Highly Efficient Hydrosilylation of Alkenes by Organoyttrium Catalysts with Sterically Demanding Amidinate and Guanidinate Ligands

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The sterically demanding guanidine ArNHC(NMe_2)NAr (Ar = 2,6-diisopropylphenyl, H**L**) reacts with $Y(CH_2SiMe_3)_3(THF)_2$ to give the yttrium dialkyl complex (**L**)$Y(CH_2SiMe_3)_2(THF)$ (**1**), which was structurally characterized. Electronic interaction of the $-NMe_2$ group with the conjugated ligand backbone can be inferred from structural and spectroscopic data. The new yttrium guanidinate complex **1** and its related amidinate analogue [PhC($NAr)_2$]$Y(CH_2SiMe_3)_2(THF)$ (**2**) are highly active and selective catalysts for alkene hydrosilylation with $PhSiH_3$ (tof > 600 h^{-1} at 23 °C). For unfunctionalized olefins, full selectivity toward anti-Markovnikov products was obtained. The more electron donating guanidinate ligand affords the highest activities with heteroatom-functionalized substrates.

Introduction

Metal-catalyzed hydrosilylation of alkenes is the most straightforward and atom-economic way to synthesize organosilanes. These can be converted to the corresponding alcohols by oxidation[1] or used as monomers for the production of silicon-based polymers, applied as rubbers, paper release coatings, and pressure-sensitive adhesives.[2] Pt-based catalysts are known to catalyze hydrosilylation with very high efficiency,[3] but when $RSiH_3$ is employed as the silylating reagent, they tend to form mixtures of reduced olefin R′H, $RR'SiH_2$, RR'_2SiH, and RR'_3Si.[3a] Disubstituted dihydrosilanes $RR'SiH_2$ are monomers for the production of poly(silylenes), which exhibit electronic properties similar to those of π-conjugated polymers due to σ-electron delocalization over the polymer backbone.[4] Catalysts based on early transition metals,[5] actinides,[6] and rare-earth metals[7] have been reported to show good selectivity for $PhRSiH_2$ in the hydrosilylation of olefins with $PhSiH_3$. Nevertheless, the low turnover frequency of these catalysts limits their application in synthesis. To date, the most efficient catalyst from this family is $Me_2SiCp''_2SmCH(SiMe_3)_2$ (tof = 120 h^{-1} at room temperature for 1-hexene), remarkably with a high selectivity for the Markovnikov product (76%).[7c] [$Me_2Si(C_5Me_4)(\mu$-PCy)$LuCH_2SiMe_3]_2$ has been reported to catalyze the hydrosilylation of 1-hexene with a similar efficiency and full selectivity for the anti-Markovnikov product, when a 25% excess of $PhSiH_3$ and 5 mol % of catalyst are used.[7j] Here we describe highly efficient and regioselective hydrosilylation catalysis by mono(amidinate)- and mono(guanidinate)yttrium catalysts. The new guanidinate catalyst shows a particularly good performance with heteroatom-containing substrates.

Amidinates and guanidinates have been used extensively as ligands in organometallic chemistry.[8] In recent years, we have used the sterically demanding amidinates $[(C_6R_5)C(NAr)_2]^-$ (Ar = 2,6-diisopropylphenyl; R = H, F) to good effect as ligands for rare-earth-metal catalysts for ethylene polymerization and hydroamination−cyclization.[9] Extension to sterically demanding guanidinates, with an R_2N- group on the ligand backbone, should allow us to access catalysts that are less strongly electron deficient, due to the possibility of the lone pair of the R_2N- group to interact with the conjugated NCN ligand moiety.[8c] Only very recently, the first examples of mono(guanidinate)dialky-

