ray diffraction studies confirm that they consist of the isostructural complexes

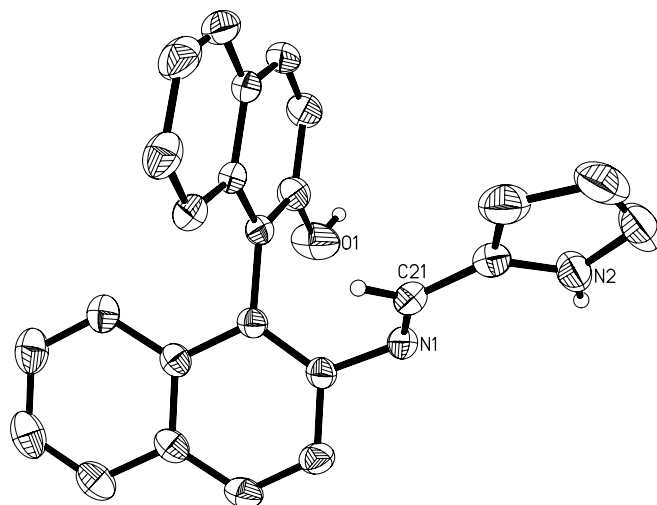


Fig. 1. Molecular structure of **1H**₂ (thermal ellipsoids drawn at the 35% probability level).

(**1**)₃Ln₂(thf)₂ and show three toluene molecules and three benzene molecules of solvation for **3** and **4**, respectively. Coordination of three ligand anions **1** and two THF molecules around two lanthanide ions results in the formation of the dinuclear complexes (**1**)₃Ln₂(thf)₂ (Figs. 2a and 3a). Figs. 2b and 3b show that one Ln³⁺ is σ-bound to two nitrogen atoms and three oxygen atoms from the ligands and one oxygen atom from THF in a distorted-octahedron geometry with the average distance of Ln–N (2.397(9) Å) for Y and (2.348(8) Å) for Yb, respectively, and the average distance of Ln–O (2.275(7) Å) for Y and (2.237(2) Å) for Yb, respectively. The other Ln³⁺ is σ-bound to four nitrogen atoms and two oxygen atoms from the ligands and one oxygen atom from THF in a distorted-pentagonal-bipyramidal geometry with the average distance of Ln–N (2.436(9) Å) for Y and (2.395(7) Å) for Yb, respectively, and the average distance of Ln–O (2.338(6) Å) for Y and (2.275(7) Å) for Yb, respectively. The average Ln–O–Ln angles are 104.9(3)° for Y and 104.7(2)° for Yb complexes, respectively. The structural data agree with those reported in the literature for similar structures [2a]. The naphthylene units are twisted with respect to the imine group by 30.2–60.1° for **3** and 29.6–69.4° for **4**, respectively. The twisting between the naphthylene rings of torsion angles are 64.9–65.8° for **3** and 62.8–66.5° for **4**, which are smaller than that (81.1(2)°) found in **1H**₂. The combination of these twists gives rise to the formation of the dinuclear structure, the chirality of the arrays being prescribed by the chiral twist inherent in the binaphthyl unit. The two Ln³⁺ centers within the dications are separated by 3.660(6) Å for Y and 3.594(2) Å for Yb, respectively.

The solid-state structures of **5** · 2C₆H₆ and **6** · 2C₆H₆ confirm that they are isostructural and show two benzene molecules of solvent in the lattice. Coordination of two ligand anions **1** and two amino N(SiMe₃)₂ groups around two lanthanide ions results in the formation of the dimeric complexes {**1**-LnN(SiMe₃)₂}₂ (Figs. 4 and 5). Each Ln³⁺ is

