Chiral Amido Alkyl Rare Earth Complexes: A New Family of Asymmetric Intramolecular Hydroamination Catalysts

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New chiral binaphthylamido alkyl ate and neutral yttrium and ytterbium complexes have been synthesized and characterized. X-ray structures have been obtained for ate alkyl complexes [(*R*)-$C_{20}H_{12}(NC_5H_9)_2$]Y[(μ-Me)$_2$Li(THF)$_2$(μ-Me)Li(THF)] and [(*R*)-$C_{20}H_{12}(NC_5H_9)_2$]Ln[(μ-Me)$_2$Li(TMEDA)(μ-Me)Li(OEt$_2$)] (Ln = Y, Yb) and for the neutral complex [(*R*)-$C_{20}H_{12}(NC_5H_9)_2$]YCH$_2$SiMe$_3$(DME). Both types of complexes can be easily prepared in a one-pot procedure starting from yttrium and ytterbium chlorides and used *in situ*. They proved to be very efficient catalysts for enantioselective intramolecular hydroamination of aminopentenes or aminohexene at room temperature with enantiomeric excesses up to 83%.

Introduction

Asymmetric intramolecular hydroamination (AIH) as an elegant and atom-economic method for the preparation of scalemic nitrogen-containing heterocycles has been recently the subject of intense work summarized in several reviews.[1] Most of the enantioselective catalysts for the cyclization of aminoalkenes described up to now are rare earth-based,[2−7] although chiral complexes of zirconium[8] and lithium-based catalysts[9] proved recently to be efficient for the synthesis of nitrogen heterocycles. Nevertheless, successful catalysts affording enantiomeric excesses above 90% are until now scarcely reported,[4b,8b,d,9b] and those high asymmetric inductions are observed for only one or two substrates. Moreover the enantioselective cyclization of aminoolefins reported to date is in general facilitated by Thorpe−Ingold effects due to a *gem*-disubstitution and/or by the presence of a terminal double bond. The by far less studied enantioselective hydroamination of more sterically demanding substrates generally requires high temperatures.[10] There is thus an imperative need for more active intramolecular hydroamination catalysts to open the locks toward more sophisticated scalemic nitrogen heterocycles.

Our previous research focused on a new family of chiral lanthanide ate complexes {Li(THF)$_4$}{Ln[(*R*)-$C_{20}H_{12}(NR)_2$]$_2$} (Ln = Nd, Sm, Yb, Lu, Y; R = CH_2CMe_3, CH_2CHMe_2, CH_2Ph, CH_2Ar, *i*Pr, Ph, cyclohexyl, cyclopentyl) derived from chiral disubstituted (*R*)-binaphthylamido ligands as easily accessible and efficient intramolecular hydroamination catalysts.[11] These compounds consist of a complex anion resulting from coordination of two (*R*)-binaphthylamine ligands to the lanthanide atom and a discrete counterion $(Li(THF)_4)^+$. Aiming to optimize the enantioselectivity of the transformation, we screened various lanthanides and nitrogen substituents on the chiral ligand and obtained the highest enantioselective enantiomeric excesses (up to 87% for substrates with a terminal double bond) using a

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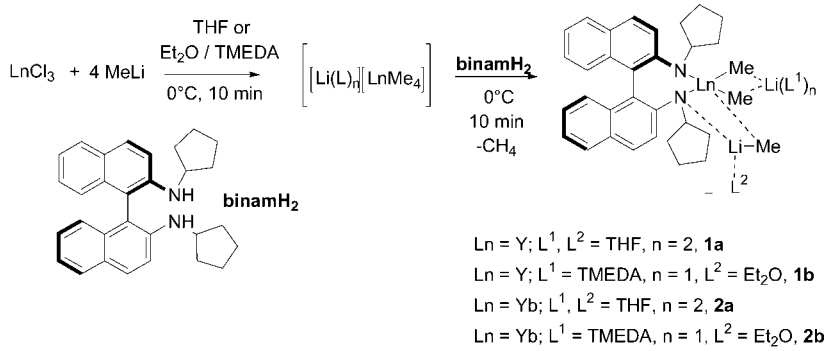
Scheme 1. Synthesis of Yttrium and Ytterbium Amido Alkyl Ate Complexes



Ln = Y; L^1, L^2 = THF, n = 2, **1a**
Ln = Y; L^1 = TMEDA, n = 1, L^2 = Et_2O, **1b**
Ln = Yb; L^1, L^2 = THF, n = 2, **2a**
Ln = Yb; L^1 = TMEDA, n = 1, L^2 = Et_2O, **2b**

complex with a small metal (ytterbium) and large cyclopentyl groups on the ligand.[11d] A ytterbium ate complex bearing benzyl-substituted ligands was interestingly a more active and enantioselective catalyst for substrates with an internal double bond.[11e] The activity of our binaphthylamido chiral catalysts for AIH could be further increased by the preparation of a neutral heteroleptic tris(amido)yttrium complex with a unique *N*-isopropyl-bis-substituted binaphthylamido ligand and a diisopropylamido moiety. Although this complex was more active for AIH than our previous reported ate complexes, its synthesis was not straightforward due to subtle stepwise metathesis reactions that could not be easily performed with other binaphthylamine ligands.[12] For the design of a rapid synthetic method for efficient AIH catalysts avoiding the tedious isolation of complexes or their precursors, we developed a new "one-pot" procedure. By the combination of a yttrium chloride precursor, a chiral diamine, and *n*-BuLi we prepared yttrium precatalysts showing higher activities than the corresponding amido ate complexes previously studied without noticeable erosion of the enantioselectivity.[13] An amido ate alkyl yttrium structure has been considered for these species. In order to develop new highly active defined structures as AIH catalysts, we focused on the synthesis of chiral alkyl rare earth complexes. We now report the synthesis, characterization, and catalytic behavior of new alkyl ate and neutral yttrium and ytterbium complexes coordinated by chiral binaphthylamido ligands.

Results and Discussion

The first studies reported by Marks' group on the mechanism of the hydroamination reaction established that alkyl and amido complexes were suitable precatalysts, which first reacted with the aminoolefin to form an intermediate amido species.[14] Reactions of homoleptic tris-amido rare earth precursors with various ligands have been employed by different teams as a route to chiral amido rare earth catalysts, but in numerous cases the reaction with the easily available $Ln[N(TMS)_2]_3$ did not lead to the targeted complex and other tris-amido derivatives have thus been used.[3a,4a] Homoleptic tris-alkyl complexes have been less exploited due to their lack of stability, although the tris-aryl rare earth complexes $[Ln(o\text{-}C_6H_4CH_2NMe_2)_3]$ have been successfully used by Hultszch for the preparation of related derivatives supported by binaphtholate[4b] and biphenolate ligands.[15]

Despite the progress that was recently made in the field of the synthesis of alkyl rare earth complexes in a noncyclopentadienyl coordination environment,[16] bis-amido alkyl derivatives are not well documented. These complexes were prepared by two-step metathetic reactions from lanthanide halides and the corresponding ligand alkaline salts.[17] More recently the use of homoleptic neutral tris-alkyl and to a lesser extent of ate tetra-alkyl rare earth complexes as precursors for the synthesis of various amido complexes by alkane elimination has been developed.[18] These alkyl precursors were either isolated or used *in situ* depending on their stability. To the best of our knowledge, the sole examples of chiral bis-amido alkyl rare earth complexes are prepared from yttrium chloride by successive metathesis reactions.[19] In order to propose a facile synthetic route to new efficient, thermally stable, and easily available amido alkyl rare earth AIH catalysts, we investigated the reactions of a binaphthylamine ligand with *in situ* obtained neutral $Ln(CH_2SiMe_3)_3(THF)_2$ and anionic $[\{LiL_n\}\{LnMe_4\}]$ (Ln = Y, Yb, L = THF, Et_2O, TMEDA) rare earth alkyl complexes.

