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Synthesis of Amidolanthanides with New Chiral Biaryl-Based NNO Ligands and Their Use as Catalysts for Enantioselective Hydroamination/Cyclization

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A new series of amidolanthanides have been prepared from the reactions between $Ln[N(SiMe_3)_2]_3$ and the chiral NNO ligands, (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl (**2**H_2) and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (**3**H_2), which are synthesized from the condensation of pyrrole-2-carboxaldehyde with 1 equiv of (*S*)-2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl or (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-amino-2′-hydroxy-1,1′-binaphthyl, in the presence of molecular sieves at 70 °C, respectively. Treatment of **2**H_2 with 1 equiv of $Ln[N(SiMe_3)_2]_3$ (Ln = Sm, Yb) in toluene under reflux, followed by recrystallization from a toluene solution, gives the dimeric amido complexes, $\{$**2**-$SmN(SiMe_3)_2\}_2 \cdot 0.5C_7H_8$ (**6** $\cdot 0.5C_7H_8$) and $\{$**2**-$YbN(SiMe_3)_2\}_2 \cdot 1.5C_7H_8$ (**8** $\cdot 1.5C_7H_8$), in good yields. While under similar reaction conditions, the reaction of **2**H_2 with 1 equiv of $Y[N(SiMe_3)_2]_3$ leads to the isolation of a mixture of $\{$**2**-$YN(SiMe_3)_2\}_2$ (**7a**) and $\{(\mathbf{2})_2Y\}Y[N(SiMe_3)_2]_2$ (**7b**) in 82% total yield; the reaction of **3**H_2 with 1 equiv of $Ln[N(SiMe_3)_2]_3$ (Ln = Y, Yb) gives the trinuclear complexes, $\{(\mathbf{3})_2Ln\}_2LnN(SiMe_3)_2 \cdot 1.5C_7H_8$ (Ln = Y (**9** $\cdot 1.5C_7H_8$), Yb (**10** $\cdot 1.5C_7H_8$)), in good yields. All compounds have been characterized by various spectroscopic techniques and elemental analyses. The solid-state structures of compounds **2**H_2 and **6**−**10** have been further confirmed by X-ray diffraction analyses. Complexes **6**−**9** are active catalysts for the asymmetric hydroamination/cyclization of aminoalkenes, affording cyclic amines in good yields with moderate ee values.

Introduction

Hydroamination is a highly atom economical process in which an amine N−H bond is added to an unsaturated carbon−carbon bond, leading to the formation 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] Since the pioneering work of Marks and co-workers in 1992,[3a,b] many chiral catalysts based on

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(1) (a) For general hydroamination reviews, see: Odom, A. L. *Dalton Trans.* **2005**, 225–233. (b) Doye, S. *Synlett* **2004**, 1653–1672. (c) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104–114. (d) Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, 935–946. (e) Seayad, J.; Tillack, A.; Hartung, C. G.; Beller, M. *Adv. Synth. Catal.* **2002**, *344*, 795–813. (f) Nobis, M.; Driessen-Hölscher, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3983–3985. (g) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675–704.

(2) (a) For reviews of asymmetric hydroamination, see: Roesky, P. W.; Müller, T. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 2708–2710. (b) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673–686. (c) Hultzsch, K. C. *Org. Biomol. Chem.* **2005**, *3*, 1819–1824. (d) Hultzsch, K. C. *Adv. Synth. Catal.* **2005**, *347*, 367–391. (e) Hii, K. K. *Pure Appl. Chem.* **2006**, *78*, 341–349. (f) Aillaud, I.; Collin, J.; Hannedouche, J.; Schulz, E. *Dalton Trans.* **2007**, 5105–5118.

(3) (a) For selected papers for asymmetric hydroaminations using lanthanide metal catalysts with chiral Cp ligands, see: Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275–294. (b) Gagné, M. R.; Brard, L.; Conticello, V. P.; Giardello, M. A.; Stern, C. L.; Marks, T. J. *Organometallics* **1992**, *11*, 2003–2005. (c) Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241–10245. (d) Vitanova, D. V.; Hampel, F.; Hultzsch, K. C. *J. Organomet. Chem.* **2007**, *692*, 4690–4701, and references therein.

(4) Hong, S.; Tian, S.; Metz, M. V.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14768–14783.

(5) (a) O'Shaughnessy, P. N.; Knight, P. D.; Morton, C.; Gillespie, K. M.; Scott, P. *Chem. Commun.* **2003**, 1770–1771. (b) O'Shaughnessy, P. N.; Gillespie, K. M.; Knight, P. D.; Munslow, I. J.; Scott, P. *Dalton Trans.* **2004**, 2251–2256.

(6) Kim, J. Y.; Livinghouse, T. *Org. Lett.* **2005**, *7*, 1737–1739.

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lanthanide metals, main group metals, group 4 metals, and late transition metals with C_1-symmetric Cp ligands[3] and chiral non-Cp ligands have been widely studied.[4–10] Among these, 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. 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), Cu(II), Zr(IV), and Zn(II) complexes are useful catalysts for a wide range of transformations.[11] More recently, we have reported a new catalytic enantioselective hydroamination/cyclization of aminoalkenes, which is promoted by bis(pyrrolate) lanthanide amides [(*R*)-$C_{20}H_{12}(NCHC_4H_3N)_2$]LnN(SiMe$_3$)$_2$(thf) and [(*S*)-2-($Me_2N$)-$C_{20}H_{12}$-2′-($NCHC_4H_3N$)]$_2$-LnN(SiMe$_3$)$_2$ (Ln = Sm, Y, Yb), and in this transformation, excellent conversions (up to 98%) and good enantioselectivities (up to 71% ee) have been obtained.[12] In our ongoing research, we are now focusing on the preparation of lanthanide catalysts coordinated by chiral C_1-symmetric tridentate ligands, and to our best knowledge, no chiral lanthanide catalyst based on 2-amino-2′-hydroxy-1,1′-binaphthyl or 2-amino-2′-hydroxy-1,1′-biphenyl has been reported, in contrast to the cases of binaphthol, biphenol, binaphthylamine, and biphenylamine.[13] More recently, we have reported a new series of amidolanthanides with the chiral tridentate ligand, (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (**1**H_2), which is derived from (*S*)-2-amino-2′-hydroxy-1,1′-binaphthyl (Scheme 1).[14] These amides can initiate the polymerization of methyl methacrylate (MMA), but the reactivity is very low.[14] In our endeavor to further explore this chiral tridentate NNO-ligand system, we have recently extended our work to new chiral tridentate ligands, (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl (**2**H_2) and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (**3**H_2), which are derived from (*S*)-2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-amino-2′-hydroxy-1,1′-binaphthyl, respectively. We report here the synthesis and the properties of these new chiral ligands, (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl (**2**H_2) and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (**3**H_2), their use in the coordination chemistry of lanthanides, and the applications of the resulting complexes as catalysts for the hydroamination/cyclization reactions. The differences and similarities between the (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (**1**H_2), (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl (**2**H_2), and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (**3**H_2) ligand systems will also be discussed in this contribution.

Experimental Section

General Methods. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture by 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′-hydroxy-6,6′-dimethyl-1,1′-biphenyl,[15] (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-amino-2′-hydroxy-1,1′-binaphthyl,[16] {**1**-YN(SiMe$_3$)$_2$}$_2$ (**4**),[14]

(7) (a) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748–3759. (b) Gribkov, D. V.; Hultzsch, K. C. *Chem. Commun.* **2004**, 730–731. (c) Gribkov, D. V.; Hampel, F.; Hultzsch, K. C. *Eur. J. Inorg. Chem.* **2004**, 4091–4101. (d) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *Chem.—Eur. J.* **2003**, *9*, 4796–4810. (e) Yu, X.; Marks, T. J. *Organometallics* **2007**, *26*, 365–376. (f) Heck, R.; Schulz, E.; Collin, J.; Carpentier, J.-F. *J. Mol. Catal. A: Chem.* **2007**, *268*, 163–168.

