A Chiral-Bridged Aminotroponiminate Complex of Lutetium as Catalyst for the Asymmetric Hydroamination

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The enantiomerically pure bridged aminotroponiminate *S,S*-H_2{(*i*PrATI)$_2$diph}, in which two amino-isopropyl-troponimine moieties are linked by 1,2-(*S,S*)-diamino-1,2-diphenylethane, has been prepared. The chiral lutetium alkyl complex of composition [(*R,R*)-{(*i*PrATI)$_2$diphLuCH$_2$SiMe$_3$(THF)] (**3**) was obtained via two synthetic approaches. In the first approach the dipotassium salt [(*S,S*)-K_2{(*i*PrATI)$_2$-diph}] (**1**) of the ligand was reacted via a salt metathesis with lutetium trichloride to give [(*S,S*)-{(*i*PrATI)$_2$diph}LuCl(THF)] (**2**). Reaction of **2** with LiCH$_2$SiMe$_3$ resulted in **3**. Compound **3** can also be obtained by the reaction of [Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$] with (*S,S*)-H_2{(*i*PrATI)$_2$diph} under elimination of Me$_4$Si. The alkyl complex **3** was used as catalyst in the intramolecular hydroamination reaction of nonactivated terminal aminoolefins. Good catalytic activities and moderate enantioselectivties were observed.

Introduction

The catalytic addition of an organic amine R_2N-H bond to alkenes or alkynes (hydroamination) to give nitrogen-containing molecules is of great interest for academic research and industrial products, since most amines are made today in multistep syntheses.[1] Over the years it turned out that early transition metals (group 4[1e] and especially the lanthanides[1g]) are highly efficient catalysts for the hydroamination reaction of various compounds containing C−C multiple bonds. In lanthanide chemistry amido and alkyl metallocene complexes have proven to be active catalysts for the hydroamination/cyclization of primary aminoolefins, allenes, and alkynes.[2] Besides the well-established metallocenes, today a number of non-cyclopentadienyl lanthanide complexes, which are based on amido and alkoxide ligands, are known to be efficient in hydroamination/cyclization catalysis.[3−9] The first non-cyclopentadienyl organolanthanide catalyst for the hydroamination/cyclization reaction, which used aminotroponiminates as a cyclopentadienyl alternative, was developed by us.[3] Based on the non-cyclopentadienyl (post-metallocene) lanthanide complexes, a number of asymmetric catalysts were developed recently.[5−9] Using these kinds of catalysts enantioselectivities up to more than 90% were obtained.[10] As chiral ligands basically chiral bis(oxazolinates), bis(phenolates),[9] bis(naphtholates),[6] and bis(naphtholamides)[5,7] were used. All of these kinds of ligands were recently classified as privileged ligands.[11] Herein, we report the synthesis of a new enantiomerically pure ligand (a chiral bridged aminotroponiminate), its use in the coordination chemistry of lutetium, and the application of the resulting complex as a catalyst for the hydroamination/cyclization reaction.

Experimental Section

General Considerations. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual-manifold Schlenk line, interfaced to a high-vacuum (10^{-4} Torr) line, or in an argon-filled M. Braun glovebox. Tetrahydrofuran was predried over Na wire and distilled under nitrogen from Na/K benzophenone ketyl prior to use. Hydrocarbon solvents (toluene

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and *n*-pentane) were distilled under nitrogen from $LiAlH_4$. All solvents for vacuum line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all ≥99 atom % D) and were dried, degassed, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on a JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and $CFCl_3$ (^{19}F NMR), respectively. Mass spectra were recorded at 70 eV on a Varian MAT 711. GC/MS measurements were performed with a Varian Saturn 2100 GC/MS system with GC-3900 using a VF-5 MS, 30 m × 0.25 mm × 0.25 μm df fused silica capillary column. Elemental analyses were carried out with an Elementar vario EL. 2-(*N*-Isopropylamino)tropone,[12] 1,2-(*S*,*S*)-diamino-1,2-diphenylethane,[13] and $[Lu(CH_2SiMe_3)_3(THF)_2]$[14] were prepared according to literature procedures.

