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Yttrium Alkyl Complexes with Triamino−Amide Ligands

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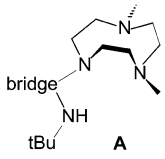
Two new monoanionic tetradentate triamino−amide ligands, $[(Me_2NCH_2CH_2)_2N\text{-}B\text{-}N(t\text{-}Bu)]^-$ (B = $(CH_2)_2$, $\mathbf{L^1}$; $SiMe_2$, $\mathbf{L^2}$) were prepared. Reaction of $\mathbf{L^1}H$ with $Y(CH_2SiMe_3)_3(THF)_2$ yielded $\mathbf{L^1}Y(CH_2SiMe_3)_2$ (**1**), which was structurally characterized. Compound **1** decomposes at ambient temperature via metalation of one of the NMe_2 methyl groups to give $\{[(CH_2)MeN(CH_2)_2][Me_2N(CH_2)_2]N(CH_2)_2N(t\text{-}Bu)\}Y(CH_2SiMe_3)$ (**2**). Attempts to prepare $\mathbf{L^2}Y(CH_2SiMe_3)_2$ resulted in very rapid ligand metalation. Both **1** and **2** react with $[PhNMe_2H][B(C_6F_5)_4]$ to generate the cation $[(\mathbf{L^1})YCH_2SiMe_3]^+$. The combination of **1** and $[Ph_3C][B(C_6F_5)_4]$ is active in catalytic ethene polymerization, but with a short catalyst lifetime. The metalated complex **2** reacts with ethene and with pyridine by stoichiometric insertion into the $Y-CH_2N$ bond, and the latter product was structurally characterized. In $\mathbf{L^1}Y(X)(CH_2SiMe_3)$ complexes, the Y−amine distance trans to X is very sensitive to the nature of X, suggesting the presence of a trans influence.

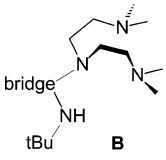
Introduction

Cyclic triamines and tetraamines, especially 1,3,5-triazacyclohexanes and 1,4,7-triazacyclononanes, have proven to be very useful ligand moieties for use in transition-metal and lanthanide coordination chemistry and catalysis.[1,2] Although these molecules are interesting ligands themselves, they also give access to functionalized derivatives with one or more additional pendant functionalities, usually connected to the cyclic polyamine moeity via its N-atoms.[3] Of particular interest to catalysis are cyclic polyamine ligands with one pendant functionality.[4] Earlier, we have successfully used tetradentate monoanionic 1,4,7-triazacyclononane−amide ligands as ancillary ligands to access triazacyclononane−amide dialkyl complexes of group 3 and lanthanide metals.[5,6] These compounds could be converted into cationic monoalkyl species that were found to be active ethene polymerization catalysts.[5,7]

These 1,4,7-triazacyclononane−amide (TACN−amide) ligands **A** are conformationally fairly rigid, due to the cyclic nature of the triamine moiety (that caps a trigonal face on the metal center) and the bridge between the cyclic triamine and amide functionalities. To investigate the way in which the chemistry of these species is affected when these conformational constraints are relaxed, we prepared monoanionic tetradentate ligands **B** based on a linear triamine moiety, and studied their



A



B

behavior as ancillary ligands for yttrium alkyl species. The resulting complexes were found to be much more

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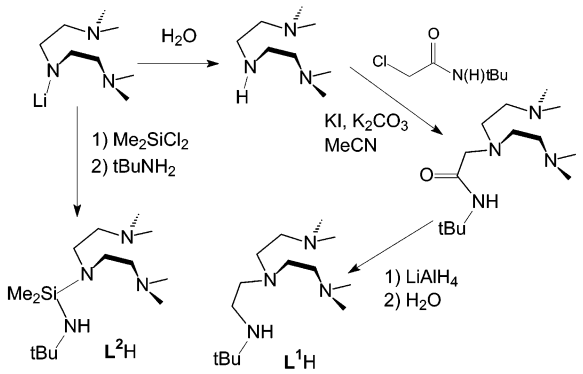
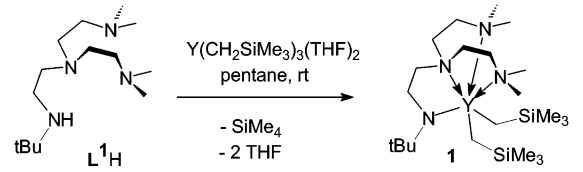
Scheme 1



Scheme 2



fluxional, and significantly more susceptible to ligand metalation processes, than the related TACN−amide complexes.

Results and Discussion

Ligand Synthesis. The tetraamine $[Me_2N(CH_2)_2]_2N(CH_2)_2NH(t\text{-Bu})$ (H**L**[1]) was prepared starting from bis(*N*,*N*-dimethyl-2-aminoethyl)amine. This compound was prepared from tris(*N*,*N*-dimethyl-2-aminoethyl)amine via a modification of a literature procedure[8] in which one of the sidearms is selectively cleaved by reaction with *t*-BuLi (the modification involving the isolation of the intermediate Li−amide prior to subsequent hydrolysis). Following the procedure described earlier for the TACN−amide analogue,[5] the bis(*N*,*N*-dimethyl-2-aminoethyl)amine was coupled with *N*-*tert*-butylchloroacetamide, followed by reduction with $LiAlH_4$ and subsequent hydrolysis to yield H**L**[1] (Scheme 1). The analogous ligand with a $SiMe_2$ bridge between the triamine and *tert*-butylamine moieties, $[Me_2N(CH_2)_2]_2N(SiMe_2)NH(t\text{-Bu})$ (H**L**[2]), was obtained by reaction of the isolated lithium[bis(*N*,*N*-dimethyl-2-aminoethyl)amide] with Me_2SiCl_2 followed by reaction with *tert*-butylamine (Scheme 1).

Synthesis and Characterization of {[Me$_2$N(CH$_2$)$_2$]$_2$N(CH$_2$)$_2$N(*t*-Bu)}Y(CH$_2$SiMe$_3$)$_2$ (1). Reaction of the amine H**L**[1] with the yttrium trialkyl $Y(CH_2SiMe_3)_3(THF)_2$[9] in pentane, followed by extraction with and crystallization from the same solvent, afforded the yttrium dialkyl complex $\{[Me_2N(CH_2)_2]_2N(CH_2)_2N(t\text{-Bu})\}Y(CH_2SiMe_3)_2$ **(1)** as white crystals in 68% isolated yield (Scheme 2).

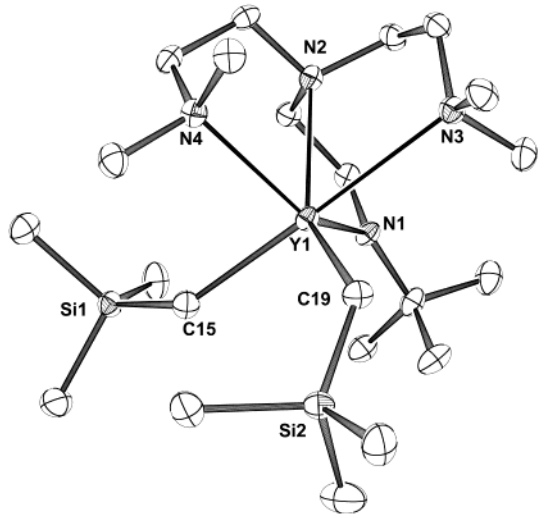


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

Y(1)−N(1)	2.226(2)	Y(1)−N(4)	2.587(2)
Y(1)−N(2)	2.530(2)	Y(1)−C(15)	2.463(2)
Y(1)−N(3)	2.870(2)	Y(1)−C(19)	2.452(2)
N(1)−Y(1)−N(2)	72.69(5)	N(3)−Y(1)−C(15)	178.46(6)
N(2)−Y(1)−N(3)	69.67(5)	N(3)−Y(1)−C(19)	78.05(6)
N(2)−Y(1)−N(3)	65.75(5)	N(4)−Y(1)−C(15)	87.17(6)
N(1)−Y(1)−C(15)	92.74(6)	N(4)−Y(1)−C(19)	96.47(6)
N(1)−Y(1)−C(19)	123.78(6)	N(1)−Y(1)−N(3)	88.53(5)
C(15)−Y(1)−C(19)	101.96(6)	N(1)−Y(1)−N(4)	128.63(5)
Y(1)−C(15)−Si(1)	140.0(1)	Y(1)−C(19)−Si(2)	130.5(1)

