Synthesis, Structural Characterization, and Reactivity of Organolanthanides Derived from a New Chiral Ligand, (*R*)-Bis(pyrrol-2-ylmethyleneamino)-1,1′-binaphthyl

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Condensation of (*R*)-2,2′-diamino-1,1′-binaphthyl with 2 equiv of pyrrole-2-carboxaldehyde in toluene in the presence of molecular sieves at 70 °C gives (*R*)-bis(pyrrol-2-ylmethyleneamino)-1,1′-binaphthyl (**1**H_2) in 85% yield. Deprotonation of **1**H_2 with NaH in DME, followed by reaction with YCl_3 in DME gives the complex **1**-YCl(dme) (**2**) in 75% yield. A salt metathesis reaction between **2** and $(Me_3Si)_2NNa$ in a mixed solvent of THF and toluene (1:1) gives the organoyttrium amide **1**-Y[N(SiMe$_3$)$_2$](thf)·C_7H_8 (**4**) in 70% yield. Alternatively, the organolanthanide amides may also be prepared by silylamine elimination. For example, treatment of **1**H_2 with 1 equiv of Ln[N(SiMe$_3$)$_2$]$_3$ in toluene at reflux gives, after recrystallization from a mixed toluene and THF solution, organolanthanide amides **1**-Ln[N(SiMe$_3$)$_2$](thf)·$(C_7H_8)_n$ (n = 1, Ln = Sm (**3**); n = 1, Ln = Y (**4**); n = 0, Ln = Yb (**5**)) in good yields. Reaction of **4** with one equiv of Me_3N·HCl or excess of Me_3Al leads to formation of **1**-YCl(dme) (**2**) and **1**-Y(μ-Me)$_2$AlMe$_2$ (**6**), respectively. Treatment of **5** with excess of **1**H_2 in toluene at reflux gives, after recrystallization from a benzene solution, the dinuclear complex $\{(\mathbf{1})_3Yb_2\}_3$·$2C_7H_8$·$2C_6H_6$ (**7**) in 65% yield. All compounds have been characterized by various spectroscopic techniques and elemental analyses. The solid-state structures of compounds **2**−**4** and **7** have been further established by single X-ray diffraction analyses. Organolanthanide amides **3**−**5** are active catalysts for asymmetric hydroamination/cyclization of aminoalkenes and polymerization of MMA, affording cyclic amines in good yields with moderate ee values and syn-rich poly(MMA)s, respectively.

Introduction

The hydroamination is a highly atom economical process in which an amine N−H bond is added to an unsaturated carbon−carbon bond. This reaction is of great potential interest for the waste-free synthesis of basic and fine chemicals, pharmaceuticals, and other industrially relevant building blocks starting from inexpensive precursors.[1−10] Therefore, it is not surprising that recent efforts have focused on the development of chiral catalysts for intramolecular asymmetric alkene hydroamination.[2−10] To date, the catalysts based on lanthanide metals have shown the most promising for this purpose.[3−10] However, even within this class only a small number (4) of highly enantioselective reaction (>90% ee) have been reported.[7a] Thus, alkene hydroamination remains an open area of research.

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Although many chiral lanthanide catalysts based on C_1-symmetric Cp ligands,[3] and non-Cp ligands such as bis(oxazolinato),[4] bis(phenolate),[5] bis(thiolate),[6] biphenolates and binaphtholates,[7] and other complexes[8] have been studied, the development of new lanthanide catalysts for asymmetric alkene hydroamination 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), and Ag(I) complexes are useful catalysts for a range of transformations.[11] In our attempt to further explore the chiral N_4-ligand system and their application in lanthanide chemistry, we have recently studied a new chiral tetradentate ligand, (*R*)-bis(pyrrol-2-ylmethyleneamino)-1,1′-binaphthyl (**1**H_2), and found it useful to stablize the amido lanthanide complexes, which are potential catalysts for the asymmetric hydroamination/cyclization of primary aminoolefins, allenes, and alkynes. We report herein the synthesis and property of this new chiral ligand, (*R*)-bis(pyrrol-2-ylmethyleneamino)-1,1′-binaphthyl (**1**H_2), its use in the coordination chemistry of lanthanide, and the applications of the resulting complexes as catalysts for the hydroamination/cyclization reaction and the polymerization of methyl methacrylate (MMA).

Experimental Section

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 CaH_2 immediately prior to use. (*R*)-2,2′-diamino-1,1′-binaphthyl,[12] Ln[N(SiMe$_3$)$_2$]$_3$,[13] 2,2-dimethylpent-4-enylamine,[6] pent-4-enylamine,[6] 2,2′-dimethylhex-5-enylamine,[6] *N*-methylpent-4-enylamine,[6] and 1-(aminomethyl)-1-allylcyclohexane[8a] were prepared according to literature methods. All other chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. and 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. ^{1}H and ^{13}C 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.

Preparation of (*R*)-Bis(pyrrol-2-ylmethyleneamino)-1,1′-binaphthyl (1H_2). Pyrrole-2-carboxaldehyde (1.90 g, 20.0 mmol) was mixed with (*R*)-2,2′-diamino-1,1′-binaphthyl (2.84 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 2 days at this temperature. The solution was filtered, and the solvent was removed under reduced pressure. The resulting brown solid was recrystallized from mixed solvents (30 mL) of toluene and *n*-hexane (1:1) to give **1**H_2 as an orange solid. Yield, 3.72 g (85%); mp 189−191 °C. ^{1}H NMR (C_6D_6): δ 8.44 (br, s, 2H), 7.82 (s, 2H), 7.75−7.71 (m, 4H), 7.56 (d, J = 8.4 Hz, 2H), 7.17−7.00 (m, 6H), 6.24 (m, 2H), 5.95 (t, J = 2.7 Hz, 2H), 5.88 (s, 2H). ^{13}C NMR (C_6D_6): δ 150.6, 149.8, 134.2, 132.0, 131.1, 129.4, 127.8, 127.5, 127.2, 126.8, 124.9, 122.8, 120.2, 116.1, 109.9. IR (KBr, cm^{-1}): ν 3411 (s), 3052 (w), 2894 (w), 1623 (s), 1608 (s), 1586 (s), 1447 (s), 1350 (m), 1122 (s), 1085 (s), 1032 (s), 833 (s), 803 (s), 737 (s). Anal. Calcd for $C_{30}H_{22}N_4$: C, 82.2; H, 5.06; N, 12.8. Found: C, 82.0; H, 5.18; N, 12.5.