(8) (a) Riegert, D.; Collin, J.; Meddour, A.; Schulz, E.; Trifonov, A. *J. Org. Chem.* **2006**, *71*, 2514–2517. (b) Collin, J.; Daran, J. C.; Jacquet, O.; Schulz, E.; Trifonov, A. *Chem.—Eur. J.* **2005**, *11*, 3455–3462. (c) Collin, J.; Daran, J. C.; Schulz, E.; Trifonov, A. *Chem. Commun.* **2003**, 3048–3049. (d) O'Shaughnessy, P. N.; Scott, P. *Tetrahedron: Asymmetry* **2003**, *14*, 1979–1983. (e) Meyer, N.; Zulys, A.; Roesky, P. W. *Organometallics* **2006**, *25*, 4179–4182. (f) Riegert, D.; Collin, J.; Daran, J. C.; Fillebeen, T.; Schulz, E.; Lyubov, D.; Fukin, G.; Trifonov, A. *Eur. J. Inorg. Chem.* **2007**, 1159–1168. (g) Kim, H.; Kim, Y. K.; Shim, J. H.; Kim, M.; Han, M.; Livinghouse, T.; Lee, P. H. *Adv. Synth. Catal.* **2006**, *348*, 2609–2618. (h) Aillaud, I.; Wright, K.; Collin, J.; Schulz, E.; Mazaleyrat, J.-P. *Tetrahedron: Asymmetry* **2008**, *19*, 82–92. (i) Aillaud, I.; Collin, J.; Duhayon, C.; Guillot, R.; Lyubov, D.; Schulz, E.; Trifonov, A. *Chem.—Eur. J.* **2008**, *14*, 2189–2200.

(9) (a) For asymmetric hydroamination using late transition metal catalysts, see: Löber, O.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 4366–4367. (b) Patil, N. T.; Lutete, L. M.; Wu, H.; Pahadi, N. K.; Gridnev, I. D.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 4270–4279. (c) Hu, A.; Ogasaware, M.; Sakamoto, T.; Okada, A.; Nakajima, K.; Takahashi, T.; Lin, W. *Adv. Synth. Catal.* **2006**, *348*, 2051–2056. (d) LaLonde, R. L.; Sherry, B. D.; Kang, E. J.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 2452–2453. (e) Zhang, Z.; Bender, C. F.; Widenhoefer, R. A. *Org. Lett.* **2007**, *9*, 2887–2889. (f) Zhang, Z.; Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2007**, *129*, 14148–14149.

(10) (a) For examples of asymmetric hydroamination using other metal catalysts, see: Knight, P. D.; Munslow, I.; O'Shaughnessy, P. N.; Scott, P. *Chem. Commun.* **2004**, 894–895. (b) Gribkov, D. V.; Hultzcsh, K. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5542–5546. (c) Martinez, P. H.; Hultzsch, K. C.; Hampel, F. *Chem. Commun.* **2006**, 2221–2223. (d) Watson, D. A.; Chiu, M.; Bergman, R. G. *Organometallics* **2006**, *25*, 4731–4733. (e) Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 354–358. (f) Gott, A. L.; Clarke, A. J.; Clarkson, G. J.; Scott, P. *Organometallics* **2007**, *26*, 1729–1737. (g) Ogata, T.; Ujihara, A.; Tsuchida, S.; Shimizu, T.; Kaneshige, A.; Tomioka, K. *Tetrahedron Lett.* **2007**, *48*, 6648–6650.

(11) (a) Zi, G.-F.; Yin, C.-L. *Acta Chim. Sin.* **1998**, *56*, 484–484. (b) Zi, G.-F.; Yin, C.-L. *J. Mol. Catal. A: Chem.* **1998**, *132*, L1–L4. (c) Zi, G.; Xiang, L.; Zhang, Y.; Wang, Q.; Yang, Y.; Zhang, Z. *J. Organomet. Chem.* **2007**, *692*, 3949–3956. (d) Zhang, Z.; Li, M.; Zi, G. *Chirality* **2007**, *19*, 802–808. (e) Zhang, Y.; Xiang, L.; Wang, Q.; Duan, X.-F.; Zi, G. *Inorg. Chim. Acta* **2008**, *361*, 1246–1254. (f) Xiang, L.; Song, H.; Zi, G. *Eur. J. Inorg. Chem.* **2008**, 1135–1140.

(12) (a) Xiang, L.; Wang, Q.; Song, H.; Zi, G. *Organometallics* **2007**, *26*, 5323–5329. (b) Zi, G.; Xiang, L.; Song, H. *Organometallics* **2008**, *27*, 1242–1246.

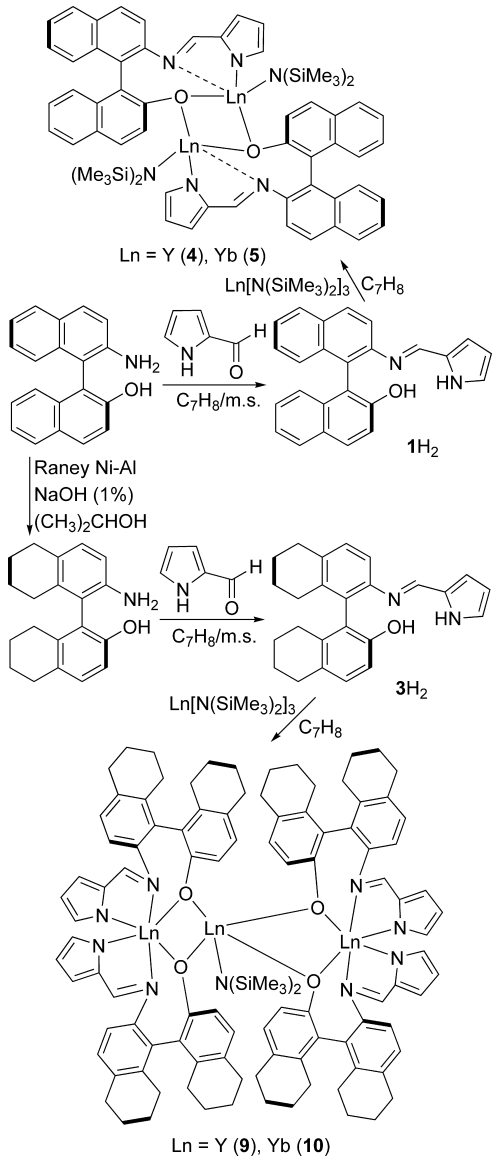
(13) (a) For selected recent reviews, see: Shibasaki, M.; Yoshikawa, N. *Chem. Rev.* **2002**, *102*, 2187–2210. (b) Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. L. *Chem. Rev.* **2002**, *102*, 2227–2302. (c) Aspinall, H. C. *Chem. Rev.* **2002**, *102*, 1807–1850. (d) Che, C.-M.; Huang, J.-S. *Coord. Chem. Rev.* **2003**, *242*, 97–113. (e) Knight, P. D.; Scott, P. *Coord. Chem. Rev.* **2003**, *242*, 125–143. (f) Kočovský, P.; VyskočilŠ.; Smrčina, M. *Chem. Rev.* **2003**, *103*, 3213–3246. (g) Ding, K.; Li, X.; Ji, B.; Guo, H.; Kitamura, M. *Curr. Org. Synth.* **2005**, *2*, 499–545. (h) Ding, K.; Guo, H.; Li, X.; Yuan, Y.; Wang, Y. *Top. Catal.* **2005**, *35*, 105–116. (i) Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857–898.

(14) Wang, Q.; Xiang, L.; Zi, G. *J. Organomet. Chem.* **2008**, *693*, 68–76.

(15) Liang, Y.; Gao, S.; Wan, H.; Wang, J.; Chen, H.; Zheng, Z.; Hu, X. *Tetrahedron: Asymmetry* **2003**, *14*, 1267–1273.

(16) Guo, H.; Ding, K. *Tetrahedron Lett.* **2000**, *41*, 10061–10064.

Scheme 1



{**1**-YbN(SiMe$_3$)$_2$}$_2$ (**5**),[14] Ln[N(SiMe$_3$)$_2$]$_3$,[17] 2,2-dimethylpent-4-enylamine,[6] 2,2′-dimethylhex-5-enylamine,[6] and 1-(aminomethyl)-1-allylcyclohexane[8a] were prepared according to literature methods. The aminoalkenes were dried over Na_2SO_4 or sodium and freshly distilled immediately prior to use. 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′-hydroxy-6,6′-dimethyl-1,1′-biphenyl (2H$_2$). Pyrrole-2-carboxaldehyde (0.95 g, 10.0 mmol) was mixed with (*S*)-2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl (2.13 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 at this temperature for two days. The solution was filtered, and the solvent was removed under reduced pressure. The resulting orange solid was recrystallized from benzene (10 mL) to give **2**H$_2$ as yellow crystals. Yield: 2.32 g (80%); mp 158–160 °C. ^{1}H NMR ($CDCl_3$): δ 9.26 (br, s, 1H), 8.07 (d, J = 11.1 Hz, 1H), 7.31 (m, 2H), 7.16 (m, 2H), 6.93–6.60 (m, 3H), 6.59 (d, J = 2.7 Hz, 1H), 6.24 (d, J = 2.1 Hz, 1H), 2.02 (s, 3H), 1.90 (s, 3H); the proton of OH was not observed. ^{13}C NMR ($CDCl_3$): δ 152.5, 151.0, 149.3, 138.6, 137.5, 130.5, 129.2, 129.0, 128.2, 127.5, 125.7, 123.2, 121.9, 116.9, 116.7, 113.4, 110.3, 19.9, 19.7. IR (KBr, cm^{-1}): ν 3354 (s), 3065 (w), 2917 (w), 1619 (vs), 1589 (s), 1548 (s), 1465 (s), 1414 (s), 1347 (s), 1281 (s), 1033 (vs), 948 (s), 739 (s). Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.62; H, 6.49; N, 9.61.

