Single-Component Polymerization Catalysts for Ethylene and Styrene: Synthesis, Characterization, and Reactivity of Alkyl and Hydrido Yttrium Complexes Containing a Linked Amido−Cyclopentadienyl Ligand

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Yttrium alkyl complexes $Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(CH_2SiMe_3)(THF)$ (R = Me, Et) and $Y(\eta^5:\eta^1\text{-}C_9H_6SiMe_2NCMe_3)(CH_2SiMe_3)(THF)$ can be prepared in high yields by a σ-bond metathesis reaction between $Y(CH_2SiMe_3)_3(THF)_2$ and amino-functionalized cyclopentadienes or indene. The structure of $Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)(CH_2SiMe_3)(THF)$ was shown by single-crystal X-ray diffraction to be that of a three-legged piano stool. Reaction of $Y(CH_2SiMe_3)_3(THF)_2$ with the tridentate linked amido−cyclopentadienyl ligands $(C_5Me_4H)SiMe_2NHR$ (R = CH_2CH_2OMe, $CH_2CH_2NMe_2$, $CH_2CH_2CH_2OMe$, CMe_2CH_2OMe), which contain an additional donor site, results in the cleavage of the silicon−cyclopentadienyl bond and the formation of the tetramethylcyclopentadienyl complexes $Y(\eta^5\text{-}C_5Me_4H)\{N(SiMe_2CH_2SiMe_3)(R)\}(CH_2SiMe_3)(THF)_x$ ($x = 0, 1$). The dimeric hydrido complexes $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(THF)(\mu\text{-}H)]_2$ are prepared in good yields by hydrogenolysis of the corresponding alkyl complexes. Variable-temperature ^1H, ^{13}C, ^{29}Si, and ^{89}Y NMR spectroscopic data show that the hydrido complexes retain their dimeric structure in solution on the NMR time scale but that they undergo fluxional processes which include THF dissociation and cis−trans isomerization. The presence of monomeric species is inferred from ^1H NMR spectroscopic detection of the crossover product $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)_2Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)(THF)]$, which forms within minutes at 50 °C when $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(THF)(\mu\text{-}H)]_2$ with R = Me and Et are mixed in C_6D_6. Ethylene is polymerized with moderate activity by the hydrido complexes, whereas styrene derivatives and 1-hexene are cleanly converted into the monoinsertion products. 1,5-Hexadiene reacts with the hydrido complexes to give the monomeric cyclopentylmethyl complex $Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{CH_2CH(CH_2)_4\}(THF)$. The 1-phenylethyl complexes $Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{CH(CH_3)(C_6H_3\text{-}2\text{-}R\text{-}4\text{-}R')\}(THF)$ (R = R′ = H; R = H, R′ = OMe; R = R′ = Me), selectively formed by secondary insertion of the corresponding styrene derivatives, show fluxional η^3-coordination in solution. A monomeric structure with a weak η^3-interaction was confirmed by single-crystal X-ray diffraction of $Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)\{CH(CH_3)(C_6H_4\text{-}4\text{-}t\text{Bu})\}(THF)$. The insertion product of 1-hexene is dimeric in solution, but partially loses THF under vacuum. This product initiates the polymerization of styrene to give atactic polystyrenes with narrow molecular weight distributions (M_w/M_n 1.10−1.23) and microstructures enriched in syndiotacticity ($rr \approx 70\%$).

Introduction

For homogeneous, cocatalyst-free polymerization catalysis of both nonpolar and polar monomers, rare-earth metal centers are conventionally supported by the bis(cyclopentadienyl) ligand framework to give structurally well-characterized organometallic complexes such as lanthanocene hydride and alkyls of the type $[(\eta^5\text{-}C_5R_5)_2LnX]_2$ (X = H, alkyl).[1,2] To gain control over the stereochemical selectivity of lanthanide-catalyzed polymerizations, *ansa*-metallocenes, most successful in group 4 chemistry,[3] have also been introduced.[4] However, epimerization of planar chiral systems[4b,5] and intermolecular ligand scrambling to give so-called flyover complexes[6] often make it difficult to identify the structure of the catalyzing species and to allow rational

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control. One solution to this problem is to link the two cyclopentadienyl ligands with an additional donor functionality such as a 2,6-lutidinediyl group.[7] An alternative approach would be to tether a non-cyclopentadienyl ligand to the cyclopentadienyl periphery.[8] Such a pendant ligand system is the linked amido−cyclopenadienyl ligand, which has, since the original introduction by Bercaw et al. a decade ago,[9] advanced to be one of the most versatile ligands for polymerization catalysts based on group 4 metals, in particular, titanium.[10−14] Catalysts based on this type of ligand are closer to systems based on complexes with only one cyclopentadienyl ligand, which are anticipated to be more active toward sterically more demanding monomers.[15] Conventional synthesis of mono(cyclopentadienyl) rare-earth complexes ($(\eta^5\text{-}C_5R_5)LnX_2(L)_n$), where at least one X ligand is hydride or an alkyl, is often hampered by ate-complex formation with concomitant alkali-metal salt incorporation.[16] Therefore, save for Schaverien's pioneering synthesis of a series of mono(cyclopentadienyl) lanthanide complexes,[15] only a very limited number of this type of half-sandwich complexes have been synthesized and have had their reactivity studied.[16g,17] We report here a facile access route[18] to alkyl and hydrido yttrium complexes of the type $(\eta^5\text{-}C_5R_4SiMe_2NR'')YX(L)$, the reactivity of these complexes toward unsaturated substrates, and some results on the polymerization of ethylene and styrene using these complexes.

Results and Discussion

Synthesis and Characterization of $Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(CH_2SiMe_3)(THF)$. Addition of 1 equiv of $(C_5Me_4H)SiMe_2NHCMe_2R$ (R = Me, Et) to a solution of $Y(CH_2SiMe_3)_3(THF)_2$ (**1**) in pentane at 0 °C results in the formation of the yttrium complexes $Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2R)(CH_2SiMe_3)(THF)$ (R = Me (**2a**), Et (**2b**)), in quantitative yield (by NMR spectroscopy), within 2 h, with simultaneous formation of tetramethylsilane (Scheme 1). Crystallization from pentane at −30 °C provides **2** in high yield as colorless crystals, soluble in aliphatic and aromatic hydrocarbons. A one-

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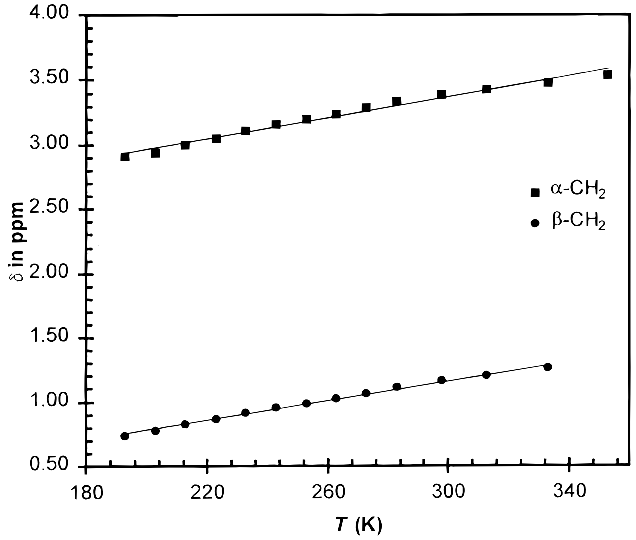
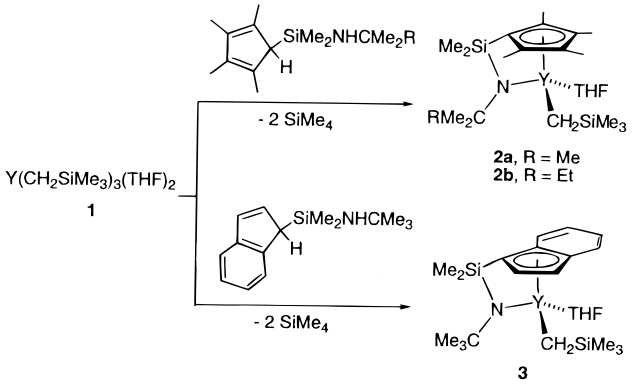


Figure 1. Temperature dependence of the chemical shift of the α- and β-CH$_2$ protons of the coordinated THF molecule in **2a** in toluene-d_8.

Scheme 1



pot synthesis, starting with anhydrous yttrium trichloride, to prepare **2** on a gram scale, is also possible. Although NMR spectroscopic data at room temperature indicate the presence of a mirror plane in the molecule, the chiral structure was confirmed by single-crystal X-ray structural analysis of complex **2b** (vide infra). The tris(alkyl) complexes Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y) have been previously used in alkane elimination reactions,[19] and the synthesis of linked amido−cyclopentadienyl scandium alkyl complexes of a modified ligand system was reported by Piers et al. Analogous yttrium complexes, however, have not been obtained so far.[19c]

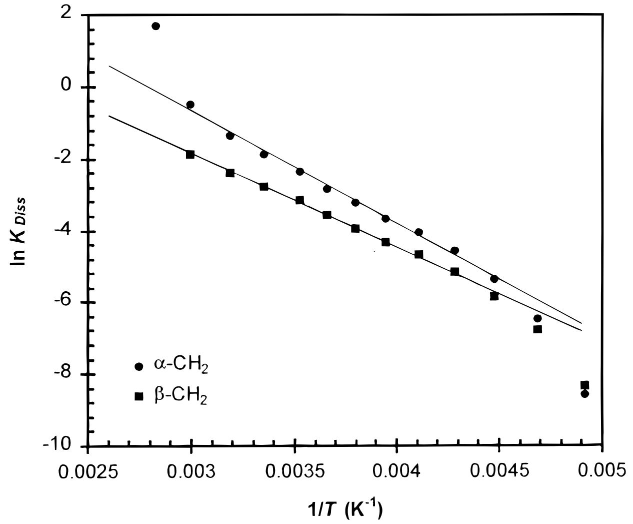


Figure 2. Plot of ln K_{diss} versus 1/T.

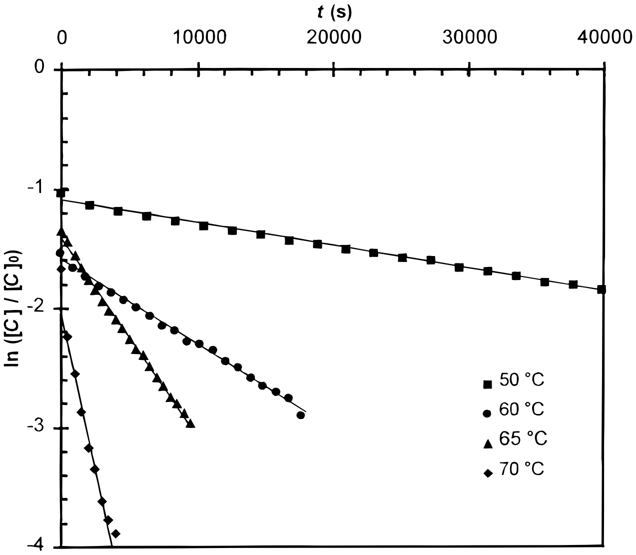


Figure 3. Thermal decomposition of **2a** at different temperatures in C$_6$D$_6$.

The coordinated THF ligands in **2** are labile on the NMR time scale, as indicated by the temperature dependence of the chemical shifts of the THF methylene protons, which undergo substantial high-field shifts upon cooling (Figure 1). The signals decoalesce at −80 °C. When more than 1 equiv of THF is present in the solution of **2a**, low-field shift of the THF signals occurs, approaching the values of free THF. Addition of excess THF-d_8 resulted in the instantaneous exchange of all coordinated THF. These observations are in agreement with the existence of THF-free **2a′** and the THF adduct **2a**, which interconvert via a dissociation equilibrium, fast on both the chemical and NMR time scales. The temperature dependence of the equilibrium constant is obtained from the chemical shifts of α- and β-CH$_2$[10b,20] The plot of ln K_{diss} versus 1/T gives the thermodynamic parameters $\Delta_rH = 24 \pm 3$ kJ mol^{-1} and $\Delta_rS = 61 \pm 12$ J K^{-1} mol^{-1} for **2a** (Figure 2). The positive reaction entropy and enthalpy is in accordance with a dissociative process. The bond enthalpy is somewhat smaller than the value of 30.6 ± 1.7 kJ mol^{-1} observed for the first coordinated THF molecule in Cp*$_2$Sm.[21] The alkyl complexes **2** are thermally quite robust. By NMR spectroscopy, **2a** was found to decompose by a first-order rate law (Figure 3) with a half-life of $t_{1/2} = 600 \pm 10$ min ($k_1 = 1.92 \pm 4 \times 10^{-5}$ s^{-1}) at 50 °C in C$_6$D$_6$, to form

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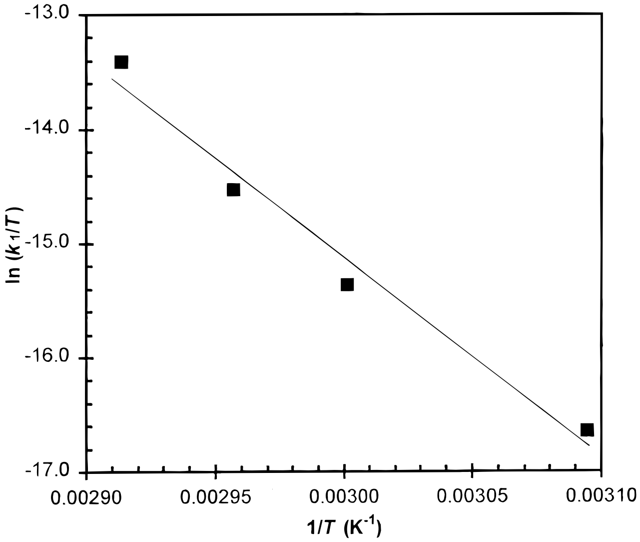


Figure 4. Eyring plot for the thermal decomposition of **2a** in C_6D_6.

tetramethylsilane and other unidentified products of C−H activation. The activation parameters $\Delta H^{\ddagger} = 145 \pm 16$ kJ mol^{-1} and $\Delta S^{\ddagger} = 110 \pm 50$ J K^{-1} mol^{-1} are obtained from the temperature dependence of the rate constants for the decomposition of **2a** (Figure 4).[19a]

A procedure similar to that used for the preparation of the tetramethylcyclopentadienyl analogues is employed to obtain the mono(indenyl) complex **3** from the tris(alkyl) **1** and the linked amido−indene $(C_9H_7)SiMe_2(NHCMe_3)$. The reaction proceeds significantly slower than the reaction leading to **2**, but no intermediate such as the bis(alkyl) amido complex can be detected by NMR spectroscopy. Complex **3** was isolated as colorless crystals, moderately soluble in aliphatic and soluble in aromatic hydrocarbons, in 69% yield after 17 h reaction time at room temperature. The ^{1}H NMR spectrum of **3** at room temperature contains two well-separated singlets for the methyl protons on the silicon atom due to the planar chirality of the indenyl ligand. Only one signal is observed for the *tert*-butyl group of the amido nitrogen atom and for the $SiMe_3$ group of the trimethylsilylmethyl ligand. The diastereotopic methylene protons of the trimethylsilylmethyl group give rise to a pair of double doublets ($^2J_{YH} = 2.7$ Hz, $^2J_{HH} = 11.0$ Hz). The indenyl ligand shows a typical coupling pattern,[10e,12c] with two doublets for the ring protons of the five-membered ring and three multiplets for those of the six-membered ring. The THF ligand in **3** is more labile than that in the tetramethylcyclopentadienyl complex **2a**, as shown by the lower reaction enthalpy for the dissociation process, $\Delta_r H = 17 \pm 1$ kJ mol^{-1}, obtained from the temperature dependence of the chemical shifts of the methylene protons of the THF ligand. The reaction entropy of $\Delta_r S = 30 \pm 2$ J K^{-1} mol^{-1} is also significantly smaller than that of **2a**.

Table 1. Experimental Data of the Crystal Structure Determination of Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$)(CH_2SiMe_3)(THF) (2b) and Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$){CH(CH_3)-C_6H_4-4-*t*Bu}(THF) (9c)

	2b	**9c**
	Crystal Data	
empirical formula	$C_{24}H_{48}NOSi_2Y$	$C_{32}H_{54}NOSiY$
fw	511.72	585.76
cryst color	colorless	yellow
cryst size, mm	0.50 × 0.50 × 0.30	0.55 × 0.40 × 0.28
cryst syst	monoclinic	monoclinic
space group	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	14.912(4)	9.073(3)
b, Å	11.162(4)	21.817(6)
c, Å	17.527(4)	17.127(5)
β, deg	99.24(3)	100.11(3)
V, Å^3	2880(1)	3338(2)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.180	1.166
μ(Mo Kα), mm^{-1}	2.122	1.805
F(000)	1096	1256
data collection		
wavelength	Mo Kα (0.71070 Å)	Mo Kα (0.71070 Å)
T, K	213(2)	296(2)
θ range	3−26	3−26
index ranges	h, −14 to 18; k, 0 to 13; l, −21 to 21	h, 0 to 11; k, −20 to 26; l, −21 to 20
	Solution and Refinement	
no. of rflns measd	6259	10183
no. of indep rflns	5660 ($R_{int} = 0.0729$)	6521 ($R_{int} = 0.0524$)
no. of obsd rflns	3248 ($I > 2\sigma(I)$)	3327 ($I > 2\sigma(I)$)
GOF	1.16	1.14
final R indices R_1, wR_2 (obsd data)	0.0742, 0.1203	0.0613, 0.0997
final R indices R_1, wR_2 (all data)	0.1598, 0.1678	0.1743, 0.1457
largest e-max, e-min, e·Å^{-3}	0.580, −0.736	0.550, −0.470

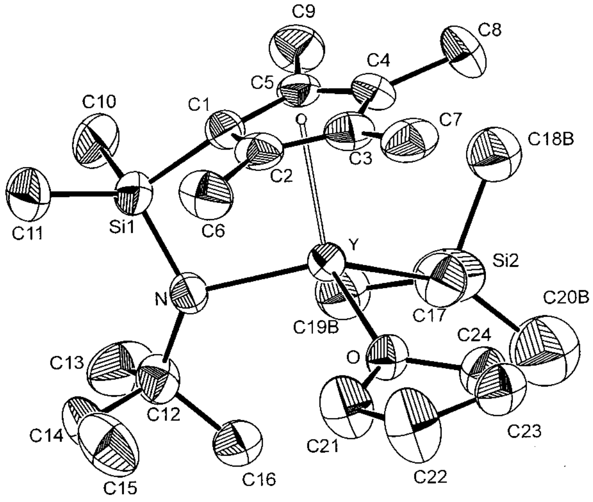
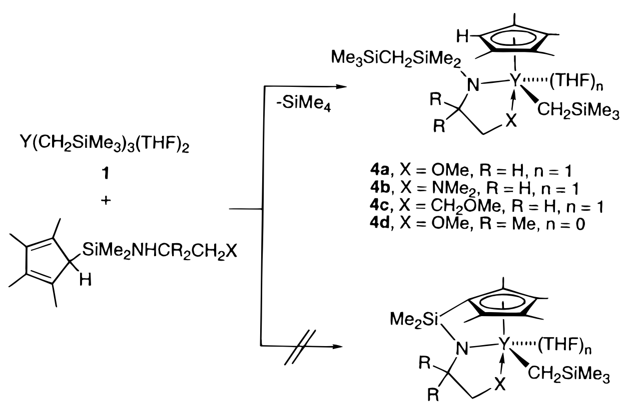


Figure 5. ORTEP diagram[22] of the molecular structure of **2b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and three positions of the disordered atoms C18, C19, and C20 are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Y−N 2.208(6), Y−C17 2.388(7), Y−O 2.319(5), Cp_{Cent}−Y 2.333(7), Cp_{Cent}−Y−N 97.1(2), Cp_{Cent}−Y−C17 118.8(3), Cp_{Cent}−Y−O 112.1(2), N−Y−C17 119.4(3), N−Y−O 114.5(2), O−Y−C17 96.0(2), N−Si1−C1 97.0(3).