Preparation and Characterization of New Chiral Ate Amido Alkyl Lanthanide Complexes. The anionic alkyl complexes $[LiL_n][LnR_4]$ (R = CH_2SiMe_3, CMe_3; Ln = Y, Sm, Er, Tb, Yb, Lu; L = THF, Et_2O, TMEDA) and $[LiL_n]_3[LnMe_6]$ (Ln = Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu; L = TMEDA, DME) have been first described in the late 1970s and attracted considerable attention due to their high reactivity.[20] We generated anionic complexes $[LiL_n][LnMe_4]$ by reacting anhydrous rare earth chlorides $LnCl_3$ (Ln = Y, Yb) with 4 equiv

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of MeLi in THF or Et_2O−TMEDA mixtures at 0 °C. Addition of an equimolar amount of (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl (**binamH$_2$**) to the resulting solutions occurred with methane evolution (Scheme 1).

Evaporation of THF under vacuum, extraction of the solid residue with toluene, and subsequent recrystallization of the product from THF−hexane mixtures (**1a**, **2a**) or diethyl ether (**1b**, **2b**) produced complexes **1a**, **1b**, **2a**, and **2b** (Scheme 1) in 58, 62, 64, and 62% yields, respectively. Formation of complexes **1a**, **1b**, **2a**, and **2b** was unexpected since their composition requires the presence of five methyl groups in the transient alkyl derivative. Noteworthy, the yield of complex **1b** can be increased from 62 up to 87% if the metathesis reaction of YCl_3 with MeLi was carried out in the molar ratio 1:5.[21] We suppose that the reaction of YCl_3 with 4 and 5 equiv of MeLi results in a complex mixture of mixed-ligand alkyl chlorido yttrium species whose interaction with **binamH$_2$** affords complexes **1a**, **1b**, **2a**, and **2b**. New complexes were isolated as orange (**1a**,**b**) and yellow (**2a**,**b**) air- and moisture-sensitive crystalline solids that are soluble in THF, Et_2O, and toluene and poorly soluble in hexane.

The ^{1}H and ^{13}C NMR spectra of the diamagnetic complexes **1a**,**b** in C_7D_8 were registrated in a wide temperature region (−60 to +30 °C) and demonstrated the expected sets of signals corresponding to the binaphthyldiamido ligands. The two different types of μ-bridging methyl ligands bound to the yttrium and lithium atoms in the ^{1}H NMR spectra give rise to two broadened singlets (**1a**: −1.39 and −0.54; **1b**: −1.45 and −0.52 ppm) with the integral intensities ratio 2:1. In the ^{13}C{^{1}H} NMR spectra two broadened singlets at 9.8 and 11.7 (for **1a**) and 7.3 and 12.4 ppm (for **1b**) correspond to these groups. The ^{7}Li NMR spectra of **1a**,**b** contain two resonances (**1a**: −0.86, 0.64; **1b**: −0.95, 0.54) due to two lithium atoms in different coordination environments.

Crystals suitable for single-crystal X-ray diffraction studies were obtained by slow condensation of hexane into the THF solutions at −20 °C (**1a** and **2a**) or by slow cooling of concentrated solutions in diethyl ether to −30 °C (**1b** and **2b**). The molecular structures of **1a**, **1b**, and **2b** are depicted in Figures 1, 2, and 3, respectively; the crystal and structural refinement data are listed in Table 1. Complexes **1a**, **1b**, and **2b** crystallize in the monoclinic space group $P2_1$ (no. 4) with four molecules in the unit cell for **1a** and two molecules for **1b** and **2b**. Compound **1a** crystallizes with two crystallographically independent molecules in the asymmetric unit. Those molecules are named A and B (caption, Figure 1 for the description of selected bond distances and angles). The single-crystal X-ray structure determinations revealed that **1a**, **1b**, and **2b** are monomeric heterobimetallic complexes that contain one rare earth metal atom and two lithium atoms. The coordination sphere of the rare earth metal atom is set up by the two nitrogen atoms of the chelating binaphthylamido ligand and the three carbon atoms of the μ^2-bridging methyl groups, thus resulting in a formal coordination number 5. One of the lithium atoms is bound with two carbon atoms of the methyl fragments and coordinated by two THF molecules in the case of **1a** or one TMEDA molecule in the cases of **1b** and **2b**. The second lithium atom is coordinated by the μ^2-bridging methyl group, the nitrogen atom of the binaphthylamido ligand, and one THF (**1a**) or diethyl ether molecule (**1b**, **2b**). The short contacts between the lanthanide atoms and the carbon atoms in *ipso*- and *ortho*-positions to the amido groups of the binaphthylamido ligand have been found in complexes **1a** (2.848(3), 2.747(3), 2.825(4), 2918(2) Å), **1b** (2.949(3), 2.895(3), 3.051(3), 2.776(3) Å), and **2b** (2.791(2), 3.020(2), 3.135(2), 2.933(2) Å). The Y−C bond lengths in the four-membered metallacycle YMe_2Li of **1a** (2.530(4), 2.528(4), 2.537(5), 2.503(5) Å) and **1b** (2.517(3),

(21) It has to be noticed that when the reaction was performed with 4 equiv of MeLi, the presence of unreacted ligand was observed in the ^{1}H NMR spectrum of the crude product.