Preparation of (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (3H$_2$). This compound was prepared as yellow microcrystals from the reaction of (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-amino-2′-hydroxy-1,1′-binaphthyl (1.47 g, 5.0 mmol) with pyrrole-2-carboxaldehyde (0.48 g, 5.0 mmol) in dry toluene (25 mL) in the presence of 4 Å molecular sieves at 70 °C and from recrystallization from cyclohexane by a similar procedure, as outlined for the synthesis of **2**H$_2$. Yield: 1.39 g (75%); mp 112–114 °C. ^{1}H NMR ($CDCl_3$): δ 8.05 (s, 1H), 7.17 (d, J = 8.1 Hz, 1H), 6.98 (m, 2H), 6.72 (s, 1H), 6.78 (d, J = 8.3 Hz, 1H), 6.59 (d, J = 2.6 Hz, 1H), 6.25 (t, J = 2.9 Hz, 1H), 2.83 (m, 2H), 2.73 (m, 2H), 2.33–2.13 (m, 4H), 1.78–1.62 (m, 8H); the protons of OH and NH were not observed. ^{13}C NMR (CDCl): δ 150.1, 148.8, 148.2, 136.9, 135.8, 135.4, 130.4, 129.7, 129.3, 129.1, 129.0, 125.1, 123.0, 116.9, 116.5, 113.4, 110.0, 29.7, 29.3, 27.5, 27.1, 27.0, 23.2, 23.0, 22.7. IR (KBr, cm^{-1}): ν 3289 (br, m), 2925 (s), 2850 (m), 1612 (s), 1583 (s), 1547 (s), 1471 (s), 1419 (s), 1342 (s), 1244 (s), 1201 (s), 1157 (s), 1095 (s), 1033 (s), 932 (s), 811 (s), 736 (s). Anal. Calcd for $C_{25}H_{26}N_2O$: C, 81.05; H, 7.07; N, 7.56. Found: C, 80.82; H, 6.89; N, 7.61.

Preparation of {2-SmN(SiMe$_3$)$_2$}$_2$·0.5C$_7$H$_8$ (6·0.5C$_7$H$_8$). A toluene solution (10 mL) of **2**H$_2$ (0.29 g, 1.0 mmol) was slowly added to a toluene solution (10 mL) of Sm[N(SiMe$_3$)$_2$]$_3$ (0.63 g, 1.0 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. After this solution stood at room temperature for three days, **6**·0.5C$_7$H$_8$ was isolated as yellow crystals. Yield: 0.50 g (80%); mp 258–260 °C (dec). IR (KBr, cm^{-1}): ν 2945 (w), 1612 (w), 1582 (s), 1556 (s), 1449 (m), 1385 (s), 1298 (s), 1257 (s), 1179 (s), 1035 (s), 988 (s), 837 (s). Anal. Calcd for $C_{107}H_{144}N_{12}O_4Si_8Sm_4$: C, 51.64; H, 5.83; N, 6.75. Found: C, 51.53; H, 5.96; N, 6.52.

Preparation of {2-YN(SiMe$_3$)$_2$}$_2$ (7a) and {(2)$_2$Y}Y[N(SiMe$_3$)$_2$]$_2$ (7b). A toluene solution (10 mL) of **2**H$_2$ (0.29 g, 1.0 mmol) was slowly added to a toluene solution (10 mL) of Y[N(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 solution was filtered, and the filtrate was concentrated to about 5 mL. After this solution stood at room temperature for three days, yellow crystals were isolated, which were identified to contain both complex {**2**-YN(SiMe$_3$)$_2$}$_2$ (**7a**) and complex {(**2**)$_2$Y}Y[N(SiMe$_3$)$_2$]$_2$ (**7b**), by using X-ray crystallography. Total yield: 0.44 g (82%). **7a**, ^{1}H NMR (C_6D_6): δ 7.97 (s, 1H), 7.73 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.27–7.19 (m, 4H), 7.11 (m, 1H), 6.93–6.68 (m, 8H), 6.58 (d, J = 7.5 Hz, 1H), 6.37 (d, J = 1.9 Hz, 1H), 6.28 (s, 1H), 6.12 (d, J = 2.0 Hz, 1H), 1.97 (s, 6H), 1.85 (s, 6H), 0.61 (s, 18H, ((CH$_3$)$_3$Si)$_2$N), –0.19 (s, 18H, ((CH$_3$)$_3$Si)$_2$N). ^{13}C NMR (C_6D_6): δ 157.6, 157.5, 147.2, 140.5, 139.1, 137.8, 130.3, 129.9, 128.9, 128.4,

(17) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021–1023.

Table 1. Crystal Data and Experimental Parameters for Compounds $2H_2$ and **6**−**10**

	$2H_2$	$6\cdot 0.5C_7H_8$	**7** (**7a** + **7b**)	$8\cdot 1.5C_7H_8$	$9\cdot 1.5C_7H_8$	$10\cdot 1.5C_7H_8$
formula	$C_{19}H_{18}N_2O$	$C_{53.5}H_{72}N_6O_2Si_4Sm_2$	$C_{100}H_{136}N_{12}O_4Si_8Y_4$	$C_{60.5}H_{78}N_6O_2Si_4Yb_2$	$C_{116.5}H_{126}N_9O_4Si_2Y_3$	$C_{116.5}H_{126}N_9O_4Si_2Yb_3$
fw	290.35	1244.23	2150.57	1379.73	2039.17	2291.56
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$C121$	$P2_12_12_1$	$P12_11$	$P12_11$	$P12_11$
a (Å)	7.859(2)	22.086(2)	12.574(1)	15.191(1)	14.969(1)	14.770(1)
b (Å)	12.133(2)	13.099(1)	19.183(1)	13.196(1)	22.379(2)	22.014(1)
c (Å)	16.954(3)	20.235(2)	45.840(3)	31.126(1)	31.488(3)	31.236(2)
β (deg)	90	98.219(8)	90	92.699(2)	100.767(7)	100.426(3)
V (Å^3)	1616.5(5)	5794.2(8)	11056.7(10)	6233.6(2)	10362.7(15)	9988.4(9)
Z	4	4	4	4	4	
D_{calc} (g/cm^3)	1.193	1.426	1.292	1.470	1.307	1.524
μ(Mo Kα)$_{calc}$ (mm^{-1})	0.075	2.132	2.217	3.104	1.746	2.869
size (mm)	0.26 × 0.24 × 0.20	0.28 × 0.26 × 0.24	0.14 × 0.12 × 0.06	0.32 × 0.30 × 0.20	0.20 × 0.18 × 0.14	0.04 × 0.03 × 0.02
F(000)	616	2524	4480	2780	4260	4632
2θ range (deg)	4.12−52.79	3.62−52.00	3.36−52.06	3.04−55.76	3.28−50.00	2.66−50.00
no. of reflns, collected	9276	24842	88689	57649	78828	76143
no. of unique reflns	1900 (R_{int} = 0.043)	11152 (R_{int} = 0.062)	21744 (R_{int} = 0.115)	29048 (R_{int} = 0.043)	35801 (R_{int} = 0.120)	35126 (R_{int} = 0.078)
no. of obsd reflns	1900	11152	21744	29048	35801	35126
abs cor (T_{max}, T_{min})	0.99, 0.98	0.63, 0.59	0.88, 0.75	0.58, 0.44	0.79, 0.72	0.94, 0.89
R	0.034	0.029	0.061	0.042	0.114	0.071
R_w	0.087	0.046	0.115	0.077	0.267	0.114
R_{all}	0.051	0.036	0.081	0.049	0.169	0.087
GOF	1.01	0.779	1.06	1.01	1.04	1.13

128.3, 128.2, 127.6, 127.2, 126.3, 125.9, 123.3, 123.1, 120.9, 120.1, 118.4, 117.3, 113.0, 20.1, 19.3, 5.9, 1.9. **7b**, ^{1}H NMR (C_6D_6): δ 7.97 (s, 1H), 7.73 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.27–7.19 (m, 4H), 7.11 (m, 1H), 6.93–6.68 (m, 8H), 6.58 (d, J = 7.5 Hz, 1H), 6.37 (d, J = 1.9 Hz, 1H), 6.28 (s, 1H), 6.12 (d, J = 2.0 Hz, 1H), 2.09 (s, 6H), 2.04 (s, 6H), 0.29 (s, 36H, $((CH_3)_3Si)_2N$). ^{13}C NMR (C_6D_6): δ 157.6, 157.5, 147.2, 140.5, 139.1, 137.8, 130.3, 129.9, 128.9, 128.4, 128.3, 128.2, 127.6, 127.2, 126.3, 125.9, 123.3, 123.1, 120.9, 120.1, 118.4, 117.3, 113.0, 20.0, 19.3, 4.6.