Clear colorless crystals of **2b** suitable for X-ray diffraction analysis are obtained by slow cooling of a pentane solution. Crystallographic data are compiled in Table 1. The trimethylsilyl group shows positional disorder with four split positions for the methyl carbon atoms C18, C19, and C20 (each 25% occupancy). For the sake of clarity only one position is shown in the ORTEP diagram of the structure of **2b** in Figure 5. The molecule contains a chiral yttrium atom coordinated in a pseudo-tetrahedral fashion similar to the geometry found in Sc(η^5:η^1-C_5H_3tBuSiMe$_2$NCMe$_3$)(CH_2SiMe_3)(PMe_3).[9a] The cyclopentadienyl, the chelating amido, and the trimethylsilylmethyl ligand, as well as one THF molecule each occupy one of the coordination sites.

The yttrium−ligand bond lengths are significantly shorter than those observed in the heterobimetallic yttrocenes $Li[Y(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NCH_2CH_2X)_2]$ (C_5R_4 = C_5Me_4, C_5H_3tBu; X = OMe, NMe_2)[5a] and the half-sandwich complex $[Li(THF)][Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(o\text{-}C_6H_4CH_2NMe_2)Cl]$,[23] in accordance with the smaller coordination number and decreased electron density at the metal center. The Y−N bond of 2.208(6) Å is similar to the value of 2.184(7) Å found in $Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{N(SiMe_3)_2\}$[24] and one of the shortest yttrium−amide bond distances observed so far.[25] Similarly, the Y−O bond of 2.319(5) Å is at the short end of the usual 2.35−2.45 Å range found in other THF-containing yttrium complexes.[26] The Y−C17 bond of 2.388(7) Å is at the lower end of the yttrium−carbon bond lengths found in other yttrium alkyl complexes.[27] The geometry around nitrogen is trigonal planar, with the sum of the bond angles at 359.5°, in contrast to the significant deviation from planarity observed in $Li[Y(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NCH_2CH_2X)_2]$ (C_5R_4 = C_5Me_4, C_5H_3tBu; X = OMe, NMe_2)[5a] and $[Li(THF)][Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(o\text{-}C_6H_4CH_2NMe_2)Cl]$.[23]

Scheme 2



4a, X = OMe, R = H, n = 1
4b, X = NMe_2, R = H, n = 1
4c, X = CH_2OMe, R = H, n = 1
4d, X = OMe, R = Me, n = 0

Continuing our previous work on linked amido−cyclopentadienyl complexes of yttrium,[5a,23] we initially began to study the reactivity of $Y(CH_2SiMe_3)_3(THF)_2$ (**1**) with the tridentate variant of the linked amido−cyclopentadienyl ligand $(C_5Me_4H)SiMe_2NHR$ (R = CH_2CH_2OMe, $CH_2CH_2NMe_2$, $CH_2CH_2CH_2OMe$, CMe_2CH_2OMe), which contains an additional donor site.[5a,10c,f,g,j,k,23] When the reaction of **1** with 1 equiv of the linked amino−cyclopentadiene is followed by ^1H NMR spectroscopy, a rapid decrease of the doublet for the methylene protons at the yttrium in **1** at −0.71 ppm is observed with concomitant formation of tetramethylsilane. Upon removal of excess THF and tetramethylsilane in a vacuum, colorless oils of **4a**−**d** are isolated. Unexpectedly, the coordination of the cyclopentadienyl ligand proceeds by cleavage of the silicon− rather than hydrogen−cyclopentadienyl bond to give a tetramethylcyclopentadienyl derivative. (Scheme 2)

Both the ^1H and ^{13}C NMR spectra indicate an asymmetric coordination sphere around yttrium. The ring proton resonance appears in the range 5.4−5.7 ppm in the ^1H NMR spectrum and is correlated to the ring carbon atom at around 110 ppm in the ^{13}C NMR spectrum. The ^{29}Si NMR spectra contain three signals, two in the range of 2 to −2 ppm and one at −8 to −18 ppm. The ^1H NMR spectra show the presence of 1 equiv of coordinated THF per yttrium, with the exception of **4d**. The increased steric bulk of the amido side chain obviously impedes a tight bonding of THF at yttrium. The ^1H NMR spectrum of **4d** (Figure 6) shows the

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(23) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 485.

(24) Mu, Y.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J. *Can. J. Chem.* **1995**, *73*, 2233.

(25) (a) $Y\{N(SiMe_3)_2\}_3$: Y−N = 2.224(6) Å, $[Li(THF)_4][Y\{N(SiMe_3)_2\}_3Cl]$: Y−N = 2.25 Å average, $[Y\{N(SiMe_3)_2\}_3(NCPh)_2]$: Y−N = 2.248(4)−2.265(4) Å, see: Westerhausen, M.; Hartmann, M.; Pfitzner, A.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 837. (b) $Y\{N(SiHMe_2)_2\}_3(THF)_2$: Y−N = 2.229(4)-2.276(4) Å, see: Herrmann, W. A.; Anwander, R.; Munck, F. C.; Scherer, W.; Dufaud, V.; Huber, N. W.; Artus, G. R. J. *Z. Naturforsch.* **1994**, *49b*, 1789. (c) $Y\{N(SiHMe_2)_2\}_3(carbene)_2$: Y−N = 2.288(6)−2.322(6) Å, $Y\{N(SiHMe_2)_2\}_3(carbene)$: Y−N = 2.237(6)−2.248(6) Å, see: Herrmann, W. A.; Munck, F. C.; Artus, G. R. J.; Runte, O.; Anwander, R. *Organometallics* **1997**, *16*, 682. (d) (salen)Y$\{N(SiHMe_2)_2\}(THF)$: Y−N = 2.27 Å, see: Runte, O.; Priermeier, T.; Anwander, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1385. (e) $Cp^*_2YN(SiMe_3)_2$: Y−N = 2.274(5), 2.253(5) Å, see: den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726. (f) $(\eta^5\text{-}C_5Me_4Et)_2YN(SiMe_3)_2$: Y−N = 2.276(3) Å, see: Schumann, H.; Rosenthal, E. C. E.; Kociok-Köhn, G.; Molander, G. A.; Winterfeld, J. *J. Organomet. Chem.* **1995**, *496*, 233. (g) (*R*)-$\{Me_2Si(C_5Me_4)[(-)\text{-menthylCp}]\}YN(SiMe_3)_2$: Y−N = 2.281(8), 2.211(8) Å, see: ref 4b. (h) *rac*-$\{(\eta^5\text{-}C_9H_5\text{-}2\text{-}Me)_2SiMe_2\}YN(SiHMe_2)_2$: Y−N = 2.237(4) Å, see: Hermann, W. A.; Eppinger, J.; Spiegel, M.; Runte, O.; Anwander, R. *Organometallics* **1997**, *9*, 11813. (i) $\{Me_2Si(NCMe_3)(OCMe_3)\}_2YCH(SiMe_3)_2$: Y−N = 2.195(16), 2.316(13) Å, see: Duchateau, R.; Tuinstra, T.; Brussee, E. A. C.; Meetsma, A.; T., v. D. P.; Teuben, J. H. *Organometallics* **1997**, *16*, 3511. (j) $Y(OSi\{tBu\}\{o\text{-}C_6H_4(CH_2NMe_2)\}_2)\{N(SiMe_3)_2\}_2$ $Y-N(SiMe_3)_2$ = 2.221(9), 2.237(9) Å, see: Shao, P.; Berg, D. J.; Bushnell, G. W. *Inorg. Chem.* **1994**, *33*, 6334. (k) $HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3Y(OEt_2)$: Y−N = 2.235(9)−2.265(9) Å, see: Memmler, H.; Walsh, K.; Gade, L. H.; Lauher, J. W. *Organometallics* **1995**, *14*, 5021. (l) $[(iPr)_2ATI]Y\{N(SiMe_3)_2\}_2$: $Y-N(SiMe_3)_2$ = 2.236(3) Å, Y−N(ATI) = 2.315(3) Å, see: Bürgstein, M. R.; Berberich, H.; Roesky, P. W. *Organometallics* **1998**, *17*, 1452.

(26) (a) $[(C_5H_4Me)_2Y(THF)(\mu\text{-}H)]_2$: Y−O = 2.460(8) Å, see: Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008. (b) $[(C_5H_3Me_2)_2Y(THF)(\mu\text{-}H)]_2$: Y−O = 2.491(5) Å, see: Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Doedens, R. J. *Organometallics* **1987**, *6*, 2279. (c) $Y_2(OC_6H_3Me_2\text{-}2,6)_6(THF)_2$: Y−O = 2.348(6) Å, see: Evans, W. J.; Olofson, J. M.; Ziller, J. W. *Inorg. Chem.* **1989**, *28*, 4308. (d) $[Y_3(OCMe_3)_7Cl(THF)_3][BPh_4]$: Y−O = 2.35(1)−2.37(1) Å, see: Evans, W. J.; Olofson, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2308. (e) $Cp^*_2Y(CH_2Ph)(THF)$: Y−O = 2.398(4) Å, see: ref 17d. (f) $CpYCl_2(THF)_3$: Y−O = 2.34(2)−2.50(2) Å, see: Zhou, X.; Wu, Z.; Ma, H.; Xu, Z.; You, X. *Polyhedron* **1994**, *13*, 375. (g) $Cp^*_2YMe(THF)$: Y−O = 2.379(8) Å, see: den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1987**, *327*, 31. (h) $(Me_3SiCH_2)_2Y(OC_6H_3tBu_2\text{-}2,6)(THF)_2$: Y−O = 2.343(9) Å, see: Evans, W. J.; Broomhall-Dillard, R. N. R.; Ziller, J. W. *Organometallics* **1996**, *15*, 1351.

(27) (a) $Y\{CH(SiMe_3)_2\}_3$: Y−C = 2.357(7) Å, see: Westerhausen, M.; Hartmann, M.; Schwarz, W. *Inorg. Chim. Acta* **1998**, *269*, 91. (b) $Cp^*_2YCH(SiMe_3)_2$: Y−C = 2.468(7) Å, see: ref 25e. (c) $Cp^*_2Y(\mu\text{-}CCCMe_3)_2Li(THF)$: Y−C = 2.38(2) Å, see: Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; M., O. J. *J. Organomet. Chem.* **1989**, *376*, 311. (d) $\{Cp_2Y(CH_2SiMe_3)_2\}_2Li_2(DME)_2(THF)$: Y−C = 2.402(6), 2.445(6) Å, see: Evans, W. J.; Dominguez, R.; Levan, K. R.; Doedens, R. J. *Organometallics* **1985**, *4*, 1836. (e) $Y(DAC)(CH_2SiMe_3)$: Y−C = 2.45(2) Å, see: ref 19a. (f) *trans*-$Y(MAC)(CH_2SiMe_3)_2$: Y−C = 2.461(4) Å, see: ref 19b. (g) $Cp^*_2Y(\eta^2\text{-}C\{CH_2(3,5\text{-}Me_2C_6H_3)\}{=}N(2,6\text{-}Me_2C_6H_3)\}(THF)$: Y−C = 2.392(3) Å, see: den Haan, K. H.; Luinstra, G. A.; Meetsma, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1509. (h) $Me_2Si(C_5Me_4)_2YCH(SiMe_3)_2$: Y−C = 2.418(6) Å, see: ref 6b. (i) (*R*)-$\{Me_2Si(C_5Me_4)[(-)\text{-menthylCp}]\}YCH(SiMe_3)_2$: Y−C = 2.40(1), 2.41(1) Å, (*S*)-$\{Me_2Si(C_5Me_4)[(+)\text{-neomenthylCp}]\}YCH(SiMe_3)_2$: Y−C = 2.36(1) Å, see: ref 4b. (j) $Cp^*_2YMe(THF)$: Y−C = 2.44(2) Å, see: ref 26g. (k) $\{(Me_3Si)_2CH\}_2Y(\mu\text{-}OCMe_3)_2Li(THF)$: Y−C = 2.440(9), 2.462(9) Å, see: ref 26h. (l) $\{(Me_3SiCH_2)_2Y(OC_6H_3tBu_2\text{-}2,6)_2\}\{[(THF)_3Li]_2Cl\}$: Y−C = 2.404(8), 2.420(8) Å, see: Evans, W. J.; Broomhall-Dillard, R. N. R. *J. Organomet. Chem.* **1998**, *569*, 89. (m) $\{p\text{-}MeOC_6H_4C(NSiMe_3)_2\}_2YCH(SiMe_3)_2$: Y−C = 2.431(5) Å, see: Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279.

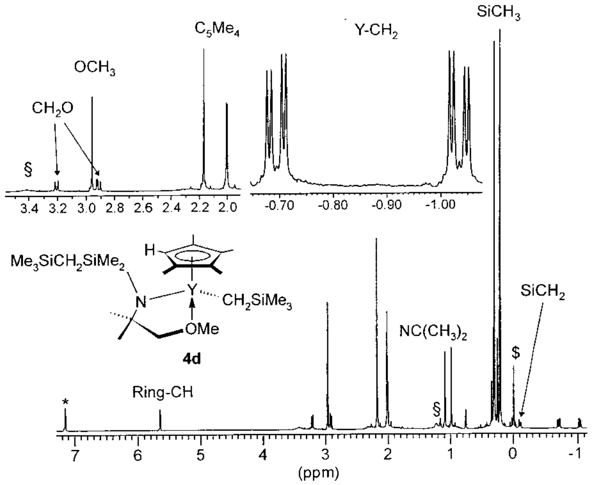
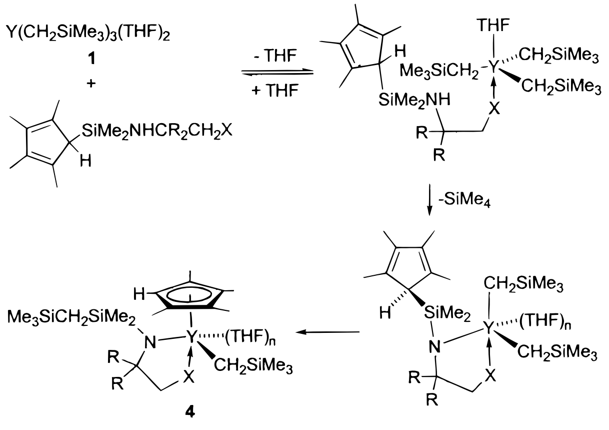


Figure 6. ^{1}H NMR spectrum of **4d** in C_6D_6 (*) at 25 °C ($ = trace SiMe$_4$, § = residual THF).

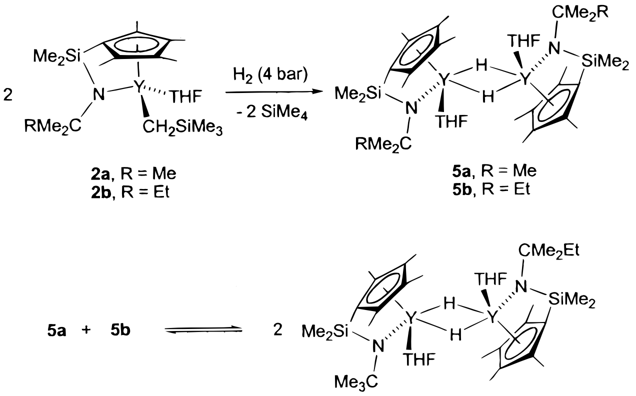
diastereotopic methylene protons at yttrium as a pair of double doublets at −1.03 and −0.69 ppm ($^2J_{YH}$ = 3.1 Hz, $^2J_{HH}$ = 11.0 Hz). The ring proton gives rise to a singlet at 5.65 ppm with an intensity of 1. The methyl protons on the cyclopentadienyl ring appear as three singlets in a 6:3:3 ratio. The two methyl groups bonded to the amido carbon atom appear as two singlets at 0.99 and 1.09 ppm, whereas the ether methylene group gives rise to an AB spin system at 2.92 and 3.21 ppm ($^2J_{HH}$ = 7.8 Hz). The ^{13}C NMR spectrum is in agreement with the asymmetric structure. The YCH$_2$ group is shifted to higher field by 6.5 ppm relative to the tris(alkyl) **1**, to 27.2 ppm ($^1J_{YC}$ = 44.9 Hz). The ^{13}C DEPT spectrum shows the presence of a SiCH$_2$ group besides four SiCH$_3$ groups.

