Monoanionic *fac*-κ^3 Ligands Derived from 6-Amino-1,4-diazepine: Ligand Dependence of Stability and Catalytic Activity of Their Scandium Alkyl Derivatives

Shaozhong Ge, Auke Meetsma, and Bart Hessen*

Center for Catalytic Olefin Polymerization, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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Two new monoanionic *fac*-κ^3 tridentate ligands [6-RN-1,4,6-trimethyl-1,4-diazepine]$^-$ (R = CH_3, $\mathbf{L}^1$; R = $PhMe_2Si$, $\mathbf{L}^2$) were prepared. Reactions of ligands H$\mathbf{L}^1$ and H$\mathbf{L}^2$ with $Sc(CH_2SiMe_3)_3(THF)_2$ yielded ($\mathbf{L}^1$)$Sc(CH_2SiMe_3)_2(THF)$ (**1**) and ($\mathbf{L}^2$)$Sc(CH_2SiMe_3)_2(THF)$ (**2**), respectively. In toluene solvent, **1** loses a THF molecule and decomposes via metalation of the methyl group of the amido functionality to give {[CH_2(μ-N)-1,4,6-trimethyl-1,4-diazepine]$Sc(CH_2SiMe_3)$}$_2$ (**3**), whereas **2** loses a THF molecule to give stable ($\mathbf{L}^2$)$Sc(CH_2SiMe_3)_2$ (**4**). In THF, both **1** and **2** react with [$PhNMe_2H$][$B(C_6H_5)_4$] to generate the ionic monoalkyl compounds [(L)$Sc(CH_2SiMe_3)(THF)_2$][$B(C_6H_5)_4$] (**5**, L = $\mathbf{L}^1$, **6**, L = $\mathbf{L}^2$). Nevertheless, only the THF-free system **4**/[$PhNMe_2H$][$B(C_6F_5)_4$] shows good ethylene polymerization activity, showing that a single THF molecule per Sc suffices to quench the catalysis. Dinuclear **3** reacts with ethylene via stoichiometric insertion into the Sc−CH_2N bond to yield {[$CH_2CH_2CH_2$(μ-N)-1,4,6-trimethyl-1,4-diazepine]$Sc(CH_2SiMe_3)$}$_2$ (**7**).

Introduction

Cationic alkyl complexes of rare-earth metals are an emerging class of catalytically active species for olefin polymerization and other transformations.[1] Although a range of ancillary ligand types has been used to stabilize these species,[2−6] little is known about ligand effects on catalyst performance and stability. Neutral nitrogen-based facial tridentate ligand moieties, such as triazacyclononane,[3] tris(pyrazolyl)methane,[3b] and tris(oxazolinyl)methane,[6c,g] have been successfully applied, but are relatively inconvenient to modify. Monoanionic N-based *fac*-κ^3 ligands have seen very limited service thus far in organo rare-earth metal chemistry.[6a,d] Deprotonated diisopropyl-1,4,7-triazacyclononane was reported as a monoanionic ligand for both main group and transition metals,[7] but provides very little protection for the N(amide)−M bond.

Recently we reported the successful use of the 6-amino-1,4,6-trimethyl-1,4-diazepine moiety as an ancillary ligand framework for neutral and cationic organo rare-earth metal chemistry.[8] This framework also allows the facile synthesis of monoanionic 6-*amido*-1,4-diazepines, where the substituent on the amide group is readily varied. Here we describe the synthesis of two such ligands and their neutral and cationic scandium alkyl derivatives. It is seen that the amide substitution pattern has a great influence on complex stability and catalytic performance.

Results and Discussion

Ligand Synthesis. The ligands employed in this study are 6-methylamino-1,4,6-trimethyl-1,4-diazepine (H$\mathbf{L}^1$) and 6-(dimethylphenylsilyl)amino-1,4,6-trimethyl-1,4-diazepine (H$\mathbf{L}^2$). H$\mathbf{L}^1$ was prepared by reaction of known 6-amino-1,4,6-trimethyl-1,4-diazepine[9] with ethyl formate under refluxing conditions, followed by reduction with $LiAlH_4$ in refluxing diethyl ether. Ligand H$\mathbf{L}^1$ was isolated as a colorless oil in 74% yield after hydrolysis and distillation (Scheme 1). Ligand H$\mathbf{L}^2$ was prepared by treating 6-amino-1,4,6-trimethyl-1,4-diazepine with *n*-BuLi,

* Corresponding author. E-mail: B.Hessen@rug.nl.

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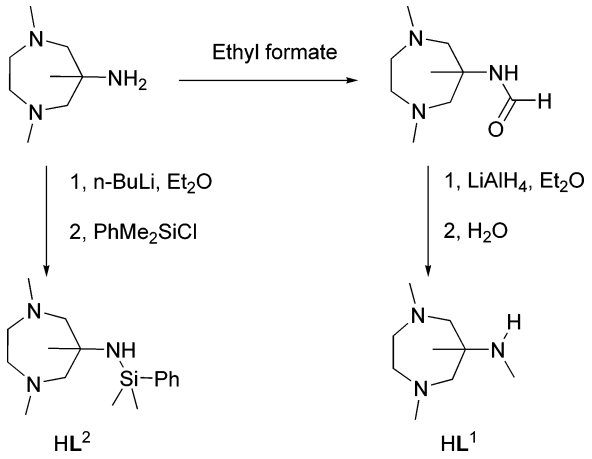
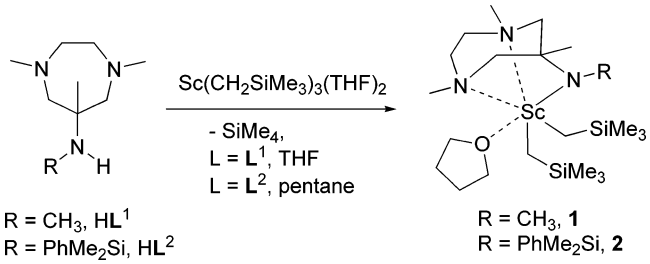
Scheme 1



Scheme 2



followed by addition of $Me_2PhSiCl$ (Scheme 1). It was isolated as a colorless liquid (95% purity by ^1H NMR) in 74% yield after distillation.

Synthesis and Characterization of Scandium Dialkyls Supported by L^1 and L^2. Reaction of the amines HL^1 and HL^2 with the scandium trisalkyl $Sc(CH_2SiMe_3)_3(THF)_2$,[10] as shown in Scheme 2, afforded the scandium dialkyl complexes $(L)Sc(CH_2SiMe_3)_2(THF)$ (L = L^1, **1**, L = L^2, **2**) as pale yellow crystals after crystallization (yield: **1**, 78% from toluene/THF; **2**, 83% from pentane). The ambient-temperature ^1H NMR spectrum of **1** in THF-d_8 shows a single resonance for the four $ScCH_2Si$ methylene protons (δ −0.85 ppm, ^{13}C δ 30.9 ppm, $^1J_{CH}$ = 97 Hz) of the CH_2SiMe_3 groups, whereas for **2** two doublets are seen (δ −0.32 and −0.51 ppm, $^2J_{HH}$ = 10.7 Hz, ^{13}C δ 35.2 ppm, $^1J_{CH}$ = 98 Hz). This suggests that, in THF solvent, the compound with the least sterically demanding amide substituent more readily inverts the configuration of the metal center.