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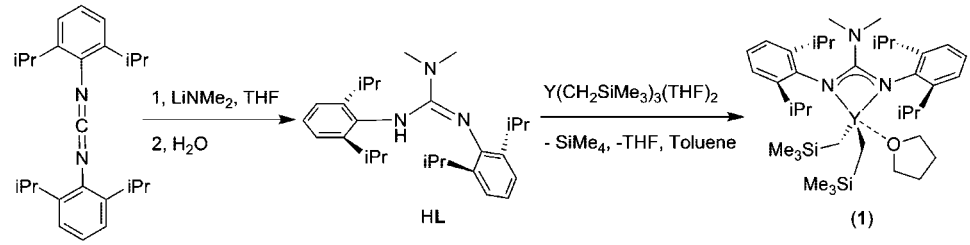
Scheme 1. Synthesis of the Ligand HL and Complex 1



lyttrium compounds, $[(SiMe_3)_2NC(NR)_2]Y(CH_2SiMe_3)_2(THF)_2$ (R = Cy,[10a] *i*-Pr[10b]), were reported.

Results and Discussion

Catalyst Synthesis and Characterization. The guanidine ArNHC(NMe$_2$)NAr (Ar = 2,6-diisopropylphenyl, H**L**) was described previously in the patent literature as an insecticidal agent and was synthesized by the reaction of the carbodiimide ArN═C═NAr with dimethylamine under forcing conditions.[11] We prepared H**L** in 85% isolated yield by hydrolysis of the lithium guanidinate Li[Me$_2$NC(NAr)$_2$], which was generated by reaction of LiNMe$_2$ with 1 equiv of ArN═C═NAr in THF (Scheme 1).

Reaction of H**L** with 1 equiv of $Y(CH_2SiMe_3)_3(THF)_2$ in toluene afforded the colorless dialkyl complex (**L**)Y(CH$_2$SiMe$_3$)$_2$(THF) (**1**) in 78% yield after crystallization from pentane (Scheme 1). Room-temperature NMR spectra of **1** in C_6D_6 suggest an (averaged) C_{2v} symmetry in solution, indicating fast rearrangement around the metal center on the NMR time scale. The YC*H*$_2$ resonances (C_6D_6, 23 °C) for **1** are found at δ −0.31 ppm (^{1}H, d, J_{YH} = 2.9 Hz) and δ 37.6 ppm (^{13}C, dt, J_{CH} = 98.5 Hz, J_{YC} = 38.9 Hz). The latter is upfield-shifted relative to the equivalent resonance in the related amidinate complex [PhC(NAr)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF) (**2**; dt, 39.5 ppm, J_{CH} = 100.1 Hz, J_{YC} = 40.3 Hz),[9a] suggesting that the guanidinate is the more electron donating of the two ligands. Compound **1** contains only a single coordinated THF molecule, while there are two in the related guanidinate yttrium dialkyl compounds $[(SiMe_3)_2NC(NR)_2]Y(CH_2SiMe_3)_2(THF)_2$ (R = Cy,[10a] *i*-Pr[10b]). This indicates that the ligand [Me$_2$NC(NAr)$_2$]$^-$ (**L**, Ar = 2,6-diisopropylphenyl) is the more sterically demanding of the three.

Compound **1** was characterized by single-crystal X-ray diffraction, and its structure is shown in Figure 1. In overall geometry, it is similar to the related amidinate complex **2**.[9a] The Y−C bond distances (2.388(2) and 2.407(2) Å) in **1** are somewhat longer than those in **2** (2.374(4) and 2.384(4) Å). The angles C1−N1−Y = 137.40(19)° and C16−N2−Y = 138.89(18)° in **1** are noticeably smaller than the corresponding angles (C8−N1−Y = 144.25(19)°, C20−N2−Y = 143.31(19)°) in **2**, indicating that the guanidinate **L** is more sterically demanding than the amidinate ligand [PhC(Ar)$_2$]$^-$. There appears to be considerable interaction of the lone pair of Me$_2$N with the conjugated NCN moiety, as seen from the following structural features in **1**:[8c] (i) The three C−N distances in the CN$_3$ guanidinate moiety are all very similar (C13−N1 = 1.342(4) Å, C13−N2 = 1.359(4) Å, C13−N3 = 1.367(4) Å); (ii) the geometry around N in the Me$_2$N− group is essentially planar (angle sum at N3: 359.7°); (iii) the dihedral angle formed by the planes C14−N2−C15 and N1−C13−N3 is only 27.3(4)°. This interaction should make the yttrium center in **1** less electron deficient than that in **2**, which is confirmed by NMR spectroscopy (see above). In the other reported guanidinate dialkylyttrium compounds [(RN)$_2$CN(SiMe$_3$)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$,[10] this delocalization can be ruled out by the R−N−C−N dihedral angles of around 90° and the corresponding elongation of the R$_2$N−C bond by about 0.1 Å relative to the other C−N bonds in the ligand.