Preparation of 1-YCl(dme) (2). A solution of **1**H_2 (0.22 g, 0.5 mmol) in DME (20 mL) was stirred with NaH (0.50 g, 20.8 mmol) at room temperature for 2 h and then filtered; the filtrate was added to a suspension of YCl_3 (0.10 g, 0.5 mmol) in DME (10 mL) at room temperature with stirring. The mixture was stirred at room temperature overnight and filtered. The filtrate was concentrated to about 2 mL. **2** was isolated as yellow crystals after this solution stood at room temperature for 3 days. Yield, 0.24 g (75%); mp 252−254 °C (dec). ^{1}H NMR (C_6D_6): δ 7.77 (m, 6H), 7.41 (d, J = 8.4 Hz, 2H), 7.35−7.25 (m, 6H), 7.06 (t, J = 8.0 Hz, 2H), 6.74 (d, J = 3.0 Hz, 2H), 6.57 (t, J = 1.4 Hz, 2H), 3.25 (s, 4H, DME), 3.17 (s, 6H, DME). ^{13}C NMR (C_6D_6): δ 159.2, 147.0, 142.1, 138.6, 134.1, 131.6, 128.7, 128.3, 128.1, 126.6, 126.5, 124.9, 123.2, 121.5, 113.3, 72.0, 58.5. IR (KBr, cm^{-1}): ν 3045 (w), 2961 (w), 1620 (w), 1590 (m), 1567 (s), 1433 (m), 1389 (s), 1292 (s), 1261 (s), 1083 (m), 1034 (s), 805 (m), 746 (m). Anal. Calcd for $C_{34}H_{30}N_4ClO_2Y$: C, 62.7; H, 4.64; N, 8.61. Found: C, 62.5; H, 4.72; N, 8.53.

Preparation of 1-Sm[N(SiMe$_3$)$_2$](thf)·C$_7$H$_8$ (3). A toluene solution (10 mL) of **1**H_2 (0.22 g, 0.5 mmol) was slowly added to a toluene solution (10 mL) of Sm[N(SiMe$_3$)$_2$]$_3$ (0.32 g, 0.5 mmol) with stirring at room temperature. The resulting solution was refluxed for 2 days and filtered. The filtrate was concentrated to about 2 mL, and three drops of THF were added. **2** was isolated as yellow crystals after this solution was allowed to stand at room temperature for one week. Yield, 0.36 g (80%); mp 190−192 °C (dec). IR (KBr, cm^{-1}): ν 3059 (w), 2925 (w), 2883 (w), 1623 (w), 1595 (w), 1564 (s), 1504 (m), 1432 (m), 1387 (m), 1294 (s), 1259 (s), 1179 (m), 1034 (s), 809 (s), 748 (s). Anal. Calcd for $C_{47}H_{54}N_5OSi_2Sm$: C, 61.9; H, 5.97; N, 7.68. Found: C, 61.7; H, 5.96; N, 7.47.

Preparation of 1-Y[N(SiMe$_3$)$_2$](thf)·C$_7$H$_8$ (4). Method A. This compound was prepared as orange crystals from the reaction of **1**H_2 (0.22 g, 0.5 mmol) with Y[N(SiMe$_3$)$_2$]$_3$ (0.29 g, 0.5 mmol) in toluene (20 mL) and recrystallization from mixed solvents of toluene and THF (20:1) by a similar procedure as in the synthesis of **3**. Yield, 0.32 g (75%); mp 145−147 °C (dec). ^{1}H NMR (C_6D_6): δ 7.86 (s, 2H), 7.78 (m, 4H), 7.45 (s, 2H), 7.27−7.12 (m, 11H), 7.02 (t, J = 7.5 Hz, 2H), 6.77 (s, 2H), 6.54 (s, 2H), 3.43 (m, 2H, THF), 3.34 (m, 2H, THF), 2.23 (s, 3H), 1.18 (m, 4H, THF), 0.27 (s, 18H). ^{13}C NMR (C_6D_6): δ 160.0, 146.8, 140.0, 138.3, 134.6, 131.9, 129.5, 129.1, 128.3, 128.2, 128.1, 126.9, 126.8, 126.7, 125.4, 125.0, 123.7, 122.5, 113.1, 70.3, 24.7, 21.2, 4.5. IR (KBr, cm^{-1}): ν 3064 (w), 2961 (m), 2891 (w), 1612 (w), 1597 (m), 1565 (s), 1494 (m), 1433 (s), 1388 (s), 1325 (s), 1291 (s), 1260 (s), 1181 (s), 1093 (s), 1034 (s), 1011 (s), 991 (s), 868 (m), 809 (s), 748 (s). Anal. Calcd for $C_{47}H_{54}N_5OSi_2Y$: C, 66.4; H, 6.40; N, 8.24. Found: C, 66.7; H, 6.66; N, 8.18.

Method B. A toluene (5 mL) solution of (Me$_3$Si)$_2$NNa (37 mg, 0.2 mmol) was added to a THF (5 mL) solution of **1**-YCl(dme) (**2**; 130 mg, 0.2 mmol) with stirring at room temperature. This mixture was stirred at room temperature overnight and filtered. The filtrate was concentrated to about 1 mL. Orange crystals were isolated after this solution stood at room temperature for two weeks, which were identified as **4** by X-ray diffraction analysis. Yield, 119 mg (70%).