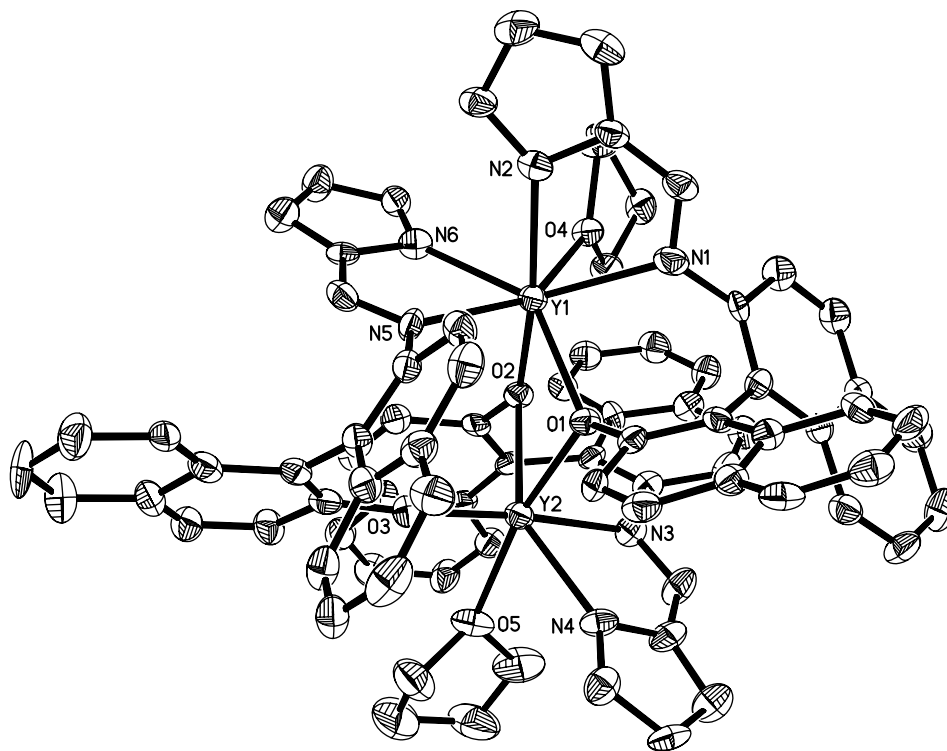


Fig. 2a. Molecular structure of **3** (thermal ellipsoids drawn at the 35% probability level).

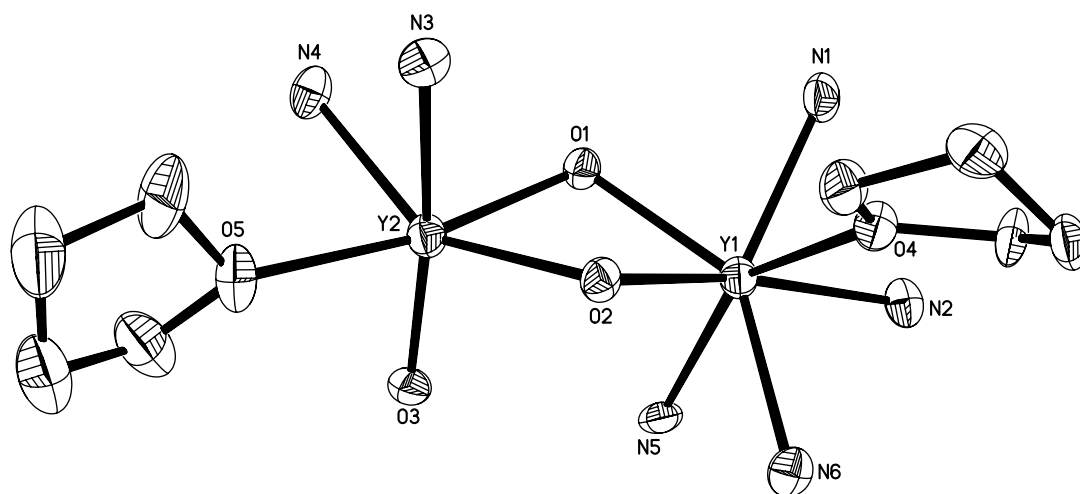


Fig. 2b. Core structure of **3**.

σ -bound to two nitrogen atoms and two oxygen atoms from the ligand anions **1** and one nitrogen atom from the amino $\text{N}(\text{SiMe}_3)_2$ group in a distorted-trigonal-bipyramidal geometry with the average distance of $\text{Ln}-\text{N}$ (2.322(3) Å) for Y and (2.290(3) Å) for Yb, respectively, and the average distance of $\text{Ln}-\text{O}$ (2.250(2) Å) for Y and (2.230(2) Å) for Yb, respectively. The average $\text{Ln}-\text{O}-\text{Ln}$ angles are $104.9(1)^\circ$ for Y and $104.4(1)^\circ$ for Yb complexes, respectively. These structural data are close to those found in **3** and **4** (Table 2). The average distance of $\text{Ln}-\text{N}(\text{SiMe}_3)_2$ (2.216(3) Å) for Y and (2.177(3) Å) for Yb are very close to