Hydrosilylation of Terminal Alkenes Catalyzed by Yttrium Catalysts 1 and 2. The guanidinate complex **1** and the amidinate complex **2** both proved to be highly effective catalysts for alkene hydrosilylation reactions using PhSiH$_3$ in small (4%) excess (Scheme 2). A range of terminal alkenes were tested as substrates, and the results are summarized in Table 1. For all the substrates (**3a**−**i**), the reaction went essentially to completion and Lewis basic acetal or 1,3-dithiane groups pose no problems. No side reactions (such as olefin hydrogenation, dimerization of alkenes, and dehydrogenative coupling of organosilanes, which are known to occur with rare-earth-metal or actinide catalysts[6,7h]) were observed for catalysts **1** and **2**. Full selectivity for anti-Markovnikov products was obtained when unfunctionalized olefins were employed as substrates (entries 1−5). For 3,3-dimethylbut-1-ene (**3e**), the amidinate catalyst **2** is noticeably faster than the guanidinate catalyst **1**, probably due to the greater steric demand of the ligand in the latter (see above). For alkenes

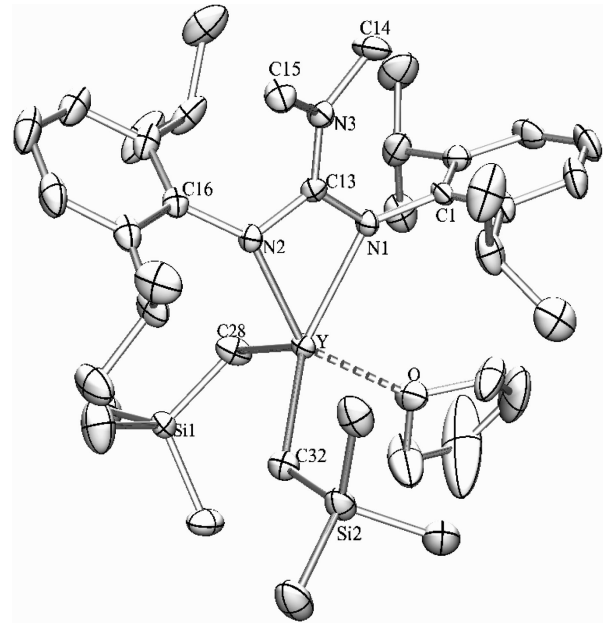
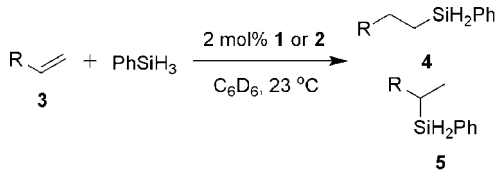


Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Y−N1 = 2.345(2), Y−N2 = 2.338(2), Y−O = 2.363(2), Y−C28 = 2.388(3), Y−C32 = 2.407(3), C13−N1 = 1.342(4), C13−N2 = 1.359(4), C13−N3 = 1.367(4); N1−Y−N2 = 57.47(8), N1−Y−O = 88.66(8), N1−Y−C28 = 114.29(9), N1−Y−C32 = 132.45(9), N2−Y−C28 = 105.84(10), N2−Y−C32 = 103.26(9), N2−Y−O = 145.45(8), C28−Y−C32 = 112.8(1), C28−Y−O = 93.57(10), C32−Y−O = 94.76(10), C1−N1−Y = 137.40(19), C16−N2−Y = 138.89(18).

