Neutral and Cationic Rare Earth Metal Alkyl and Benzyl Compounds with the 1,4,6-Trimethyl-6-pyrrolidin-1-yl-1,4-diazepane Ligand and Their Performance in the Catalytic Hydroamination/ Cyclization of Aminoalkenes

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A new neutral tridentate 1,4,6-trimethyl-6-pyrrolidin-1-yl-1,4-diazepane (**L**) was prepared. Reacting **L** with trialkyls $M(CH_2SiMe_3)_3(THF)_2$ (M = Sc, Y) and tribenzyls $M(CH_2Ph)_3(THF)_3$ (M = Sc, La) yielded trialkyl complexes (**L**)$M(CH_2SiMe_3)_3$ (M = Sc, **1**; M = Y, **2**) and tribenzyl complexes (**L**)$M(CH_2Ph)_3$ (M = Sc, **3**; M = La, **4**). Complexes **1** and **2** can be converted to their corresponding ionic compounds [(**L**)$M(CH_2SiMe_3)_2(THF)][B(C_6H_5)_4]$ (M = Sc, **5**; M = Y, **6**) by reaction with $[PhNMe_2H][B(C_6H_5)_4]$ in THF. Complexes **3** and **4** can be converted to cationic species $[(L)M(CH_2Ph)_2]^+$ by reaction with $[PhNMe_2H][B(C_6F_5)_4]$ in C_6D_5Br in the absence of THF. The neutral complexes **1**−**4** and their cationic derivatives were studied as catalysts for the hydroamination/cyclization of 2,2-diphenylpent-4-en-1-amine and *N*-methylpent-4-en-1-amine reference substrates and compared with ligand-free Sc, Y, and La neutral and cationic catalysts. The most effective catalysts in the series were the cationic **L**-yttrium catalyst (for 2,2-diphenylpent-4-en-1-amine) and the cationic lanthanum systems (for *N*-methylpent-4-en-1-amine). For the La catalysts, evidence was obtained for release of **L** from the metal during catalysis.

Introduction

Neutral and cationic rare earth metal alkyl species are catalytically active for a range of transformations,[1] such as olefin polymerization,[2] dimerization of alkynes,[3] and the hydroamination,[4] hydrophosphination,[5] or hydrosilylation[6] of alkenes. Neutral nitrogen-based facial tridentate ancillary ligands, such as 1,4,7-trimethyltriazacyclononane, tris(pyrazolyl)methane, and tris(oxazolinyl)methane, have been reported to stabilize these species, but rare earth metal compounds bearing these ligands were reported only for metals in the small to medium ionic size range (Sc, Y, Dy−Lu),[7] mainly due to the availability of the corresponding isolated trialkyl starting materials $M(CH_2SiMe_2R)_3(THF)_n$ (M = Sc, Y, Dy−Lu; R = Me or Ph; n = 1, 2). Recent isolation of the tribenzyl complex of lanthanum (the largest rare earth metal), $La(CH_2Ph)_3(THF)_3$, and its Sc and Lu congeners[8] offers an opportunity to investigate the chemistry of larger lanthanides with this type of neutral κ^3 nitrogen-based ancillary ligands.

Recently we communicated the successful use of the 6-amino-1,4-diazepane moiety as a ligand framework for neutral and cationic Sc and Y complexes.[9] Here we describe the synthesis of a new neutral ligand, 1,4,6-trimethyl-6-pyrrolidin-1-yl-1,4-diazepane (**L**), from this ligand motif, its application in the synthesis of neutral and cationic alkyl (for Sc and Y) and benzyl

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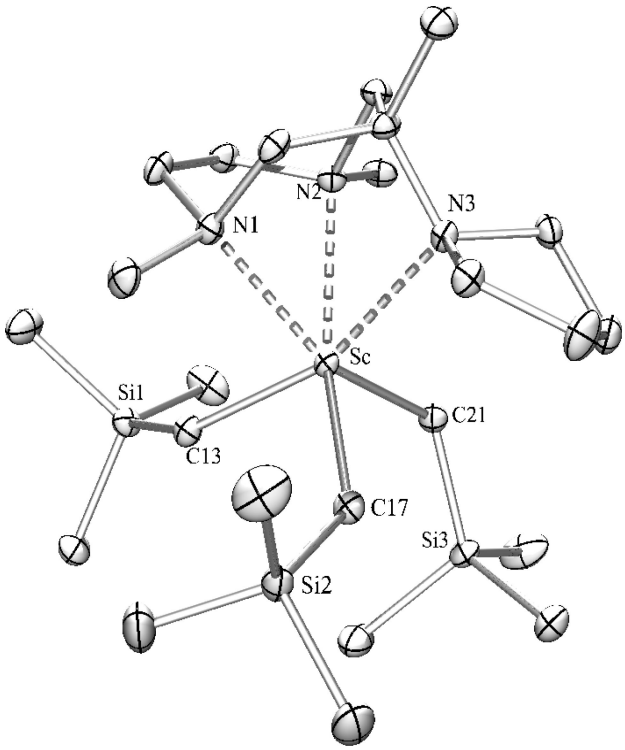
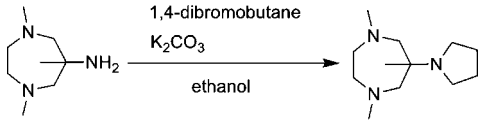


Figure 1. Molecular structure of **1** (hydrogen atoms are omitted for clarity, thermal ellipsoids drawn at 50% probability level).

Scheme 1. Synthesis of Ligand L



complexes (for Sc and La, the smallest and largest metals in rare earth metal series), and a comparative study of their performance in the catalytic hydroamination/cyclization of two commonly used standard substrates, 2,2-diphenylpent-4-en-1-amine (**S1**) and *N*-methylpent-4-en-1-amine (**S2**). Earlier, it was shown that the nature of monoanionic ancillary ligands can have a significant influence on the relative rate of conversion for hydroamination/cyclization reactions catalyzed by neutral rare earth metal complexes versus their corresponding cationic species.[10] Here we have probed the dependence of the relative catalyst performance of neutral and cationic species on the metal size for the neutral N_3 ancillary ligand system.

Results and Discussion

Ligand Synthesis. In an earlier communication, we used 6-dimethylamino-1,4,6-trimethyl-1,4-diazepane (**L′**) to test the suitability of the 6-amino-1,4-diazepane group as an ancillary ligand moiety for rare earth metal alkyl chemistry.[9] The synthesis of **L′** is a two-step reaction: the condensation of 6-amino-1,4,6-trimethyl-1,4-diazepane[11] with formaldehyde followed by reduction over $Na(CN)BH_3$ under acidic conditions. The latter requires control of the pH, as this reaction may potentially release HCN gas. The ligand employed in the present study, 1,4,6-trimethyl-6-pyrrolidin-1-yl-1,4-diazepane (**L**), can be conveniently prepared by reaction of 6-amino-1,4,6-trimethyl-1,4-diazepane with1,4-dibromobutane in the presence of K_2CO_3 in ethanol, as shown in Scheme 1. The ligand was isolated as a colorless liquid with a yield of 57% after distillation.

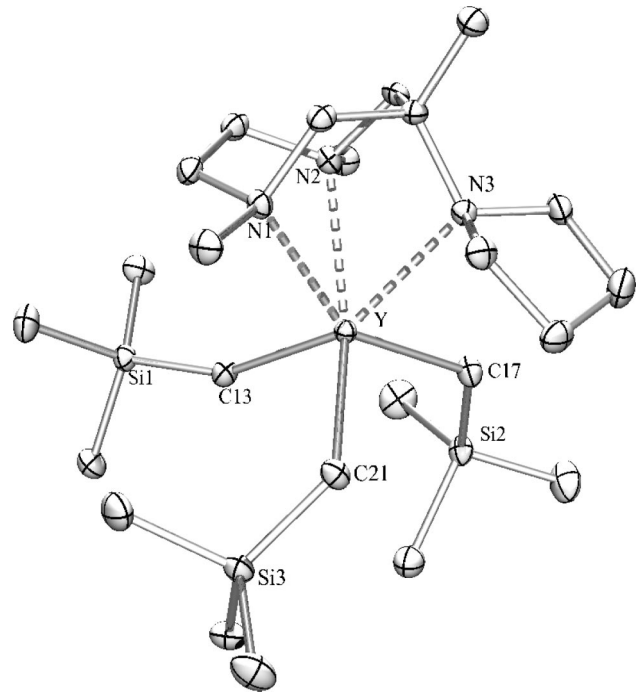
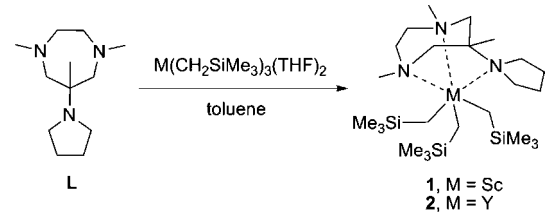


Figure 2. Molecular structure of **2** (hydrogen atoms are omitted for clarity, thermal ellipsoids drawn at 50% probability level).

