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Yttrium Hydrido Complexes that Contain a Less "Constrained Geometry" Ligand: Synthesis, Structure, and Efficient Hydrosilylation Catalysis

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σ-Bond metathesis of the new linked amino-cyclopentadiene $(C_5Me_4H)CH_2SiMe_2NHCMe_3$ with $Y(CH_2SiMe_3)_3(THF)_2$ gave the alkyl-yttrium complex $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)\text{-}(CH_2SiMe_3)(THF)]$ (**1**) in 66% yield. Compound **1** was characterized by NMR spectroscopy and X-ray crystal structure analysis. By hydrogenolysis, **1** was quantitatively converted into the dimeric hydride $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ (**2**). X-ray crystal structure analysis revealed a Y_2H_2 core connected to two $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(THF)]$ fragments in a skewed manner, with a relatively long yttrium−yttrium distance of 3.7085(8) Å. In solution, two diastereomers were observed by ^1H NMR spectroscopy at −78 °C. Dimer **2** was shown to efficiently catalyze the hydrosilylation of 1-decene with $PhSiH_3$ to give the terminal silane $^nC_{10}H_{21}SiH_2Ph$ exclusively. Although the product of addition of the yttrium-hydride complex **2** to styrene, $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)\{CH(CH_3)Ph\}(THF)]$ (**3**), contains a 1-phenethyl ligand derived from internal addition, hydrosilylation of styrene with $PhSiH_3$ catalyzed by **2** gave both terminal- and internal-hydrosilylated products in a ratio of 1:1.4.

Introduction

Organolanthanide-catalyzed hydrosilylations of alkenes and alkynes give organosilanes, which can be further oxidized to the corresponding alcohols.[1] By utilizing the decamethylyttrocene alkyls Cp^*_2YR ($Cp^* = \eta^5\text{-}C_5Me_5$; R = Me, $CH(SiMe_3)_2$) as precursors for the catalytically active hydride Cp^*_2YH,[2] Molander et al. have developed this method into a versatile organolanthanide-catalyzed transformation.[3] More recently, Marks et al. reported that lanthanide alkyl and amido complexes containing the linked amido-cyclopentadienyl ligand $(C_5Me_4SiMe_2NCMe_3)^{2-}$, originally designed by Bercaw et al. for scandium centers,[4] catalyze the cyclization/hydroamination of α,ω-aminoolefins[5] with higher activity than that of lanthanocenes. This observation was ascribed to the so-called "constrained geometry" structure,[4,6] which allows easier access of the substrate molecule to the trivalent lanthanide metal center. Previously Teuben et al. and we have noted that the use of the prototypical $(C_5Me_4SiMe_2NCMe_3)^{2-}$ system as ancillary ligand for group 4 metals may not be universally suitable.[7] We report here that yttrium-alkyl and -hydrido complexes containing a linked amido-cyclopentadienyl ligand with a longer two-atom backbone,[8] viz., $(C_5Me_4CH_2SiMe_2NCMe_3)^{2-}$, are easily accessible and, moreover, that their activity in the

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[1] (a) Sakakura, T.; Lautenschläger, H. J.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, 40. (b) Onozawa, S.; Sakakura, T.; Tanaka, M. *Tetrahedron Lett.* **1994**, *35*, 8177. (c) Beletskaya, I. P.; Voskoboinikov, A. Z.; Parshina, I. N.; Magomedov, G. K. I. *Izv. Akad. Nauk. SSR, Ser. Khim.* **1990**, 693. (d) For hydrosilylation of internal alkynes, see: Molander, G. A. Retsch, W. H. *Organometallics* **1995**, *14*, 4570. (e) For sequential cyclization/hydrosilylation, see: Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1995**, *117*, 4415. (f) For enantioselective hydrosilylation, see: Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157.

[2] den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053.

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[5] (a) Tian, S.; Arrendondo, V. M.; Stern, S. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2568. (b) Arrendondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633.

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[7] The activity of titanium catalysts of the type $[Ti(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}CH_2SiMe_2NCMe_3)Cl_2]$/MAO for ethylene polymerization was not found to be significantly different from that of the prototypical systems $[Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)Cl_2]$: Eberle, T. E. Doctoral Dissertation, University of Mainz, 1999. See also: (a) Okuda, J.; Eberle, T.; Spaniol, T. P.; Piquet-Fauré, V. *J. Organomet. Chem.* **1999**, *591*, 127. (b) Sinnema, P.-J.; Hessen, B.; Teuben, J. H. *J. Mol. Catal. A: Chem.* **1998**, *128*, 143.

[8] For examples of amido-cyclopentadienyl ligands with a longer link than $SiMe_2$, see: (a) Sinnema, P.-J.; van der Veen, L.; Spek, A. L.; Veldman, N. M.; Teuben, J. H. *Organometallics* **1997**, *17*, 44245. (b) Dias, H. V. R.; Wang. Z. *J. Organomet. Chem.* **1997**, *539*, 77. (c) van Leusen, D.; Beetstra, D. J.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 4084.