(*S*,*S*)-H_2{(*i*PrATI)$_2$diph}. 2-(*N*-Isopropylamino)tropone (1.65 g, 9.4 mmol) in 10 mL of methylene chloride was slowly added to a solution of $Me_3O{\cdot}BF_4$ (1.39 g, 9.4 mmol) in 10 mL of CH_2Cl_2 under an argon atmosphere. After stirring at room temperature for 3 h 1.4 mL (9.4 mmol) of Et_3N was added to the orange solution. The mixture was stirred for another 15 min, and then 1 g (4.7 mmol) of 1,2-(*S*,*S*)-diamino-1,2-diphenylethane was added to the mixture and the solution turned yellow immediately. After stirring for 18 h the volatiles were removed in vacuo. The residue was extracted twice with 10 mL of toluene. The solution was concentrated under vacuum to 5 mL, and 10 mL of pentane was added to obtain the product as a yellow powder. Yield: 1.45 g (2.8 mmol, 60%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.29 (d, 6 H, CH(CH_3)$_2$, J(H,H) = 6.4 Hz), 1.31 (d, 6 H, CH(CH_3)$_2$, J(H,H) = 6.4 Hz), 3.83 (sept, 2 H, CH(CH$_3$)$_2$, J(H,H) = 6.2 Hz), 4.95 (s, 2 H, CH), 6.01 (t, 2 H, CH$_{ring}$, J(H,H) = 9.3 Hz), 6.14 (d, 2H, CH$_{ring}$, J(H,H) = 11.4 Hz), 6.22 (d, 2 H, CH$_{ring}$, J(H,H) = 11.0 Hz), 6.50 (t, 2 H, CH$_{ring}$, J(H,H) = 10.4 Hz), 6.69 (t, 2 H, CH$_{ring}$, J(H,H) = 10.6 Hz), 7,14−7,20 (m, 10 H, Ph), 8,42 (br, 2 H, NH). ^{13}C NMR ($CDCl_3$, 100.4 MHz, 25 °C): δ 23.0, 45.1, 67.1, 108.1, 113.2, 117.1, 126.6, 127.7, 128.2, 132.6, 133.1, 141.3, 151.2, 153.3. MS (EI, 70 eV, 200 °C): *m*/*z* (%) 503 $[M]^+$ (7). MS (FAB): *m*/*z* (%) $[M + H]^+$ 503 (15), $[M/2]^+$ 251 (100). Anal. Calcd for $C_{34}H_{38}N_4$: C, 81.23, H, 7.62, N, 11.15. Found: C, 81.16, H, 7.61, N, 10.78.

[(*S*,*S*)-K_2{(*i*PrATI)$_2$diph}] (1). To a suspension of 140 mg (3.4 mmol) of KH in 10 mL of THF was slowly added a solution of 770 mg (1.5 mmol) of (*S*,*S*)-H_2{(*i*PrATI)$_2$diph} in 30 mL of THF. Gas evolution was observed and the solution turned to dark orange immediately. After stirring overnight at room temperature, the solution was filtered. The product was obtained as an orange powder after evaporating the solvent and washing with pentane (10 mL). Yield: 750 mg (1.3 mmol, 87%). ^1H NMR (THF-d_8, 400 MHz, 25 °C): δ 1.11 (d, 6 H, CH(CH_3)$_2$, J(H,H) = 6.2 Hz), 1.14 (d, 6 H, CH(CH_3)$_2$, J(H,H) = 6.2 Hz), 3.67 (sept, 2 H, CH(CH$_3$)$_2$, J(H,H) = 6.2 Hz), 4.49 (s, 2 H, CH), 5.08 (t, 2 H, CH$_{ring}$, J(H,H) = 8.5 Hz), 5.59 (d, 2 H, CH$_{ring}$, J(H,H) = 11.0 Hz), 5.68 (d, 2 H, CH$_{ring}$, J(H,H) = 11.4 Hz), 6.00 (t, 2 H, CH$_{ring}$, J(H,H) = 9.4 Hz), 6.19 (m, 2 H, CH$_{ring}$), 6.81−6.85 (m, 10 H, Ph). ^{13}C NMR (THF-d_8, 100.4 MHz, 25 °C): δ 24.3, 50.0, 73.3, 106.5, 106.8, 107.3, 125.8, 127.4, 129.7, 132.1, 132.6, 146.6, 163.2, 164.7.