Scheme 2. Synthesis of Compounds 1 and 2



Synthesis and Characterization of Trialkyl Compounds (L)M(CH$_2$SiMe$_3$)$_3$ (M = Sc, Y). Reaction of the group 3 metal trialkyls $M(CH_2SiMe_3)_3(THF)_2$[12] (M = Sc and Y) with **L** afforded compounds (**L**)$M(CH_2SiMe_3)_3$ (**1**, M = Sc; **2**, M = Y) as crystalline materials after crystallization from toluene/hexane solution (isolated yields: **1**, 70%; **2**, 61%), as shown in Scheme 2. When the reactions are performed in C_6D_6, **1** and **2** are formed quantitatively, as seen by ^{1}H NMR spectroscopy. For both **1** and **2** in C_6D_6, the 1,4-diazepane and pyrrolidinyl ring methylene protons are diastereotopic, indicating that in solution ligand **L** is κ^3 bound to the $M(CH_2SiMe_3)_3$ fragments.

The structures of (isomorphous) **1** and **2** were determined by single-crystal X-ray diffraction. Their molecular structures are

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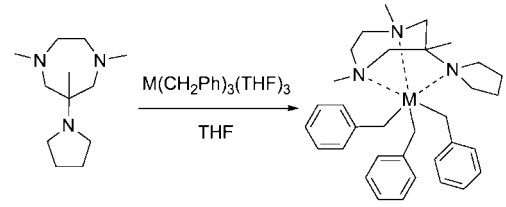
Table 1. Selected Geometrical Data of Compounds 1, 5, and 2

1		5		2	
		Bond Lengths (Å)			
Sc−N1	2.4532(13)	Sc1−N11	2.441(4)	Y−N1	2.6419(16)
Sc−N2	2.5098(13)	Sc1−N12	2.460(5)	Y−N2	2.5647(16)
Sc−N3	2.5270(12)	Sc1−N13	2.396(5)	Y−N3	2.6726(17)
Sc−C13	2.2699(16)	Sc1−C113	2.236(5)	Y−C13	2.388(2)
Sc−C17	2.2735(16)	Sc1−C117	2.289(6)	Y−C17	2.444(2)
Sc−C21	2.2818(16)	Sc1−O11	2.219(4)	Y−C21	2.454(2)
		Bond Angles (deg)			
N1−Sc−N2	66.46(4)	N11−Sc1−N12	67.11(15)	N1−Y−N2	63.65(5)
N2−Sc−N3	69.88(4)	N11−Sc1−N13	73.73(14)	N2−Y−N3	70.26(5)
N1−Sc−N3	73.33(4)	N12−Sc1−N13	77.29(15)	N1−Y−N3	65.98(5)
N1−Sc−C21	154.93(5)	N11−Sc1−C117	158.07(16)	N1−Y−C17	150.40(6)
N2−Sc−C17	159.61(5)	N12−Sc1−C113	168.37(18)	N2−Y−C21	157.89(6)
N3−Sc−C13	160.48(5)	N13−Sc1−O11	160.63(14)	N3−Y−C13	157.85(6)

shown in Figures 1 and 2, respectively. The geometrical data are compiled in Table 1. The metal center in both **1** and **2** has approximately octahedral coordination geometry with a facially coordinated N_3 ligand and three alkyl ligands. In overall geometry, compound **1** is similar to the related trialkyl scandium complex with 6-dimethylamino-1,4,6-trimethyl-1,4-diazepane, (**L′**)Sc(CH_2SiMe_3)$_3$.[9] There is a noticeable difference in the bonding of the three amine donors for these two scandium complexes: the Sc−N distance for the NMe_2 group is intermediate between the other two Sc−N distances in (**L′**)Sc(CH_2SiMe_3)$_3$, whereas the Sc−N distance for the pyrrolidinyl group is the longest of the three Sc−N distances in **1**. The coordination of **L** is to a large extent dictated by minimizing the intramolecular interaction between the pyrrolidinyl group and the trimethylsilylmethyl groups. This can also be seen by the significant difference in orientation of one of the alkyl groups in **1** versus (**L′**)Sc(CH_2SiMe_3)$_3$: the torsion angle of N3−Sc−C17−Si2 in **1** is 100.51(13)° and the corresponding torsion angle in (**L′**)Sc(CH_2SiMe_3)$_3$ is −58.1(3)°. For compound **2**, the average Y−N distance (2.625 Å) is slightly longer than that reported for (Me_3[9]aneN_3)Y(CH_2SiMe_3)$_3$[13] (Y−N 2.601 Å; Y−C 2.427 Å), whereas the average Y−C bond lengths in the two compounds are very similar (Y−C 2.429 Å for **2**). Comparing the average M−N and M−C distances for **1** and **2** indicates that those for Sc are 0.13−0.14 Å shorter, corresponding to the difference in ionic radius between Sc (0.75 Å) and Y (0.90 Å) for a coordination number of 6.[14]

Synthesis and Characterization of Tribenzyl Compounds (L)M(CH_2Ph)$_3$ (M = Sc, La). The rare earth tribenzyl compounds M(CH_2Ph)$_3$(THF)$_3$ are convenient organo rare earth metal starting materials that are readily accessible by reaction of metal trihalides $MX_3(THF)_n$ with benzyl potassium.[8] The tribenzyl complexes (**L**)M(CH_2Ph)$_3$ (**3**, M = Sc; **4**, M = La) were synthesized by reaction of M(CH_2Ph)$_3$(THF)$_3$ (M = Sc, La) with **L** in THF (Scheme 3) and were isolated as crystalline solids by crystallization from THF (isolated yield: **3**, 80%; **4**, 75%). Compounds **3** and **4** are rather poorly soluble in hydrocarbon solvents and sparingly soluble in THF and C_6H_5Br. The ^{1}H NMR resonances for ligand **L** in the compounds **3** and **4** are very similar to those in compounds **1** and **2**. Solution NMR spectroscopy of the Sc compound **3** in C_6D_5Br at ambient temperature showed two sets of signals for three benzyl groups in a ratio of 1:2. The ^{1}H NMR resonances of Sc-CH_2 are found at δ 2.60 and 2.41 ppm and the corresponding ^{13}C NMR resonances at δ 61.6 and 60.7 ppm. This indicates that compound **3** is geometrically rigid in solution on the NMR time scale. In contrast, NMR spectroscopy of the La compound **4** in C_6D_5Br at ambient temperature showed that the three benzyl groups on the lanthanum center are equivalent, indicative of fluxionality of **4** in solution on the NMR time scale, and the resonances of La-CH_2 are found at δ 1.68 ppm (^{1}H) and 69.2 ppm (^{13}C). Once dissolved in THF-d_8 ([La] = 10 mM), compound **4** partially loses the ligand **L** and forms a mixture of La(CH_2Ph)$_3$(THF-d_8)$_3$ and **4** with $K_{eq} = 1.01 \times 10^{-6}$ at 25 °C,[15] as seen by ^{1}H NMR spectroscopy. This ligand dissociation was not observed for the scandium compound **3** in THF-d_8.

Scheme 3. Synthesis of Compounds 3 and 4



Crystal structure determinations of **3** and **4** were performed, and their structures are shown in Figures 2 and 3, respectively, and the geometrical data are listed in Table 2. Compound **3**, like compound **1**, features an approximately octahedral Sc center with the coordination sphere composed of three nitrogen atoms of ligand **L** and three η^1-bound benzyl ligands, with $Sc-CH_2-C_{ipso}$ angles of 115.7(13)−132.7(14)°. The three Sc−N distances (2.4292(19), 2.4331(17), and 2.4512(16) Å) in **3** are comparable, and noticeably shorter than those in **1** (2.4532(13), 2.5098(13), and 2.5270 Å). Unlike its precursor La(CH_2Ph)$_3$(THF)$_3$, which has three η^2-bound benzyl groups, **4** contains one η^1-bound, one η^2-bound, and one η^3-bound benzyl group with $La-CH_2-C_{ipso}$ angles of 121.3(5)°, 96.6(4)°, and 87.7(4)°, respectively. The η^3-bound benzyl has a phenyl group that is significantly tilted, with the difference of 0.61 Å between the two La−C_o distances (La−C33 = 3.177(8) Å and La−C29 = 3.785(8) Å). Benzyl groups η^3-bound to a rare earth metal center have precedent, for example, in [PhC(NAr)$_2$]La(CH_2Ph)$_2$(THF) (Ar = 2,6-diisopropylphenyl)[8c] and (C_5Me_5)$_2$MCH_2Ph (M = Sm[16a] and Ce[16b]).