Because cyclopentadienes are more acidic than amines,[28] one would expect the cyclopentadiene to react more easily with the alkyl complex **1** than with the amine. However, one of the coordinated THF molecules in **1** seems to be displaced by the additional donor site in the side chain of the linked amido−cyclopentadienyl ligand. The close proximity of the amine proton to the yttrium center then promotes the aminolysis of the yttrium−alkyl bond to give a bis(alkyl) amido intermediate (Scheme 3), followed by the complexation of the cyclopentadienyl ligand via silicon−cyclopentadienyl bond cleavage. The four-center transition state leading to the product of alkane elimination probably is disfavored due to the strong chelation of the donor in the amido side chain. The outcome of this reaction is independent of the spacing between the amido and the additional donor (C$_2$ vs C$_3$ chain) and steric demand of the amido side chain (NCH$_2$ vs NCMe$_2$). The reaction proceeds in the same manner in THF-d_8, although the overall rate of complexation is somewhat decreased compared to the reaction in noncoordinating solvents.

Scheme 3



Scheme 4



Synthesis and Characterization of Hydrido Complexes. In contrast to the numerous, mostly dimeric, lanthanocene hydrido complexes described in the literature,[29,30] only a small number of half-sandwich hydrido complexes have been reported so far.[9,15,19c,31] Hydrogenolysis of **2** in pentane at room temperature gives the dimeric hydrido complexes **5** as colorless microcrystals in good yield (Scheme 4). The dimeric deuteride **5a-*d*$_2$** may be obtained analogously. The hydrides are insoluble in aliphatic solvents, but are soluble in aromatic and ethereal solvents.

Although the ^{1}H NMR spectrum of **5a** at 50 °C, in toluene-d_8 solution (Figure 7), with only one hydride triplet at 5.50 ppm with $^1J_{YH}$ = 28.8 Hz, (Table 2) agrees with a molecule containing an internal mirror plane, this spectrum has to be considered as the result of fast interconversion between two asymmetric diastereomers. The fluxional process is slowed sufficiently at −40 °C, resulting in an ^{1}H NMR spectrum that shows two triplets for the bridging hydrides at 5.27 and 5.45 ppm with $^1J_{YH}$ = 29.0 and 28.6 Hz, respectively, as well as the doubling up of all other signals. The signal ratio shows that **5a** exists as a 4:1 mixture of two asymmetric diastereomers in toluene-d_8 solution. This ratio is shifted toward 8:1 for **5a** in THF-d_8 at −60 °C. The ratio for **5b** is approximately 6:1 in toluene-d_8 solution. The

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(28) (a) Cyclopentadiene pK_a = 18 in DMSO, indene pK_a = 20.1 in DMSO, pentamethylcyclopentadiene pK_a = 26.1 in DMSO, see: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456. (b) HN(CHMe$_2$)$_2$ pK_a = 35.7 in THF, HN(CMe$_3$)(SiMe$_3$) pK_a = 33.6 in THF, see: Fraser, R. R.; Mansour, T. S. *J. Org. Chem.* **1984**, *49*, 3442. (c) HN(SiMe$_3$)$_2$ pK_a = 25.8 in THF, see: Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232. (d) Higher acidity of the ring proton of the cyclopentadienyl ligand compared with the amine proton has also been confirmed by the X-ray structural analysis of the monopotassium salt K[(C$_5$Me$_4$)SiMe$_2$(NHCMe$_3$)](THF), see: Schaefer, W. P.; Cotter, W. D.; Bercaw, J. E. *Acta Crystallogr.* **1993**, *C49*, 1489.

(29) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193.

(30) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263.

(31) (a) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126. (b) Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1992**, 11.

Table 2. Chemical Shifts and ^{89}Y−^{1}H Coupling Constants in ^{1}H NMR Spectra of Dimeric Yttrium Hydrido Complexes at Room Temperature

compd	δ (ppm)	$^{1}J_{YH}$ (Hz)	ref
5a	5.27, 5.45^{a} (−40 °C), 5.50^{a} (50 °C)	29.0, 28.6, 28.8	this work
5b	5.23, 5.42^{a} (−40 °C), 5.44^{b} (50 °C)	29.0, 28.6, 28.8	this work
$[Cp_2Y(THF)(\mu\text{-}H)]_2$	2.02^{c}	27.0	26a
$[(C_5H_4Me)_2Y(THF)(\mu\text{-}H)]_2$	2.31^{c}	27.2	26a
$[(C_5H_3Me_2)_2Y(THF)(\mu\text{-}H)]_2$	2.82^{c}	28	26b
$[(t\mathrm{Bu}C_5H_4)Y(\mu\text{-}H)]_2$	3.09^{b}	32.8	32a
$[(2,4,7\text{-}Me_3C_9H_4)_2Y(\mu\text{-}H)]_2$	2.69^{a}	32.7	32b
$[Y(C_5H_4CH_2CH_2OMe)_2(\mu\text{-}H)]_2$	1.85^{c}	28.3	32c
$[(CH_2)_3(C_5H_4)_2YH(THF)]_2$	2.16^{c}	23.8	32d
rac-$[(Bp)Y(\mu\text{-}H)]_2$^{d}	4.87^{b}	31	4a
rac-$[(BnBp)Y(\mu\text{-}H)]_2$^{e}	4.98^{b}	31.4	32e
(R,S)-$[Me_2Si(C_5Me_4)\{(+)\text{-neomenthylCp}\}YH]_2$	4.28^{b}	32	4b
$[Me_2Si(C_5Me_4)_2Y(\mu\text{-}H)]_2$^{f}	5.286^{b}	33.3	27h
$[Y_2(\mu\text{-}\{Et_2Si(C_5Me_4)Cp\})_2(\mu\text{-}H)_2]$	3.03^{b}	35.3	6a
$[Y_2(\mu\text{-}\{Me_2Si(C_5Me_4)_2\})_2(\mu\text{-}H)_2]$	3.867^{b}	34.4	6b
$[Cp^{*}Y(OAr)(\mu\text{-}H)]_2$	5.64^{b}	35.2	15
$[\{PhC(NSiMe_3)_2\}_2Y(\mu\text{-}H)]_2$	8.28^{b}	27.6	27m
$[\{p\text{-}MeO\text{-}C_6H_4C(NSiMe_3)_2\}_2Y(\mu\text{-}H)]_2$	8.31^{b}	27.8	27m

[a] In toluene-d_8. [b] In C_6D_6. [c] In THF-d_8. [d] Bp = $Me_2Si\{C_5H_2(CMe_3)(SiMe_3)\}_2$. [e] BnBp = (R,S)-$(C_{20}H_{12}O_2)Si\{C_5H_2(CMe_3)(SiMe_3)\}_2$. [f] Unstable.

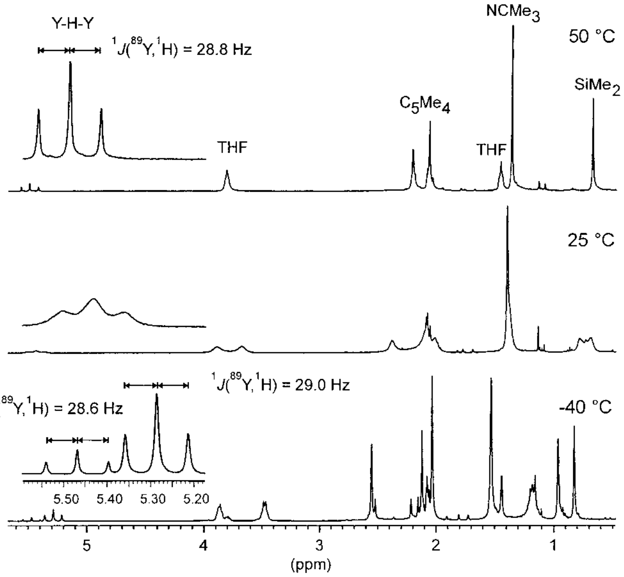


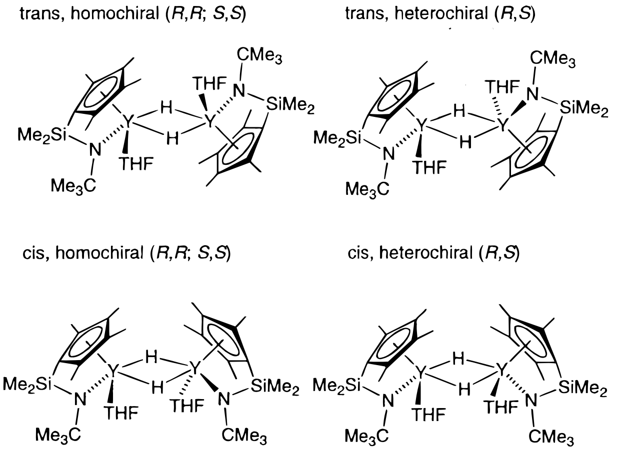
Figure 7. Temperature dependence of the ^{1}H NMR spectrum of **5a** in toluene-d_8.

crystallographic characterization of the C_2-symmetric homochiral dimer, reported earlier,[18] shows one of the possible diastereomers with transoid disposition of the cyclopentadienyl ligands. We propose the other diastereomers to be either the heterochiral (meso) form and/or isomers containing cisoid arrangement of the two THF ligands (Scheme 5).

In the presence of 11 equiv of trimethylphosphine, fast exchange of THF occurs on the NMR time scale, and a mixture of several different yttrium species containing trimethylphosphine is observed according to the ^{1}H and ^{31}P NMR spectra in toluene-d_8 at −40 °C. Hydrogenolysis of **2a** in the presence of 5 equiv of trimethylphosphine produced pure **5a**.

In the ^{89}Y NMR DEPTND spectrum of **5a** in C_6D_6 at 50 °C a triplet is observed as a result of coupling between one ^{89}Y nucleus (I = 1/2) and two protons (Figure 8). No monomeric species can be detected spectroscopically in the range −80 to +80 °C. However, the existence of a monomer−dimer equilibrium can be inferred from spectroscopic detection of the crossover

Scheme 5



product in an equimolar mixture of **5a** and **5b**.[33] In addition to the signals from **5a** and **5b**, a triplet in the statistically predicted 1:2:1 ratio can be observed in the ^{1}H NMR spectrum after 10 min at 50 °C (Figure 9). Likewise, in an equimolar mixture of the hydride **5b** and the deuteride **5a-*d*₂** the deuterium was distributed statistically over all three complexes within 10 min. Contrary to well-documented C−H activation reactions of dimeric lanthanocene hydrides $[Cp^{*}_2LnH]_2$,[2,34] no reaction with deuterated solvents is observed with **5** (50 °C, C_6D_6, > 24 h).

Reaction of the Hydrido Complexes with Olefins and Ethylene Polymerization. Insertion reactions involving metal−hydride bonds are usually more facile and significantly faster than analogous reactions involv-

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[32] (a) Voskoboynikov, A. Z.; Parshina, I. N.; Shestakova, A. K.; Butin, K. P.; Beletskaya, I. P.; Kuz'mina, L. G.; Howard, J. A. K. *Organometallics* **1997**, *16*, 4041. (b) Kretschmer, W. P.; Troyanov, S. I.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 284. (c) Deng, D.; Jiang, Y.; Qian, C.; Wu, G.; Zheng, P. *J. Organomet. Chem.* **1994**, *470*, 99. (d) Ye, C.; Qian, C.; Yang, X. *J. Organomet. Chem.* **1991**, *407*, 329. (e) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045.

[33] When the yttrium hydrido complex **5a** ($I(^{89}Y)$ = 1/2) is mixed with the analogous lutetium hydrido complex ($I(^{175}Lu)$ = 7/2), the resulting heterobimetallic crossover product shows a doublet for the hydrido ligands ^{1}H NMR spectrum: Arndt, S.; Okuda, J. Unpublished results. See also ref 32a.

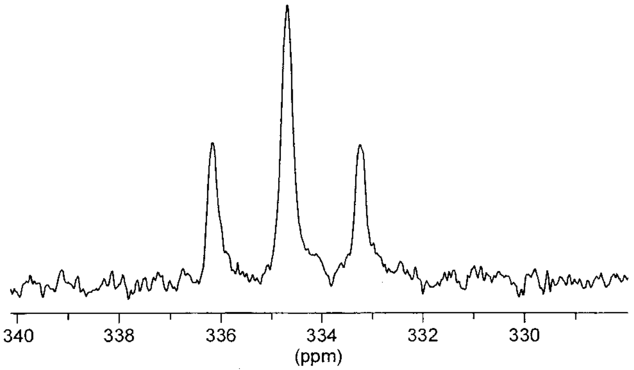


Figure 8. ^{89}Y NMR DEPTND spectrum of **5a** in C_6D_6 at 50 °C.

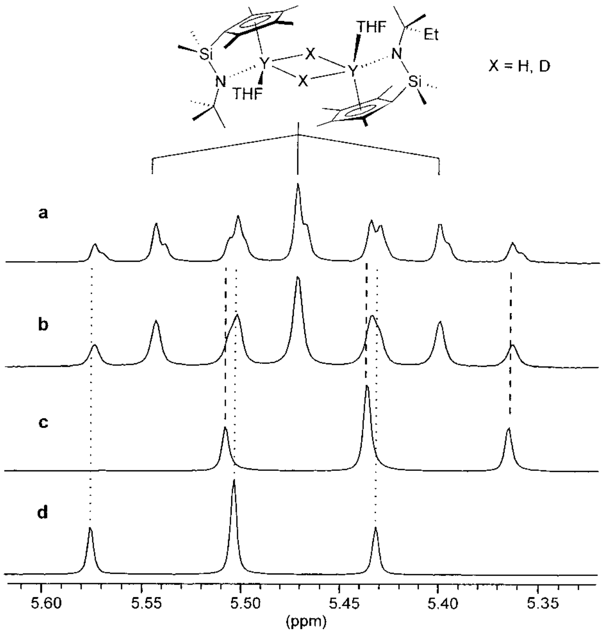
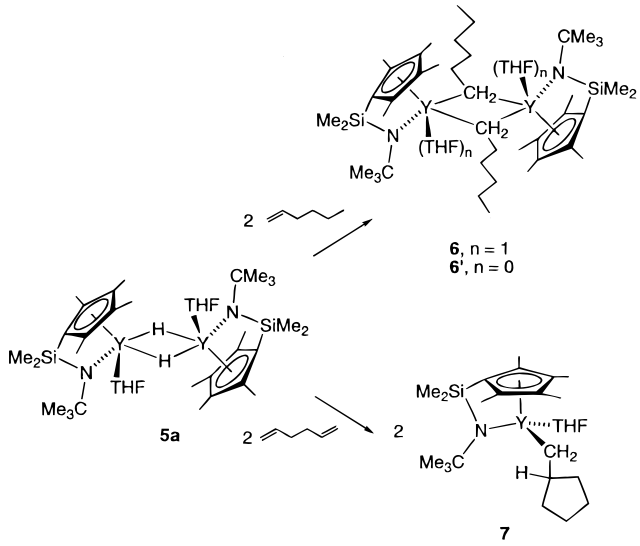


Figure 9. ^{1}H NMR spectra of (a) a 1:1 mixture of **5a**-d_2 and **5b**; (b) a 1:1 mixture of **5a** and **5b**; (c) pure complex **5b**; (d) pure complex **5a**. All spectra were run in C_6D_6 at 50 °C.

ing metal−alkyl bonds.[35a] Whereas the alkyl and hydrido complexes **2a** and **5a** polymerize ethylene under ambient conditions, the alkyl complex **2a** does not react with 1-hexene or styrene (C_6D_6, room temperature, 1 week). The moderate activity for ethylene polymerization (activity: 0.21 and 0.08 g polyethylene/mmol Y·h·bar for **2a** and **5a**, respectively) as compared with that of lanthanocene hydrides is due to the occupation of the free coordination site by a THF molecule. The polyethylenes obtained with these catalysts are strictly linear, as judged by ^{13}C NMR spectroscopy, and highly crystalline, showing melting temperatures of 136 °C.

Scheme 6



1-Hexene slowly reacts with **5a** to give the monoinsertion product **6** as colorless microcrystals, soluble in aromatic hydrocarbons, according to Scheme 6 (2 equiv of 1-hexene, 12 h, 25 °C). Complete conversion is reached within 2 h at room temperature in the presence of 6 equiv of 1-hexene, leaving excess olefin unreacted in the reaction mixture. Even at higher temperatures (5 days, 60 °C), no polymerization of 1-hexene is observed.

The complex **6** shows C_{2h}-symmetry which is caused by a fast site exchange of the coordinated THF molecule. Its dimeric structure in solution is suggested by the triplet for the α-methylene carbon atom in the ^{13}C NMR spectrum at 39.8 ppm with $^1J_{YC} = 21.9$ Hz. The methyl groups on the cyclopentadienyl ligand give rise to two signals and the methyl group on the silicon gives one signal in the ^{1}H and ^{13}C NMR spectrum. The methylene protons at the bridging carbon are observed as a broad pseudotriplet at −0.24 ppm with $^3J_{HH} = 9$ Hz. The other diastereotopic methylene protons form a complex pattern that is partially obscured by the signal of the *tert*-butyl amido group and the coordinated THF ligand. The insertion appears to be reversible, as indicated by the observation of deuterium in free 1-hexene in the reaction with **5a-*d*$_2$** at higher temperatures. The coordinated THF ligand in **6** is more labile than in **5a**. About 50−60% of the THF can be removed in vacuo (1 h, 5×10^{-3} mmHg) to give what we believe is a mixture of THF-free complex **6′** and **6**.[35b] This mixture exhibits polymerization activity toward styrene, although complete removal of THF invariably results in decomposition.

1,5-Hexadiene reacts with **5a** by cyclization to give the cyclopentylmethyl complex **7** (Scheme 6).[41] The ^{1}H

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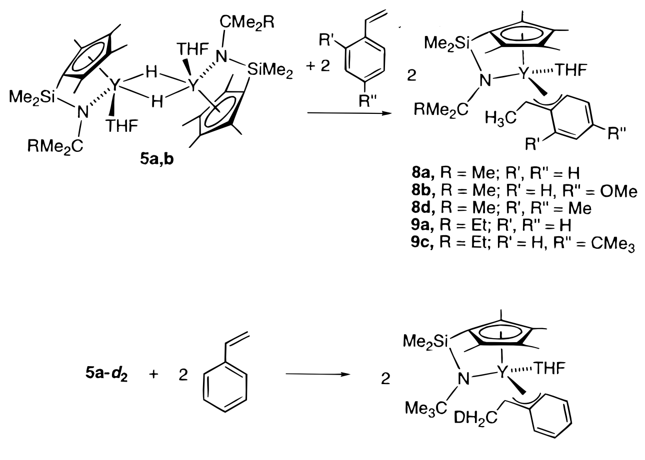
(34) (a) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (c) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (d) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053. (e) Booij, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531.

