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Rare-Earth-Metal Complexes Supported by New Chiral Tetra-Azane Chelating Ligands: Synthesis, Characterization, and Catalytic Properties for Intramolecular Asymmetric Hydroamination

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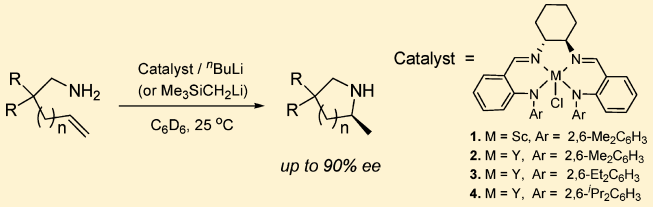
Supporting Information

ABSTRACT: A number of new chiral tetra-azane proligands (1*R*,2*R*)-*N*,*N*′-bis(*o*-arylamino-benzylidene)-1,2-diaminocyclohexane ((1*R*,2*R*)-[(ArHN)C_6H_4CH=N]$_2C_6H_{10}$, Ar = 2,6-$Me_2C_6H_3$ (L^1H_2), 2,6-$Et_2C_6H_3$ (L^2H_2), 2,6-$^iPr_2C_6H_3$ (L^3H_2)) have been synthesized via a nucleophilic displacement of the two fluorine atoms in (*o*-C_6H_4FCH=N)$_2C_6H_{10}$ with the lithium salt of the corresponding aniline derivative. Their rare-earth-metal complexes $L^1ScCl_2Li(THF)_3$ (**1**), $L^1YCl_2Li(THF)_3$ (**2**), $L^2YCl_2Li(THF)_3$ (**3**), and $L^3YCl_2Li(THF)_2$ (**4**) were synthesized in good yields via the salt metathesis of MCl_3 (M = Sc, Y) with the dilithium salts of the ligands $L^1Li_2(THF)_4$, $L^2Li_2(THF)_4$, and $L^3Li_2(THF)_4$, respectively. Further more, the two diethylamido complexes $L^1Y(NEt_2)ClLi(THF)_3$ (**5**) and $L^3Y(NEt_2)ClLi(THF)_2$ (**6**) were also synthesized from reactions of the corresponding chloride complexes **2** and **4** with diethylamidolithium. The new proligands L^1H_2–L^3H_2 and their rare-earth-metal complexes **1**–**6** have been characterized by elemental analyses and ^{1}H and ^{13}C NMR spectroscopy. The structures of complexes **1**, **2**, and **4** have been further confirmed by single-crystal X-ray diffraction analysis. The molecular structural analysis reveals that the metal centers in complexes **1**, **2**, and **4** acquire a distorted-octahedral coordination environment in their solid-state structures by sharing the chloride with a LiCl(THF)$_n$ moiety. After in situ treatment with ^{n}BuLi or Me_3SiCH_2Li, complexes **1**–**4** show reasonable catalytic activity and good enantioselectivity (up to 90%) for intramolecular asymmetric hydroamination reactions of terminal aminoalkenes. The amido complexes **5** and **6** can catalyze the intramolecular hydroamination reaction directly and show catalytic activities and enantioselectivities similar to those of the in situ formed alkyl complexes.



INTRODUCTION

The intramolecular selective addition of N–H to a C=C bond, a highly atom economical process for the formation of nitrogen-containing heterocyclic compounds, has received extensive attention in recent years.[1] The process can be efficiently catalyzed by some chiral organometallic complexes to produce chiral nitrogen-containing heterocyclic compounds, which is the so-called catalytically asymmetric intramolecular hydroamination of alkenes (AIHA).[2] The first example of the AIHA reaction was reported by Marks' group in 1992 with C_1-symmetrical *ansa*-lanthanocene complexes as the catalysts, and chiral pyrrolidines were afforded in up to 74% ee from their work.[3] The cyclopentadienyl-based ligands of these complexes were found to undergo a reversible protonation/deprotonation process, which leads to a facile epimerization of the catalysts.[4] Since then, major research works have been focused on the development of new chiral catalysts with noncyclopentadienyl ligands. So far, most of the known efficient catalysts for the AIHA reaction are rare-earth-metal complexes,[5−7] although some chiral complexes of zirconium,[8] alkali metals,[9] and alkaline-earth metals[10] were also found to be efficient for the transformation. In 2001, complexes of the type Ln[N(SiMe$_3$)$_2$]$_3$ were reported to show catalytic activity for the intramolecular hydroamination of alkenes.[11] Thereafter, a large number of rare-earth-metal complexes with chiral bi-,[5] tri-,[6] and tetradentate[7] ligands have been reported to be promising catalysts for the AIHA reaction. In comparison to the bi- and tridentate ligands, the tetradentate ligands seem to be more suitable for forming the rare-earth-metal complexes and can be modified with plentiful structural diversity.[7] Several typical rare-earth-metal catalysts with chiral tetradentate ligands are summarized in Chart 1. Complexes **A**, the first rare-earth-metal catalysts chelated with chiral tetradentate ligands, were reported to exhibit poor catalytic activity for the AIHA reaction, due probably to a migratory insertion taking place at the imine C=N double bond in their tetradentate salicylaldimine ligands.[7a] The related complex **B** with an N-methylated reductive chiral salicylaldimine ligand was found to show good catalytic activity for the AIHA reaction with up to 61% ee.[7a] Similar complexes of yttrium(III), **C**, with chiral bisthiolate ligands were reported to display significantly high enantioselectivity (up to 89% ee) for the AIHA reaction.[7b] Some lanthanide complexes **D** with organophosphine oxide and sulfide substituted tetradentate binaphtholate ligands were also studied as catalysts for the AIHA reaction, and modest

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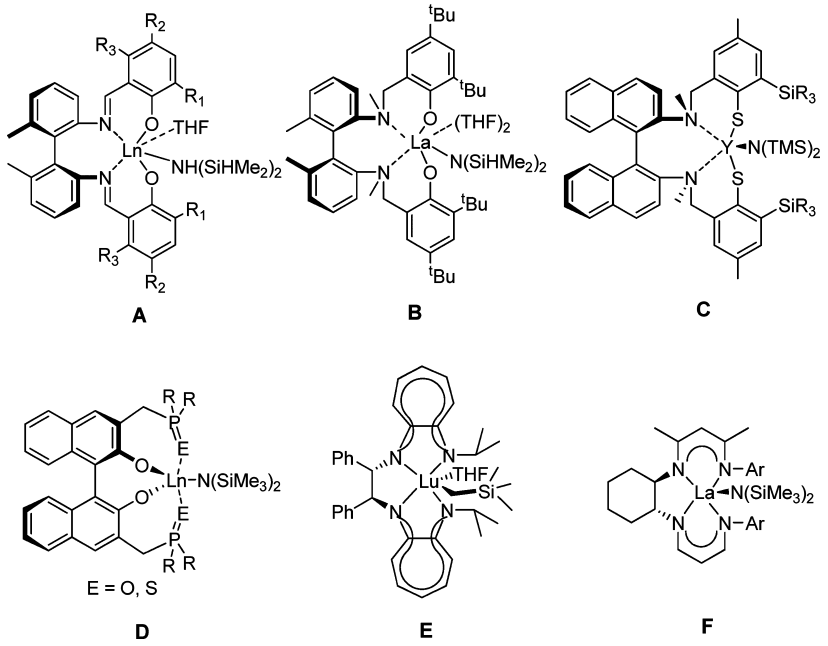
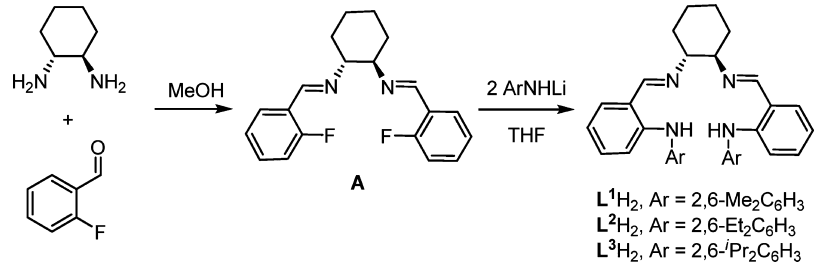
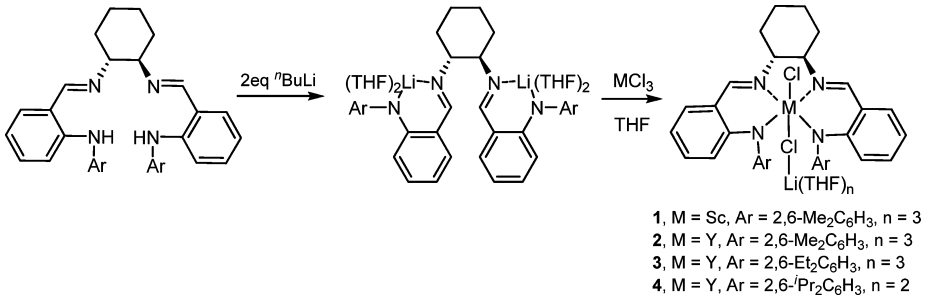
Chart 1. Representative Rare-Earth-Metal Catalysts with Chiral Tetradentate Ligands for the AIHA Reaction