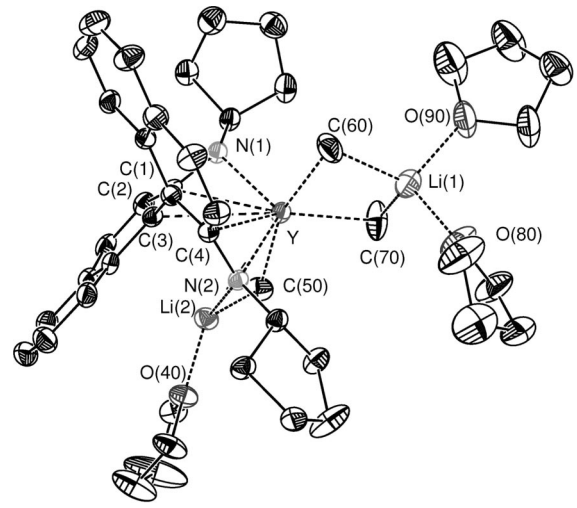

Figure 1. ORTEP diagram (30% probability thermal ellipsoids) of **1a** showing atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Y(1A)−N(1A) 2.295(3), Y(1A)−N(2A) 2.393(3), Y(1A)−C(50A) 2.555(4), Y(1A)−C(60A) 2.530(4), Y(1A)−C(70A) 2.537(5), Y(2B)−C(50B) 2.543(4), Y(2B)−C(60B) 2.528(4), Y(2B)−N(1B) 2.288(3), Y(2B)−N(2B) 2.398(3), Y(2B)−C(70B) 2.503(5), O(80B)−Li(1B) 1.955(9), O(90B)−Li(1B) 1.936(8), N(2A)−Li(2A) 2.068(8), N(2B)−Li(2B) 2.041(8), O(40A)−Li(2A) 1.911(8), O(80A)−Li(1A) 1.934(9), O(40B)−Li(2B) 1.941(8), C(50A)−Li(2A) 2.174(8), C(60A)−Li(1A) 2.158(8), C(70A)−Li(1A) 2.228(8), O(80A)−Li(1A) 1.934(9), O(90A)−Li(1A) 1.941(8), C(50B)−Li(2B) 2.175(8), C(60B)−Li(1B) 2.166(10), C(70B)−Li(1B) 2.184(10), N(1A)−Y(1A)−N(2A) 116.49(11), C(50B)−Y(2B)−C(60B) 164.24(16), C(50B)−Y(2B)−C(70B) 79.91(15), C(60B)−Y(2B)−C(70B) 88.70(16).

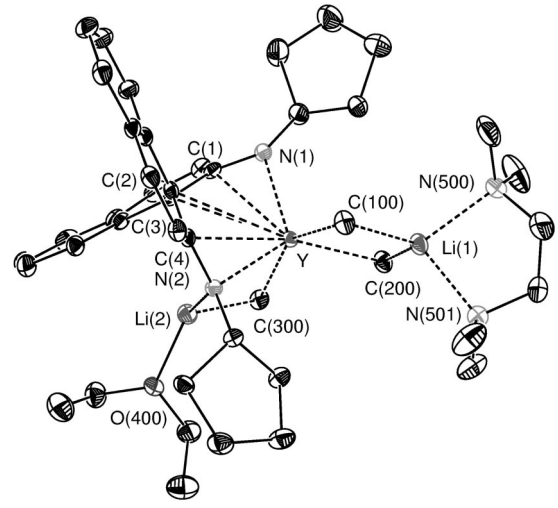

Figure 2. ORTEP diagram (30% probability thermal ellipsoids) of **1b** showing atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Y−N(1) 2.2674(19), Y−N(2) 2.362(2), Y−C(100) 2.517(3), Y−C(200) 2.520(3), Y −C(300) 2.541(3), O(400)−Li(1) 1.962(5), N(2)−Li(1) 2.054(5), C(100)−Li(2) 2.181(5), C(200)−Li(2) 2.188(5), C(300)−Li(1) 2.170(5), N(1)−Y−N(2) 113.82(8), C(100)−Y−C(200) 90.08(10), C(100)−Y−C(300) 152.42(9), C(200)−Y−C(300) 77.65(10).

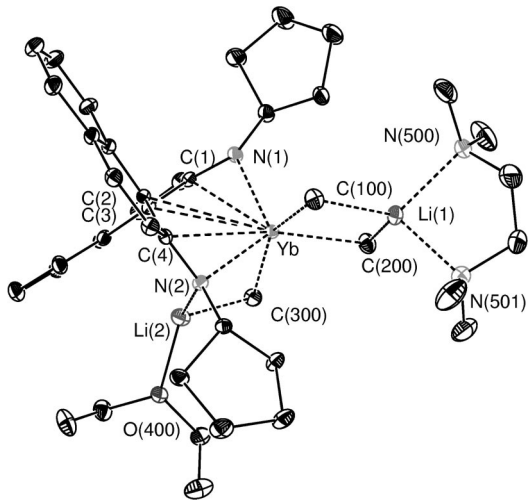

Figure 3. ORTEP diagram (30% probability thermal ellipsoids) of **2b** showing atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Yb−N(1) 2.2378(15), Yb−N(2) 2.3342(17), Yb−C(100) 2.466(3), Yb−C(200) 2.468(3), Yb−C(300) 2.491(2), O(400)−Li(2) 1.970(5), N(2)−Li(2) 2.056(5), C(100)−Li(1) 2.172(5), C(200)−Li(1) 2.188(5), C(300)−Li(2) 2.178(5), N(1)−Yb−N(2) 111.77(7), C(100)−Yb−C(200) 90.90(10), C(100)−Yb−C(300) 155.65(8), C(200)−Yb−C(300) 78.78(9).

2.520(3) Å) are somewhat shorter than the related distances in the YMeLiN metallacycle (**1a**: 2.555(4), 2.543(4) Å; **1b**: 2.541(3) Å). The terminal Y−N bond lengths in **1a** (2.295(3), 2.288(3) Å) and **1b** (2.2674(19) Å) are predictably shorter compared to the μ-bridging ones (**1a**: 2.393(3), 2.398(3) Å). A similar pattern was observed in complex **2b** (Yb−N: 2.2378(15), 2.3342(17) Å; Yb−C: 2.466(3), 2.468(3), 2.491(3) Å).

Preparation and Characterization of New Chiral Neutral Alkyl Amido Lanthanide Complexes. For the preparation of neutral amido alkyl complexes we used the reactions of equimolar amounts of (*R*)-(+)-2,2′-bis(cyclopentylamino)-1,1′-binaphthyl with $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y,[21] Yb[20a]) isolated or obtained *in situ* by reacting $LnCl_3(THF)_{3.5}$ and $Li(CH_2SiMe_3)_3$ (1:3 molar ratio, hexane, −15 °C) (Scheme 2). Concentration of resulting solutions under vacuum and cooling to −20 °C afforded neutral amido alkyl complexes **3a** and **4** in 89 and 75% yields, respectively. The treatment of complex **3a** with DME and subsequent recrystallization of the product from hexane allowed isolation of complex **3b** containing the coordinated DME molecule in 92% yield. Complexes **3a**,**b** and **4** were obtained as highly air- and moisture-sensitive crystalline solids that are highly soluble in THF and toluene and sparingly soluble in hexane. In an inert atmosphere, complexes **3a**,**b** and **4** can be stored in crystalline state at 0 °C without decomposition, while in the C_6D_6 solution at 20 °C they slowly decompose with elimination of Me_4Si. Thus for compounds **3a**,**b** in 2 weeks under these conditions the decomposition was just 7 and 12%, respectively. In the ^{1}H NMR spectra of complexes **3a**,**b** (C_6D_6, 20 °C) the hydrogen atoms of the methylene group attached to the yttrium atom appear as a set of two doublets of doublets at −0.91 and −0.73 ppm ($^2J_{HH}$ = 11.0 Hz, $^2J_{YH}$ = 3.1 Hz) for **3a** and at −1.28 and −1.02 ppm ($^2J_{HH}$ = 11.2 Hz, $^2J_{YH}$ = 3.0 Hz) for **3b**. In the $^{13}C\{^1H\}$ NMR spectra the appropriate carbon gives rise to a doublet at 29.8 ppm ($^1J_{YC}$ = 40.6 Hz) in the case of **3a** and at 30.2 ppm ($^1J_{YC}$ = 43.3 Hz) in the case of **3b**. Chemical shifts and coupling constants of the signals of methylene groups YCH_2 in **3a**,**b** are in a good agreement with the values published for related alkyl yttrium species supported by nitrogen-containing ligands.[22] The binaphthylamido and THF (DME) ligands give expected sets of signals in the ^{1}H and ^{13}C NMR spectra.

