Rare-Earth Metal Alkyl and Hydrido Complexes Containing a Thioether-Functionalized Bis(phenolato) Ligand: Efficient Catalysts for Olefin Hydrosilylation

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Rare-earth metal alkyl complexes with tridentate [OSO]-type and tetradentate [OSSO]-type bis(phenolato) ligands, $[Ln(L)(CH_2SiMe_3)(THF)_n]$ (LH_2 = 2,2′-thiobis(6-*tert*-butyl-4-methylphenol) ($tbmpH_2$), 1,3-dithiapropanediylbis(6-*tert*-butyl-4-methylphenol) ($mtbmpH_2$), 1,4-dithiabutanediylbis(6-*tert*-butyl-4-methylphenol) ($etbmpH_2$); Ln = Y (**1**−**3**), Sc (**4**, **5**), Lu (**7**), Ho (**9**, **10**)), were synthesized from the reactions of the tris(alkyl) complexes $[Ln(CH_2SiMe_3)_3(THF)_2]$ with the corresponding bis(phenol) via alkane elimination. The alkyl complexes were characterized by NMR spectroscopy (Y, Sc, Lu) and elemental analysis as well as by X-ray crystal structure analysis (**5**, **7**). The reaction of $[Lu(CH_2SiMe_3)_3(THF)_2]$ with H_2etbmp in a 1:2 ratio led to the formation of the bis(phenolato)-bridged dinuclear complex $[Lu_2(etbmp)_3(THF)_2]$ (**8**). The reaction of the holmium alkyl complexes **9** and **10** with $PhSiH_3$ resulted in the formation of the corresponding hydrido complexes $[Ho(L)(\mu\text{-}H)(THF)_n]_2$ (L = tbmp, n = 3, **11**; L = etbmp, n = 2, **12**). The formation of the yttrium analogues could be observed by NMR spectroscopy. Complexes **2**, **4**, and **5** were tested in the hydrosilylation of a wide variety of aliphatic and aromatic 1-alkenes and 1,5-hexadiene with various silanes ($PhSiH_3$, $^nBuSiH_3$, and Ph_2SiH_2). In the case of terminal aliphatic alkenes an anti-Markovnikov (1,2) addition takes place with 80−99% regioselectivity. The hydrosilylation of styrene afforded the Markovnikov (2,1) addition product $PhHC(SiH_2Ph)Me$ with 97% regioselectivity. The hydrosilylation of 1,5-hexadiene by $PhSiH_3$ catalyzed by **2** resulted in the formation of a linear product, 1,6-bis(phenylsilyl)hexane (ca. 90%), and a cyclic product, (phenylsilylmethyl)cyclopentane (ca. 10%), whereas with $^nBuSiH_3$ 84% of the cyclic product was obtained.

Introduction

Catalytic hydrosilylation of α-olefins is one of the most versatile and efficient methods for the synthesis of alkylsilanes and the production of organosilicon compounds on the industrial scale.[1] Rare-earth metal alkyl, amido, and hydrido complexes[2] with metallocene[3] or mono(cyclopentadienyl)[4] ligands have proven to be efficient catalyst precursors for the hydrosilylation of olefins. The mechanism of the hydrosilylation catalytic cycle most probably involves hydride complexes.[3d,m] In contrast to the well-established and numerous cyclopentadienyl complexes of the rare-earth metals, there are only a few types of complexes with a non-cyclopentadienyl ancillary ligand environment that have been reported to be active in olefin hydrosilylation catalysis. Examples include trivalent yttrium and lanthanide amido,[5] silylamido,[6] and silanolate[7] complexes as well as divalent lanthanide imine or diketoiminate complexes.[8] Recently,

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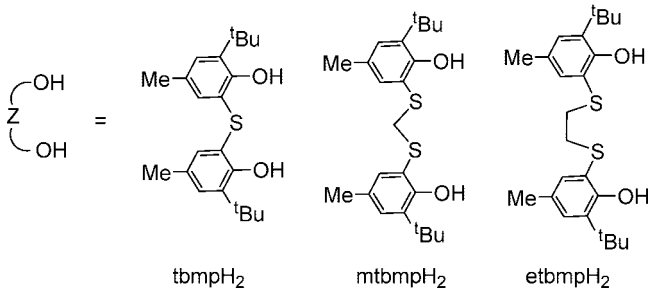
Scheme 1



we reported that lutetium alkyl and hydrido complexes supported by an [OSO]- or [OSSO]-type bis(phenolato) ligand framework are active in 1-hexene hydrosilylation.[9] Here we report the synthesis of the alkyl complexes of other rare-earth metals with linked bis(phenolato) ligands as well as the catalytic activity of the scandium and yttrium alkyl complexes in the hydrosilylation of a wide range of terminal aliphatic and aromatic olefins as well as of 1,5-hexadiene.