Compounds **1** and **2** were characterized by single-crystal X-ray diffraction, and their structures are shown in Figures 1 and 2, respectively. Both compounds contain a monoanionic *fac*-tridentate ligand in which the nitrogen N3 on the 6-position of the 1,4-diazepine moiety is an amide. The THF molecule is located in a *trans* position relative to the amide nitrogen. One remarkable structural feature of **1** is the large difference of 0.276 Å between the two Sc−N(amine) distances. In fact, the distance Sc−N2 of 2.710(3) Å is easily the longest Sc−N(amine) distance reported thus far.[11] This extreme elongation seems to be associated with the *trans* orientation of one of the alkyl groups relative to this amine: N2−Sc−C14 = 172.09(12)°.[12]

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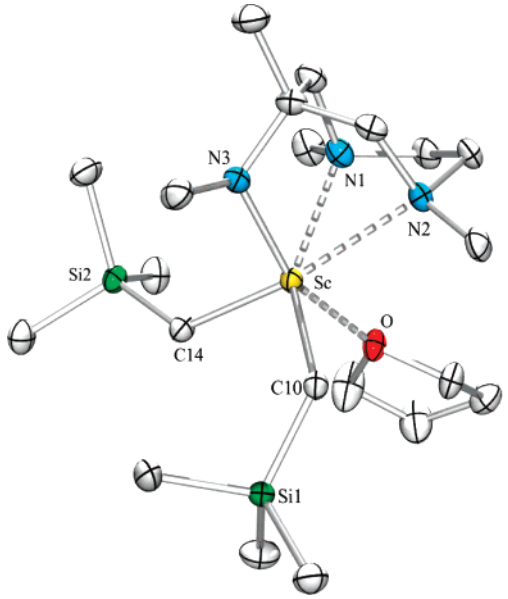


Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Sc−O = 2.274(3), Sc−N1 = 2.434(3), Sc−N2 = 2.710(3), Sc−N3 = 2.040(3), Sc−C10 = 2.282(4), Sc−C14 = 2.273(4), N1−Sc−C10 = 145.82(12), O−Sc−N3 = 158.80(13), N2−Sc−C14 = 172.09-(12), N3−Sc−C10 = 102.83(13), N3−Sc−C14 = 98.35(14).

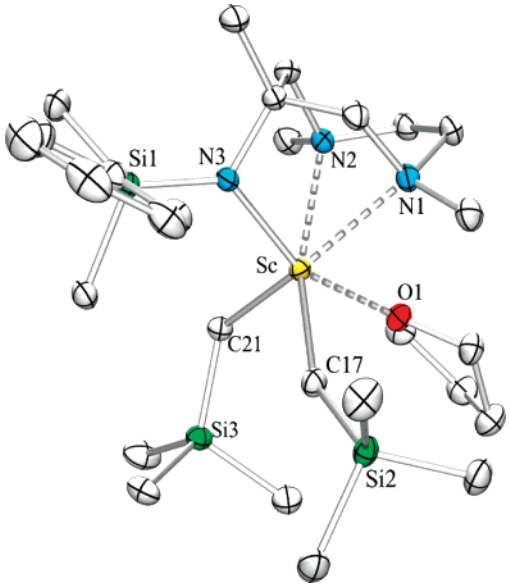


Figure 2. Molecular structure of **2**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Sc−O1 = 2.3228(11), Sc−N1 = 2.5114(13), Sc−N2 = 2.4404-(12), Sc−N3 = 2.1100(12), Sc−C17 = 2.2612(16), Sc−C21 = 2.2936(14), N1−Sc−C21 = 162.43(5), O1−Sc−N3 = 158.02(4), N2−Sc−C17 = 161.66(5), N3−Sc−C17 = 104.78(5), N3−Sc−C21 = 104.88(5).

In **2**, the larger amide substituent changes the placement of the alkyl groups to the extent that now the corresponding angle N1−Sc−C21 = 162.43(5)° is smaller and the *trans* Sc−N1 distance is less elongated. Additionally, the Sc−O(THF) distance in **2** is 0.05 Å longer than in **1**.

Thermal Stability of the Dialkyl Compounds 1 and 2. Upon standing in toluene-d_8 solution at ambient temperature for about 8 h, the dialkyl compound **1** decomposed cleanly to

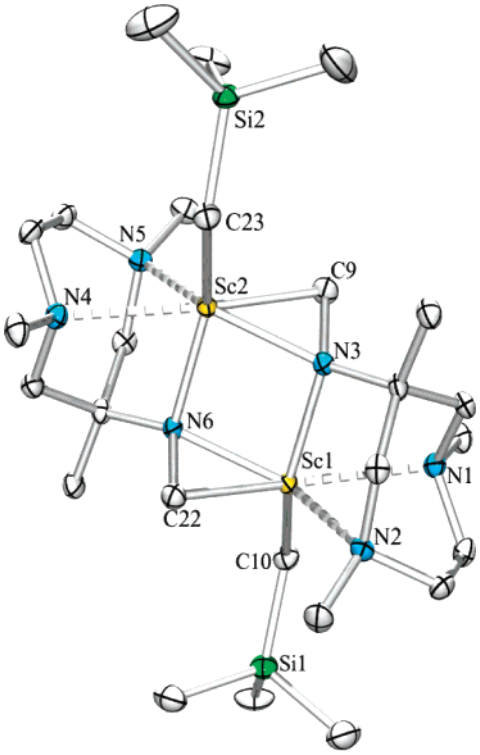
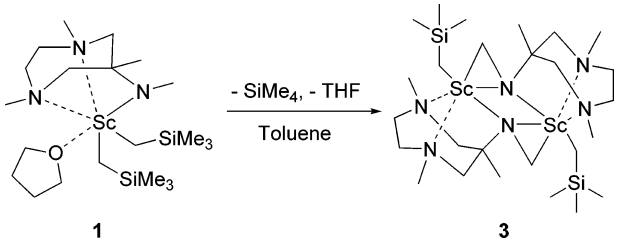


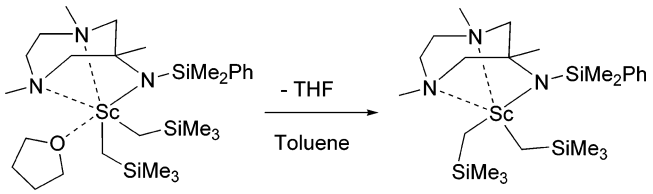
Figure 3. Molecular structure of **3**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Sc1−N1 = 2.5000(19), Sc1−N2 = 2.3652(19), Sc1−N3 = 2.1943(19), Sc1−N6 = 2.1119(19), Sc1−C10 = 2.328(3), Sc1−C22 = 2.202(3), Sc2−N4 = 2.479(2), Sc2−N5 = 2.4255(17), Sc2−N6 = 2.1802(19), Sc2−N3 = 2.1098(19), Sc2−C9 = 2.190(3), Sc2−C23 = 2.314(3), N1−Sc1−C22 = 155.25(8), N2−Sc1−N6 = 126.69(7), N3−Sc1−C10 = 147.06(8), N4−Sc2−C9 = 160.27(8), N5−Sc2−N3 = 124.74(7), N6−Sc2−C23 = 146.77(8).