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(15) Equation used to calculate the equilibrium constant K_{eq}: (**L**)La(CH_2Ph)$_3$ + 3 THF-d_8 ⇌ La(CH_2Ph)$_3$(THF-d_8)$_3$ + **L**: K_{eq} = [La(CH_2Ph)$_3$(THF-d_8)$_3$][**L**]/[(**L**)La(CH_2Ph)$_3$][THF-d_8]^3. In a solution of (**L**)La(CH_2Ph)$_3$ (10 mM) in THF-d_8, (**L**)La(CH_2Ph)$_3$ (6.5 mM), La(CH_2Ph)$_3$(THF-d_8) (3.5 mM), and **L** (3.5 mM) were detected by ^{1}H NMR spectroscopy. [THF-d_8] (12.3 M) was used to calculate K_{eq}.

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Table 2. Geometrical Data of Compounds 4 and 5

4		5	
	Bond Lengths (Å)		
Sc−N1	2.4292(19)	La−N1	2.736(5)
Sc−N2	2.4331(17)	La−N2	2.816(6)
Sc−N3	2.4512(18)	La−N3	2.775(5)
Sc−C13	2.341(2)	La−C13	2.716(7)
Sc−C20	2.314(2)	La−C20	2.633(7)
		La−C21	3.154(7)
Sc−C27	2.295(2)	La−C27	2.661(7)
		La−C28	2.965(7)
		La−C33	3.177(8)
	Bond Angles (deg)		
N1−Sc−N2	68.09(6)	N1−La−N2	59.82(17)
N2−Sc−N3	73.68(6)	N1−La−N3	63.19(16)
N1−Sc−N3	72.16(6)	N2−La−N3	64.89(17)
N1−Sc−C13	157.15(6)	N1−La−C20	141.2(2)
N2−Sc−C20	168.34(7)	N2−La−C27	151.57(19)
N3−Sc−C27	161.00(7)	C3−La−C13	150.20(18)
Sc−C13−C14	115.72(17)	La−C13−C14	121.3(5)
Sc−C20−C21	125.21(14)	La−C20−C21	96.6(4)
Sc−C27−C28	132.73(14)	La−C27−C28	87.7(4)

Generation and Characterization of Ionic Dialkyl and Dibenzyl Compounds. Upon reaction of the trialkyl complexes **1** and **2** with $[PhNMe_2H][B(C_6F_5)_4]$ in the weakly coordinating solvent C_6D_5Br, instantaneous liberation of 3 equiv of TMS was observed by ^1H NMR spectroscopy, and no well-defined cations could be identified. Apparently, the initially formed dialkyl cation is thermally labile, decomposing through ligand H-abstraction processes. This decomposition of the dialkyl cations can be prevented when the reactions are carried out in THF (Scheme 4). The ionic compounds $[(\mathbf{L})M(CH_2SiMe_3)_2(THF)][B(C_6H_5)_4]$ (M = Sc, **5**; M = Y, **6**) were isolated as analytically pure, white, microcrystalline powders by layering their THF solutions with *n*-hexane (isolated yield: **5**, 84%; **6**, 86%). The compounds contain one THF molecule per metal center, as seen by elemental analysis.

The structure of **5** was established by single-crystal X-ray diffraction and is shown in Figure 4 (for easy comparison, the geometrical data of **5** are listed in Table 1 together with those of **1**). The geometry around the scandium center in the cation of **5** is again distorted octahedral, as in its neutral trialkyl precursor **1**. The ligand in **5** is bound more tightly to the Sc center than in **1**, as seen by the shorter Sc−N average distance and the larger N−Sc−N angles in **5** compared with those in **1**, indicating that the Sc center in the cation of **5** is more electrophilic. The differences between the corresponding Sc−C and Sc−N distances in neutral and cationic species are relatively small, with one notable exception. The position taken in the neutral compound **1** by the alkyl group *trans* to the pyrrolidinyl nitrogen, with the shortest Sc−C13 distance (2.2699 Å) and largest N3−Sc−C13 angle (160.48°), is occupied in the ionic compound **5** by the coordinated THF molecule. With this, the longest Sc−N (2.527 Å) bond (to the pyrrolidinyl nitrogen N3) in **1** becomes the shortest Sc1−N13 (2.396 Å) bond with N13−Sc1−O11 = 160.63° in **5**, indicating that the Sc−N(amine) distances in these complexes are very sensitive to the nature of the group *trans* to it. Similar phenomena were observed previously in various triamine-amide and 6-amide-1,4-diazepane rare earth metal alkyl complexes.[17]

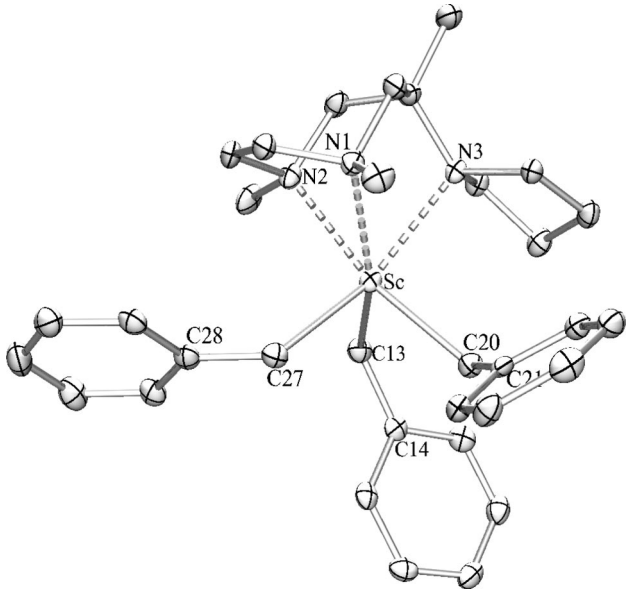


Figure 3. Molecular structure of **3** (hydrogen atoms are omitted for clarity, thermal ellipsoids drawn at 50% probability level).

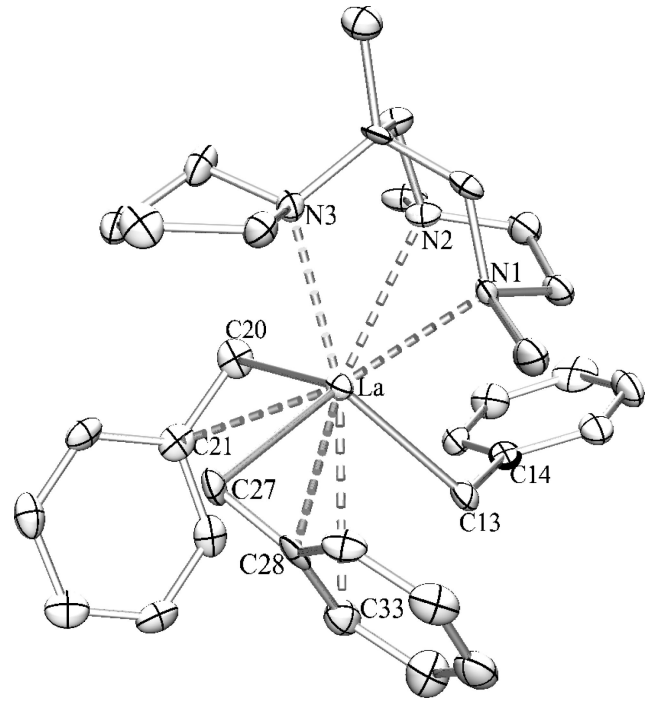
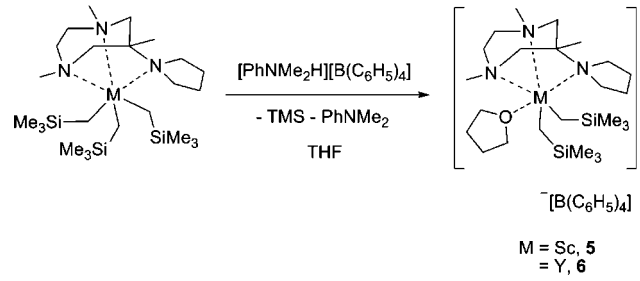


Figure 4. Molecular structure of **4** (hydrogen atoms are omitted for clarity, thermal ellipsoids drawn at 50% probability level).