The compound was characterized by single-crystal X-ray diffraction and its structure is shown in Figure 1 with pertinent interatomic distances and angles in Table 1. It shows a monomeric complex with a coordination geometry similar to that of the $[(i\text{-Pr})_2TACN(CH_2)_2N(t\text{-Bu})]Y(CH_2SiMe_3)_2$ complex reported earlier by us.[5] The triamine moiety is capping a trigonal face of the 6-coordinate complex, and the geometry is distorted to minimize the steric interaction between the alkyl groups and the Me substituents of the ligand. One remarkable feature is the very large difference in Y−N distance between the two NMe_2 groups of the ligand. The distance Y−N(3) of 2.870(2) Å is 0.280 Å longer than that to the other NMe_2 nitrogen N(4), and is to our knowledge by far the longest Y−amine distance reported. Two representative examples are a distance of 2.576(4) Å in the amidinate−amine dialkyl complex $[PhC(NSiMe_3)N(CH_2)_2NMe_2]Y[CH(SiMe_3)_2]_2$[10] and of 2.588(2) Å in the cyclopentadienyl−amide−amine alkyl complex $[C_5Me_4CH_2SiMe_2N(CH_2)_2NMe_2]Y(CH_2SiMe_3)(THF)$.[11] The N(4) amine nitrogen in **1** is located trans to one of the alkyl groups, N(4)−Y−C(15) = 178.45(6)°, which may suggest the presence of a trans influence from this diagonal alkyl group. In the structure of the related $[(i\text{-Pr})_2TACN(CH_2)_2N(t\text{-Bu})]Y(CH_2SiMe_3)_2$ complex the difference between the two (*i*-Pr)N−Y distances is smaller (0.122 Å),[6] but again the nitrogen that is approximately trans to an alkyl group (C−Y−N =

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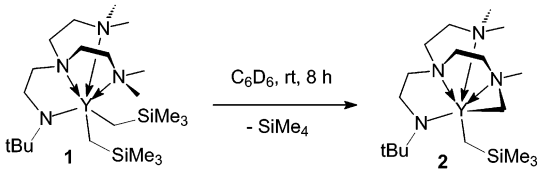
Scheme 3



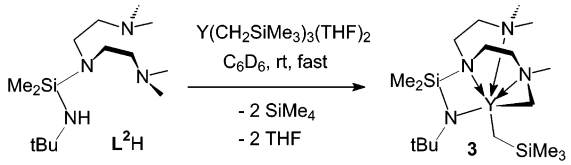
155.3°) shows the longest Y−N distance. The Y−N distance also appears to be very sensitive to changes in the nature of the ligand trans to it (vide infra).

The ^{1}H NMR spectrum of **1** at ambient temperature shows a broadened AB system for the YCH_2Si methylene protons, indicating an averaged C_s symmetry, and a single broad resonance for the four NMe_2 methyl groups. This indicates rapid dissociation and inversion of the amine groups on the NMR time scale at this temperature. Indeed, cooling a toluene-d_8 solution of **1** to −50 °C shows a spectrum consistent with a fully asymmetric structure, with four NMe resonances of 3H intensity each, and two inequivalent trimethylsilylmethyl goups. Unfortunately the coalescence of the NMe resonances is too much obscured by other ligand resonances to establish an activation barrier, but from the coalescence of the $SiMe_3$ resonances the $\Delta G_{Tc}^{\ddagger}$ for the symmetrization to C_s was determined at 11.7 kcal mol^{-1} (T_c = 242 K). For the analogous Me_2TACN−amide complex this is 14.7 kcal mol^{-1} (T_c = 291 K).

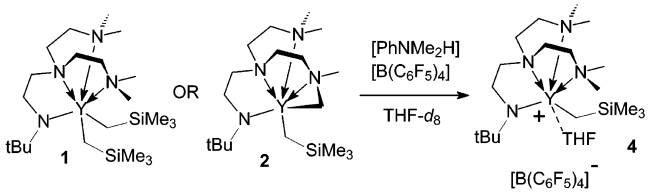
Ligand Metalation. Upon standing in solution at ambient temperature, the dialkyl complex **1** is converted gradually (full conversion in C_6D_6 in about 8 h, in 2 days in the Lewis basic solvent THF-d_8) and cleanly to a single organometallic product with release of 1 equiv of $SiMe_4$. Attempts to isolate this product from a preparative scale reaction only yielded an oil that could not be crystallized, but for spectroscopic characterization and reactivity studies the compound is conveniently and quantitatively generated from **1** in solution, as described above. By ^{1}H and ^{13}C NMR spectroscopy the product was characterized as {[(CH_2)MeN$(CH_2)_2$][Me_2N$(CH_2)_2$]N-$(CH_2)_2$N(*t*-Bu)}Y(CH_2SiMe_3) (**2**, Scheme 3), deriving from intramolecular metalation of one of the ligand NMe groups.[12]

The NCH_2 methylene proton resonances are found at δ 1.72 and 1.50 ppm (d, $^2J_{HH}$ = 11.5 Hz, $^2J_{YH}$ coupling not resolved), whereas the methylene proton resonances for the remaining CH_2SiMe_3 group are found at δ −0.81 and −0.93 ppm ($^2J_{HH}$ = 11.1 Hz, $^2J_{YH}$ = 2.1 and 2.7 Hz, respectively). The monomeric nature of the complex is deduced from the ^{13}C NMR data, where the NCH_2Y and $SiCH_2Y$ carbon resonances show coupling to a single ^{89}Y nucleus (I = $^1/_2$). This is in contrast with the observation for the significantly larger metal lanthanum, where a dinuclear species {[(μ-CH_2)MeTACNSiMe_2N(*t*-Bu)]La-(CH_2SiMe_3)}$_2$ is formed by metalation of one of the NMe groups of the TACN−amide ligand.[6] As may be anticipated for the proposed structure of **2**, the NCH_2Y carbon resonance (δ 63.4 ppm, $^1J_{CH}$ = 126 Hz, $^1J_{YC}$ = 30 Hz) is shifted significantly downfield from the $SiCH_2Y$ carbon resonance (δ 27.1 ppm, $^1J_{CH}$ = 100 Hz, $^1J_{YC}$ = 36 Hz), and displays the larger $^1J_{CH}$ and the smaller $^1J_{YC}$ coupling constant of the two methylene groups.

Scheme 4



Scheme 5



Attempts to generate the yttrium dialkyl complex (**L**^{2})Y$(CH_2SiMe_3)_2$, with the Me_2Si-bridged triamine−amide ligand, by reaction of Y$(CH_2SiMe_3)_3(THF)_2$ with H**L**^{2} led to rapid ligand cyclometalation to give {[(CH_2)-MeN$(CH_2)_2$][Me_2N$(CH_2)_2$]NSiMe_2N(*t*-Bu)}Y$(CH_2$-$SiMe_3)$ (**3**, Scheme 4), and we were unable to isolate or observe the intermediate dialkyl species. Thus changing the ligand bridge from $(CH_2)_2$ to Me_2Si makes the system much more reactive with respect to ligand metalation, a conclusion we could also draw for the Me_2-TACN−(bridge)−amide ligand system when applied to lanthanum.[6] Again, attempts to isolate **3** from preparative scale reaction only yielded the compound as an oil. The ^{1}H and ^{13}C NMR spectroscopic characteristics of **3** are very similar to those of **2**, indicating a similar monomeric structure in solution.