the corresponding values of 2.223 Å for Y and 2.183 Å for Yb found in the starting materials $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ [12] and $\text{Yb}[\text{N}(\text{SiMe}_3)_2]_3$ [13]. The naphthylene units are twisted with respect to the imine group by $31.7(1)^\circ$ and $32.4(1)^\circ$ for Y and $31.8(1)^\circ$ and $33.7(1)^\circ$ for Yb, respectively. The twisting between the naphthylene rings of torsion angles are $66.7(1)^\circ$ and $72.8(1)^\circ$ for Y and $64.7(1)^\circ$ and $71.6(1)^\circ$ for Yb. The two Ln^{3+} centers within the dication are separated by 3.571(1) Å for Y and 3.525(1) Å for Yb, respectively. These structural data are comparable to those found in **3** and **4** (Table 2).

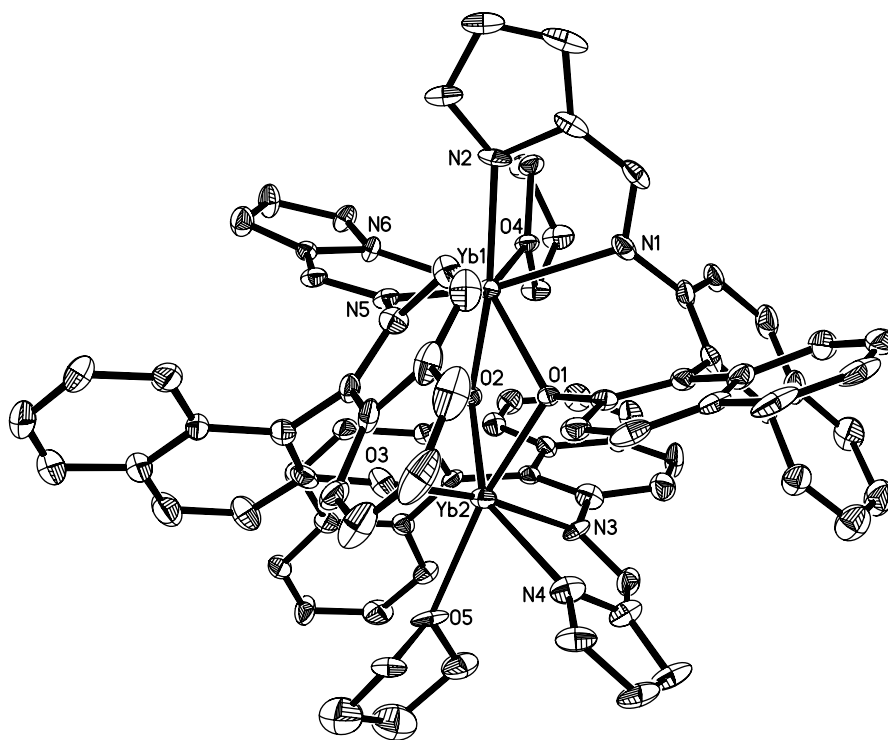


Fig. 3a. Molecular structure of **4** (thermal ellipsoids drawn at the 35% probability level).

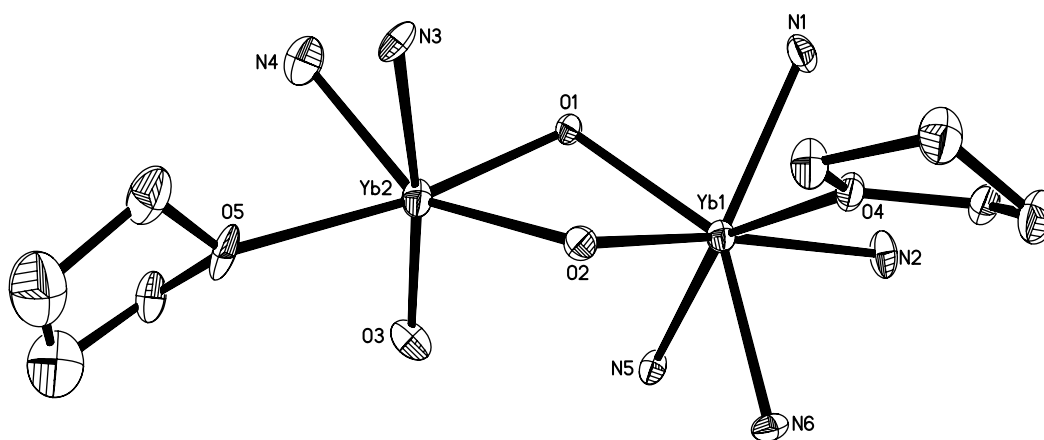


Fig. 3b. Core structure of **4**.