Scheme 3

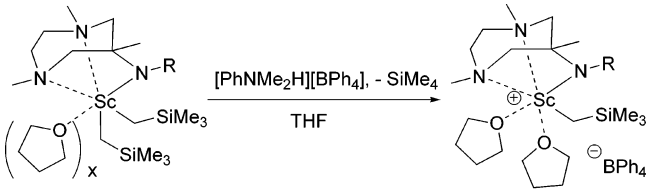


a single organometallic product with release of 1 equiv of $SiMe_4$ and 1 equiv of THF. This product was obtained in 68% isolated yield by simply dissolving **1** in toluene at ambient temperature, followed by removal of the volatiles and crystallization from a toluene/pentane mixture. Single-crystal X-ray diffraction (Figure 3) showed that the product can be formulated as $\{[CH_2(\mu\text{-}N)\text{-}1,4,6\text{-trimethyl-}1,4\text{-diazepine}]Sc(CH_2SiMe_3)\}_2$ (**3**, Scheme 3), derived from metalation of the amide methyl substituent.[13] The NCH_2Sc methylene proton resonances of **3** are found at δ 2.07 and 1.29 ppm (d, $^2J_{HH}$ = 7.2 Hz), whereas the methylene proton resonances for the remaining CH_2SiMe_3 group are found at δ −0.31 and −0.64 ppm (d, $^2J_{HH}$ = 11.2 Hz). The NCH_2Sc carbon resonance (δ 53.5 ppm, $^1J_{CH}$ = 130 Hz) is shifted significantly downfield relative to the $ScCH_2SiMe_3$ group (δ 19.9 ppm, $^1J_{CH}$ = 100 Hz).

Scheme 4



Scheme 5



The structural analysis of **3** shows it to be a binuclear complex with the amide nitrogen bridging two scandium centers. The geometry around each Sc center is approximately octahedral. The core of the structure is the four-membered ring Sc1−N6−Sc2−N3, which is essentially planar (max. deviation from the plane 0.015 Å), annelated with two three-membered rings (Sc1−N6−C22 and Sc2−C9−N3) *trans* to each other. The angles between these rings and the core plane are 105.44° and 113.60°, respectively. The bond distances of Sc−N(bridging amide) in compound **3** are longer than the Sc−N(amide) distances and shorter than the Sc−N(amine) distances in compound **1**.

Although compound **2** also readily loses its coordinated THF molecule (it could be converted to the THF-free dialkyl compound **4** by simply pumping a toluene solution of **2** to dryness, Scheme 4), the resulting dialkyl complex **4** is stable at ambient temperature in toluene solution for at least 1 day. On a preparative scale, **4** was obtained as a pale yellow powder in 95% yield by reaction of HL^2 with $Sc(CH_2SiMe_3)_3(THF)_2$ in toluene, followed by removal of the volatiles. The observations made above show that the stability of the scandium dialkyl compounds is greatly affected by the nature of the amide substituent.

Generation and Characterization of the Ionic Compounds $[(L)Sc(CH_2SiMe_3)(THF)_2]^+[B(C_6H_5)_4]^-$ (5, L = L^1; 6, L = L^2). The dialkyl compounds **1** and **2** can be converted in THF solvent to the monoalkyl cations $[(L)Sc(CH_2SiMe_3)(THF)_2]^+$ by reaction with $[PhNMe_2H][B(C_6H_5)_4]$ (Scheme 5). The ionic compounds $[(L)Sc(CH_2SiMe_3)(THF)_2]^+[B(C_6H_5)_4]^-$ (L = L^1, **5**; L = L^2, **6**) were isolated as analytically pure white microcrystalline powders by layering their THF solutions with apolar solvents (yield: **5**, 82% from *n*-hexane/THF; **6**, 67% from toluene/THF). The ^{13}C NMR resonance of the Sc−CH_2 group in **5** (δ 34.0 ppm) shows a typical downfield shift, relative to its dialkyl precursor **1** (δ 30.9 ppm), associated with conversion to a cationic species. The compounds contain two THF molecules per Sc center, as seen by elemental analysis. Their room-temperature ^1H NMR spectra show broad resonances, indicating fluxionality. Cooling THF-d_8 solutions of compound **5** or **6** to −50 °C slows this dynamic process, revealing an asymmetric structure consistent with a *cis* configuration of the two strongest σ-donors in the complex (alkyl and amide).

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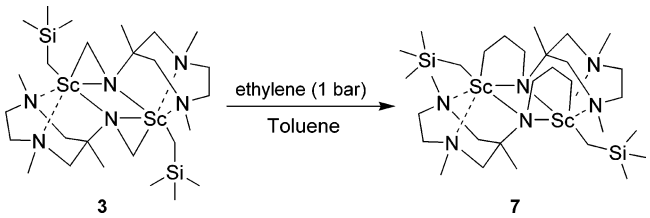
Scheme 6



Reactivity toward Ethylene. When a toluene solution of the dinuclear compound **3** was exposed to 1 bar of ethylene, one molecule of ethylene per scandium was selectively inserted into the Sc−CH_2N bond to give the compound {[$CH_2CH_2CH_2$(μ-N)-1,4,6-trimethyl-1,4-diazepine]Sc(CH_2SiMe_3)}$_2$ (**7**, Scheme 6) within 3 h at room temperature. This indicates that the Sc−C bond in the Sc−C−N three-membered ring is more reactive than the Sc−CH_2SiMe_3 bond. Compound **7** was isolated as colorless crystals in a yield of 71% by crystallization from a mixture of toluene and pentane. The identity of compound **7** was confirmed by a combination of 1D and 2D (COSY and HSQC) NMR techniques and single-crystal X-ray diffraction (Figure 4). The ^{1}H NMR resonances of the Sc- and N-methylene protons of the Sc$CH_2CH_2CH_2$N moiety are found at δ 0.93 and 0.76 ppm and δ 3.53 and 1.70 ppm, respectively. The corresponding ^{13}C NMR resonances are at δ 47.9 and 56.0 ppm, respectively. For the remaining trimethylsilylmethyl group the methylene ^{1}H and ^{13}C NMR resonances are found at δ −0.42 and 0.69 ppm and δ 32.1 ppm.