Scheme 2

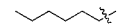
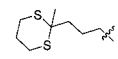
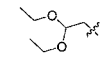


with a 1,3-dithiane functionality (entries 6 and 7), the guanidinate catalyst **1** is clearly the most efficient. Apparently, catalyst **2** is more susceptible to inhibition by (reversible) coordination of the heteroatom, although as yet it cannot be determined whether this is due to steric or electronic factors. 4,4-Diethoxybut-1-ene (**3h**) is remarkably rapidly hydrosilylated but now yields predominantly the Markovnikov product (entry 8), and differences between **1** and **2** are visible in both activity and selectivity. The guanidinate catalyst **1** is clearly faster but yields a 3:1 M:AM isomer mixture, whereas **2** has a 93% selectivity for the branched product. As the olefin in substrate **3h** is not expected to have an electronic preference for 2,1-insertion into an Y−H species (metal hydrides are the proposed active species in rare-earth-metal-catalyzed hydrosilylation[7h,k,12]), the preference for the branched (Markovnikov) product is likely to stem from interaction of the substrate ether groups with the metal center. The most stable chelate (with intramolecular Y−O coordination), resulting from insertion of the olefin into the Y−H bond, is likely to be the five-membered chelate (from 2,1-insertion) rather than the six-membered chelate (from 1,2-insertion). It could also be possible that ether coordination precedes olefin insertion, in which case the geometry for 2,1-insertion is likely to be the most favorable. Although we did not succeed in observing organometallic intermediates in the reactions, it can be expected that an increased affinity of the metal for the ether function will lead to an increased selectivity for the branched product **5h**. This would lead to the conclusion that the metal center in the guanidinate catalyst **1** is less electrophilic than that in the amidinate catalyst **2**, which is consistent with the structural and spectroscopic observations made above. Styrene requires a higher temperature (80 °C) to give conversion and then yields the benzylic silane **5g** as the main product (entry 9). That styrene hydrosilylation is more sluggish may be due to η^3 coordination of the 1-phenylethyl group formed by 2,1-insertion of styrene into a Y−H species. An yttrium η^3-1-phenylethyl complex was reported from the reaction of styrene with $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)(THF)(\mu\text{-}H)]_2$.[13] Internal olefins (e.g., *cis*-4-octene and cyclohexene) are not converted under the applied conditions.

Conclusions

Yttrium catalysts with sterically demanding amidinate or guanidinate ancillary ligands thus appear to be excellent catalysts for the hydrosilylation of terminal alkenes with phenylsilane.

Table 1. Hydrosilylation of Alkenes by Y-Based Catalysts 1 and 2[a]

Entry (Substrate)	R	catalyst	Time (min)	Olefin Conv. (%)[b]	Product Select. (%)[b] 4	5
1 (**3a**)		**1**	<5	100	>99	
		2	<5	100	>99	
2 (**3b**)		**1**	<5	100	>99	
		2	<5	100	>99	
3 (**3c**)		**1**	<5	100	>99	
		2	<5	100	>99	
4 (**3d**)		**1**	<5	100	>99	
		2	<5	100	>99	
5 (**3e**)		**1**	300	98	>99	
		2	60	100	>99	
6 (**3f**)		**1**	<5	100	>99	
		2	90	100	>99	
7 (**3g**)		**1**	240	98	96	4
		2	720	98	96	4
8 (**3h**)		**1**	25	100	26	74
		2	90	100	7	93
9 (**3i**)[c]		**1**	70	100	33	67
		2	190	100	23	77

[a] Reaction conditions: catalyst **1** or **2** (10 μmol), olefin (0.5 mmol), $PhSiH_3$ (0.52 mmol), 23 °C, solvent C_6D_6 (0.3 mL). [b] Determined by GC-MS and in situ ^1H NMR spectroscopy. [c] 80°C.