3.4. Reactivity of amido lanthanide complexes

It has been reported that the addition of excess Me_3SiCl or Me_3Al to the metal amide complexes results in the clean formation of chloride or methyl derivatives [14]. Treatment of $\mathbf{6} \cdot 2\text{C}_6\text{H}_6$ with 2 equiv. of Me_3SiCl in benzene at 60°C gives, after recrystallization from THF and benzene (about 1:20), the complex $(\mathbf{1})_3\text{Yb}_2(\text{thf})_2 \cdot 3\text{C}_6\text{H}_6$ ($\mathbf{4} \cdot 3\text{C}_6\text{H}_6$) in 45% yield, instead of the organoytterbium chloride complex (Scheme 1). The primarily ionic bonding between Ln^{3+} and ligands is the driving forces for this reaction. The reaction between Me_3Al and $\mathbf{5} \cdot 2\text{C}_6\text{H}_6$ or $\mathbf{6} \cdot 2\text{C}_6\text{H}_6$ is very complicated, and no pure product has been isolated [15].

These results show that organolanthanide amide complexes exhibit very different reactivity patterns from their d-block transition metal counterparts due to the difference in bonding between metal ions and ligands.

To examine the catalytic ability of amido lanthanide complexes $\mathbf{5} \cdot 2\text{C}_6\text{H}_6$ and $\mathbf{6} \cdot 2\text{C}_6\text{H}_6$ toward polar monomers, polymerization of methyl methacrylate (MMA) has been tested under the conditions given in Table 3. The polymerization data show that conversion of MMA is low over the various reaction temperatures. The sterically encumbered environment around the metal center coupled with the relatively low reactivity of the amido complex compared to the corresponding alkyl or hydride derivatives

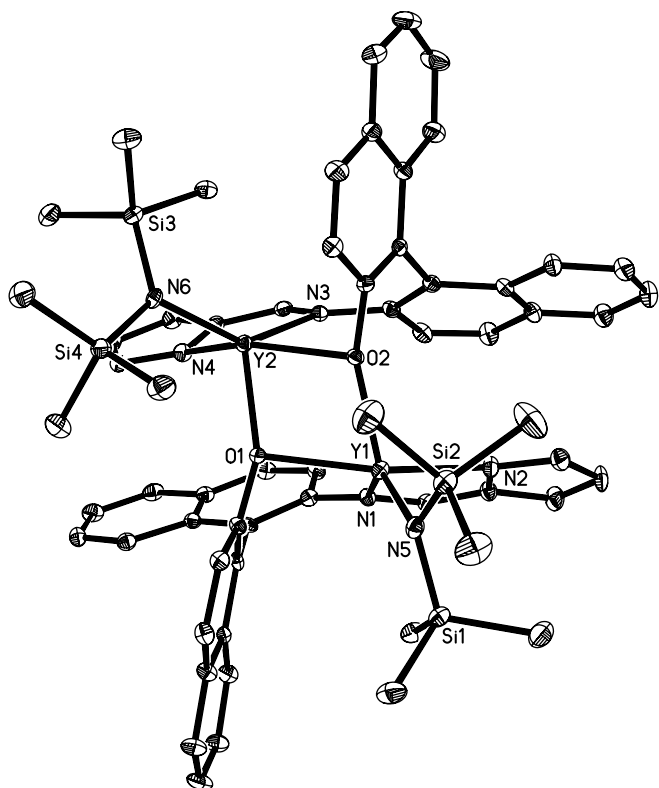


Fig. 4. Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level).