Scheme 4. Generation of the Ionic Compounds 5 and 6



In contrast to the trialkyl complexes **1** and **2**, the tribenzyl compounds **3** and **4** can be cleanly converted to the corresponding cations $[(\mathbf{L})M(CH_2Ph)_2]^+$ by reaction with $[PhNMe_2H][B(C_6F_5)_4]$ in C_6D_5Br (as seen by NMR spec-

(17) (a) Ge, S.; Meetsma, A; Hessen, B. *Organometallics* **2007**, *26*, 5278. (b) Bambirra, S.; Meetsma, A.; Hessen, B.; Bruins, A. P. *Organometallics* **2006**, *25*, 3486. (c) Bambirra, S.; Boot, S. J.; van. Leusen, D.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, *23*, 1891.

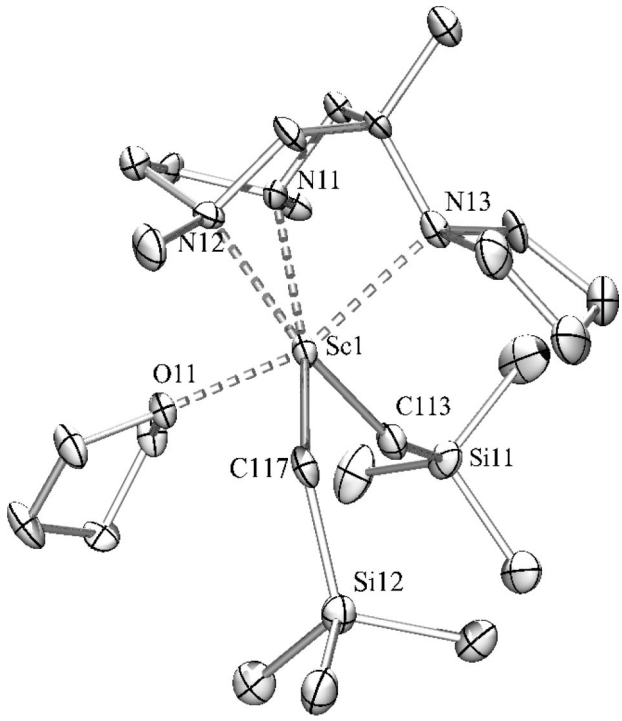


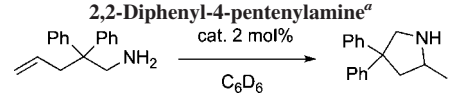
Figure 5. Molecular structure of **5** (hydrogen atoms and anion $[B(C_6H_5)_4]^-$ are omitted for clarity, thermal ellipsoids drawn at 50% probability level).

troscopy), accompanied by release of toluene and free $PhNMe_2$. Both cations are thermally robust and can be stored in C_6D_5Br solution for at least one day without decomposition. This enhanced thermal stability in the absence of THF might be due to η^n-coordination of the remaining benzyl groups. The ^{13}C NMR resonances of the M-$\underline{C}H_2Ph$ groups are found at δ 64.7 ppm for $[(\mathbf{L})Sc(CH_2Ph)_2]^+$ and δ 71.7 ppm for $[(\mathbf{L})La(CH_2Ph)_2]^+$, showing a typical downfield shift compared with their neutral precursors (61.1 ppm for **3** and 69.2 ppm for **4**), associated with generation of cationic species.[2c,h]

Comparative Catalysis Study of Intramolecular Hydroamination/Cyclization of Aminoalkenes. The intramolecular hydroamination/cyclization of aminoalkenes by organo rare earth metal catalysts has been extensively investigated.[4] Nevertheless, only a limited number of reports exist concerning the comparative study of neutral catalysts versus their cationic congeners.[8c,10,18] In this contribution, we have compared the activities of the neutral and cationic rare earth metal alkyl or benzyl complexes reported here in the hydroamination/cyclization of 2,2-diphenylpent-4-en-1-amine (**S1**) and *N*-methylpent-4-en-1-amine (**S2**). Control experiments with $Sc(CH_2Ph)_3(THF)_3$, $Y(CH_2SiMe_3)_3(THF)_3$, $La(CH_2Ph)_3(THF)_3$, and their monocationic derivatives were also carried out. All cationic species were generated *in situ* from neutral precursors by reaction with $[PhNMe_2H][B(C_6F_5)_4]$.

For substrate **S1** (Table 3), a comparison of the neutral and cationic catalyst species shows that for both types of species the reactions are first order in substrate concentration over the full conversion range (see Supporting Information). Most

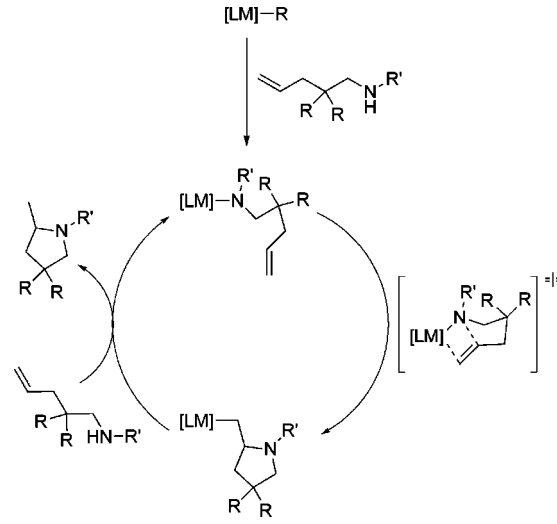
Table 3. Catalytic Hydroamination/Cyclization of 2,2-Diphenyl-4-pentenylamine[a]



entry	catalyst	time (min)	conv (%)[c]	k (L mol^{-1} s^{-1})
1	$Sc(CH_2Ph)_3(THF)_3$	600[b]	40	4.74×10^{-4}
2	**1** or **3**	600[b]	54	9.00×10^{-4}
3	$Sc(CH_2Ph)_3(THF)_3$/**B**	500[b]	>99	5.34×10^{-3}
4	**1** or **3**/**B**	240[b]	0	
5	$Y(CH_2SiMe_3)_3(THF)_3$	600[b]	>99	3.68×10^{-3}
6	**2**	400[b]	>99	7.48×10^{-3}
7	$Y(CH_2SiMe_3)_3(THF)_2$/**B**	180	88	[d]
8	**2**/**B**	5	>99	8.11×10^{-1}
9	$La(CH_2Ph)_3(THF)_3$	200	>99	1.98×10^{-2}
10	**4**	200	>99	1.99×10^{-2}
11	$La(CH_2Ph)_3(THF)_3$/**B**	240	51	[d]
12	**4**/**B**	70	>99	6.48×10^{-2}

[a] Conditions: C_6D_6 solvent (total volume 0.5 mL), 60 °C, catalyst (10 μmol), and activator $[PhNMe_2H][B(C_6F_5)_4]$ (**B**, 10 μmol) where appropriate, substrate (500 μmol). [b] 80 °C. [c] Determined by *in situ* NMR spectroscopy. [d] Not determined, due to the poor solubility of the catalyst.

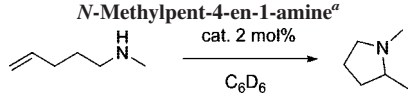
Scheme 5



catalyzed cyclizations of **S1** and related substrates show a zero-order dependence on substrate concentration, consistent with rate-determining intramolecular insertion of the olefin into the metal–nitrogen bond (Scheme 5).[4j–l] Deviations from this behavior are often found at higher substrate conversions, where they are associated with product inhibition (formation of metal secondary amide species).[4g,h,j,k] We observed a few instances of first-order behavior over the full conversion range with nonmetallocene rare earth metal catalysts before,[10] but as yet have no unambiguous explanation for this phenomenon. For neutral catalysts **1**–**4**, compound **4**, with the largest metal (La), shows the highest activity (entries 2, 6, and 10). No catalytic activity was observed for the cationic Sc system (entry 4), and the cationic Y and La species show higher activities than their neutral precursors (entries 6 and 8; 10 and 12). Remarkably, the activity of the Y catalyst increases substantially when converted to the cationic species (entry 6 and 8), producing easily the most active catalyst in the entire series. The control experiments (entries 1, 5, and 9) indicate that the neutral ligand **L** does enhance the activity (except for the neutral La system), especially for the cationic systems where the catalysts are sparingly soluble without **L** and precipitate as oily materials during the catalysis. For the neutral La system, **4** and

(18) Lauterwasser, F.; Hayes, P. G.; Bräse, S.; Piers, W. E.; Schafer, L. L. *Organometallics* **2004**, *23*, 2234.
(19) (a) De Kimpe, N.; De Smaele, D.; Hofkens, A.; Dejaegher, Y.; Kesteleyn, B. *Tetrahedron* **1997**, *53*, 10803–10816. (b) Tokuda, M.; Yamada, Y.; Takagi, T.; Suginome, H. *Tetrahedron* **1987**, *43*, 281.