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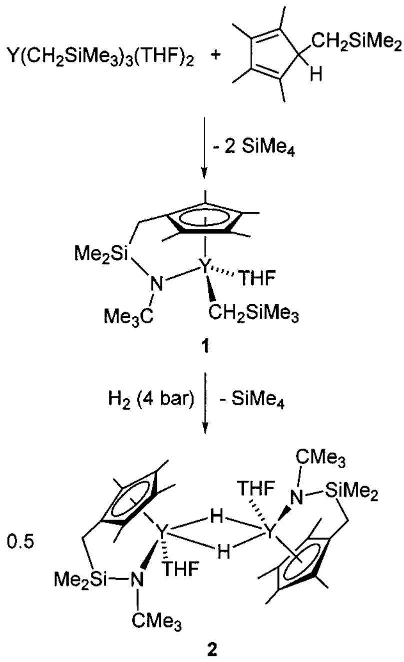
Scheme 1



hydrosilylation of α-olefins is *higher* than that of analogues containing a shorter $SiMe_2$ link.

Results and Discussion

Lanthanide alkyl complexes with a linked amido-cyclopentadienyl ligand have previously been synthesized by σ-bond metathesis of homoleptic tris(alkyl) complexes with cyclopentadienes.[5a,9,10] Following an analogous procedure for the synthesis of $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$,[9b] we prepared the new alkyl complex $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ (**1**) in 66% yield as hydrocarbon-soluble, colorless crystals by reaction of $(C_5Me_4H)CH_2SiMe_2NHCMe_3$ with $Y(CH_2SiMe_3)_3(THF)_2$[11] in hexane at 0 °C (Scheme 1). Variable-temperature ^1H and ^{13}C NMR spectroscopic data for **1** indicate a labile THF ligand over the temperature range of +80 to −80 °C,[11] which results in an apparent mirror plane within the molecule. In contrast to the analogue with the $SiMe_2$ link, $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$,[9b] no decoalescence of any of the diastereotopic signals was observed, even at −80 °C.[12] The chiral structure derived from the three-legged piano-stool configuration was confirmed by a crystal structure analysis of **1** (Figure 1). Metrical parameters of **1** are comparable with those of $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)(CH_2SiMe_3)(THF)]$.[9b] The only notable differences are in the three angles at the sp^2-hybridized nitrogen atom of the amido group Si−N−Y, Y−N−C13, and Si−N−C13. As a consequence of the longer bridge in **1**, the Si−N−Y angle of 121.74(9)° is much larger than 104.9(3)° in $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)(CH_2SiMe_3)(THF)]$. Similarly, the "bite angle" Cp_{cent}−Y−N in **1** is 106.5(7)°, compared to 97.1(2)° in $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_2Et)(CH_2SiMe_3)(THF)]$. This is in agreement with the presence of a less strained chelating ligand resulting from the longer link in **1**. At the same time, the coordination sphere appears to be more crowded.

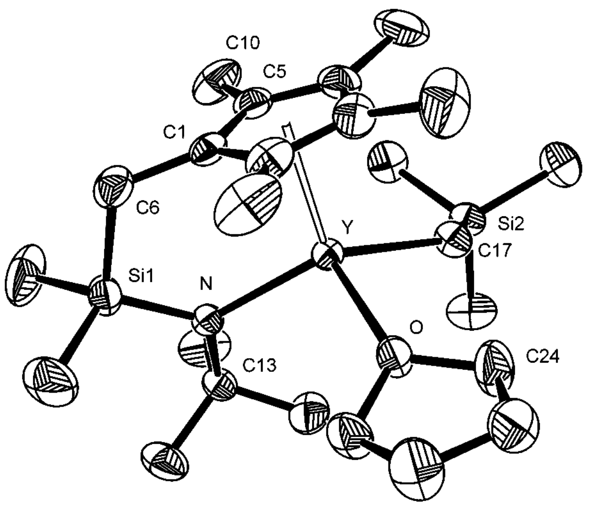


Figure 1. ORTEP diagram of the molecular structure of $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ (**1**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Y−N 2.236(2), Y−C17 2.425(2), Y−O 2.327(1), Cp_{Cent}−Y 2.332(2), Cp_{Cent}−Y−N 106.5(7), Cp_{Cent}−Y−C17 113.5(8), Cp_{Cent}−Y−O 111.5(7), N−Y−C17 126.09(7), N−Y−O 103.72(5), O−Y−C17 93.75(7), N−Si1−C6 107.0(1), Y−C17−Si2 135.4(1).

Hydrogenolysis of alkyl **1** with dihydrogen in hexane (4 bar, 25 °C) or reaction of **1** with $PhSiH_3$ results in clean formation of the colorless dimeric hydrido complex $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ (**2**), isolated as colorless microcrystals in quantitative yield. Compared with the analogous complex with a $SiMe_2$ link, $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$,[9] complex **2** is highly fluxional, showing one sharp triplet for the hydrido ligand at 5.50 ppm with J_{YH} = 26.8 Hz in the temperature range of +40 to −60 °C in the ^1H NMR spectra. Below −60 °C, the hydride signal decoalesces, and at −80 °C, three triplets in a ratio of 1:2.4:1 are observed (Figure 2). We assign the two resonances at δ 4.75 ($^1J_{YH}$ = 22.6 Hz) and δ 5.94 ($^1J_{YH}$ = 30.8 Hz) to the inequivalent hydride ligands of the C_2-symmetric homochiral dimer, whereas the third resonance at δ 5.47 ($^1J_{YH}$ = 26.6 Hz) is assigned to the centrosymmetric heterochiral diastereomer (Figure 3).[9] Crystallization of **2** by slow evaporation of the benzene solution at 25 °C resulted in single crystals of the benzene solvate $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2{\cdot}C_6H_6$. The X-ray structure analysis confirms the dimeric structure with homochiral configuration at the metal centers (Figure 3). Most remarkably, the disposition of the two ring ligands is such that the dihedral angle $Cp_{cent.}$−Y−Y′−$Cp_{cent.}$′ is 97°, in contrast to 169.9° found in

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[9] (a) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227. (b) Hultzsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228. (c) Arndt, S.; Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 4690.