(35) (a) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566. (b) The X-ray structural analysis of the ytterbium analogue [Yb(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(μ-$CH_2CH_2CH_2CH_2CH_2CH_3$)]$_2$ confirms the structure of the bridging alkyl with trans-disposed chelate ligands: Arndt. S.; Spaniol, T. P.; Okuda, J. Unpublished results.

(36) (a) Cotton, F. A.; La Prade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418. (b) Patterman, S. P.; Karle, I. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150. (c) Chappell, S. D.; Cole-Hamilton, D. J.; Galas, A. M. R.; Hursthouse, M. B.; Walker, N. P. C. *Polyhedron* **1985**. *4*, 121. (d) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (e) Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 3246. (f) Adams, H.; Bailey, N. A.; Winter, M. J.; Woodward, S. *J. Organomet. Chem.* **1991**, *418*, C39. (g) Wang, T.-F.; Hwu, C.-C.; Tsai, C.-W.; Wen, Y.-S. *J. Chem. Soc., Dalton Trans.* **1998**, 2091. (h) Carmona, E.; Marin, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757. (i) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 4693.

Scheme 7



and ^{13}C NMR spectroscopic data for the linked amido–cyclopentadienyl ligand in **7** is analogous to those observed in **2**. In the ^{13}C NMR spectrum the doublet of the methylene carbon atom bonded to yttrium at 47.4 ppm shows an unusually large coupling constant, $^{1}J_{YC} = 54.7$ Hz. The two protons bonded to this carbon are observed as a double doublet at −0.06 ppm ($^{2}J_{YH} = 3.1$ Hz, $^{3}J_{HH} = 7.0$ Hz) in the ^{1}H NMR spectrum. Thus, complex **7** remains monomeric in solution with a labile THF ligand similar to the trimethylsilylmethyl complexes **2**, probably due to an increased steric demand of the tertiary β-carbon atom compared with the secondary β-carbon atom in the linear alkyl complex **6**.

Reaction of the Hydrido Complexes with Styrene and Styrene Polymerization. Reaction of the hydrido complexes **5** with various styrene derivatives leads to the quantitative (by NMR spectroscopy) formation of the monomeric complexes **8** and **9** resulting from the secondary insertion (Scheme 7). No further reaction is observed with excess styrene (6 days). The yellow to orange complexes **8** and **9** are moderately soluble in aliphatic hydrocarbons and highly soluble in aromatic hydrocarbons. The color indicates a charge transfer between the π-electrons of the phenyl ring and the yttrium center. The monomeric structure in solution is suggested by the observation that in the $^{13}C\{^{1}H\}$ NMR spectra the methine carbon bonded to the yttrium atom appears as a doublet in the region 48−53 ppm with a small coupling constant $^{1}J_{YC} = 21$ to 26 Hz. The monomeric structure in the crystalline state is confirmed by a single-crystal X-ray structural analysis of complex **9c** (vide infra).

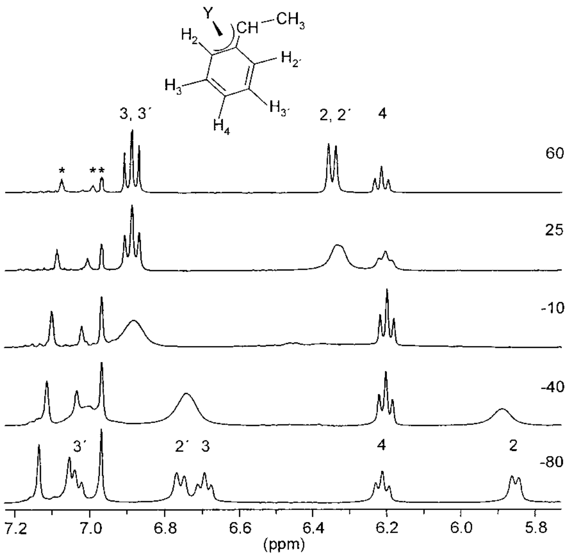


Figure 10. Temperature dependence of the ^{1}H NMR spectrum (aromatic region) of **8a** in toluene-d_8 (*).

The strong temperature dependence of the NMR spectra indicates a fluxional coordination of the 1-phenylethyl ligand. This fluxional process may be slowed sufficiently at −80 °C to give rise to five inequivalent signals for the aromatic ring protons in the ^{1}H NMR spectrum (Figure 10). The significant upfield shift of one of the ortho ring protons suggests an η^3-coordination[36] due to hindered rotation of the phenyl ring on the NMR time scale. The chemical shift of the triplet of the para proton and the signals of the linked amido−cyclopentadienyl ligand framework show no temperature dependence. Over the temperature range +80 to −80 °C four signals for the diastereotopic methyl groups on the cyclopentadienyl ring as well as two signals for the methyl groups on the silicon atom are observed. Yttrium becomes chiral at low temperatures ($T \leq -10$ °C) due to tight binding of the THF molecule on the NMR time scale. However, even at −80 °C only one diastereomer was observed. We suggest that the diastereomer with either R_Y,R_C or S_Y,S_C configuration is stable (Scheme 8).[37]

Although it is well-known that secondary insertion of styrene into the metal hydride bond is preferred on electronic grounds,[38] this result differs from the observations made by Bercaw et al. for the reaction of styrene with the scandium hydrido complex $[Sc(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}H)(PMe_3)]_2$ giving the bis(insertion)

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(37) Insertion of the prochiral styrene into the yttrium hydride bond generates a new chiral center at the methine carbon atom. Such chiral carbon atoms do not racemize during $\eta^1-\eta^3$ rearrangement, see: Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 845. Yet another complication is conceivable: Similar to "prone" and "supine" isomers in diene complexes $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NR_1)$(diene), the η^3-benzyl ligand may be oriented in two fashions relative to the linked amido−cyclopentadienyl ligand to give "prone" and "supine" isomers; see ref 11b. In the case of complex **9c**, the phenyl ring is oriented toward the amido ligand, similar to the observation that linked *tert*-butylamido cyclopentadienyl titanium complexes of branched dienes such as isoprene and 1,3-pentadiene prefer the "supine" isomer (with the "cup" of the diene oriented toward the cyclopentadienyl ligand), whereas unbranched dienes prefer the "prone" isomer (with the "cup" of the diene oriented toward the amido ligand).

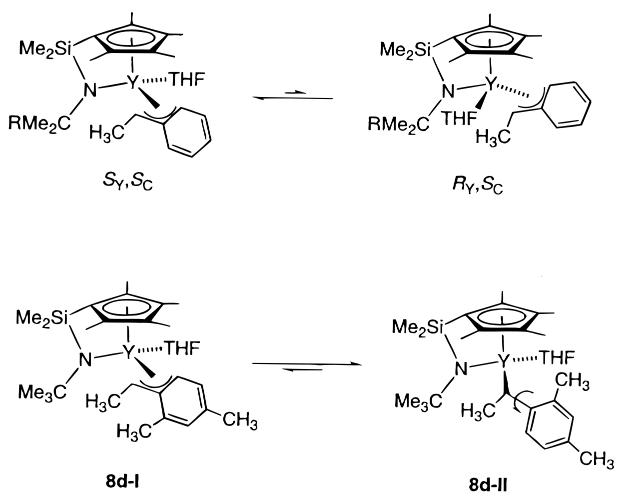
(38) (a) Zambelli, A.; Longo, P.; Pellecchia, C.; Grassi, A. *Macromolecules* **1987**, *20*, 2035. (b) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134. (c) Zambelli, A.; Pellecchia, C.; Proto, A. *Makromol. Chem., Macromol. Symp.* **1995**, *89*, 373. (d) LaPointe, A. M.; Rix, F. C.; Brookhart, M. **1997**, *119*, 906.

(39) (a) Mandel, A.; Magull, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1542. (b) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 135. (c) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219.

(40) Whereas the THF ligands in complex **5** are tightly bonded to yttrium at −40 °C on the ^{1}H NMR time scale, $[Sc(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}H)(PMe_3)]_2$ appears to be a single species over the temperature range from −80 to 25 °C. The ^{31}P NMR spectrum shows two signals at −66 °C in a 4:1 ratio; see ref 9d.

(41) There is a fine balance between catalytic cyclization and cyclopolymerization reaction of α,ω-dienes. Lanthanocene hydrides are known to catalyze cyclization of α,ω-dienes, see: (a) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976. (b) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406. (c) Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1992**, *114*, 3123. (d) Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415. 1,5-Hexadiene may be polymerized using the mono(cyclopentadienyl) yttrium hydrido complex $[Cp^*Y(OC_6H_3\text{-}2,6\text{-}tBu_2)(\mu\text{-}H)]_2$; see ref 15. An yttrium alkyl alkene intermediate was observed spectroscopically at low temperatures, see: (f) Casey, C. P.; Hallenbeck, S. L.; Wright, J. M.; Landis, C. R. *J. Am. Chem. Soc.* **1997**, *119*, 9680. (g) Casey, C. P.; Fagan, M. A.; Hallenbeck, S. L. *Organometallics* **1998**, *17*, 287.

Scheme 8



product [Sc(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$){CH(Ph)CH_2CH_2-CH_2Ph}(PMe_3)] as a result of primary insertion followed by a secondary insertion.[9a,d] Similarly, Teuben et al. reported that catalytic dimerization of styrene utilizing lanthanocene hydrides preferably gives the tail-to-tail coupled product *trans*-1,4-diphenylbut-1-ene.[32b] The selective formation of secondary monoinsertion products observed at room temperature is explained by a *reversible* secondary insertion of styrene into the metal–hydride bond. A second insertion of another styrene molecule is only possible with the sterically less hindered primary insertion product. In contrast, the reaction of styrene with **5** appears to be irreversible, as can be concluded from the selective formation of product [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$){CH(Ph)CH_2D}(THF)] (**8a-*d*$_1$**), from excess styrene and the deuteride **5a-*d*$_2$**.

Insertion of the sterically more demanding styrene 2,4-dimethylstyrene proceeds significantly slower (12 h) than with sterically less demanding derivatives. In the NMR spectra of the oily, yellow product **8d** at −20 °C two diastereomers in a 2:1 ratio are observed. The resonances of the aromatic ring protons of the major isomer fall within the normal region (6.49–6.82 ppm), while the ortho-ring proton of the minor isomer is found at 6.11 ppm. Similarly, compared to the major isomer, the doublet for the methyl group bonded to the methine carbon atom and the singlet for the amido *tert*-butyl group appear at higher field by 0.36 and 0.26 ppm, respectively. The minor isomer **8d-I** is thought to have an η^3-coordinated 1-phenylethyl ligand involving the unsubstituted ortho-ring carbon. There is an unfavorable steric interaction between the ortho-methyl group and the methyl group bonded to the methine carbon atom (Scheme 8). The major isomer **8d-II**, which results from the rotation of the phenyl ring, is supposed to have an η^1-bonded benzyl ligand due to the steric bulk of the methyl group at the ortho-carbon atom. No reaction to give characterizable products is observed when higher substituted styrene derivatives such as 2,4,6-trimethylstyrene, α-methylstyrene, or *trans*-stilbene (several hours, 60–80 °C) are employed.

X-ray diffraction analysis of **9c** was performed using clear yellow cubes obtained by recrystallization from toluene/pentane. Crystallographic data are compiled in Table 1. ORTEP diagrams of the structure of **9c** are shown in Figure 11. Complex **9c** is monomeric, with the

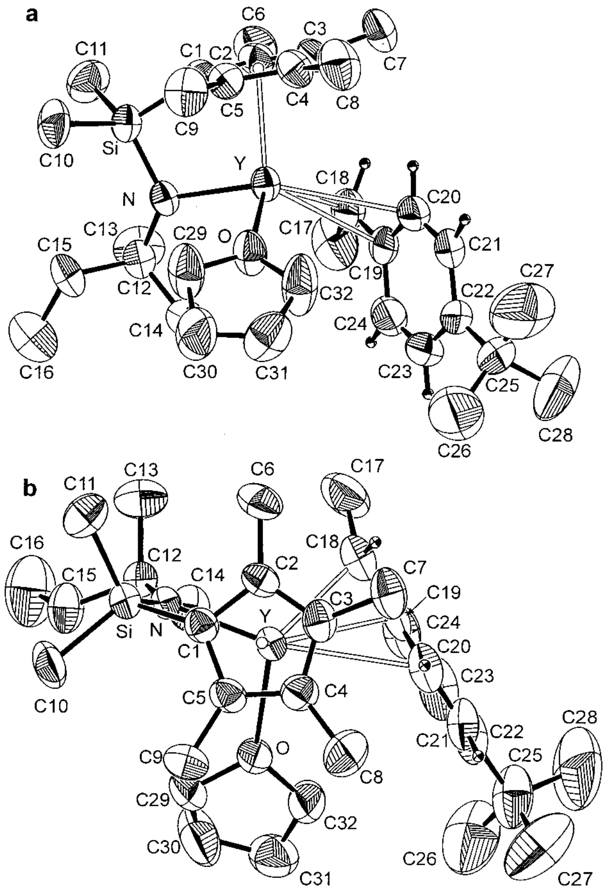


Figure 11. (a) ORTEP diagram[22] of the molecular structure of **9c**. (b) Alternative view from the top. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are partly omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Y–N 2.223(4), Y–C18 2.494(7), Y–C19 2.806(6), Y–C20 3.078(7), Y···C24 3.711(8), Y–O 2.374(4), Cp_{Cent}–Y 2.347(6), C19–C20 1.413(9), C19–C24 1.41(1), C20–C21 1.390(9), C21–C22 1.371(9), C22–C23 1.39(1), C23–C24 1.38(1), Cp_{Cent}–Y–N 97.5(2), Cp_{Cent}–Y–C18 111.7(2), Cp_{Cent}–Y–C20 103.4(2), Cp_{Cent}–Y–O 114.1(2), Y–C18–C19 86.9(4), N–Y–C18 109.0(2), N–Y–C20 155.9(2), N–Y–O 96.5(2), O–Y–C18 123.3(2), O–Y–C20 85.9(2), N–Si–C1 97.3(2), C24–C19–C20 113.6(7), C19–C20–C21 122.6(7), C20–C21–C22 123.1(7), C21–C22–C23 114.5(8), C22–C23–C24 123.8(7), C19–C24–C23 122.2(8).

yttrium atom adopting a pseudotetrahedral coordination geometry similar to that found for complex **2b**. Although the Y–N bond length (2.223(4) Å) and the Y–Cp_{Cent} distance (2.347(6) Å) are similar to those found in **2b**, the Y–O bond (2.374(4) Å) as well as the Y–C18 bond (2.494(7) Å) are significantly longer than those in **2b** and fall in the normal range of Y–O and Y–C bond lengths.[26,27] Most strikingly, there is a weak interaction between the yttrium atom and the ortho ring carbon atom of the benzylic ligand (Y–C20 3.078(7) Å, in agreement with the solution ground-state structure as observed by NMR spectroscopy at low temperatures. Another feature of the interaction of the yttrium atom with the aromatic ring system is a small Y–C18–C19 angle, which is significantly smaller than those found in η^1-bonded benzyl ligands. The bond distances of the ipso-carbon atom to the two ortho-carbon ring atoms are slightly longer than the other aromatic ring carbon–carbon bond lengths (C21–C22 1.371(9) Å, C23–C24

Table 3. Comparison of Metrical Parameters in Various Rare-Earth Benzyl Complexes

complex	Ln−C_α	Ln−C_{ipso}	Ln−C_{ortho}	Ln− C_α−C_{ipso}	ref
9c	2.494(7)	2.806(6)	3.078(7)	86.7	this work
[Cp*Gd($CH_2Ph)_2$(THF)]	2.460(7)−2.489(7)	2.889−3.069	3.168 −3.778	91.9(4)−98.9(4)	17d
[Cp*$_2$Sm]$_2$(μ-η^2:η^4-CH_2CHPh)	2.73(2)	2.85(2)	2.77(2)	79.5(9)	39c
[Cp*$_2$Ce(η^3-CH_2Ph)]	2.596(5)	2.885(5)	2.882(6)	86.0(3)	36e
[(tmeda)($PhCH_2)_2$Y(μ-Br)$_2$Li(tmeda)]	2.418(6), 2.440(6)	3.511, 3.53	4.208, 4.186	127−130	39a
[Cp*$_2$Y(CH_2Ph)(THF)]	2.484(6)	3.444	3.942	118.3(4)	17d
[Cp*$_2$Sm(CH_2Ph)(THF)]	2.528(8)	3.349	3.852	111.2(5)	39b

Table 4. Polymerization of Styrene with 1-Hexyl Yttrium Complex 6′[a]

run no.	t (h)	T (°C)	[M_0]/[cat]	yield (%)	M_n (10^{-3} g mol^{-1})	M_w (10^{-3} g mol^{-1})	M_w/M_n	efficiency (%)
1	24	25	50	100	24.1	26.6	1.10	21
2	40	25	115	99	34.3	38.4	1.12	35
3	72	25	240	90	61.3	75.4	1.23	37
4	24	50	130	90	30.9	43.0	1.39	39
5	24	75	130	100	8.0	15.3	1.91	169

[a] Conditions of polymerization: 19 μmol catalyst, 1.5 mL benzene.

Table 5. Triad and Pentad Analysis of Polystyrene[a]

run no.	*mm* (%)	*mr* (%)	rr (%)	*mmmm* + *mmmr* (%)	*rmmr* (%)	*mmrm* + *rmrm* (%)	*mmrr* + *rmrr* (%)	*rr* (%)
1	0	29.5	70.5	0	0	10	19.5	70.5
	(2.6)	(26.9)	(70.5)	(0.8)	(1.8)	(4.3)	(22.6)	(70.5)
2	1.3	26.2	72.5	0	1.3	7.6	18.6	72.5
	(2.2)	(25.3)	(72.5)	(0.6)	(1.6)	(3.8)	(21.5)	(72.5)
4	5.1	32.1	62.8	0	5.1	6.3	25.8	62.8
	(4.3)	(32.9)	(62.8)	(1.6)	(2.7)	(6.8)	(26.1)	(62.8)
5	6.4	40.4	53.2	0	6.4	12.3	28.1	53.2
	(7.3)	(39.5)	(53.2)	(3.4)	(3.9)	(10.7)	(28.8)	(53.2)

[a] Values in parentheses are the expected values by Bernoullian statistic.