Table 2. Crystal Data and Data Collection Parameters of Complex 1

compd	**1**
formula	$C_{39}H_{70}N_3OSi_2Y$
fw	743.08
cryst color	colorless
cryst size (mm)	0.56 × 0.46 × 0.42
cryst syst	orthorhombic
space group	$P2_12_12_1$
a (Å)	12.9822(8)
b (Å)	17.6370(11)
c (Å)	18.8875(12)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	4324.6(5)
Z	4
ρ_{calcd}, g cm^{-3}	1.140
μ, cm^{-1}	14.34
F(000), electrons	1600
θ range (deg)	2.67−26.37
index ranges(h,k,l)	±16, −20 to +22, −23 to +22
no. of rflns collected	34 204
no. of unique rflns	8832
no. of reflns with $F_o \geq 4\sigma(F_o)$	7374
$R_w(F^2)$	0.0906
a, *b*	0.0468, 0.8703
R (*F*)	0.0399
T (K)	100(1)
GOF	1.023

Significantly higher turnover frequencies (>600 h^{-1}, 23 °C) are achieved than with other rare-earth-metal or early-transition-metal catalysts, and heteroatom-containing substrates can also be converted with high efficiency. The performance of this catalyst family with functionalized substrates may be tuned by

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(12) Evidence that hydride species of the type "(**L**)YH_2" are the active species in the present system was obtained from the reaction of (**L**)$Y(CH_2SiMe_3)_2(THF)$ (**1**) with 2 equiv of $PhSiH_3$. Although this did not produce a stable, well-defined Y-hydride complex, the formation of 2 equiv of $PhSiH_2CH_2SiMe_3$ was observed, a clear indication of smooth Y−H formation.

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modifying the electrophilicity of the catalyst (viz. amidinate vs guanidinate).

Experimental Section

General Remarks. All reactions and manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk, vacuum line, and glovebox techniques, unless mentioned otherwise. Toluene and pentane (Aldrich, anhydrous, 99.8%) were passed over columns of Al_2O_3 (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). THF (Aldrich, anhydrous, 99.8%) was dried over Al_2O_3 (Fluka). All solvents were degassed prior to use and stored under nitrogen. C_6D_6 was vacuum-transferred from Na/K alloy. NMR spectra were recorded on Varian Gemini VXR 300, Varian Gemini VXR 400, and Varian Inova 500 spectrometers in NMR tubes equipped with a Teflon (Young) valve. The ^{1}H NMR spectra were referenced to resonances of residual protons in deuterated solvents. The ^{13}C NMR spectra were referenced to carbon resonances of deuterated solvents and reported in ppm relative to TMS (δ 0 ppm). GC-MS measurements were performed on an HP 6890 series GC system coupled with an HP 5973 mass-selective detector. Column: HP-5MS 5% phenyl methyl siloxane 30 m × 250 μm capillary column. Temperature profile: start at 35 °C (hold for 10 min), increase to 280 °C at a rate of 20 °C/min, and then hold at 280 °C for 10 min. The olefins 1-hexene, 1-octene, vinylcyclohexane, 4-vinyl-1-cyclohexene, and 3,3-dimethyl-1-butene were commercial samples stirred for at least 4 h over Na/K alloy and then distilled under nitrogen. Styrene was dried over molecular sieves and distilled before use. Phenylsilane (Aldrich, 99%) was saturated with nitrogen and used as purchased. Bis(2,6-diisopropylphenyl)carbodiimide (TCI Europe Organic Chemicals, >98%) was used as purchased. 2-(3′-Butenyl)-2-methyl-1,3-dithiane,[14] 2-(4′-pentenyl)-2-methyl-1,3-dithiane,[14] and 4,4-diethoxylbut-1-ene[15] were prepared according to literature procedures.