Scheme 1. Synthesis of Chiral Tetra-Azane Proligands



Scheme 2. Synthesis of Rare Earth Complexes with Chiral Tetra-Azane Chelating Ligands



enantioselectivity (up to 65% ee) was achieved.[7c] In addition, the lutetium complex **E** with a chiral tetra-azane chelating ligand was reported to be an effective catalyst for the AIHA reaction as well.[7d] Very recently, some new lanthanum complexes **F** with chiral bis(β-diketiminato) tetra-azane chelating ligands were found to show relatively high enantioselectivity for the AIHA reaction with up to 76% ee.[7e] We have synthesized a number of new chiral tetra-azane proligands and their complexes of rare-earth metals, as shown in Scheme 1 and 2, and evaluated the catalytic performance of these complexes for the AIHA reaction. It was found that these new rare earth metal complexes show moderate catalytic activity and relatively high enantioselectivity (up to 90% ee) at room temperature. Herein, we report the synthesis of the new chiral tetra-azane proligands (1*R*,2*R*)-*N*,*N*′-bis(*o*-arylaminobenzylidene)-1,2-diaminocyclohexane ((1*R*,2*R*)-[(ArHN)-$C_6H_4CH{=}N]_2C_6H_{10}$, Ar = 2,6-$Me_2C_6H_3$ ($\mathbf{L^1H_2}$), 2,6-$Et_2C_6H_3$ ($\mathbf{L^2H_2}$), 2,6-$^iPr_2C_6H_3$ ($\mathbf{L^3H_2}$)) and their rare-earth-metal complexes $\mathbf{L^1}ScCl_2Li(THF)_3$ (**1**), $\mathbf{L^1}YCl_2Li(THF)_3$ (**2**), $\mathbf{L^2}YCl_2Li(THF)_3$ (**3**), $\mathbf{L^3}YCl_2Li(THF)_2$ (**4**), $\mathbf{L^1}Y(NEt_2)ClLi(THF)_3$ (**5**), and $\mathbf{L^3}Y(NEt_2)ClLi(THF)_2$ (**6**), the structures of complexes **1**, **2**, and **4**, and the catalytic performance of these complexes in the AIHA reaction.

RESULTS AND DISCUSSION

Synthesis of Proligands. The preligand compound (**A** in Scheme 1) was prepared according to a literature procedure[12] in moderate yields by condensation reaction of *o*-fluorobenzal-

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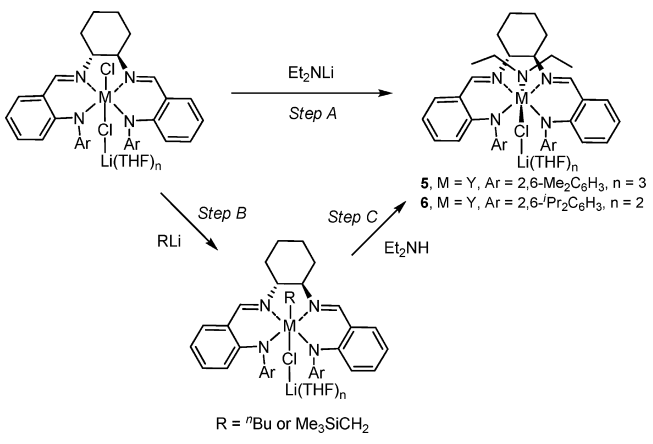
dehyde with $^1/_2$ equiv of chiral (1*R*,2*R*)-cylclohexanediamine in MeOH. The new chiral proligands $\mathbf{L}^1H_2$, $\mathbf{L}^2H_2$, and $\mathbf{L}^3H_2$ were synthesized by using a procedure similar to that described for the synthesis of bidentate anilido-imine ligands[13] via a nucleophilic displacement of the fluorine atoms in **A** by the lithium salt of a corresponding aniline derivative, as shown in Scheme 1. The proligands $\mathbf{L}^1H_2$, $\mathbf{L}^2H_2$, and $\mathbf{L}^3H_2$ were characterized by ^{1}H and ^{13}C NMR spectroscopy along with elemental analyses. ^{1}H NMR spectra of the proligands $\mathbf{L}^1H_2$, $\mathbf{L}^2H_2$, and $\mathbf{L}^3H_2$ exhibit resonances in the range of δ 8.28−8.31 for the imino N=CH protons, with the corresponding ^{13}C NMR resonances around δ 163.3−163.4. The NH resonances in the ^{1}H NMR spectra appear at characteristically low field, about δ 10.55−10.59. The hydrogen atoms on the chiral carbon atoms have resonances at δ 3.20−3.24.[14]

Synthesis of Complexes. The proligands $\mathbf{L}^1H_2$, $\mathbf{L}^2H_2$, and $\mathbf{L}^3H_2$ were treated with 2 equiv of ^{n}BuLi in THF at −78 °C, respectively, to form their lithium salts $\mathbf{L}^1Li_2(THF)_4$, $\mathbf{L}^2Li_2(THF)_4$, and $\mathbf{L}^3Li_2(THF)_4$ in high yields and used without isolation for synthetic purposes. Pure lithium salts can be obtained by removing the solvent THF and washing with hexane. $\mathbf{L}^1Li_2(THF)_4$, $\mathbf{L}^2Li_2(THF)_4$, and $\mathbf{L}^3Li_2(THF)_4$ have been characterized by ^{1}H NMR spectroscopy, and the structure of $\mathbf{L}^1Li_2(THF)_4$ has been determined by single-crystal X-ray diffraction. Complex **1** was synthesized from the reaction of $ScCl_3$ with $\mathbf{L}^1Li_2(THF)_4$ in THF, and complexes **2**−**4** were obtained from the reactions of YCl_3 with $\mathbf{L}^1Li_2(THF)_4$, $\mathbf{L}^2Li_2(THF)_4$, and $\mathbf{L}^3Li_2(THF)_4$, respectively, in good yields as described in Scheme 2. No distinguishable product has been isolated from the reactions of $ScCl_3$ with $\mathbf{L}^2Li_2(THF)_4$ and $\mathbf{L}^3Li_2(THF)_4$. These complexes are all air and moisture sensitive and have to be treated and stored under an inert atmosphere. They are soluble in THF, toluene, and benzene but only slightly soluble in *n*-hexane. All new complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy along with elemental analyses. The disappearance of the NH signal of the ligands in these complexes in the low-field region of their ^{1}H NMR spectra demonstrates the formation of the desired complexes **1**−**4**. The structures of **1**, **2**, and **4** were confirmed by X-ray crystallography.

The diethylamido complexes **5** and **6** were synthesized in high yields from the reactions of the chloride complexes **2** and **4** with diethylamidolithium in toluene (step A in Scheme 3). Complexes **5** and **6** are both soluble in common organic solvents. They were found to be more sensitive to air and moisture than the chloride complexes. Both complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy along with elemental analyses. The presence of a diethylamido group in **5** and **6** is clearly indicated by a multiplet resonance at 3.05 ppm and a triplet resonance at 0.92 ppm for the N−CH_2CH_3 protons.[5j,16] All the resonances observed for the chiral tetra-azane ligands in complexes **5** and **6** from their ^{1}H and ^{13}C NMR spectra are similar to (but not the same as) those observed for the chloride complexes **2** and **4**, respectively, indicating that complexes **5** and **6** retain the same skeleton structures as their chloride precursors **2** and **4**. Integrations on the resonances in their ^{1}H NMR spectra demonstrate that the amounts of the coordinated THF molecules in complexes **5** and **6** are also the same as those in complexes **2** and **4**. Unfortunately, attempts to grow single crystals of complexes **5** and **6** suitable for X-ray structural analysis were unsuccessful.

Alkyl complexes could be generated in situ in an NMR tube by treating the corresponding chloride complexes with ^{n}BuLi or Me_3SiCH_2Li (step B in Scheme 3), and their ^{1}H NMR spectra could be obtained. However, attempts to isolate the resulting alkyl complexes or record their ^{13}C NMR spectra have been unsuccessful so far, due to their poor stability. It has been reported that alkyl migratory insertion into the imine C=N double bond of the ligand in similar alkyl complexes could take place.[7a,15] Through aminolysis of the alkyl complexes by adding diethylamine to the reaction mixtures of the chloride complexes with an alkyllithium reagent, it was found that the in situ formed alkyl complexes could be converted immediately to the diethylamido complexes (step C in Scheme 3), as observed previously by other groups.[5j,16] A typical ^{1}H NMR spectrum for the relatively stable alkyl complex $\mathbf{L}^3Y(CH_2SiMe_3)ClLi(THF)_2$ (**7**), generated from the reaction of complex **4** with $LiCH_2SiMe_3$ (1 equiv) in C_6D_6, is shown in Figure 1 together with the ^{1}H NMR spectrum of complex **4** for comparison purposes. The resonances of the two protons of the methylene group attached to the yttrium atom in complex **7** appear as two sets of doublets of doublets at −0.45 and −0.99 ppm ($^2J_{H-H}$ = 11.5 Hz, J_{Y-H} = 3.1 Hz) due to the asymmetrical environment around the metal center, as observed in related yttrium alkyl complexes.[5j,k] All the resonances for the protons in the chiral tetra-azane ligand of complex **7** appear with patterns and positions similar to those seen in complex **4**, indicating that the chiral ligand in complex **7** was not attacked by the alkyl nucleophile during the short period of reaction.

