Enantioselective Hydroamination/Cyclization Catalyzed by Organolanthanide Amides Derived from a New Chiral Ligand, (*S*)-2-(Pyrrol-2-ylmethyleneamino)-2′-(dimethylamino)-1,1′-binaphthyl

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A new series of bis-ligated organolanthanide amides, (**1**)$_2$-LnN(SiMe$_3$)$_2$·C$_7$H$_8$ (Ln = Sm (**2**), Y (**3**), Yb (**4**)), have been prepared by the reaction of Ln[N(SiMe$_3$)$_2$]$_3$ with the ligand (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-(dimethylamino)-1,1′-binaphthyl (**1**H) in good yields. They are active catalysts for the asymmetric hydroamination/cyclization reaction of aminoalkenes, affording cyclic amines in moderate to good conversions with moderate to good ee values.

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 synthesis of nitrogen heterocycles that are found in numerous biologically and pharmacologically active compounds.[1] Therefore, it is not surprising that recent efforts have focused on the development of chiral catalysts for intramolecular asymmetric alkene hydroamination.[2–10] Over the years it has been shown that the catalysts based on early transition metals (group 4 and especially the lanthanides) are the most promising for this purpose.[3–10] However, even within this class only a small number of highly enantioselective reactions (>90% ee) have been reported.[7a,10e,f] Thus, alkene hydroamination remains an open area of research.

Although many chiral lanthanide catalysts based on C_1-symmetric Cp ligands[3] and chiral non-Cp ligands[4–8] have been studied, the development of new lanthanide catalysts for asymmetric alkene hydroamination is still a desirable and challenging goal. In recent years, we have developed a series of chiral non-Cp multidentate ligands, and their Ir(I), Rh(I), Ti(IV), Ag(I), Zn(II), Zr(IV), and lanthanide complexes are useful catalysts for a wide range of transformations.[11] More recently, we have reported a new catalytic enantioselective hydroamination/cyclization of aminoalkenes promoted by the bis(pyrrolate) lanthanide amides [(*R*)-C$_{20}$H$_{12}$(NCHC$_4$H$_3$N)$_2$]-LnN(SiMe$_3$)$_2$(thf) (Ln = Sm, Y, Yb) in which good yields but low enantioselectivities (<24% ee) have been achieved.[12] In

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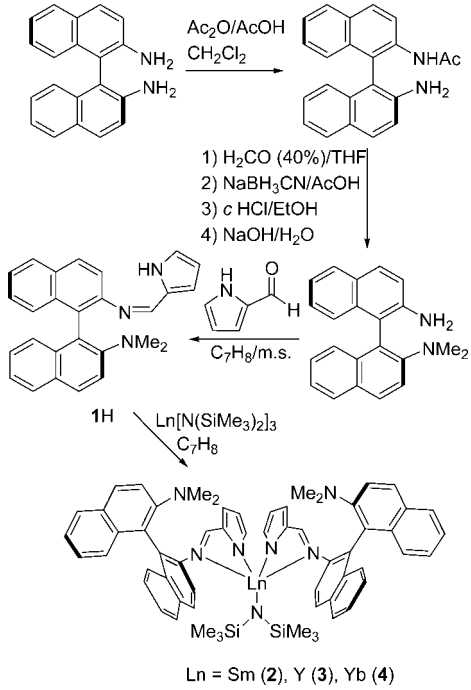
Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 2–4