Ligand (HL) Synthesis. To a solution of bis(2,6-diisopropylphenyl)carbodiimide (3.62 g, 10 mmol) in THF (20 mL) was added a solution of lithium dimethylamide (0.53 g, 10.4 mmol) in THF (10 mL). The resulting solution was stirred for 2 h at room temperature. Then water (0.20 g, 11 mmol) was added, and the mixture was stirred for another 10 min. Diethyl ether (100 mL) was added, and the mixture was dried over Na_2SO_4 and filtered. The volatiles were removed under reduced pressure to yield the title compound (3.47 g, 8.5 mmol, 85%) as an off-white solid, which can be used without further purification. ^{1}H NMR (300 MHz, C_6D_6, δ): 7.26 (d, 2H, J_{HH} = 7.41 Hz, *m-H* Ph), 7.09 (m, 2H, *p-H* Ph), 7.00 (d, 2H, J_{HH} = 7.41 Hz, *m-H* Ph), 5.25 (s, 1H, N=CN*H*), 3.45 (sept, 2H, J_{HH} = 6.87 Hz, C*H*(CH$_3$)$_2$), 3.27 (sept, 2H, J_{HH} = 6.87 Hz, C*H*(CH$_3$)$_2$), 2.47 (s, 6H, N(C*H*$_3$)$_2$), 1.39 (d, 6H, J_{HH} = 6.49 Hz, CH(C*H*$_3$)$_2$), 1.37 (d, 6H, J_{HH} = 6.49 Hz, CH(C*H*$_3$)$_2$), 1.17 (br, 6H, CH(C*H*$_3$)$_2$), 0.97 (br, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.6 MHz, C_6D_6, δ): 152.2 (N*C*N), 151.3 (N*C*N), 144.9 (*ipso-C* Ph), 140.3 (*o-C* Ph), 127.0 (*p-C* Ph), 124.1 (*m-C* Ph), 123.5 (*m-C* Ph), 123.3 (*p-C* Ph), 39.4 (N*C*H$_3$), 28.9 (*C*H iPr), 28.7 (*C*H iPr), 24.6 (*C*H$_3$ iPr), 22.5 (*C*H$_3$ iPr). Anal. Calcd for $C_{27}H_{41}N_3$: C, 79.55; H, 10.14; N, 10.31. Found: C, 79.50; H, 10.19; N, 10.15.

Synthesis of (L)Y(CH$_2$SiMe$_3$)$_2$(THF) (1). To a solution of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (268 mg, 0.541 mmol) in toluene (20 mL) was added a solution of H**L** (221 mg, 0.541 mmol) in toluene (5 mL). The resulting solution was stirred for 20 min at room temperature. Then volatiles were removed under reduced pressure and the residue was dissolved in pentane (4 mL). Cooling to −30 °C overnight afforded well-formed crystals. The mother liquor was decanted and the solid was dried under vacuum, yielding the title compound (316 mg, 0.415 mmol, 78%) as an off-white solid. ^{1}H NMR (400 MHz, C_6D_6, δ): 7.08 (m, 6H, *m-H*, *p-H* Ph), 3.61 (sept, 4H, J_{HH} = 6.67 Hz, C*H* iPr), 3.56 (m, 4H, α-*H* THF), 2.01 (s, 6H, NC*H*$_3$), 1.40 (d, 12H, J_{HH} = 6.97 Hz, C*H*$_3$ iPr), 1.23 (d, 12H, J_{HH} = 6.97 Hz, C*H*$_3$ iPr), 1.12 (m, 4H, *β-H* THF), 0.26 (s, 18H, Si(C*H*$_3$)$_3$), −0.31 (d, 4H, J_{HH} = 2.9 Hz, YC*H*$_2$). ^{13}C NMR (100.6 MHz, C_6D_6, δ): 166.7 (s, N*C*N), 144.0 (s, *ipso-C* Ph), 142.4 (s, *o-C* Ph), 124.0 (d, J_{CH} = 156.3 Hz, *m-C* Ph), 123.9 (d, J_{CH} = 159.1 Hz, *p-C* Ph), 70.5 (t, J_{CH} = 150.2 Hz, α-*C* THF), 39.6 (q, J_{CH} = 138.1 Hz, N*C*H$_3$), 37.6 (dt, J_{YC} = 38.9 Hz, J_{CH} = 98.5, Y*C*H$_2$), 28.1 (d, J_{CH} = 127.7 Hz, *C*H iPr), 25.9 (q, J_{CH} = 123.8 Hz, *C*H$_3$ iPr), 24.9 (t, J_{CH} = 133.6 Hz, *β-C* THF), 23.8 (q, J_{CH} = 125.6 Hz, *C*H$_3$ iPr), 4.4 (q, J_{CH} = 115.6 Hz, Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{39}H_{70}N_3OSi_2Y$: C, 63.12; H, 9.51; N, 5.66. Found: C, 62.95; H, 9.56; N, 5.55.