Scheme 3. Synthesis of Diethylamido Complexes from Chloride Complexes



X-ray Crystallography Studies. Single crystals of the lithium salt $\mathbf{L}^1Li_2(THF)_4$ suitable for X-ray crystallographic analysis were obtained from a solution of the complex in a THF/hexane mixture, and the molecular structure of $\mathbf{L}^1Li_2(THF)_4$ has been determined. The molecular structure of $\mathbf{L}^1Li_2(THF)_4$ (in ORTEP form), together with selected bond distances and angles, is shown in Figure 2. The molecule of $\mathbf{L}^1Li_2(THF)_4$ possesses a C_2-symmetric structure, with both lithium atoms being coordinated by one imine group, one amido group, and two THF molecules in a distorted-tetrahedral coordination environment. The torsion angle N2−C8−C13−N3 (65.69°) is much larger than the same angles in complexes **1**, **2**, and **4**.

Single crystals of complexes **1**, **2**, and **4** suitable for X-ray crystal structure analysis were grown from their solutions in a THF/hexane mixture, and their crystal structures have been determined. The molecular structures of complexes **1**, **2**, and **4** are shown in Figures 3−5, respectively, and their selected bond

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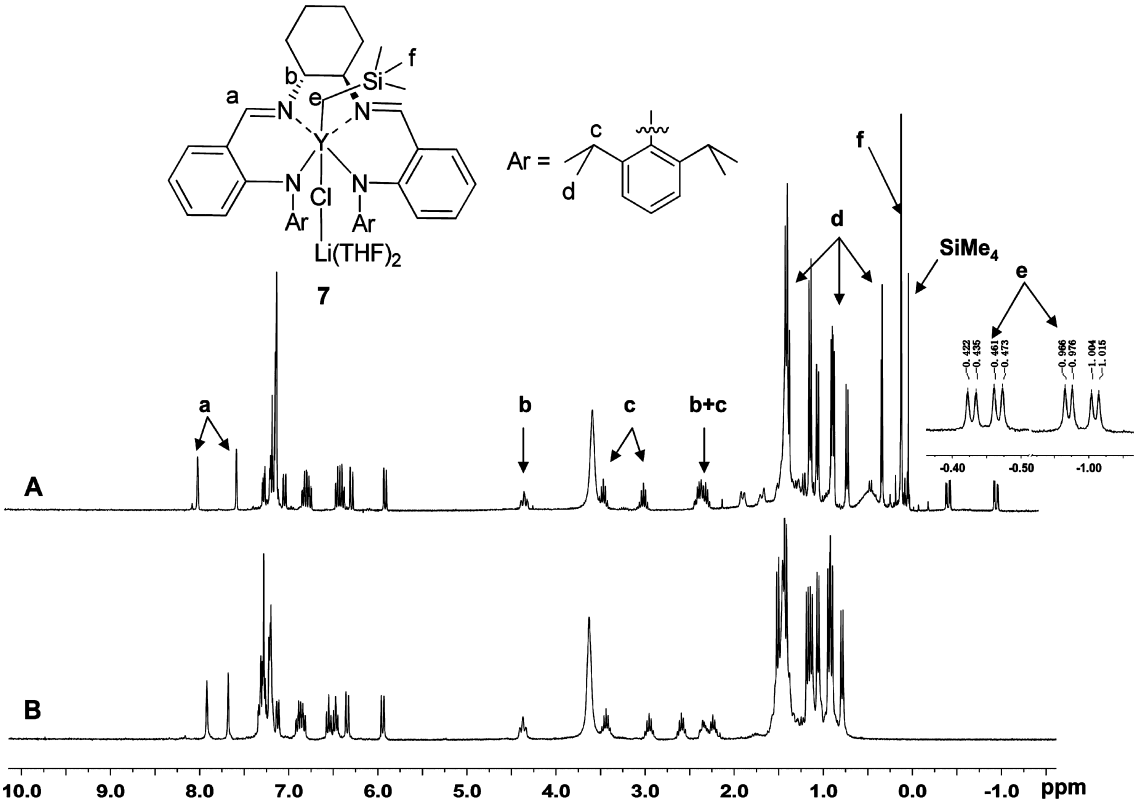

Figure 1. ^{1}H NMR spectra of (A) in situ formed alkyl complex **7** from the reaction of complex **4** with $LiCH_2SiMe_3$ (1 equiv) and (B) complex **4** in C_6D_6 at 25 °C (300 MHz).

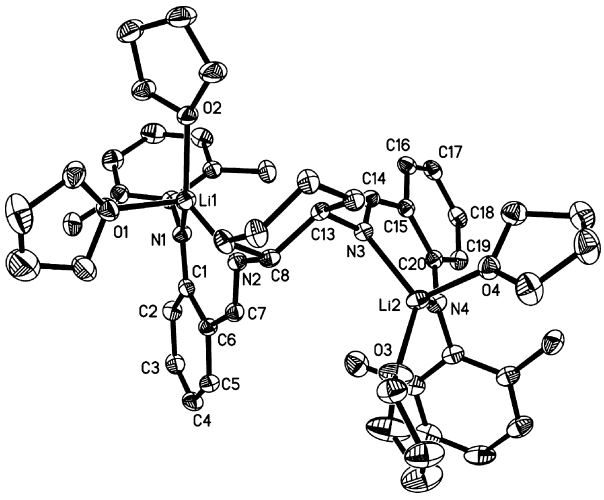

Figure 2. Perspective view of the complex $\mathbf{L}^1Li_2(THF)_4$ with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)–Li(1) = 1.966(7), N(2)–Li(1) = 1.995(6), N(3)–Li(2) = 1.992(6), N(4)–Li(2) = 1.963(6), Li(1)–O(2) = 1.969(6), Li(1)–O(1) = 2.051(7), Li(2)–O(4) = 1.965(6), Li(2)–O(3) = 2.033(7); N(1)–Li(1)–N(2) = 95.3(3), N(4)–Li(2)–N(3) = 94.9(3).

lengths and angles are given in Table 1. The X-ray diffraction analysis confirms the configuration of these complexes and reveals that these complexes exist in a scandium–lithium or yttrium–lithium binuclear form with a LiCl·3THF or LiCl·2THF unit being attached to the scandium or yttrium atom by sharing one or two chloride atom(s). The central metal scandium or yttrium atom in these complexes is coordinated by two imine N atoms, two amido N atoms, and two chloride atoms in a distorted-octahedral coordination environment. In complexes **1** and **2**, the tetra-azane chelating ring adopts a roughly planar geometry, with the two chloride atoms occupying the axial positions around the central metal

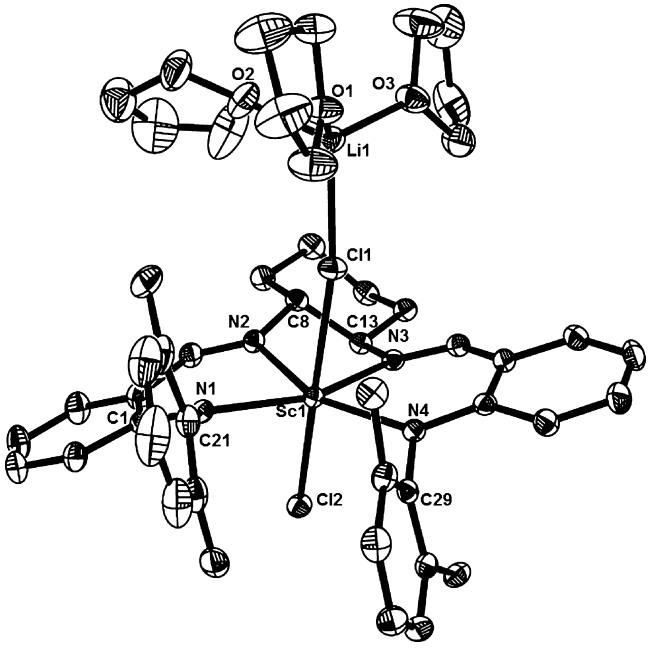

Figure 3. Perspective view of complex **1** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and a solvated THF molecule are omitted for clarity.

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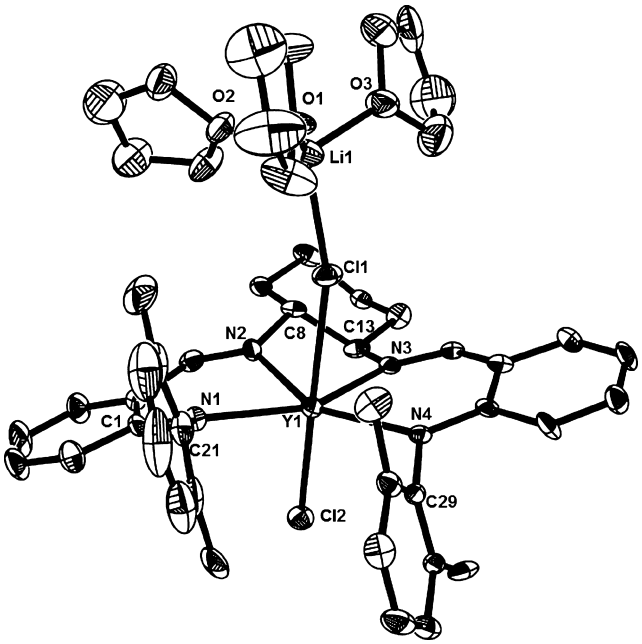

Figure 4. Perspective view of complex **2** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and a solvated THF molecule are omitted for clarity.