Reactivity Studies. To compare its behavior to the [Me_2TACN$(CH_2)_2$N(*t*-Bu)]Y(CH_2SiMe_3) cation, which was found to be an active ethene polymerization catalyst,[5,7] the generation of the **L**^{1}YCH_2SiMe_3 cation was studied. It was seen that the reaction of the Brønsted acid [PhNMe_2H][B$(C_6F_5)_4$] with either the dialkyl **1** or the metalated complex **2** results in formation of [**L**^{1}-YCH_2SiMe_3][B$(C_6F_5)_4$] (**4**, Scheme 5).

Unlike its Me_2TACN−amide analogue (which is stable for some time in neat bromobenzene-d_5 solvent), **4** needs the presence of THF to be sufficiently stable for spectroscopic characterization. The ^{13}C NMR spectrum of **4** (in THF-d_8) shows the YCH_2Si resonance at δ 33.5 ppm ($^1J_{CH}$ = 94 Hz, $^1J_{YC}$ = 38 Hz), shifted downfield relative to the dialkyl **1**, and with a smaller $^1J_{CH}$ and a larger $^1J_{YC}$ coupling constant. This behavior is similar to that observed in the generation of other yttrium monoalkyl cations.[5,13] The observation that **4** can be generated from **1** as well as **2** indicates that the YCH_2N group in **2** is more reactive than the YCH_2Si group. This is also borne out by other reactivity studies (vide infra). A catalytic ethene polymerization experiment with **1**/[PhNMe_2H]-[B$(C_6F_5)_4$] did not show any activity, but the combina-

(12) For related C−H activation of NMe_2 functionalities in group 3 metal complexes, see: (a) Booij, M.; Kiers, N. H.; Meetsma, A.; Teuben, J. H. *Organometallics* **1989**, *8*, 2454. (b) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720. (c) Hayes, P. G.; Piers, W. P.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. J. R.; Clegg, W. *Organometallics* **2001**, *20*, 2533.

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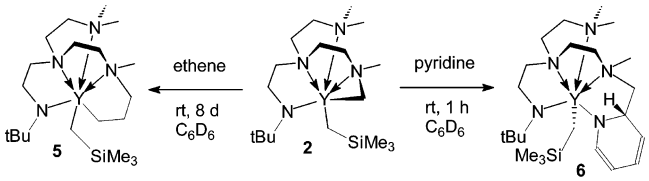
Scheme 6



tion **1**/$[Ph_3C][B(C_6F_5)_4]$, which does not generate the free Lewis base $PhNMe_2$ upon activation, showed initial polymerization activity (toluene solvent, 50 °C, 5 bar of ethene, 15 min run time), but rapid catalyst deactivation (within 4 min). The polyethene produced was characteristic of a single site catalyst ($M_w = 55 \times 10^3$, $M_w/M_n = 2.2$), with a productivity of 20 kg PE mol(Y)$^{-1}$ in the 4 min that the catalyst was active. Under comparable conditions, the $Me_2TACN-(CH_2)_2N(t\text{-}Bu)$-catalyst produced 940 kg PE mol(Y)$^{-1}$ in 10 min.[5,7] Clearly, the removal of the conformational constraint in the triamine ligand moiety leads to a dramatic decrease in catalyst performance.

The reactivity of the metalated complex **2** was further investigated by studying its reaction with ethene and with pyridine. With ethene, **2** reacts very sluggishly at ambient temperature (8 days to full conversion) by stoichiometric insertion into the $Y-CH_2N$ bond. The resulting product **5** (Scheme 6) was identified by a combination of 1D and 2D (COSY, HSQC) NMR techniques. The yttrium- and nitrogen-bound methylene groups of the $YCH_2CH_2CH_2N$ moiety give rise to ^1H resonances at δ 0.69 and 0.21 ppm and at δ 2.70 and 2.37 ppm, respectively. The corresponding ^{13}C resonances are found at δ 32.3 ppm ($^1J_{YC} = 41$ Hz, $^1J_{CH} = 110$ Hz) and δ 65.0 ppm ($^1J_{CH} = 135$ Hz), respectively. The YCH_2SiMe_3 moiety is retained in **5**, as seen, e.g., from the methylene ^{13}C resonance at δ 27.8 ppm ($^1J_{YC} = 34$ Hz, $^1J_{CH} = 101$ Hz). Apparently the reactivity is associated with the strain in the metalated moiety of **2**, as no evidence was found for the occurrence of subsequent ethene insertions.

The reaction of **2** with pyridine proceeds much faster than that with ethene, and is complete within an hour upon addition of the reagent at ambient temperature. The product is again derived from (1,2-)insertion into the $Y-CH_2N$ bond,[14] resulting in complex **6** (Scheme 6) that was characterized by single-crystal X-ray diffraction (Figure 2, pertinent interatomic distances and angles in Table 2). The overall coordination geometry of the metal center in **6** is very similar to that in the dialkyl complex **1**, with one alkyl group being replaced by the vinylamide moiety resulting from the 1,2-insertion of the pyridine into the $Y-CH_2N$ bond. Differences in metal−ligand bond distances between **1** and **6** are within 3−4 σ, with two notable exceptions. First, the amine nitrogen to which the reduced pyridine is attached has moved somewhat closer to the metal (by 0.030 Å), probably in response to the five-membered-ring chelate arrangement. Second, the Y−amine distance to the NMe_2 group trans to the vinylamide, $Y-N(4) = 2.670(2)$ Å, is much shorter (by 0.170 Å) than that for the amine trans to the C(15) alkyl group in **1**. Evidently, this Y−amine distance is very sensitive to the nature of the group trans to it. In recent years there have been several observations that suggest the presence of a kind of trans influence in group 3 metal and lanthanide complexes, but the source of this phenomenon is still subject to debate.[15] As the effects seen in the present system (with distance differences in the order of 0.2 Å) are significantly larger than those observed thus far (in the order of 0.06 Å), the $\mathbf{L^1}Y(X)(CH_2SiMe_3)$ system seems suitable for a further study of this phenomenon. A range of compounds of this type should be readily accessible from **2**.

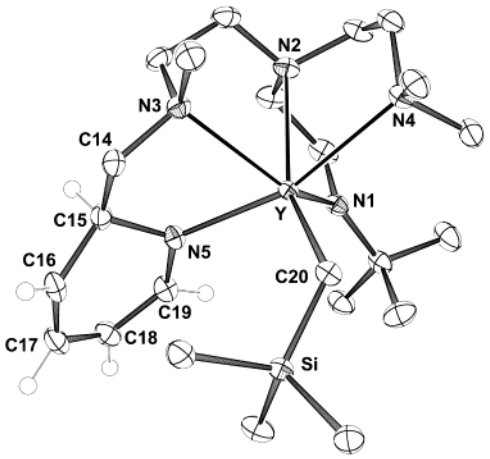


Figure 2. Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity, except for those on the C_6H_6N fragment.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6

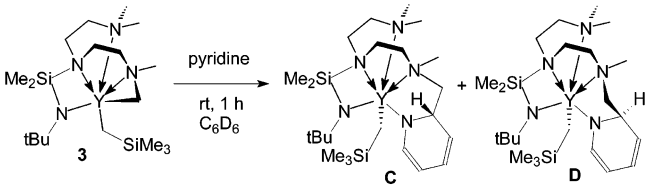
Y−N(1)	2.234(2)	N(5)−C(15)	1.472(2)
Y−N(2)	2.522(2)	C(15)−C(16)	1.506(3)
Y−N(3)	2.557(2)	C(16)−C(17)	1.335(3)
Y−N(4)	2.670(2)	C(17)−C(18)	1.440(3)
Y−N(5)	2.295(2)	C(18)−C(19)	1.364(3)
Y−C(20)	2.448(2)	C(19)−N(5)	1.360(2)
N(3)−C(14)	1.488(2)	C(14)−C(15)	1.521(3)
N(1)−Y−N(2)	73.04(5)	N(3)−Y−N(5)	68.99(5)
N(1)−Y−N(3)	135.45(5)	N(4)−Y−N(5)	162.26(5)
N(1)−Y−N(4)	95.55(5)	N(3)−Y−C(20)	102.88(6)
N(1)−Y−N(5)	95.69(5)	N(4)−Y−C(20)	82.40(5)
N(1)−Y−C(20)	121.53(6)	N(5)−Y−C(20)	103.18(6)
N(2)−Y−N(3)	70.04(5)	Y−N(5)−C(15)	123.0(1)
N(2)−Y−N(4)	68.56(5)	Y−N(5)−C(19)	125.1(1)
N(2)−Y−N(5)	101.86(5)	N(5)−C(15)−C(14)	109.4(2)
N(3)−Y−N(4)	93.42(5)	N(5)−C(15)−C(16)	110.7(2)
		C(14)−C(15)−C(16)	112.1(2)