The structural analysis of compound **7** shows it to be a binuclear complex with an amide nitrogen bridging the two scandium centers, and the geometry around each scandium center is approximately octahedral. The core of the structure is the four-membered ring Sc1−N6−Sc2−N3, which is similar to that in compound **3**, but it is more twisted with a maximum deviation from the least-squares plane of 0.14 Å. The two five-membered rings (Sc1−N6−C24−C25−C26 and Sc2−N3−C9−C10−C11) are annelated with the four-membered core. Interestingly, the remaining two alkyl groups now have a *cis* arrangement relative to the core plane (in contrast to the *trans* arrangement in **3**). The Sc−N bond lengths to the bridging nitrogen atom in compound **7** are on average longer than in compound **3**.

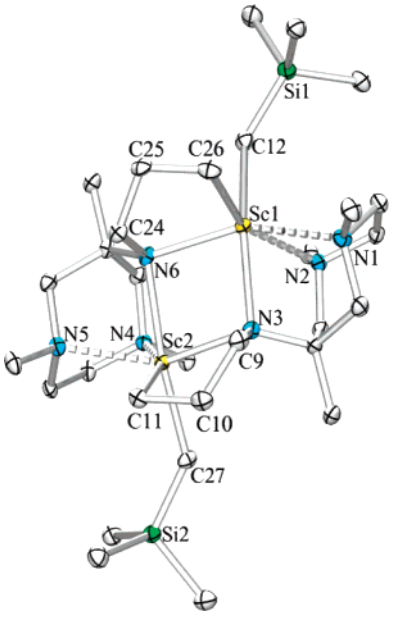


Figure 4. Molecular structure of **7**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Sc1−N1 = 2.452(3), Sc1−N2 = 2.479(2), Sc1−N3 = 2.302(2), Sc1−N6 = 2.277(3), Sc1−C12 = 2.306(3), Sc1−C26 = 2.251(3), Sc2−N4 = 2.454(2), Sc2−N5 = 2.442(2), Sc2−N6 = 2.311(2), Sc2−N3 = 2.280(3), Sc2−C11 = 2.229(3), Sc2−C27 = 2.308(3), N1−Sc1−N6 = 150.83(9), N2−Sc1−C26 = 153.86(11, N3−Sc1−C12 = 158.23(10), N4−Sc2−C11 = 154.30(9), N5−Sc2−N3 = 150.91-(8), N6−Sc2−C27 = 161.42(10), Sc1−N6−Sc2 = 97.86(9), N6−Sc2−N3 = 80.20(9), Sc2−N3−Sc1 = 98.03(9), N3−Sc1−N6 = 80.45(9).

Catalytic ethylene polymerization experiments in toluene solvent using the THF complex **1** or **2** in conjunction with [$PhNMe_2H$][$B(C_6F_5)_4$] activator did not show any activity. In contrast, the combination of the THF-free dialkyl compound **4** with [$PhNMe_2H$][$B(C_6F_5)_4$] afforded an active, single-site ethylene polymerization catalyst, with a productivity of 584 kg (PE)(mol Sc)$^{-1}$ h^{-1} bar^{-1} (toluene solvent, 5 bar, 50 °C, 10 min run time), producing PE with $M_w = 1.2 \times 10^6$, M_w/M_n = 1.9. Thus it appears that even a single THF molecule can shut down the catalytic activity, suggesting that the actual active species is a THF-free (6-amido-1,4,6-trimethyl-1,4-diazepine)-Sc(alkyl) cation.

Conclusions

We have prepared in a straightforward manner two examples of a new monoanionic diamino-amide *fac* tridentate ligand, 6-amido-1,4,6-trimethyl-1,4-diazepine, which was used as ancillary ligand for neutral and cationic scandium alkyl species. The stability and reactivity characteristics of these species depend considerably on the substituent on the amide group. We expect this ligand family to be useful ancillary ligands for rare-earth metal and transition-metal based electrophilic catalysts.

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. 6-Amino-1,4,6-trimethyl-1,4-diazepine was prepared following a procedure from ref 5. Ethyl formate (96.0%, Fluka), $LiAlH_4$ (Acros Organics), *n*-BuLi (1.6 M in *n*-hexane, Acros), and chlorodimethylphenylsilane (95%, Acros Organics) were used as purchased. 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 Gemini VXR 400, Varian Gemini VXR 300, 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). GPC analyses were performed by A. Jekel on a Polymer Laboratories Ltd. (PL-GPC210) chromatograph with 1,2,4-trichlorobenzene (TCB) as the mobile phase at 150 °C and with polystyrene references. Elemental analyses were performed at the Microanalytical Department of the University of Groningen.

Synthesis of 6-Methylamino-1,4,6-trimethyl-1,4-diazepine (HL^1). To a 250 mL two-necked flask equipped with a water condenser were added 6-amino-1,4,6-trimethyl-1,4-diazepine (10.5 g, 66.8 mmol) and ethyl formate (80 mL). The resulting mixture was refluxed for 2 days, and GC indicated that the reaction was complete. Removal of volatiles under reduced pressure yielded a

yellow residue. The residue (12.0 g, 64.8 mmol) was dissolved in diethyl ether (50 mL), and the resulting solution was slowly added to a suspension of $LiAlH_4$ (7.1 g, 187 mmol) in 200 mL of diethyl ether. The mixture was refluxed for 4 h, and then water (20 mL) was slowly added dropwise (CAUTION: vigorous reaction). After stirring for another 2 h, Na_2SO_4 was added, and the salts were filtered and washed with five portions of diethyl ether (50 mL each). The filtrate was concentrated and the residue was distilled to give 6-methylamino-1,4,6-trimethyl-1,4-diazepine (8.5 g, 49.6 mmol, 74%) as a colorless oil (90 °C, 330 mbar). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.56 (m, 2H, NCH_2), 2.40 and 2.26 (AB system, 4H, CCH_2), 2.26 (s, 6H, N(CH_3)$_2$), 2.22 (s, 3H, NCH_3), 0.84 (s, 3H, CCH_3). {^{1}H}^{13}C NMR (100.5 MHz, $CDCl_3$, δ): 67.4 (CCH_2), 60.3 (NCH_2), 55.1 (*C*CH$_3$), 48.9 (NCH_3), 28.1 (H_3CNC), 22.3 (C*C*H$_3$). Anal. Calc for $C_9H_{21}N_3$: C, 63.11; H, 12.36; N, 24.53. Found: C, 63.14; H, 12.40; N, 24.12.