Preparation of 1-Yb[N(SiMe$_3$)$_2$](thf) (5). This compound was prepared as orange microcrystals from the reaction of **1**H_2 (0.22 g, 0.5 mmol) with Yb[N(SiMe$_3$)$_2$]$_3$ (0.33 g, 0.5 mmol) in toluene (20 mL) and recrystallization from mixed solvents of toluene and THF (20:1) by a similar procedure as in the synthesis of **3**. Yield, 0.29

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Table 1. Crystal Data and Experimental Parameters for Compounds 2−4 and 7

	2	3	4	7
formula	$C_{34}H_{30}N_4ClO_2Y$	$C_{47}H_{54}N_5OSi_2Sm$	$C_{47}H_{54}N_5OSi_2Y$	$C_{98.67}H_{69.33}N_{12}Yb_2$
fw	650.98	911.48	850.04	1769.07
cryst syst	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P12_11$	$P2_12_12_1$	$P2_12_12_1$	$C121$
a (Å)	14.688(1)	11.236(2)	11.179(3)	25.536(3)
b (Å)	23.835(2)	17.360(4)	17.442(5)	22.103(2)
c (Å)	21.211(2)	68.727(14)	68.466(19)	25.583(3)
β (deg)	102.57(1)	90	90	111.31(1)
V (Å^3)	7247.8(11)	13406(5)	13350(7)	13453(3)
Z	8	12	12	6
D_{calcd} (g/cm^3)	1.193	1.355	1.269	1.310
μ(Mo Kα)$_{calcd}$ (mm^{-1})	1.714	1.408	1.404	2.124
size (mm)	0.30 × 0.28 × 0.22	0.22 × 0.18 × 0.16	0.22 × 0.20 × 0.18	0.14 × 0.12 × 0.10
F(000)	2672	5628	5352	5312
2θ range (deg)	3.32−50.00	3.34−52.04	3.34−52.02	3.22−55.74
no. of reflns, collected	54829	62550	62330	63422
no. of unique reflns	24906 (R_{int} = 0.1026)	20400 (R_{int} = 0.055)	23852 (R_{int} = 0.065)	31053 (R_{int} = 0.064)
no. of obsd reflns	24906	20400	23852	31053
abscorr (T_{max}, T_{min})	0.70, 0.63	0.81, 0.75	0.79, 0.75	0.82, 0.76
R	0.077	0.048	0.053	0.060
R_w	0.178	0.073	0.057	0.120
R_{all}	0.111	0.062	0.102	0.070
GOF	0.98	1.01	0.82	1.05

g (70%); mp 196−198 °C (dec). IR (KBr, cm^{-1}): ν 3054 (w), 2962 (m), 2918 (w), 1619 (w), 1596 (s), 1580 (s), 1388 (m), 1260 (s), 1091 (vs), 1032 (vs), 800 (vs). Anal. Calcd for $C_{40}H_{46}N_5OSi_2Yb$: C, 57.1; H, 5.51; N, 8.32. Found: C, 57.3; H, 5.80; N, 8.33.

Reaction of 4 with Me_3N·HCl. A solid of Me_3N·HCl (19 mg, 0.2 mmol) was added to a DME (10 mL) solution of **1**-Y[N(SiMe$_3$)$_2$]-(thf)·C_7H_8 (**4**; 170 mg, 0.2 mmol) with stirring at room temperature. This mixture was stirred at room temperature overnight and filtered. The filtrate was concentrated to about 1 mL. Yellow crystals were isolated after this solution stood at room temperature for two weeks, which were identified as **1**-YCl(dme) (**2**) by X-ray diffraction analysis. Yield, 49 mg (38%).

Reaction of 4 with Me_3Al. NMR Scale. To a J. Young NMR tube charged with **1**-Y[N(SiMe$_3$)$_2$](thf)·C_7H_8 (**3**; 17 mg, 0.02 mmol) and C_6D_6 (0.5 mL) was added Me_3Al (11 mg, 0.15 mmol). The color of the solution immediately changed from orange to pale-yellow. The ^{1}H NMR spectrum contained resonances consistent with **1**-Y(μ-Me)$_2$AlMe$_2$ (**6**) (^{1}H NMR (C_6D_6): δ 7.73 (t, J = 8.3 Hz, 4H), 7.50 (s, 2H), 7.27 (m, 4H), 7.04 (m, 6H), 6.78 (d, J = 3.6 Hz, 2H), 6.42 (m, 2H), −0.50 (s, 6H), −1.42 (s, 6H)) and (Me$_3$-Si)$_2$NAlMe$_2$ (^{1}H NMR (C_6D_6): δ 0.36 (s, 18H, CH_3Si), −0.21 (s, 6H, CH_3Al)) (100% conversion). **6** was not isolated as a pure compound on a synthetic scale, since it is an oily residue and very soluble in solvents such as toluene, *n*-hexane, and the adduct (Me$_3$-Si)$_2$NAlMe$_2$(AlMe$_3$)$_n$ cannot be removed under vacuum.

Reaction of 5 with $1H_2$. A toluene solution (5 mL) of **1**H_2 (44 mg, 0.1 mmol) was slowly added to a toluene solution (5 mL) of **1**-Yb[N(SiMe$_3$)$_2$](thf) (**5**; 84 mg, 0.1 mmol) with stirring at room temperature. The resulting solution was refluxed for 2 days, and the solvent was removed under vacuum. The resulting oily residue was extracted with benzene (5 mL × 2), and the benzene solution was combined and concentrated to about 1 mL. Orange-red crystals were isolated after this solution stood at room temperature for two weeks, which were identified as {(**1**)$_3$Yb$_2$}$_3$·2C_7H_8·2C_6H_6 (**7**) by X-ray diffraction analysis. Yield, 57 mg (65%); mp 270−272 °C (dec). IR (KBr, cm^{-1}): ν 3044 (w), 2962 (m), 1615 (w), 1593 (m), 1568 (s), 1431 (m), 1388 (m), 1293 (m), 1260 (s), 1092 (s), 1033 (s), 1020 (s), 800 (s). Anal. Calcd for $C_{296}H_{208}N_{36}Yb_6$: C, 67.0; H, 3.95; N, 9.50. Found: C, 67.2; H, 3.74; N, 9.42.

General Procedure for Asymmetric Hydroamination/Cyclization. The cyclization of 2,2-dimethylpent-4-enylamine by catalyst **3** is representative. In a nitrogen-filled glovebox, **1**-Sm-[N(SiMe$_3$)$_2$](thf)·C_7H_8 (**3**; 14.6 mg, 0.016 mmol), C_6D_6 (0.7 mL), and 2,2-dimethylpent-4-enylamine (36 mg, 45.2 μL, 0.32 mmol) were introduced sequentially into a J. Young NMR tube equipped with Teflon screw cap. The reaction mixture was subsequently kept at 21 °C or heated at 60 °C to achieve hydroamination, and the reaction was monitored periodically by ^{1}H NMR spectroscopy. The cyclic amine 2,4,4-trimethylpyrrolidine was vacuum transferred from the J. Young NMR tube into a 25 mL Schlenk flask which contained 62 mg (0.32 mmol) of (*S*)-(+)-*O*-acetylmandelic acid (or (*S*)-(−)-Mosher's acid in the case of 2-methyl-*N*-methylpyrrolidine). This transfer was quantitated by washing the NMR tube with a small amount of $CDCl_3$. The resulting mixture was stirred at room temperature for 2 h and the volatiles were removed *in vacuo*. The resulting diastereomeric salt was then dissolved in $CDCl_3$ and the enantiomeric excesses were determined by ^{1}H NMR spectroscopy.[6]

General Procedure for Polymerization of MMA. A 2.0 mL (1.86 g, 18.6 mmol) portion of methyl methacrylate was added into a toluene (2 mL) solution of **3** (0.034 g, 0.037 mmol) at room temperature with stirring. After the reaction mixture was vigorously stirred for 60 h at room 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.