The solution ^1H and ^{13}C NMR spectra of **6** (including COSY and HSQC experiments) are fully consistent with the structure as observed in the single-crystal structure determination. The resonances of the $YNCH(CH_2)$ moiety are found at δ 4.02 ppm (^1H NMR, with two different couplings to the protons of the adjacent methylene group) and δ 54.5 ppm (^{13}C NMR, $J_{CH} = 131.5$ Hz), and

(14) For other examples of pyridine 1,2-insertion into Y−H/alkyl bonds, see: (a) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291. (b) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291. (c) Duchateau, R.; Brussee, E. A. C.; Meetsma, A.; Teuben, J. H. *Organometallics* **1997**, *16*, 5506. (d) Gountchev, T. I.; Tilley, T. D. *Organometallics* **1999**, *18*, 2896.

(15) See: (a) Domingos, A.; Elsegood, M. R. J.; Hillier, A. C.; Lin, G.; Liu, S. Y.; Lopes, I.; Marques, N.; Maunder, G. H.; McDonald, R.; Sella, A.; Steed, J. W.; Takats, J. *Inorg. Chem.* **2002**, *41*, 6761. (b) Kornienko, A.; Melman, J. H.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **2002**, *41*, 121. (c) Freedman, D.; Melman, J. H.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1998**, *37*, 4162 and references cited therein.

Scheme 7



the coupling constants are consistent with the geometry of this specific diastereomer, the only product formed in the reaction.

In contrast, reaction between pyridine and the metalated complex with the $SiMe_2$ bridge in the ligand (**3**) shows formation of two diastereomers in approximately a 1:1 ratio (Scheme 7). The NMR resonances for the two diastereomers could be assigned with the aid of COSY and HSQC measurements. For the H-endo isomer (**D** in Scheme 7) the YN*CH*(CH_2) proton resonance is shifted upfield by 0.78 ppm relative to that in the H-exo isomer **C**. The increased geometrical constraint of the ligand $SiMe_2$ bridge versus the $(CH_2)_2$ bridge apparently opens up the complex sufficiently to lose diastereoselectivity in the pyridine insertion reaction. It appears that the H-exo isomer (**C** in Scheme 7) is formed faster initially, making it unclear whether the obtained diastereomer ratio is kinetically or thermodynamically determined.

Conclusions

Monoanionic tetradentate triamine−amide ligands based on bis(*N*,*N*-dimethyl-2-aminoethyl)amine, with a pendant amide functionality attached to the central triamine nitrogen atom through a $(CH_2)_2$ or a $SiMe_2$ bridge, are readily accessible. These ligands can be attached to an yttrium dialkyl fragment by using the same methodology as used previously to prepare complexes with a triamine−amide ligand containing a cyclic triamine (TACN) moiety. Nevertheless, the lack of geometrical constraint in the open triamine fragment makes the system very susceptible to ligand cyclometalation, and results in a very poor catalyst performance in ethene polymerization. The enhanced reactivity of the "open" triamine ligand moiety versus the TACN fragment may be compared to that of "open" pentadienyl versus cyclopentadienyl ligands,[16] with the distinction that the reactivity of the pentadienyl group stems both from the greater conformational freedom as well as from the enhanced nucleophilicity of the pentadienyl methylene groups.

The kinetic lability of the NMe_2 groups in the triamine−amide yttrium complexes is seen by NMR spectroscopy, showing rapid dissociation and inversion of these groups at ambient temperature, and is probably related to the presence of one extemely long Y−NMe_2 dative bond, as seen in the crystal structure of the dialkyl complex **1**. This Y−amine distance appears to be very sensitive to the ligand trans to it. Thus the (triamine-amido)M(X)(CH_2SiMe_3) system could be very suitable for the investigation of trans influence phenomena for group 3 metals and lanthanides, the nature of which is presently unclear. As reactivity studies of the metalated complex **2** have shown, the Y−CH_2N bond is significantly more reactive than the Y−CH_2Si bond. This should provide a convenient access to (triamine-amido)M(X)(CH_2SiMe_3) complexes.

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, or dried over and distilled from CaH_2 (C_6D_5Br) prior to use. The reagents Me_3SiCH_2Li,[17] $YCl_3(THF)_{3.5}$,[18] $Y(CH_2SiMe_3)_3(THF)_2$,[9] tris(2-dimethylaminoethyl)amine,[19] and *N*-*tert*-butylchloroacetamide[5] were prepared according to published procedures. Tris(2-aminoethyl)amine (Aldrich), $[PhNMe_2H][B(C_6F_5)_4]$, and $[Ph_3C][B(C_6F_5)_4]$ (Asahi Glass Co.) were used as received. NMR spectra were recorded on 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 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.

Synthesis of *N*-*tert*-Butylaminoethylbis(2-dimethylaminoethyl)amine (L^{1}H). (a) Li[bis(2-dimethylaminoethyl)amide]. A solution of *t*-BuLi (1.5 M, 20.0 mL, 30.0 mmol) was slowly added to a solution of 6.5 g (28.2 mmol) of tris(2-dimethylaminoethyl)amine in hexane (50 mL, −40 °C). The reaction mixture was allowed to warm to ambient temperature and was stirred for an additional 2 h. The solution was concentrated to 20 mL and cooled overnight (−30 °C) providing yellowish crystals of Li[bis(2-dimethylaminoethyl)-amide] (3.90 g, 23.7 mmol, 84%) that were isolated by filtration. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 3.45 (m, 4H, NCH_2), 3.10 (m, 2H, NCH_2), 2.25 (m, 2H, NCH_2), 2.06 (m, 4H, NCH_2), 2.03 (br s, 6H, NCH_3), 2.00 (br s, 6H, NCH_3). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 20 °C): δ 63.7 (NCH_2), 58.3 (NCH_2), 47.3 (NCH_3), 41.8 (NCH_3).

(b) Bis(2-dimethylaminoethyl)amine. Li[bis-(2-dimethylaminoethyl)amide] (3.50 g, 21.2 mmol) was dissolved in 15 mL of hexane, after which 10 mL of water was added. The mixture was subsequently extracted with $CHCl_3$ (3 × 100 mL). The combined extracts were dried over Na_2SO_4 after which the solvent was removed in vacuo to yield bis(2-dimethylaminoethyl)amine (3.20 g, 21.1 mmol, 95%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ 2.68 (t, J = 6.2 Hz, 4H, NCH_2), 2.39 (t, J = 6.2 Hz, 4H, NCH_2), 2.21 (s br, 1H, NH), 2.19 (s, 12 H, NCH_3). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 20 °C): δ 57.4 (NCH_2), 53.0 (NCH_2), 45.9 (NCH_3).

(c) *N*-*tert*-Butylbis(2-dimethylaminoethyl)amino Acetamide. A mixture of bis(2-dimethylaminoethyl)amine (4 g, ca. 25 mmol), *N*-*tert*-butylchloroacetamide (3.8 g, 26 mmol), acetonitrile (10 mL), potassium iodide (0.3 g), and 4 g of powdered

(16) See e.g.: (a) Hylakryspin, I.; Waldman, T. E.; Mendelez, E.; Trakarnpruk, W.; Arif, A. M.; Ziegler, M. L.; Ernst, R. D.; Gleiter, R. *Organometallics* **1995**, *14*, 5030. (b) Tomaszewski, R.; Arif, A. M.; Ernst, R. D. *J. Chem. Soc., Dalton Trans.* **1999**, 1883. (c) Ernst, R. D. *Comments Inorg. Chem. A* **1999**, *21*, 285 and references cited therein.