Table 4. Catalytic Hydroamination/Cyclization of *N*-Methylpent-4-en-1-amine[a]



entry	catalyst	time/(min)	conv/(%)[b]	k/s^{-1}[c]
1	$Sc(CH_2Ph)_3(THF)_3$	30	>99	1.10×10^{-1} L.mol^{-1}.s^{-1}
2	**1**	30	>99	9.88×10^{-2} L.mol^{-1}.s^{-1}
3	$Sc(CH_2Ph)_3(THF)_3$/**B**	240	72	4.50×10^{-3} L.mol^{-1}.s^{-1}
4	**1/B**	240	0	
5	$Y(CH_2SiMe_3)_3(THF)_2$	25	>99	4.18×10^{-2}
6	**2**	40	>99	4.12×10^{-2}
7	$Y(CH_2SiMe_3)_3(THF)_2$/**B**	40	>99	2.58×10^{-2}
8	**2/B**	275	>99	4.50×10^{-3}
9	$La(CH_2Ph)_3(THF)_3$	15	>99	9.15×10^{-2}
10	**4**	15	>99	1.00×10^{-1}
11	$La(CH_2Ph)_3(THF)_3$/**B**	10	>99	1.31×10^{-1}
12	**4/B**	10	>99	1.32×10^{-1}

[a] Conditions: C_6D_6 solvent (total volume 0.5 mL), 60 °C, catalyst (10 μmol), and activator $[PhNMe_2H][B(C_6F_5)_4]$ (**B**, 10 μmol), where appropriate, substrate (500 μmol). [b] Determined by *in situ* NMR spectroscopy. [c] Calculated over the first 50% conversion.

$La(CH_2Ph)_3(THF)_3$ show the same activity, indicating that **L** may dissociate from the metal in the presence of excess amine **S1**. This is plausible, considering our observation (described above) that dissociation of **L** occurs when **4** is dissolved in neat THF.

Another substrate employed in this study is the secondary amine **S2**, and the results are summarized in Table 4. All the reactions essentially go to completion (except for **1**/B), and the catalysts with the metal with the largest ionic radius (La) show higher activity. For Sc catalysts, **1** and $Sc(CH_2Ph)_3(THF)_3$ show similar reaction rates (entry 1 and 2), and no conversion was observed for the cationic system **1/B**. For the Y catalysts, the cationic species in this case is less active than its neutral precursor (entries 6 and 8), but the cationic system is more active for the La systems (entries 10 and 12). The control experiments indicated that **L** actually slows down the catalysis by the Y catalysts (entries 5 and 6; 7 and 8). This might be due to the increased steric demand of the secondary amine substrate **S2** relative to **S1** and relatively strong coordination of the ligand to the Y center during the catalysis, thus making the Y center sterically more crowded. This can also be seen by the observation that all alkyl groups of $Y(CH_2SiMe_3)_3(THF)_2$ were instantaneously protonated upon mixing with **S2**, whereas some of the alkyl groups attached to the Y center in **2** were still detectable even after 20 min at 60 °C during the catalysis. For the larger metal La, **L** does not influence the catalysis by either neutral or cationic catalysts. For substrate **S2**, the catalysis by Y and La systems shows a zero-order dependence in substrate concentration over the first 50% conversion (characteristic of rate-limiting intramolecular alkene insertion into the metal−amido bond; Scheme 5), indicating a change in rate-determining step at lower substrate concentrations (likely to reflect substrate inhibition, see above). In contrast, a first-order dependence on the substrate concentration was observed for the Sc catalysts.

Conclusion

We have shown that the 1,4,6-trimethyl-6-pyrrolidin-1-yl-1,4-diazepane ligand (**L**) is suitable to support well-defined neutral and cationic alkyl and benzyl scandium, yttrium, and lanthanum complexes and can thus be applied over the full size range of the rare earth metals. The benzyl group imparts greater stability to these complexes than the trimethylsilyl group. This is likely to be due to the possibility of multihapto bonding of the benzyl groups, illustrated, for example, by the structure of (**L**)$La(CH_2Ph)_3$ (**4**), which contains one η^1, one η^2, and one η^3 group. Whereas the tridentate ligand **L** is apparently tightly bound to Sc and Y, it is readily displaced from the large La center by a large excess of monodentate Lewis bases.

The prepared neutral compounds and their monocationic derivatives catalyze the intramolecular hydroamination/cyclization of primary and secondary aminoalkenes. The substrates display quite different requirements for effective catalysis: the primary amine 2,2-diphenylpent-4-en-1-amine is most efficiently converted by the cationic (**L**)Y catalyst, but the secondary amine *N*-methylpent-4-en-1-amine simply prefers the least sterically demanding catalyst (the cationic La system).

Experimental Section

General Remarks. All preparations were performed under an inert nitrogen atmosphere, using standard Schlenk or glovebox techniques, unless mentioned otherwise. Toluene, pentane, and hexane (Aldrich, anhydrous, 99.8%) were passed over columns of Al_2O_3 (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Diethyl ether and THF (Aldrich, anhydrous, 99.8%) were dried over Al_2O_3 (Fluka). All solvents were degassed prior to use and stored under nitrogen. Deuterated solvents (C_6D_6, C_7D_8, C_4D_8O; Aldrich) were vacuum-transferred from Na/K alloy. NMR spectra were recorded on Varian VXR 300, Varian Mercury 400, or Varian Inova 500 spectrometers in NMR tubes equipped with a Teflon (Young) valve. The ^{1}H NMR spectra were referenced to resonances of residual protons in deuterated solvents. The ^{13}C NMR spectra were referenced to carbon resonances of deuterated solvents and reported in ppm relative to TMS (δ 0 ppm). 6-Amino-1,4,6-trimethyl-1,4-diazepine,[9] $M(CH_2SiMe_3)_3(THF)_2$ (M = Sc and Y),[12] $Sc(CH_2Ph)_3(THF)_3$,[8a] $La(CH_2Ph)_3(THF)_3$,[8c] 2,2-diphenyl-4-pentenylamine,[19a] and *N*-methyl-4-pentenylamine[19b] were prepared according to published procedures.

Synthesis of 6-Pyrrolidinyl-1,4,6-trimethyl-1,4-diazepine (L). A mixture of 6-amino-1,4,7-trimethyl-1,4-diazepine (4.20 g, 26.7 mmol), 1,4-dibromobutane (5.77 g, 26.7 mmol), and K_2CO_3 (3.69 g, 26.7 mmol) in ethanol (80 mL) was stirred for 36 h at 60 °C. H_2O (40 mL) was added to the mixture, and the resulting solution was acidified (pH < 1) with 35% HCl solution. All the volatiles were removed under reduced pressure, and the residue was redissolved in water (40 mL) and then made basic (pH > 12) with 40% NaOH solution. The mixture was extracted twice with CH_2Cl_2 (70 mL), and the combined organic layer was dried over Na_2SO_4. All the volatiles were removed under reduced pressure, and the residue was purified by Kugelrohr distillation to give the title compound (3.22 g, 15.2 mmol, 57%) as a colorless liquid. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 2.84 and 2.26 (AB system, 4H, CCH_2), 2.73 (m, 4H, Py α-*H*), 2.38 (m, 4H, NCH_2), 2.19 (s, 6H, NCH_3), 1.62 (m, 4H, Py β-*H*), 1.18 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 25 °C): δ 66.3 (CCH_2), 62.4 (NCH_2), 58.6 (CCH_3), 49.1 (NCH_3), 46.3 (Py α-*C*), 24.5 (CCH_3), 24.1 (Py β-*C*). Anal. Calc for $C_{12}H_{25}N_3$: C, 68.20; H, 11.92; N, 19.88. Found: C, 67.41; H, 11.97; N, 19.75.