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 M*o* Kα radiation (λ = 0.71070 Å). An empirical absorption correction was applied using the SADABS program.[14] All structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL-97 program package.[15] All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and experimental data for **2**−**4** and **7** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Results and Discussion

Ligand. The C_2-symmetric pyrrole imine ligand, (*R*)-bis-(pyrrol-2-ylmethyleneamino)-1,1′-binaphthyl (**1**H_2), is readily prepared by condensation of (*R*)-2,2′-diamino-1,1′-binaphthyl

(14) Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.

(15) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structure from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1997.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 2−4 and 7

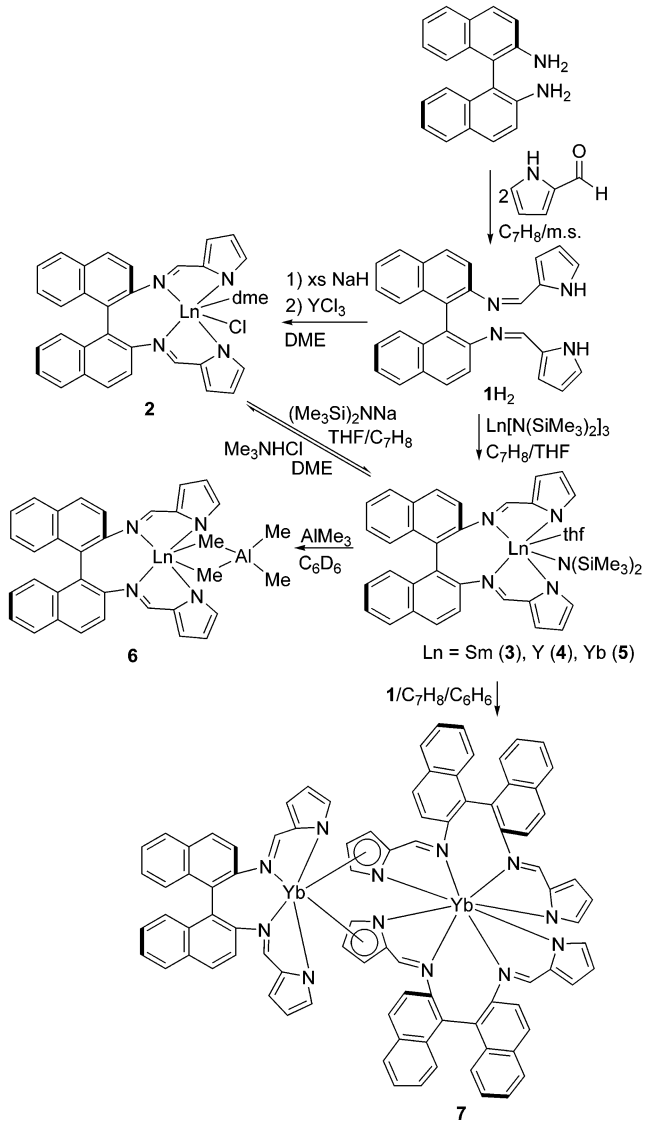
	compound **2**		
Y(1)−N(1)	2.467(7)	Y(1)−N(2)	2.445(8)
Y(1)−N(3)	2.432(8)	Y(1)−N(4)	2.392(7)
Y(1)−O(1)	2.425(7)	Y(1)−O(2)	2.447(6)
Y(1)−Cl(1)	2.579(2)	O(1)−Y(1)−O(2)	67.0(2)
N(1)−Y(1)−N(2)	74.6(3)	N(1)−Y(1)−N(3)	68.8(3)
N(2)−Y(1)−N(4)	68.3(3)	N(3)−Y(1)−N(4)	161.7(3)
torsion (aryl−aryl)	70.1(3)		
	compound **3**		
Sm(1)−N(1)	2.527(4)	Sm(1)−N(2)	2.506(5)
Sm(1)−N(3)	2.460(5)	Sm(1)−N(4)	2.478(5)
Sm(1)−N(5)	2.477(4)	Sm(1)−O(1)	2.438(4)
N(1)−Sm(1)−N(2)	77.1(2)	N(1)−Sm(1)−N(3)	67.8(2)
N(2)−Sm(1)−N(4)	68.2(2)	N(3)−Sm(1)−N(4)	155.2(2)
torsion (aryl−aryl)	69.2(6)		
	compound **4**		
Y(1)−N(1)	2.468(4)	Y(1)−N(2)	2.445(4)
Y(1)−N(3)	2.396(4)	Y(1)−N(4)	2.398(4)
Y(1)−N(5)	2.227(4)	Y(1)−O(1)	2.368(3)
N(1)−Y(1)−N(2)	77.8(2)	N(1)−Y(1)−N(3)	69.3(2)
N(2)−Y(1)−N(4)	69.8(2)	N(3)−Y(1)−N(4)	153.3(2)
torsion (aryl−aryl)	67.3(4)		
	compound **7**		
Yb(1)−N(1)	2.430(7)	Yb(1)−N(2)	2.456(6)
Yb(1)−N(3)	2.364(6)	Yb(1)−N(4)	2.347(7)
Yb(1)−N(7)	3.012(7)	Yb(1)−N(11)	2.774(7)
Yb(1)−Cent(ring)	2.625(8) 2.526(8)	Yb(2)−N(5)	2.644(7)
Yb(2)−N(6)	2.437(5)	Yb(2)−N(7)	2.383(7)
Yb(2)−N(8)	2.366(7)	Yb(2)−N(9)	2.631(6)
Yb(2)−N(10)	2.437(6)	Yb(2)−N(11)	2.407(6)
Yb(2)−N(12)	2.337(7)	N(1)−Yb(1)−N(2)	68.4(2)
N(1)−Yb(1)−N(3)	70.0(2)	N(2)−Yb(1)−N(4)	70.2(2)
Cent(ring)−Yb(1)−ent(ring)	105.1(7)	N(5)−Yb(2)−N(6)	68.13(19)
N(5)−Yb(2)−N(7)	66.1(2)	N(6)−Yb(2)−N(8)	69.3(2)
N(7)-Yb(2)−N(11)	69.9(2)	N(9)−Yb(2)−N(10)	68.68(19)
N(9)−Yb(2)-N(11)	66.1(2)	torsion (aryl−aryl)	70.7(9) 75.3(9) 82.7(9)