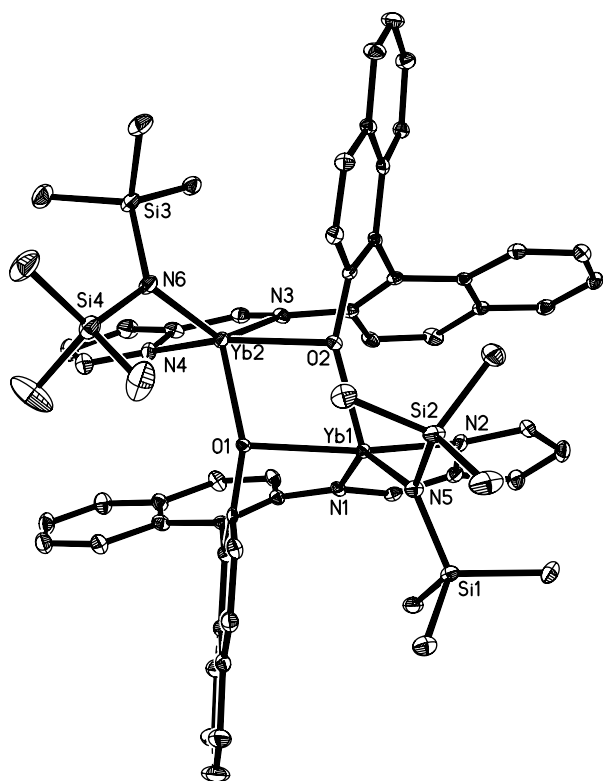


Fig. 5. Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).

Table 3

MMA polymerization results by chiral organolanthanide complexes **5** and **6**^a

Entry	Precat.	<i>T</i> (°C)	Conv. (%)	<i>m</i> ^b (%)	<i>rr</i> ^b (%)	<i>M</i> _n (kg/mol) ^c	<i>M</i> _w / <i>M</i> _n ^c
1	5	20	3.5	24	58	27.0	1.82
2	5	0	5.0	26	59	42.3	1.87
3	5	−20	7.0	25	54	47.8	1.99
4	6	20	3.2	28	45	32.6	2.28
5	6	0	3.7	25	57	34.8	2.32
6	6	−20	5.5	23	55	33.2	2.19

^a Conditions: precat./MMA (mol/mol) = 1/500; polymerization time, 3 h; solvent, 2 mL of toluene; MMA/solvent (v/v) = 1/1.

^b Triad values from methyl region of ¹H NMR spectra in CDCl₃ at 25 °C; isotactic (*mm*), δ 1.23 ppm; heterotactic (*mr*), δ 1.05 ppm; syndiotactic (*rr*), δ 0.85 ppm.

^c Measured by GPC (using polystyrene standards in THF).

[16] seems to be a major reason for such a low conversion. Although both the complexes **5** and **6** can initiate the polymerization of MMA, the conversion ceases after 2 or 3 h. Since this catalytic reaction goes by the 1,4-addition initiation and followed by conjugate addition propagation, and involves the intermediacy of an organolanthanide enolate species [17], which could be stopped by 1,2-migratory insertion at a carbonyl unit of the MMA. The resulting poly(MMA)s are all syn-rich under the conditions examined. Molecular weights and polydispersities of the polymers produced ranged from 27.0 to 47.8 kg mol^{−1} and 1.82 to 2.32, respectively. Our results show that the catalytic activities of **5** · 2 C₆H₆ and **6** · 2 C₆H₆ resemble that of [Me₂Si(C₁₃H₈)(C₅Me₄)]YN(SiMe₃)₂ [18], while the microstructure of the resulting poly(MMA)s are similar to those initiated by [¹Pr₂NB(C₉H₆)(C₂B₁₀H₁₀)]NdN(SiHMe₂)₂(THF) [19] and [Me₂Si(C₅Me₄)(C₅H₃R*)]LnE(SiMe₃)₂ (E = CH, N; R* = (−)-menthyl) [17]. Under similar reaction conditions, no detectable polymerization activity is observed for complexes **3** and **4**, even at room temperature for one week.

4. Conclusions

A new chiral tridentate ligand has been prepared from the reaction between pyrrole-2-carboxaldehyde and (*S*)-2-amino-2'-hydroxy-1,1'-binaphthyl, which can effectively go by silylamine elimination with Ln[N(SiMe₃)₂]₃ to give amido lanthanide complexes. These amido complexes can initiate the polymerization of MMA, leading to syn-rich poly(MMA)s, but the reactivity is very low. Further efforts will focus on the applications of these chiral amido lanthanide complexes toward asymmetric reactions and the exploration of new organolanthanide complexes based on chiral ligands.