Crystals suitable for single-crystal X-ray diffraction studies were obtained by slow cooling of the hexane solution of **3b** to −20 °C. The molecular structure of **3b** is shown in Figure 4, and the crystal and structure refinement data are listed in Table 1. Complex **3b** crystallizes in the orthorhombic space group $P2_12_12_1$ (no. 19) with four molecules in the unit cell. The X-ray diffraction study revealed that complex **3b** is monomeric, where the yttrium atom is coordinated by two nitrogen atoms of one bidentate binaphthylamido ligand, one carbon atom of the alkyl group, and two oxygen atoms of the DME molecule, thus having formal coordination number 5. The presence in complex **3b** of the short contacts between the metal atom and the carbon atoms in *ipso*- and *ortho*-positions to the amido groups (Y−C(1) 2.6868(18), Y−C(2) 2.7455(18) Å) comparable to that reported for the yttrium π-complexes ({[PhP($CH_2SiMe_2NSiMe_2$-CH_2)$_2$PPh]Y}$_2${η^6:η^6-(C_6H_5)$_2$}: 2.699(1)−2.738(4) Å;[23] Y(O-2,6-$Ph_2C_6H_3$)$_3$: 2.84(1)−3.38(1) Å)[24] probably reflects η^2-interaction of the yttrium atom with the aromatic rings of the binaphthyl ligand, which leads to a saturation of the coordination sphere of the yttrium atom. The average Y−N bond length in **3b** (2.269 Å) is slightly shorter than those in anionic amido alkyl yttrium complexes **1a** (2.343(3) Å) and **1b** (2.314(2) Å), obviously reflecting the lesser extent of steric repulsion of binaphthylamido ligand and metal-alkyl fragments. The Y−C bond length in **3b** (2.423(2) Å) is comparable to the values reported for related alkylyttrium complexes.[22]

Catalytic Hydroamination Tests. All complexes were immediately used *in situ* after their preparation for catalytic intramolecular hydroamination tests. They were all active for the hydroamination/cyclization of various aminopentene derivatives, and they also promoted the intramolecular hydroamination of C-(1-but-3-enylcyclohexyl)methylamine **5d** toward the formation of a piperidine. These complexes were also tested in their recrystallized form as catalysts for the cyclization of substrate **5a** leading to the expected compound **6a** with the same efficiencies as those obtained with the catalysts formed *in situ*.

C-(1-allylcyclohexyl)-methyl amine **5a** was thus cyclized with complex **1a** in about 2 h with 75% ee (Table 2, entry 1). The analogous complex **1b** prepared in a mixture of Et_2O−TMEDA (50/1) afforded similarly the pyrrolidine **6a** in 3 h with 73% ee. The use of another solvent for the preparation of this yttrium complex thus did not modify its activity or its enantioselectivity. The analogous complex prepared in the presence of 5 equiv of MeLi led also to the same results. The rate and enantioselectivity of the cyclization of substrate **5a** with complex **1a** or **1b** are furthermore identical to those obtained with the catalyst prepared *in situ* using *n*-BuLi in a one-pot procedure (2 h, 75% ee).[13] These similar results suggest the formation of the same active catalytic species using the three above-mentioned preparation methods.

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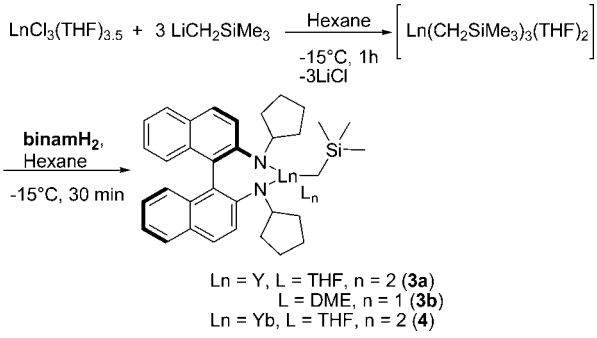
Table 1. Crystallographic Data and Structure Refinement Details for 1a, 1b, 2b, and 3b

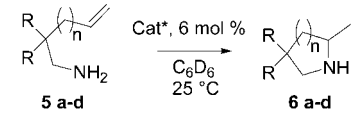
	1a	1b	2b	3b
formula	$C_{45}H_{54}Li_2N_2O_3Y$	$C_{43}H_{56}Li_2N_4OY$	$C_{43}H_{65}Li_2N_4OYb$	$C_{38}H_{51}N_2O_2SiY$
M_r	773.69	747.71	831.84	684.81
cryst size, mm^3	0.12 × 0.09 × 0.06	0.24 × 0.18 × 0.06	0.42 × 0.28 × 0.09	0.120 × 0.090 × 0.030
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1$	$P2_1$	$P2_1$	$P2_12_12_1$
a, Å	16.7670(11)	13.3537(7)	13.4102(12)	13.3372(5)
b, Å	13.5953(10)	10.5126(5)	10.5451(9)	15.3845(7)
c, Å	18.3666(14)	15.1380(8)	15.0029(13)	17.3891(9)
α, deg	90	90	90	90
β, deg	90.8860(10)	97.682(3)	97.492(3)	90
γ, deg	90	90	90	90
cell volume, Å^3	4186.2(5)	2106.03(19)	2103.5(3)	3568.0(3)
Z	4	2	2	4
T, K	100(1)	100(1)	100(1)	100(1)
F_{000}	1628	790	852	1448
μ, mm^{-1}	1.433	1.419	2.258	1.679
2θ range, deg	1.63−30.67	1.54−30.61	1.53−43.38	1.77−30.53
reflns collected	69 634	42 603	68 689	57 758
reflns unique	24 802	12 643	27 506	10 819
R_{int}	0.0844	0.0694	0.0419	0.0586
GOF	0.988	0.995	1.003	0.959
reflns obsd ($I > 2\sigma(I)$)	15505	9834	23423	10819
params	955	466	466	402
Flack param	0.022(4)	0.005(4)	0.006(5)	0.018(3)
wR_2 (all data)	0.1427	0.1038	0.0838	0.0681
R value ($I > 2\sigma(I)$)	0.0592	0.0443	0.0363	0.0338
largest diff peak and hole (e− Å^{-3})	0.801/−0.497	0.782/−0.755	0.705/−0.464	0.450/−0.353