[10] (a) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720. (b) Mu, Y.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J. *Can. J. Chem.* **1995**, *73*, 2233.

[11] Lappert, M. F.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1973**, 126.

[12] The apparently less labile THF in the lutetium analogue of **1**, $[Lu(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$, gives rise to the expected AB signal pattern for the methylene protons of the CH_2SiMe_3 group below $T_c = -8$ °C ($\Delta G^{\ddagger} = 53.98$ kJ mol^{-1}): Trifonov, A. A.; Spaniol, T. P.; Okuda, J. Unpublished results.

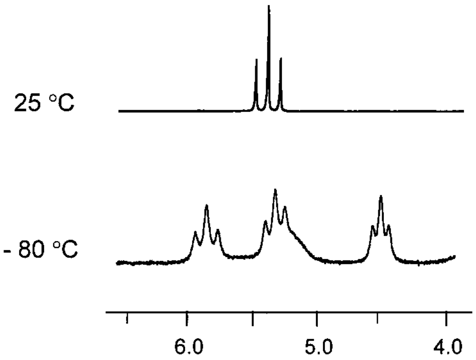

Figure 2. Hydride region in the ^{1}H NMR spectra of the hydride complex in toluene-d_8.

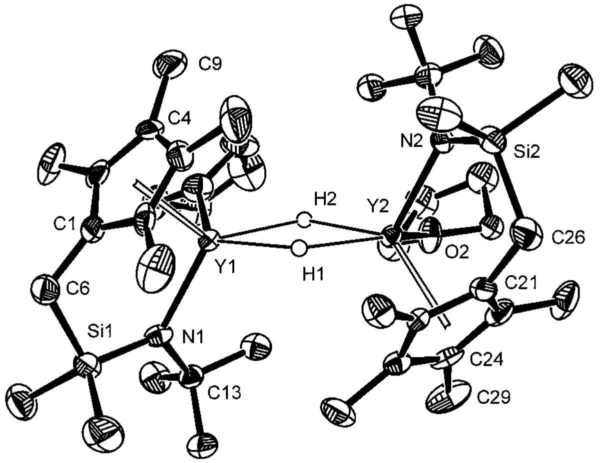

Figure 3. ORTEP diagram of the molecular structure of [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$)(THF)(μ-H)]$_2$ (**2**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for the two bridging hydrides H1 and H2, are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Y1−Y2 3.7085(8), Y1−H1 2.30(4), Y1−H2 2.07(6), Y1−N1 2.253(4), Y1−O1 2.440(4), Y1−Cp$_{Cent}$1 2.360(5), Y2−H1 2.03(4), Y2−H2 2.16(6), Y2−N2 2.268(4), Y2−O2 2.413(4), Y2−Cp$_{Cent}$2 2.371(5); Y1−H1−Y2 118(2); Y1−H2−Y2 122(2); Cp$_{Cent}$1−Y1−N1 104.9(2); Cp$_{Cent}$2−Y2−N2, 104.3(2). Cp$_{Cent}$1: centroid of C1, C2, C3, C4, C5; Cp$_{Cent}$2: centroid of C21, C22, C23, C24, C25.

[Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)(μ-H)]$_2$.[9a] With a CH_2 group added to the bridge between the amido and tetramethylcyclopentadienyl moieties, the dimerization of the two homochiral monomeric units results in a dimer structure with a configuration that is intermediate between cis and trans. This may reflect steric strain in **2**, although the Y···Y distance of 3.7085(8) Å is comparable to that of 3.672(1) Å in [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)(μ-H)]$_2$.[9a] The bite angles for the ancillary ligands are an average of 104.6(2)° as compared to 97.6(2)° in [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)(μ-H)]$_2$[9a]. We have previously noted that the relative arrangement of the monomeric units within the dimer structure of the type [Ln(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(L)(μ-X)]$_2$ (Ln = Sc, Y, Lu; L = THF, PMe_3; X = H, Cl) critically depends on the nature of the ligands L and X.[9c]

Hydrido complex **2** shows high reactivity toward a variety of unsaturated substrates. It polymerizes ethylene to give high molecular weight polyethylene (activity, 0.4 g/mmol Y h bar; $M_n \approx 10^4$), whereas 1-hexene is slowly oligomerized to a mixture of dimers and trimers. In contrast to the hydride with the more "constrained" ligand, [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_3$)(THF)(μ-H)]$_2$, where products of 1-alkene mono(insertion) can be isolated and fully characterized, rapid polymerization by **2** precludes observation of any alkyls of the type [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$)(CH_2CH_2R)(THF)] or [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$)(μ-CH_2CH_2R)]$_2$.[9b,13]