	2 (Ln = Sm)	**3** (Ln = Y)	**4** (Yb)		**2** (Ln = Sm)	**3** (Ln = Y)	**4** (Ln = Yb)
Ln(1)−N(1)	2.476(2)	2.419(3)	2.385(3)	Ln(1)−N(3)	2.376(2)	2.300(3)	2.283(3)
Ln(1)−N(4)	2.497(2)	2.425(3)	2.389(3)	Ln(1)−N(6)	2.402(2)	2.319(3)	2.266(4)
Ln(1)−N(7)	2.258(2)	2.208(3)	2.169(3)	N(1)−Ln(1)−N(3)	69.6(1)	71.8(1)	72.8(1)
N(1)−Ln(1)−N(4)	142.6(1)	144.3(1)	145.1(1)	N(1)−Ln(1)−N(6)	94.4(1)	92.2(1)	89.6(1)
N(1)−Ln(1)−N(7)	106.8(1)	106.7(1)	108.7(1)	N(3)−Ln(1)−N(4)	88.4(1)	89.3(1)	91.4(1)
N(3)−Ln(1)−N(6)	119.1(1)	122.2(1)	123.2(1)	N(3)−Ln(1)−N(7)	118.2(1)	116.9(1)	120.8(1)
N(4)−Ln(1)−N(6)	69.8(1)	72.2(1)	72.9(1)	N(4)−Ln(1)−N(7)	110.2(1)	108.9(1)	106.2(1)
N(6)−Ln(1)−N(7)	122.7(1)	120.9(1)	116.1(1)	Si(1)−N(7)−Si(2),	122.2(1)	120.3(2)	119.7(2)
Si(1)−N(7)−Ln(1)	121.1(1)	121.4(2)	118.5(2)	Si(2)−N(7)−Ln(1)	116.8(1)	118.3(2)	121.7(2)
torsion (aryl−aryl)	69.2(1)	69.6(3)	69.0(2)				
	76.1(1)	76.6(3)	76.6(2)				

Scheme 1. Synthesis of Organolanthanides



Ln = Sm (**2**), Y (**3**), Yb (**4**)

our ongoing research, we are now focusing on the preparation of lanthanide catalysts coordinated by a new chiral C_1-symmetric versatile ligand, (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-(dimethylamino)-1,1′-binaphthyl (**1**H), which contains three σ-donating nitrogen atoms that can act in a bidentate or tridentate fashion.[13] In contrast to organolanthanides with C_2-symmetric ligands,[4–8,12] as far as we know, no organolanthanide with a C_1-symmetric non-Cp ligand for the hydroamination/cyclization has been reported yet. We report here the synthesis and properties of the new chiral ligand, its use in the coordination chemistry of lanthanide, and the applications of the resulting complexes as catalysts for the hydroamination/cyclization reaction.

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. (*S*)-2-amino-2′-dimethylamino-1,1′-binaphthyl,[14] Ln[N(SiMe$_3$)$_2$]$_3$,[15] 2,2-dimethylpent-4-enylamine (**5a**),[6] pent-4-enylamine (**6a**),[6] 2,2-dimethylhex-5-enylamine (**7a**),[6] and 1-(aminomethyl)-1-allylcyclohexane (**8a**)[8a] were prepared according to literature methods. All chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. and were used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. ^{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 (*S*)-2-(Pyrrol-2-ylmethyleneamino)-2′-(dimethylamino)-1,1′-binaphthyl (1H). Pyrrole-2-carboxaldehyde (0.95 g, 10.0 mmol) was mixed with (*S*)-2-amino-2′-(dimethylamino)-1,1′-binaphthyl (3.12 g, 10.0 mmol) in dry toluene (50 mL). A few 4 Å molecular sieves were added, and the solution was warmed 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 methanol (40 mL) to give **1**H·CH$_3$OH as yellow crystals. Yield: 3.58 g (85%). Mp: 82–84 °C. ^{1}H NMR (C$_6$D$_6$): δ 8.03 (s, 1H, aryl H), 7.77–7.70 (m, 4H, aryl H), 7.44 (d, J = 8.4 Hz, 2H, aryl H), 7.26–6.96 (m, 6H, aryl H), 6.39 (d, J = 2.4 Hz, 1H, aryl H), 6.07 (s, 1H, aryl H), 6.02 (m, 1H, aryl H), 2.87 (s, 3H, C*H*$_3$OH), 2.30 (s, 6H, N(C*H*$_3$)$_2$); protons of O*H* and N*H* were not observed. ^{13}C NMR (C$_6$D$_6$): δ 151.0, 150.6, 148.8, 134.6, 134.5, 132.3, 131.1, 130.3, 129.2, 129.1, 128.5, 128.4, 128.2, 127.8, 127.0, 126.8, 126.5, 126.4, 124.9, 124.0, 123.2, 120.4, 119.9, 116.6, 110.0, 49.8, 43.6. IR (KBr, cm^{-1}): ν 3407 (br, m), 3052 (m), 2934 (m), 2780 (w), 1625 (vs), 1609 (vs), 1586 (vs), 1503 (s), 1418 (s), 1032 (s), 747 (s). Anal. Calcd for C$_{28}$H$_{27}$N$_3$O: C, 79.8; H, 6.46; N, 9.97. Found: C, 79.8; H, 6.52; N, 9.83. The solvate methanol can be easily removed under vacuum at 50 °C overnight to give pure compound **1**H.