Synthesis of (L)Sc(CH$_2$SiMe$_3$)$_3$ (1). To a solution of $Sc(Me_3SiCH_2)_3(THF)_2$ (0.44 g, 0.98 mmol) in toluene (20 mL) was added dropwise a solution of **L** (0.21 g, 0.99 mmol) in toluene (20 mL) while stirring. The mixture was stirred at room temperature for 30 min, and then the volatiles were removed under reduced pressure. The slightly yellow residue was dissolved in toluene (3 mL), and pentane (5 mL) was layered on top. Upon cooling to −30 °C, crystalline material formed, including material suitable for X-ray diffraction. The mother liquor was decanted and the solid was dried under reduced pressure, yielding the title compound as a slightly yellow solid (0.37 g, 0.71 mmol, 72%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 3.10 (m, 2H, Py α-*H*), 3.08 (m, 2H, NCH_2), 2.25 (d, 2H, J_{HH} = 14.0 Hz, CCH_2), 2.19 (s, 6H, NCH_3), 2.02 (m, 2H, Py α-*H*), 1.76 (m, 2H, Py β-*H*), 1.54 (m, 2H, NCH_2), 1.35 (d, 2H, J_{HH} = 14.0 Hz, CCH_2),

1.31 (m, 2H, Py β-*H*), 0.47 (s, 27H, Si(C*H*$_3$)$_3$), −0.0 (s, 3H, CC*H*$_3$), −0.11 (br, 6H, ScC*H*$_2$). ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 70.5 (t, J_{CH} = 138.1 Hz, C*C*H$_2$), 59.5 (s, *C*CH$_3$), 59.1 (t, J_{CH} = 138.4 Hz, N*C*H$_2$), 50.8 (q, J_{CH} = 136.6 Hz, N*C*H$_3$), 48.1 (t, J_{CH} = 134.8 Hz, Py α-*C*), 39.7 (br, Sc*C*H$_2$, the J_{CH} coupling on ScCH$_2$ is not resolved), 24.5 (t, J_{CH} = 131.3 Hz, Py β-*C*), 12.2 (q, J_{CH} = 127.3 Hz, C*C*H$_3$), 4.7 (q, J_{CH} = 117.0 Hz, Si(*C*H$_3$)$_3$). Anal. Calc for $C_{24}H_{58}N_3Si_3Sc$: C, 55.65; H, 11.29; N, 8.11. Found: C, 55.48; H, 11.26; N, 7.81.

Synthesis of (L)Y(CH$_2$SiMe$_3$)$_3$ (2). To a solution of Y(Me$_3$SiCH$_2$)$_3$(THF)$_2$ (0.49 g, 0.99 mmol) in toluene (30 mL) was added dropwise a solution of **L** (0.21 g, 0.99 mmol) in toluene (20 mL) while stirring. The mixture was stirred at room temperature for 30 min, and then the volatiles were removed under reduced pressure. The slightly yellow residue was dissolved in toluene (3 mL), and pentane (6 mL) was layed on top. Upon cooling to −30 °C, crystalline material formed, including material suitable for X-ray diffraction. The mother liquor was decanted and the solid was dried under reduced pressure, yielding the title compound as a white solid (0.34 g, 0.61 mmol, 61%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 3.07 (m, 2H, NC*H*$_2$), 3.06 (m, 2H, Py α-*H*), 2.17 (d, 2H, J_{HH} = 14.3 Hz, CC*H*$_2$), 2.16 (s, 6H, NC*H*$_3$), 2.03 (m, 2H, Py α-*H*), 1.75 (m, 2H, Py β-*H*), 1.53 (m, 2H, NC*H*$_2$), 1.32 (m, 2H, Py β-H), 1.31 (d, 2H, J_{HH} = 14.3 Hz, CC*H*$_2$), 0.47 (s, 27H, Si(C*H*$_3$)$_3$), −0.03 (s, 3H, CC*H*$_3$), −0.54 (d, 6H, J_{YH} = 2.8 Hz, YC*H*$_2$). ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 69.9 (t, J_{CH} = 135.1 Hz, C*C*H$_2$), 59.7 (s, *C*CH$_3$), 58.2 (t, J_{CH} = 138.3 Hz, N*C*H$_2$), 49.7 (q, J_{CH} = 136.0 Hz, N*C*H$_3$), 47.0 (t, J_{CH} = 138.3 Hz, Py α-*C*), 35.5 (dt, J_{CH} = 96.5 Hz, J_{YC} = 36.2 Hz, Y*C*H$_2$), 24.6 (t, J_{CH} = 134.3 Hz, Py β-*C*), 12.2 (q, J_{CH} = 129.0 Hz, C*C*H$_3$), 4.9 (q, J_{CH} = 115.8 Hz, Si(*C*H$_3$)$_3$). Anal. Calc ($C_{24}H_{58}N_3Si_3Y$): C, 51.3; H, 10.40; 7.48. Found: C, 51.0; H, 10.42; N, 7.46.

Synthesis of (L)Sc(CH$_2$Ph)$_3$ (3). To a solution of Sc(CH$_2$Ph)$_3$(THF)$_3$ (0.242 g, 0.453 mmol) in THF (10 mL), was added a solution of **L** (0.096 g, 0.454 mmol) in THF (10 mL). The resulting mixture was stirred at room temperature for 30 min and then concentrated to 4 mL. Upon cooling to −30 °C, colorless crystalline material formed. The mother liquor was decanted and the solid was dried under vacuum to give the title compound (**L**)Sc(CH$_2$Ph)$_3$·(THF) (0.217 g, 0.361 mmol, 80%) as colorless crystals. Crystals suitable for X-ray analysis were grown from a saturated THF solution. ^{1}H NMR (500 MHz, C_6D_5Br, 25 °C): δ 7.15 (t, 4H, J_{HH} = 7.43 Hz, *m-H* Ph), 7.07 (t, 2H, J_{HH} = 7.47 Hz, *m-H* Ph), 7.04 (d, 4H, J_{HH} = 7.54 Hz, *o-H* Ph), 6.89 (d, 4H, J_{HH} = 7.58 Hz, *o-H* Ph), 6.74 (t, 2H, J_{HH} = 7.24 Hz, *p-H* Ph), 6.68 (t, 1H, J_{HH} = 7.11 Hz, *p-H* Ph), 2.99 (m, 2H, Py α-*H*), 2.74 (m, 2H, NC*H*$_2$), 2.60 (br, 2H, ScC*H*$_2$), 2.41 (br, 4H, ScC*H*$_2$), 2.41 (d, 2H, J_{HH} = 14.0 Hz, CC*H*$_2$), 2.03 (s, 6H, NC*H*$_3$), 1.97 (m, 2H, Py α-*H*), 1.74 (m, 2H, Py β-*H*), 1.67 (m, 2H, NC*H*$_2$), 1.63 (d, 2H, J_{HH} = 14.0 Hz, CC*H*$_2$), 1.33 (m, 2H, Py β-*H*), 0.26 (s, 3H, CC*H*$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_5Br, 25 °C): δ 154.4 (*ipso-C* Ph), 154.1 (*ipso-C* Ph), 128.0 (*m-C* Ph), 127.9 (*m-C* Ph), 124.3 (*o-C* Ph), 123.5 (*o-C* Ph), 117.5 (*p-C* Ph), 117.4 (*p-C* Ph), 70.8 (C*C*H$_2$), 61.6 (br, Sc*C*H$_2$), 60.7 (br, Sc*C*H$_2$), 59.6 (*C*CH$_3$), 58.1 (N*C*H$_2$), 49.7 (N*C*H$_3$), 47.5 (Py α-*C*), 24.7 (Py β-*C*), 11.9 (C*C*H$_3$). Anal. Calcd for $C_{37}H_{54}N_3OSc$: C, 73.84; H, 9.04; N, 6.98. Found: C, 73.31; H, 8.93; N, 6.96.