Scheme 2. Synthesis of Yttrium and Ytterbium Neutral Amido Alkyl Complexes



The ytterbium ate alkyl complex **2a** is clearly less active but slightly more enantioselective than the yttrium complex **1a**. It promoted the cyclization of substrate **5a** in 1 day with 79% ee (Table 2, entry 2). The yttrium neutral alkyl complex **3a** is less active than the yttrium alkyl complex **1a** since pyrrolidine **6a** was obtained with complex **3a** in more than 3 h with 75% ee (Table 2, entry 3). By contrast the ytterbium ate alkyl complex **2a** and the ytterbium neutral alkyl complex **4** display the same reactivity and enantioselectivity: the cyclization of **5a** was performed in 1 day with 81% ee with complex **4** (Table 2, entry 4). For the formation of pyrrolidine **6a** yttrium complexes **1a** and **3a** are more efficient than ytterbium complexes **2** and **4**, and the yttrium ate alkyl complex **1a** proved to be the more active species of the series. Similar trends were observed for the transformation of the more reactive substrate 2,2-diphenyl-pent-4-enylamine **5b**. The pyrrolidine **6b** was formed within about 2 h with respectively 72 and 66% ee using yttrium alkyl complex **1a** or **3a**, while ytterbium alkyl complexes **2a** and **4** promoted the cyclization of **5b** in 7 h with 75% ee (Table 2, entries 5−8). Similar conclusions could be drawn using the more demanding substrates 2,2-dimethylpent-4-enylamine **5c** (Table 2, entries 9−14) and the aminohexene derivative **5d** (Table 2, entries 15−19). They were interestingly cyclized with complex **1a** at room temperature respectively in 2 days with 75% ee and 5 days with 33% ee. Compound **6c** was previously cyclized

Table 2. Hydroamination Reactions Catalyzed by Ate and Neutral Amido Alkyl Complexes



5 a-d **6 a-d**

a, n= 1, R,R = -$(CH_2)_5$-
b, n= 1, R,R = Ph
c, n= 1, R,R = CH_3
d, n= 2, R,R = -$(CH_2)_5$-

entry	product	catalyst	time (h)	conversion (%)	ee (%)
1	**6a**	**1a**	2.3	90	75
2		**2a**	24	92	79
3		**3a**	3.3	89	75
4		**4**	23	92	81
5	**6b**	**1a**	1.9	100	72
6		**2a**	7	85	74
7		**3a**	2.3	100	66
8		**4**	7	100	75
9	**6c**	**1a**	48	92	75
10		**2a**	144	21	83
11		**2a**	22[a]	90	74
12		**3a**	144	94	77
13		**3a**	3.3[a]	92	64
14		**4**	23[a]	95	69
15	**6d**	**1a**	120	87	33
16		**2a**	29[a]	100	39
17		**3a**	576	65	29
18		**3a**	27[a]	100	25
19		**4**	23[a]	100	38

[a] Reactions were performed at 60 °C.

with the corresponding yttrium amido ate complex[11d] with at least a 4 times longer reaction period. Concerning compound **6d**, its synthesis required a reaction temperature of at least 60 °C with our former complexes. Thus this new series of catalyst demonstrates improved activities. The dramatic positive effect of the temperature on the catalyst activity was accompanied with only a slight decrease in the enantioselectivity values (Table 2, see entries 10 and 11, 12 and 13, 17 and 18). These results allow concluding that yttrium alkyl complexes are by far more active but slightly less enantioselective than ytterbium alkyl

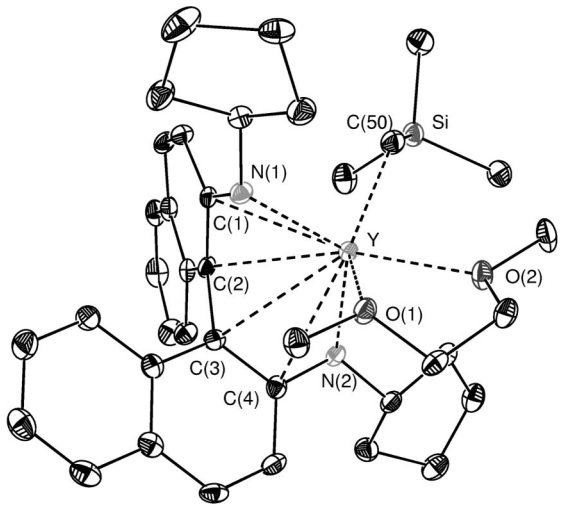


Figure 4. ORTEP diagram (30% probability thermal ellipsoids) of **3b** showing atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Y−N(1) 2.2894(16), Y−N(2) 2.2506(16), Y−C(50) 2.423(2), Y−O(1) 2.4055(13, Y−O(2) 2.4366(14), Y−C(1) 2.6868(18), Y−C(2) 2.7455(18).

complexes, as both neutral or ate complexes. The difference in terms of activity may be explained by the lower stability of the ytterbium alkyl precatalytic species. Such a conclusion already arose from a previous study[11d] in which we compared analogous yttrium and ytterbium amido ate complexes.

The new methodology presented here thus allows the facile preparation of both neutral and ate alkyl chiral amido complexes starting from yttrium and ytterbium chlorides. To the best of our knowledge, the chiral complexes we have described represent the first examples of fully characterized alkyl amido neutral or ate complexes that are directly prepared in a one-pot procedure from commercially available rare earth metal halides, an alkyllithium reagent, and a chiral amido ligand. These yttrium and ytterbium complexes promoted efficiently the intramolecular enantioselective hydroamination of several aminopentenes and an aminohexene derivative. The best results in terms of turnover for the cyclization of different aminoalkenes were obtained in the presence of the yttrium-based catalysts, and particularly the ate alkyl chiral amido species. Up to 83% ee could be reached in the preparation of 2,4,4-trimethylpyrrolidine. Work is ongoing for the use of such catalysts in the hydroamination/cyclization of more demanding and functionalized substrates.

Experimental Section

General Considerations. All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. THF and diethyl ether were distilled from sodium benzophenone ketyl and degassed immediately prior to use. Hexane and toluene were distilled from CaH_2 and degassed immediately prior to use. Deuterated benzene and toluene were dried with sodium benzophenone ketyl and vacuum-transferred. Anhydrous $YbCl_3$, YCl_3, (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine, and MeLi solution in Et_2O were purchased. (*R*)-(+)-2,2′-Bis(cyclopentylamino)-1,1′-binaphthyl[11d] and Me_3SiCH_2Li[25] were prepared according to reported procedures. All other commercially available chemicals were used after the appropriate purification. Bruker AM 250, AV 300, AV 360 NMR, and Avance III 400 NMR spectrometers (operating at 250, 300, 360, and 400 MHz respectively) were used for recording the NMR spectra. Chemical shifts for ^1H and ^{13}C spectra were referenced internally according to the residual solvent resonances and reported relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer as Nujol mulls and are reported in cm^{-1}. Enantiomeric excesses of the products have been determined by GC (GC Fisons 800, column DB1 30 m × 0.32 mm × 0.5 μm) or HPLC (Thermo Separation Product Spectra Series tsp 100 P100/UV100 or Perkin-Elmer Pump Series 200/DAD 200) analyses after derivatization and compared to racemic products prepared with $Y[N(TMS)_2]_3$ as previously reported.[11c,d]