1.38(1) Å). A limited number of rare-earth metal benzyl complexes exhibit a related geometry of the benzylic ligand (Table 3).

The monoinsertion product of 1-hexene **6′** initiates the polymerization of styrene after partial removal of the coordinated THF (50−60%). The polystyrene obtained at room temperature has a narrow molecular weight distribution (Table 4); at higher temperatures a significant increase is observed. The catalyst efficiency[42] is in the range 20−40% at room temperature probably due to incomplete removal of coordinated THF as well as impurities in the solvent and the monomer. Efficiencies above 100% observed at higher temperatures are most likely caused by chain transfer reactions. The polymer is insoluble in methyl ethyl ketone at room temperature and has a syndiotactic-enriched microstructure[43] (Figure 12) showing a decrease in stereoregularity with increasing temperature. The polymer is amorphous with no melting temperatures, but a glass transition at 100 °C is observed by differential scanning calorimetry. The titanium-catalyzed polymerization of styrene is known to proceed by a chain-end control mechanism,[38c,44] with the microstructure described by Bernoullian statistics.[45] Analysis of triads and pentads of the polystyrene obtained from **6′** shows that the observed values deviate significantly from those expected (Table 5).

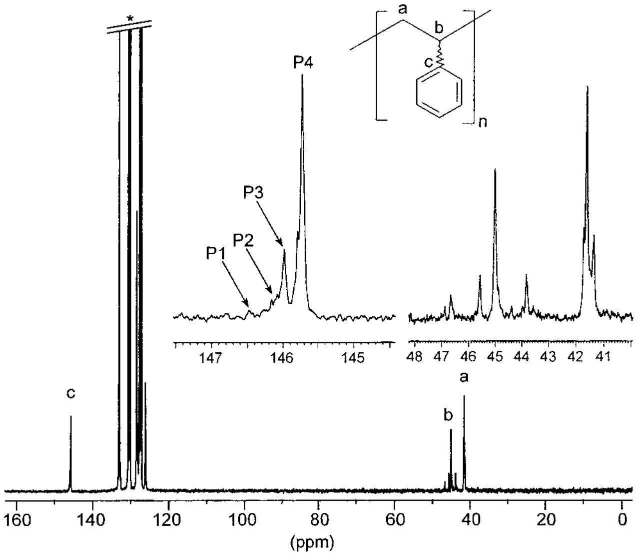


Figure 12. ^{13}C NMR spectrum of polystyrene from run no. 2 in *o*-dichlorobenzene-d_4 (*) at 100 °C. Pentads: P1 = *rmmr*; P2 = *mmrm* + *rmrm*; P3 = *mmrr* + *rmrr*; P4 = *rr*.

Conclusion

Using the linked amido−cyclopentadienyl ligand, a series of alkyl and hydrido complexes of yttrium became readily accessible, although all complexes are stabilized with one THF ligand. The stronger binding of THF to yttrium in the complexes employed in the present work compared with binding of trimethylphosphine to scandium in complexes Sc(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)R(PMe_3) reported by Bercaw et al. may explain the lower activity of the yttrium complexes toward α-olefins such as 1-hexene.[40] Stable dimeric alkyl-bridged complexes as

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[42] Defined as the percentage of active initiators, calculated from the observed number of polymer chains relative to the theoretical ones, assuming that each yttrium complex initiates one polymer chain.

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observed for the scandium complexes $[Sc(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(\mu\text{-}R)]_2$ (R = *n*Pr, *n*Bu)[9d] and the yttrium complex $[Cp^*Y(OC_6H_3\text{-}2,6\text{-}tBu_2)]_2(\mu\text{-}H)(\mu\text{-}R)$ (R = Et, *n*Pr, *n*Bu, nC_6H_{13})[15a] have not been isolated so far using the $Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)$ fragment. We suggest that the THF-depleted monoinsertion product of 1-hexene **6′** adopts a similar structure.[35b] The rate of insertion of ethylene in such bridging alkyl lanthanide bonds is decreased by several orders of magnitude (10^8-10^{10} times in the case of *μ*-H ligands[6a,15]), whereas such dimeric structures are strongly disfavored in the highly active permethyl lanthanocenes.

Since the discovery of syndiotactic polystyrene by Ishihara in 1986,[46] a range of catalyst systems based on MAO-, borane-, or borate-activated half-sandwich titanium complexes have been reported.[47] The polymers obtained with the catalysts of the type $[Ti(\eta^5\text{-}C_5R'_5)R]^+$ are highly syndiotactic (typical *rr* > 97%) with polydispersities > 1.5.[44,47b,c,f,n,p] Control over syndiotacticity and molecular weight with low polydispersity has not been achieved so far. The few lanthanide-based catalytic systems give mostly atactic polystyrene.[48] The reason for the lower syndiotacticity using **6′** can be ascribed to the decreased differentiation of the incoming styrene. Based on the pronounced interaction of the phenyl group of the last inserted monomeric unit in the growing polymer chain with the yttrium center, the strict differentiation would require the styrene monomer to approach from the side opposite the site occupied by THF according to a model based on the crystal structure of **9c**. The linked amido−cyclopentadienyl ligand framework may not be capable of strictly enforcing such a situation under the condition examined.

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous yttrium trichloride (ALFA) was used as received. The linked amido−cyclopentadienyl ligands $(C_5Me_4H)SiMe_2NHR$ (R = CH_2CH_2OMe, $CH_2CH_2NMe_2$, $CH_2CH_2CH_2OMe$, CMe_3, $CHMe_2$) and the indenyl ligand $(C_9H_7)SiMe_2NHCMe_3$ were prepared from the reaction of $(C_5Me_4H)SiMe_2Cl$ and $(C_9H_7)SiMe_2Cl$, respectively, with Li(NHR) according to published procedures.[9,10c,e,i,j] The new ligands $(C_5Me_4H)SiMe_2NHCMe_2Et$ and $(C_5Me_4H)SiMe_2NHCMe_2CH_2OMe$) were prepared by analogous procedures. All other chemicals were commercially available and used as received unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 spectrometer (^1H, 400 MHz; ^{13}C, 101 MHz; ^{89}Y, 19.6 MHz; ^{29}Si, 79.5 MHz) in C_6D_6 at 25 °C, unless otherwise stated. Chemical shifts for ^1H and ^{13}C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ^{89}Y spectra were referenced externally to a 1 M solution of YCl_3 in D_2O; ^{29}Si spectra, to tetramethylsilane. Elemental analyses were performed by the Microanalytical Laboratory of this department. GPC analyses of the isolated polymers were performed using a SpectraSeries P100 pump, a SDV 5*μ* 60 cm column, two 100 A 5*μ* columns with lengths of 5 and 30 cm, respectively, and a Shodex-RI-71 detector. THF was used as eluent; flow rate 1 mL/min. Molecular weights of polystyrenes were determined relative to polystyrene standards. DSC analyses were performed on a Netzsch DSC 204.

$Y(CH_2SiMe_3)_3(THF)_2$ (1). Anhydrous yttrium trichloride (586 mg, 3.00 mmol) was slurried in THF (30 mL) and stirred at 55 °C for 30 min. The solvent was removed in vacuo, and the solid residue was suspended in hexane (40 mL). The suspension was cooled to −78 °C, and a solution of $LiCH_2SiMe_3$ (856 mg, 9.10 mmol) in hexane (20 mL) was added. The suspension was stirred at 0 °C for 3 h. The reaction mixture was filtered, and the white solid was extracted with an additional 2 × 10 mL hexane. LiCl was filtered off, and the solvent was removed from the filtrate in vacuo to yield 1.22 g (82%) of colorless microcrystals. ^1H NMR *δ*: −0.71 (d, $^2J_{YH}$ = 2.3 Hz, 6 H, YCH_2), 0.27 (s, 27 H, $SiCH_3$), 1.30 (m, 8 H, THF), 3.93 (m, 8 H, THF). $^{13}C\{^1H\}$ NMR *δ*: 4.6 ($SiCH_3$), 25.0 (THF), 33.7 (d, $^1J_{YC}$ = 35.7 Hz, YCH_2), 70.8 (THF). $^{29}Si\{^1H\}$ NMR *δ*: −4.1.

$Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)$ (2a). Method A. To a solution of **1** (250 mg, 0.51 mmol) in pentane (10 mL) was added a solution of $(C_5Me_4H)SiMe_2(NHCMe_3)$ (128 mg, 0.51 mmol) in pentane (3 mL) at 0 °C. After stirring for 2 h at this temperature, the reaction mixture was decanted and concentrated in vacuo. The crude product was recrystallized from pentane at −30 °C to give 233 mg (92%) of **2a** as colorless microcrystals.

Method B. Anhydrous yttrium trichloride (586 mg, 3.00 mmol) was slurried in THF (20 mL) and stirred at 60 °C for 30 min. The solvent was removed in vacuo and the solid residue was suspended in pentane (20 mL). The suspension was cooled to −78 °C, a solution of $LiCH_2SiMe_3$ (860 mg, 9.13 mmol) in pentane (20 mL) was added, and the suspension was stirred at 0 °C for 2 h. The suspension was filtered, and the white solid was extracted with an additional 2 × 10 mL of pentane. LiCl was filtered off, and a solution of $(C_5Me_4H)SiMe_2(NHCMe_3)$ (715 mg, 2.84 mmol) in pentane (5 mL) was added at 0 °C. After stirring at this temperature for 2 h, the solution was decanted and concentrated in vacuo. The crude product was recrystallized from pentane at −30 °C to give 1.27 g (90%) of **2a** as colorless microcrystals. ^1H NMR *δ*: −0.93 (d, $^2J_{YH}$ = 3.1 Hz, 2 H, YCH_2), 0.28 (s, 9 H, CH_2SiCH_3), 0.74 (s, 6 H, $SiCH_3$), 1.02 (m, 4 H, *β*-CH_2, THF), 1.38 (s, 9 H, $C(CH_3)_3$), 2.04, 2.19 (s, 6 H, ring CH_3), 3.30 (m, 4 H, α-CH_2, THF). ^{13}C NMR *δ*: 4.7 (q, $^1J_{CH}$ = 115.9 Hz, CH_2SiCH_3), 8.4 (q, $^1J_{CH}$ = 117.1 Hz, $NSiCH_3$), 11.5 (q, $^1J_{CH}$ = 125.5 Hz, ring CH_3), 14.0 (q,

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$^1J_{\mathrm{CH}}$ = 125.5 Hz, ring CH$_3$), 24.7 (t, $^1J_{\mathrm{CH}}$ = 133.5 Hz, β-CH$_2$, THF), 26.2 (dt, $^1J_{\mathrm{CH}}$ = 100.1 Hz, $^1J_{\mathrm{YC}}$ = 44.9 Hz, YCH$_2$), 36.0 (q, $^1J_{\mathrm{CH}}$ = 123.7 Hz, C(*C*H$_3$)$_3$), 54.0 (*C*(CH$_3$)$_3$), 70.7 (t, $^1J_{\mathrm{CH}}$ = 149.8 Hz, α-CH$_2$, THF), 106.6 (ring C attached to SiMe$_2$), 122.3, 126.4 (ring CH$_3$). ^{29}Si{^{1}H} NMR δ: −25.0 (NSiMe$_2$), −2.7 (d, $^2J_{\mathrm{YSi}}$ = 1.9 Hz, CH$_2$SiMe$_3$). Anal. Calcd for C$_{23}$H$_{46}$NOSi$_2$Y: C, 55.51; H, 9.32; N, 2.81. Found: C, 55.67; H, 9.28; N, 3.17.

Thermal Decomposition of 2a. A 5 mm NMR tube with a Teflon valve was charged with approximately 20 mg (40 μmol) of **2a** and 0.45 mL of C$_6$D$_6$. The sample was inserted into the thermostated probe (±0.5 °C) of the spectrometer, and an initial (t = 0) ^{1}H NMR spectrum was recorded. The integral of the methylene protons at −0.93 ppm was monitored as a function of time; the concentration of the alkyl complex was determined relative to the area of the integral of the residual undeuterated solvent. The samples were allowed to reach equilibrium, and a final spectrum was recorded. The data were fit by linear least-squares analysis to a first-order rate expression for the decomposition. The plot of ln([C]/[C]$_0$) (where [C]$_0$ is the initial concentration, [C] the concentration of **2a** at time t) versus time afforded k_1 from the slope a. The rate constants obtained at different temperatures were fit to the Eyring equation by linear least-squares analysis. Δ$H^‡$ and Δ$S^‡$ were obtained from the slope and the axial section.

Determination of K_{diss} from the Temperature Dependence of the Chemical Shift of the THF Methylene Protons. The observed chemical shifts of the THF protons δ_{obs} are the mean chemical shifts of free (δ_{free}) and coordinated (δ_{coord}) THF weighted by their molar fraction x of free THF.

$$\delta_{\mathrm{obs}} = (1 - x)\delta_{\mathrm{coord}} + N\delta_{\mathrm{free}} \qquad (1)$$

The dissociation constant K_{diss} can be obtained from eq 2.

$$K_{\mathrm{diss}} = (\delta_{\mathrm{obs}} - \delta_{\mathrm{coord}})^2 c/(\delta_{\mathrm{free}} - \delta_{\mathrm{coord}})(\delta_{\mathrm{free}} - \delta_{\mathrm{obs}}) \qquad (2)$$

Y(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCMe$_2$Et)(CH$_2$SiMe$_3$)(THF) (2b). To a solution of **1** (990 mg, 2.00 mmol) in pentane (10 mL) was added a solution of (C$_5$Me$_4$H)SiMe$_2$(NHCMe$_2$Et) (531 mg, 2.00 mmol) in pentane (10 mL) at 0 °C. After stirring at this temperature for 2 h, the solution was decanted and concentrated in vacuo. The crude product was recrystallized from pentane at −30 °C to give 810 mg (79%) of **2b** as colorless microcrystals. ^{1}H NMR δ: −0.93 (d, $^2J_{\mathrm{YH}}$ = 3.1 Hz, 2 H, YCH$_2$), 0.27 (s, 9 H, CH$_2$SiC*H*$_3$), 0.73 (s, 6 H, SiCH$_3$), 0.98 (t, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 3 H, NC(CH$_3$)$_2$CH$_2$C*H*$_3$), 1.12 (br m, 4 H, β-CH$_2$, THF), 1.29 (s, 6 H, NC(C*H*$_3$)$_2$CH$_2$CH$_3$), 1.59 (q, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 2 H, NC(CH$_3$)$_2$C*H*$_2$CH$_3$), 2.03, 2.20 (s, 6 H, ring CH$_3$), 3.43 (br m, 4 H, α-CH$_2$, THF). ^{13}C NMR δ: 4.7 (q, $^1J_{\mathrm{CH}}$ = 116.6 Hz, CH$_2$-Si*C*H$_3$), 8.4 (q, $^1J_{\mathrm{CH}}$ = 117.3 Hz, NSi*C*H$_3$), 10.6 (q, $^1J_{\mathrm{CH}}$ = 124.2 Hz, NC(CH$_3$)$_2$CH$_2$*C*H$_3$), 11.5 (q, $^1J_{\mathrm{CH}}$ = 125.2 Hz, ring CH$_3$), 14.0 (q, $^1J_{\mathrm{CH}}$ = 125.2 Hz, ring CH$_3$), 24.8 (t, $^1J_{\mathrm{CH}}$ = 132.7 Hz, β-CH$_2$, THF), 25.9 (dt, $^1J_{\mathrm{CH}}$ = 99.6 Hz, $^1J_{\mathrm{YC}}$ = 43.9 Hz, YCH$_2$), 32.6 (q, $^1J_{\mathrm{CH}}$ = 124.5 Hz, NC(*C*H$_3$)$_2$CH$_2$CH$_3$), 40.6 (t, $^1J_{\mathrm{CH}}$ = 123.2 Hz, NC(CH$_3$)$_2$*C*H$_2$CH$_3$), 56.8 (N*C*(CH$_3$)$_2$CH$_2$CH$_3$), 70.6 (t, $^1J_{\mathrm{CH}}$ = 148.5 Hz, α-CH$_2$, THF), 106.5 (ring C attached to SiMe$_2$), 122.4, 126.3 (ring CH$_3$). ^{29}Si{^{1}H} NMR δ: −25.6 (NSiMe$_2$), −2.6 (d, $^2J_{\mathrm{YSi}}$ = 2.3 Hz, CH$_2$SiMe$_3$). Anal. Calcd for C$_{24}$H$_{48}$NOSi$_2$Y (511.72): C, 56.33; H, 9.45; N, 2.74. Found: C, 56.15; H, 9.37; N, 2.86.