with 2 equiv of pyrrole-2-carboxaldehyde in the presence of molecular sieves in toluene at 70 °C (Scheme 1). The product is isolated in 85% yield after recrystallization from toluene and *n*-hexane (1:1).

Ligand $\mathbf{1}H_2$ is air-stable, but sensitive to hydrolysis, and very soluble in CH_2Cl_2, $CHCl_3$, toluene, and benzene, but only slightly soluble in *n*-hexane. It has been fully characterized by various spectroscopic techniques and elemental analyses. Both the ^{1}H and ^{13}C NMR spectra of $\mathbf{1}H_2$ indicate that it is symmetrical on the NMR time scale, which is consistent with its C_2-symmetric structure. The IR spectrum of $\mathbf{1}H_2$ shows characteristic N−H and N═C absorptions at 3411 and 1623 cm^{-1}, respectively.

Organolanthanide Complexes. Deprotonation of the chiral ligand $\mathbf{1}H_2$ is achieved by reaction with an excess of NaH in DME. The resulting disodium salt $\mathbf{1}Na_2$ thus formed is reacted with 1 equiv of YCl_3 in DME to give the complex **1**-YCl(dme) (**2**) in 75% yield (Scheme 1). Salt metathesis reaction between **2** and $(Me_3Si)_2NNa$ in mixed solvents of THF and toluene (1:1) gives the organoyttrium amide **1**-Y[N(SiMe$_3$)$_2$](thf)·C_7H_8 (**4**) in 70% yield. It has been documented that amido lanthanide complexes also can be efficiently prepared via silylamine elimination reactions of Ln[N(SiMe$_3$)$_2$]$_3$ and protic reagents.[6,7,8g] It is rational to propose that two acidic protons in the ligand $\mathbf{1}H_2$ would also allow the similar silylamine elimination to occur between $\mathbf{1}H_2$ and metal amides. In fact, treatment of $\mathbf{1}H_2$ with 1 equiv of Ln[N(SiMe$_3$)$_2$]$_3$ in toluene at reflux temperature gives, after recrystallization from a mixed toluene and THF solution, organolanthanide amides **1**-Ln[N(SiMe$_3$)$_2$](thf)·$(C_7H_8)_n$ (n = 1, Ln = Sm (**3**); n = 1, Ln = Y (**4**); n = 0, Ln = Yb (**5**)) in good yields (Scheme 1).

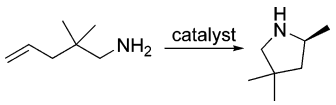
Scheme 1. Synthesis of Organolanthanides



These complexes are stable in dry nitrogen atmosphere, while they are very sensitive to moisture. They are soluble in organic solvents such as THF, DME, pyridine, toluene, and benzene, but only slightly soluble in *n*-hexane. They have been characterized by various spectroscopic techniques and elemental analyses. The ^{1}H NMR spectrum of **2** supports the ratio of DME and ligand **1** is 1:1, and the ^{1}H NMR spectrum of **4** supports the ratio of THF, toluene, amino group N(SiMe$_3$)$_2$, and ligand **1** is 1:1:1:1. The ^{1}H NMR spectra of the hydrolytic products of **3** and **5** support the ratio of THF, amino group N(SiMe$_3$)$_2$, and ligand **1** is 1:1:1 for **3** and **5**. Their IR spectra exhibit a weak typical characteristic N═C absorption at about 1620 cm^{-1}. The solid-state structures of the complexes **2**−**4** have been further confirmed by single-crystal X-ray diffraction analyses.

Reactivity. It has been reported that the addition of excess Me_3SiCl or a stoichiometric amount of Me_3N·HCl to the metal amide complexes results in the clean formation of chloride derivatives.[16] Treatment of **1**-Y[N(SiMe$_3$)$_2$](thf)·C_7H_8 (**4**) with 1 equiv of Me_3N·HCl in DME gives **1**-YCl(dme) (**2**) (Scheme 1), while the reaction between Me_3SiCl and **4** is very complicated, and no pure product has been isolated. In an NMR tube, treatment of **1**-Y[N(SiMe$_3$)$_2$](thf)·C_7H_8 (**4**) with excess of Me_3-

Table 3. Enantioselective Hydroamination/Cyclization of 2,2-Dimethylpent-4-enylamine[a]



entry	catalyst (Ln; mol %)	*T* (°C)	time (h)	conversion (%)[b]	ee (%)[c]
1	**3** (Sm; 5%)	21	20	51	21
2	**3** (Sm; 5%)	60	6	44	24
3	**4** (Y; 1%)	21	20	59	24
4	**4** (Y; 3%)	21	20	97	21
5	**4** (Y; 5%)	21	20	98	18
6	**4** (Y; 5%)	60	6	93	20
7	**5** (Yb; 5%)	21	20	35	7.2
8	**5** (Yb; 5%)	60	6	50	5.4
9	**7** (Yb; 5%)	120	160	N.R.	N.A.

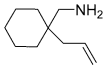
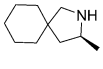
[a] Conditions: C_6D_6 (0.70 mL), 2,2-dimethylpent-4-enylamine (0.32 mmol, 45.2 μL). [b] Determined by ^{1}H NMR. N.R. = no reaction. [c] Determined by ^{1}H NMR of its diastereomeric (*S*)-(+)-*O*-acetylmandelic acid salt.[6] N. A. = not applicable.