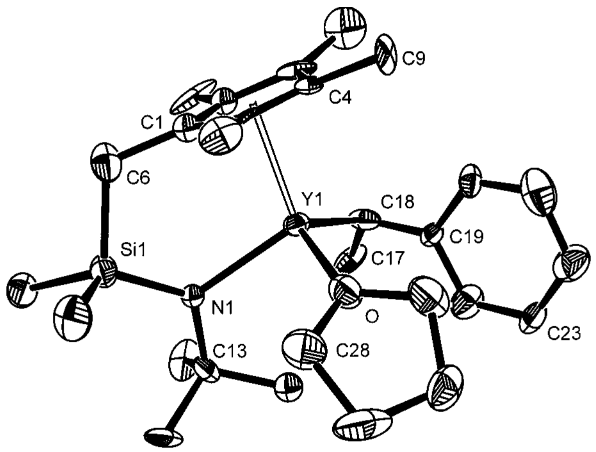

Figure 4. ORTEP diagram of the molecular structure of [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$){CH(CH_3)Ph}(THF)] (**3**). Only one of two independent molecules is shown. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for the two bridging hydrides, are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Y1−C18 2.52(1), Y1−N1 2.237(8), Y1−O1 2.350(8), Y1−C19 2.90(1), Y1−C20 3.28(1), Y1−Cp$_{Cent}$ 2.35(1), N1−Y1−C18 112.3(4), N1−Y1−O1 94.3(3), O1−Y1−C18 122.3(4), Cp$_{Cent}$−Y1−C18 111.1(4), Cp$_{Cent}$−Y1−N1 104.6(3), Cp$_{Cent}$−Y1−O1 110.0(3). Cp$_{Cent}$: centroid of C1, C2, C3, C4, C5.

Styrene forms a monomeric mono(insertion) product upon reaction with **2** and is isolated as its yellow THF adduct [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$){CH(CH_3)Ph}(THF)] (**3**). Variable-temperature ^{1}H and ^{13}C NMR spectroscopic data as well as a single-crystal X-ray structure analysis (Figure 4) showed that terminal addition of the Y−H bond to styrene had taken place. As was observed with systems with the shorter $SiMe_2$ bridge,[9b] no evidence for formation of the internal addition product, [Y(η^5:η^1-$C_5Me_4CH_2SiMe_2NCMe_3$)(CH_2CH_2Ph)(THF)], was found. A comparison of the X-ray structural analysis data of **3** with those of [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$){CH(CH_3)C_6H_4-4-CMe_3}(THF)][9b] shows that the metal−ligand bond distances are similar within the standard error: Y−C18 2.52(1), Y−N 2.237(8), Y−O 2.350(8), and Y−Cp$_{cent}$ 2.35(1) Å for one of the two independent molecules of **3**; Y−C18 2.494(7), Y−N 2.223(4), Y−O 2.374(4), and Y−Cp$_{cent}$ 2.347(6) Å for [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$){CH(CH_3)C_6H_4-4-CMe_3}(THF)].[9b] However, the η^3-coordination of the phenyl ring is no longer present in **3**, as indicated by the large values for the Y−C19 and Y−C20 distances of 2.90(1) and 3.28(1) Å, respectively (2.806(6) and 3.078 Å in [Y(η^5:η^1-$C_5Me_4SiMe_2NCMe_2Et$){CH(CH_3)C_6H_4-4-CMe_3}(THF)]). No further reaction of **2** with excess styrene at ambient temperature was observed.

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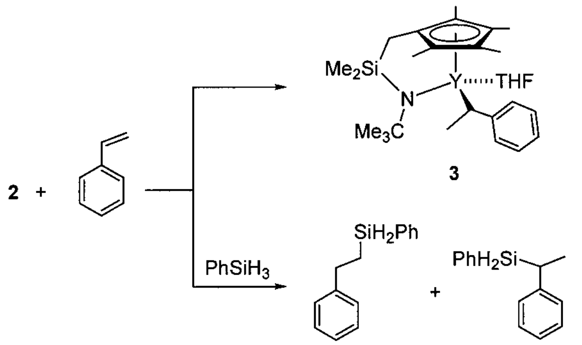
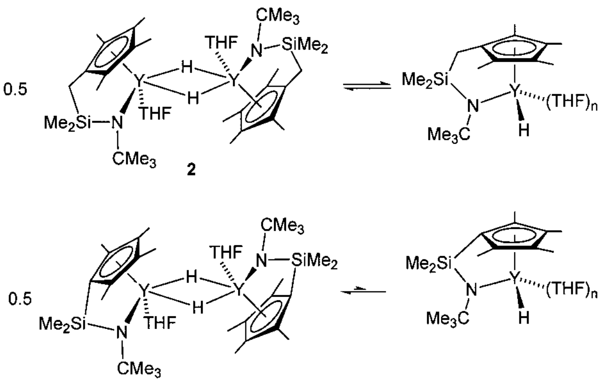
(13) Arndt, S.; Voth, P.; Spaniol, T. P.; Okuda, J. Unpublished results.