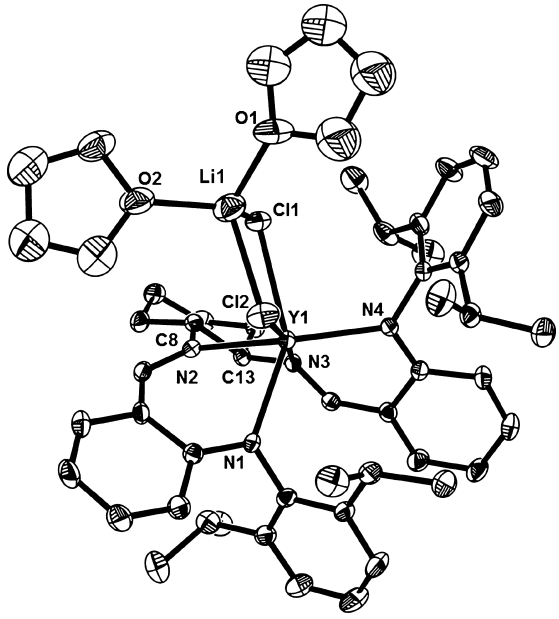

Figure 5. Perspective view of complex **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

atom, while the tetra-azane chelating ring in complex **4** is distorted, with the two chloride atoms being shared by the yttrium and lithium atoms in cis positions. The N2−C8−C13−N3 torsion angles in complexes **1** (54.45°) and **2** (55.40°) are much larger than the corresponding angle observed in complex **4** (43.96°). On the other hand, the angle between the N1−Sc−N2 and N3−Sc−N4 planes in complex **1** (5.32°) and that between the N1−Y−N2 and N3−Y−N4 planes in complex **2** (6.07°) are remarkably smaller than the same angle between the N1−Y−N2 and N3−Y−N4 planes (80.12°) in complex **4**, due to the N1 atom in the chelating ring of complex **4** being pushed to the axial position by one of the two bridging chlorides.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1, 2, and 4[a]

	1	2	4
M−N(1)	2.186(2)	2.299(6)	2.344(7)
M−N(2)	2.252(2)	2.378(6)	2.374(7)
M−N(3)	2.264(2)	2.380(6)	2.398(7)
M−N(4)	2.189(2)	2.300(6)	2.334(6)
M−Cl(1)	2.5603(8)	2.6921(19)	2.667(2)
M−Cl(2)	2.4652(8)	2.597(2)	2.663(2)
N(1)−M−N(2)	81.51(8)	78.47(19)	72.9(2)
N(2)−M−N(3)	73.21(8)	70.28(19)	66.5(2)
N(3)−M−N(4)	82.40(8)	78.9(2)	75.0(2)
N(1)−M−N(4)	122.80(8)	132.1(2)	117.6(2)
N(1)−M−-N(3)	154.72(8)	148.8(2)	88.2(2)
N(2)−M−N(4)	155.03(8)	148.6(2)	140.0(2)
Cl(1)−M(1)−Cl(2)	171.27(3)	171.02(7)	81.47(8)

[a]M = Sc for **1**; M = Y for **2** and **4**.

In complex **1**, the Sc−Cl1(LiCl) bond length (2.5603(8) Å) is obviously longer than that of Sc−Cl2 (2.4652(8) Å), which is in agreement with the coordination bond character of the Sc−Cl1 bond. The Sc−Cl1 bond distance is comparable to that reported in the dimeric Sc complex $[Sc[N(SiHMe_2)_2]_2(\mu\text{-}Cl)(thf)]_2$ (average Sc−Cl = 2.56 Å),[17] while the Sc−Cl2 distance is close to the terminal Sc−Cl distance in the similar complex (SALEN)ScCl(thf) (2.438(2) Å).[18] The Sc−N(imine) bond distances (2.252(2) and 2.264(2) Å) are much longer than the Sc−N(amido) distances (2.186(2) and 2.189(2) Å), indicating the Sc−N(imine) coordination bond character. The Sc−N(imine) distances in complex **1** are longer than the values (2.237(6) and 2.245(6) Å) reported for the complex (SALEN)ScCl(thf).[18] Similar to the case discussed above for complex **1**, the Y−N(amido) distances (2.299(6) and 2.300(6) Å) in complex **2** are shorter than the Y−N(imine) distances (2.378(6) and 2.380(6) Å) as well. Both the Y−N(amido) and Y−N(imine) distances in complex **2** are shorter than those reported for related bidentate (Y−N(amido) = 2.324(3) Å and Y−N(imine) = 2.454(3) Å))[13e] and tridentate (Y−N(amido) = 2.332(4) Å and Y−N(imine) = 2.494(4) Å))[19] yttrium complexes, due probably to the compression of its nearly planar tetra-azane chelating ring. The coordination bond Y−Cl1(LiCl) (2.6921(19) Å) is obviously longer than the Y−Cl2 (2.597(2) Å) bond. The latter is close to the terminal Y−Cl distance in the related bis(amido)yttrium chloride complex $[(R)\text{-}C_{20}H_{12}(N^iPr)_2]YCl(thf)_2$ (2.5835(14) Å, where the ligand is (*R*)-*N*,*N*′-diisopropyl-1,1′-binaphthyl-2,2′-diamide),[5e] while the former is comparable to those found in complexes containing a $[Y(\mu\text{-}Cl)]_2$ unit such as $[(salen)Y(\mu\text{-}Cl)(thf)]_2$ (2.734(1)−2.759(1) Å)[20] and $[(Me_3SiC_5H_4)_2Y(\mu\text{-}Cl)]_2$ (2.684(1) and 2.704(1) Å).[21] In a way similar to that observed for complex **2**, the Y−N(amido) distances (2.334(6) and 2.344(7) Å) in complex **4** are also shorter than the Y−N(imine) distances (2.374(7) and 2.398(7) Å). In contrast to the case for complex **2**, the bond lengths Y−Cl1 (2.667(2) Å) and Y−Cl2 (2.663(2) Å) in complex **4** are close to each other due to the formation of the bridged $Y(\mu\text{-}Cl)_2Li$ binuclear structure.

Asymmetric Hydroamination Reaction. Complexes **1**−**6** have been tested as procatalysts in the intramolecular hydroamination reaction of a number of terminal aminoalkenes,

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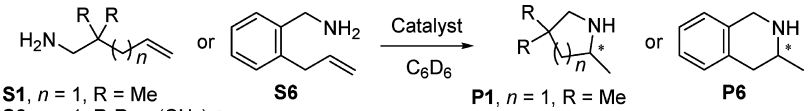
Scheme 4. Catalytic Intramolecular Hydroamination Reaction



S1, *n* = 1, R = Me
S2, *n* = 1, R-R = -$(CH_2)_4$-
S3, *n* = 1, R = Ph
S4, *n* = 2, R = Me
S5, *n* = 1, R = H

P1, *n* = 1, R = Me
P2, *n* = 1, R-R = -$(CH_2)_4$-
P3, *n* = 1, R = Ph
P4, *n* = 2, R = Me
P5, *n* = 1, R = H

Table 2. Results of the Catalytic Intramolecular Hydroamination Reactions[a]

entry	substrate	cat.	temp (°C)	time (h)	conversn[b] (%)	N_t (h^{-1})[c]	ee (%)[d]
1	**S1**	**1**/^{n}BuLi	25	310	90	0.07	85
2	**S1**	**1**/Me_3SiCH_2Li	25	300	90	0.07	84
3	**S1**	**1**/^{n}BuLi	70	63	92	0.4	71
4	**S1**	**2**/^{n}BuLi	25	8.6	95	2.8	62
5	**S1**	**2**/Me_3SiCH_2Li	25	9.0	95	2.7	62
6	**S1**	**3**/^{n}BuLi	25	9.0	94	2.6	63
7	**S1**	**3**/Me_3SiCH_2Li	25	8.9	95	2.8	64
8	**S1**	**4**/^{n}BuLi	25	27	95	0.9	90
9	**S1**	**4**/Me_3SiCH_2Li	25	27	93	1.0	90
10	**S1**	**5**	25	9.5	95		61
11	**S1**	**6**	25	29	95		90
12	**S2**	**1**/^{n}BuLi	25	76	90	0.4	71
13	**S2**	**2**/^{n}BuLi	25	1.0	93	23	60
14	**S2**	**5**	25	1.9	90		61
15	**S2**	**3**/^{n}BuLi	25	1.2	94	20	62
16	**S2**	**4**/^{n}BuLi	25	2.8	90	7.9	78
17	**S3**	**1**/^{n}BuLi	25	45	95	0.5	28
18	**S3**	**2**/^{n}BuLi	25	0.8	93	32	16
19	**S3**	**3**/^{n}BuLi	25	0.9	95	28	18
20	**S3**	**4**/^{n}BuLi	25	1.7	90	13	64
21	**S4**	**1**/^{n}BuLi	25	336	20		n.d.[e]
22	**S4**	**2**/^{n}BuLi	25	20	90	1.2	38
23	**S4**	**3**/^{n}BuLi	25	24	92	0.9	40
24	**S4**	**4**/^{n}BuLi	25	70	87	0.3	73
25	**S5**	**4**/^{n}BuLi	25	240	0		n.d.[e]
26	**S5**	**4**/^{n}BuLi	70	336	13		n.d.[e]
27	**S6**	**4**/^{n}BuLi	25	240	32		n.d.[e]
28	**S6**	**4**/^{n}BuLi	70	10	90		75[f]

[a]Reaction conditions: catalyst, 0.007 mmol; ^{n}BuLi, 0.007 mmol; substrate, 0.14 mmol; C_6D_6, 0.6 mL. [b]Determined by ^{1}H NMR based on *p*-xylene as the internal standard. [c]The turnover frequency, N_t, was calculated from the least-squares-determined slope (m) according to eq 2. [d]Determined by ^{1}H NMR of their diastereomeric (*R*)-(−)-*O*-acetylmandelates unless otherwise noted. [e]The product was not isolated and determined. [f]Determined by HPLC on a chiral stationary phase.

as shown in Scheme 4, and the results of typical catalytic reactions are given in Table 2. After treatment with ^{n}BuLi (or Me_3SiCH_2Li), complexes **1**−**4** were found to show moderate to good catalytic activity and enantioselectivity at room temperature for the AIHA reactions of the *gem*-dialkyl-substituted aminoalkenes. Considering that similar catalytic results were obtained from the reactions activated by ^{n}BuLi or Me_3SiCH_2Li, most of the catalytic reactions were carried out with ^{n}BuLi as the alkylation reagent.