Preparation of (1)$_2$-SmN(SiMe$_3$)$_2$·C$_7$H$_8$ (2). A toluene solution (10 mL) of **1**H (0.19 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 overnight to give a yellow solution. The solution was filtered, and the filtrate was concentrated to about 5 mL. **2** was isolated as yellow crystals

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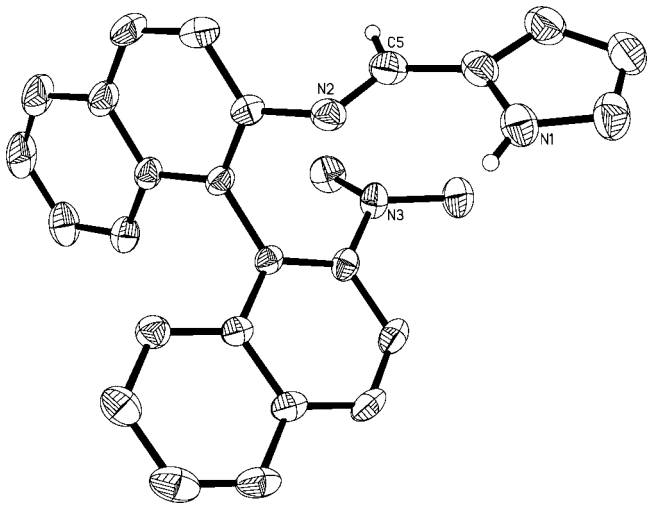


Figure 1. Molecular structure of **1**H (35% probability ellipsoids). Selected distances (Å) and angles (deg): N(2)−C(5), 1.286(4); torsion (aryl−aryl), 75.6(3).

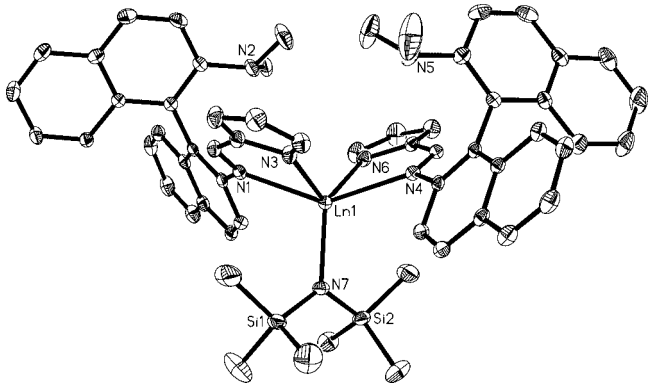


Figure 2. Molecular structures of **2** (Ln = Sm), **3** (Ln = Y), and **4** (Ln = Yb) (35% probability ellipsoids).

after this solution stood at room temperature for 3 days. Yield: 0.23 g (78%). Mp: 186–188 °C (dec). IR (KBr, cm^{-1}): ν 3056 (w), 2961 (m), 2846 (w), 1615 (w), 1594 (m), 1567 (s), 1503 (s), 1434 (m), 1390 (m), 1300 (s), 1259 (s), 1093 (s), 1034 (vs), 801 (s). Anal. Calcd for $C_{67}H_{70}N_7Si_2Sm$: C, 68.2; H, 5.98; N, 8.31. Found: C, 67.9; H, 6.24; N, 8.52.