(17) Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664.

(18) (a) Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387. (b) Sobota, P.; Utko, J.; Szafert, S. *Inorg. Chem.* **1994**, *33*, 5203.

(19) Mizzoni, R. H.; Hennessey, M. A.; Scholz, C. R. *J. Am. Chem. Soc.* **1954**, *76*, 2414.

K_2CO_3 was stirred at ambient temperature for 20 h. The solids were filtered off and washed with ether (3 × 25 mL). The filtrates were combined and concentrated. The residue was extracted with three 25-mL portions of warm ether. The extracts were combined and after removal of the solvent the residue was distilled with a Kugelrohr apparatus (oven 180 °C, 0.4 Torr) to give 2.1 g (37%) of product. ^{1}H NMR (300 MHz, 20 °C, $CDCl_3$): δ 7.9 (br, 1H, NH), 2.95 (s, 2H, NCH_2), 2.57 (t, J = 7.4 Hz, NCH_2), 2.27 (t, J_{HH} = 7.4 Hz, 4H, NCH_2), 2.16 (s, 12H, NCH_3), 1.29 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C, $CDCl_3$): δ 168.9 (C=O), 57.2 (NCH_2), 56.7 (NCH_2), 55.1 (NCH_2), 51.7 (*t*-Bu C), 43.2 (NCH_3), 26.1 (*t*-Bu Me).

(d) *N*-*tert*-Butylaminoethylbis(2-dimethylaminoethyl)amine. A solution of *N*-*tert*-butylbis(2-dimethylaminoethyl)-amino acetamide (1.5 g, 5.5 mmol) was reduced with ca. 1 g of $LiAlH_4$ in 10 mL of dimethoxyethane (18 h at reflux). Water (2 mL) was slowly added while the mixture was cooled and stirred. Stirring was continued until the color of the mixture was white. After filtration the solids were washed with ether. The combined filtrates were dried over Na_2SO_4, filtered, and concentrated, using a rotary evaporator. Subsequent Kugelrohr distillation (1.5 Torr, 150 °C) yielded 1.5 g (83%) of the title compound as a colorless oil. ^{1}H NMR (300 MHz, 20 °C, $CDCl_3$): δ 2.28−2.54 (m, 12H, NCH_2), 2.16 (s, 12H, NCH_3), 1.03 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C, $CDCl_3$): δ 56.8 (NCH_2), 55.0 (NCH_2), 52.7 (NCH_2), 50.3 (*t*-Bu C), 43.4 (NCH_3), 37.6 (NCH_2), 26.5 (*t*-Bu Me). MS(CI) for $C_{14}H_{34}N_4$ *m*/*z* 259 $(M + H)^+$.

Synthesis of *N*-*tert*-Butylaminodimethylsilylbis(2-dimethylaminoethyl)amine (L^2H). Li[bis(2-dimethylaminoethyl)amide] (3.37 g, 20.4 mmol) was dissolved in 40 mL of hexane and slowly added to a solution of dichlorodimethylsilane (10 mL, 10.6 g, 82.1 mmol) in 20 mL of hexane. The reaction mixture turned yellow and was stirred for 4 h. The solvent and excess Me_2SiCl_2 was removed under reduced pressure and the residue was redissolved in hexane (50 mL). The solution was then reacted with *t*-$BuNH_2$ (12 mL, 114.2 mmol) at room temperature, resulting in precipitation of [*t*-$BuNH_3$][Cl]. After 18 h the hexane and excess amine was removed under vacuum. The remaining sticky residue was extracted with hexane (3 × 100 mL). Evaporation of the solvent yielded 4.44 g (13.0 mmol, 64%) of the title compound as a colorless oil that was >95% pure by NMR spectrocopy. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ 3.03 (t, J = 7.2 Hz, 4H, NCH_2), 2.36 (t, J = 7.2 Hz, 4H, NCH_2), 2.14 (s, 12H, NMe_2), 1.17 (s, 9H, *t*-Bu), 0.21 (s, 6H, $SiMe_2$). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 20 °C): δ 60.9 (NCH_2), 48.7 (*t*-Bu C), 46.1 (NMe_2), 45.9 (NMe_2), 33.7 (*t*-Bu Me), 1.4 ($SiMe_2$).

Synthesis of [{$Me_2N(CH_2)_2$}$_2$N$(CH_2)_2$N(*t*-Bu)]Y(CH_2SiMe_3)$_2$ (1). A solution of L^1H (0.51 g, 2.00 mmol) in pentane (10 mL) was added dropwise to a solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.98 g, 2.00 mmol) in pentane (50 mL) at ambient temperature. The reaction mixture was stirred for 4 h, after which the volatiles were removed in vacuo. The residue was stripped of residual THF by stirring with pentane (5 mL), which was subsequently removed in vacuo. The resulting sticky solid was extracted with pentane (2 × 50 mL). Concentrating and cooling the extract to − 30 °C gives **1** as a crystalline solid (0.70 g, 1.36 mmol, 68%). ^{1}H NMR (500 MHz, 20 °C, C_6D_6): δ 3.34 (m, 1 H, NCH_2), 3.23 (m, 1 H, NCH_2), 3.08 (t, J = 6.0 Hz, 2 H, NCH_2), 2.57 (m, 2 H, NCH_2), 2.02 (s, 12 H, NMe_2), 1.59−1.52 (m, 6 H, NCH_2), 1.46 (s, 9 H, *t*-Bu), 0.43 (s, 18 H, $SiMe_3$), −0.54 (br, 2 H, YCH_2), −0.81 (br, 2 H, YCH_2). ^{1}H NMR (500 MHz, −70 °C, C_7D_8): δ 3.11 (m, 2 H, NCH_2), 2.81 (m, 2 H, NCH_2), 3.50 (m, 2 H, NCH_2), 2.40 (s, 3 H, NMe_2), 2.15 (s, 3 H, NMe_2), 1.89 (m, 1 H, NCH_2), 1.76 (s, 3 H, NMe_2), 1.53 (s, 9 H, *t*-Bu), 1.44 (m, 1 H, NCH_2), 1.35 (s, 3 H, NMe_2), 1.04−0.90 (m, 4 H, NCH_2), 0.65 (s, 9 H, $SiMe_3$), 0.53 (s, 9 H, $SiMe_3$), −0.02 (d, J = 9.0 Hz, 1 H, YCH_2), −0.51 (d, J = 9.0 Hz, 1 H, YCH_2), −1.03 (d, J = 10.5 Hz, 1 H, YCH_2), −1.15 (d, J = 10.5 Hz, 1 H, YCH_2). The J_{YH} coupling on the YCH_2 protons is unresolved. ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C, C_6D_6): δ 71.6 (NCH_2), 70.1 (NCH_2), 59.0 (NCH_2), 57.0 (NCH_2), 55.9 (NCH_2), 53.7 (s, *t*-Bu C), 50.9 (NMe_2), 47.3 (NMe_2), 44.4 (NCH_2), 30.9 (d, J_{YC} = 36.6 Hz, YCH_2), 29.9 (*t*-Bu Me), 5.2 (Me_3SiCH_2Y). Anal. Calcd for $C_{22}H_{55}N_4Si_2Y$: C, 50.74; H, 10.64; N, 10.76. Found: C, 50.86; H, 10.55; N, 10.97.