Note that the ^{1}H NMR spectra of **7a** and **7b** could not be assigned unambiguously, but according to the analogue complex {**1**-YN-$(SiMe_3)_2$}$_2$ (**4**),[14] their amino groups $(Me_3Si)_2N$ were assigned clearly, which showed the ratio of **7a/7b** is about 1:1.1. The mixture of **7a** and **7b** could not be isomerized to one isomer even after heating at 120 °C for one week, which was monitored by ^{1}H NMR in a J. Young NMR tube with the deuterated solvent of C_6D_6.

Preparation of {2-YbN(SiMe$_3$)$_2$}$_2$·1.5C$_7$H$_8$ (8·1.5C$_7$H$_8$). This compound was prepared as yellow crystals from the reaction of $2H_2$ (0.29 g, 1.0 mmol) with Yb[N(SiMe$_3$)$_2$]$_3$ (0.65 g, 1.0 mmol) in toluene (20 mL) by a similar procedure as in the synthesis of $6\cdot 0.5C_7H_8$. Yield: 0.52 g (75%); mp 260–262 °C (dec). IR (KBr, cm^{-1}): ν 3056 (w), 2958 (s), 1617 (s), 1586 (s), 1560 (s), 1449 (s), 1298 (s), 1259 (vs), 1034 (vs), 933 (s), 799 (s). Anal. Calcd for $C_{121}H_{156}N_{12}O_4Si_8Yb_4$: C, 52.67; H, 5.70; N, 6.09. Found: C, 52.78; H, 5.43; N, 6.16.

Preparation of {(3)$_2$Y}$_2$YN(SiMe$_3$)$_2$·1.5C$_7$H$_8$ (9·1.5C$_7$H$_8$). This compound was prepared as yellow crystals from the reaction of $3H_2$ (0.37 g, 1.0 mmol) with Y[N(SiMe$_3$)$_2$]$_3$ (0.57 g, 1.0 mmol) in toluene (20 mL) by a similar procedure as in the synthesis of $6\cdot 0.5C_7H_8$. Yield: 0.33 g (65%); mp 264–266 °C (dec). ^{1}H NMR (C_5D_5N): δ 8.30 (s, 2H), 8.07 (s, 2H), 7.79 (s, 2H), 7.32 (m, 10H), 7.15 (m, 6H), 7.02 (s, 2H), 6.89–6.74 (m, 30H), 6.58 (m, 3H), 6.47 (m, 10H), 6.32 (d, J = 1.5 Hz, 2H), 6.15 (d, J = 1.6 Hz, 2H), 6.10 (d, J = 3.2 Hz, 2H), 6.01 (d, J = 3.3 Hz, 2H), 5.85 (d, J = 2.1 Hz, 2H), 5.22 (d, J = 7.8 Hz, 2H), 3.00 (m, 12H), 2.75 (m, 18H), 2.45 (m, 12H), 2.25 (m, 8H), 2.19 (s, 9H), 1.98 (m, 26H), 1.60–1.31 (m, 42H), 1.15 (m, 10H), 0.13 (s, 36H). ^{13}C NMR (C_5D_5N): δ 160.4, 160.2, 158.1, 158.0, 155.3, 149.9, 148.4, 147.3, 146.4, 145.1, 140.6, 139.4, 139.2, 139.1, 138.5, 138.3, 138.2, 138.0, 137.9, 136.7, 135.8, 135.6, 134.9, 134.7, 133.7, 132.6, 130.9, 130.3, 130.2, 129.8, 129.7, 129.6, 129.0, 128.0, 125.8, 124.0, 123.2, 122.4, 121.4, 120.7, 120.5, 120.1, 119.8, 118.5, 113.8, 113.3, 112.5, 31.6, 31.4, 31.0, 30.7, 30.6, 30.3, 30.0, 29.7, 29.4, 29.0, 27.0, 25.9, 25.3, 25.2, 25.0, 24.7, 24.6, 24.4, 24.0, 23.9, 23.8, 23.7, 22.2, 3.6. IR (KBr, cm^{-1}): ν 2928 (m), 2853 (w), 1595 (s), 1567 (s), 1461 (s), 1386 (s), 1296 (s), 1260 (s), 1239 (s), 1091 (s), 1035 (s), 801 (s). Anal. Calcd for $C_{233}H_{252}N_{18}O_8Si_4Y_6$: C, 68.62; H, 6.23; N, 6.18. Found: C, 68.42; H, 6.39; N, 6.23.

Preparation of {(3)$_2$Yb}$_2$YbN(SiMe$_3$)$_2$·1.5C$_7$H$_8$ (10·1.5C$_7$H$_8$). This compound was prepared as yellow crystals from the reaction of $3H_2$ (0.37 g, 1.0 mmol) with Yb[N(SiMe$_3$)$_2$]$_3$ (0.65 g, 1.0 mmol) in toluene (20 mL) by a similar procedure as in the synthesis of $6\cdot 0.5C_7H_8$. Yield: 0.40 g (70%); mp 260–262 °C (dec). IR (KBr, cm^{-1}): ν 2925 (m), 2854 (w), 1595 (s), 1570 (s), 1460 (m), 1426 (m), 1384 (s), 1296 (s), 1260 (s), 1089 (s), 1035 (s), 799 (s). Anal. Calcd for $C_{233}H_{252}N_{18}O_8Si_4Yb_6$: C, 61.06; H, 5.54; N, 5.50. Found: C, 61.32; H, 5.29; N, 5.33.

General Procedure for Asymmetric Hydroamination/Cyclization. In a nitrogen-filled glovebox, precatalyst (0.016 mmol, based on the LnN(SiMe$_3$)$_2$ group), C_6D_6 (0.7 mL), and aminoalkene (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 room temperature, at 60 °C, or at 120 °C to achieve hydroamination, and the reaction was monitored periodically by ^{1}H NMR spectroscopy. The cyclic amine was vacuum transferred from the J. Young NMR tube into a 25 mL Schlenk flask that 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 were carried out on a Rigaku Saturn CCD diffractometer at 113(2) K using graphite monochromated Mo Kα radiation (λ = 0.71070 Å). An empirical absorption correction was applied using the SADABS program.[18] All structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the