General Procedure for Catalytic Hydrosilylation of Alkenes. An NMR tube equipped with a Teflon Young valve was charged in a glovebox with (**L**)Y(CH$_2$SiMe$_3$)$_2$(THF) (**1**) or [PhC(NC$_6$H$_3$*i*-Pr-2,6)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF) (**2**) (10 μmol), PhSiH$_3$ (0.52 mmol), olefin (0.5 mmol), and C_6D_6 (0.3 mL). The tube was closed and taken out of the glovebox. The dispearance of the substrates and formation of new organosilanes can be conveniently monitored by NMR. The products were characterized by ^{1}H (and for new compounds ^{13}C) NMR spectrometry and GC-MS.

Characterization of New Silanes. 2-(5′-Phenylsilylpentyl)-2-methyl-1,3-dithiane (4f). ^{1}H NMR (400 MHz, C_6D_6, δ): 7.49 (m, 2H), 7.19 (m, 3H), 4.45 (t, 2H, J_{HH} = 3.59 Hz, Si*H*$_2$), 2.47 (m, 4H), 1.84 (m, 2H), 1.58 (m, 2H), 1.54 (s, 3H), 1.47 (m, 2H), 1.37 (m, 2H), 1.24 (m, 2H), 0.81 (m, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, δ): 135.5 (*m-C* Ph), 132.7 (*ipso-C* Ph), 129.8 (*p-C* Ph), 128.3 (*o-C* Ph), 49.4 (S$_2$*C*CH$_3$), 42.0 (S*C*H$_2$), 33.3, 28.1, 26.5, 25.6, 25.3, 24.5, 10.3 (SiH$_2$*C*H$_2$). GC-MS: *m*/*z* 310 (M$^+$).

2-(3′-Phenylsilylpropyl)-2-methyl-1,3-dithiane (4g). ^{1}H NMR (400 MHz, C_6D_6, δ): 7.49 (m, 2H), 7.17 (m, 3H), 4.45 (t, 2H, J_{HH} = 3.70 Hz, Si*H*$_2$), 2.42 (m, 4H), 1.93 (m, 2H), 1.69 (m, 2H), 1.54 (m, 2H), 1.48 (s, 3H), 0.80 (m, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, δ): 135.5 (*m-C* Ph), 132.5 (*ipso-C* Ph), 129.9 (*p-C* Ph), 128.3 (*o-C* Ph), 49.3 (S$_2$*C*CH$_3$), 45.1 (S*C*H$_2$), 28.0, 26.5, 25.5, 20.6, 10.4 (SiH$_2$*C*H$_2$). GC-MS: *m*/*z* 282 (M$^+$). Retention time: 21.6 min.

2-(2′-Phenylsilylpropyl)-2-methyl-1,3-dithiane (5g). ^{1}H NMR (400 MHz, C_6D_6, δ): 4.41 (m, PhSi*H*$_2$), 1.49 (s, S$_2$CC*H*$_3$), 1.15 (d, J_{HH} = 7.35 Hz, SiH$_2$C*H*CH$_3$), other resonances are overlapped with **4g**. GC-MS: *m*/*z* 282 (M$^+$). Retention time: 21.3 min.