[(*R*)-$C_{20}H_{12}(NC_5H_9)_2$]Y[(μ-Me)$_2$Li(THF)$_2$(μ-Me)Li(THF)] (1a). A solution of MeLi in THF (0.396 mL, 3 M, 1.188 mmol) was added to a suspension of YCl_3 (0.058 g, 0.297 mmol) in THF (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, and a solution of **binamH$_2$** (0.125 g, 0.297 mmol) in THF (10 mL) was added. When the gas evolution was finished, the orange solution was stirred at 0 °C for 10 min and allowed to warm to room temperature. The solvent was evaporated under vacuum, and the solid residue was extracted with toluene (2 × 15 mL). Filtration of the solution, evaporation of toluene by vacuum condensation, and recrystallization of the product by slow hexane condensation into the THF solution at −20 °C allowed isolating complex **1a** as an orange crystalline solid (0.135 g, 58%). IR (Nujol, KBr, cm^{-1}): 2725 m, 2670 w, 1610 s, 1590 s, 1540 m, 1495 m, 1420 m, 1335 s, 1290 m, 1240 s, 1210 w, 1170 m, 1150 m, 1090 m, 1040 m, 945 w, 915 w, 890 m, 855 s, 810 s, 775 w, 745 s. ^1H NMR (400 MHz, C_7D_8, 293 K): −1.39 (br s, 6 H, Y(μ-C*H*$_3$)$_2$Li(THF)$_2$), −0.54 (br s, 3 H; Y(μ-C*H*$_3$)Li(THF)), 1.12 (m, 12 H, β-C*H*$_2$ THF), 1.25 (m, 2 H, C*H*$_2$, C_5H_9), 1.58 (m, 2 H, C*H*$_2$, C_5H_9), 1.66 (m, 4 H, C*H*$_2$, C_5H_9), 1.76 (m, 4 H, C*H*$_2$, C_5H_9), 2.44 (m, 2 H, C*H*$_2$, C_5H_9), 2.70 (m, 2 H, C*H*$_2$, C_5H_9), 2.93 (m, 6 H, α-C*H*$_2$ THF), 2.98 (m, 6 H, α-C*H*$_2$ THF), 4.10 (m, 2 H, C*H*, C_5H_9), 7.06 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, C*H*, Ar), 7.13 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, C*H*, Ar), 7.21 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, C*H*, Ar), 7.48 (m, 2 H, C*H*, Ar), 7.75 (d,$^3J_{HH}$ = 7.5 Hz, 2 H, C*H*, Ar), 7.84 (m, 2 H, C*H*, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_7D_8, 293 K): 9.8 (br s, Y(μ-*C*H$_3$)$_2$Li(THF)$_2$), 11.7 (br s, Y(μ-*C*H$_3$)Li(THF)), 23.1 (s, *C*H$_2$, C_5H_9), 24.5 (s, *C*H$_2$, β-THF), 26.2 (s, *C*H$_2$, C_5H_9), 36.1 (s, *C*H$_2$, C_5H_9), 37.4 (s, *C*H$_2$, C_5H_9), 57.5 (s, *C*H, C_5H_9), 68.3 (s, *C*H$_2$ α-THF), 112.7 (s, Ar), 116.2 (s, Ar), 119.8 (s, Ar), 123.9 (s, Ar; C), 126.4 (s, Ar), 126.8 (s, Ar), 128.1 (s, Ar), 132.3 (s, Ar), 137.9 (s, Ar), 150.5 (s, Ar) ppm. ^7Li NMR (155.4 MHz, C_7D_8, 293 K): −0.86 (s), 0.64 (s) ppm. Anal. Calcd for $C_{45}H_{63}Li_2N_2O_3Y$ (782.8): C 69.05, H 8.11, N 3.58, Y 11.36. Found: C 68.77, H 8.37, N 3.84, Y 11.59.

[(*R*)-$C_{20}H_{12}(NC_5H_9)_2$]Y[(μ-Me)$_2$Li(TMEDA)(μ-Me)Li(OEt$_2$)] (1b) (*method a*, molar ratio YCl_3:MeLi = 1:4). A solution of MeLi in THF (0.436 mL, 3 M, 1.308 mmol) was added to a suspension of YCl_3 (0.064 g, 0.327 mmol) in Et_2O (15 mL) and TMEDA (0.157 g, 1.308 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, and a solution of **binamH$_2$** (0.137 g, 0.327 mmol) in Et_2O (10 mL) was added. When the gas evolution was finished, the orange solution was stirred at 0 °C for 10 min and allowed to warm to the room temperature. The volatiles were evaporated under vacuum, and the solid residue was extracted with toluene (2 × 20 mL). Filtration of the solution, evaporation of toluene by vacuum condensation, and recrystallization of the product by slow cooling of the solution in diethyl ether to −30 °C allowed isolating complex **1b** as an orange crystalline solid (0.135 g, 62%). IR (Nujol, KBr, cm^{-1}): 2725 m, 2670 w, 1610 s, 1590 s, 1535 m, 1420 m, 1340 s, 1300 m, 1245 s, 1220 w, 1170 m, 1150 m, 1125 w, 1095 w, 1070 m, 1030 w, 1020 m, 965 w, 945 m, 930 w, 890 m, 845 s, 810 s, 785 w, 770 w, 745 s. ^1H NMR (400 MHz, C_7D_8, 293 K): −1.45 (br s, 6 H, Y(μ-C*H*$_3$)$_2$Li(TMEDA)), −0.52 (br s, 3 H, Y(μ-C*H*$_3$)Li(OEt$_2$)), 1.04 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, C*H*$_3$, Et$_2$O), 1.25

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(m, 8 H, CH_2, C_5H_9), 1.78 (s, 4 H, CH_2 TMEDA), 1.87 (m, 8 H, C_5H_9), 1.96 (s, 12 H, CH_3, TMEDA), 3.18 (q, $^3J_{HH}$ = 7.0 Hz, 4 H, CH_2, Et_2O), 4.24 (m, 2 H, CH, C_5H_9), 6.99 (m, 6 H, Ar), 7.43 (d, $^3J_{HH}$ = 9.0 Hz, 2 H, Ar), 7.61 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, Ar), 7.80 (d, $^3J_{HH}$ = 9.0 Hz, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_7D_8, 293 K): 7.3 (br s, Y(μ-CH_3)$_2$Li(TMEDA)), 12.4 (br s, Y(μ-CH_3)Li(OEt_2)), 15.7 (s, CH_3, Et_2O), 24.6 (s, CH_2, C_5H_9), 27.3 (s, CH_2, C_5H_9), 35.4 (s, CH_2, C_5H_9), 38.2 (s, CH_2, C_5H_9), 46.3 (s, CH_2, TMEDA), 54.5 (s, CH, C_5H_9), 57.3 (s, CH_3, TMEDA), 66.2 (s, CH_3, Et_2O), 110.3 (s, Ar), 116.0 (s, Ar), 117.7 (s, Ar), 122.4 (s, Ar), 126.9 (s, Ar), 127.5 (s, Ar), 129.0 (s, Ar), 133.1 (s, Ar), 138.5 (s, Ar), 153.2 (s, Ar) ppm. ^{7}Li NMR (155.4 MHz, C_7D_8, 293 K): −0.95 (s), 0.54 (s) ppm. Anal. Calcd for $C_{43}H_{65}Li_2N_4OY$ (756.8): C 68.24, H 8.66, N 7.40, Y 11.75. Found: C 68.05, H 8.82, N 7.53, Y 11.67. **Method b, molar ratio YCl_3:MeLi = 1:5:** The procedure analogous to *method a* was used. YCl_3 (0.060 g, 0.307 mmol) in Et_2O (15 mL) and TMEDA (0.185 g, 1.534 mmol); MeLi in THF (0.512 mL, 3 M, 1.535 mmol); **binamH$_2$** (0.129 g, 0.307 mmol) in Et_2O (10 mL). Complex **1b** was obtained in 87% yield (0.202 g).