The scandium complex **1**/^{n}BuLi system was found to show much lower catalytic activity for the intramolecular hydroamination reaction of these substrates at 25 °C than its yttrium analogue **2**/^{n}BuLi system (comparing entries 1, 12, 17, and 21 with 4, 13, 18, and 22 in Table 2). However, the complex **1**/^{n}BuLi system produces products with relatively good enantioselectivity (85% ee for product **P1**) in comparison to the complex **2**/^{n}BuLi system, and the enantioselectivity of the **1**/^{n}BuLi system does not decrease as quickly as the reactivity increases when the reaction temperature changes from 25 to 70 °C (comparing entries 1 and 3 in Table 2). The relatively high enantioselectivity of the **1**/^{n}BuLi system may be the result of the atomic radius of scandium being smaller than that of yttrium and thus complex **1** has a more crowded coordination environment than complex **2**. For the yttrium complex **2**−**4**/^{n}BuLi systems, the catalytic activity decreases and the enantioselectivity increases from **2** to **4** as their chiral tetraazane chelating ligands become bulkier and bulkier.

The catalytic activity and enantioselectivity of these systems were also found to be significantly dependent on the nature of the substrates. For the *gem*-dialkyl-substituted aminoalkenes **S1**−**S4**, the substrates **S2** and **S3** show relatively high reactivity and low enantioselectivity in comparison to **S1**. The highest enantioselectivity up to 90% ee was achieved from the reaction of substrate **S1** with the complex **4**/^{n}BuLi (or Me_3SiCH_2Li) catalyst system at 25 °C (Table 2, entries 8 and 9). To our knowledge, this result is among the best obtained so far with

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chiral rare-earth-metal catalysts.[5−7] Although the formation of the six-membered-ring product **P4** from the substrate **S4** was also achieved with these catalyst systems (Table 2, entries 21−24), the reactions were found to be much slower than those reactions for the formation of the five-membered-ring products under similar conditions. It has been reported in the literature that the cyclization reaction for the formation of six-membered-ring products from aminoalkenes is slower than that for the formation of five-membered-ring products.[7b,5n] The enantioselectivity for the formation reactions of **P4** is also lower than that for the formation reactions of the corresponding five-membered-ring product **P1**. In contrast to the reactions of the *gem*-dialkyl-substituted aminoalkenes **S1**−**S3**, the complex **4**/^{n}BuLi catalyst system shows very low catalytic activity for the reactions of the corresponding unsubstituted aminopentene **S5** (Table 2, entries 25 and 26), revealing that the Thorp−Ingold acceleration of the two *gem* substituents is a necessary requirement for efficient intramolecular hydroamination/cyclization with our new catalysts.[22] Similarly, the reactions of the *o*-allylbenzylamine **S6** (Table 2, entries 27 and 28) are also slower than the corresponding reactions of the *gem*-dimethyl-substituted aminoalkene **S4**.

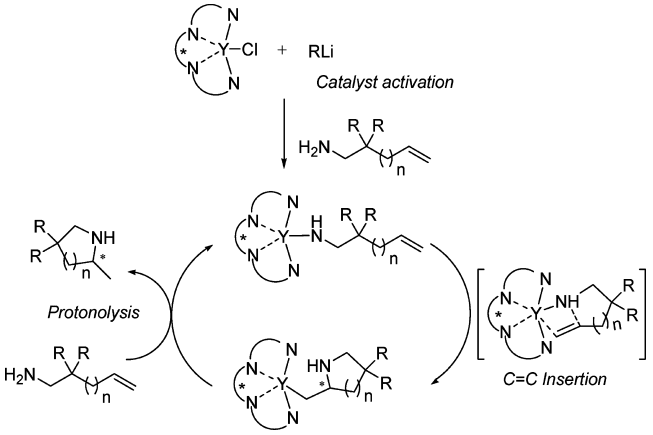
We have also studied the catalytic performance of the diethylamido complexes **5** and **6** in the intramolecular hydroamination reaction (Table 2, entries 10, 11, and 14). In comparison to the corresponding alkyl-activated catalyst systems ((complex **2** or **4**)/(^{n}BuLi or Me_3SiCH_2Li); see entries 4, 5, 8, 9, and 13 in Table 2), the amido complexes show relatively low catalytic activity, due probably to the exchanging reactions of the aminoalkene substrates with the amido complexes being much slower than the corresponding reactions with the alkyl complexes.

Kinetic studies on these intramolecular hydroamination reactions of substrates **S1**−**S4** catalyzed by **1**−**4**/^{n}BuLi catalyst systems indicate that these reactions are zero order in substrate concentration over a period of ∼80% substrate conversion (Figure S16−S20, Supporting Information), meaning that the intramolecular C═C insertion is the reaction rate limiting step in the catalytic cycle, as pointed out previously in the literature.[3] On the basis of the aforementioned results from the synthetic and catalytic reactions and the observed structural evidence of the alkyl and amido complexes, and with reference to the generally accepted reaction mechanism in the literature,[3] a reasonable catalytic cycle for our new chiral rare-earth-metal catalytic system can be proposed as shown in Scheme 5.

CONCLUSIONS

A number of new chiral tetra-azane chelating ligands (1*R*,2*R*)-*N*,*N*′-bis(*o*-arylamino-benzylidene)-1,2-diaminocyclohexane and their rare-earth-metal chloride complexes **1**−**4** have been synthesized in good yields. From reactions of complexes **2** and **4** with Et_2NLi, the corresponding amido complexes **5** and **6** were also obtained. By treatment of complex **4** with Me_3SiCH_2Li, the alkyl complex **7** has been generated in situ and observed by ^{1}H NMR spectroscopy. After treatment with RLi (^{n}BuLi or Me_3SiCH_2Li), complexes **1**−**4** show reasonable catalytic activity and good enantioselectivity for the intramolecular asymmetric hydroamination reactions of terminal aminoalkenes. The complex **4**/RLi catalyst system gives the highest enantioselectivity, up to 90% ee for the reaction of substrate **S1** at 25 °C. Kinetic studies indicate that these reactions are zero order in substrate concentration over a period of ∼80% substrate conversion. The amido complexes **5** and **6** were found to show lower catalytic activity than the corresponding in situ generated alkyl catalyst systems.

Scheme 5. Proposed Catalytic Cycle for the Intramolecular Hydroamination Reaction of Aminoalkenes by 1−4/RLi Catalyst Systems



EXPERIMENTAL SECTION

General Considerations. All manipulations for air- and moisture-sensitive compounds were performed under an inert atmosphere of nitrogen using standard Schlenk or glovebox techniques. Solvents were dried and purified by known procedures and distilled under nitrogen prior to use. (1*R*,2*R*)-(−)-1,2-Diaminocyclohexane (Aldrich, ≥99% ee) and (*R*)-(−)-*O*-acetylmandelic acid (Aldrich, ≥99% ee) were used as received. 2,2-Dimethylpent-4-en-1-amine (**S1**),[23] 2,2-dicyclohexane-4-en-1-amine (**S2**),[23] 2,2-diphenylpent-4-en-1-amine (**S3**),[23] and 2,2-dimethyl-5-hexen-1-amine (**S4**),[7b] 1-amino-4-pentene (**S5**),[7b] and *o*-allylbenzylamine (**S6**)[24] were prepared according to reported procedures.