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

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds $2H_2$ and **6**−**10**

			Compound $2H_2$				
N(1)−C(15)	1.273(3)	torsion (pyrrolyl-imine)	5.6(2)	torsion (aryl-imine)	58.0(2)	torsion (aryl-aryl)	76.7(2)
			Compound $6\cdot 0.5C_7H_8$				
Sm(1)−O(1)	2.446(3)	Sm(1)−O(2)	2.239(3)	Sm(1)−Sm(2)	3.7270(4)	Sm(1)−O(1)−Sm(2)	105.17(11)
Sm(1)−N(1)	2.563(4)	Sm(1)−N(2)	2.394(4)	Sm(1)−O(2)−Sm(2)	105.93(11)	torsion (aryl-imine)	38.9(2)
Sm(1)−N(5)	2.245(3)	Sm(2)−O(1)	2.244(3)				41.5(2)
Sm(2)−O(2)	2.427(3)	Sm(2)−N(3)	2.524(4)	torsion (aryl-aryl)	76.3(2)		
Sm(2)−N(4)	2.390(4)	Sm(2)−N(6)	2.259(4)		72.8(2)		
			Compound **7** (**7a** + **7b**)				
Y(1)−O(1)	2.362(4)	Y(1)−O(2)	2.176(4)	Y(4)−O(4)	2.223(4)	Y(4)−N(11)	2.239(5)
Y(1)−N(1)	2.495(5)	Y(1)−N(2)	2.339(5)	Y(4)−N(12)	2.252(5)	Y(3)−Y(4)	3.6858(8)
Y(1)−N(5)	2.226(5)	Y(2)−O(1)	2.181(3)	Y(1)−O(1)−Y(2)	104.90(14)	Y(1)−O(2)−Y(2)	105.15(15)
Y(2)−O(2)	2.359(4)	Y(2)−N(3)	2.512(4)	Y(3)−O(3)−Y(4)	108.30(14)	Y(3)−O(4)−Y(4)	107.52(15)
Y(2)−N(4)	2.330(5)	Y(2)−N(6)	2.227(5)	torsion (aryl-imine) (**7a**)	37.3(6)	torsion (aryl-aryl) (**7a**)	70.5(6)
Y(1)−Y(2)	3.6028(8)	Y(3)−O(3)	2.342(4)		41.0(6)		71.5(6)
Y(3)−O(4)	2.346(4)	Y(3)−N(7)	2.438(5)	torsion (aryl-imine) (**7b**)	36.5(6)	torsion (aryl-aryl) (**7b**)	69.0(6)
Y(3)−N(8)	2.318(5)	Y(3)−N(9)	2.447(5)		38.3(6)		70.8(6)
Y(3)−N(10)	2.342(5)	Y(4)−O(3)	2.204(3)				
			Compound $8\cdot 1.5C_7H_8$				
Yb(1)−O(1)	2.305(3)	Yb(1)−O(2)	2.172(3)	Yb(1)−Yb(2)	3.5596(3)	Yb(1)−O(1)−Yb(2)	105.52(14)
Yb(1)−N(1)	2.429(5)	Yb(1)−N(2)	2.280(5)	Yb(1)−O(2)−Yb(2)	105.82(14)	torsion (aryl-imine)	32.9(2)
Yb(1)−N(5)	2.195(5)	Yb(2)−O(1)	2.165(3)				35.3(2)
Yb(2)−O(2)	2.289(4)	Yb(2)−N(3)	2.456(5)	torsion (aryl-aryl)	69.5(2)		
Yb(2)−N(4)	2.266(5)	Yb(2)−N(6)	2.160(5)		69.9(2)		
			Compound $9\cdot 1.5C_7H_8$				
Y(1)−O(1)	2.357(8)	Y(1)−O(2)	2.344(9)	Y(1)−O(2)−Y(3)	108.1(3)	Y(2)−O(3)−Y(3)	107.3(4)
Y(1)−N(1)	2.460(12)	Y(1)−N(2)	2.348(11)	Y(2)−O(4)−Y(3)	107.0(3)	torsion (aryl-imine)	27.9(4)
Y(1)−N(3)	2.447(11)	Y(1)−N(4)	2.391(13)				36.0(4)
Y(1)−Y(3)	3.7320(18)	Y(2)−O(3)	2.334(9)				44.2(4)
Y(2)−O(4)	2.348(9)	Y(2)−N(5)	2.449(11)				49.1(4)
Y(2)−N(6)	2.388(11)	Y(2)−N(7)	2.457(12)	torsion (aryl-aryl)	66.9(4)		
Y(2)−N(8)	2.355(14)	Y(2)−Y(3)	3.6927(19)		68.2(4)		
Y(3)−O(1)	2.197(9)	Y(3)−O(2)	2.265(8)		72.3(4)		
Y(3)−O(3)	2.249(9)	Y(3)−O(4)	2.244(8)		74.5(4)		
Y(3)−N(9)	2.231(10)	Y(1)−O(1)−Y(3)	110.0(4)				
			Compound $10\cdot 1.5C_7H_8$				
Yb(1)−O(1)	2.266(9)	Yb(1)−O(2)	2.309(8)	Yb(1)−O(2)−Yb(3)	107.6(3)	Yb(2)−O(3)−Yb(3)	106.5(4)
Yb(1)−N(1)	2.370(10)	Yb(1)−N(2)	2.276(12)	Yb(2)−O(4)−Yb(3)	107.8(4)	torsion (aryl-imine)	26.7(4)
Yb(1)−N(3)	2.357(10)	Yb(1)−N(4)	2.342(12)				32.5(4)
Yb(1)−Yb(2)	3.647(10)	Yb(2)−O(3)	2.302(8)				42.3(4)
Yb(2)−O(4)	2.274(9)	Yb(2)−N(5)	2.367(10)				46.6(4)
Yb(2)−N(6)	2.303(10)	Yb(2)−N(7)	2.397(9)	torsion (aryl-aryl)	62.6(4)		
Yb(2)−N(8)	2.267(11)	Yb(2)−Yb(3)	3.616(10)		67.3(4)		
Yb(3)−O(1)	2.198(8)	Yb(3)−O(2)	2.210(8)		69.7(4)		
Yb(3)−O(3)	2.211(9)	Yb(3)−O(4)	2.202(8)		70.5(4)		
Yb(3)−N(9)	2.174(12)	Yb(1)−O(1)−Yb(3)	109.6(3)				

SHELXL-97 program package.[19] All the hydrogen atoms were geometrically fixed using the riding model. The crystal data and the experimental data for $2H_2$ and **6**−**10** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Results and Discussion

Ligands. The C_1-symmetric pyrrole imine ligands, (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl ($2H_2$) and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl ($3H_2$), are readily prepared by condensation of pyrrole-2-carboxaldehyde with 1 equiv of (*S*)-2-amino-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl or (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-amino-2′-hydroxy-1,1′-binaphthyl, respectively, in good yields, in the presence of molecular sieves in toluene at 70 °C (Schemes 1 and 2).

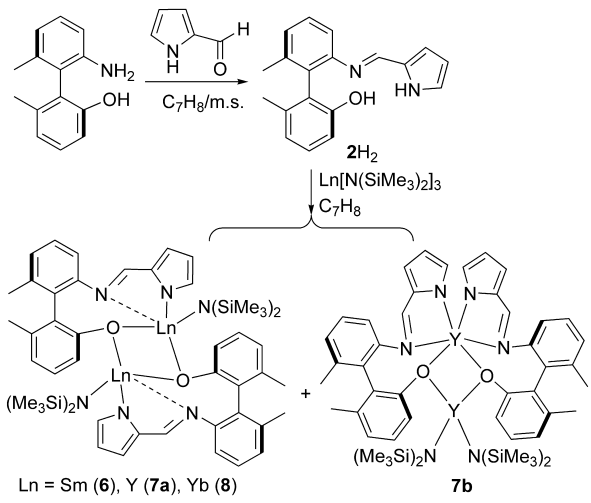
(19) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structure from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1997.

Both $2H_2$ and $3H_2$ are air-stable but sensitive to hydrolysis; they are soluble in CH_2Cl_2, $CHCl_3$, toluene, and benzene and only slightly soluble in *n*-hexane. They have been fully characterized by various spectroscopic techniques and elemental analyses. Their IR spectra show a typical characteristic N═C absorption at about 1619 cm^{-1}. The solid-state structure of $2H_2$ has been further confirmed by single-crystal X-ray analysis.

The molecular structure of $2H_2$ shows that it crystallizes in a C_1 symmetric distorted-tetrahedral geometry (Figure 1). As expected, the distance (1.273(3) Å) of the C═N is in agreement with a C═N double bond. The phenyl units are twisted with the imine group (the torsion angle is 58.0(2)°), and a more dramatic twisting is observed between the phenyl rings, which are almost perpendicular to each other (the torsion angles are 76.7(2)°).

Amidolanthanide Complexes. Our previous work has shown that the interaction between (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl ($1H_2$) and Ln[N-

Scheme 2



$(SiMe_3)_2]_3$ in toluene results in the clean formation of the dimeric amidolanthanides $\{\mathbf{1}\text{-LnN}(SiMe_3)_2\}_2$ (Ln = Y (**4**), Yb (**5**)) (Scheme 1).[14] The two acidic protons in the ligand $\mathbf{2}H_2$ or $\mathbf{3}H_2$ would allow a similar silylamine elimination to occur between $\mathbf{2}H_2$ or $\mathbf{3}H_2$ and metal amides. In fact, treatment of $\mathbf{2}H_2$ with 1 equiv of $Ln[N(SiMe_3)_2]_3$ (Ln = Sm, Yb) in toluene under reflux followed by recrystallization from a toluene solution gives the dimeric amide complexes $\{\mathbf{2}\text{-SmN}(SiMe_3)_2\}_2 \cdot 0.5C_7H_8$ (**6**·$0.5C_7H_8$) and $\{\mathbf{2}\text{-YbN}(SiMe_3)_2\}_2 \cdot 1.5C_7H_8$ (**8**·$1.5C_7H_8$) in good yields (Scheme 2). Under similar reaction conditions, reaction of $\mathbf{2}H_2$ with 1 equiv of $Y[N(SiMe_3)_2]_3$ leads to the isolation of a mixture of $\{\mathbf{2}\text{-YN}(SiMe_3)_2\}_2$ (**7a**) and $\{(\mathbf{2})_2Y\}Y[N(SiMe_3)_2]_2$ (**7b**) in 82% total yield (Scheme 2); the reaction of $\mathbf{3}H_2$ with 1 equiv of $Ln[N(SiMe_3)_2]_3$ (Ln = Y, Yb) gives the trinuclear complexes $\{(\mathbf{3})_2Ln\}_2LnN(SiMe_3)_2 \cdot 1.5C_7H_8$ (Ln = Y (**9**$1.5C_7H_8$), Yb (**10**·$1.5C_7H_8$)) in good yields (Scheme 1).