Preparation of (1)$_2$-YN(SiMe$_3$)$_2$·C$_7$H$_8$ (3). This compound was prepared as yellow crystals from the reaction of **1**H (0.19 g, 0.5 mmol) with Y[N(SiMe$_3$)$_2$]$_3$ (0.28 g, 0.5 mmol) in toluene (20 mL) under reflux for 2 days and recrystallization from a toluene solution by a procedure similar to that used in the synthesis of **2**. Yield,: 0.21 g (74%). Mp: 216–218 °C dec. ^{1}H NMR (C_6D_6): δ 8.50 (m, 2H, aryl H), 8.13 (d, J = 8.6 Hz, 2H, aryl H), 7.83 (m, 6H, aryl H), 7.55–7.04 (m, 21H, aryl H), 6.71 (s, 2H, aryl H), 6.20 (d, J = 3.1 Hz, 2H, aryl H), 5.94 (m, 2H, aryl H), 2.23 (s, 3H, $C_6H_5CH_3$), 2.13 (s, 12 H, N(CH_3)$_2$), 0.43 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 158.6, 150.0, 143.4, 139.9, 136.7, 135.5, 129.9, 129.3, 129.0, 128.5, 128.3, 127.8, 127.6, 127.4, 127.1, 125.9, 125.4, 125.1, 124.7, 123.9, 120.4, 113.1, 43.7, 21.2, 4.4; other carbon resonances were not observed. IR (KBr, cm^{-1}): ν 3056 (w), 2960 (m), 2823 (w), 1617 (m), 1595 (m), 1564 (vs), 1504 (s), 1392 (s), 1258 (s), 1035 (vs), 814 (s). Anal. Calcd for $C_{67}H_{70}N_7Si_2Y$: C, 72.0; H, 6.31; N, 8.77. Found: C, 71.7; H, 6.36; N, 9.12.

Preparation of (1)$_2$-YbN(SiMe$_3$)$_2$·C$_7$H$_8$ (4). This compound was prepared as yellow crystals from the reaction of **1**H (0.19 g, 0.5 mmol) with Yb[N(SiMe$_3$)$_2$]$_3$ (0.17 g, 0.25 mmol) in toluene (20 mL) and recrystallization from a toluene solution by a procedure similar to that used in the synthesis of **2**. Yield: 0.21 g (70%). Mp: 188–190 °C dec. IR (KBr, cm^{-1}): ν 3055 (w), 2961 (m), 2924 (m), 1617 (m), 1594 (m), 1571 (s), 1502 (s), 1390 (s), 1301 (s), 1260 (vs), 1093 (s), 1033 (vs), 801 (s). Anal. Calcd for $C_{67}H_{70}N_7Si_2Yb$: C, 66.9; H, 5.87; N, 8.15. Found: C, 67.2; H, 5.68; N, 7.83.

This complex can also be prepared in 64% yield (0.19 g) from the reaction of **1**H (0.19 g, 0.5 mmol) with Yb[N(SiMe$_3$)$_2$]$_3$ (0.33 g, 0.5 mmol) in toluene (20 mL).

General Procedure for Asymmetric Hydroamination/Cyclization. The cyclization of 2,2-dimethylpent-4-enylamine (**5a**) catalyzed by **2** is representative. In a nitrogen-filled glovebox, (**1**)$_2$-Sm[N(SiMe$_3$)$_2$]·C$_7$H$_8$ (**2**; 18.9 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 a Teflon screw cap. The reaction mixture was subsequently kept at 21 °C or heated to 60 or 120 °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. 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]