[(*R*)-$C_{20}H_{12}(NC_5H_9)_2$]Yb[(μ-Me)$_2$Li(THF)$_2$(μ-Me)Li(THF)] (2a). The procedure analogous to the synthesis of **1a** was used. $YbCl_3$ (0.103 g, 0.368 mmol) in THF (15 mL); MeLi in THF (0.491 mL, 3 M, 1.473 mmol) (molar ratio $YbCl_3$: MeLi = 1: 4); **binamH$_2$** (0.155 g, 0.368 mmol) in THF (10 mL). Complex **2a** was isolated as a yellow crystalline solid (0.204 g, 64%). IR (Nujol, KBr, cm^{-1}): 2720 m, 2670 w, 1610 s, 1590 s, 1540 m, 1490 m, 1415 m, 1330 s, 1290 m, 1245 s, 1210 w, 1170 m, 1150 m, 1090 m, 1040 m, 940 w, 910 w, 890 m, 855 s, 810 s, 775 w, 745 s. Anal. Calcd for $C_{45}H_{63}Li_2N_2O_3Yb$ (866.9): C 62.35, H 7.32, N 3.23, Yb 19.96. Found: C 61.99, H 7.05, N 2.89, Yb 19.85.

[(*R*)-$C_{20}H_{12}(NC_5H_9)_2$]Yb[(μ-Me)$_2$Li(TMEDA)(μ-Me)Li(OEt_2)] (2b). The procedure analogous to the synthesis of **1b** was used. $YbCl_3$ (0.108 g, 0.386 mmol) in Et_2O (15 mL) and TMEDA (0.157 g, 1.308 mmol); MeLi in THF (0.436 mL, 3 M, 1.308 mmol) (molar ratio $YbCl_3$:MeLi = 1:4); **binamH$_2$** (0.137 g, 0.327 mmol) in Et_2O (10 mL). Complex **2b** was isolated as a yellow crystalline solid in 62% yield (0.135 g). IR (Nujol, KBr, cm^{-1}): 2725 m, 2670 w, 1610 s, 1590 s, 1535 m, 1420 m, 1340 s, 1300 m, 1245 s, 1220 w, 1170 m, 1150 m, 1125 w, 1095 w, 1070 m, 1030 w, 1020 m, 965 w, 945 m, 930 w, 890 m, 845 s, 810 s, 785 w, 770 w, 745 s. Anal. Calcd for $C_{43}H_{65}Li_2N_4OYb$ (840.8): C 61.42, H 7.79, N 6.66, Yb 20.58. Found: C 61.09, H 8.00, N 6.37, Yb 20.49.

[(*R*)-$C_{20}H_{12}(NC_5H_9)_2$]YCH$_2$SiMe$_3$(THF)$_2$ (3a). A solution of **binamH$_2$** (0.087 g, 0.206 mmol) in hexane (15 mL) was added to a solution of $(Me_3SiCH_2)_3Y(THF)_2$ (0.102 g, 0.206 mmol) in hexane (15 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, concentrated approximately to 1/10 of its initial volume, and kept overnight at −20 °C. Complex **3a** was isolated as a yellow crystalline solid (0.135 g, 89%). IR (Nujol, KBr, cm^{-1}): 2720 m, 2970 w, 1610 s, 1590 s, 1540 m, 1490 m, 1425 m, 1335 s, 1300 m, 1280 w, 1250 s, 1210 w, 1170 m, 1150 m, 1073 m, 1020 m, 960 w, 920 w, 890 m, 858 s, 810 s, 775 w, 740 s. ^{1}H NMR (400 MHz, C_6D_6, 293 K): −0.91 (dd, $^2J_{HH}$ = 11.0 Hz, $^2J_{YH}$ = 3.1 Hz, 1 H, YCH_2), −0.73 (dd, $^2J_{HH}$ = 11.0 Hz, $^2J_{YH}$ = 3.1 Hz, 1 H, YCH_2), 0.29 (s, 9 H, Si(CH_3)$_3$), 1.08 (m, 8 H, β-CH_2 THF), 1.46 (m, 2 H, CH_2, C_5H_9), 1.65 (m, together 10 H, CH_2, C_5H_9), 2.22 (m, 2 H, CH_2, C_5H_9), 2.32 (m, 2 H, CH_2, C_5H_9), 3.13 (m, 4 H, α-CH_2 THF), 3.37 (m, 4 H, α-CH_2 THF), 4.17 (q, $^3J_{HH}$ = 6.8 Hz, 2 H, CH, C_5H_9), 7.07 (m, together 6 H, CH, Ar), 7.28 (d, $^3J_{HH}$ = 9.2 Hz, 2 H, CH, Ar), 7.58 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, CH, Ar), 7.63 (d, $^3J_{HH}$ = 9.2 Hz, 2 H, CH, Ar) ppm. ^{13}C NMR (100 MHz, C_6D_6, 293 K): 4.4 (s, Si(CH_3)$_3$), 24.4 (s, CH_2, C_5H_9), 24.9 (s, CH_2 β-THF), 25.0 (s, CH_2, C_5H_9), 29.8 (d, $^1J_{YC}$ = 40.6 Hz, YCH_2), 35.0 (s, CH_2, C_5H_9), 36.1 (s, CH_2, C_5H_9), 58.2 (s, NCH, C_5H_9), 69.9 (s, CH_2, α-THF), 113.3 (s, CH Ar), 116.8 (s, CH Ar), 120.7 (s, CH Ar), 124.6 (s, CH Ar), 126.5 (s, CH Ar), 127.0 (s, C Ar), 127.2 (s, CH Ar), 130.8 (s, CH Ar), 136.4 (s, C Ar), 151.5 (s, C Ar) ppm. Anal. Calcd for $C_{42}H_{57}N_2O_2SiY$ (738.9): C 68.27, H 7.78, N 3.79, Y 12.03. Found: C 67.93, H 8.00, N 3.84, Y 12.28.