Y(η^5:η^1-C$_9$H$_6$SiMe$_2$NCMe$_3$)(CH$_2$SiMe$_3$)(THF) (3). Anhydrous yttrium trichloride (391 mg, 2.00 mmol) was slurried in THF (15 mL) and stirred at 60 °C for 30 min. The solvent was removed in vacuo, and the solid was suspended in pentane (20 mL). The suspension was cooled to −78 °C, and a solution of LiCH$_2$SiMe$_3$ (571 mg, 6.06 mmol) in pentane (15 mL) was added. The suspension was stirred at 0 °C for 1 h. The suspension was filtered, and the white solid was extracted with an additional 2 × 8 mL of pentane. LiCl was filtered off, and a solution of (C$_9$H$_7$)SiMe$_2$(NHCMe$_3$) (445 mg, 1.81 mmol) in pentane (8 mL) was added at 0 °C. After stirring at room temperature for 17 h, the solution was filtered and concentrated in vacuo. The crude product was recrystallized from pentane at −30 °C to give 610 mg (69%) of **3** as colorless microcrystals. ^{1}H NMR δ: −0.98, (dd, $^2J_{\mathrm{YH}}$ = 2.7 Hz, $^2J_{\mathrm{HH}}$ = 11.0 Hz, 1 H, YCH$_2$), −0.81 (dd, $^2J_{\mathrm{YH}}$ = 3.5 Hz, $^2J_{\mathrm{HH}}$ = 11.0 Hz, 1 H, YCH$_2$), 0.35 (s, 9 H, CH$_2$SiC*H*$_3$), 0.77, 0.90 (s, 3 H, SiCH$_3$), 1.02 (br s, 4 H, β-CH$_2$, THF), 1.29 (s, 9 H, C(CH$_3$)$_3$), 3.04 (br s, 4 H, α-CH$_2$, THF), 6.75 (m, 2 H, H-6, H-7), 7.01 (d, $^2J_{\mathrm{HH}}$ = 3.1 Hz, 1 H, H-2), 7.12 (d, $^2J_{\mathrm{HH}}$ = 3.1 Hz, 1 H, H-3), 7.50, 7.83 (m, 1 H, H-5, H-8). ^{13}C{^{1}H} NMR δ: 4.3 (NSi*C*H$_3$), 4.6 (CH$_2$Si*C*H$_3$), 6.2 (NSi*C*H$_3$), 24.9 (β-CH$_2$, THF), 30.0 (d, $^1J_{\mathrm{YC}}$ = 44.6 Hz, YCH$_2$), 35.8 (C(*C*H$_3$)$_3$), 53.8 (*C*(CH$_3$)$_3$), 70.0 (α-CH$_2$, THF), 100.4 (C-1), 104.5 (C-3), 121.0, 121.2 (C-6, C-7), 122.5, 123.8 (C-5, C-8), 132.1, 134.7 (C-4, C-9), the signal of C-2 is obscured by the signal of the solvent. ^{29}Si{^{1}H} NMR δ: −24.1 (NSiMe$_2$), −2.8 (CH$_2$SiMe$_3$). Anal. Calcd for C$_{23}$H$_{40}$NOSi$_2$Y: C, 56.19; H, 8.20; N, 2.85. Found: C, 55.50; H, 6.41; N, 2.91.

Y(η^5-C$_5$Me$_4$H){N(SiMe$_2$CH$_2$SiMe$_3$)(CH$_2$CH$_2$OMe)}(CH$_2$SiMe$_3$)(THF) (4a). A 5 mm NMR tube was charged with **1** (41 mg, 83 μmol), C$_6$D$_6$ (0.50 mL) and (C$_5$Me$_4$H)SiMe$_2$(NHCH$_2$CH$_2$OMe) (21 mg, 83 μmol) in this order. After 1 h all volatiles were removed in vacuo, and the residue was redissolved in C$_6$D$_6$ (0.45 mL). ^{1}H NMR δ: −1.18 (d, $^2J_{\mathrm{YH}}$ = 2.7 Hz, 2 H, YCH$_2$), −0.09 (s, 2 H, SiCH$_2$Si), 0.20 (s, 9 H, SiCH$_2$Si(CH$_3$)$_3$), 0.21 (s, 6 H, NSi(CH$_3$)$_2$), 0.28 (s, 9 H, YCH$_2$Si(CH$_3$)$_3$), 1.38 (β-CH$_2$, THF), 2.04, 2.12 (s, 6 H, C$_5$Me$_4$), 3.13 (s, 3 H, OCH$_3$), 3.16 (m, 2 H, NCH$_2$), 3.23 (m, 2 H, CH$_2$O), 3.57 (α-CH$_2$, THF), 5.71 (s, 1 H, ring H); ^{13}C{^{1}H} NMR δ: 1.8 (SiCH$_2$Si(*C*H$_3$)$_3$), 3.1 (NSi(CH$_3$)$_2$), 5.0 (YCH$_2$Si(*C*H$_3$)$_3$), 6.7 (SiCH$_2$Si), 11.8, 13.5 (ring CH$_3$), 22.8 (d, $^1J_{\mathrm{YC}}$ = 42.5 Hz, YCH$_2$), 25.6 (THF, β-CH$_2$), 44.7 (NCH$_2$), 60.8 (OCH$_3$), 68.5 (α-CH$_2$, THF), 83.0 (CH$_2$O), 109.5 (ring CH), 117.5, 118.2 (ring C).

Y(η^5-C$_5$Me$_4$H){N(SiMe$_2$CH$_2$SiMe$_3$)(CH$_2$CH$_2$NMe$_2$)}(CH$_2$SiMe$_3$)(THF) (4b). A 5 mm NMR tube was charged with **1** (41 mg, 83 μmol), C$_6$D$_6$ (0.50 mL), and (C$_5$Me$_4$H)SiMe$_2$(NHCH$_2$CH$_2$NMe$_2$) (22 mg, 83 μmol) in this order. After 1 h all volatiles were removed in vacuo, and the residue was redissolved in C$_6$D$_6$ (0.45 mL). ^{1}H NMR δ: −1.04 (d, $^2J_{\mathrm{YH}}$ = 3.1 Hz, 2 H, YCH$_2$), −0.07 (s, 2 H, SiCH$_2$Si), 0.21 (s, 9 H, SiCH$_2$Si(C*H*$_3$)$_3$), 0.22 (s, 6 H, NSi(C*H*$_3$)$_2$), 0.30 (s, 9 H, YCH$_2$Si(C*H*$_3$)$_3$), 1.35 (br s, 4 H, β-CH$_2$, THF), 1.85 (s, 6 H, N(CH$_3$)$_2$), 1.95 (C*H*$_2$NMe$_2$), 2.05, 2.13 (s, 6 H, C$_5$Me$_4$), 2.98 (t, $^3J_{\mathrm{HH}}$ = 5.5 Hz, 2 H, NC*H*$_2$CH$_2$NMe$_2$), 3.55 (br s, 4 H, α-CH$_2$, THF), 5.45 (s, 1 H, ring H). ^{13}C{^{1}H} NMR δ: 1.2 (NSi(*C*H$_3$)$_2$), 1.7 (SiCH$_2$Si(*C*H$_3$)$_3$), 1.9 (SiCH$_2$Si), 4.8 (YCH$_2$Si(*C*H$_3$)$_3$), 11.9, 13.6 (ring CH$_3$), 27.5 (d, $^1J_{\mathrm{YC}}$ = 46.8 Hz, YCH$_2$), 25.5 (β-CH$_2$, THF), 43.5 (N*C*H$_2$CH$_2$NMe$_2$), 45.1 (N(CH$_3$)$_2$), 63.3 (NCH$_2$*C*H$_2$NMe$_2$), 68.7 (α-CH$_2$, THF), 110.5 (ring CH), 119.3, 119.7 (ring C). ^{29}Si{^{1}H} NMR δ: 1.2, −2.5 (d, $^2J_{\mathrm{YSi}}$ = 2.0 Hz, CH$_2$SiMe$_3$), −8.7.

Y(η^5-C$_5$Me$_4$H){N(SiMe$_2$CH$_2$SiMe$_3$)(CH$_2$CH$_2$CH$_2$OMe)}(CH$_2$SiMe$_3$)(THF) (4c). A 5 mm NMR tube was charged with **1** (37 mg, 75 μmol), C$_6$D$_6$ (0.50 mL) and (C$_5$Me$_4$H)SiMe$_2$(NHCH$_2$CH$_2$CH$_2$OMe) (20 mg, 75 μmol) in this order. After 1 h all volatiles were removed in vacuo, and the residue was redissolved in C$_6$D$_6$ (0.45 mL). ^{1}H NMR δ: −0.96 (d, $^2J_{\mathrm{YH}}$ = 2.0 Hz, 2 H, YCH$_2$), 0.09 (s, 2 H, SiCH$_2$Si), 0.23 (s, 9 H, SiCH$_2$Si(C*H*$_3$)$_3$), 0.26 (s, 9 H, YCH$_2$Si(C*H*$_3$)$_3$), 0.27 (s, 6 H, NSi(C*H*$_3$)$_2$), 1.37 (β-CH$_2$, THF), 1.45 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$O), 2.01, 2.14 (s, 6 H, C$_5$Me$_4$), 2.89 (s, 3 H, OCH$_3$), 3.03 (m, 2 H, NCH$_2$), 3.12 (m, 2 H, CH$_2$O), 3.57 (α-CH$_2$, THF), 5.69 (s, 1 H, ring H). ^{13}C{^{1}H} NMR δ: 1.3 (NSi(*C*H$_3$)$_2$), 1.8 (SiCH$_2$Si(*C*H$_3$)$_3$), 4.4 (SiCH$_2$Si), 4.8 (YCH$_2$Si(*C*H$_3$)$_3$), 11.6, 13.6 (ring CH$_3$), 24.8 (d, $^1J_{\mathrm{YC}}$ = 45.5 Hz, YCH$_2$), 25.6 (THF, β-CH$_2$), 34.2 (NCH$_2$*C*H$_2$CH$_2$O), 45.2 (NCH$_2$), 60.7 (OCH$_3$), 68.7 (α-CH$_2$, THF), 77.3 (CH$_2$O), 109.9 (ring CH), 118.6, 118.8 (ring C). ^{29}Si{^{1}H} NMR δ: 1.2, −1.4, −10.2.

Y(η^5-C$_5$Me$_4$H){N(SiMe$_2$CH$_2$SiMe$_3$)(CMe$_2$CH$_2$OMe)}(CH$_2$SiMe$_3$) (4d). A 5 mm NMR tube was charged with **1** (41 mg, 83 μmol), C$_6$D$_6$ (0.50 mL) and (C$_5$Me$_4$H)SiMe$_2$(NHCMe$_2$CH$_2$OMe) (24 mg, 85 μmol) in this order. After 1 h all volatiles were removed in vacuo, and the residue was redissolved in $\mathrm{C_6D_6}$ (0.45 mL). ^{1}H NMR δ: -1.03, -0.69 (dd, $^{2}J_{\mathrm{YH}} = 3.1$ Hz, $^{2}J_{\mathrm{HH}} = 11.0$ Hz, 1 H, $\mathrm{YCH_2}$), -0.10 (d, $^{2}J_{\mathrm{HH}} = 10.2$ Hz, 1 H, $\mathrm{SiCH_2Si}$), 0.01 (d, 1 H, $\mathrm{SiCH_2Si}$, partially obscured by $\mathrm{SiMe_4}$), 0.21 (s, 9 H, $\mathrm{SiCH_2Si(C\mathit{H}_3)_3}$), 0.25 (s, 3 H, $\mathrm{NSi(CH_3)_2}$), 0.30 (s, 9 H, $\mathrm{YCH_2Si(C\mathit{H}_3)_3}$), 0.32 (s, 3 H, $\mathrm{NSi(CH_3)_2}$), 0.99, 1.09 (s, 3 H, $\mathrm{NC(CH_3)_2}$), 2.01, 2.02 (s, 3 H, ring $\mathrm{CH_3}$), 2.18 (s, 6 H, ring $\mathrm{CH_3}$), 2.92 (d, 1 H, $^{2}J_{\mathrm{HH}} = 7.8$ Hz, $\mathrm{CH_2O}$), 2.97 (s, 3 H, $\mathrm{OCH_3}$), 3.21 (d, 1 H, $^{2}J_{\mathrm{HH}} = 7.8$ Hz, $\mathrm{CH_2O}$), 5.65 (s, 1 H, ring H). ^{13}C{^{1}H} NMR δ: = 2.0 ($\mathrm{SiCH_2Si(\mathit{C}H_3)_3}$), 4.8 ($\mathrm{YCH_2Si(\mathit{C}H_3)_3}$), 5.1, 5.2 ($\mathrm{NSi(CH_3)_2}$), 5.5 ($\mathrm{SiCH_2Si}$), 11.5, 11.7, 13.8, 13.9 (ring $\mathrm{CH_3}$), 27.2 (d, $^{1}J_{\mathrm{YC}} = 44.9$ Hz, $\mathrm{YCH_2}$), 29.8, 31.8 ($\mathrm{NC(\mathit{C}H_3)_2}$), 56.0 ($\mathrm{N\mathit{C}(CH_3)_2}$), 60.6 ($\mathrm{OCH_3}$), 91.8 ($\mathrm{CH_2O}$), 110.5 (ring CH), 118.7, 118.8, 119.1, 119.2 (ring C). ^{29}Si{^{1}H} NMR δ: 2.0, -2.4, -18.0.

$[\mathrm{Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2}$ (5a). A solution of **2a** (630 mg, 1.27 mmol) in pentane (10 mL) was loaded in a thick-walled 100 mL glass vessel. Dihydrogen (4 atm) was charged at room temperature, and the reaction mixture was stirred vigorously. After stirring for 7 h, the white precipitate of **5a** was collected by decanting the solution; yield 335 mg (64%) of a colorless powder. ^{1}H NMR (toluene-d_8, 50 °C) δ: 0.69 (s, 6 H, $\mathrm{SiCH_3}$), 1.36 (s, 9 H, $\mathrm{C(CH_3)_3}$), 1.46 (br m, 4 H, β-$\mathrm{CH_2}$, THF), 2.09, 2.22 (s, 6 H, ring $\mathrm{CH_3}$), 3.82 (br m, 4 H, α-$\mathrm{CH_2}$, THF), 5.50 (t, 1 H, $^{1}J_{\mathrm{YH}} = 28.8$ Hz, $\mathrm{Y_2H_2}$). ^{13}C{^{1}H} NMR (toluene-d_8, 50 °C) δ: 8.6 ($\mathrm{Si\mathit{C}H_3}$), 12.2, 14.3 (ring $\mathrm{CH_3}$), 25.2 (β-$\mathrm{CH_2}$, THF), 36.8 ($\mathrm{C(\mathit{C}H_3)_3}$), 55.0 ($\mathrm{\mathit{C}(CH_3)_3}$), 72.1 ($\alpha$-$\mathrm{CH_2}$, THF), 108.5 (ring C attached to $\mathrm{SiMe_2}$), 125.8 (ring C), one signal of a ring carbon atom is covered by a signal of the solvent. ^{29}Si{^{1}H} NMR (toluene-d_8, 50 °C) δ: -25.5. ^{89}Y NMR ($\mathrm{C_6D_6}$, 50 °C) δ: 334.7 (t, $^{1}J_{\mathrm{YH}} = 28.6$ Hz). Major isomer: ^{1}H NMR (toluene-d_8, -40 °C) δ: 0.81, 0.95 (s, 3 H, $\mathrm{SiCH_3}$), 1.17 (m, 4 H, β-$\mathrm{CH_2}$, THF), 1.52 (s, 9 H, $\mathrm{C(CH_3)_3}$), 2.02 (s, 6 H, ring $\mathrm{CH_3}$), 2.11, 2.54 (s, 3 H, ring $\mathrm{CH_3}$), 3.47, 3.85 (br m, 2 H, α-$\mathrm{CH_2}$, THF), 5.27 (t, 1 H, $^{1}J_{\mathrm{YH}} = 29.0$ Hz, $\mathrm{Y_2H_2}$). ^{13}C{^{1}H} NMR (toluene-d_8, -40 °C) δ: 8.2, 9.3 ($\mathrm{Si\mathit{C}H_3}$), 12.1, 12.3, 13.9, 14.7 (ring $\mathrm{CH_3}$), 25.0 (β-$\mathrm{CH_2}$, THF), 36.3 ($\mathrm{C(\mathit{C}H_3)_3}$), 54.7 ($\mathrm{\mathit{C}(CH_3)_3}$), 72.7 ($\alpha$-$\mathrm{CH_2}$, THF), 107.1 (ring C attached to $\mathrm{SiMe_2}$), 119.6, 122.8, 126.0, 126.2 (ring C). ^{29}Si{^{1}H} NMR (toluene-d_8, -40 °C) δ: -25.6. ^{89}Y NMR (toluene-d_8, -40 °C) δ: 337.5 (t, $^{1}J_{\mathrm{YH}} = 29.0$ Hz). Minor isomer: ^{1}H NMR (toluene-d_8, -40 °C) δ: 1.20 (m, 4 H, β-$\mathrm{CH_2}$, THF), 1.44 (s, 9 H, $\mathrm{C(CH_3)_3}$), 2.05, 2.14, 2.20, 2.51 (s, 3 H, ring $\mathrm{CH_3}$), 3.78 (br m, 4 H, α-$\mathrm{CH_2}$, THF), 5.45 (t, 1 H, $^{1}J_{\mathrm{YH}} = 28.6$ Hz, $\mathrm{Y_2H_2}$). ^{13}C{^{1}H} NMR (toluene-d_8, -40 °C) δ: 8.5, 9.0 ($\mathrm{Si\mathit{C}H_3}$), 11.6, 13.3, 14.1, 15.2 (ring $\mathrm{CH_3}$), 24.9 (β-$\mathrm{CH_2}$, THF), 36.4 ($\mathrm{C(\mathit{C}H_3)_3}$), 55.0 ($\mathrm{\mathit{C}(CH_3)_3}$), 72.4 ($\alpha$-$\mathrm{CH_2}$, THF), 107.7 (ring C attached to $\mathrm{SiMe_2}$), 119.9, 123.3, 125.8 (ring C). ^{29}Si{^{1}H} NMR (toluene-d_8, -40 °C) δ: -25.7. ^{89}Y NMR (toluene-d_8, -40 °C) δ: 335.3 (t, $^{1}J_{\mathrm{YH}} = 28.6$ Hz). Spectra obtained in THF-d_8: ^{1}H NMR (THF-d_8, 50 °C) δ: 0.41 (s, 6 H, $\mathrm{SiCH_3}$), 1.24 (s, 9 H, $\mathrm{C(CH_3)_3}$), 2.03, 2.08 (s, 6 H, ring $\mathrm{CH_3}$), 5.44 (t, 1 H, $^{1}J_{\mathrm{YH}} = 28.8$ Hz, $\mathrm{Y_2H_2}$). ^{13}C{^{1}H} NMR (THF-d_8, 50 °C) δ: 8.5 ($\mathrm{Si\mathit{C}H_3}$), 12.0, 14.2 (ring $\mathrm{CH_3}$), 36.7 ($\mathrm{C(\mathit{C}H_3)_3}$), 55.2 ($\mathrm{\mathit{C}(CH_3)_3}$), 108.2 (ring C attached to $\mathrm{SiMe_2}$), 122 (very broad, ring C), 125.8 (ring C). ^{29}Si{^{1}H} NMR (THF-d_8, 50 °C) δ: -27.9. ^{89}Y NMR (THF-d_8, 50 °C) δ: 331.2 (t, $^{1}J_{\mathrm{YH}} = 28.8$ Hz). ^{1}H NMR (THF-d_8, -60 °C) δ: 0.36, 0.40 (s, 3 H, $\mathrm{SiCH_3}$), 1.25 (s, 9 H, $\mathrm{C(CH_3)_3}$), 1.93, 1.99, 2.01, 2.06 (s, 3 H, ring $\mathrm{CH_3}$), 5.12 (t, 1 H, $^{1}J_{\mathrm{YH}} = 29.0$ Hz, $\mathrm{Y_2H_2}$, major isomer), 5.37 (t, $^{1}J_{\mathrm{YH}} =$ ca. 30 Hz, $\mathrm{Y_2H_2}$, minor isomer). ^{13}C{^{1}H} NMR (THF-d_8, -60 °C) δ: 8.1, 8.9 ($\mathrm{Si\mathit{C}H_3}$), 11.8, 12.2, 13.6, 14.5 (ring $\mathrm{CH_3}$), 36.2 ($\mathrm{C(\mathit{C}H_3)_3}$), 54.7 ($\mathrm{\mathit{C}(CH_3)_3}$), 106.5 (ring C attached to $\mathrm{SiMe_2}$), 120.2, 123.0, 125.6, 126.3 (ring C). ^{29}Si{^{1}H} NMR (THF-d_8, -60 °C) δ: -28.3. ^{89}Y NMR (THF-d_8, -60 °C) δ: 331.6 (t, $^{1}J_{\mathrm{YH}} = 29.0$ Hz). Anal. Calcd for $\mathrm{C_{38}H_{72}N_2O_2Si_2Y_2}$: C, 55.46; H, 8.82; N, 3.40. Found: C, 54.62; H, 8.33; N, 3.29.