X-ray Crystallography. Single-crystal X-ray diffraction measurements of compounds **1**H and **2**−**4** were carried out on a Rigaku Saturn CCD diffractometer at 113(2) K using graphite-monochromated Mo Kα radiation (λ = 0.710 70 Å). An empirical absorption correction was applied using the SADABS program.[16] All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package.[17] All of the hydrogen atoms were geometrically fixed using the riding model. Crystal data for **1**H·CH$_3$OH: $C_{28}H_{27}N_3O$, fw 421.53, monoclinic, $P2_1$, a = 8.893(2) Å, b = 14.556(3) Å, c = 9.416(2) Å, β = 107.08(1)°, V = 1165.0(4) Å^3, Z = 2, R1 = 0.042 for 2470 reflections ($I > 2\sigma(I)$), wR2 = 0.112 (all data). Crystal data for **2**: $C_{67}H_{70}N_7Si_2Sm$, fw 1179.83, orthorhombic, $P2_12_12_1$, a = 11.515(2) Å, b = 21.460(4) Å, c = 24.200(5) Å, V = 5980(2) Å^3, Z = 4, R1 = 0.032 for 14 236 reflections ($I > 2\sigma(I)$), wR2 = 0.069 (all data). Crystal data for **3**: $C_{67}H_{70}N_7Si_2Y$, fw 1118.39, orthorhombic, $P2_12_12_1$, a = 11.444(2) Å, b = 21.508(2) Å, c = 24.216(2) Å, V = 5960.6(8) Å^3, Z = 4, R1 = 0.066 for 12 997 reflections ($I > 2\sigma(I)$), wR2 = 0.114 (all data). Crystal data for **4**: $C_{67}H_{70}N_7Si_2Yb$, fw 1202.52, orthorhombic, $P2_12_12_1$, a = 11.438(3) Å, b = 21.506(5) Å, c = 24.243(7) Å, V = 5963.3(3) Å^3, Z = 4, R1 = 0.041 for 14 022 reflections ($I > 2\sigma(I)$), wR2 = 0.080 (all data). Selected bond lengths and angles for complexes **2**–**4** are given in Table 1.

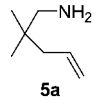
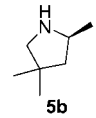
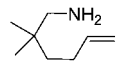
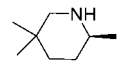
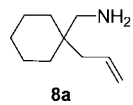
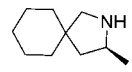
Results and Discussion

Ligand. The C_1-symmetric pyrrole imine ligand (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-(dimethylamino)-1,1′-binaphthyl (**1**H) is readily prepared by condensation of pyrrole-2-carboxaldehyde with 1 equiv of (*S*)-2-amino-2′-(dimethylamino)-1,1′-binaphthyl, which is derived from (*S*)-1,1′-binaphthyl-2,2′-diamine by a five-step procedure,[14] in the presence of molecular sieves in toluene at 70 °C (Scheme 1). The product is isolated in 85% yield after recrystallization from a methanol solution.

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

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

Table 2. Enantioselective Hydroamination/Cyclization of Aminoalkenes[a]

entry	catalysts (Ln; mol%)	substrate	product	*T* (°C)	time (h)	conversion (%)[b]	ee (%)[c]
1	**2** (Sm; 5)			21	24	77	55
2	**3** (Y; 5)	**5a**	**5b**	21	24	92	60
3	**4** (Yb; 5)			21	24	7.0	71
4	**4** (Yb; 5)			60	24	56	65
5	**2** (Sm; 3)			60	36	80	38
6	**3** (Y; 3)	**6a**	**6b**	60	36	95	48
7	**4** (Yb; 3)			60	36	32	56
8	**2** (Sm; 5)			120	60	46	16
9	**3** (Y; 5)	**7a**	**7b**	120	60	92	25
10	**4** (Yb; 5)			120	160	N.R.	N.A.
11	**2** (Sm; 3)			60	36	88	33
12	**3** (Y; 3)	**8a**	**8b**	60	36	100	42
13	**4** (Yb; 3)			60	36	31	51

[a] Conditions: C_6D_6 (0.70 mL), aminoalkene (0.32 mmol). [b] Determined by ^{1}H NMR with *p*-xylene as the internal standard. N.R. = no reaction. [c] Determined by ^{1}H NMR of its diastereomeric (*S*)-(+)-*O*-acetylmandelic acid salt.[6] N.A. = not applicable.