Scheme 2



Scheme 3



The yttrium hydride **2**, conveniently prepared in-situ from the alkyl **1**, catalyzes the hydrosilylation of olefins under standard conditions ($PhSiH_3$, 25 °C).[3,14] Thus, 1-decene is quantitatively converted to the anti-Markovnikov product $^nC_{10}H_{21}SiH_2Ph$ within 1 h. In contrast, $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ gives only 80% yield of a 96:4 mixture of both $^nC_{10}H_{21}SiH_2Ph$ and $^nC_8H_{17}CH(CH_3)SiH_2Ph$ after more than 7 h. We postulate a 14-electron species $[Y(\eta^5:\eta^1\text{-}C_5Me_4ZNCMe_3)H(THF)]$ (Z: CH_2SiMe_2 or $SiMe_2$) with a labile THF ligand as the active species in the hydrosilylation catalyzed by the hydrido complexes. The superior hydrosilylation activity of **2** compared to that of $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ is tentatively ascribed to the shift of the dimer-to-monomer dissociation equilibrium to the monomer side (Scheme 3). This may be caused by the increased steric demand of the $(C_5Me_4CH_2SiMe_2NCMe_3)^{2-}$ ligand with a CH_2SiMe_2 link, as became evident in the molecular structure of hydride **2**. At the same time, the increased lability of the coordinated THF will influence the rate of the 1-alkene addition and insertion step.

With styrene, **2** gives a 1:1.4 mixture of the two regioisomers $PhCH_2CH_2SiH_2Ph$ and $PhCH(CH_3)SiH_2Ph$ in a somewhat slower reaction (94% yield after 8 h), whereas the hydride with a $SiMe_2$ link affords a 1:7.3 mixture of the two regioisomers (85% yield after 8 h). The latter observations seem to contradict our failure to observe terminal addition products of styrene with **2**. However, the regioisomer of **3**, $[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(CH_2CH_2Ph)(THF)]$, is presumably present in only (undetectably) low concentrations and reacts considerably faster with $PhSiH_3$ to give $PhCH_2CH_2SiH_2Ph$ and **2** (or the monomeric hydride in the catalytic cycle). The terminal addition products of styrene for related systems are reported to display higher reactivity: The reaction of styrene with the scandium-hydride complex $[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(PMe_3)(\mu\text{-}H)]_2$ gives the bis(insertion) product $[Sc(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{CH(Ph)CH_2CH_2CH_2Ph\}(PMe_3)]$, as a result of terminal addition followed by an internal addition.[4c] Similarly, styrene dimerization by bis(indenyl)yttrium complexes[14] preferentially gives the tail-to-tail coupled product *trans*-1,4-diphenylbut-1-ene. The higher amount of the terminal hydrosilylation product $PhCH_2CH_2SiH_2Ph$ when **2** is used, compared to when $[Y(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ is used, may be due to the steric strain within the coordination sphere of the ligand with the longer link.[15] The higher proportion of the internal regioisomer from lanthanocene-catalyzed styrene hydrosilylation was reported for larger metals and more open *ansa*-type ligand systems.[1f]

In conclusion, we have demonstrated that the linked amido-cyclopentadienyl ligand with the longer backbone can easily be coordinated at the yttrium center. It generates an apparently sterically more crowded ligand sphere, affecting the structure and dynamic of the hydride dimer and, more significantly, results in higher hydrosilylation activity. Thus, the amido-cyclopentadienyl ligand with a shorter link, $(C_5Me_4SiMe_2NCMe_3)^{2-}$, cannot be regarded as the optimal coordination environment for yttrium. Further experiments aimed at elucidation of the mechanism and exploration of the scope of the catalytic activity of the yttrium-hydrido complex **2** are underway.

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon and by 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 or Strem) was used as received. All other commercially available chemicals were used after appropriate purification. 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 according to 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. Gas chromatographic analyses were performed on a Fisons GC 8000 Top instrument using a capillary column (30 m × 0.32 mm). Elemental analyses were performed by the Microanalytical Laboratory of this department.

5-(Chlorodimethylsilylmethyl)-1,2,3,4-tetramethylcyclopentadiene. Solid $Li(C_5Me_4H)$ (10.08 g, 79 mmol) was slowly added to a solution of $ClSiMe_2CH_2Cl$ (11.26 g, 79 mmol) in 250 mL of THF at room temperature, and the reaction mixture was stirred for 14 h. THF was evaporated in vacuo, and the resulting residue was extracted with 200 mL of hexane. The extract was filtered and concentrated by rotary evaporation. Purification of the pale yellow oil by Kugelrohr distillation gave 17.08 g (95%) of $(C_5Me_4H)CH_2SiMe_2Cl$. ^1H

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[14] Kretschmer, W. P.; Troyanov, S. I.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 284.

[15] It is well-known for styrene hydroboration that the regioselectivity can be influenced by the steric bulk of the boron substituent to give predominantly the terminal addition product: Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765.

NMR ($CDCl_3$, 25 °C): δ 0.12 (s, 6 H, $SiCH_3$), 1.82 (s, 6 H, ring CH_3), 1.94 (s, 6 H, ring CH_3), 2.71 (s, 2 H, CH_2), 2.94 (s, 1 H, C_5Me_4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ −5.0 ($SiCH_3$), 11.2, 14.3 (ring CH_3), 30.2 (CH_2), 53.1 (ring C attached to CH_2), 132.2, 136.4 (ring C). EI MS *m*/*z* (%): 228 (34%, M^+), 193 (7%, $M^+ - Cl$), 178 (43%, $M^+ - Cl, - Me$), 121 (27%, C_5Me_4H). Anal. Calcd for $C_{12}H_{21}ClSi$: C, 62.98; H, 9.25. Found: C, 62.76; H, 9.37.