Synthesis of L^1H_2. A solution of ^{n}BuLi (2 M in hexane, 30.0 mL, 60.0 mmol) was added to a solution of 2,6-dimethylaniline (7.39 mL, 60.0 mmol) in THF (60 mL) at −78 °C. The mixture was warmed to room temperature and stirred for 6 h. The resulting solution was transferred into a solution of **A** (9.79 g, 30.0 mmol) in THF (60 mL) At 25 °C. After it was stirred for 24 h, the reaction mixture was quenched with H_2O (25 mL) and extracted with ether, and the organic phase was evaporated to dryness in vacuo to give the crude product as a yellow solid. Pure product was obtained by recrystallization from MeOH at −20 °C as a white solid (10.2 g, 19.3 mmol, 64%). Anal. Calcd for $C_{36}H_{40}N_4$ (528.73): C, 81.78; H, 7.63; N, 10.60. Found: C, 81.72; H, 7.66; N, 10.62. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 10.55 (s, 2H, ArN*H*Ar), 8.28(s, 2H, C*H*═N), 6.95−7.20 (m, 10H, Ar*H*), 6.56 (t, 2H, $^3J_{H,H}$ = 7.5 Hz, Ar*H*), 6.12 (d, 2H, $^3J_{H,H}$ = 8.4 Hz, Ar*H*), 3.24 (m, 2H, CH═NC*H*), 2.21 (s, 6H, ArCH_3), 2.04 (s, 6H, ArCH_3), 1.51 (m, 2H, CH_2), 1.76 (m, 2H, CH_2), 1.93 (m, 4H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 293 K): δ 163.3, 147.7, 138.3, 136.7, 133.5, 130.8, 128.4, 128.3, 126.0, 117.2, 115.19, 111.3, 75.2, 33.6, 24.6,18.5.

Synthesis of L^2H_2. The proligand was synthesized in the same manner as for L^1H_2 with 2,6-diethylaniline (9.88 mL, 60.0 mmol), ^{n}BuLi (2.00 M in hexane, 30.0 mL, 60.0 mmol), and **A** (9.79 g, 30.0 mmol) as starting materials. Pure L^2H_2 was obtained as a white powder (10.2 g, 17.4 mmol, 58%). Anal. Calcd for $C_{40}H_{48}N_4$ (584.84): C, 82.15; H, 8.27; N, 9.58. Found: C, 82.20; H, 8.24; N, 9.56. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 10.58 (s, 2H, N*H*), 8.31 (s, 2H, C*H*═N), 7.17−7.24 (m, 6H, Ar*H*), 7.09 (d, 2H, $^3J_{H,H}$ = 6.6 Hz, Ar*H*), 7.00 (t, 2H, $^3J_{H,H}$ = 7.8 Hz, Ar*H*), 6.56 (t, 2H, $^3J_{H,H}$ = 7.2 Hz, Ar*H*), 6.12 (d, 2H, $^3J_{H,H}$ = 8.1 Hz, Ar*H*), 3.24 (m, 2H, CH═NC*H*), 2.53 (m, 8H, ArCH_2CH_3), 1.86 (m, 4H, CH_2), 1.69 (m, 2H, CH_2), 1.44 (m, 2H, CH_2), 1.15 (t, 6H, $^3J_{H,H}$ = 7.5 Hz, ArCH$_2$CH_3), 1.00 (t, 6H, $^3J_{H,H}$ = 7.5 Hz, ArCH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 293 K): δ = 163.4, 148.5, 143.0, 142.9, 133.5, 130.8, 126.8, 126.7, 126.6, 116.7, 114.8, 111.2, 75.1, 33.7, 25.2, 25.0, 24.6, 15.3,14.9.

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Synthesis of L^3H_2. The proligand was synthesized in the same manner as for L^1H_2 with 2,6-diisopropylaniline (14.8 mL, 90.0 mmol), ^{n}BuLi (2.00 M in hexane, 45.0 mL, 90.0 mmol), and **A** (9.79 g, 30.0 mmol) as starting materials. Pure L^3H_2 was obtained as a white powder (10.6 g, 16.5 mmol, 55%). Anal. Calcd for $C_{44}H_{56}N_4$ (640.94): C, 82.45; H, 8.81; N, 8.74. Found: C, 82.41; H, 8.82; N, 8.88. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 10.59 (s, 2H, NH), 8.29 (s, 2H, CH=N), 7.24−7.36 (m, 6H, ArH), 7.11 (d, 2H, $^3J_{H,H}$ = 7.5 Hz, ArH), 7.01 (t, 2H, $^3J_{H,H}$ = 7.8 Hz, ArH), 6.56 (t, 2H, $^3J_{H,H}$ = 7.5 Hz, ArH), 6.15 (d, 2H, $^3J_{H,H}$ = 8.1 Hz, ArH), 3.20 (m, 2H, CH=NCH), 3.09 (m, 4H, $CH(CH_3)_2$), 1.86 (m, 4H, CH_2), 1.66 (m, 2H, CH_2), 1.43 (m, 2H, CH_2), 1.15 (m, 12H, $CH_2(CH_3)_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 293 K): δ 163.4, 149.2, 147.7, 135.2, 133.4, 130.8, 127.1, 123.7, 123.6, 116.5, 114.7, 111.3, 74.8, 33.6, 28.4, 25.2, 25.0, 24.4, 22.7.

Synthesis of $L^1Li_2(THF)_4$. A solution of ^{n}BuLi in hexanes (2.00 M, 1.00 mL, 2.00 mmol) was added dropwise to a solution of L^1H_2 (529 mg, 1.00 mmol) in THF (20 mL) at −78 °C. The mixture was warmed to room temperature. After 24 h the product was obtained as a yellow powder (731 mg, 0.89 mmol, 89%) after evaporating the solvent under reduced pressure and washing with hexane. Anal. Calcd for $C_{52}H_{70}Li_2N_4O_4$ (829.02): C, 75.34; H, 8.51; N, 6.76. Found: C, 75.30; H, 8.55; N, 6.72. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.13 (s, 2H, CH=N), 7.10−6.90 (m, 14H, ArH), 3.38 (m, 8H, THF), (m, 2H, CH=NCH), 2.21 (s, 6H, $ArCH_3$), 2.21 (s, 6H, $ArCH_3$), 1.85 (m, 2H, CH_2), 1.69 (m, 2H, CH_2), 1.43−1.32 (m, 4H, CH_2), 1.30 (m, 8H, THF) ppm. ^{13}C NMR (75 MHz, C_6D_6, 293 K): δ 167.7, 157.3, 152.7, 137.8, 132.9, 132.1, 128.6, 128.1, 127.8, 121.4, 116.4, 115.0, 112.4, 108.5, 76.2, 68.1, 36.3, 25.44, 18.8, 18.5.

Synthesis of $L^2Li_2(THF)_4$. The complex was synthesized in the same manner as for $L^1Li_2(THF)_4$ with L^2H_2 (585 mg, 1.00 mmol) and ^{n}BuLi (2.00 M in hexane, 1.00 mL, 2.00 mmol) as starting materials. Pure $L^1Li_2(THF)_4$ was obtained as a yellow powder (814 mg, 0.92 mmol, 92%). Anal. Calcd for $C_{56}H_{78}Li_2N_4O_4$ (885.13): C, 75.99; H, 8.88; N, 6.33. Found: C, 75.60; H, 8.70; N, 6.36%. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.09 (s, 2H, CH=N), 7.17−6.92 (m, 10H, ArH), 6.37−6.30 (m, 4H, ArH), 3.62 (m, 4H, THF), 3.15 (m, 4H, THF), 3.02 (m, 2H, CH=NCH), 2.63 (m, 4H, $ArCH_2CH_3$), 2.45 (m, 4H, $ArCH_2CH_3$), 1.85 (m, 2H, CH_2), 1.69 (m, 2H, CH_2), 1.43−1.21 (m, 4H, CH_2), 1.10 (m, 14H, THF and $ArCH_2CH_3$), 0.97 (t, 6H, $ArCH_2CH_3$) ppm. ^{13}C NMR (75 MHz, C_6D_6, 293 K): δ 167.2, 157.6, 151.4, 138.5, 137.7, 137.7, 132.4, 126.4, 125.9, 121.7, 116.2, 115.3, 108.1, 76.9, 68.4, 35.9, 25.5, 25.1, 25.0, 24.9, 15.1, 14.8.

Synthesis of $L^3Li_2(THF)_4$. The complex was synthesized in the same manner as for $L^1Li_2(THF)_4$ with L^3H_2 (641 mg, 1.00 mmol) and ^{n}BuLi (2.00 M in hexane, 1.00 mL, 2.00 mmol) as starting materials. Pure $L^3Li_2(THF)_4$ was obtained as a yellow powder (814 mg, 0.92 mmol, 92%). Anal. Calcd for $C_{60}H_{86}Li_2N_4O_4$ (941.23): C, 76.56; H, 9.21; N, 5.95. Found: C, 76.20; H, 9.21; N, 5.99. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.03 (s, 2H, CH=N), 7.17−6.87 (m, 10H, ArH), 6.32−6.24 (m, 4H, ArH), 3.34 (m, 4H, $CH(CH_3)_2$), 3.28 (m, 4H, THF), 3.17 (m, 4H, THF), 2.96 (m, 2H, CH=NCH), 1.81 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 1.41−1.25 (m, 4H, CH_2), 1.13 (m, 8H, THF), 1.09−0.97 (m, 24H, $CH(CH_3)_2$) ppm. ^{13}C NMR (75 MHz, C_6D_6, 293 K): δ 162.0, 152.9, 144.8, 137.8, 137.2, 132.6, 126.9, 118.3, 117.9, 116.9, 110.7, 102.67, 71.7, 63.2, 30.7, 22.7, 22.4, 20.2, 19.8, 19.1, 18.9, 18.8.