Al in C_6D_6 at room temperature gives the resonances consistent with the dinuclear complex **1**-Y(μ-Me)$_2$AlMe$_2$ (**6**) with 100% conversion (Scheme 1).[17] Treatment of **1**-Yb[N(SiMe$_3$)$_2$](thf) (**5**) with excess of **1**H$_2$ in toluene at reflux gives, after recrystallization from a benzene solution, the dinuclear complex {(**1**)$_3$Yb$_2$}$_3$·2C$_7$H$_8$·2C$_6$H$_6$ (**7**) in 65% yield (Scheme 1). **7** is stable in a dry nitrogen atmosphere, while it is very sensitive to moisture. It is soluble in organic solvents such as THF, DME, pyridine, toluene, and benzene, but only slightly soluble in *n*-hexane. It has been characterized by infrared spectroscopy, elemental analyses, and single-crystal X-ray analysis.

To examine the catalytic ability of the organolanthanide amides **3**−**5**, the asymmetric hydroamination/cyclization of aminoalkenes and polymerization of methyl methacrylate (MMA) have been tested under the conditions given in Tables 3 and 4 and Table 5, respectively.

The results of the hydroamination/cyclization of 2,2-dimethylpent-4-enylamine show that the Sm^{3+} ion gives noticeably better ee values (Table 3, entries 1 and 2), but the rate is slow. On moving to the smaller Y^{3+} ion (Table 3, entries 5 and 6), the rate increases while the ee falls slightly. Decreasing the ratio of the catalyst **4** to 2,2-dimethylpent-4-enylamine, increases the enantioselectivity of 2,4,4-trimethylpyrrolidine (Table 3, entries 3−5), and the best enantioselectivity (24% ee) is obtained when 1 mol % of **4** is used (Table 3, entry 3). However, the smaller Yb^{3+} ion results largely in decrease ee values with moderate conversions (Table 3, entries 7 and 8).[18] This result maybe due to the inversion of the product configuration for smaller Ln^{3+} ion, which has also been observed by Marks and co-worker for their binaphtholate catalysts.[7e] Variations in the reaction temperature have no profound effects on enantioselectivity compared to those of ionic radius, as shown in Table 3. Enantioselectivity increases slightly as temperature is increased in some cases, whereas in other cases it declines modestly. Under similar reaction conditions, no detectable hydroamination activity is observed for complex **7**, even at 120 °C for one week (Table 3, entry 9).

Table 4. Enantioselective Hydroamination/Cyclization of Aminoalkenes[a]

entry	catalyst (Ln)	substrate	product	conv. (%)[b]	ee (%)[c]
1	**3** (Sm)			46	7.4
2	**4** (Y)			86	12
3	**5** (Yb)			35	2.6
4	**3** (Sm)			40	11
5	**4** (Y)			75	14
6	**5** (Yb)			28	4.6
7	**3** (Sm)			50	19
8	**4** (Y)			82	22
9	**5** (Yb)			43	5.7
10	**3** (Sm)			25	5.6[d]
11	**4** (Y)			68	10[d]
12	**5** (Yb)			30	2.2

[a] Conditions: C_6D_6 (0.70 mL), aminoalkene (0.32 mmol), catalyst (0.016 mmol), at 60 °C, 6 h. [b] Determined by ^{1}H NMR. [c] Determined by ^{1}H NMR of its diastereomeric (*S*)-(+)-*O*-acetylmandelic acid salt.[6] [d] Determined by ^{1}H NMR of its diastereomeric (*S*)-(−)-Mosher's acid salt.[6]

Table 5. MMA Polymerization Results[a]

entry	precatalyst	conversion (%)	mr[b] (%)	rr[b] (%)	M_n (kg/mol)[c]	M_w/M_n[c]
1	**3**	4.5	25	60	26.9	1.79
2	**4**	7.5	29	56	42.7	1.74
3	**5**	5.2	29	51	47.2	1.94

[a] Conditions: precat./MMA (mol/mol) = 1/500, 2 mL of toluene, MMA/solvent (v/v) = 1/1, at room temperature, 60 h. [b] Triad values from methyl region of ^{1}H NMR spectra in $CDCl_3$ at 25 °C. [c] Measured by GPC (using polystyrene standards in THF).

Other aminoalkene substrates have also been investigated for hydroamination/cyclization activity in forming five- and six-membered heterocycles (Table 4). Similar to the results obtained for 2,2-dimethylpent-4-enylamine, the bis(pyrrolate) catalysts exhibit moderate to good reaction rates with low enantioselectivities regardless of the size of the lanthanide ions and substrates (Table 4, entries 1−12). The best enantioselectivity for 1-(aminomethyl)-1-allylcyclohexane is only 22% ee, mediated by the catalyst **4** (Table 4, entry 8). Our results show that the catalytic activities of the bis(pyrrolate) resemble those of biphenolates and binaphtholates,[7] while the enantiomeric excesses of the resulting cyclic amines are similar to those initiated by bis(phenolate).[5] Although the enantiomeric excesses obtained are modest, it should be noted that there are only few catalysts for these reactions that give a significant ee at all.[7a]

The polymerization data (Table 5) show that the conversion of MMA is low regardless of the metal ions. The reasons for the low conversion are not clear at this time; however, 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[19] seems to be a major reason for such a low conversion. The

(16) For selected recent papers, see: (a) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4045. (b) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (c) Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572. (d) Zi, G.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 3580.

(17) Anwander and co-workers have reported the first example of silylamide elimination between amino lanthanide complexes (C_5Me_4R)Ln[N(SiHMe$_2$)$_2$]$_2$ and AlMe$_3$ gives the bis(tetramethylaluminate) complexes (C_5Me_4R)Ln(AlMe$_4$)$_2$, see: Anwander, R.; Klimpel, M. G.; Martin Dietrich, H.; Shorokhov, D. J.; Scherer, W. *Chem. Commun.* **2003**, 1008.

(18) For the ionic radius of yttrium (Y^{3+} = 0.88 Å), samarium (Sm^{3+} = 0.964 Å), and ytterbium (Yb^{3+} = 0.858 Å), see: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980; p 982.

(19) Yasuda, H. *J. Polym. Sci., Polym. Chem.* **2001**, *39*, 1955.