Generation of {[$(CH_2)MeN(CH_2)_2$][$Me_2N(CH_2)_2$]N$(CH_2)_2$N-(*t*-Bu)}Y(CH_2SiMe_3) (2) from 1. A solution of **1** (40.0 mg, 76.8 μmol) in benzene-d_6 (0.6 mL) was allowed to stand overnight at 20 °C. Monitoring the solution by NMR spectroscopy showed clean conversion to **2** and $SiMe_4$, going to completion in approximately 8 h. ^{1}H NMR (500 MHz, 20 °C, C_6D_6): δ 3.34 (m, 1 H, NCH_2), 3.26 (m, 1 H, NCH_2), 2.85−2.74 (m, 2 H, NCH_2), 2.48 (s, 3 H, NMe), 2.33 (m, 4 H, NCH_2), 2.00 (br s, 6 H, NMe_2), 1.99−1.93 (m, 4 H, NCH_2), 1.72 (d, J_{HH} = 11.5 Hz, 1 H YCH_2N), 1.50 (d, J_{HH} = 11.5 Hz, 1 H YCH_2N), 1.46 (s, 9 H, *t*-Bu), 0.47 (s, 9 H, $SiMe_3$), −0.93 (dd, J_{YH} = 2.7 Hz, J_{HH} = 11.1 Hz, 1 H YCH_2Si), −0.81 (dd, J_{YH} = 2.1 Hz, J_{HH} = 11.1 Hz, 1 H YCH_2Si). The J_{YH} coupling on the NCH_2Y protons is not resolved. ^{13}C NMR (75.4 MHz, 20 °C, C_6D_6): δ 72.1 (t, J = 139.5 Hz, NCH_2), 70.6 (t, J = 143.3 Hz, NCH_2), 63.4 (dt, J_{YC} = 29.8 Hz, J_{CH} = 125.7 Hz, YCH_2N), 63.0 (t, J = 132.0 Hz, NCH_2), 59.2 (t, J = 137.5 Hz, NCH_2), 59.1 (t, J = 134.5 Hz, NCH_2), 54.5 (s, *t*-Bu C), 53.8 (q, J = 137.0 Hz, NMe), 51.0 (q, J = 135.8 Hz, NMe), 50.2 (t, J = 132.0 Hz, NCH_2), 45.8 (t, J = 127.0 Hz, NCH_2), 31.6 (q, J = 122.7 Hz, *t*-Bu Me), 27.1 (dt, J_{YC} = 36.0 Hz, J_{CH} = 99.5 Hz, YCH_2Si), 5.2 (t, J = 114.4 Hz, $SiMe_3$).

Synthesis of {[$(CH_2)MeN(CH_2)_2$][$Me_2N(CH_2)_2$]N$SiMe_2$N-(*t*-Bu)}Y(CH_2SiMe_3) (3). A solution of L^2H (0.37 g, 1.07 mmol) in hexane (15 mL) was added to a solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.53 g, 1.07 mmol) in hexane (20 mL) at ambient temperature. The reaction mixture was stirred for 4 h, after which the volatiles were removed in vacuo. The residue was stripped of residual THF by stirring with pentane (5 mL), which was subsequently removed in vacuo. The resulting sticky solid was extracted with pentane (30 mL). Concentration of the extract and cooling to −80 °C did not result in crystallization. The solvent was evaporated, yielding 420 mg of **3** as an oil (0.76 mmol, 70%) that was essentially pure by NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 3.09 (dt, J = 13.4 Hz, 4.7 Hz, 1H, NCH_2), 2.51 (dddd, J = 14.5, 3.8, 6.2, 9.9 Hz, 1H NCH_2), 2.54 (s, 3H, NMe), 2.35 (dt, J = 12.5, 5.1 Hz, 1H, NCH_2), 2.26 (m, 1H, NCH_2), 2.05 (s, 3H, NMe), 1.97 (ddd, J = 12.8, 3.8, 9.0 Hz, 1H, NCH_2), 1.93 (s, 3H, NMe), 1.87 (dd, J = 12.0, 4.9 Hz, 1H, NCH_2), 1.81 (dd, J = 4.9, 13.9 Hz, 1H, NCH_2), 1.76 (d, 1H, J_{HH} = 11.9 Hz, YCH_2N), 1.75 (m, 1H, NCH_2), 1.48 (s, 9H, *t*-Bu), 1.43 (dd, J_{YH} = 2.0 Hz, J_{HH} = 11.9 Hz, 1H, YCH_2N), 0.46 (s, 9H, $SiMe_3$), 0.28 (s, 3H, SiMe), 0.12 (s, 3H, SiMe), −0.75 (dd, J_{YH} = 2.4 Hz, J_{HH} = 11.0 Hz, 1H, YCH_2Si), −0.88 (dd, J_{YH} = 2.0 Hz, J_{HH} = 11.0 Hz, 1H, YCH_2Si). ^{13}C NMR (125.8 MHz, C_6D_6, 298 K): δ 63.2 (t, J = 126.3 Hz, NCH_2), 63.1 (dt, J_{YC} = 29.1 Hz, J_{CH} = 122.5 Hz, YCH_2N), 63.0 (t, J = 125.4 Hz, NCH_2), 62.5 (t, J = 134.2 Hz, NCH_2), 59.6 (t, J = 133.3 Hz, NCH_2), 50.2 (q, J = 132.3 Hz, NMe), 48.4 (t, J = 135.3 Hz, NCH_2), 46.1 (s, *t*-Bu C), 46.2 (q, J = 135.3 Hz, NMe), 45.9 (t, J = 136.2 Hz, NCH_2), 45.8 (q, J = 135.3 Hz, NMe), 37.5 (q, J = 124.0 Hz, *t*-Bu Me), 29.4 (dt, J_{YC} = 38.0 Hz, J_{CH} = 98.7 Hz, YCH_2Si), 5.5 (q, J = 117.7 Hz, SiMe), 5.0 (q, J = 115.5 Hz, SiMe), 3.4 (q, J = 116.9 Hz, $SiMe_3$).

Generation of {[$Me_2N(CH_2)_2]_2N(CH_2)_2N$(*t*-Bu)}Y($CH_2$-$SiMe_3$)(THF-$d_8$)$_n$[$B(C_6F_5)_4$] (4). (a) From 1. A solution of **1** (20.8 mg, 40.0 μmol) in THF-d_8 (0.6 mL) was added to solid [$HNMe_2Ph$][$B(C_6F_5)_4$] (32.0 mg, 40.0 μmol). The obtained solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the cationic species **4**, $SiMe_4$, and free $PhNMe_2$.

(b) From 2. A solution of **2**, generated from **1** (15.6 mg, 30.0 μmol) in THF-d_8 (0.6 mL) by allowing this solution to stand at ambient temperature for 2 days, was added to solid [$HNMe_2$-Ph][$B(C_6F_5)_4$] (24.0 mg, 30.0 μmol). NMR spectroscopy showed

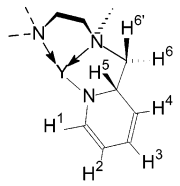
clean formation of **4** and free $PhNMe_2$. ^1H NMR (300 MHz, 20 °C, THF-d_8): δ 3.11 (m, 2 H, NCH_2), 2.83 (m, 2 H, NCH_2), 2.60 (s, 6H, NMe_2), 2.59−2.45 (m, 8H, NCH_2), 2.55 (s, 6H, NMe_2), 1.22 (s, 9 H, *t*-Bu), −0.05 (s, 9 H, $SiMe_3$), −1.10 (d, J_{YH} = 2.6 Hz, 2 H, YCH_2). Free $PhNMe_2$: δ 7.14 (t, J = 7.9 Hz, 2H, *m*-H), 6.69 (d, J = 7.9 Hz, 2H, *o*-H), 6.60 (t, J = 7.3 Hz, 1H, *p*-H), 2.89 (s, 6H, NMe_2). ^{13}C NMR (75.4 MHz, 20 °C, THF-d_8): δ 59.2 (t, J = 134.5 Hz, NCH_2), 56.0 (t, J = 136.5 Hz, NCH_2), 52.1 (t, J = 136.4 Hz, NCH_2), 48.6 (q, J = 140.5 Hz, NMe_2), 47.3 (q, J = 140.5 Hz, NMe_2), 46.8 (s, *t*-Bu C), 44.8 (t, J = 132.2 Hz, NMe_2), 33.5 (dt, J_{YC} = 38.2 Hz, J_{CH} = 94.0 Hz, YCH_2), 30.3 (q, J = 124.0 Hz, *t*-Bu Me), 5.0 (q, J = 116.6 Hz, $SiMe_3$). Free $PhNMe_2$: δ 152.3 (ipso-C), 130.0 (Ph CH), 117.6 (Ph CH), 113.8 (Ph CH), 41.1 (q, J = 134.7 Hz, NMe_2).