[(*S*,*S*)-{(*i*PrATI)$_2$diph}LuCl(THF)] (2). THF (10 mL) was condensed at −196 °C onto a mixture of 360 mg (1.3 mmol) of $LuCl_3$ and 1 mmol (580 mg) of **1**, and the mixture was stirred for 18 h at room temperature. The solution was then evaporated, and the remaining yellow residue was extracted with hot toluene (20 mL). The toluene was evaporated, and the product was crystallized from THF as yellow crystals. Yield: 430 mg (0.6 mmol, 60%). ^1H NMR (THF-d_8, 400 MHz, 25 °C): δ 1.58 (d, 6 H, CH(CH_3)$_2$, J(H,H) = 6.4 Hz), 1.67 (d, 6 H, CH(CH_3)$_2$, 6 H, J(H,H) = 6.4 Hz), 4.20 (sept, 2 H, CH(CH$_3$)$_2$, J(H,H) = 6.4 Hz), 5.34 (s, 2 H, CH), 6.08 (d, 2 H, CH$_{ring}$, J(H,H) = 9.2 Hz), 6.13 (d, 2 H, CH$_{ring}$, J(H,H) = 10.6 Hz), 6.62−6.68 (m, 2 H, CH$_{ring}$), 6.88−6.91 (m, 4 H, CH$_{ring}$), 7.08−7.23 (m, 6 H, Ph), 7.60 (d, 4 H, Ph, J(H,H) = 7,4 Hz). ^{13}C NMR (THF-d_8, 100.4 MHz, 25 °C): δ 22.1, 50.1, 74.5, 114.8, 116.5, 118.2, 127.2, 127.9, 129.0, 129.6, 134.5, 135.1, 145.4, 166.3. Anal. Calcd for $C_{38}H_{44}ClLuN_4O$: C, 58.27, H, 5.66, N, 7.15. Found: C, 57.96, H, 5.72, N, 6.92.

[(*S*,*S*)-{(*i*PrATI)$_2$diph}Lu(CH$_2$SiMe$_3$)(THF)] (3). Route A: THF (10 mL) was condensed at −196 °C onto a mixture of 0.4 mmol (300 mg) of **2** and 0.4 mmol (40 mg) of $LiCH_2SiMe_3$, and the mixture was stirred for 18 h at room temperature. The solvent was then evaporated in vacuo, and the remaining solid was extracted with 20 mL of pentane. After evaporating the solvent the product was obtained as a yellow powder. Yield: 120 mg (0.14 mmol, 36%). Route B (NMR scale): In a NMR tube C_6D_6 was condensed at −196 °C to a mixture of (*S*,*S*)-H_2{(*i*PrATI)$_2$diph} (0.05 mmol, 26 mg) and $[Lu(CH_2SiMe_3)_3(THF)_2]$ (0.05 mmol, 30 mg) and stirred for 8 h at room temperature. Then the solvent was evaporated to remove $SiMe_4$, and again C_6D_6 was condensed onto the mixture. NMR shows the product in quantitative yield. ^1H NMR (C_6D_6, 400 MHz, 25 °C): δ −0.84 (d, 1 H, CH_2Si(CH$_3$)$_3$, J(H,H) = 11.6 Hz) −0.60 (d, 1 H, CH_2Si(CH$_3$)$_3$, J(H,H) = 11.6 Hz), 0.14 (s, 9 H, CH$_2$Si(CH_3)$_3$), 1.17 (m, 4 H, THF), 1.26 (d, 2 H, CH(CH_3)$_2$, J(H,H) = 6.5 Hz), 1.42 (d, 2 H, CH(CH_3)$_2$, J(H,H) = 6.5 Hz), 1.49 (d, 2 H, CH(CH_3)$_2$, J(H,H) = 6.5 Hz), 1.62 (d, 2 H, CH(CH_3)$_2$, J(H,H) = 6.5 Hz), 3.47 (m, 4 H, THF), 3.88 (sept, 1 H, CH(CH$_3$)$_2$, J(H,H) = 6.7 Hz), 4.10 (sept, 1 H, CH(CH$_3$)$_2$, J(H,H) = 6.4 Hz), 5.47 (d, 1 H, CH, J(H,H) = 2.7), 5.68 (d, 1 H, CH, J(H,H) = 2.7), 6.08 (m, 2 H, CH$_{ring}$), 6.37 (m, 4 H, CH$_{ring}$), 6.53−6.64 (m, 4 H, CH$_{ring}$), 6.79−7.15 (m, 10 H, Ph), 7.46 (d, 4 H, Ph, J(H,H) = 7.4 Hz). ^{13}C NMR (d_8-THF, 100.4 MHz, 25 °C): δ 0.0, 4.6, 25.4, 38.1, 49.5, 71.9, 113.3, 114.8, 117.9, 127.1, 128.4, 128.7, 142.7, 144.5, 164.6, 165.8. MS (EI, 70 eV, 240 °C): *m*/*z* (%) 836 $[M + 2H]^+$ (2), 764 $[M - THF]^+$ (3), 692 $[M - THF - SiMe_3 + 2H]^+$ (2), 675 $[M - THF - SiMe_4]^+$ (1), 634 $[M - THF - SiMe_4 - iPr]^+$ (1) 28 $[C_2H4]^+$ (100). Anal. Calcd for $C_{42}H_{55}LuN_4OSi$: C, 60.42, H, 6.64, N, 6.71. Found: C, 59.83, H, 6.70, N, 6.26.