5. Supplementary material

CCDC 650930, 650727, 650728, 650729 and 650730 contain the supplementary crystallographic data for **1H**₂, **3**, **4**, **5** and **6**. These data can be obtained free of charge from

The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20602003). We greatly thank Dr. Haibin Song (at the Analytical Laboratory, Nankai University, Tianjin, China) for his help with the crystallography.

References

- [1] For selected recent reviews, see (a) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem., Int. Ed.* 38 (1999) 428; (b) W. Kaminsky, M. Arndt, *Adv. Polym. Sci.* 127 (1997) 144; (c) M. Bochmann, *J. Chem. Soc., Dalton Trans.* (1996) 255; (d) W. Kaminsky, *Macromol. Chem. Phys.* 197 (1996) 3907; (e) H.H. Brintzinger, D. Fisher, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem., Int. Ed.* 34 (1995) 1143; (f) T.J. Marks, *Acc. Chem. Res.* 25 (1992) 57; (g) R.F. Jordan, *Adv. Organomet. Chem.* 32 (1991) 325; (h) J.A. Gladysz, *Chem. Rev.* 100 (2000) (issue 4, special issue for *Frontiers in Metal-Catalyzed Polymerization*); (i) H.B. Kagan, *Chem. Rev.* 102 (2002) (issue 6, special issue for *Frontiers in Lanthanide Chemistry*); (j) V.C. Gibson, S.K. Spitzmesser, *Chem. Rev.* 103 (2003) 283; (k) W.E. Piers, D.J.H. Emslie, *Coord. Chem. Rev.* 233–234 (2002) 131; (l) J. Gromada, J.F. Carpentier, A. Mortreux, *Coord. Chem. Rev.* 248 (2004) 397.
- [2] For selected recent reviews, see (a) H. Schumann, J.A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* 95 (1995) 865; (b) S. Arndt, J. Okuda, *Chem. Rev.* 102 (2002) 1953.
- [3] For selected recent reviews and papers, see (a) R. Duchateau, C.T. van Wee, A. Meetsma, J.H. Teuben, *J. Am. Chem. Soc.* 115 (1993) 4931; (b) P.J. Bailey, S. Pace, *Coord. Chem. Rev.* 214 (2001) 91; (c) G.R. Giesbrecht, G.D. Whitener, J. Arnold, *J. Chem. Soc., Dalton Trans.* (2001) 923; (d) Z. Lu, G.P.A. Yap, D.S. Richeson, *Organometallics* 20 (2001) 706; (e) P.G. Hayes, W.E. Piers, L.W.M. Lee, L.K. Knight, M. Parvez, M.R.J. Elsegood, W. Clegg, *Organometallics* 20 (2001) 2533; (f) D.J.H. Emslie, W.E. Piers, M. Parvez, R. McDonald, *Organometallics* 21 (2002) 4226; (g) Y.M. Yao, M.T. Ma, X.P. Xu, Y. Zhang, Q. Shen, W.T. Wong, *Organometallics* 24 (2005) 4014; (h) D.V. Gribkov, K.C. Hultsch, F. Hampel, *Chem. Eur. J.* 9 (2003) 4796; (i) C.X. Cai, A. Amgoune, C.W. Lehmann, J.F. Carpentier, *Chem. Commun.* (2004) 330; (j) T. Katsuki, *Adv. Synth. Catal.* 344 (2002) 131; (k) O. Runte, T. Priermeier, R. Anwander, *J. Chem. Soc., Chem. Commun.* (1996) 1385; (l) W. Miao, S. Li, D. Cui, B. Huang, *J. Organometal. Chem.* 692 (2007) 3823.
- [4] H.C. Aspinall, *Chem. Rev.* 102 (2002) 1807.