Synthesis of Complex 1. A solution of ^{n}BuLi in hexanes (2.00 M in hexane, 1.00 mL, 2.00 mmol) was added dropwise to a solution of L^1H_2 (529 mg, 1.00 mmol) in THF (20 mL) at −78 °C. The mixture was stirred for 0.5 h at room temperature, and then a slurry of $ScCl_3$ (151 mg, 1.00 mmol) in THF (10 mL) was added. The solution was stirred at room temperature for 12 h and then was warmed to 60 °C. After 24 h the volatiles were removed under reduced pressure. The residue was extracted into toluene and the extract filtered. The product (450 mg, 0.52 mmol, 52%) was obtained as a bright yellow powder after evaporating the solvent and washing with THF/hexane. Crystals of **1** suitable for an X-ray structural determination were grown in THF/hexane mixed solution. Anal. Calcd for $C_{48}H_{62}Cl_2LiN_4O_3Sc$ (865.83): C, 66.58; H, 7.22; N, 6.47. Found: C, 66.64; H, 7.25; N, 6.43. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.88 (s, 1H, CH=N), 7.80 (s, 1H, CH=N), 7.21−6.83 (m, 10H, ArH), 6.51 (m, 2H, ArH), 6.17 (d, 1H, $^3J_{H,H}$ = 9.0 Hz, ArH), 5.96 (d, 1H, $^3J_{H,H}$ = 9.0 Hz, ArH), 4.10 (t, 1H, $^3J_{H,H}$ = 9.0 Hz, CH=NCH), 3.67 (br, 12H, THF), 2.71 (t, 1H, $^3J_{H,H}$ = 9.0 Hz, CH=NCH), 2.28, 2.26, 1.77, 1.69 (each s, 3H, $ArCH_3$), 1.38 (br, 12H, THF), 1.58−1.40, 1.22−1.05 (each m, 2H, CH_2), 0.94−0.78 (m, 4H, CH_2) ppm. ^{13}C NMR (75 MHz, C_6D_6, 293 K): δ 165.0, 160.8, 154.0, 143.4, 138.9, 136.8, 136.1, 135.9, 135.5, 135.0, 134.9, 134.5, 130.5, 129.4, 129.3, 128.8, 126.1, 125.1, 119.7, 119.4, 118.4, 115.3, 115.2, 115.1, 72.5, 68.6, 65.5, 32.5, 27.7, 25.6, 24.8, 24.2, 19.8, 18.1,18.0.

Synthesis of Complex 2. Complex **2** was synthesized in the same manner as for **1** with L^1H_2 (529 mg, 1.00 mmol), ^{n}BuLi (2.00 M in hexane, 1.00 mL, 2.00 mmol), and YCl_3 (195 mg, 1.00 mmol) as starting materials. Complex **2** was obtained as a bright yellow powder (450 mg, 0.52 mmol, 52%). Crystals of **2** suitable for an X-ray structural determination were grown in THF/hexane mixed solution. Anal. Calcd for $C_{48}H_{62}Cl_2LiN_4O_3Y$ (909.78): C, 63.37; H, 6.87; N, 6.16. Found: C, 63.40; H, 6.85; N, 6.21. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.08 (s, 1H, CH=N), 7.90 (s, 1H, CH=N), 7.37 (d, 1H, $^3J_{H,H}$ = 7.5 Hz, ArH), 6.92−6.77 (m, 9H, ArH), 6.56 (t, 1H, $^3J_{H,H}$ = 7.1 Hz, ArH), 6.49 (t, 1H, $^3J_{H,H}$ = 7.1 Hz, ArH), 6.13 (d, 1H, $^3J_{H,H}$ = 9.0 Hz, ArH), 5.98 (d, 1H, $^3J_{H,H}$ = 9.0 Hz, ArH), 4.22 (br, 1H, CH=NCH), 3.55 (br, 12H, THF), 2.83 (br, 1H, CH=NCH), 2.21, 2.12, 1.74, 1.61 (each s, 3H, $ArCH_3$), 1.41 (br, 12H, THF), 1.23−1.10 (m, 4H, CH_2), 0.92−0.87 (m, 4H, CH_2) ppm. ^{13}C NMR (75 MHz, C_6D_6, 293 K): δ 166.0, 161.5, 155.8, 154.0, 145.5, 147.7, 138.6, 137.2, 136.9, 136.5, 136.1, 134.0, 133.8, 133.5, 129.82, 129.7, 128.8, 128.7, 124.8, 124.4, 120.4, 119.7, 118.0, 116.9, 114.0, 113.6, 72.9, 67.9, 64.6, 31.3, 29.3, 25.6, 25.1, 24.5, 19.9, 19.5, 18.8, 18.5.

Synthesis of Complex 3. Complex **3** was synthesized in the same manner as for **1** with L^2H_2 (585 mg, 1.00 mmol), ^{n}BuLi (2.00 M in hexane, 1.00 mL, 2.00 mmol), and YCl_3 (195 mg, 1.00 mmol) as starting materials. Complex **3** was obtained as a bright yellow powder (513 mg, 0.54 mmol, 54%). Anal. Calcd for $C_{52}H_{70}Cl_2LiN_4O_3Y$ (965.89): C, 64.66; H, 7.30; N, 5.80. Found: C, 64.52; H, 7.34; N, 5.76. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.20 (s, 1H, CH=N), 8.04 (s, 1H, CH=N), 7.31−6.87 (m, 10H, ArH), 6.54 (m, 2H, ArH), 6.20 (d, 1H, $^3J_{H,H}$ = 9.0 Hz, ArH), 6.07 (d, 1H, $^3J_{H,H}$ = 9.0 Hz, ArH), 4.59 (br, 1H, CH=NCH), 3.65 (br, 12H, THF), 2.94 (br, 1H, CH=NCH), 2.77−2.13 (m, 8H, $ArCH_2CH_3$), 2.02−1.50 (m, 8H, CH_2), 1.41 (br, 12H, THF), 1.23−0.91 (m, 12H, ArH_2CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6, 293 K): δ = 166.5, 162.0, 156.4, 155.1, 143.5, 141.6, 140.2, 137.5, 137.4, 133.89, 133.3, 126.9, 126.7, 126.6, 126.5, 125.6, 125.3, 119.8, 119.5, 118.5, 117.3, 113.8, 113.5, 72.7, 68.6, 65.1, 31.9, 29.2, 25.6, 25.2, 24.7, 24.5, 24.0, 23.5, 15.5, 14.9, 14.4, 14.2.

Synthesis of Complex 4. The complex **4** was synthesized in the same manner as for **1** with L^3H_2 (641 mg, 1.00 mmol), ^{n}BuLi (2.00 M in hexane, 1.00 mL, 2.00 mmol), and YCl_3 (195 mg, 1.00 mmol) as starting materials. Complex **4** was obtained as a bright yellow powder (599 mg, 0.63 mmol, 63%). Crystals of **4** suitable for an X-ray structural determination were grown in THF/hexane mixed solution. Anal. Calcd for $C_{52}H_{70}Cl_2LiN_4O_2Y$ (949.89): C, 65.75; H, 7.43; N, 5.90. Found: C, 65.70; H, 7.32; N, 6.10. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.85 (s, 1H, CH=N), 7.60 (s, 1H, CH=N), 7.38−6.67 (m, 10H, ArH), 6.50 (t, 1H, $^3J_{H,H}$ = 7.3 Hz, ArH), 6.43 (t, 1H,$^3J_{H,H}$ = 7.3 Hz, ArH), 6.30 (d, 1H, $^3J_{H,H}$ = 8.8 Hz, ArH), 5.90 (d, 1H,$^3J_{H,H}$ = 8.8 Hz, ArH), 4.30 (t, 1H, $^3J_{H,H}$ = 9.6 Hz, CH=NCH), 3.55 (br, 8H, THF) 3.37 (m, 1H, $CH(CH_3)_2$), 2.87 (m, 1H, $CH(CH_3)_2$), 2.53 (m, 1H, $CH(CH_3)_2$), 2.25 (m, 1H, CH=NCH), 2.17 (m, 1H, $CH(CH_3)_2$), 1.35 (br, 8H, THF), 1.46, 1.37, 1.13, 1.09, 1.01, 0.90, 0.85, 0.74 (each d, 3H, $^3J_{H,H}$ = 6.7 Hz, $CH(CH_3)_2$), 1.34−1.20 (m, 8H, CH_2) ppm. ^{13}C NMR (75 MHz, C_6D_6, 293 K): δ 166.1, 161.2, 158.9, 156.2, 149.6, 146.7, 145.6, 145.4, 145.1, 139.1, 137.1, 136.7, 133.9, 133.8, 125.9, 125.6, 124.6, 123.3, 122.1, 119.5, 119.4, 118.2, 114.6, 114.2, 73.8, 67.8, 65.6, 35.0, 31.8, 31.7, 30.3, 27.7, 26.8, 26.7, 26.3, 25.9, 25.6, 25.3, 25.2, 25.0, 24.8, 24.6, 24.4, 22.9, 21.6.