$[\mathrm{Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}D)]_2}$ (5a-d_2). A solution of **2a** (1.00 g, 2.01 mmol) in pentane (15 mL) was loaded in a thick-walled 100 mL glass vessel. Deuterium (4.5 atm) was charged at room temperature, and the reaction mixture was stirred vigorously. After stirring for 20 h, the white precipitate of **5a-d_2** was collected by decanting the solution; yield 624 mg (75%) of a colorless powder. ^{2}H NMR ($\mathrm{C_6H_6}$, 50 °C) δ: 5.54 (t, $^{1}J_{\mathrm{YD}} = 4.5$ Hz, $\mathrm{Y_2D_2}$).

$[\mathrm{Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)(THF)(\mu\text{-}H)]_2}$ (5b). A solution of **2b** (600 mg, 1.17 mmol) in pentane (8 mL) was loaded in a thick-walled 100 mL glass vessel. Dihydrogen (5 atm) was charged at room temperature, and the reaction mixture was stirred vigorously. After stirring for 7 h, the white precipitate of **5b** was collected by decanting the solution; yield 275 mg (55%) of a colorless powder. ^{1}H NMR ($\mathrm{C_6D_6}$, 50 °C) δ: 0.77 (s, 6 H, $\mathrm{SiCH_3}$), 1.04 (t, $^{3}J_{\mathrm{HH}} = 7.4$ Hz, 3 H, $\mathrm{NC(CH_3)_2CH_2C\mathit{H}_3}$), 1.35 (s, 6 H, $\mathrm{NC(C\mathit{H}_3)_2CH_2CH_3}$), 1.38 (br m, 4 H, β-$\mathrm{CH_2}$, THF), 1.66 (q, $^{3}J_{\mathrm{HH}} = 7.4$ Hz, 2 H, $\mathrm{NC(CH_3)_2C\mathit{H}_2CH_3}$), 2.08, 2.27 (s, 6 H, ring $\mathrm{CH_3}$), 3.80 (br s, 4 H, α-$\mathrm{CH_2}$, THF), 5.44 (t, 1 H, $^{1}J_{\mathrm{YH}} = 28.8$ Hz, $\mathrm{Y_2H_2}$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 50 °C) δ: 8.8 ($\mathrm{NSi\mathit{C}H_3}$), 10.7 ($\mathrm{NC(CH_3)_2CH_2\mathit{C}H_3}$), 12.2, 14.3 (ring $\mathrm{CH_3}$), 25.1 (β-$\mathrm{CH_2}$, THF), 33.1 ($\mathrm{NC(\mathit{C}H_3)_2CH_2CH_3}$), 41.2 ($\mathrm{NC(CH_3)_2\mathit{C}H_2CH_3}$), 57.7 ($\mathrm{N\mathit{C}(CH_3)_2CH_2CH_3}$), 72.2 ($\alpha$-$\mathrm{CH_2}$, THF), 108.4 (ring C attached to $\mathrm{SiMe_2}$), 125.8, 128.6 (ring $\mathrm{CH_3}$). ^{29}Si{^{1}H} NMR δ: -25.9. Major isomer: ^{1}H NMR (toluene-d_8, -40 °C) δ: 0.81, 0.92 (s, 3 H, $\mathrm{SiCH_3}$), 1.09 (br s, 3 H, $\mathrm{NC(CH_3)_2CH_2C\mathit{H}_3}$), 1.2 (m, β-$\mathrm{CH_2}$, THF), 1.42, 1.44 (s, 3 H, $\mathrm{NC(C\mathit{H}_3)_2CH_2CH_3}$) 1.72 (br m, 2 H, $\mathrm{NC(CH_3)_2C\mathit{H}_2CH_3}$), 2.02 (s, 6 H, ring $\mathrm{CH_3}$), 2.11, 2.54 (s, 3 H, ring $\mathrm{CH_3}$), 3.53, 3.91 (br m, 2 H, α-$\mathrm{CH_2}$, THF), 5.23 (t, 1 H, $^{1}J_{\mathrm{YH}} = 29.0$ Hz, $\mathrm{Y_2H_2}$). ^{13}C{^{1}H} NMR (toluene-d_8, -40 °C) δ: 8.1, 9.7 ($\mathrm{NSi\mathit{C}H_3}$), 10.9 ($\mathrm{NC(CH_3)_2CH_2\mathit{C}H_3}$), 12.1, 12.2, 13.9, 14.6 (ring $\mathrm{CH_3}$), 25.1 (β-$\mathrm{CH_2}$, THF), 32.2, 34.2 ($\mathrm{NC(\mathit{C}H_3)_2CH_2CH_3}$), 40.2 ($\mathrm{NC(CH_3)_2\mathit{C}H_2CH_3}$), 57.4 ($\mathrm{N\mathit{C}(CH_3)_2CH_2CH_3}$), 72.9 ($\alpha$-$\mathrm{CH_2}$, THF), 107.2 (ring C attached to $\mathrm{SiMe_2}$), 119.9, 123.0, 125.9, 126.2 (ring $\mathrm{CH_3}$). ^{29}Si{^{1}H} NMR (toluene-d_8, -40 °C) δ: -26.0. Minor isomer: ^{1}H NMR (toluene-d_8, -40 °C) δ: 2.14, 2.20, 2.37, 2.50 (s, 3 H, ring $\mathrm{CH_3}$), 5.42 (t, 1 H, $^{1}J_{\mathrm{YH}} = 28.6$ Hz, $\mathrm{Y_2H_2}$). ^{13}C{^{1}H} NMR (toluene-d_8, -40 °C) δ: 9.3, 9.4 ($\mathrm{NSi\mathit{C}H_3}$), 11.0 ($\mathrm{NC(CH_3)_2CH_2\mathit{C}H_3}$), 11.7, 13.3, 14.0, 15.2 (ring $\mathrm{CH_3}$), 24.9 (β-$\mathrm{CH_2}$, THF), 33.5 ($\mathrm{NC(\mathit{C}H_3)_2CH_2CH_3}$), 39.2 ($\mathrm{NC(CH_3)_2\mathit{C}H_2CH_3}$), 57.6 ($\mathrm{N\mathit{C}(CH_3)_2CH_2CH_3}$), 72.7 ($\alpha$-$\mathrm{CH_2}$, THF), 108.1 (ring C attached to $\mathrm{SiMe_2}$), 120.3, 124.1, 124.6 (ring $\mathrm{CH_3}$). ^{29}Si{^{1}H} NMR (toluene-d_8, -40 °C) δ: -26.2. Anal. Calcd for $\mathrm{C_{40}H_{76}N_2O_2Si_2Y_2}$: C, 56.45; H, 9.00; N, 3.29. Found: C, 53.84; H, 8.81; N, 3.38.

$[\mathrm{Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}CH_2CH_2CH_2CH_2CH_2CH_3)]_2}$ (6). A 5 mm NMR tube was charged with **5a** (26 mg, 32 μmol) and $\mathrm{C_6D_6}$ (0.45 mL). A solution of 1-hexene (70 μL, 1 M in $\mathrm{C_6D_6}$) was added at room temperature. After 20 h the solvent was removed in vacuo to give **6** as colorless microcrystals. ^{1}H NMR δ: -0.24 (br t, $^{3}J_{\mathrm{HH}} = 9$ Hz, 2 H, $\mathrm{YCH_2}$), 0.74 (s, 6 H, $\mathrm{SiCH_3}$), 0.90 (t, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, 3 H, $\mathrm{CH_2CH_2CH_2CH_2CH_2C\mathit{H}_3}$), 1.2–1.3 (m, 4 H, $\mathrm{CH_2CH_2CH_2C\mathit{H}_2C\mathit{H}_2CH_3}$), 1.28 (s, 9 H, $\mathrm{C(CH_3)_3}$), 1.42 (m, 4 H, $\mathrm{CH_2C\mathit{H}_2C\mathit{H}_2CH_2CH_2CH_3}$), 1.43 (br s, 4 H, β-$\mathrm{CH_2}$, THF), 1.95, 2.46 (s, 6 H, ring $\mathrm{CH_3}$), 3.62 (br s, 4 H, α-$\mathrm{CH_2}$, THF). ^{13}C{^{1}H} NMR δ: 8.2 ($\mathrm{NSi\mathit{C}H_3}$), 11.6 (ring $\mathrm{CH_3}$), 14.1 ($\mathrm{CH_2CH_2CH_2CH_2CH_2\mathit{C}H_3}$), 14.5 (ring $\mathrm{CH_3}$), 22.7 ($\mathrm{CH_2CH_2CH_2CH_2\mathit{C}H_2CH_3}$), 25.1 ($\beta$-$\mathrm{CH_2}$, THF), 28.3 ($\mathrm{CH_2CH_2CH_2\mathit{C}H_2CH_2CH_3}$), 31.5 ($\mathrm{CH_2CH_2\mathit{C}H_2CH_2CH_2CH_3}$), 36.2 ($\mathrm{C(\mathit{C}H_3)_3}$), 36.9 ($\mathrm{CH_2\mathit{C}H_2CH_2CH_2CH_2CH_3}$), 39.8 (t, $^{1}J_{\mathrm{YC}} = 21.9$ Hz, $\mathrm{YCH_2}$), 54.3 ($\mathrm{\mathit{C}(CH_3)_3}$), 106.3 (ring C attached to $\mathrm{SiMe_2}$), 121.8, 126.2 (ring C), α-$\mathrm{CH_2}$ of THF was not detected. ^{29}Si{^{1}H} NMR δ: -24.9.

$\mathrm{Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{CH_2CH(CH_2)_4\}(THF)}$ (7). A 5 mm NMR tube was charged with **5a** (25 mg, 30 μmol) and $\mathrm{C_6D_6}$ (0.45 mL). A solution of 1,5-hexadiene (85 μL, 1 M in $\mathrm{C_6D_6}$) was added at room temperature. After 3 h the solvent was removed in vacuo to give **7** as a slight yellow powder in quantitative yield. ^{1}H NMR δ: -0.06 (dd, $^{2}J_{\mathrm{YH}} = 3.1$ Hz, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 2 H, $\mathrm{YCH_2}$), 0.77 (s, 6 H, $\mathrm{SiCH_3}$), 1.17 (br s, 4 H, β-$\mathrm{CH_2}$, THF), 1.3 (m, 2 H, $\mathrm{C_5H_9}$, α-$\mathrm{CH_2}$), 1.40 (s, 9 H, $\mathrm{C(CH_3)_3}$), 1.7, 1.9 (m, 2 H, $\mathrm{C_5H_9}$, β-$\mathrm{CH_2}$), 2.0 (m, 2 H, $\mathrm{C_5H_9}$, α-$\mathrm{CH_2}$), 2.05, 2.24 (s, 6 H, ring $\mathrm{CH_3}$), 2.36 (m, 1 H, $\mathrm{YCH_2C\mathit{H}}$), 3.42 (br s, 4 H, α-$\mathrm{CH_2}$, THF); ^{13}C{^{1}H} NMR δ: 8.5 ($\mathrm{NSi\mathit{C}H_3}$), 11.2, 13.9 (ring $\mathrm{CH_3}$), 25.0 (β-$\mathrm{CH_2}$, THF), 25.8 ($\mathrm{C_5H_9}$, β-$\mathrm{CH_2}$), 36.1 ($\mathrm{C(\mathit{C}H_3)_3}$), 40.7 ($\mathrm{C_5H_9}$, α-$\mathrm{CH_2}$), 43.3 ($\mathrm{YCH_2\mathit{C}H}$), 47.4 (d, $^{1}J_{\mathrm{YC}} = 54.7$ Hz, $\mathrm{YCH_2}$), 53.8 ($\mathrm{\mathit{C}(CH_3)_3}$), 70.1 ($\alpha$-$\mathrm{CH_2}$, THF), 106.3 (ring C attached to $SiMe_2$), 121.8, 126.2 (ring C). ^{29}Si{^{1}H} NMR δ: −25.2.

Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$){CH(CH_3)Ph}(THF) (8a). To a solution of **5a** (84 mg, 102 μmol) in benzene (1.0 mL) was added styrene (44 mg, 0.42 mmol) at room temperature. After stirring for 3 h, all volatiles were removed in vacuo. The crude product was recrystallized from pentane/benzene (10:1) at −30 °C to give 95 mg (90%) of **8a** as yellow powder. ^{1}H NMR δ: 0.68, 0.81 (s, 3 H, $SiCH_3$), 1.03 (br s, 4 H, β-CH_2, THF), 1.27 (s, 9 H, $C(CH_3)_3$), 1.90 (d, $^{3}J_{HH}$ = 6.7 Hz, 3 H, $CHC\mathit{H}_3$) 1.92, 2.06 (s, 3 H, ring CH_3), 2.17 (m, 1 H, $C\mathit{H}CH_3$), 2.20, 2.41 (s, 3 H, ring CH_3), 3.13 (br s, 4 H, α-CH_2, THF), 6.23 (br t, $^{3}J_{HH}$ = 6.7 Hz, 4-C_6H_5), 6.40 (br s, 2 H, 2-C_6H_5), 6.92 ("t", $^{3}J_{HH}$ = 7.4 Hz, 2 H, 3-C_6H_5). ^{13}C{^{1}H} NMR δ: 8.3, 8.7 (NSi$\mathit{C}H_3$), 11.3, 12.6, 14.1, 14.3 (ring CH_3), 16.1 (CH$\mathit{C}H_3$), 25.0 (β-CH_2, THF), 35.3 (C($\mathit{C}H_3)_3$), 52.9 (d, $^{1}J_{YC}$ = 21.6 Hz, YCH), 54.8 ($\mathit{C}(CH_3)_3$), 71.9 (α-CH_2, THF), 107.2 (ring C attached to $SiMe_2$), 115.0, 117.0 (C_6H_5), 120.6, 123.3, 124.6, 127.2 (ring C), 132.2 (C_6H_5), 155.0 (1-C_6H_5). ^{29}Si{^{1}H} NMR δ: −24.9 (d, $^{2}J_{YSi}$ = 2 Hz, $NSiMe_2$). ^{1}H NMR (toluene-d_8, −80 °C) δ: 0.79 (s, 3 H, $SiCH_3$), 0.80 (br s, 4 H, β-CH_2, THF), 0.94 (s, 3 H, $SiCH_3$), 1.30 (s, 9 H, $C(CH_3)_3$), 1.93 (s, 3 H, ring CH_3), 2.06 (br s, 6 H, ring CH_3, $CHC\mathit{H}_3$) 2.22 (s, 3 H, ring CH_3), 2.31 (m, 1 H, $C\mathit{H}CH_3$), 2.52 (s, 3 H, ring CH_3), 2.88, 3.05 (m, 2 H, α-CH_2, THF), 5.86 (d, $^{3}J_{HH}$ = 7.4 Hz, 1 H, 2-C_6H_5), 6.21 (t, $^{3}J_{HH}$ = 7.0 Hz, 1 H, 4-C_6H_5), 6.70 ("t", 1 H, 3-C_6H_5), 6.76 (d, $^{3}J_{HH}$ = 8.2 Hz, 1 H, 2′−C_6H_5), 7.04 ("t", 1 H, 3′−C_6H_5). ^{13}C{^{1}H} NMR (toluene-d_8, −80 °C) δ: 8.4, 8.8 (NSi$\mathit{C}H_3$), 11.5, 12.8, 14.1, 14.6 (ring CH_3), 16.3 (CH$\mathit{C}H_3$), 24.9 (β-CH_2, THF), 34.9 (C($\mathit{C}H_3)_3$), 52.4 (d, $^{1}J_{YC}$ = 20.3 Hz, YCH), 54.9 ($\mathit{C}(CH_3)_3$), 72.2 (α-CH_2, THF), 106.2 (ring C attached to $SiMe_2$), 112.6, 114.6, 119.2 (C_6H_5), 120.0, 122.8, 124.5, 126.7 (ring C), 132.4, 133.2 (C_6H_5), 154.4 (1-C_6H_5). Anal. Calcd for $C_{27}H_{44}NOSiY$: C, 62.89; H, 8.60; N, 2.72. Found: C, 60.25; H, 8.56; N, 3.22.

Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$){CH(CH_2D)Ph}(THF) (8a-*d*$_1$). A 5 mm NMR tube was charged with **5a-*d*$_2$** (21 mg, 25 μmol), C_6D_6 (0.45 mL) and styrene (7 μL, 58 μmol) was added. The solution was kept at 5 °C for 15 h. ^{1}H NMR δ: 0.68, 0.81 (s, 3 H, $SiCH_3$), 1.03 (br s, 4 H, β-CH_2, THF), 1.27 (s, 9 H, $C(CH_3)_3$), 1.90 (br m, 2 H, $CHC\mathit{H}_2D$) 1.92, 2.06 (s, 3 H, ring CH_3), 2.17 (br m, 1 H, $C\mathit{H}CH_2D$), 2.20, 2.42 (s, 3 H, ring CH_3), 3.14 (br s, 4 H, α-CH_2, THF), 6.23 (br t, $^{3}J_{HH}$ = 6.7 Hz, 4-C_6H_5), 6.40 (br s, 2 H, 2-C_6H_5), 6.92 ("t", $^{3}J_{HH}$ = 7.4 Hz, 2 H, 3-C_6H_5). ^{13}C{^{1}H} NMR δ: 8.3, 8.7 (NSi$\mathit{C}H_3$), 11.3, 12.6, 14.1, 14.3 (ring CH_3), 15.8 (t, $^{1}J_{CD}$ = 18.9 Hz, CH$\mathit{C}H_2D$), 25.1 (β-CH_2, THF), 35.3 (C($\mathit{C}H_3)_3$), 52.8 (d, $^{1}J_{YC}$ = 20.9 Hz, YCH), 54.8 ($\mathit{C}(CH_3)_3$), 71.9 (α-CH_2, THF), 107.2 (ring C attached to $SiMe_2$), 115.0, 117.0 (C_6H_5), 120.6, 123.3, 124.6, 127.2 (ring C), 132.2 (C_6H_5), 155.0 (1-C_6H_5). ^{2}H NMR (C_6H_6) δ: 1.87 (br m, $CHCH_2D$).

Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$){CH(CH_3)(C_6H_4-4-OMe)}(THF) (8b). A 5 mm NMR tube was charged with **5a** (25 mg, 30 μmol) and C_6D_6 (0.40 mL). A solution of 4-methoxystyrene (85 μL, 1 M in C_6D_6) was added at room temperature. The solvent was removed after 2 h in vacuo to give **8b** as an orange powder in quantitative yield. ^{1}H NMR δ: 0.69, 0.83 (s, 3 H, $SiCH_3$), 1.02 (br s, 4 H, β-CH_2, THF), 1.30 (s, 9 H, $C(CH_3)_3$), 1.92 (s, 3 H, ring CH_3), 1.93 (m, 3 H, $CHC\mathit{H}_3$) 1.99 (br m, 1 H, $C\mathit{H}CH_3$), 2.07, 2.24, 2.44 (s, 3 H, ring CH_3), 3.10 (br s, 4 H, α-CH_2, THF), 3.32 (s, 3 H, OCH_3), 6.43, 6.63 (br d, $^{3}J_{HH}$ = 7.4 Hz, 2 H, C_6H_4). ^{13}C{^{1}H} NMR δ: 8.3, 8.8 (NSi$\mathit{C}H_3$), 11.3, 12.7, 14.1, 14.4 (ring CH_3), 17.1 (CH$\mathit{C}H_3$), 24.8 (β-CH_2, THF), 35.4 (C($\mathit{C}H_3)_3$), 49.7 (d, $^{1}J_{YC}$ = 25.7 Hz, YCH), 54.7 ($\mathit{C}(CH_3)_3$), 55.5 (OCH_3), 71.9 (α-CH_2, THF), 107.0 (ring C attached to $SiMe_2$), 118.2, 119.0 (2-,3-C_6H_4), 120.2, 123.1, 124.3, 127.1 (ring C), 148.7, 151.9 (1-, 4-C_6H_4). ^{29}Si{^{1}H} NMR δ: −25.1 (d, $^{2}J_{YSi}$ = 1.5 Hz, $NSiMe_2$).

Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$){CH(CH_3)(C_6H_3-2,4-Me_2)}(THF) (8d). A 5 mm NMR tube was charged with **5a** (23 mg, 28 μmol), C_6D_6 (0.45 mL), and 2,4-dimethylstyrene (9 μL, 61 μmol) was added. The solvent was removed after 13 h in vacuo to give **8d** as a yellow oil in quantitative yield. Major isomer: ^{1}H NMR (toluene-d_8, −20 °C) δ: 0.69, 0.82 (s, 3 H, $SiCH_3$), 0.94 (m, 4 H, β-CH_2, THF), 1.39 (s, 9 H, $C(CH_3)_3$), 1.61 (d, $^{3}J_{HH}$ = 6.7 Hz, 3 H, $CHC\mathit{H}_3$), 1.81, 1.85, 1.96, 2.10, 2.27, 2.35 (s, 3 H, ring CH_3 and $C_6H_3(C\mathit{H}_3)_2$), 2.1 (m, 1 H, $C\mathit{H}CH_3$), 2.92, 2.98 (m, 2 H, α-CH_2, THF), 6.49 (s, 1 H, 3-$C_6\mathit{H}_3(CH_3)_2$), 6.57, 6.82 (d, $^{3}J_{HH}$ = 7.8 Hz, 1 H, 5-, 6-$C_6\mathit{H}_3(CH_3)_2$). ^{13}C{^{1}H} NMR (toluene-d_8, −20 °C) δ: 8.5, 9.5 (NSi$\mathit{C}H_3$), 11.5, 12.5, 13.9, 14.4 (ring CH_3), 15.6 (CH$\mathit{C}H_3$), 20.8, 21.2 ($C_6H_3(\mathit{C}H_3)_2$), 25.1 (β-CH_2, THF), 36.6 (C($\mathit{C}H_3)_3$), 48.4 (d, $^{1}J_{YC}$ = 23.6 Hz, YCH), 54.0 ($\mathit{C}(CH_3)_3$), 71.9 (α-CH_2, THF), 107.3 (ring C attached to $SiMe_2$), 116.0 ($C_6H_3(CH_3)_2$, aryl-H), 120.4, 123.2, 124.6, 124.7, 127.5 (ring C and $\mathit{C}_6H_3(CH_3)_2$ attached to CH_3), 129.1 ($\mathit{C}_6H_3(CH_3)_2$, aryl-H), 130.3 ($\mathit{C}_6H_3(CH_3)_2$ attached to CH_3), 131.6 ($\mathit{C}_6H_3(CH_3)_2$, aryl−H), 148.4 (1-$\mathit{C}_6H_3(CH_3)_2$). ^{29}Si{^{1}H} NMR (toluene-d_8, −20 °C) δ: −24.9. Minor isomer: ^{1}H NMR (toluene-d_8, −20 °C) δ: 0.67, 0.83 (s, 3 H, $SiCH_3$), 1.03 (m, 4 H, β-CH_2, THF), 1.12 (s, 9 H, $C(CH_3)_3$), 1.25 (d, $^{3}J_{HH}$ = 7.0 Hz, 3 H, $CHC\mathit{H}_3$), 1.94, 2.13, 2.19, 2.25, 2.39 (s, 3 H, ring CH_3 and $C_6H_3(C\mathit{H}_3)_2$), 2.1 ($C\mathit{H}CH_3$, obscured by other signals), 3.11, 3.19 (m, 2 H, α-CH_2, THF), 6.11 (d, $^{3}J_{HH}$ = 7.4 Hz, 1 H, 6-$C_6\mathit{H}_3(CH_3)_2$), 6.72 (s, 1 H, 3-$C_6\mathit{H}_3(CH_3)_2$), 6.94 (d, $^{3}J_{HH}$ = 7.4 Hz, 1 H, 5-$C_6\mathit{H}_3(CH_3)_2$). ^{13}C{^{1}H} NMR (toluene-d_8, −20 °C) δ: 8.3 (NSi$\mathit{C}H_3$), 11.4, 12.3, (ring CH_3), 14.6 (2 C, ring CH_3), 16.1 (CH$\mathit{C}H_3$), 21.0, 21.7 ($C_6H_3(\mathit{C}H_3)_2$), 24.9 (β-CH_2, THF), 35.8 (C($\mathit{C}H_3)_3$), 46.6 (d, $^{1}J_{YC}$ = 23.0 Hz, YCH), 53.8 ($\mathit{C}(CH_3)_3$), 72.4 (α-CH_2, THF), 113.5 ($C_6H_3(CH_3)_2$, aryl−H), 120.9, 123.3, 124.1, 126.4 (ring C and $\mathit{C}_6H_3(CH_3)_2$ attached to CH_3), 128.3 ($\mathit{C}_6H_3(CH_3)_2$, aryl−H), 130.3 ($\mathit{C}_6H_3(CH_3)_2$ attached to CH_3), 132.2 ($\mathit{C}_6H_3(CH_3)_2$, aryl−H), 148.8 (1-$\mathit{C}_6H_3(CH_3)_2$). ^{29}Si{^{1}H} NMR (toluene-d_8, −20 °C) δ: −25.2.

Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$){CH(CH_3)C_6H_5}(THF) (9a). A 5 mm NMR tube was charged with **5b** (31 mg, 36 μmol), C_6D_6 (0.5 mL), and styrene (10 μL, 77 μmol). After 12 h the solvent was removed in vacuo, to give **9a** as a yellow powder in 68% yield. ^{1}H NMR δ: 0.68, 0.81 (s, 3 H, $SiCH_3$), 0.95 (t, $^{3}J_{HH}$ = 7.4 Hz, 3 H, $CH_2C\mathit{H}_3$), 1.02 (m, 4 H, β-CH_2, THF), 1.18 (s, 6 H, $C(CH_3)_2$), 1.50 (m, $^{2}J_{HH}$ = 12.5 Hz, $^{3}J_{HH}$ = 7.4 Hz, 2 H, $CC\mathit{H}_2CH_3$), 1.89 (d, $^{3}J_{HH}$ = 6.3 Hz, 3 H, $CHC\mathit{H}_3$), 1.92, 2.09, 2.20, 2.43 (s, 3 H, ring CH_3), 3.12 (br s, 4 H, α-CH_2, THF), 6.25 ("t", 1 H, 4-C_6H_5), 6.42 (br s, 2 H, 2-C_6H_5), 6.93 ("t", 2 H, 3-C_6H_5). ^{13}C{^{1}H} NMR δ: 8.0, 8.3 ($NSiCH_3$), 10.2 ($NC(CH_3)_2CH_2\mathit{C}H_3$), 10.9, 12.3, 13.7, 13.9 (ring CH_3), 15.9 (CH$\mathit{C}H_3$), 24.7 (β-CH_2, THF), 30.7, 31.0 (C($\mathit{C}H_3)_2$), 40.0 ($C\mathit{C}H_2CH_3$), 52.3 (d, $^{1}J_{YC}$ = 22.3 Hz, YCH), 56.0 ($\mathit{C}(CH_3)_2$), 71.4 (α-CH_2, THF), 106.8 (ring C attached to $SiMe_2$), 116.8, 118.8 (C_6H_5), 124.1, 125.3, 125.8, 126.8 (ring C), 131.6 (C_6H_5), 154.6 (1-C_6H_5). ^{29}Si{^{1}H} NMR δ: −25.6.

Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$){CH(CH_3)C_6H_4-4-*t*Bu}(THF) (9c). To a solution of **5b** (50 mg, 59 μmol) in benzene (6.0 mL) was added *p*-*tert*-butylstyrene (13 mg, 125 μmol) at room temperature. After stirring for 3 h, the solution was concentrated in vacuo to a volume of 0.75 mL and the solution layered with 5 mL of hexane. After standing for 5 days at 5 °C, yellow crystals were collected by decantation of the mother liquor: yield 35 mg (51%). ^{1}H NMR (toluene-d_8, −60 °C) δ: 0.74, 0.88 (s, 3 H, $SiCH_3$), 0.78 (m, 4 H, β-CH_2, THF), 0.98 (t, $^{3}J_{HH}$ = 7.0 Hz, 3 H, $CH_2C\mathit{H}_3$), 1.18 (s, 9 H, $C(CH_3)_3$), 1.26 (s, 6 H, $C(CH_3)_2$), 1.40, 1.49 ("d", $^{2}J_{HH}$ = 7.0 Hz, 1 H, $CC\mathit{H}_2CH_3$), 1.95, 2.07, 2.33, 2.54 (s, 3 H, ring CH_3), 2.01 (d, $^{3}J_{HH}$ = 6.4 Hz, 3 H, $CHC\mathit{H}_3$), 2.12 (m, 1 H, $C\mathit{H}CH_3$), 2.77, 2.88 (d, 2 H, α-CH_2, THF), 6.03 (d, $^{3}J_{HH}$ = 6.6 Hz, 1 H, 2-C_6H_4), 6.76 (d, $^{3}J_{HH}$ = 7.8 Hz, 1 H, 3-C_6H_4), 6.85 (d, $^{3}J_{HH}$ = 6.6 Hz, 1 H, 2-C_6H_4), 6.98 (d, $^{3}J_{HH}$ = 7.8 Hz, 1 H, 3-C_6H_4). ^{1}H NMR (toluene-d_8) δ: 0.64, 0.76 (s, 3 H, $SiCH_3$), 0.96 (t, $^{3}J_{HH}$ = 7.4 Hz, 3 H, $CH_2C\mathit{H}_3$), 1.09 (m, 4 H, β-CH_2, THF), 1.15 (s, 9 H, $C(CH_3)_3$), 1.17 (s, 6 H, $C(CH_3)_2$), 1.51 (m, 2 H, $CC\mathit{H}_2CH_3$), 1.84 (d, $^{3}J_{HH}$ = 6.2 Hz, 3 H, $CHC\mathit{H}_3$), 1.97, 2.09, 2.25, 2.39 (s, 3 H, ring CH_3), 2.11 (m, 1 H, $C\mathit{H}CH_3$), 3.02, 3.11 (br s, 2 H, α-CH_2, THF), 6.43 (d, $^{3}J_{HH}$ = 6.7 Hz, 2 H, 2-C_6H_4), 6.98 (d, 2 H, 3-C_6H_4). ^{13}C{^{1}H} NMR (toluene-d_8) δ: 8.3, 8.8 ($NSiCH_3$), 10.2 ($NC(CH_3)_2CH_2\mathit{C}H_3$), 11.2, 12.2, 13.5, 13.7 (ring CH_3), 16.3 (CH$\mathit{C}H_3$), 25.4 (β-CH_2, THF), 30.6, 30.9

(C(*C*H$_3$)$_2$), 31.3 (C(*C*H$_3$)$_3$), 32.5 (*C*(CH$_3$)$_3$), 40.9 (C*C*H$_2$CH$_3$), 50.4 (d, $^1J_{YC}$ = 23.0 Hz, YCH), 57.1 (*C*(CH$_3$)$_2$), 71.4 (α-CH$_2$, THF), 106.6 (ring C attached to SiMe$_2$), 117.7, 118.0 (C$_6$H$_4$), 120.1, 124.1, 125.1, 127.0 (ring C), 152.2 (1-C$_6$H$_4$). ^{29}Si{^{1}H} NMR (toluene-d_8) δ: −25.9 (NSiMe$_2$). ^{1}H NMR (toluene-d_8, 60 °C) δ: 0.59, 0.67 (s, 3 H, SiCH$_3$), 0.91 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, CH$_2$C*H*$_3$), 1.13 (s, 9 H, C(CH$_3$)$_3$), 1.24 (m, 4 H, β-CH$_2$, THF), 1.28 (s, 6 H, C(CH$_3$)$_2$), 1.46 (m, 2 H, CC*H*$_2$CH$_3$), 1.75 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, CHC*H*$_3$), 1.92 (m, 1 H, C*H*CH$_3$), 1.96, 2.16, 2.20, 2.28 (s, 3 H, ring CH$_3$), 3.32 (br s, 4 H, α-CH$_2$, THF), 6.41 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, 2-C$_6$H$_4$), 6.97 (d, 2 H, 3-C$_6$H$_4$). Anal. Calcd for $C_{32}H_{54}NOSiY$: C, 65.50; H, 9.28; N, 2.39. Found: C, 62.84; H, 9.46; N, 2.34.

Ethylene Polymerization. A solution of the catalyst (50 μmol) in toluene (50 mL) was loaded in a thick-walled 200 mL glass vessel. The reaction vessel was charged with ethylene (4.5 atm) at room temperature, and the reaction mixture was stirred vigorously. After 2 h the glass vessel was vented, and the reaction mixture was drained into methanol (200 mL) and acidified with concentrated hydrochloric acid. The polymer was collected by filtration, washed with methanol, and dried under vacuum to constant weight.

Styrene Polymerization. To a solution of **5a** (16 mg, 19 μmol) in benzene (0.5 mL) was added 1-hexene (18 mg, 0.21 mmol) at room temperature. The solvent was removed after 1 h in vacuo (1 h, 5×10^{-3} Torr). The solid was dissolved in benzene (1.5 mL), and styrene (ca. 0.25 mL) was added. After a given time period the solvent was removed in vacuo. The polymer was redissolved in chloroform (2 mL) and precipitated into methanol (100 mL). The polymer was collected by filtration, washed with methanol, and dried under vacuum to constant weight.

X-ray Crystal Structure Analysis of 2b and 9c. Relevant crystallographic data for **2b** and **9c** are summarized in Table 1. Single crystals suitable for X-ray crystal structure analysis were obtained by slow cooling of a concentrated pentane solution to −30 °C (**2b**) or by layering of a concentrated toluene solution with pentane at 5 °C (**9c**). Data collections were performed using ω scans on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation at 213(2) K for **2b** and at 296(2) K for **9c**. Data correction for Lorentz polarization and absorption (empirically using ψ scans) was carried out using the program system MolEN.[49a] The structures were solved by Patterson methods (SHELXS-86).[49b] From the measured reflections, all independent reflections were used, and the parameters were refined by full-matrix least-squares against all F_o^2 data (SHELXL-93)[49c] and difference Fourier syntheses and refined with anisotropic thermal parameters for all non-hydrogen atoms except for the atoms of the disordered SiMe$_3$ group in **2b**. This fragment was refined with four independent orientations (each with a multiplicity of 0.25) and isotropic thermal parameters for the carbon atoms. Hydrogen atoms were calculated at their idealized positions for **2b**. For **9c** the hydrogen atoms of the styryl fragment were located in difference Fourier syntheses and refined in their positions (with fixed isotropic thermal parameters). The remaining hydrogen atoms were included into idealized positions.

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Supporting Information Available: Tables of all crystal data and refinement parameters and atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles for **2b** and **9c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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