Although we have attempted to separate complexes **7a** and **7b** by recrystallization in various solvents, such as toluene,

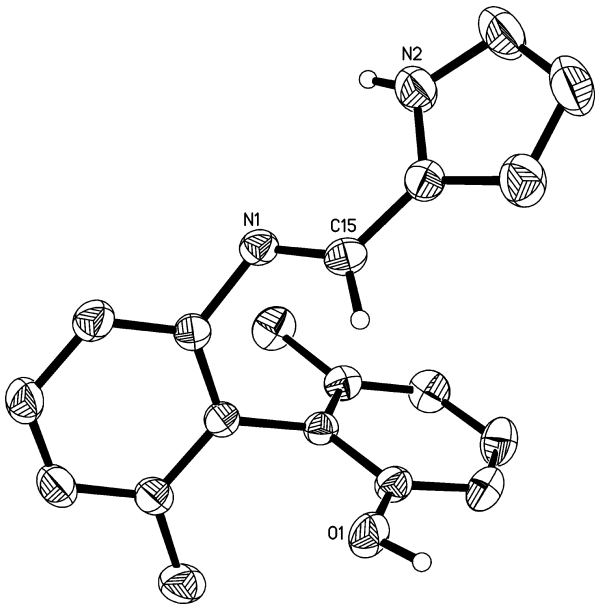


Figure 1. Molecular structure of $\mathbf{2}H_2$ (thermal ellipsoids drawn at the 35% probability level).

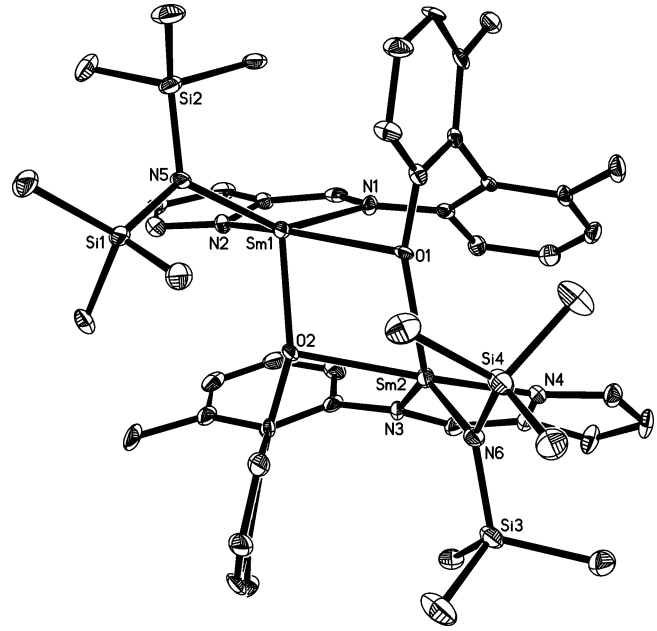


Figure 2. Molecular structure of **6** (thermal ellipsoids drawn at the 35% probability level).

benzene, *n*-hexane, cyclohexane, DME, dioxane, THF, and some mixed solvents, no pure complex of **7a** or **7b** has been isolated due to their similar solubilities. The formation process of **7a** and **7b** can be monitored by ^{1}H NMR. This transformation does not occur at room temperature, 60 °C, or 90 °C. But it occurs at 120 °C, and this conversion could be completed in about one day. The ^{1}H NMR spectra of **7a** and **7b** could not be assigned unambiguously, but according to the ^{1}H NMR spectrum of the analogue complex $\{\mathbf{1}\text{-YN}(SiMe_3)_2\}_2$ (**4**),[14] their amino groups $(Me_3Si)_2N$ were assigned clearly, which shows the ratio of **7a**/**7b** is about 1:1.1, and the ^{1}H NMR experiment shows that the mixture of **7a** and **7b** cannot be isomerized to one isomer even when heated at 120 °C for one week.

All the complexes are stable in a dry nitrogen atmosphere, but 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 single-crystal X-ray diffraction analyses show that there are two molecules of $\{\mathbf{2}\text{-LnN}(SiMe_3)_2\}_2$, one solvate toluene molecule for **6**, and three solvate toluene molecules for **8** in the lattice. Coordination of the two ligand anions **2** and two amino $N(SiMe_3)_2$ groups around two lanthanide ions results in the formation of the dimeric complexes $\{\mathbf{2}\text{-LnN}(SiMe_3)_2\}_2$ (Figures 2 and 3). Each Ln^{3+} is covalently bound to two nitrogen atoms and two oxygen atoms from the ligand anions **2** and one nitrogen atom from the amino $N(SiMe_3)_2$ group, in a distorted-trigonal-bipyramidal geometry with the average distance of Ln−N 2.396(4) Å for the Sm and 2.298(5) Å for the Yb, respectively, and the average distance of Ln−O 2.339(4) Å for the Sm and 2.233(3) Å for the Yb, respectively. The average Ln−O−Ln angles are 105.6(1)° for the Sm and 105.7(1)° for the Yb complexes, respectively. The average distance of $Ln-N(SiMe_3)_2$ is

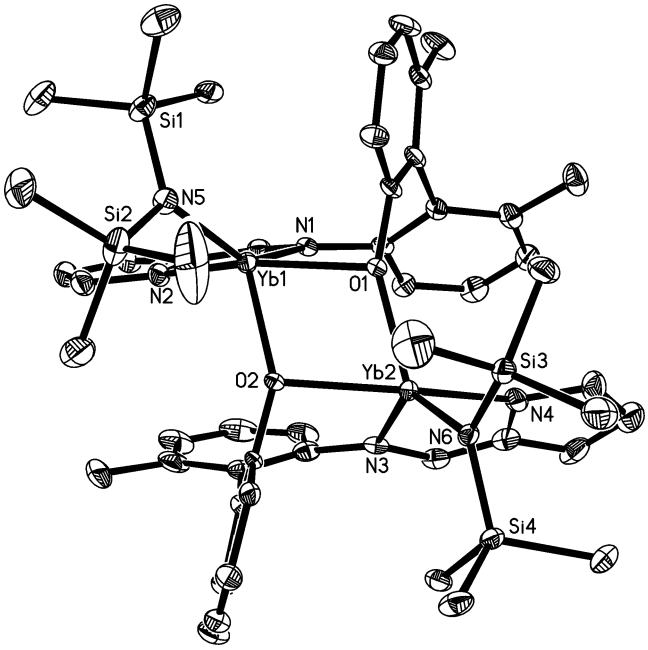


Figure 3. Molecular structure of **8** (thermal ellipsoids drawn at the 35% probability level).

2.252(4) Å for the Sm and 2.178(5) Å for the Yb. These structural data are close to those found in {**1**-LnN-$(SiMe_3)_2$}$_2$.[14] The phenyl units are twisted with respect to the imine group by 38.9(2)° and 41.5(2)° for the Sm and 32.9(2)° and 35.3(2)° for the Yb, respectively. The twisting between the phenyl rings of the torsion angles is 72.8(2)° and 76.3(2)° for the Sm and 69.5(2)° and 69.9(2)° for the Yb. The distance of two ions of Ln^{3+} is 3.727(1) Å for the Sm and 3.560(1) Å for the Yb, respectively, which are close to those found in {**1**-LnN$(SiMe_3)_2$}$_2$.[14]

The single-crystal X-ray diffraction analysis shows that there is a molecule of {**2**-YN$(SiMe_3)_2$}$_2$ (**7a**) and a molecule of {(**2**)$_2$Y}Y[N$(SiMe_3)_2$]$_2$ (**7b**) in the lattice. Coordination of two ligand anions **2** and two amino N$(SiMe_3)_2$ groups around two Y^{3+} results in the formation of the dimeric complexes {**2**-YN$(SiMe_3)_2$}$_2$ (**7a**) (Figure 4a). Each Y^{3+} is covalently bound to two nitrogen atoms and two oxygen atoms from the ligand anions **2** and one nitrogen atom from the amino N$(SiMe_3)_2$ group, in a distorted-trigonal-bipyramidal geometry with the average distance of Y−N 2.355(5) Å and the average distance of Y−O 2.270(4) Å. The average Y−O−Y angle is 105.0(2)°. The average distance of Y−N$(SiMe_3)_2$ is 2.227(5) Å. These structural data are close to those found in {**1**-YN$(SiMe_3)_2$}$_2$.[14] The phenyl units are twisted with respect to the imine group by 37.3(6)° and 41.0(6)°, and the twisting between the phenyl rings of torsion angles is 70.5(6)° and 71.5(6)°, which is comparable to those found in **6** and **8** (Table 2). The distance of two ions of Y^{3+} is 3.603(1) Å, which is close to that (3.571(1) Å) found in {**1**-YN$(SiMe_3)_2$}$_2$.[14] In **7b** (Figure 4b), one Y^{3+} is covalently bound to four nitrogen atoms and two oxygen atoms from two ligand anions **2** in a distorted-octahedron geometry with the average distance of Y−N 2.386(5) Å and the average distance of Y−O 2.344(4) Å. The other Y^{3+} is σ-bound to