5-(*tert*-Butylaminodimethylsilylmethyl)-1,2,3,4-tetramethylcyclopentadiene. A suspension of $Li(NHCMe_3)$ (2.93 g, 3.71 mmol) in 150 mL of hexane was treated with 5-(chlorodimethylsilylmethyl)-1,2,3,4-tetramethylcyclopentadiene (8.48 g, 3.71 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 14 h. After filtration, volatiles were evaporated in vacuo and the residue was distilled. The fraction boiling at 60−65 °C and 8×10^{-3} mbar was collected to give 5.90 g (60%) of $(C_5Me_4H)CH_2SiMe_2NHCMe_3$ as a mixture of isomers. ^1H NMR ($CDCl_3$, 25 °C): δ 0.24, 0.26, 0.27 (s, 6 H, $SiCH_3$), 0.61, 0.68, 1.03 (s, 1 H, NH), 1.11, 1.13, 1.16, 1.17, 1.18 (br, 2 H, CH_2), 1.23 (s, 9 H, $C(CH_3)_3$), 1.80, 1.83, 1.88, 1.91, 1.92, 1.95, 2.05, 2.09 (s, 12 H, ring CH_3), 2.56, 2.68, 2.81 (1 H, C_5Me_4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 1.8, 1.9, 2.3 ($SiCH_3$), 11.4, 11.9, 12.0, 12.8, 14.9, 18.2, 19.4 (ring CH_3, CH_2), 33.9 ($C(CH_3)_3$), 49.4, 51.3, 51.7, 83.0 ($C(CH_3)_3$), ring C attached to CH_2), 132.0, 134.3, 134.6, 136.5, 136.6, 138.2, 140.2 (C_5Me_4). EI MS *m*/*z* (%): 265 (100%, M^+), 192 (12%, $C_5Me_4CH_2SiMe_2{}^+$), 177 (6%, $C_5Me_4CH_2SiMe^+$), 129 (100%, $CH_2SiMeNHCMe_3{}^+$), 121 (15%, $C_5Me_4H^+$). Anal. Calcd for $C_{16}H_{31}NSi$: C, 72.38; H, 11.77; N, 5.27. Found: C, 71.94; H, 11.39; N, 5.12.

$[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$ (1). A suspension of $YCl_3(THF)_{3.5}$ (1.352 g, 3.02 mmol) in hexane (20 mL) was treated with a solution of $LiCH_2SiMe_3$ (0.866 g, 9.20 mmol) in 20 mL of hexane at −78 °C and stirred at 0 °C for 2 h. After filtration, the resulting white solid was extracted with hexane (2 × 10 mL). A solution of $(C_5Me_4H)CH_2SiMe_2NHCMe_3$ (0.758 g, 2.86 mmol) in 5 mL of hexane was added at 0 °C to the extracts, and the reaction mixture was stirred for 2 h. The solution was decanted and concentrated in vacuo. Recrystallization of the crude product from hexane at −30 °C gave colorless microcrystals of **1**, yield: 1.01 g (66%). ^1H NMR: δ −0.94 (br s, 2 H, YCH_2), 0.27 (s, 9 H, CH_2SiCH_3), 0.42 (s, 6 H, $SiCH_3$), 1.17 (br s, 4 H, β-CH_2, THF), 1.37 (s, 9 H, $C(CH_3)_3$), 2.03, 2.04 (br s, 2 × 6 H, ring CH_3), 2.13 (s, 2 H, CH_2SiN), 3.40 (br s, 4 H, α-CH_2, THF). $^{13}C\{^1H\}$ NMR: δ 4.4 (CH_2SiCH_3), 7.8 ($NSiCH_3$), 10.8, 11.0 (ring CH_3), 17.3 (CH_2SiN), 24.1 (β-CH_2, THF), 26.8 (d, $^1J_{YC} = 42.6$ Hz, YCH_2), 34.7 ($C(CH_3)_3$), 53.3 ($C(CH_3)_3$), 70.1 (α-CH_2, THF), 114.5, 115.4, (ring C), 136.9 (ring C attached to CH_2). ^{89}Y NMR: δ 450.1. Anal. Calcd for $C_{24}H_{48}NOSi_2Y$: C, 56.37; H, 9.38; N, 2.73. Found: C, 55.88; H, 9.63; N, 2.85.

X-ray Crystal Structure Analysis of 1. Single crystals suitable for X-ray crystal structure analysis were obtained by cooling of concentrated hexane solutions to −30 °C. Crystal data: $C_{24}H_{48}NOSi_2Y$, $M_r = 511.73$, monoclinic, 0.35 × 0.16 × 0.01 mm, $P2_1/n$ (No. 14), $a = 8.4212(5)$ Å, $b = 20.729(1)$ Å, $c = 16.759(1)$ Å, $\beta = 102.371(1)°$, $V = 2857.6(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.189$ Mg/m^3, Mo Kα ($\lambda = 0.71073$ Å), Bruker AXS diffractometer, semiempirical absorption correction, $T = 293$ K, ω scans, 3 ° < θ < 28 °, $F(000) = 1096$, μ(Mo Kα) = 2.14 mm^{-1}, number of reflections measured 25 723, 7060 independent reflections. The structure was solved by direct methods (SHELXS-86)[17a] and refined (SHELXS-97)[17b] against all F^2 data, resulting in $R_1 = 0.0321$ and $wR_2 = 0.0617$ for all observed reflections with $I > 2\sigma(I)$, GOF = 0.888.