General Considerations for the Hydroamination Reaction (NMR-scale reaction). Compound **3** was weighed under argon gas into an NMR tube. C_6D_6 (∼0.7 mL) was condensed into the NMR tube, and the mixture was frozen to −196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before the insertion into the core of the NMR machine (t_0). The ratio between the reactant and the product was exactly calculated by comparison of the integrations of the corresponding signals.

Preparation of Mosher Amides.[6] A solution of the amine in C_6D_6 (0.5 mL) was treated with Hünig's base and (*R*)-(+)-α-methoxy-α-trifluoro-methylphenylacetic acid chloride. Enantiomeric excesses were determined in comparison to racemic samples by ^{19}F NMR spectroscopy. Spectra were collected at 60 or 100 °C with a pulse delay of 5.3 s. Furthermore, the amides were purified by chromatography on silica by using hexanes/EtOAc (10:1) as eluent dissolved in acetone and then injected into a GC/MS.

X-ray Crystallographic Studies. Crystals of **2** were grown from THF. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C cold N_2 stream of a Stoe IPDS 2T diffractometer. Subsequent computations were carried out on an Intel Pentium IV PC.

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Table 1. Crystallographic Data of [(*S,S*)-{(*i*PrATI)$_2$Diph}LuCl(THF)] (2)[a]

	2·2 THF
formula	$C_{46}H_{60}ClLuN_4O_3$
fw	927.40
space group	$P2_1$ (No. 4)
a, Å	8.7215(3)
b, Å	15.9505(7)
c, Å	15.7992(5)
β, deg	103.551(3)
V, Å^3	2136.68(14)
Z	2
density (g/cm^3)	1.441
radiation	Mo Kα (λ = 0.71073 Å)
μ, mm^{-1}	2.417
absorp corr	integration
no. of reflns collected	36 746
no. of unique reflns	10 463 [R_{int} = 0.0331]
no. of obsd reflns	9866
no. of data; params	10 463; 421
R_1[b]; wR_2[c]	0.0253; 0.0655

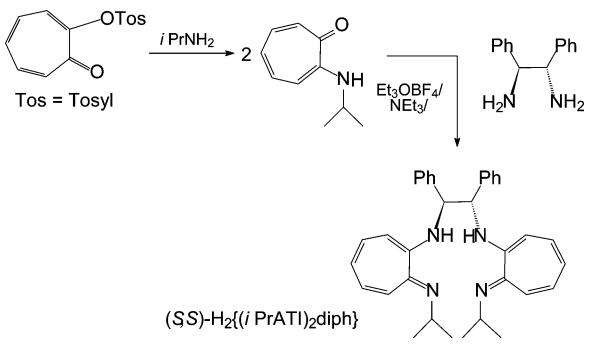
[a] All data collected at 203 K. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

All structures were solved by the Patterson method (SHELXS-86[15] and SHELXS-97[16]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-93 and SHELXL-97, respectively.[17] In the final cycles of each refinement, all non-hydrogen atoms except C30−C32 and the solvent-noncoordinated THF molecules in **2** were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. The hydrogen atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-61399. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk). Data collection parameters are given in Table 1.