Synthesis of 6-Dimethylphenylsilylamino-1,4,6-trimethyl-1,4-diazepine (HL^2). To a solution of 6-amino-1,4,6-trimethyl-1,4-diazepine (5.03 g, 32 mmol) in diethyl ether (60 mL) was added dropwise *n*-BuLi solution (20 mL, 32 mmol, 1.6 M in *n*-hexane) at −40 °C. After addition, the resulting solution was stirred at room temperature for another 3 h and then cooled to −40 °C. Chlorodimethylphenylsilane (5.46 g, 32 mmol) was added, and the resulting suspension was stirred overnight at room temperature. The suspension was filtrated, and the filtrate was dried under vacuum to give a yellow residue. The residue was purified by distillation (140 °C, 176 mbar) to yield the title compound (7.24 g, 23.6 mmol, 74%) as a colorless liquid. Its ^{1}H NMR spectrum indicated that it contains 5% of residual chlorodimethylphenylsilane. ^{1}H NMR (300 MHz, C_6D_6, δ): 7.69 (d, 2H, J_{HH} = 7.43 Hz, *o*-Ph), 7.25 (t, 2H, J_{HH} = 7.36 Hz, *m*-Ph), 7.22 (t, 1H, J_{HH} = 6.75 Hz, *p*-Ph), 2.44 (m, 2H, NCH_2), 2.36 (m, 4H, CCH_2), 2.26 (m, 2H, NCH_2), 2.17 (s, 6H, N(CH_3)$_2$), 1.97 (b, 1H, N*H*), 1.03 (s, 3H, CCH_3), 0.38 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (75.4 MHz, C_6D_6, δ): 142.3 (s, *ipso-Ph*), 134.0 (d, J_{CH} = 155.0 Hz, *o-Ph*), 129.1 (d, J_{CH} = 157.8 Hz, *m-Ph*), 127.9 (d, J_{CH} = 158.5 Hz, *o-Ph*), 73.6 (t, J_{CH} = 136.3 Hz, CCH_2), 61.1 (t, J_{CH} = 130.9 Hz, NCH_2), 55.0 (s, *C*CH$_3$), 49.0 (q, J_{CH} = 132.5 Hz, NCH_3), 26.3 (q, J_{CH} = 127.7 Hz, C*C*H$_3$), 1.5 (q, J_{CH} = 116.4 Hz, Si(*C*H$_3$)$_2$). Anal. Calc for [95% $C_{16}H_{29}N_3Si$ + 5% $C_8H_{11}ClSi$]: C, 65.44; H, 9.85; N, 13.69. Found: C, 65.20; H, 10.09; N, 13.50.

Synthesis of (L^1)Sc(CH$_2$SiMe$_3$)$_2$(THF) (1). To a solution of Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (626 mg, 1.39 mmol) in 20 mL of THF was added dropwise a solution of 6-methylamino-1,4,6-trimethyl-1,4-diazepine H**L**^{1} (238 mg, 1.39 mmol) in 20 mL of THF while stirring. The mixture was stirred at room temperature for 30 min and then was concentrated to 1 mL under reduced pressure. On top of the resulting yellow solution, 5 mL of pentane was carefully layered. Upon standing in the refrigerator (−30 °C) overnight, crystalline material was formed and part of the crystals were suitable for X-ray analysis. The mother liquor was decanted and the solid was dried under reduced pressure, yielding the title compound as a pale yellow solid (497 mg, 1.08 mmol, 78%). ^{1}H NMR (400 MHz, THF-d_8, δ): 3.61 (m, 4H, α-*H*-THF), 3.22 (m, 2H, NCH_2), 2.86 (s, 3H, CNCH_3), 2.85 (d, 2H, J_{HH} = 12.3 Hz, CCH_2), 2.50 (m, 2H, NCH_2), 2.46 (s, 6H, NCH_3), 2.44 (d, 2H, J_{HH} = 12.3 Hz, CCH_2), 1.77 (m, 4H, *β-H*-THF), 0.76 (s, 3H, CCH_3), −0.06 (s, 18H, Si(CH_3)$_3$), −0.85 (s, 4H, ScCH_2). ^{13}C NMR (100.5 MHz, THF-d_8, δ): 77.9 (t, J_{CH} = 134.0 Hz, CCH_2), 69.4 (t, J_{CH} = 140.4 Hz, α-*C*-THF), 60.3 (t, J_{CH} = 136.7 Hz, NCH_2), 59.2 (s, *C*CH$_3$), 51.9 (q, J_{CH} = 135.2 Hz, NCH_3), 37.1 (q, J_{CH} = 127.6 Hz, CN*C*H$_3$), 30.9 (t, J_{CH} = 96.9 Hz, ScCH_2), 27.5 (t, J_{CH} = 132.7 Hz, *β-C*-THF), 21.1 (t, J_{CH} = 125.0 Hz, C*C*H$_3$), 5.8(q, J_{CH} = 115.5 Hz, Si(*C*H$_3$)$_3$). Anal. Calc for $C_{21}H_{50}N_3OScSi_2$: C, 54.62; H, 10.91; N, 9.10. Found: C, 54.15; H, 10.84; N, 9.41.

Synthesis of (L^2)Sc(CH$_2$SiMe$_3$)$_2$(THF) (2). To a solution of Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (416 mg, 0.92 mmol) in 30 mL of pentane was added dropwise a solution of 6-dimethylphenylsilylamino-1,4,6-trimethyl-1,4-diazepine H**L**^{2} (269 mg, 0.92 mmol) in 10 mL of pentane while stirring. The mixture was stirred at room temperature for 30 min, and then the mixture was concentrated to 5 mL under reduced pressure. Upon standing in the refrigerator (−30 °C) overnight, crystalline material had formed and part of the crystals were suitable for X-ray analysis. The mother liquor was decanted and the solid was dried under reduced pressure, yielding the title compound as an off-white solid (445 mg, 0.76 mmol, 83%). ^{1}H NMR (400 MHz, THF-d_8, δ): 7.65 (d, 2H, J_{HH} = 6.69 Hz, *o*-Ph), 7.19 (t, 2H, J_{HH} = 6.90 Hz, *m*-Ph), 7.15 (t, 1H, J_{HH} = 7.44 Hz, *p*-Ph), 3.61 (m, 4H, α-*H*-THF), 3.25 (m, 2H, NCH_2), 2.81 (d, 2H, J_{HH} = 12.0 Hz, CCH_2), 2.56 (s, 6H, NCH_3), 2.49 (m, 2H, NCH_2), 2.43 (d, 2H, J_{HH} = 12.0 Hz, CCH_2), 1.77 (m, 4H, *β-H*-THF), 0.76 (s, 3H, CCH_3), 0.46 (s, 6H, Si(CH_3)$_2$), −0.03 (s, 18H, Si(CH_3)$_3$), −0.32 (d, J_{HH} = 10.7 Hz, 2H, ScCH*H*), −0.51 (d, J_{HH} = 10.7 Hz, 2H, ScC*H*H). ^{13}C NMR (100.5 MHz, THF-d_8, δ): 151.1 (s, *ipso-Ph*), 135.5 (d, J_{CH} = 155.5 Hz, *o-Ph*), 129.1 (d, J_{CH} = 156.6 Hz, *m-Ph*), 129.0 (d, J_{CH} = 157.9 Hz, *o-Ph*), 82.4 (t, J_{CH} = 134.1 Hz, CCH_2), 69.3 (α-*C*-THF, J_{CH} unresolved due to overlap with THF-d_8), 60.5 (t, J_{CH} = 140.7 Hz, NCH_2), 58.1 (s, *C*CH$_3$), 52.9 (q, J_{CH} = 136.0 Hz, NCH_3), 35.2 (t, J_{CH} = 98.1 Hz, Sc*C*H$_2$), 27.6 (*β-C*-THF, J_{CH} unresolved due to overlap with THF-d_8), 26.6 (q, J_{CH} = 124.8 Hz, C*C*H$_3$), 6.3 (q, J_{CH} = 117.1 Hz, Si(*C*H$_3$)$_3$), 6.0 (q, J_{CH} = 116.4 Hz, Si(*C*H$_3$)$_2$). Anal. Calc for $C_{28}H_{58}N_3OScSi_3$: C, 57.78; H, 10.04; N, 7.22. Found: C, 58.30; H, 10.18; N, 7.15.