Ligand **1**H is air-stable, but sensitive to hydrolysis, is soluble in CH_2Cl_2, $CHCl_3$, toluene, and benzene, and is only slightly soluble in *n*-hexane. It has been fully characterized by various spectroscopic techniques, elemental analyses, and single-crystal X-ray diffraction analysis. The ^{1}H and ^{13}C NMR spectra of **1**H indicate that it is nonsymmetrical on the NMR time scale, which is consistent with its C_1-symmetric structure. The IR spectrum of **1**H shows typical characteristic N−H and N═C absorptions at 3407 and 1625 cm^{-1}, respectively.

The molecular structure of **1**H·CH_3OH shows there is one **1**H molecule and one methanol molecule in the lattice. The **1**H crystallizes in a C_1-symmetric distorted-tetrahedral geometry (Figure 1). As expected, the distance (1.286(4) Å) of C═N is in agreement with a C═N double bond. The twisting between the naphthyl rings gives a torsion angle of 75.6(3)°, which is larger than that (63.9(6)°) found in (*R*)-2,2′-diamino-1,1′-binaphthyl.[18]

Organolanthanide Amides. Our previous work has shown that interaction between (*R*)-$C_{20}H_{12}(NCHC_4H_4N)_2$[12] or (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl[11f] and $Ln[N(SiMe_3)_2]_3$ in toluene results in the clean formation of the corresponding organolanthanide amide compounds. The acidic proton in the ligand **1**H would allow a similar silylamine elimination to occur between **1**H and metal amides. In fact, treatment of **1**H with 1 or 0.5 equiv of $Ln[N(SiMe_3)_2]_3$ in toluene under reflux, followed by recrystallization from a toluene solution, gives the bis-ligated organolanthanide amides $(\mathbf{1})_2$-$LnN(SiMe_3)_2 \cdot C_7H_8$ (Ln = Sm (**2**), Y (**3**), Yb (**4**)) (Scheme 1), in good yields. These amides are stable under 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 diffraction analyses. The ^{1}H NMR spectrum of **3** supports a ratio of toluene, amino group $N(SiMe_3)_2$, and ligand **1** of 1:1:2, and the ^{1}H NMR spectra of the hydrolytic products of **2** and **4** support that the ratio of toluene, amido group $N(SiMe_3)_2$, and ligand **1** is also 1:1:2 for **2** and **4**. Their IR spectra exhibit a weak characteristic N═C absorption at about 1617 cm^{-1}.

The solid-state structures of **2**–**4** confirm that they are isostructural and show one toluene molecule of solvent in the lattice. The substituted Me_2N groups are far away from the metal center, and the Ln^{3+} is σ-bound to four nitrogen atoms from the ligand **1** and one nitrogen atom from amido group $N(SiMe_3)_2$ in a distorted-tetragonal-pyramidal geometry (Figure 2) with average Ln−N distances of 2.402(2) Å for Sm, 2.334(3) Å for Y, and 2.298(4) Å for Yb. The average N−Ln(1)−N angles are 104.2(1)° for Sm, 104.5(1)° for Y, and 104.7(1)° for Yb, respectively. The average Si−N(7)−Ln(1) angles are 121.7(1)° for Sm, 120.9(2)° for Y, and 119.1(2)° for Yb. The Si(1)−N(7)−Si(2)

(18) Jones, M. D.; Almeida Paz, F. A.; Davies, J. E.; Johnson, B. F. G. *Acta Crystallogr.* **2003**, *E59*, o910.