Synthesis of Complex 5. A solution of complex **2** (455 mg, 0.50 mmol) in toluene (10 mL) was mixed with diethylamidolithium (39.5 mg, 0.50 mmol) at room temperature. The suspension was stirred for 12 h and filtered to afford a clear filtrate. After the solvent was

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Table 3. Summary of Crystallographic Data for Complexes $L^1Li_2(THF)_4$, 1, 2, and 4

	$L^1Li_2(THF)_4$	1·THF	2·THF	4
formula	$C_{52}H_{70}Li_2N_4O_4$	$C_{52}H_{70}Cl_2LiN_4O_4Sc$	$C_{52}H_{70}Cl_2LiN_4O_4Y$	$C_{52}H_{70}Cl_2LiN_4O_2Y$
fw	829.00	937.92	981.87	534.45
cryst syst	triclinic	orthorhombic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	9.6598(14)	12.6508(9)	12.3497(16)	13.2799(9)
b (Å)	16.151(3)	17.9350(12)	18.816(3)	13.9219(9)
c (Å)	17.149(3)	22.2951(15)	22.036(3)	27.5159(18)
α (deg)	65.550(2)	90	90	90
β (deg)	88.613(3)	90	90	90
γ (deg)	78.037(3)	90	90	90
V (Å^3)	2377.0(6)	5058.6(6)	5120.5(12)	5087.2(6)
Z	2	4	4	4
μ (mm^{-1})	0.072	0.298	1.290	1.293
R_{int}	0.0417	0.0305	0.1630	0.0370
GOF	1.011	1.119	0.945	0.996
R1	0.0790	0.0466	0.0741	0.0406
wR2	0.1601	0.1178	0.1063	0.0990

evaporated under reduced pressure, the product **5** was obtained as a brown powder (445 mg, 0.47 mmol, 94%). Anal. Calcd for $C_{52}H_{72}ClLiN_5O_3Y$ (946.46): C, 65.99; H, 7.67; N, 7.40. Found: C, 65.54; H, 7.31; N, 7.49. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.11 (s, 1H, C*H*=N), 7.90 (s, 1H, C*H*=N), 7.31 (d, 1H, $^3J_{H,H}$ = 7.8 Hz, Ar*H*), 7.20−6.79 (m, 9H, Ar*H*), 6.58−6.43 (m, 2H, Ar*H*), 6.20 (d, 1H, $^3J_{H,H}$ = 7.8 Hz, Ar*H*), 6.10 (d, 1H, $^3J_{H,H}$ = 7.8 Hz, Ar*H*), 4.04 (t, 1H, $^3J_{H,H}$ = 8.9 Hz, CH=NC*H*), 3.54 (br, 8H, THF), 3.05 (qd, 4H, J = 6.7, 2.8 Hz, NC*H*$_2$CH$_3$), 2.69−2.54 (m, 1H, CH=NC*H*), 2.27, 2.21, 1.78, 1.72 (each s, 3H ArC*H*$_3$), 1.65−1.43 (m, 4H, C*H*$_2$), 1.38 (m, 12H, THF), 1.26−0.95 (m, 4H, C*H*$_2$), 0.92 (t, $^3J_{H,H}$ = 6.9 Hz, NCH$_2$C*H*$_3$) ppm. ^{13}C NMR (75 MHz, C_6D_6, 293 K): δ 166.10, 161.46, 156.82, 154.82, 149.00, 144.09, 137.71, 137.48, 137.15, 135.11, 134.79, 134.16, 129.99, 129.79, 129.67, 129.29, 125.71, 123.96, 119.15, 118.43, 115.39, 113.56, 113.13, 72.63, 67.86, 65.65, 44.11, 42.66, 33.14, 27.99, 25.66, 24.99, 24.78, 18.84, 18.61, 18.00, 17.88, 15.88, 15.57.

Synthesis of Complex 6. A solution of complex **4** (475 mg, 0.50 mmol) in toluene (10 mL) was mixed with diethylamidolithium (39.5 mg, 0.50 mmol) at room temperature. The suspension was stirred for 12 h and filtered to afford a clear filtrate. After the solvent was evaporated under reduced pressure, the product **6** was obtained as a brown powder (445 mg, 0.47 mmol, 94%). Anal. Calcd for $C_{56}H_{80}ClLiN_5O_2Y$ (986.57): C, 68.18; H, 8.17; N, 7.10. Found: C, 67.64; H, 7.72; N, 7.45. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.07 (s, 1H, C*H*=N), 7.75 (s, 1H, C*H*=N), 7.37−7.21 (m, 7H, Ar*H*), 7.15 (dd, 1H, J = 7.9, 1.7 Hz, Ar*H*), 6.93 (m, 1H, Ar*H*), 6.84 (m, 1H, Ar*H*), 6.56−6.40 (m, 2H, Ar*H*), 6.41 (d, 1H, $^3J_{H,H}$ = 8.6 Hz, Ar*H*), 6.08 (d, 1H, $^3J_{H,H}$ = 8.6 Hz, Ar*H*), 4.32 (t, 1H, $^3J_{H,H}$ = 10.5 Hz, CH=NC*H*), 3.62 (br, 8H, THF), 3.39 (m, 1H, C*H*(CH$_3$)$_2$), 3.07 (m, 5H, NC*H*$_2$CH$_3$ and C*H*(CH$_3$)$_2$), 2.55 (m, 1H, C*H*(CH$_3$)$_2$), 2.37 (m, 1H, CH=NC*H*), 2.29 (m, 1H, C*H*(CH$_3$)$_2$), 1.83−1.66 (m, 2H, C*H*$_2$), 1.45 (m, 8H, THF), 1.39, 1.32, 1.19, 1.14, 1.11, 0.92, 0.86, 0.77 (each d, 3H, $^3J_{H,H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 0.73 (t, 6H, $^3J_{H,H}$ = 6.9 Hz, NCH$_2$C*H*$_3$) ppm. ^{13}C NMR (75 MHz, C_6D_6, 293 K): δ 166.42, 160.34, 159.51, 156.97, 148.77, 148.65, 145.11, 144.77, 141.74, 137.35, 136.85, 133.18, 133.09, 127.06, 126.46, 126.13, 124.73, 124.65, 123.39, 122.93, 119.59, 118.57, 114.01, 112.97, 73.88, 67.86, 65.96, 40.58, 35.57, 31.61, 30.52, 27.61, 27.51, 27.01, 26.61, 26.13, 25.95, 25.70, 25.21, 25.15, 25.05, 24.92, 24.62, 21.27, 14.07.

In Situ Generation of Complex 7 in an NMR Tube. Complex **4** (32.2 mg, 40 μmol) and $LiCH_2SiMe_3$ (3.8 mg, 40 μmol) were dissolved in 0.6 mL of C_6D_6 in an NMR tube in the drybox. The NMR tube was sealed and taken out of the drybox, and the ^{1}H NMR experiment was carried out immediately.

General Procedure for Asymmetric Hydroamination/Cyclization. A solution of Me_3SiCH_2Li or ^{n}BuLi (2.0 M in hexane, 3.5 μL, 7.0 μmol) was added via a microsyringe to a solution of a chloride complex (7.0 μmol) in C_6D_6 (0.60 mL, contains 0.067 M *p*-xylene as an internal standard) in a NMR tube at room temperature. After the mixture was shaken by hand, an aminoalkene substrate (0.14 mmol) was added and the NMR tube was sealed. The reaction mixture was kept at 25 or 70 °C, and the reaction was monitored periodically by ^{1}H NMR spectroscopy. The substrate concentration was measured from the olefinic peak area standardized to the methyl peak area of the *p*-xylene internal standard. After an appropriate time, the reaction was quenched with $CHCl_3$. The produced cyclic amine was vacuum-transferred into a 10 mL Schlenk flask containing (*R*)-(−)-*O*-acetylmandelic acid (25 mg, 0.14 mmol). The mixture was stirred at room temperature for 2 h, and the volatiles were removed in vacuo. The resulting diastereomeric salt was then dissolved in $CDCl_3$ (0.6 mL) for ^{1}H NMR determination, and the enantiomeric excesses were calculated on the basis of the ^{1}H NMR data as previously reported in the literature.[6a,7b] For the hydroamination product **P6**, the ee value was determined by chiral stationary phase HPLC analysis using a Regis (*S*,*S*)-Whelk O1 column (eluent ratio hexane/^{i}PrOH 70/30, flow rate 1 mL/min) after derivatization of **P6** as 1-naphthoylamide treated with 1-naphthoyl chloride and Et_3N in Et_2O. The HPLC analysis methods are the same as those reported previously.[5l,7c]

For the zero-order reactions, the turnover frequency, N_t (h^{-1}), was calculated from the least-squares-determined slope (m) in the reaction rate eq according to eqs 1 and 2, where [substrate], [substrate]$_0$, and [catalyst] are the substrate concentration, the initial substrate concentration, and the catalyst concentration, respectively.[5l,p,7c]

$$[\text{substrate}] = mt + [\text{substrate}]_0 \quad (1)$$

$$N_t\ (\text{h}^{-1}) = -\frac{60\ \text{min}}{\text{h}} \times \frac{m}{[\text{catalyst}]} \quad (2)$$

Crystal Structure Determination. The crystals of the complexes $L^1Li_2(THF)_4$, **1**, **2**, and **4** were obtained from a THF/hexane mixed solvent system. The data were obtained with the ω−2θ scan mode on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at −70 °C. All structures were solved using direct methods[25] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All calculations were performed using SHELXTL crystallographic software packages.[26] Details of the crystal data, data collections, and structure refinements are summarized in Table 3.

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■ ASSOCIATED CONTENT

Supporting Information

CIF files giving X-ray crystallographic data for complexes $L^1Li_2(THF)_4$, **1**, **2**, and **4** and figures giving selected ^1H NMR spectra of the products **P1**−**P4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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