$[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ (2). A solution of **1** (0.95 g, 1.85 mmol) in hexane (25 mL) was loaded in a thick-walled 200 mL glass vessel. Dihydrogen (4 bar) was charged at room temperature, the vessel was sealed, and the reaction mixture was stirred vigorously. After stirring for 12 h, the solution was concentrated in vacuo and cooled to −70 °C to give 0.76 g (97%) of **2** as colorless microcrystals. ^1H NMR (toluene-d_8, 25 °C): δ 0.48 (s, 6 H, $SiCH_3$), 1.40 (br s, 4 H, β-CH_2, THF), 1.44 (s, 9 H, $C(CH_3)_3$), 2.09 (s, 6 H, ring CH_3), 2.14 (s, 2 H, CH_2), 2.17 (s, 6 H, ring CH_3), 3.87 (br s, 4 H, α-CH_2, THF), 5.50 (t, 1 H, $^1J_{YH} = 26.8$ Hz, Y_2H_2). $^{13}C\{^1H\}$ NMR (toluene-d_8, 25 °C): δ 8.4 ($SiCH_3$), 12.2, 12.7, (ring CH_3), 17.6 (CH_2), 24.4 (β-CH_2, THF), 36.2 ($C(CH_3)_3$), 54.9 ($C(CH_3)_3$), 71.3 (α-CH_2, THF), 113.9, 114.7 (ring C), 136.9 (ring C attached to CH_2). ^{89}Y NMR (toluene-d_8, 25 °C): δ 310.6 (t, $^1J_{YH} = 26.7$ Hz). Anal. Calcd for $C_{40}H_{76}N_2O_2Si_2Y_2$: C, 56.45; H, 9.00; N, 3.29. Found: C, 56.17; H, 8.65; N, 3.20.

X-ray Crystal Structure Analysis of 2. Single crystals of the benzene solvate suitable for X-ray crystal structure analysis were obtained by slow concentration of benzene solutions at room temperature. Crystal data: $C_{46}H_{82}N_2O_2Si_2Y_2$, $M_r = 929.14$, 0.19 × 0.17 × 0.06 mm, monoclinic, $C2/c$ (No. 15), $a = 19.919(2)$ Å, $b = 11.6534(9)$ Å, $c = 43.245(3)$ Å, $\beta = 97.414(1)°$, $V = 9954(1)$ Å^3, $Z = 8$, $\rho_{calc} = 1.240$ Mg/m^3, Mo Kα radiation ($\lambda = 0.71073$ Å), Bruker AXS diffractometer, semiempirical absorption correction, $T = 293$ K, ω scans, 3° < θ < 28°, $F(000) = 3952$, μ(Mo Kα) = 2.40 mm^{-1}, number of reflections measured 44 611, 12 312 independent reflections. The structure was solved by direct methods (SHELXS-86)[17a] and refined (SHELXS-97)[17b] against all F^2 data, resulting in $R_1 = 0.0570$, $wR_2 = 0.1198$ for all observed reflections with $I > 2\sigma(I)$, GOF = 0.886.

$[Y(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2NCMe_3)\{CH(CH_3)Ph\}(THF)]$ (3). To a solution of **2** (0.300 g, 0.35 mmol) in 10 mL of toluene was added styrene (0.073 g, 0.70 mmol) at room temperature. After stirring for 2 h, the solution was concentrated and cooled to −30 °C to give 0.330 g (88%) of yellow crystals. ^1H NMR: δ 0.39, 0.54 (s, 2 × 3 H, $SiCH_3$), 1.07 (br s, 4 H, β-CH_2, THF), 1.20 (s, 9 H, $C(CH_3)_3$), 1.86 (d, $^3J_{HH} = 6.4$ Hz, 3 H, $CHCH_3$), 1.92, 1.96 (s, 3 H, ring CH_3), 2.10, 2.14 (s, 2 × 1 H, CH_2), 2.21 (m, 1 H, $CHCH_3$), 2.24, 2.27 (s, 2 × 3 H, ring CH_3), 3.17 (br s, 4 H, THF), 6.46 (br t, $^3J_{HH} = 6.8$ Hz, 1 H, para-C_6H_5), 6.60 (d, $^3J_{HH} = 8.0$ Hz, 2 H, ortho-C_6H_5), 7.04 (t, $^3J_{HH} = 7.2$ Hz, 2 H, meta-C_6H_5). $^{13}C\{^1H\}$ NMR (toluene-d_8, 25 °C): δ 7.3, 7.7 ($NSiCCH_3$), 10.2, 10.6, 11.2, 12.3 (ring CH_3), 16.5 (CH_2), 17.1 ($CHCH_3$), 24.1 (β-CH_2, THF), 33.1 ($C(CH_3)$), 49.5 (d, $^1J_{YC} = 26.2$ Hz, YCH), 52.8 ($C(CH_3)_3$), 71.2 (α-CH_2, THF), 113.7, 115.0 (C_6H_5), 115.4, 116.2, 118.3 (ring C), 136.7 (ring C attached to CH_2), 130.1 (C_6H_5), 154.3 (ipso-C_6H_5). ^{89}Y NMR: δ 286.2. Anal. Calcd for $C_{28}H_{46}NOSiY$: C, 63.49; H, 8.68, N, 2.64. Found: C, 63.44; H, 8.68; N, 2.76.