Ethene Polymerization with 1 and $[Ph_3C][B(C_6F_5)_4]$. In a drybox, solutions were prepared of **1** (10 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (10 μmol), each in 10 mL of toluene in separate septum-capped vials. Polymerization was performed in a stainless steel 0.5-L autoclave (predried in vacuo at 80 °C and then cooled and flushed with nitrogen), charged with 150 mL of dry toluene. After equilibration at the desired reaction temperature (50 °C), the reactor was pressurized with ethene (5 bar). The solution of $[Ph_3C][B(C_6F_5)_4]$ was injected into the reactor first (using a pneumatically operated injector), and the reaction was started by subsequently injecting the solution of **1**. The ethylene pressure was kept constant during the reaction by replenishing flow, and the ethene uptake was monitored continuously. The reactor was stirred for 15 min and then vented. The polymer was repeatedly rinsed with methanol and dried in a vacuum oven, yielding 0.2 g of polyethylene (M_w = 55 000; M_w/M_n = 2.18 by GPC). The same experiment, but with $[PhNMe_2H][B(C_6F_5)_4]$ activator, did not yield any polymer.

Reaction of 2 with Ethene. A solution of **2** (C_6D_6, 0.6 mL, generated from 27.0 mg, 51.8 μmol of **1**) was placed in an NMR tube with a Teflon (Young) valve, and the tube was attached to a vacuum line. The solution was frozen in liquid nitrogen and evacuated, after which ethylene (60.0 μmol) was condensed into the tube. The tube was closed, carefully thawed out, and brought to ambient temperature. The reaction was monitored by ^1H NMR spectroscopy. After 8 days **1** was fully converted to the insertion product **5**. Assignment of the NMR resonances was aided by COSY and HSQC experiments. ^1H NMR (500 MHz, C_6D_6, 20 °C): δ 3.17 (m, 2H, NCH_2), 2.97 (m, 2H, NCH_2), 2.78 (m, 1H, NCH_2), 2.70 (m, 1H, YCH_2CH_2CHH), 2.58 (m, 2H, NCH_2), 2.49 (m, 1H, YCH_2CHH), 2.47 (m, 1H, NCH_2), 2.37 (m, 1H, YCH_2CH_2CHH), 2.20 (m, 2H, NCH_2), 2.14 (m, 1H, YCH_2CHH), 2.12 (m, 2H, NCH_2), 2.00 (br, 6H, NMe_2), 1.94 (s, 3H, NMe), 1.63 (m, 2H, NCH_2), 1.46 (s, 9H, *t*-Bu), 1.28 (m, H, NCH_2), 1.21 (m, H, NCH_2), 0.69 (m, 1H, $YCHHCH_2$), 0.50 (s, 9H, $SiMe_3$), 0.21 (m, 1H, $YCHHCH_2$), −1.00 (dd, J_{HH} = 10.7 Hz, J_{YH} = 2.5 Hz, 1H, $YCHHSi$), −1.06 (dd, J_{HH} = 10.7 Hz, J_{YH} = 2.2, 1H, $YCHHSi$). ^{13}C NMR (125.7 MHz, C_6D_6, 20 °C): δ 65.0 (t, J = 134.5 Hz, $YCH_2CH_2CH_2$), 58.4 (t, J = 132.2 Hz, NCH_2), 54.1 (t, J = 132.8 Hz, NCH_2), 53.3 (t, J = 133.9 Hz, NCH_2), 51.1 (t, J = 133.9 Hz, NCH_2), 50.3 (*t*-Bu C), 49.5 (t, J = 134.0 Hz, NCH_2), 47.2 (br q, J = 133.8 Hz, NMe_2), 45.4 (t, J = 127.9 Hz, NCH_2), 43.2 (q, J = 135.4 Hz, NMe), 32.3 (dt, J_{YC} = 41.2 Hz, J_{CH} = 109.9 Hz, YCH_2CH_2), 30.5 (q, J = 123.9 Hz, *t*-Bu Me), 27.8 (d, J_{YC} = 33.5 Hz, J_{CH} = 101.2 Hz, YCH_2-Si), 26.8 (t, J = 123.4 Hz, YCH_2CH_2), 5.3 (q, J = 117.8 Hz, $SiMe_3$).

Synthesis of {$[NC_5H_5CH_2NMe(CH_2)_2][Me_2N(CH_2)_2]N(CH_2)_2N(t\text{-}Bu)$}$Y(CH_2SiMe_3)$ (6). A solution of **2** in 0.6 mL of C_6D_6 was generated by allowing a solution of **1** (40 mg, 76.8 μmol) to stand at ambient temperature, as described above. Pyridine (6.2 μL, 76.8 μmol) was added to this solution, and ^1H NMR spectroscopy showed clean converson to **6**. From this solution, crystals of **6** gradually separated, which were isolated after decanting the supernatant. Yield 26.6 mg (52.0 μmol, 68%).

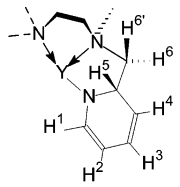
The assignment of the NMR resonances of **6** was made with



the aid of COSY and HSQC spectra. The labeling of the H/C nuclei of the $NCH_2(C_5H_5N)$ fragment is shown above. ^1H NMR (500 MHz, C_6D_6, 20 °C): δ 7.71 (d, J_{12} = 6.1 Hz, 1H, H^1), 6.52 (dd, J_{32} = 6.0 Hz, J_{34} = 8.0 Hz, 1H, H^3), 5.51 (ps t, $J_{21} = J_{23}$ = 6.0 Hz, 1H, H^2), 4.66 (d, J_{43} = 8.0 Hz, 1H, H^4), 4.02 (dd, J_{56} = 11.8 Hz, $J_{56'}$ = 4.7 Hz, 1H, H^5), 3.45 (ps t, $J_{56} = J_{66'}$ = 11.8 Hz, 1H, H^6), 3.19−2.82 (m, 4H, NCH_2), 2.56 (dt, J = 13.3, 2.9 Hz, 1H, NCH_2), 2.37 (dd, $J_{66'}$ = 11.8 Hz, $J_{56'}$ = 4.7 Hz, 1H, $H^{6'}$), 2.2−1.8 (br, 6H, NMe_2, overlaps with the following resonance), 1.97−1.72 (m, 4H, NCH_2), 1.69 (s, 3H, NMe_2), 1.37 (s, 9H, *t*-Bu), 1.07−0.96 (m, 2H, NCH_2), 0.46 (s, 9H, $SiMe_3$), −1.18 (dd, J_{HH} = 10.0 Hz, J_{YH} = 2.4, 1H, YCH_2Si), −1.11 (dd, J_{HH} = 10.0 Hz, J_{YH} = 3.0, 1H, YCH_2Si). ^{13}C NMR (125.7 MHz, C_6D_6, 20 °C): δ 149.0 (d, J = 163.1 Hz, C_1), 128.6 (d, overlap with solvent, C_2), 100.8 (d, J = 159.6 Hz, C_4), 95.9 (d, J = 161.4 Hz, C_3), 63.8 (t, J = 132.4 Hz, C_6), 58.3 (t, J = 128.0 Hz, NCH_2), 54.7 (t, J = 135.9 Hz, NCH_2), 54.5 (d, J = 131.5 Hz, C_5), 53.9 (*t*-Bu C), 51.5 (t, J = 133.3 Hz, NCH_2), 48.8 (t, J = 134.2 Hz, NCH_2), 47.3 (t, J = 134.2 Hz, NCH_2), 46.8 (br, NMe_2), 43.5 (t, J = 126.3 Hz, NCH_2), 42.7 (q, J = 135.1 Hz, NMe), 29.9 (q, J = 123.4 Hz, *t*-Bu Me), 27.8 (dt, J_{YC} = 36.6 Hz, J_{CH} = 98.6 Hz, YCH_2Si), 5.0 (q, J = 116.1 Hz, $SiMe_3$). Anal. Calcd for $C_{23}H_{48}N_5SiY$: C, 53.99; H, 9.46; N, 13.69. Found: C, 53.98; H, 9.28; N, 13.12.