Results and Discussion

Enantiomerically pure bridged aminotroponiminates, {(*R,R*)-(R-ATI)$_2$Cy}$^{2-}$ (R = Me, *i*Pr), in which two aminoisopropyltroponimine moieties are linked by (*R,R*)-1,2-diammoniumcyclohexane were reported by Lippard et al.[18] as ligand for titanium and by us as ligands for the lanthanides.[19] In this context we reported the Yb and Lu compounds [(*R,R*)-{(*i*PrATI)$_2$Cy}LnCl(THF)] (Ln = Yb, Lu).[19] We used the enantiomeric pure diamino backbone 1,2-(*S,S*)-diamino-1,2-diphenylethane[13] between the aminoisopropyltroponimine moieties to obtain the new chiral-bridged aminotroponimine (*S,S*)-H$_2${(*i*PrATI)$_2$diph}) (Scheme 1). (*S,S*)-H$_2${(*i*PrATI)$_2$diph} is obtained in a straightforward synthesis in which 2-(tosyloxo)-tropone is reacted with isopropylamine first to form 2-(*N*-isopropylamino)tropone in almost quantitative yield. Further treatment of 2-(*N*-isopropylamino)tropone with $Me_3O{\cdot}BF_4$, triethylamine, and 1,2-(*S,S*)-diamino-1,2-diphenylethane leads to the desired product as an analytically pure yellow solid in 60% yield (Scheme 1). Deprotonation with KH afforded the corresponding dipotassium salt [(*S,S*)-K$_2${(*i*PrATI)$_2$diph}] (**1**) as a yellow-brown, air-sensitive solid (Scheme 2).

Scheme 1



Transmetalation of **1** with anhydrous lutetium trichloride in THF at room temperature and crystallization from THF leads to the reaction product [(*S,S*)-{(*i*PrATI)$_2$diph}LuCl(THF)] (**2**) (Scheme 2). The new complex has been characterized by standard spectroscopic techniques, and the structure was confirmed by single-crystal X-ray diffraction in the solid state (Figure 1). **2** crystallizes in the monoclinic space group $P2_1$ having four molecules in the unit cell. Additionally, four molecules of THF are located in the unit cell. As a result of the chiralilty of the ligand, compound **2** is an enantiomerically pure complex. Four coordination sites are occupied by the chelating {(*i*PrATI)$_2$diph}$^{2-}$ ligand; furthermore a chlorine atom and a molecule of THF are coordinated to the central metal, resulting in a 6-fold coordination sphere of the ligands around the lanthanide atoms. A similar coordination polyhedron was observed in [{(*i*PrATI)$_2$Cy}LnCl(THF)] (Ln = Yb, Lu).[19] In contrast to the latter complexes in **2** the ligand is symmetrically bonded to the metal center. The Ln−N bond lengths are in the expected range of 2.264(3) to 2.339(3) Å in **2**.[20] Reaction of complex **2** with $LiCH_2SiMe_3$ in THF, followed by workup in pentane, afforded the corresponding chiral alkyl complex [(*S,S*)-{(*i*PrATI)$_2$diph}LuCH$_2$SiMe$_3$(THF)] (**3**) as a yellow crystalline solid (Scheme 2). Compound **3** was characterized by ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H and ^{13}C NMR spectra of **3** two resonances of signals for the isopropyl CH_3 groups were observed. Each set shows a diasterotopic splitting. Furthermore, the expected two signals for the methylene protons of the CH_2SiMe$_3$ group at δ −0.84 and −0.60 ppm are seen. The doublets are a result of a diasterotopic splitting concomitant with a geminal coupling of the protons. In an alternative approach compound **3** can also be obtained by reaction of [Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$] with (*S,S*)-H$_2${(*i*PrATI)$_2$diph} via an Me_4Si elimination (Scheme 2). The alkyl compound **3** is very moisture sensitive and decomposes at room temperature even

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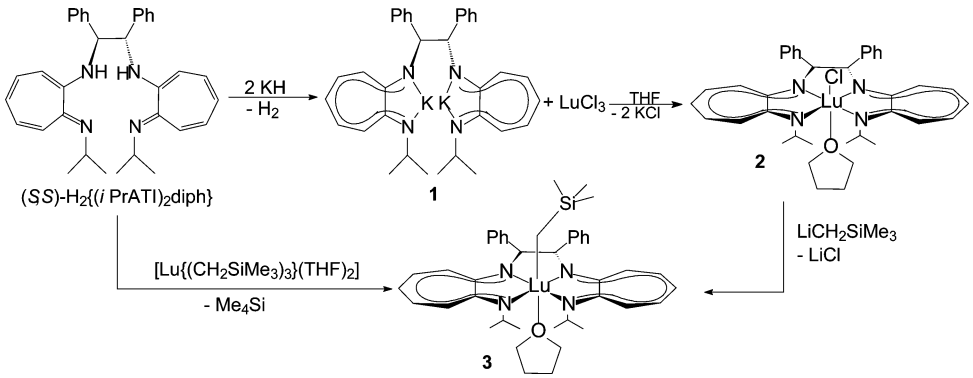
Scheme 2



in the glovebox within days. Thus, for the catalytic studies **3** was prepared in situ via the alkyl elimination route.