Synthesis of {[CH$_2$(μ-N)-1,4,6-trimethyl-1,4-diazepine]-Sc(CH$_2$SiMe$_3$)}$_2$ (3). The dialkyl compound **1** (270 mg, 585 μmol) was dissolved in toluene (20 mL) at room temperature, and the resulting solution was stirred for 10 min. All the volatiles were removed under reduced pressure, the residue was dissolved in toluene (1 mL), and pentane was added until a precipitate began to form. Upon standing in the refrigerator (−30 °C) overnight, a crystalline material had formed and part of the crystals were suitable for X-ray analysis. The mother liquor was decanted and the solid was dried under reduced pressure, yielding the title compound as a pale yellow solid (241 mg, 400 μmol, 68%). The assignment of NMR resonances was aided by COSY and HSQC experiments. ^{1}H NMR (500 MHz, C_6D_6, δ): 3.13 (d, 2H, J_{HH} = 12.2 Hz, CC*H*H), 3.05 (m, 2H, NCH_2), 2.89 (d, 2H, J_{HH} = 12.9 Hz, CC*H*H), 2.53 (s, 6H, NCH_3), 2.51 (m, 2H, NCH_2), 2.36 (s, 6H, NCH_3), 2.07 (d, 2H, J_{HH} = 7.2 Hz, ScC*H*HN), 1.97 (d, 2H, J_{HH} = 12.2 Hz, CCH*H*), 1.89 (m, 2H, NCH_2), 1.84 (d, 2H, J_{HH} = 12.9 Hz, CCH*H*), 1.65 (m, 2H, NCH_2), 1.29 (d, 2H, J_{HH} = 7.2 Hz, ScCH*H*N), 0.99 (s, 6H, CCH_3), 0.40 (s, 18H, Si(CH_3)$_3$), −0.31 (d, 2H, J_{HH} = 11.2 Hz, ScC*H*H), −0.64 (d, 2H, J_{HH} = 11.2 Hz, ScCH*H*). ^{13}C NMR (125.7 MHz, C_6D_6, δ): 77.8 (t, J_{CH} = 135.9 Hz, CCH_2), 68.2 (t, J_{CH} = 134.2 Hz, CCH_2), 60.1 (s, *C*CH$_3$), 58.8 (t, J_{CH} = 135.6 Hz, NCH_2), 55.6 (t, J_{CH} = 135.6 Hz, NCH_2), 53.5 (t, J_{CH} = 129.8 Hz, NCH_2Sc), 52.4 (q, J_{CH} = 135.6 Hz, NCH_3), 49.1 (q, J_{CH} = 135.6 Hz, NCH_3), 19.9 (q, J_{CH} = 125.7 Hz, C*C*H$_3$), 19.9 (t, J_{CH} = 100.4 Hz, ScCH_2), 5.3 (q, J_{CH} = 115.7 Hz, Si(*C*H$_3$)$_3$). Anal. Calc for $C_{26}H_{60}N_6Sc_2Si_2$: C, 51.80; N, 13.94; H, 10.03. Found: C, 51.52; N, 13.93; H, 10.03.

Synthesis of (L^2)Sc(CH$_2$SiMe$_3$)$_2$ (4). (L^2)Sc(CH$_2$SiMe$_3$)$_2$(THF) (232 mg, 0.40 mmol) was dissolved in toluene (5 mL) and the resulting solution was evaporated to dryness, yielding the title compound (194 mg, 0.38 mmol, 95%) as an off-white solid. ^{1}H NMR (300 MHz, C_6D_6, δ): 7.81 (d, 2H, J_{HH} = 8.06 Hz, *o*-Ph), 7.31 (t, 2H, J_{HH} = 7.28 Hz, *m*-Ph), 7.21 (t, 1H, J_{HH} = 7.42 Hz, *p*-Ph), 2.41 (m, 2H, NCH_2), 2.28 (d, J_{HH} = 12.0 Hz, CCH_2), 2.11 (s, 6H, N(CH_3)$_2$), 1.65 (d, J_{HH} = 12.0 Hz, CCH_2), 1.56 (m, 2H, NCH_2), 0.76 (s, 6H, Si(CH_3)$_2$), 0.59 (s, 3H, CCH_3), 0.41 (s, 18H, Si(CH_3)$_3$), −0.03 (s, 4H, ScCH_2). ^{13}C NMR (75.4 MHz, C_6D_6, δ): 145.4 (s, *ipso-Ph*), 134.1 (d, J_{CH} = 155.2 Hz, *Ph*), 128.5 (d, J_{CH} = 157.1 Hz, *m-Ph*), 127.9 (d, J_{CH} = 157.1 Hz, *o-Ph*), 76.6 (t, J_{CH} = 138.5 Hz, CCH_2), 56.9 (t, J_{CH} = 135.5 Hz, NCH_2), 54.3 (s, *C*CH$_3$), 51.3 (q, J_{CH} = 137.5 Hz, NCH_3), 35.2 (t, J_{CH} = 100.7 Hz, ScCH_2), 25.1 (q, J_{CH} = 125.6 Hz, C*C*H$_3$), 4.76 (q, J_{CH} = 116.9

Table 1. Crystal Data and Collection Parameters of Complexes 1, 2, 3, and 7

	1	2	3	7
formula	$C_{21}H_{50}N_3OSi_2Sc$	$C_{28}H_{58}N_3OScSi_3$	$C_{26}H_{60}N_6Si_2Sc_2$	$C_{30}H_{68}N_6Sc_2Si_2$
fw	461.77	582.0	602.89	658.99
cryst color	colorless	colorless	colorless	colorless
cryst size (mm)	0.45 × 0.21 × 0.12	0.45 × 0.41 × 0.36	0.44 × 0.37 × 0.19	0.37 × 0.23 × 0.07
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$	$P2_1/c$
a (Å)	8.883(2)	9.4978(4)	13.316(1)	12.866(1)
b (Å)	9.665(2)	12.0208(5)	16.815(1)	17.139(2)
c (Å)	17.508(3)	15.6141(7)	16.211(1)	16.753(2)
α (deg)	98.910(3)	79.1238(7)	90	90
β (deg)	102.205(3)	79.1083(7)	110.118(1)	93.363(2)
γ (deg)	105.553(3)	79.6515(7)	90	90
V (Å^3)	1379.2(5)	1699.85(13)	3408.3(4)	3687.9(7)
Z	2	2	4	4
ρ_{calcd} (g cm^{-3})	1.112	1.137	1.175	1.187
μ (cm^{-1})	3.69	3.46	4.92	4.6
F(000), electrons	508	636	1312	1440
θ range (deg)	2.77, 25.03	2.60, 28.28	2.42, 27.10	2.67, 26.37
index ranges (h,k,l)	±10, −11 → 10, ±20	±12, −16 → 15, ±20	−16 → 17, ±21, ±20	−16 → 15, −21 → 20, ±20
no. of reflns collected	8929	15 551	28 317	28 779
no. of unique reflns	4738	8116	7464	7459
no. of reflns with $F_o \geq 4\sigma(F_o)$	3343	6938	5637	4925
$wR(F^2)$	0.1569	0.0947	0.1070	0.1236
a, b	0.0776, 0	0.0525, 0.39	0.0552, 0.256	0.0563, 0
$R(F)$	0.0587	0.0360	0.0451	0.0529
T (K)	100(1)	100(1)	100(1)	100(1)
GOF	1.059	1.056	1.037	1.002