Reaction of 3 with Pyridine. Pyridine (6.0 μL, 75 μmol) was added to a solution of **3** (32 mg, 69 μmol) in 0.6 mL of C_6D_6. NMR spectroscopy showed clean 1,2-insertion of pyridine into the $Y-CH_2N$ bond. Full conversion is reached within 1 h, yielding a mixture of diastereomers in an approximate 1:1 ratio. The assignment of NMR resonances was aided by 2D (COSY, HSQC) experiments.

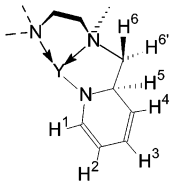
The labeling of the H-exo isomer (**C**) is given here.



^1H NMR (500 MHz, C_6D_6, 20 °C): δ 7.59 (d, J_{12} = 6.4 Hz, 1H, H^1), 6.42 (dd, J_{23} = 6.5 Hz, J_{34} = 6.9 Hz, 1H, H^3), 5.38 (t, $J_{21} = J_{23}$ = 5.7 Hz, 1H, H^2), 4.54 (d, J_{43} = 8.3 Hz, 1H, H^4), 4.14 (br d, J_{56} = 11.5 Hz, 1H, H^5), 3.39 (t, $J_{65} = J_{66'}$ = 11.6 Hz, 1H, H^6), 3.03 (t, J_{HH} = 8.3 Hz, 2H, NCH_2), 2.90 (m, 2H, NCH_2), 2.50 (m, 4H, NCH_2), 2.30 (br d, $J_{66'}$ = 11.6 Hz, 1H, $H^{6'}$), (s, 6H, NMe_2), 1.94 (s, 3H, NMe), 1.40 (s, 9H, *t*-Bu), 0.46 (s, 9H, $SiMe_3$), 0.33 (s, 3H, SiMe), 0.28 (s, 3H, SiMe), −0.92 (dd, J_{YH} = 3.0 Hz, J_{HH} = 11.0 Hz, 1H, YCH_2SiMe_3), −1.03 (dd, J_{YH} = 2.2 Hz, J_{HH} = 10.8 Hz, 1H, YCH_2SiMe_3). ^{13}C NMR (125.7 MHz, C_6D_6, 20 °C): δ 147.8 (d, J = 159.4 Hz, C^1), 129.1 (d, J = 160.2 Hz, C^3), 101.8 (d, J = 159.1 Hz, C^4), 94.2 (d, J = 158.6 Hz, C^2), 67.3 (t, J = 135.8 Hz, C^6), 61.2 (d, NCH_2), 58.4 (t, J = 133.9 Hz, NCH_2), 55.2 (d, J = 130.5 Hz, C^5), 53.8 (NCH_2), 53.0 (s, *t*-Bu C), 47.7 (NMe), 47.2 (NCH_2), 46.1 (NMe), 45.9 (NMe), 36.0 (q, J = 122.1 Hz, *t*-Bu), 29.4 (dt, J_{YC} = 38.3 Hz, J_{CH} = 99.1 Hz, YCH_2Si), 5.0 (q, J = 115.3 Hz, $SiMe_3$), 2.7 (q, J = 117.0 Hz, SiMe), 1.4 (q, J = 117.0 Hz, SiMe). Overlap of resonances prevented the determination of some coupling constants.

The labeling of the H-endo isomer (**D**) is given here.

^1H NMR (500 MHz, C_6D_6, 20 °C): δ 7.45 (d, J_{12} = 6.3 Hz, 1H, H^1), 6.37 (dd, J_{34} = 8.8 Hz, J_{23} = 5.4 Hz, 1H, H^3), 4.92 (m, 1H, H^5), 4.84 (ps t, $J \approx$ 5.8 Hz, 1H, H^2), 4.65 (dd, J_{34} = 8.8 Hz,



J_{45} = 4.2 Hz, 1H, H[4]), 3.26 (t, $J_{66'} = J_{56}$ = 11.0 Hz, 1H, H[6]), 2.96 (m, 2H, NCH_2), 2.67 (m, 2H, NCH_2), 2.58 (m, 2H, NCH_2), 2.12 (s, 6H, NMe_2), 1.81 (s, 3H, NMe), 1.71 (m, 1H, H[6′]), 1.60 (m, 2H, NCH_2), 1.39 (s, 9H, *t*-Bu), 0.45 (s, 9H, $SiMe_3$), 0.21 (s, 3H, SiMe), 0.14 (s, 3H, SiMe), −0.89 (dd, J_{YH} = 2.3 Hz, J_{HH} = 11.0 Hz, 1H, YCH_2Si), −0.98 (dd, J_{YH} = 2.6 Hz, J_{HH} = 10.8 Hz, 1H, YCH_2Si). ^{13}C NMR (125.7 MHz, C_6D_6, 20 °C): δ 147.3 (d, J = 161.0 Hz, C[1]), 128.2 (d, J = 159.9 Hz, C[3]), 103.0 (d, J = 165.9 Hz, C[4]), 88.4 (d, J = 161.9 Hz, C[2]), 67.5 (d, J = 132.2 Hz, C[6]), 60.9, (NCH_2), 60.5 (t, J = 133.9 Hz, NCH_2), 54.9 (NCH_2), 53.7 (d, J = 131.0 Hz, C[5]), 52.8 (s, *t*-Bu, C), 47.3 (NMe), 46.6 (NCH_2), 46.3 (NMe), 43.9 (q, J = 139.5 Hz, NMe), 36.2 (q, J = 122.9 Hz, *t*-Bu Me), 29.2 (dt, J_{YC} = 38.8 Hz, J_{CH} = 96.0 Hz, YCH_2Si), 4.9 (q, J = 117.0 Hz, $SiMe_3$), 3.8 (q, J = 116.4 Hz, SiMe), 1.5 (q, J = 117.1 Hz, SiMe). Overlap of resonances prevented the determination of some coupling constants.

Structure Determinations of 1 and 6. Suitable single crystals of **1** were obtained by cooling a pentane solution of the compound to −30 °C. For **6**, single crystals gradually grew from the reaction mixture 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[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 3.

Table 3. Crystal Data for Compounds 1 and 6

	1	**6**
empirical formula	$C_{22}H_{55}N_4Si_2Y$	$C_{23}H_{48}N_5SiY$
fw	520.79	511.66
temp (K)	90(2)	95(2)
cryst size (mm)	0.50 × 0.32 × 0.22	0.30 × 0.17 × 0.14
space group	$P\bar{1}$	$P2_1/c$
a (Å)	9.5799(4)	14.7891(6)
b (Å)	9.8987(5)	9.4573(4)
c (Å)	12.4468(8)	19.2445(8)
α (deg)	99.185(1)	
β (deg)	98.943(1)	91.167(1)
γ (deg)	111.086(1)	
V (Å^3)	1482.62(12)	2691.07(19)
Z	2	4
d_c (g cm^{-3})	1.167	1.263
μ (mm^{-1})	20.62	22.3
F(000)	564	1096
θ range (deg)	2.27 to 27.49	2.04 to 29.81
index range	$-12 \le h \le 10$ $-12 \le k \le 12$ $-22 \le l \le 22$	$-20 \le h \le 20$ $-13 \le k \le 12$ $-25 \le l \le 25$
no. of reflns collected	12961	25856
no. of unique reflns	6650	7205
no. of reflns with $F_o \ge 4\sigma(F_o)$	5549	5715
$wR(F^2)$	0.0581	0.0775
a, b	0.0267, 0.0	0.0379, 0.0787
$R(F)$	0.0277	0.0335
no. of data/params	6650/482	7205/463
GOF on F^2	0.936	1.039
largest diff peak/ hole (e Å^{-3})	0.62(6), −0.34(6)	0.57(7), −0.28(7)

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Supporting Information Available: Crystallographic data for **1** and **6** including atomic coordinates, full bond distances, and bond angles as well as anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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