Compound **3** was used as the catalyst in the intramolecular hydroamination/cyclization reaction of nonactivated terminal aminoolefins (Table 2). It turned out that the substrates are converted to the cyclic product at room temperature or elevated temperature in high yields. The rigorously anaerobic reaction of the catalyst with dry, degassed aminoolefin proceeds regiospecifically. Kinetic studies indicate zero-order behavior in substrate over a 10-fold concentration range. Substrates bearing bulky geminal substituents in the β-position to the amino group (Thorpe−Ingold effect)[21] could be cyclized with reasonable catalyst/activator loadings of 5 mol % within good reaction times. Substrate **4a** was the most reactive of the aminoolefins, giving the corresponding pyrrolidine within 2 h. We were pleased to find that the formation of six-membered rings can also be performed with our catalyst (entry 4). It can be concluded that the rate of cyclization for aminoalkynes follows the order 5 > 6, consistent with classical, stereoelectronically controlled, cyclization processes. Moderate enantioselectivities (up to 44%) were obtained for the cyclization of **7a** (entry 4).

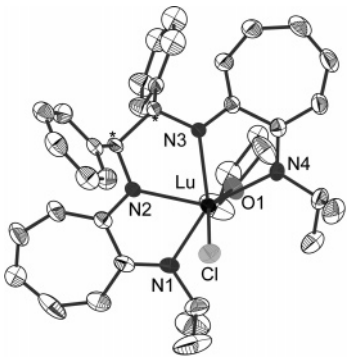
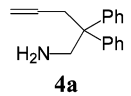
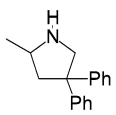
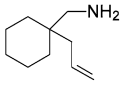
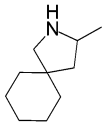
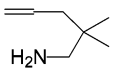
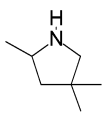
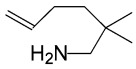
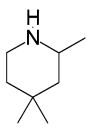


Figure 1. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Lu−N1 2.339(3), Lu−N2 2.264(3), Lu−N3 2.272(3), Lu−N4 2.329(3), Lu−O1 2.324(3), Lu−Cl 2.5492(9); N1−Lu−N2 68.65(10), N1−Lu−N3 139.21(10), N1−Lu−N4 149.85(11), N2−Lu−N3 72.42(10), N2−Lu−N4 140.86(10), N3−Lu−N4 68.56(10), N1−Lu−O1 83.61(11), N2−Lu−O1 99.91(10), N3−Lu−O1 91.59(10), N4−Lu−O1 84.23(10), N1−Lu−Cl 89.29(8), N2−Lu−Cl 102.27(7), N3−Lu−Cl 110.69(7), N4−Lu−Cl 88.84(8), O1−Lu−Cl 152.36(8).

Table 2. Hydroamination/Cyclization Reaction of Terminal Aminoolefins Catalyzed by 3[a]

Entry	Substrate	Product	T °C	Yield %[b]	t h	ee %[c]
1	 **4a**	 **4b**	RT	99	2	9
2	 **5a**	 **5b**	60	99	12	14
3	 **6a**	 **6b**	100	99	80	10
4	 **7a**	 **7b**	100	99	20	44

[a] Condition, cat. 20 mg (0.043 mM). [b] Based on ^{1}H NMR. [c] ^{19}F NMR and GC/MS analysis of the (*R*)-(+) Mosher amides.

The ee's were determined independently by ^{19}F NMR spectroscopy and GC/MS analysis of the corresponding (*R*)-(+) Mosher amides.

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Supporting Information Available: Experimental details and X-ray crystallographic files in CIF format for the structure determinations of **2** are available free of charge via the Internet at http://pubs.acs.org.

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(21) (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.