angles are 122.2(1)° for Sm, 120.3(2)° for Y, and 119.7(2)° for Yb. These structural data are comparable to those found in [(*R*)-$C_{20}H_{12}(NCHC_4H_3N)_2$]LnN($SiMe_3$)$_2$(thf).[12] The Ln−N($SiMe_3$)$_2$ distances of 2.258(2) Å for Sm, 2.208(3) Å for Y, and 2.169(3) Å for Yb are very close to the corresponding values of 2.284(5) Å for Sm, 2.223 Å for Y, and 2.183 Å for Yb found in the starting materials Sm[N($SiMe_3$)$_2$]$_3$,[19] Y[N($SiMe_3$)$_2$]$_3$,[20] and Yb[N($SiMe_3$)$_2$]$_3$.[21] The twisting between the naphthyl rings give torsion angles of 69.2(1) and 76.1(1)° for Sm, 69.6(3) and 76.6(3)° for Y, and 69.0(2) and 76.6(2)° for Yb, which are comparable to that found in **1**H of 75.6(3)°.

Asymmetric Hydroamination. Compounds **2**–**4** have been used as the catalysts in the intramolecular hydroamination/cyclization reaction of nonactivated terminal aminoalkenes (Table 2). All substrates are converted to the cyclic product at room temperature or elevated temperature in moderate to good conversions. The results of the hydroamination/cyclization of 2,2-dimethylpent-4-enylamine (**5a**) show that the samarium amide **2** (Table 2, entry 1) is noticeably good at room temperature. Not surprisingly, given a more open coordination sphere, the reaction is faster, but the ee value remains moderate. When the smaller Y^{3+} ion is used (Table 2, entry 2), the rate increases and the ee also improves slightly. However, under similar reaction conditions, the smaller Yb^{3+} ion (Table 2, entry 3) gives a rather low conversion (only 7.0%) but affords a good ee value (up to 71%), which is commensurate with the smaller metal ion radius.[22] When the temperature is increased, the rate increases but the ee value falls slightly (Table 2, entry 4). We are encouraged to find that the formation of six-membered rings can also be achieved with our catalysts **2** and **3** (Table 2, entries 8 and 9), and a moderate enantioselectivity (25%), mediated by the catalyst **3**, has been obtained (Table 2, entry 9). It can be concluded that the rate of cyclization for aminoalkenes follows the order 5 > 6, consistent with classical, stereoelectronically controlled cyclization processes.[8e] The three complexes can mediate the cyclization of the representative aminoalkenes, but the conversion ceases after 1 or 2 days due to the decomposition of the complexes by the intermediacy of the metal alkyl species via 1,2-migratory insertion at the imine unit,[5a] which makes the determination of kinetic data infeasible. Although the enantiomeric excesses obtained remain moderate to good, it should be noted that there are only a small number of catalysts for these reactions that give a significant ee (>90%) at all.[7a,9d,f,10e–g]

Conclusions

The bis-ligated lanthanide amides (**1**)$_2$-LnN($SiMe_3$)$_2$, prepared from the C_1-symmetric monopyrrole-substituted ligand **1**H, have been found to be more effective chiral catalysts for the enantioselective hydroamination/cyclization reaction than the C_2-symmetric bis(pyrrolate) lanthanide amides [(*R*)-$C_{20}H_{12}$-$(NCHC_4H_3N)_2$]LnN($SiMe_3$)$_2$(thf) (Ln = Sm, Y, Yb).[12] In some cases, the corresponding heterocyclic products have been obtained with good ee values (up to 71%) by this modified chiral 1,1′-binaphthyl-2,2′-diamine ligand. Although this modification using peripheral binaphthalene coupled with pyrrole and dimethylamine ligation in multidentate systems does not provide sufficient rigidity of the dative N-donor ligand to achieve a significant enantioselectivity (ee >90%), in contrast to the case for the binaphtholate system,[7a] the present results should significantly expand the range of possibilities in designing catalysts not only for hydroamination but also for many other reactions.[13] We are planning to synthesize a similar tridentate chiral binaphthyl embedded in a C_1-symmetric chiral scaffold in order to obtain more effective and stereoselective chiral ligands and to utilize those novel chiral ligands in this transformation and other catalytic asymmetric reactions. Work along these lines is in progress.

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Supporting Information Available: X-ray crystallographic data, in CIF format, for **1**H, **2**, **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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