X-ray Crystal Structure Analysis of 3. Single crystals suitable for X-ray crystal structure analysis were obtained by cooling of concentrated hexane solutions to −30 °C. Crystal data: $C_{28}H_{46}NOSiY$, $M_r = 529.67$, 0.346 × 0.156 × 0.014 mm, monoclinic, $P2_1$ (No. 4), $a = 8.8890(8)$ Å, $b = 29.576(3)$ Å, $c = 11.417(1)$ Å, $\beta = 110.015(2)°$, $V = 2820.3(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.247$ Mg/m^3, Mo Kα ($\lambda = 0.71073$ Å), Bruker AXS diffractometer, semiempirical absorption correction, $T = 213$ K, ω scans, 2° < θ < 28°, $F(000) = 1128$, μ(Mo Kα) = 2.13 mm^{-1}, number of reflections measured 18 007, 12 735 independent reflections. The structure was solved by direct methods (SHELXS-86)[17a] and refined (SHELXS-97)[17b] against all F^2 data, resulting in $R_1 = 0.0715$ and $wR_2 = 0.1134$ for all observed reflections with $I > 2\sigma(I)$, GOF = 0.895.

Hydrosilylation of 1-Decene. To a solution of 25.5 mg (50 μmol) of **1** in 0.5 mL of hexane were added sequentially $PhSiH_3$ (108 mg, 1.00 mmol) and 1-decene (140 mg, 1.00 mmol), and the reaction mixture was stirred at ambient temperature. Small aliquots were taken for GC analysis, and the reaction was found to be complete after 1 h. The reaction mixture was

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(16) Dinuclear intermediates cannot be ruled out in lanthanocene-catalyzed hydrosilylation: Voskoboynikov, A. Z.; Shestakova, A. K.; Beletskaya, I. P. *Organometallics* **2001**, *20*, 2794.

(17) (a) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986. (b) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

quenched with 0.5 mL of methanol, diluted with hexane, and filtered. The filtrate was concentrated and distilled in vacuo to give 230 mg (93%) of 1-(phenylsilyl)decane as a colorless oil. ^{1}H NMR (CDCl$_3$, 25 °C): δ 0.86 (m, 3 H), 0.96 (m, 2 H), 1.25−1.45 (m, 16 H), 4.28 (t, $^3J_{HH} = 3.6$ Hz, 2 H), 7.37 (m, 3 H), 7.56 (m, 2 H). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 10.0 (CH$_2$), 14.1 (CH$_2$), 22.8 (CH$_2$), 25.25 (CH$_2$), 29.0 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 29.6 (CH$_2$), 32.0 (CH$_2$), 32.9 (CH$_2$), 128.0, 129.5, 133.0, 135.2 (ring C). EI MS *m*/*z* (%): 248 (22%, M$^+$), 170 (41%, $C_{10}H_{21}SiH^+$), 127 (7%, $C_9H_{19}^+$), 99 (7%, $C_7H_{15}^+$). Anal. Calcd for $C_{16}H_{28}Si$: C, 77.34; H, 11.36. Found: C, 77.04; H, 11.22. The oxidation of the silane was performed following ref 18 to give 0.119 g (82%) of 1-decanol. 2-Decanol could not be detected by GC.

Hydrosilylation of Styrene. To a solution of 25.5 mg (50 μmol) of **1** in 0.5 mL of hexane were added sequentially $PhSiH_3$ (108 mg, 1.00 mmol) and styrene (104 mg, 1.00 mmol) under stirring at room temperature. Small aliquots were taken for GC analysis, and the reaction was found to be complete after 8 h. The reaction mixture was quenched with 0.5 mL of methanol, diluted with hexane, and purified by flash chromatography (silica gel, eluent pentane). Kugelrohr distillation gave 201 mg (94%) of a colorless oil. EI MS *m*/*z* (%): 212 (21%, M$^+$), 183 (8%, $C_{12}H_{11}Si^+$), 134 (100%, $C_8H_{11}Si^+$), 105 (45%, $C_6H_5Si^+$). Anal. Calcd for $C_{14}H_{16}Si$: C, 79.25; H, 7.55. Found: C, 79.11; H, 7.36. GC analysis and ^{1}H NMR spectra showed the presence of $PhCH_2CH_2SiH_2Ph$ and $PhCH(CH_3)SiH_2Ph$ in a 1:1.4 ratio.

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Supporting Information Available: Tables of all crystal data and refinement parameters, atomic parameters, including hydrogen atoms, thermal parameters, and bond lengths and angles for **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010518R

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(18) Molander, G. A.; Dowdy, E. D.; Noll, B. C. *Organometallics* **1998**, *17*, 3754.