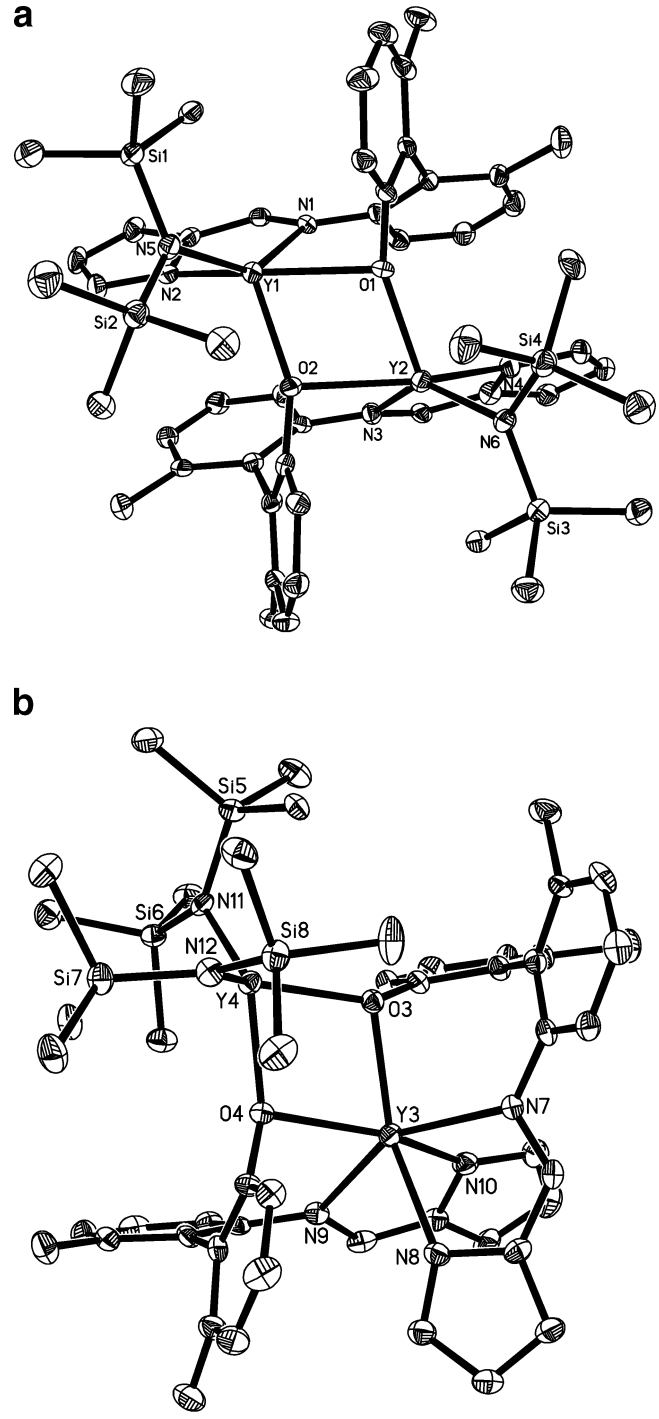


Figure 4. (a) Molecular structure of **7a** (thermal ellipsoids drawn at the 35% probability level). (b) Molecular structure of **7b** (thermal ellipsoids drawn at the 35% probability level).

two oxygen atoms from two ligand anions **2** and two nitrogen atoms from two amino N$(SiMe_3)_2$ groups in a distorted-tetrahedron geometry with the average distance of Y−O 2.214(4) Å and the average distance of Y−N$(SiMe_3)_2$ 2.246(5) Å. The average Y−O−Y angle is 107.9(2)°. The phenyl units are twisted with respect to the imine group by 36.5(6)° and 38.3(6)°, and the twisting between the phenyl rings of torsion angles is 69.0(6)° and 70.8(6)°. The distance of two ions of Y^{3+} is 3.686 Å. These structural data are comparable to those found in **7a** (Table 2).

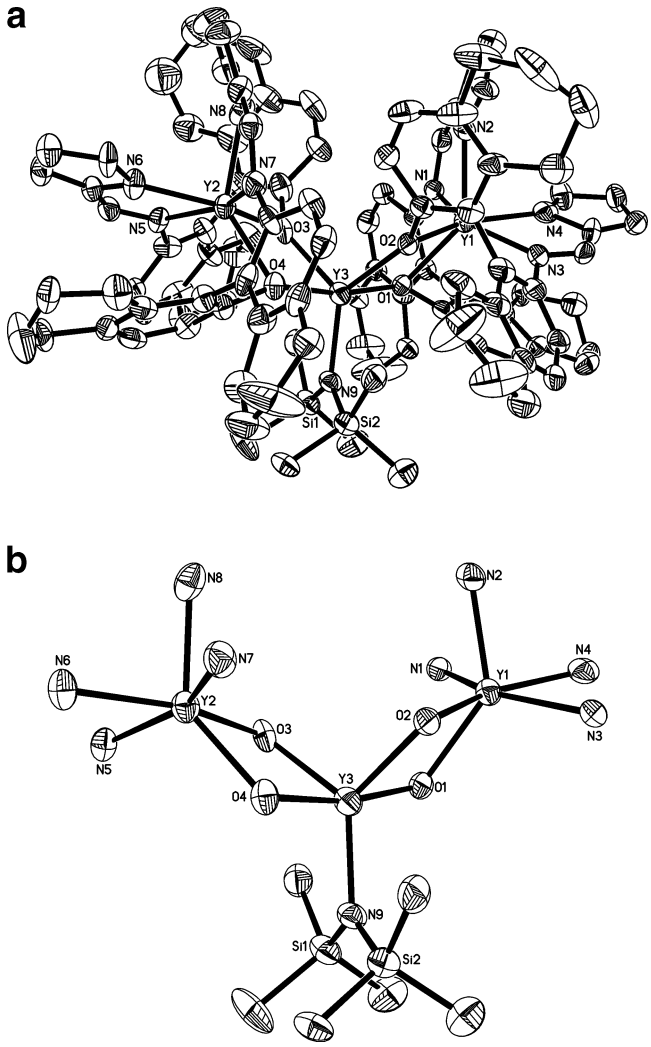


Figure 5. (a) Molecular structure of **9** (thermal ellipsoids drawn at the 35% probability level). (b) Core structure of **9**.

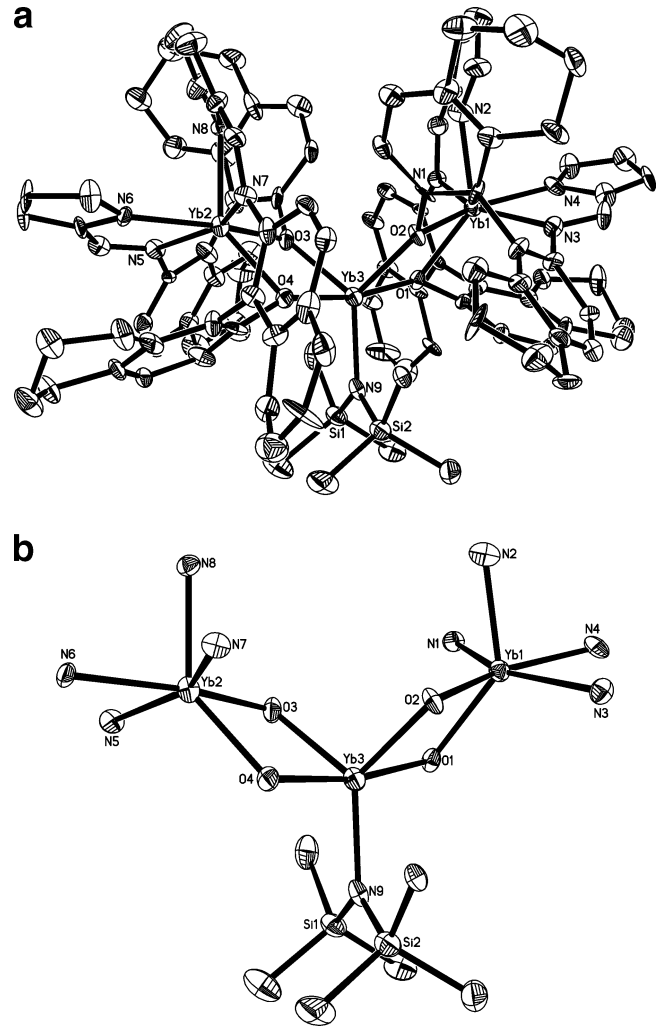


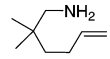
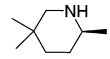
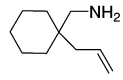
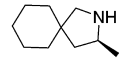
Figure 6. (a) Molecular structure of **10** (thermal ellipsoids drawn at the 35% probability level). (b) Core structure of **10**.