1,1-Diethoxyl-3-(phenylsilyl)butane (4h). ^{1}H NMR (500 MHz, C_6D_6, δ): 7.53 (m, 2H), 7.14 (m, 3H), 4.57 (t, 1H, J_{HH} = 5.89 Hz, (C$_2$H$_5$O)$_2$C*H*), 4.42 (m, 2H, Si*H*$_2$), 3.49 (m, 2H), 3.32 (m, 2H), 1.90 (m, 1H), 1.69 (m, 1H), 1.36 (m, 1H), 1.10 (t, 6H, J_{HH} = 7.13 Hz, C*H*$_3$), 1.06 (d, 3H, J_{HH} = 7.15 Hz, C*H*$_3$). ^{13}C NMR (125.7 MHz, C_6D_6, δ): 136.0 (d, J_{CH} = 158.6 Hz, *m-C* Ph), 132.3 (s, *ipso-C* Ph), 129.8 (d, J_{CH} = 159.8 Hz, *p-C* Ph), 128.2 (d, J_{CH} = 157.8 Hz, *o-C* Ph), 101.8 (d, J_{CH} = 158.1 Hz, O$_2$*C*H), 60.9 (t, J_{CH} = 140.1 Hz, O*C*H$_2$CH$_3$), 60.5 (t, J_{CH} = 140.1 Hz, O*C*H$_2$CH$_3$), 37.5 (t, J_{CH} = 125.0 Hz, O$_2$CH*C*H$_2$), 16.6 (q, J_{CH} = 124.0 Hz, PhSiH$_2$CH*C*H$_3$), 15.6 (q, J_{CH} = 124.2 Hz, OCH$_2$*C*H$_3$), 12.7 (d, J_{CH} = 112.0 Hz, PhSiH$_2$*C*H). GC-MS: *m*/*z* 252 (M$^+$). Retention time: 18.7 min.

1,1-Diethoxyl-4-(phenylsilyl)butane (5h). ^{1}H NMR (500 MHz, C_6D_6, δ): 7.47 (m, 2H), 7.13 (m, 3H), 4.38 (t, 1H, J_{HH} = 5.61 Hz, (C$_2$H$_5$O)$_2$C*H*), 4.45 (t, 2H, J_{HH} = 3.28 Hz, Si*H*$_2$), 3.49 (m, 2H), 3.31 (m, 2H), 1.90 (m, 1H), 1.67 (m, 2H), 1.54 (m, 2H), 1.10 (t, 6H, J_{HH} = 7.13 Hz, C*H*$_3$), 0.79 (m, 2H, C*H*$_2$SiH$_2$). ^{13}C NMR (125.7 MHz, C_6D_6, δ): 135.5 (d, J_{CH} = 156.2 Hz, *m-C* Ph), 132.6 (s, *ipso-C* Ph), 129.8 (d, J_{CH} = 159.8 Hz, *p-C* Ph), 128.3 (d, J_{CH} = 158.3 Hz, *o-C* Ph), 102.6 (d, J_{CH} = 156.7 Hz, O$_2$*C*H), 60.7 (t, J_{CH} = 140.1 Hz, O*C*H$_2$CH$_3$), 36.9 (t, J_{CH} = 125.0 Hz, O$_2$CH*C*H$_2$), 20.8 (t, J_{CH} = 122.1 Hz, SiH$_2$CH$_2$*C*H$_2$), 15.6 (q, J_{CH} = 124.2 Hz, OCH$_2$*C*H$_3$), 10.2 (t, J_{CH} = 118.0 Hz, PhSiH$_2$*C*H$_2$). GC-MS: *m*/*z* 252 (M$^+$). Retention time: 18.3 min.

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Structure Determination of Compound 1. Suitable crystals were obtained by crystallization from pentane. A crystal was mounted on a glass fiber inside a drybox and transferred under an inert atmosphere to the cold nitrogen stream of a Bruker SMART APEX CCD diffractometer. Intensity data were collected with Mo Kα radiation ($\lambda = 0.710\,73$ Å). Intensity data were corrected for Lorentz and polarization effects. A semiempirical absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS[16]). The structures were solved by Patterson methods, and extension of the models was accomplished by direct methods applied to difference structure factors, using the program DIRDIF.[17] In a subsequent difference Fourier synthesis all hydrogen atoms were located, the positional and isotropic displacement parameters of which were refined. All refinements and geometry calculations were performed with the program packages SHELXL[18] and PLATON.[19] Crystallographic data and the details of data collections and data refinements are given in Table 2.

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Supporting Information Available: Text giving additional characterization data for the organosilanes and a CIF file giving X-ray data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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