Results and Discussion

Alkyl and Hydrido Complexes. The bis(phenols) with an [OSO]- or [OSSO]-type framework used in this work are shown in Scheme 1. Reaction of a bis(phenol) with the tris(alkyl) precursors $[Ln(CH_2SiMe_3)_3(THF)_2]$ leads at room temperature, via $SiMe_4$ elimination, to formation of the corresponding mono(alkyl) complexes $[Ln(L)(CH_2SiMe_3)(THF)_n]$ (L = tbmp, mtbmp, etbmp; Ln = Y (**1**−**3**), Sc (**4**, **5**), Lu (**7**), Ho (**9**, **10**)) isolated in moderate to good yields (Scheme 2). The products often contain one to two THF molecules, depending on the crystallization/isolation method, but can be stored under argon at −40 °C for several weeks without decomposition.

The THF ligands in the yttrium complex **2** are labile and could be easily exchanged for pyridine to give the alkyl complex $[Y(etbmp)(CH_2SiMe_3)(C_5H_5N)_n]$ (*n* = 1, 2, **6**) (Scheme 2). The structure of the alkyl complexes **1**−**6** was confirmed by NMR spectroscopy (with the exception of holmium) and by elemental analysis.

X-ray diffraction analyses of single crystals of $[Sc(etbmp)(CH_2SiMe_3)(THF)]$ (**5**) and $[Lu(mtbmp)(CH_2SiMe_3)(THF)_2]\cdot 2$ THF (**7**), grown from a THF/pentane solution at −40 °C, were performed. As shown in Figures 1 and 2, both complexes are monomeric in the solid state. The scandium and lutetium atoms are six- and seven-coordinate, respectively. The scandium atom adopts a distorted-octahedral geometry. The alkyl ligand is located *cis* to the THF molecule and *trans* to one of the sulfur atoms, and the two oxygen donors of the ligand in **5** are arranged *trans* to each other, as indicated by the corresponding angles C1−Sc1−O3 = 96.68(14)°, C1−Sc1−S2 = 168.32(11)°, and O1−Sc1−O2 = 151.72(11)°. Analogously to the previously reported lutetium complex $[Lu(etbmp)(CH_2SiMe_3)(THF)]$,[9] the 1,4-dithiabutanediyl-bridged complex **5** adopts a *cis*-α configuration, consistently observed for group 4 metal complexes bearing this or a related ligand.[10] The molecule of **5** shows C_1 symmetry, and both enantiomers are found in the centrosymmetric crystal structure. As expected, the two bond lengths with phenoxy oxygen donors, Sc1−O1 and Sc1−O2, are shorter than the bond distance for THF oxygen donor O3 (2.003(4) and 1.985(3) Å versus 2.136(3) Å). The Sc1−C1 distance of 2.206(4) Å is shorter than the average bond length of 2.251 Å in the tris(alkyl) precursor $[Sc(CH_2SiMe_3)_3(THF)_2]$[11] and is also shorter than the median bond length of 2.25 Å (64 bonds, lower quantile 2.224, upper quantile 2.270, quantile 25%) for 27 crystallographically characterized scandium mono-, di-, and tris(alkyl) complexes with the (trimethylsilyl)methyl group. However, due to the constraints imposed by the ligand, the O1−Sc1−O2 angle of 151.72(11)° is significantly smaller than 180°. This effect was also found in a scandium amido complex bearing the 1,5-dithiapentanediylbis(6-*tert*-butyl-4-methylphenolate) ligand, $[Sc(ptbmp)\{N(SiHMe_2)_2\}(THF)]$ (151.1(2)°).[12] The two Sc1−S distances of 2.711(2) and 2.860(3) Å in **5** are apparently longer than the sum of the covalent radii ($r_c(Sc) + r_c(S) = 1.44 + 1.02 = 2.46$ Å) but still much shorter than the sum of metal radius $r_m(Sc)$ and van der Waals radius $r_v(S)$ ($r_m(Sc) + r_v(S) = 1.628 + 1.80 = 3.428$ Å),[13] indicating the presence of coordinative bonds. The Sc1−S1 and Sc1−S2 bond lengths in **5** differ from each other by 0.15 Å, and the Sc1−S2 bond *trans* to the more strongly electron donating CH_2SiMe_3 group is elongated. The coordination environment of the lutetium atom in **7** is best described as a distorted pentagonal bipyramid. The configuration of the ligand is pseudo *cis*-α with both THF and both phenoxy oxygen atoms *trans* to each other (O1−Lu1−O2 = 147.41(9)°; O3−Lu1−O4 = 166.54(8)°). As expected, the S1−Lu1−S2 angle of 58.13(2)° is smaller than the respective S1−Sc1−S2 angle in **5** (79.80(9)°). The Lu1−C24 bond distance of 2.369(3) Å is comparable with the bond length reported in the literature for $[Lu(CH_2SiMe_3)_3(THF)_2]$ (2.36 Å)[14] and slightly longer than that for $[Lu(etbmp)(CH_2SiMe_3)(THF)]$ (2.335(4) Å)[9] and than the median bond length of 2.356 Å for 30 crystallographically characterized lutetium complexes featuring the (trimethylsilyl)methyl ligand (54 bonds, lower quantile 2.336, upper quantile 2.374, quantile 25%).