The single-crystal X-ray diffraction analyses confirm that **9** and **10** are isostructural and show that there are two molecules of $\{(\mathbf{3})_2\mathrm{Ln}\}_2\mathrm{LnN}(\mathrm{SiMe_3})_2$ and three toluene molecules in the lattice. In each molecule of $\{(\mathbf{3})_2\mathrm{Ln}\}_2\mathrm{LnN}(\mathrm{SiMe_3})_2$, two of the Ln^{3+} are covalently bound to four nitrogen atoms and two oxygen atoms from two ligand anions **3** in a distorted-octahedron geometry (Figures 5 and 6) with the average distance of Ln−N 2.412(14) Å for Y and 2.335(12) Å for Yb, respectively, and the average distance of Ln−O 2.346(9) Å for Y and 2.288(9) Å for Yb, respectively. Another Ln^{3+} is covalently bound to four oxygen atoms from four ligand anions **3** and one nitrogen atom from amino group $N(SiMe_3)_2$ in a distorted-tetragonal-pyramidal geometry with the average distance of Ln−O 2.239(8) Å for Y and 2.205(9) Å for Yb, respectively. The distances of $Ln-N(SiMe_3)_2$ are 2.231(10) Å for Y and 2.174(12) Å for Yb, respectively. The average Ln−O−Ln angles are 108.1(4)° for Y and 107.9(4)° for Yb, respectively. The distances of two ions of Ln^{3+} are 3.693(2) and 3.732(2) Å for Y and 3.616(10) and 3.647(10) Å for Yb, respectively. The H_4-naphthyl units are twisted with respect to the imine group in the range from 27.9 to 44.2(2)° for Y and from 26.7 to 46.6(4)° for Yb, respectively. The twisting between the H_4-naphthyl rings of torsion angles is 66.9(4), 68.2(4), 72.3(4), and 74.5(4)° for Y and 62.6(4), 67.3(4), 69.7(4), and 70.5(4)° for Yb, respectively. These structure data are comparable to those found in $\{\mathbf{1}\text{-}\mathrm{LnN}(\mathrm{SiMe_3})_2\}_2$.[14]

Asymmetric Hydroamination. Compounds **4**−**10** have been used as the catalysts in the intramolecular hydroamination/cyclization reaction of nonactivated terminal aminoalkenes (Table 3). All the substrates are converted to the cyclic product at room temperature or elevated temperature in moderate to good yields. Substrates bearing bulky geminal substituents in the β-position to the amino group (Thorpe−Ingold effect)[20] could be cyclized with reasonable catalyst loadings of 5 mol % within good reaction times. The results of the hydroamination/cyclization of 2,2-dimethylpent-4-enylamine show that the samarium amide (**6**) (Table 3, 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. Moving to the smaller Yb^{3+} ion (Table 3, entry 2), the rate decreases but affords a better ee value (up to 43%), which is commensurate with

(20) (a) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, *107*, 1080–1106. (b) Ingold, C. K. *J. Chem. Soc.* **1921**, *119*, 305–329.

Table 3. Enantioselective Hydroamination/Cyclization of Aminoalkenes[a]

entry	catalysts (Ln)	substrate	product	T (°C)	time (h)	conv. (%)[b]	ee (%)[c]
1	**6** (Sm)			23	48	100	37
2	**8** (Yb)			23	48	55	43
3	**4** (Y)			23	48	81	5.4
4	**5** (Yb)			120	160	N.R.	N.A.
5	**9** (Y)			60	48	46	11
6	**10** (Yb)			120	60	31	61
7	**4** (Y)			120	90	9.4	24
8	**6** (Sm)			120	48	78	25
9	**8** (Yb)			120	48	75	34
10	**4** (Y)			60	90	92	11
11	**6** (Sm)			60	48	93	16
12	**8** (Yb)			60	60	96	23
13	**9** (Y)			60	60	94	29
14	**10** (Yb)			60	110	36	15

[a] Conditions: C_6D_6 (0.70 mL), aminoalkene (0.32 mmol), catalyst (0.016 mmol, based on the $LnN(SiMe_3)_2$ group). [b] Determined by ^1H NMR based on *p*-xylene as the internal standard. N.R. = no reaction. [c] Determined by ^1H NMR of its diastereomeric (*S*)-(+)-*O*-acetylmandelic acid salt.[6] N.A. = not applicable.

the smaller metal ion radius. On moving from the ligand **2** to ligand **1** and to ligand **3** (Table 3, entries 3–6), the yttrium complex **4** shows a good catalytic activity, but the ee value is very low (only 5.4%; Table 3, entry 3), while complex **9** (Y^{3+}) shows a slight improvement in the enantioselectivity with a moderate conversion at 60 °C (Table 3, entry 5). Under similar reaction conditions, no detectable hydroamination activity is observed for the ytterbium complex **5**, even at 120 °C for one week (Table 3, entry 4). However, the ytterbium complex **10** shows the best enantioselectivity (up to 61%) with a moderate catalytic activity (Table 3, entry 6). The formation of a six-membered ring can also be performed with our catalysts **4**, **6**, and **8** (Table 3, entries 7–9), and a moderate enantioselectivity (up to 34%), mediated by the catalyst **8**, has been obtained (Table 3, entry 9). The data clearly show that the rate of cyclization for aminoalkenes follows the order 5 > 6, which is consistent with the classical, stereoelectronically controlled, cyclization processes.[8e] Although the enantiomeric excesses obtained remain moderate, 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] and here, we are aware that this is the first example of the enantioselective hydroamination/cyclization catalyzed by binuclear or trinuclear lanthanide complexes in the literature.[21]

Conclusions

When a change is made from binaphthyl to biphenyl and to H_8-binaphthyl, the ligands (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (**1**H_2), (*S*)-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-6,6′-dimethyl-1,1′-biphenyl (**2**H_2), and (*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-2-(pyrrol-2-ylmethyleneamino)-2′-hydroxy-1,1′-binaphthyl (**3**H_2) exhibit different reactivity patterns. For example, reaction of **1**H_2 with $Y[N(SiMe_3)_2]_3$gives the amide {**1**-$YN(SiMe_3)_2$}$_2$ (**4**),[14] while **2**H_2 and **3**H_2 afford a mixture of {**2**-$YN(SiMe_3)_2$}$_2$ (**7a**) and {(**2**)$_2$Y}Y$[N(SiMe_3)_2]_2$ (**7b**) and a trinuclear complex {(**3**)$_2$Y}$_2$-$YN(SiMe_3)_2$ (**9**), respectively. The ytterbium amide with ligand **3** has displayed a moderate enantioselectivity (up to 61%) for the asymmetric hydroamination/cyclization of the representative aminoalkene, 2,2-dimethylpent-4-enylamine, while the amides with ligands **1** and **2** have not. Although our ligand sets using peripheral binaphthalene or biphenyl coupled with pyrrole and hydroxyl ligation in multidentate systems do not provide sufficient rigidity of the dative NNO-donor ligand to achieve a significant enantioselectivity (ee

(21) More recently, Marks and co-worker reported the first example of hydroamination/cyclization catalyzed by binuclear lanthanide complexes *p*-bis{η^5-(2,3,4,5-tetramethylcyclopentadienyl)Ln[N-$(SiHMe_2)_2]_2$}phenylene and *m*-bis{η^5-(2,3,4,5-tetramethylcyclopentadienyl) La[N$(SiHMe_2)_2]_2$}phenylene. See: Yuen, H. F.; Marks, T. J. *Organometallics* **2008**, *27*, 155–158.

>90%), in contrast to 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] Further exploration of these catalysts toward other types of transformations and the optimization of the ligand architecture to improve the enantiomeric excess for this transformation are still underway.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grant No. 20602003).

Supporting Information Available: Experimental procedure for the preparation of the chirality ligand. X-ray crystallographic data, in CIF format, for **2**H_2 and **6**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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