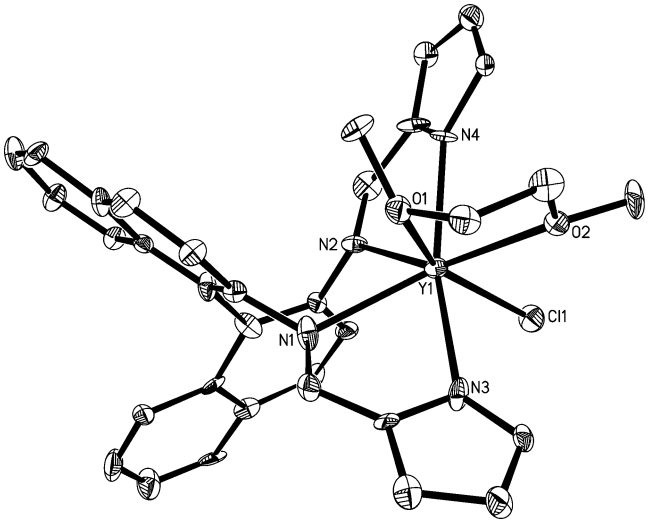


Figure 1. Molecular structure of **2** (thermal ellipsoids drawn at the 35% probability level).

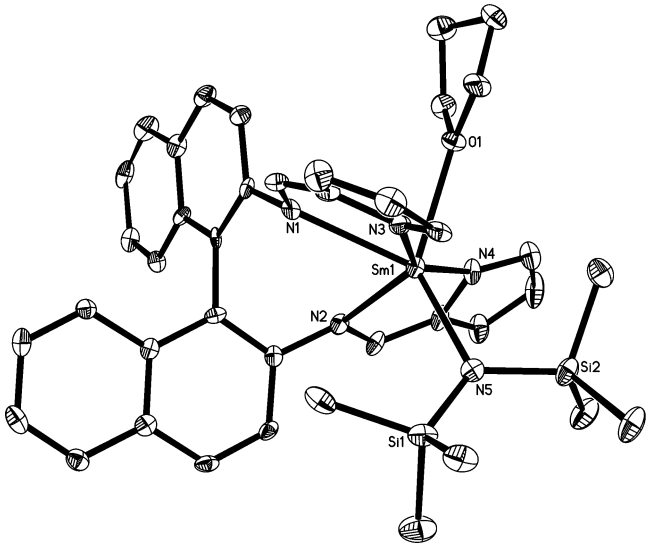


Figure 2. Molecular structure of **3** (thermal ellipsoids drawn at the 35% probability level).

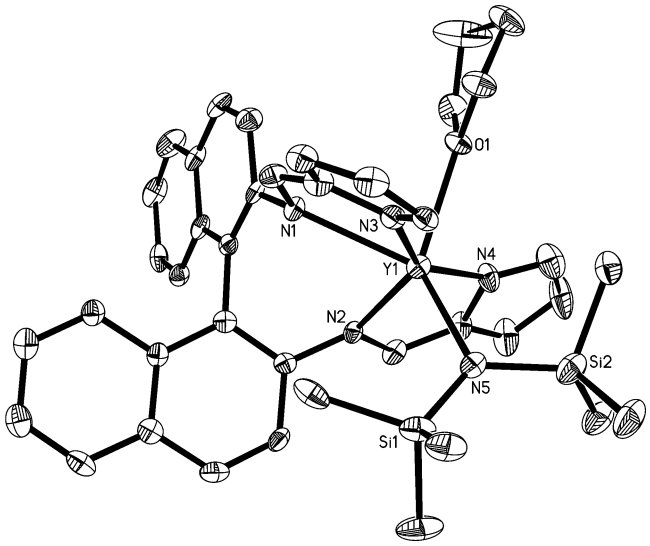


Figure 3. Molecular structure of **4** (thermal ellipsoids drawn at the 35% probability level).

resulting poly(MMA)s are all syn-rich under the conditions examined. Molecular weights and polydispersities of the polymers produced ranged from 26.9 to 47.2 kg mol^{-1} and 1.74 to 1.94, respectively. Our results show that the catalytic activities of **3**−**5** resemble that of $[Me_2Si(C_{13}H_8)(C_5Me_4)]YN(SiMe_3)_2$,[20] while the microstructure of the resulting poly(MMA)s are similar to those initiated by $[^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]NdN(SiHMe_2)_2(THF)$[21] and $[Me_2Si(C_5Me_4)(C_5H_3R^*)]LnE(SiMe_3)_2$ (E = CH, N; R* = (−)-menthyl).[22]

Molecular Structure. The solid-state structures of **2**−**4** and **7** have all been confirmed by single-crystal X-ray diffraction analyses. Selected bond distances and angles are listed in Table 2 for comparison.

The single-crystal X-ray diffraction analysis shows that there are four molecules **1**-YCl(dme) (**2**) in the lattice. In each molecule **1**-YCl(dme) (**2**), the Y^{3+} is σ-bound to the four nitrogen atoms of the ligand **1**, and two oxygen atoms from DME, and one chlorine atom in a distorted-pentagonal−bipyramidal geometry (Figure 1) with the average distance of Y−N being 2.434(8) Å, the average distance of Y−O(DME) being 2.436(7) Å, and the distance of Y−Cl being 2.579(2) Å. These structural data are close to those reported in the literature.[23] The twisting between the naphthyl rings of torsion angle is 70.1(3)°, which is larger than that (63.9(6) °) found in (*R*)-2,2′-diamino-1,1′-binaphthyl.[24]

The single-crystal X-ray diffraction analyses confirm that **3** and **4** are isostructural, and show there are three molecules **1**-Ln-$[N(SiMe_3)_2]$(thf) and three toluene molecules of solvent in the lattice. In each molecule **1**-Ln$[N(SiMe_3)_2]$(thf), the Ln^{3+} is σ-bound to four nitrogen atoms from the ligand **1**, one oxygen atom from THF, and one nitrogen atom from the amino $N(SiMe_3)_2$ group in a distorted-octahedron geometry (Figures 2 and 3) with the average distance of Ln−N being 2.490(5) Å for Sm and 2.387(4) Å for Y, respectively, and the distance of Ln−O(THF) being 2.438(4) Å for Sm and 2.368(3) Å for Y, respectively. These structural data are close to those reported in the literature.[23] The distance of Ln−$N(SiMe_3)_2$ is 2.277(4) Å for Sm and is 2.227(4) Å for Y, and these are very close to the corresponding values of 2.284(5) Å for Sm and 2.223 Å for Y found in the starting materials $Sm[N(SiMe_3)_2]_3$[25] and $Y[N(SiMe_3)_2]_3$.[26] The twisting between the naphthyl rings of torsion angle is 69.2(6)° for Sm and 67.3(4)° for Y, which is slightly smaller than that (70.1(3)°) found in **2**.