Hz, Si(CH_3)$_3$), 2.5 (q, J_{CH} = 117.8 Hz, Si(CH_3)$_2$). Anal. Calc for $C_{24}H_{50}N_3ScSi_3$: C, 56.53; H, 9.88; N, 8.24. Found: C, 56.85; H, 9.97; N, 8.02.

Synthesis of [(L^1)Sc(CH$_2$SiMe$_3$)(THF)$_2$][B(C$_6$H$_5$)$_4$] (5). A solution of 6-methylamino-1,4,7-trimethyl-1,4-diazepine H**L**^{1} (47.7 mg, 278 μmol) in THF was added to Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (126 mg, 278 μmol). The resulting homogeneous solution was added to [PhMe$_2$NH][B(C$_6$H$_5$)$_4$] (123 mg, 278 μmol). The solution was homogenized by agitation and allowed to stand for about 20 min. *n*-Hexane (6 mL) was carefully layered on the top, and a colorless crystalline material was formed upon standing at room temperature for 2 days. The mother liquor was decanted and the solid was dried under reduced pressure, yielding the title compound as a white solid (174 mg, 227 μmol, 82%). ^{1}H NMR (500 MHz, THF-d_8, 248 K, δ): 7.24 (br, 8H, *o*-*Ph*B), 6.85 (t, 8H, J_{HH} = 7.60 Hz, m-*Ph*B), 6.72 (t, 4H, J_{HH} = 7.12 Hz, *p*-*Ph*B), 3.57 (m, 8H, α-*H*-THF), 2.94 (d, 1H, J_{HH} = 12.0 Hz CC*H*H), 2.90 (m, 1H, NC*H*H), 2.80 (s, 3H, NCH_3), 2.71 (d, 1H, J_{HH} = 12.0 Hz, CC*H*H), 2.70 (m, 1H, NC*H*H), 2.69 (d, 1H, J_{HH} = 12.0 Hz, CCH*H*), 2.46 (s, 3H, NCH_3), 2.44 (m, 1H, NCH*H*), 2.41 (m, 1H, NCH*H*), 2.38 (d, 1H, J_{HH} = 12.0 Hz, CCH*H*), 2.11 (s, 3H, NCH_3), 1.72 (m, 8H, *β*-*H*-THF), 0.75 (s, 3H, CCH_3), −0.07 (s, 9H, Si(CH_3)$_3$), −0.74 (d, 1H, J_{HH} = 11.8 Hz, ScC*H*H), −0.79 (d, 1H, J_{HH} = 11.8 Hz, ScCH*H*). ^{13}C NMR (125.7 MHz, THF-d_8, 248 K, δ): 166.4 (q, J_{BC} = 49.9 Hz, *ipso*-*Ph*), 138.0 (d, J_{CH} = 151.4 Hz, *o*-*Ph*B), 126.9 (d, J_{CH} = 152.5 Hz, *m*-*Ph*B), 123.1 (d, J_{CH} = 154.7 Hz, *p*-*Ph*B), 79.3 (t, J_{CH} = 135.0 Hz, C*C*H$_2$), 69.2 (t, J_{CH} = 146.2 Hz, α-*C*-THF), 59.0 (t, J_{CH} = 135.7 Hz, N*C*H$_2$), 58.8 (t, J_{CH} = 133.7 Hz, N*C*H$_2$), 57.8 (s, Me*C*), 52.2 (q, J_{CH} = 137.7 Hz, N*C*H$_3$), 50.8 (q, J_{CH} = 136.7 Hz, N*C*H$_3$), 36.6 (q, J_{CH} = 130.7 Hz, N*C*H$_3$), 34.0 (t, J_{CH} = 99.2 Hz, Sc*C*H$_2$), 27.4 (t, J_{CH} = 132.1 Hz, *β*-*C*-THF), 20.0 (q, J_{CH} = 126.3 Hz, C*C*H$_3$), 4.8 (q, J_{CH} = 116.8 Hz, Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{45}H_{67}BN_3O_2ScSi$: C, 70.57; H, 8.82; N, 5.49. Found: C, 70.35; H, 8.81; N, 5.09.