Synthesis of (L)La(CH$_2$Ph)$_3$ (4). To a solution of La(CH$_2$Ph)$_3$(THF)$_3$ (233.8 mg, 0.372 mmol) in THF (2 mL), was added **L** (78.6 mg, 0.372 mmol). The resulting mixture was allowed to stand at room temperature overnight, and a yellow crystalline material formed, suitable for X-ray analysis. The mother liquor was decanted and the solid was dried under vacuum to give the title compound (172.6 mg, 0.278 mmol, 75%) as a yellow crystalline solid. ^{1}H NMR (500 MHz, C_6D_5Br, 25 °C): δ 7.11 (t, 6H, J_{HH} = 7.83 Hz, *m-H* Ph), 6.62 (t, 3H, J_{HH} = 7.25 Hz, *p-H* Ph), 6.60 (d, 6H, J_{HH} = 7.47 Hz, *o-H* Ph), 2.74 (m, 2H, NC*H*$_2$), 2.60 (m, 2H, Py α-*H*), 2.36 (d, 2H, J_{HH} = 14.3 Hz, CC*H*$_2$), 2.04 (s, 6H, NC*H*$_3$), 2.04 (m, 2H, Py α-*H*), 1.74 (m, 2H, NC*H*$_2$), 1.69 (d, 2H, J_{HH} = 14.3 Hz, CC*H*$_2$), 1.68 (s, 6H, LaC*H*$_2$), 1.58 (m, 2H, Py β-*H*), 1.37 (m, 2H, Py β-*H*), 0.28 (s, 3H, CC*H*$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_5Br, 25 °C): δ 151.8 (*ipso-C* Ph), 129.7 (*m-C* Ph), 121.8 (*o-C* Ph), 116.0 (*p-C* Ph), 69.6 (C*C*H$_2$), 69.2 (La*C*H$_2$), 60.5 (*C*CH$_3$), 57.0 (N*C*H$_2$), 48.7 (N*C*H$_3$), 45.7 (Py α-*C*), 25.8 (Py β-*C*), 12.5 (C*C*H$_3$). Anal. Calcd for $C_{33}H_{46}N_3La$: C, 63.55; H, 7.43; N, 6.74. Found: C, 62.82; H, 7.41; N, 6.56.

Synthesis of [(L)Sc(CH$_2$SiMe$_3$)$_2$(THF)][B(C$_6$H$_5$)$_4$] (5). THF (2 mL) was added to a mixture of **1** (77.7 mg, 150 μmol) and [PhMe$_2$NH][B(C$_6$H$_5$)$_4$] (66.2 mg, 150 μmol). The solution was homogenized by agitation and allowed to stand for about 20 min. *n*-Hexane (2 mL) was added to the mixture to form a white precipitate, and more THF was added to just dissolve this. A colorless crystalline material formed upon cooling to −30 °C. The mother liquor was decanted and the solid was dried under reduced pressure, yielding the title compound as a white solid (103.9 mg, 126 μmol, 84%). Crystals for single-crystal X-ray diffraction were obtained by recrystallization from a mixture of THF and toluene. ^{1}H NMR (500 MHz, THF-d_8, 25 °C): δ 7.32 (br, 8H, *o-H* Ph), 6.91 (t, 8H, J_{HH} = 7.62 Hz, *m-H* Ph), 6.78 (t, 4H, J_{HH} = 7.35 Hz, *p-H* Ph), 3.62 (m, 4H, α-*H* THF), 3.36 (m, 2H, Py α-*H*), 2.93 (d, 2H, J_{HH} = 14.3 Hz, CC*H*$_2$), 2.75 (m, 2H, NC*H*$_2$), 2.70 (m, 2H, Py α-*H*), 2.37 (s, 6H, NC*H*$_3$), 2.26 (m, 2H, NC*H*$_2$), 2.23 (d, 2H, J_{HH} = 14.3 Hz, CC*H*$_2$), 2.04 (m, 2H, Py β-*H*) 1.87 (m, 2H, Py β-H), 1.77 (m, 4H, β-*H* THF), 0.69 (s, 3H, CC*H*$_3$), −0.02 (s, 18H, Si(C*H*$_3$)$_3$), −0.27 (s, 4H, ScC*H*$_2$). ^{13}C NMR (125.7 MHz, THF-d_8, 25 °C): δ 166.4 (q, J_{BC} = 46.5 Hz, *ipso-C* Ph), 138.4 (d, J_{CH} = 155.9 Hz, *o-C* Ph), 127.1 (d, J_{CH} = 152.7 Hz, *m-C* Ph), 123.3 (d, J_{CH} = 159.1 Hz, *p-C* Ph), 71.6 (t, J_{CH} = 138.3 Hz, C*C*H$_2$), 69.4 (t, J_{CH} = 134.6 Hz, α-*C* THF), 63.2 (s, *C*CH$_3$), 60.2 (t, J_{CH} = 139.4 Hz, N*C*H$_2$), 52.4 (q, J_{CH} = 138.1 Hz, N*C*H$_3$), 50.5 (t, J_{CH} = 139.6 Hz, Py α-*C*), 47.6 (t, J_{CH} = 94.6 Hz, Sc*C*H$_2$), 27.6 (t, J_{CH} = 132.2 Hz, β-*C* THF), 26.6 (t, J_{CH} = 130.9 Hz, Py β-*C*), 14.4 (q, J_{CH} = 116.2 Hz, C*C*H$_3$), 4.8 (q, J_{CH} = 116.9 Hz, Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{48}H_{75}BN_3OScSi_2$: C, 70.13; H, 9.20; N, 5.11. Found: C, 70.50; H, 9.22; N, 5.15.

Synthesis of [(L)Y(CH$_2$SiMe$_3$)$_2$(THF)][B(C$_6$H$_5$)$_4$] (6). THF (2 mL) was added to a mixture of **2** (84.3 mg, 150 μmol) and [PhMe$_2$NH][B(C$_6$H$_5$)$_4$] (66.2 mg, 150 μmol). The solution was homogenized by agitation and allowed to stand for about 20 min. *n*-Hexane (2 mL) was added to the mixture to form a white precipitate, and more THF was added to just dissolve this. Upon cooling to −30 °C, a crystalline material formed. The mother liquor was decanted and the solid was dried under reduced pressure, yielding the title compound as a white solid (112 mg, 129 μmol, 86%). ^{1}H NMR (500 MHz, THF-d_8, 25 °C): δ 7.32 (br, 8H, *o-H* Ph), 6.91 (t, 8H, J_{HH} = 7.62 Hz, *m-H* Ph), 6.78 (t, 4H, J_{HH} = 7.35 Hz, *p-H* Ph), 3.61 (m, 4H, α-*H* THF), 3.19 (m, 2H, Py α-*H*), 2.94 (d, 2H, J_{HH} = 14.4 Hz, CC*H*$_2$), 2.86 (m, 2H, NC*H*$_2$), 2.72 (m, 2H, Py α-*H*), 2.43 (s, 6H, NC*H*$_3$), 2.35 (m, 2H, NC*H*$_2$), 2.32 (d, 2H, J_{HH} = 14.4 Hz, CC*H*$_2$), 1.97 (m, 2H, Py β-*H*) 1.90 (m, 2H, Py β-H), 1.77 (m, 4H, β-*H* THF), 0.72 (s, 3H, CC*H*$_3$), −0.04 (s, 18H, Si(C*H*$_3$)$_3$), −0.74 (d, 4H, J_{YH} = 3.1 Hz, YC*H*$_2$). ^{13}C{^{1}H} NMR (125.7 MHz, THF-d_8): δ 166.4 (q, J_{BC} = 46.5 Hz, *ipso-C* Ph), 138.4 (*o-C* Ph), 127.1 (*m-C* Ph), 123.3 (*p-C* Ph), 71.0 (C*C*H$_2$), 69.4 (α-*C* THF), 63.1 (*C*CH$_3$), 59.4 (N*C*H$_2$), 51.2 (Py α-*C*), 48.8 (N*C*H$_3$), 40.7 (d, J_{YC} = 42.0 Hz, Y*C*H$_2$), 27.6 (β-*C* THF), 26.5 (Py β-*C*), 14.3 (C*C*H$_3$), 5.2 (Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{46}H_{73}BN_3OSi_2Y$: C, 66.57; H, 8.73; N, 4.85. Found: C, 66.77; H, 8.55; N, 5.02.