The single-crystal X-ray diffraction analysis shows that there are three molecules of $(\mathbf{1})_3Yb_2$, two toluene molecules, and two benzene molecules of solvent in the lattice. Coordination of three ligands **1** around two Yb^{3+} ions results in the formation of the dinuclear complexes $(\mathbf{1})_3Ln_2$ (Figure 4a). Figure 4b shows that one Yb^{3+} is σ-bound to four nitrogen atoms from one ligand **1** and η^5-bound to two pyrrolyl rings from the other two ligands **1** in a distorted-octahedron geometry with the average distance of Yb(1)-N being 2.399(7) Å, which is close to those reported in the literature.[23] The distances of Yb-Cent(pyrrolyl ring) are

(20) Lee, M.-H.; Hwang, J.-W.; Kim, Y.; Kim, J.; Han, Y.; Do, Y. *Organometallics* **1999**, *18*, 5124.
(21) Zi, G.; Li, H.-W.; Xie, Z. *Organometallics* **2002**, *21*, 1136.
(22) Giardello, M. A.; Yamamoto, Y.; Brard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 3276.
(23) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.
(24) Jones, M. D.; Almeida Paz, F. A.; Davies, J. E.; Johnson, B. F. G. *Acta Cryst.* **2003**, *E59*, o910.
(25) Brady, E. D.; Clark, D. L.; Gordon, J. C.; Hay, P. J.; Keogh, D. W.; Poli, R.; Scott, B. L.; Watkin, J. G. *Inorg. Chem.* **2003**, *42*, 6682.
(26) Westerhausen, M.; Hartmann, M.; Pfitzner, A.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 837.

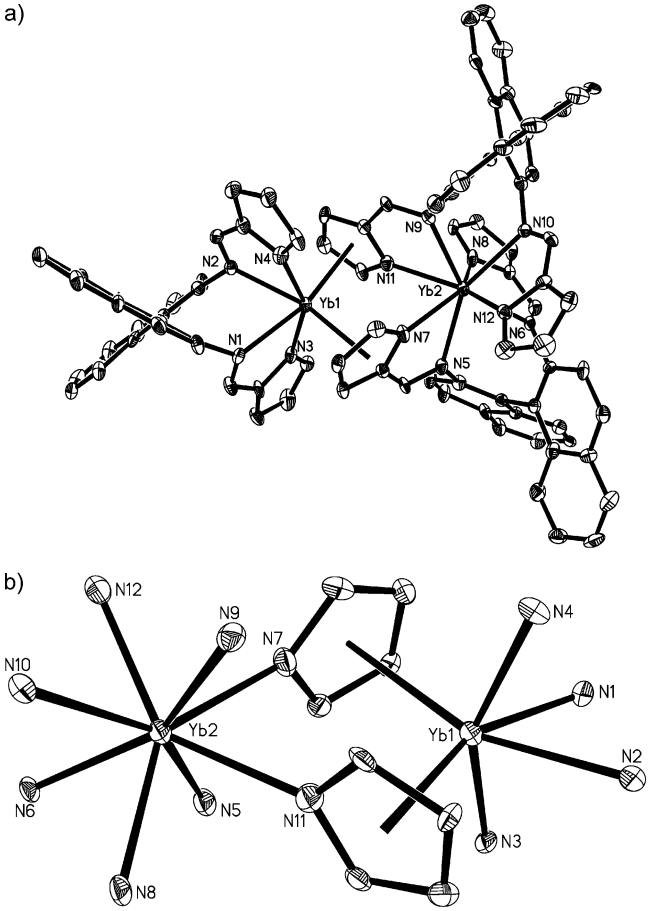


Figure 4. (a) Molecular structure of **7** (thermal ellipsoids drawn at the 35% probability level); (b) core structure of **7**.

2.625(8) and 2.526(8) Å, which is close to that found in (1,1′-dipyrrolylcyclohexanediyl-Yb)$_4$(μ-O)(thf)$_2$ (2.572(7) Å).[27] The other Yb^{3+} is σ-bound to eight nitrogen atoms from two ligands **1** in a distorted-hexagonal−bipyramidal geometry with the average distance of Yb(2)-N being 2.455(7) Å, which is slightly longer than that found for Yb(1)-N (2.399(7) Å). The twisting between the naphthyl rings of torsion angles are 70.7(9)°, 75.3(9)°, and 82.7(9)°, which are larger than those found in **2** (70.1(3)°), **3** (69.2(6)°), and **4** (67.3(4)°).

(27) Freckmann, D. M. M.; Dubé, T.; Bérubé, C. D.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2002**, *21*, 1240.

Conclusions

A new chiral tetradentate ligand has been prepared from the reaction between pyrrole-2-carboxaldehyde and (*R*)-2,2′-diamino-1,1′-binaphthyl, which can effectively go by either salt metathesis reaction or silylamine elimination reaction giving amido lanthanide complexes. These organolanthanide amides have displayed moderate to good catalytic activity for the asymmetric hydroamination/cyclization of representative aminoalkenes, although enantioselectivities have remained low (up to 24% ee). The reasons for the low enantiomeric excess are not clear at this time; however, it seems that very precise control of the metal coordination sphere is required for this to be a realistic prospect. However, it appears that our ligand set using peripheral binaphthalene coupled with pyrrole ligation in multidentate systems does not provide sufficient rigidity of the dative N-donor ligand to achieve this goal. These amido complexes can also initiate the polymerization of MMA, leading to syn-rich poly(MMA)s, but the conversion is very low. Further exploration of these catalysts toward other types of transformations and the optimization of the ligand architecture to improve the enantiomeric excess for hydroamination/cyclization are currently underway.

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Note Added after ASAP Publication. In the version of this paper published on the Web on September 19, 2007, we neglected to cite a recent report by Schafer et al. (Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 354) describing the asymmetric hydroamination of aminoalkenes catalyzed by zirconium amidate complexes to give a significant enantioselectivity (up to 93% ee). We regret the oversight and greatly thank Professor Peter Scott for his pointing out this mistake.

Supporting Information Available: X-ray crystallographic data, in CIF format, for **2**, **3**, **4**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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