- [5] For selected recent papers, see (a) S. Hong, S. Tian, M.V. Metz, T.J. Marks, *J. Am. Chem. Soc.* 125 (2003) 14768; (b) P.N. O'Shaughnessy, P.D. Knight, C. Morton, K.M. Gillespie, P. Scott, *Chem. Commun.* (2003) 1770; (c) J.Y. Kim, T. Livinghouse, *Org. Lett.* 7 (2005) 1737; (d) D.V. Gribkov, K.C. Hultsch, F. Hampel, *J. Am. Chem. Soc.* 128 (2006) 3748; (e) J. Collin, J.C. Daran, O. Jacquet, E. Schulz, A. Trifonov, *Chem.-Eur. J.* 11 (2005) 3455; (f) N. Meyer, A. Zulys, P.W. Roesky, *Organometallics* 25 (2006) 4179; (g) G.W. Coates, T.M. Ovitt, *J. Am. Chem. Soc.* 121 (1999) 4072; (h) T.M. Ovitt, G.W. Coates, *J. Am. Chem. Soc.* 124 (2002) 1316.
- [6] (a) G.-F. Zi, C.-L. Yin, *Acta Chim. Sin.* 56 (1998) 484; (b) G.-F. Zi, C.-L. Yin, *J. Mol. Catal. A: Chem.* 132 (1998) L1; (c) G. Zi, L. Xiang, Y. Zhang, Q. Wang, Y. Yang, Z. Zhang, *J. Organometal. Chem.* 692 (2007) 3949; (d) Z. Zhang, M. Li, G. Zi, *Chirality* 19 (2007) 802; (e) L. Xiang, Q. Wang, H. Song, G. Zi, *Organometallics* 26 (2007) 5323; (f) Y. Zhang, L. Xiang, Q. Wang, X.-F. Duan, G. Zi, *Inorg. Chim. Acta* (2007), doi:10.1016/j.ica.2007.08.003.
- [7] (a) R.A. Singer, J.R. Brock, E.M. Carreira, *Helv. Chim. Acta* 86 (2003) 1040; (b) G. Zi, L. Xiang, Y. Zhang, Q. Wang, Z. Zhang, *Appl. Organometal. Chem.* 21 (2007) 177.
- [8] D.C. Bradley, J.S. Ghotra, F. Alan Hart, *J. Chem. Soc., Dalton Trans.* (1973) 1021.
- [9] G.M. Sheldrick, *SADABS*, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 1996.
- [10] G.M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structure from Diffraction Data, University of Göttingen, Göttingen, Germany, 1997.
- [11] For selected recent papers, see (a) Y. Matsuo, K. Mashima, K. Tani, *Organometallics* 20 (2001) 3510; (b) A.K. Dash, A. Razavi, A. Mortreux, C.W. Lehmann, J.-F. Carpentier, *Organometallics* 21 (2002) 3238; (c) K.C. Hultsch, F. Hampel, T. Wagner, *Organometallics* 23 (2004) 2601; (d) E. Sheng, S. Wang, G. Yang, S. Zhou, L. Cheng, K. Zhang, Z. Huang, *Organometallics* 22 (2003) 684.
- [12] M. Westerhausen, M. Hartmann, A. Pfitzner, W. Schwarz, *Z. Anorg. Allg. Chem.* 621 (1995) 837.
- [13] M. Niemeyer, *Z. Anorg. Allg. Chem.* 628 (2002) 647.
- [14] For selected recent papers, see (a) G.M. Diamond, R.F. Jordan, J.L. Petersen, *Organometallics* 15 (1996) 4045; (b) A.K. Hughes, A. Meetsma, J.H. Teuben, *Organometallics* 12 (1993) 1936; (c) D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, *Organometallics* 15 (1996) 1572; (d) H. Wang, Y. Wang, H.W. Li, Z. Xie, *Organometallics* 20 (2001) 5110; (e) G. Zi, H.W. Li, Z. Xie, *Organometallics* 21 (2002) 3580.
- [15] Anwander and co-workers have reported the first example of silylamide elimination between amido lanthanide complexes (C₅Me₄R)Ln[N(SiHMe₂)₂]₂ and trimethylaluminum gives the bis(tetramethylaluminate) complexes (C₅Me₄R)Ln(AlMe₄)₂, see R. Anwander, M.G. Klimpel, H. Martin Dietrich, D.J. Shorokhov, W. Scherer, *Chem. Commun.* (2003) 1008.
- [16] H. Yasuda, *J. Polym., Sci. Polym. Chem.* 39 (2001) 1955.
- [17] M.A. Giardello, Y. Yamamoto, L. Brard, T.J. Marks, *J. Am. Chem. Soc.* 117 (1995) 3276.
- [18] M.H. Lee, J.W. Hwang, Y. Kim, J. Kim, Y. Han, Y. Do, *Organometallics* 18 (1999) 5124.
- [19] G. Zi, H.W. Li, Z. Xie, *Organometallics* 21 (2002) 1136.