Reaction of 3 with [PhNMe$_2$H[B(C$_6$F$_5$)$_4$]. In a Tomas tube, C_6D_5Br (0.6 mL) was added to a mixture of **3** (5.3 mg, 10 μmol) and [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (8.0 mg, 10 μmol), and the resulting solution was transferred to an NMR tube equipped with a Teflon (Young) valve. NMR analysis indicated clean conversion to the corresponding cationic dibenzyl species, toluene, and free PhNMe$_2$. ^{1}H NMR (500 MHz, C_6D_5Br, 40 °C): δ 7.09 (t, 4H, J_{HH} = 7.4 Hz, Ph, *m-H*), 6.92 (d, 4H, J_{HH} = 6.8 Hz, Ph *o-H*), 6.74 (t, 2H, J_{HH} = 7.4 Hz, Ph *p-H*), 2.73 (m, 2H, Py α-*H*), 2.41 (d, 2H, J_{HH} = 13.8 Hz, CC*H*$_2$), 2.23 (br, 4H, ScC*H*$_2$), 2.15 (m, 2H, Py α-*H*), 2.10 (s, 6H, NC*H*$_3$), 1.83 (d, 2H, J_{HH} = 13.8 Hz, CC*H*$_2$), 1.82 (m, 2H, NC*H*$_2$), 1.77, (m, 2H, Py β-H), 1.58

Table 5. Crystal Data and Collection Parameters of Complexes 1−5

	1	**2**	**3**·C_4H_8O	**4**	**5**·[1.5(C_7H_8)]
formula	$C_{24}H_{58}N_3Si_3Sc$	$C_{24}H_{58}N_3Si_3Y$	$C_{37}H_{54}N_3OSc$	$C_{33}H_{46}LaN_3$	$BC_{48}H_{75}N_3OSi_2Sc.1.5(C_7H_8)$
fw	517.96	561.91	601.81	623.65	960.29
cryst color	colorless	colorless	colorless	yellow	colorless
cryst size (mm)	0.53 × 0.38 × 0.24	0.41 × 0.33 × 0.22	0.34 × 0.31 × 0.15	0.54 × 0.10 × 0.03	0.44 × 0.23 × 0.06
cryst syst	orthorhombic	orthorhombic	triclinic	orthorhombic	triclinic
space group	*Pbca* (No. 61)	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	$Pna2_1$ (No. 33)	$P\bar{1}$ (No. 2)
a (Å)	18.668(2)	17.211(1)	9.5975(9)	17.907(3)	13.108(4)
b (Å)	17.479(2)	17.984(2)	9.7793(9)	12.848(2)	14.586(4)
c (Å)	19.473(2)	20.309(2)	18.7475(18)	12.995(2)	15.371(4)
α (deg)			100.6527(16)		78.892(4)
β (deg)			96.5794(17)		83.362(4)
γ (deg)			106.2471(16)		86.160(5)
V (Å^3)	6354.0(12)	6286.1(10)	1634.2(3)	2989.8(8)	2838.3(14)
Z	8	8	2	4	2
ρ_{calcd} (g cm^{-3})	1.083	1.187	1.223	1.386	1.124
μ (cm^{-1})	3.60	19.85	2.58	14.54	2.12
F(000), electrons	2288	2432	652	1288	1042
θ range (deg)	2.55, 27.10	2.26, 26.73	2.63, 26.73	2.76, 26.73	2.62, 25.03
index ranges (h,k,l)	±23, ± 22, ± 24	±21, ± 22, ± 25	±12, ± 12, ± 23	−21→22, ± 16, ± 16	−15→13, −14→17, ± 18
no. of reflns collected	50 937	49 161	12 995	22 741	15 891
no. of unique reflns	6998	6670	6707	6329	9452
no. of reflns with $F_o \geq 4\sigma(F_o)$	5990	5151	4965	4274	4167
$wR(F^2)$	0.0853	0.0688	0.1258	0.1101	0.2003
a, *b*	0.0427, 2.8215	0.0322, 2.1759	0.0722, 0	0.0142, 0	0.0784, 0
R(*F*)	0.0352	0.0289	0.0471	0.0512	0.794
T (K)	100(1)	100(1)	100(1)	100(1)	100(1)
GOF	1.056	1.039	1.042	0.963	0.926

(m, 2H, Py *β*-H), 0.36 (s, 3H, CCH_3). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_5Br, 40 °C): *δ* 148.5 (d, J_{CF} = 240.7 Hz, *o*-*C*C_6F_5), 138.3 (d, J_{CF} = 235.0 Hz, *p*-*C* Ph), 136.5 (d, J_{CF} = 242.9 Hz, *m*-*C* C_6F_5), 124.2 (br, *ipso*-*C* C_6F_5), 68.7 (NCH_2), 64.7 (br, ScCH_2), 60.0 (*C*CH_3), 56.9 (NCH_2), 49.5 (NCH_3), 47.1 (Py α-*C*), 24.4 (Py *β*-*C*), 12.6 (CCH_3). The ^{13}C signals of the benzyl aryl carbons were obscured by the solvent peaks.

Reaction of 4 with [PhNMe$_2$H[B(C$_6$F$_5$)$_4$]. In a Tomas tube, C_6D_5Br (0.6 mL) was added to a mixture of **3** (12.5 mg, 20 *μ*mol) and [PhNMe$_2$H][B(C_6F_5)$_4$] (16.0 mg, 20 *μ*mol), and the resulting solution was transferred to an NMR tube equipped with a Teflon (Young) valve. NMR analysis indicated clean conversion to the corresponding cationic dibenzyl species, toluene, and free PhNMe$_2$. NMR (500 MHz, C_6D_5Br, 10 °C): *δ* 7.03 (t, 4H, J_{HH} = 7.5 Hz, Ph, *m*-*H*), 6.59 (t, 2H, J_{HH} = 6.8 Hz, Ph *p*-*H*), 6.25 (d, 4H, J_{HH} = 7.2 Hz, Ph *o*-*H*), 2.62 (m, 2H, NCH_2), 2.29 (d, 2H, J_{HH} = 14.6 Hz, CCH_2), 2.08 (s, 6H, NCH_3), 2.03 (m, 2H, Py α-*H*), 1.95 (m, 2H, NCH_2), 1.84 (m, 2H, Py α-*H*), 1.82 (d, 2H, J_{HH} = 14.6 Hz, CCH_2), 1.79 (s, 4H, LaCH_2), 1.35 (m, 2H, Py *β*-*H*), 1.22 (m, 2H, Py *β*-*H*), 0.30 (s, 3H, CCH_3). ^{13}C NMR (125.7 MHz, C_6D_5Br, 10 °C): *δ* 148.5 (d, J_{CF} = 240.7 Hz, *o*-*C* C_6F_5), 138.3 (d, J_{CF} = 235.0 Hz, *p*-*C* Ph), 136.5 (d, J_{CF} = 242.9 Hz, *m*-*C* C_6F_5), 124.2 (br, *ipso*-*C* C_6F_5), 131.5 (d, J_{CH} = 164.0 Hz, *m*-*C*Ph), 121.7 (d, J_{CH} = 163.6 Hz, *o*-*C* Ph), 117.6 (d, J_{CH} = 156.9 Hz, *p*-*C* Ph), 71.7 (t, J_{CH} = 131.7 Hz, LaCH_2), 68.4 (t, J_{CH} = 137.4 Hz, CCH_2), 61.0 (s, *C*CH_3), 56.1 (t, J_{CH} = 137.9 Hz, NCH_2), 49.2 (q, J_{CH} = 137.4 Hz, NCH_3), 45.4 (t, J_{CH} = 139.7 Hz, Py α-*C*), 25.2 (t, J_{CH} = 132.9 Hz, Py *β*-*C*), 12.3 (q, J_{CH} = 127.2 Hz, CCH_3). The ^{13}C signal of the benzyl C_{ipso} was obscured by the solvent peaks.

General Procedure for Catalytic Hydroamination/Cyclization of Aminoalkenes. Stock solutions (1.0 mol/L in C_6D_6) of 2,2-diphenylpent-4-en-1-amine (**S1**) and *N*-methylpent-4-en-1-amine (**S2**) were prepared. In the glovebox, an NMR tube equipped with a Teflon (Young) valve was charged with the (pre)catalyst (10 *μ*mol), the activator [PhNMe$_2$H][B(C_6F_5)$_4$] (10 *μ*mol, where appropriate), and stock solution of substrate (0.5 mL). The NMR tube was taken out and followed by NMR spectrometry. The products were identified by ^1H NMR and GC-MS in comparison with literature data.[4e,f]

Structure Determinations of Compounds 1, 2, 3, 4, and 5. Suitable single crystals of the compounds were obtained by crystallization as described above. Crystals were mounted on a glass fiber inside a glovebox and transferred under an inert atmosphere to the cold nitrogen stream of a Bruker SMART APEX CCD diffractometer. Intensity data were collected with Mo Kα radiation (*λ* = 0.71073 Å). Intensity data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS[20]). The structures were solved by Patterson methods, and extension of the models was accomplished by direct methods applied to difference structure factors, using the program DIRDIF.[21] In a subsequent difference Fourier synthesis all hydrogen atoms were located, of which the positional and isotropic displacement parameters were refined. All refinements and geometry calculations were performed with the program packages SHELXL[22] and PLATON.[23] Crystallographic data and details of the data collections and structure refinements are listed in Table 5.

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Supporting Information Available: Kinetic plots to calculate the rate constants and CIF files giving the crystal data of compounds **1**, **2**, **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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