[(*R*)-$C_{20}H_{12}(NC_5H_9)_2$]YCH$_2$SiMe$_3$(DME) (3b). Complex **3a** (0.120 g, 0.162 mmol) was dissolved in DME (10 mL) and stirred at 0 °C for 15 min. The volatiles were removed under vacuum, and the resulting solid residue was recrystallized from hexane. Complex **3b** was isolated as a yellow crystalline solid (0.081 g, 73%). IR (Nujol, KBr, cm^{-1}): 2725 m, 2670 w, 1610 s, 1590 s, 1540 m, 1490 m, 1420 m, 1340 s, 1300 m, 1290 w, 1245 s, 1210 w, 1170 m, 1145 m, 1095 m, 1040 m, 955 w, 920 w, 890 m, 855 s, 810 s, 775 w, 745 s. ^{1}H NMR (400 MHz, C_6D_6, 293 K): −1.28 (dd, $^2J_{HH}$ = 11.2 Hz, $^2J_{YH}$ = 3.0 Hz, 1 H, YCH_2), −1.02 (dd, $^2J_{HH}$ = 11.2 Hz, $^2J_{YH}$ = 3.0 Hz, 1 H, YCH_2), 0.10 (s, 9 H, Si(CH_3)$_3$), 1.62 (m, 4 H, CH_2, C_5H_9), 1.66 (m, 4 H, CH_2, C_5H_9), 1.92 (m, 4 H, CH_2, C_5H_9), 2.23 (m, 4 H, CH_2, C_5H_9), 2.58 (s, 4 H, CH_2, DME), 2.67 (s, 6 H, CH_3, DME), 4.20 (m, 2 H, CH, C_5H_9), 7.04 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, Ar), 7.11 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, Ar), 7.18 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, Ar), 7.40 (m, 2 H, Ar), 7.66 (d,$^3J_{HH}$ = 7.4 Hz, 2 H, Ar), 7.80 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 293 K): 4.2 (s, Si(CH_3)$_3$), 24.1 (s, CH_2, C_5H_9), 24.8 (s, CH_2, C_5H_9), 30.2 (d, $^1J_{YC}$ = 43.3 Hz, YCH_2), 35.8 (s, CH_2, C_5H_9), 58.7 (s, CH, C_5H_9), 62.0 (s, CH_3, DME), 69.9 (s, CH_2, DME), 114.9 (s, Ar), 117.6 (s, Ar), 120.8 (s, Ar), 124.4 (s, Ar), 126.5 (s, Ar), 127.2 (s, Ar), 127.6 (s, Ar), 131.5 (s, Ar), 136.2 (s, Ar), 150.6 (s, Ar) ppm. Anal. Calcd for $C_{38}H_{51}N_2O_2SiY$ (684.8): C 66.65, H 7.51, N 4.09, Y 12.98. Found: C 66.29, H 7.36, N 4.32, Y 12.89.

[(*R*)-$C_{20}H_{12}(NC_5H_9)_2$]YbCH$_2$SiMe$_3$(THF)$_2$ (4). A solution of **binamH$_2$** (0.065 g, 0.154 mmol) in hexane (15 mL) was added to a solution of $(Me_3SiCH_2)_3Yb(THF)_2$ (0.089 g, 0.154 mmol) in hexane (15 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, concentrated approximately to 1/10 of its initial volume, and kept overnight at −20 °C. Complex **4** was isolated as a dark green crystalline solid (0.075 g, 75%). IR (Nujol, KBr, cm^{-1}): 2725 m, 2670 w, 1610 s, 1595 s, 1540 m, 1490 m, 1420 m, 1330 s, 1295 m, 1275 w, 1245 s, 1205 w, 1170 m, 1130 m, 1070 m, 1020 m, 950 w, 915 w, 895 m, 860 s, 805 s, 775 w, 740 s. Anal. Calcd for $C_{42}H_{57}N_2O_2SiYb$ (823.0): C 61.29, H 6.98, N 3.40, Yb 21.02. Found: C 60.95, H 7.29, N 3.34, Yb 21.25.

Catalytic Tests. *In situ* preparation of catalysts for asymmetric hydroamination of aminoalkenes

1a, 2a. A solution of MeLi (1.6 M in Et_2O, 0.15 mL, 0.24 mmol) was added via a microsyringe to a suspension of $LnCl_3$ (0.06 mmol) in THF (2 mL) at 0 °C in a Schlenk flask equipped with a magnetic stirring bar. The reaction mixture was stirred at 0 °C for 10 min, and a solution of **binamH$_2$** (25 mg, 0.06 mmol) in THF (0.1 mL) was added via a microsyringe. When the gas evolution was finished, the orange solution was stirred at 0 °C for 10 min and allowed to warm to room temperature. THF was evaporated *in vacuo*, and the crude mixture was directly used for the catalytic tests.

1b. A solution of MeLi (1.6 M in Et_2O, 0.15 mL, 0.24 mmol) was added via a microsyringe to a suspension of YCl_3 (12 mg, 0.06 mmol) in Et_2O (2 mL) and TMEDA (28 mg, 0.24 mmol) at 0 °C in a Schlenk flask equipped with a magnetic stirring bar. The reaction mixture was stirred at 0 °C for 10 min, and a solution of **binamH$_2$** (25 mg, 0.06 mmol) in toluene (0.1 mL) was added via a microsyringe. When the gas evolution was finished, the orange solution was stirred at 0 °C for 10 min and allowed to warm to room temperature. Et_2O was evaporated *in vacuo*, and the crude mixture was directly used for the catalytic tests.

3a, 4. In an argon-filled glovebox $LnCl_3(THF)_{3.5}$ (0.06 mmol) was dissolved in hexane and cooled at −15 °C. A solution of $LiCH_2SiMe_3$ (23 mg, 0.24 mmol) in hexane (2 mL) was added at −15 °C, and the solution was stirred for 1 h at −15 °C. A solution of **binamH$_2$** (25 mg, 0.06 mmol) in hexane was added to the filtrate, and the mixture was stirred for 30 min at −15 °C. Hexane was

evaporated *in vacuo*, and the crude mixture was directly used for the catalytic tests.

NMR Scale Asymmetric Hydroamination of Aminoalkenes. The appropriate aminoalkene (0.20 mmol) was dissolved in C_6D_6 (0.1 mL) in the glovebox and dried on 4 Å molecular sieves for 2 h at room temperature. An aliquot of the lanthanide catalyst solution ($2.4.10^{-2}$ M in C_6D_6, 500 μL, 0.012 mmol) was introduced into a J. Young NMR tube equipped with a Teflon valve, and the aminoalkene solution was then introduced. For the cyclization of aminoalkenes performed at 60 °C, the NMR tube was heated out of the glovebox. The hydroamination reaction was monitored by ^{1}H NMR by observation of the decrease of the olefinic proton signals. After the appropriate time, the reaction was quenched with CH_2Cl_2. The method for the determination of enantiomeric excesses has been previously reported.[11c,13]

X-ray Crystallography. X-ray diffraction data for **1a**, **1b**, **2b**, and **3b** were collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated Mo Kα radiation (α = 0.71073 Å). The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[27] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97[28] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[29] The absolute configuration was determined by refinement of the Flack[30] parameter based on a large number of Friedel's pairs. The drawing of the molecule was realized with the help of ORTEP32.[31]

CCDC-692553, -692554, -692555, and -692556 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

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