Synthesis of [(L^2)Sc(CH$_2$SiMe$_3$)(THF)$_2$][B(C$_6$H$_5$)$_4$] (6). THF (3 mL) was added to a mixture of 85.3 mg (147 μmol) of (**L**^{2})Sc(CH$_2$SiMe$_3$)$_2$(THF) and 64.7 mg (147 μmol) of [PhMe$_2$NH]-[B(C$_6$H$_5$)$_4$]. The solution was homogenized by agitation and allowed to stand for about 20 min. Toluene (1 mL) was added to the mixture to form a white precipitate, and more THF was added to just redissolve the precipitate. A colorless crystalline material was formed upon standing in the refrigerator (−30 °C) overnight. The mother liquor was decanted and the solid was dried under reduced pressure, yielding the title compound as a white solid (87.0 mg, 98.2 μmol, 67%). ^{1}H NMR (500 MHz, THF-d_8, 258 K, δ): 7.56 (d, 2H, J_{HH} = 7.26 Hz, *o*-*Ph*Si), 7.32 (br, 11H, *o*-*Ph*B, *m*-*Ph*Si, *p*-*Ph*Si overlap), 6.91 (t, 8H, J_{HH} = 7.40 Hz, *m*-*Ph*B), 6.78 (t, 4H, J_{HH} = 7.14 Hz, *p*-*Ph*B), 3.57 (m, 8H, α-*H*-THF), 3.01 (d, 1H, J_{HH} = 12.0 Hz CC*H*H), 2.89 (m, 1H, NC*H*H), 2.70 (d, 1H, J_{HH} = 12.2 Hz, CC*H*H), 2.64 (m, 1H, NC*H*H), 2.59 (s, 3H, NCH_3), 2.58 (d, 1H, J_{HH} = 12.0 Hz, CCH*H*), 2.43 (d, 1H, J_{HH} = 12.2 Hz, CCH*H*), 2.42 (m, 1H, NCH*H*), 2.28 (m, 1H, NCH*H*), 2.19 (s, 3H, NCH_3), 1.74 (m, 8H, *β*-*H*-THF), 0.68 (s, 3H, CCH_3), 0.38 (s, 3H, SiCH_3), 0.34 (s, 3H, SiCH_3), −0.08 (s, 9H, Si(CH_3)$_3$), −0.18 (d, 1H, J_{HH} = 11.2 Hz, ScC*H*H), −0.29 (d, 1H, J_{HH} = 11.2 Hz, ScCH*H*). ^{13}C NMR (125.7 MHz, THF-d_8, 258 K, δ): 166.4 (q, J_{BC} = 46.5 Hz, *ipso*-*Ph*), 148.1 (s, *ipso*-*Ph*Si), 138.0 (d, J_{CH} = 153.7 Hz, *o*-*Ph*B), 134.8 (d, J_{CH} = 154.3 Hz, *o*-*Ph*Si), 129.8 (d, J_{CH} = 158.4 Hz, *p*-*Ph*Si), 129.5 (d, J_{CH} = 157.1 Hz, *m*-PhSi), 127.0 (d, J_{CH} = 153.2 Hz, *m*-*Ph*B), 123.2 (d, J_{CH} = 156.5 Hz, *p*-*Ph*B), 82.3 (t, J_{CH} = 136.6 Hz, C*C*H$_2$), 82.1 (t, J_{CH} = 139.1 Hz, C*C*H$_2$), 69.2 (t, J_{CH} = 145.0 Hz, α-*C*-THF), 59.5 (t, J_{CH} = 138.5 Hz, N*C*H$_2$), 59.1 (t, J_{CH} = 139.2 Hz, N*C*H$_2$), 57.6 (s, Me*C*), 53.6 (q, J_{CH} = 138.2 Hz, N*C*H$_3$), 51.3 (q, J_{CH} = 136.7 Hz, N*C*H$_3$), 40.2 (t, J_{CH} = 92.7 Hz, Sc*C*H$_2$), 27.4 (t, J_{CH} = 131.8 Hz, *β*-*C*-THF), 25.5 (q, J_{CH} = 127.4 Hz, C*C*H$_3$), 5.4 (q, J_{CH} = 117.4 Hz, Si*C*H$_3$), 5.2 (q, J_{CH} = 116.7 Hz, Si(*C*H$_3$)$_3$), 5.0 (q, J_{CH} = 115.5 Hz, Si*C*H$_3$). Anal. Calcd for $C_{52}H_{75}BN_3O_2ScSi_2$: C, 70.48; H, 8.53; N, 4.74. Found: C, 70.70; H, 8.80; N, 4.38.

Synthesis of {[CH$_2$CH$_2$CH$_2$(*μ*-N)-1,4,6-trimethyl-1,4-diazepine]-Sc(CH$_2$SiMe$_3$)}$_2$ (7). Compound **3** (170 mg, 0.28 mmol) was dissolved in toluene (30 mL), and the resulting solution was exposed to ethylene (1 bar) with vigorous stirring for 3 h at room temperature. Then all the volatiles were removed under reduced pressure, and the residue was purified by crystallization from a toluene/pentane mixture to give **7** (134 mg, 0.20 mmol, 71%) as colorless crystals. ^{1}H NMR (500 MHz, C$_6$D$_6$, δ): 4.42 (m, 2H, NCH_2), 3.53 (m, 2H, NCH_2), 2.83 (m, 2H, CH$_2$CH_2CH$_2$), 2.76 (m, 2H, NCH_2), 2.70 (m, 2H, NCH_2), 2.59 (m, 2H, NCH_2), 2.52 (m, 2H, NCH_2), 2.51 (m, 2H, NCH_2), 2.32 (s, 6H, NCH_3), 2.00 (s, 6H, NCH_3), 1.80 (m, 2H, NCH_2), 1.73 (m, 2H, NCH_2), 1.71 (m, 2H, NCH_2), 1.70 (m, 2H, NCH_2), 1.12 (s, 6H, CCH_3), 0.93 (m, 2H, NCH_2Sc), 0.76 (m, 2H, NCH_2Sc), 0.41 (s, 18H, Si(CH_3)$_3$), −0.43

(d, 2H, J_{HH} = 10.9 Hz, $ScCH_2SiMe_3$), −0.70 (d, 2H, J_{HH} = 10.9 Hz, $ScCH_2SiMe_3$). ^{13}C NMR (125.7 MHz, C_6D_6, δ): 77.5 (t, J_{CH} = 133.6 Hz, NCH_2), 64.3 (t, J_{CH} = 136.5 Hz, NCH_2), 61.7 (s, CCH_3), 61.0 (t, J_{CH} = 135.3 Hz, NCH_2), 56.0 (t, J_{CH} = 139.5 Hz, NCH_2), 50.9 (q, J_{CH} = 135.7 Hz, NCH_3), 50.2 (q, J_{CH} = 135.7 Hz, NCH_3), 47.9 (t, J_{CH} = 116.5 Hz, NCH_2Sc), 46.5 (t, J_{CH} = 129.7 Hz, NCH_2), 33.6 (t, J_{CH} = 122.4 Hz, $CH_2CH_2CH_2$), 32.1 (t, J_{CH} = 99.0 Hz, $ScCH_2$), 22.5 (q, J_{CH} = 126.0 Hz, CCH_3), 4.9 (q, J_{CH} = 116.0 Hz, $Si(CH_3)_3$). Anal. Calc for $C_{30}H_{68}N_6Sc_2Si_2$: C, 54.68; H, 10.40; N, 12.75. Found: C, 54.36; H, 10.37; N, 12.56.

General Procedure for Ethylene Polymerization. In a typical experiment, solutions were prepared in a drybox of the complexes **1**, **2**, and **4** (10 μmol) and of $[HNMe_2Ph][B(C_6F_5)_4]$ (10 μmol), each in 5 mL of toluene in separate vials sealed with a serum cap. The autoclave was charged with 200 mL of toluene (after injection of (co)catalyst solutions and rinsing the vials, the total volume of toluene was 250 mL), equilibrated at 50 °C, and pressurized with ethylene (5 bar). The solution of $[HNMe_2Ph][B(C_6F_5)_4]$ was injected first into the reactor, and the reaction was started by subsequently injecting the solution of the catalyst precursors. The ethylene pressure was kept within 0.1 bar of the initial pressure during the reaction by replenishing flow. The polymerization was run for 10 min. The obtained polymer was rinsed with ethanol and dried in a vacuum oven (70 °C).

Structure Determinations of Compound 1, 2, 3, and 7. Suitable single crystals of the compounds were obtained by recrystallization as described above. Crystals were mounted on a glass fiber inside a drybox and transferred under 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).[14] 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.[15] 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[16] and PLATON.[17] Crystallographic data and details of the data collections and structure refinements are listed in Table 1.

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Supporting Information Available: NMR spectra of H**L**[1] and H**L**[2]. CIF files giving the X-ray data of **1**, **2**, **3**, and **7**. This material is available free of charge via Internet at http://pubs.acs.org.

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