Due to the greater constraints within the SCH_2S bridge of the mtbmp ligand, the two Lu1−S distances of 3.1671(9) and 3.1096(9) Å in **7** are different from and longer than the respective distances in $[Lu(etbmp)(CH_2SiMe_3)(THF)]$ (2.962(1) and 2.846(1) Å).[9] Analogously to the scandium complex **5**, the Lu1−S distances are longer than the sum of the covalent radii ($r_c(Lu) + r_c(S) = 1.56 + 1.02 = 2.58$ Å) but still shorter than the sum of metal radius $r_m(Lu)$ and van der Waals radius $r_v(S)$ ($r_m(Lu) + r_v(S) = 1.738 + 1.80 = 3.538$ Å).

The alkyl complexes **1**−**7** show fluxional behavior in solution, as indicated by the presence of only one set of signals observed

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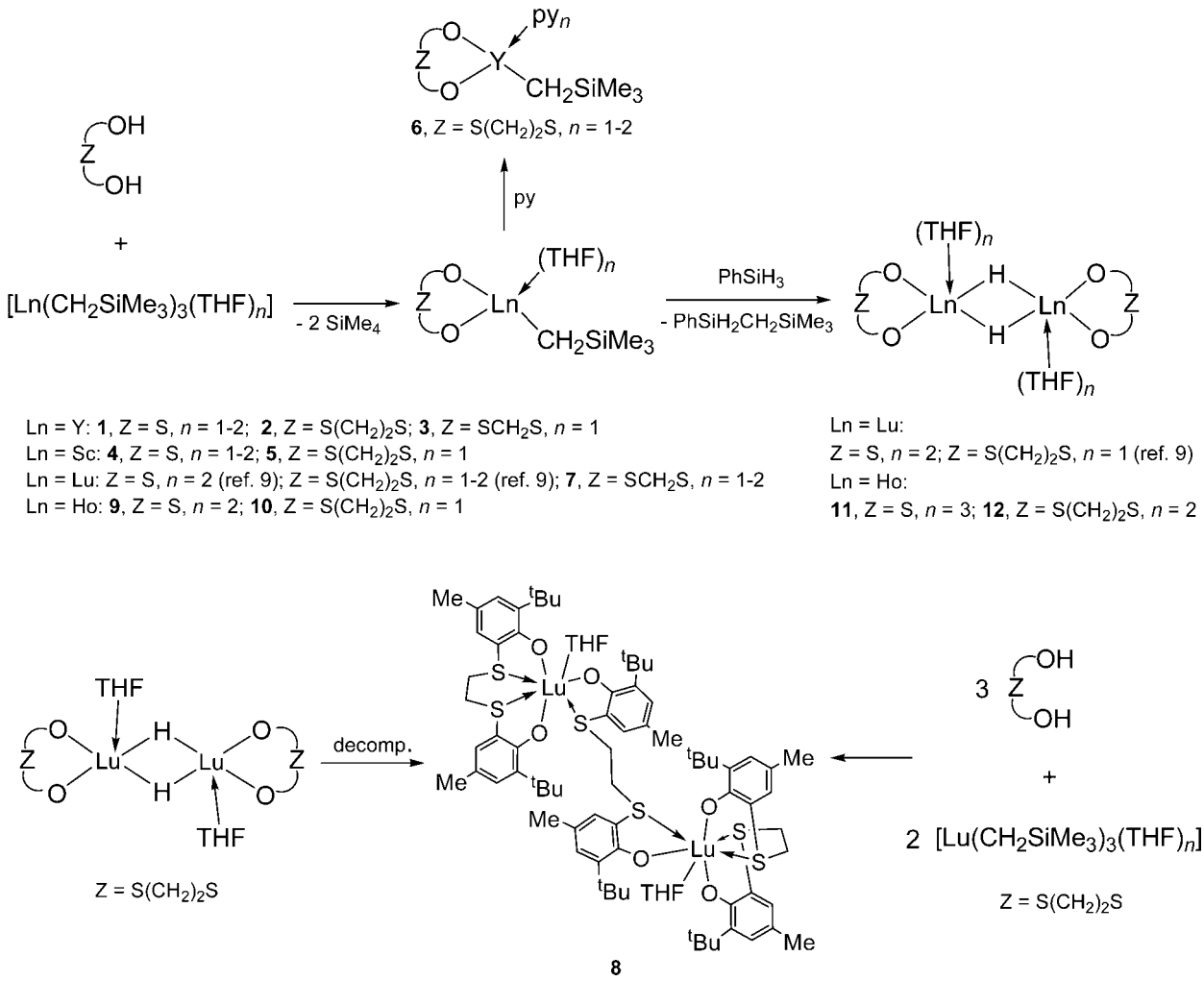
Scheme 2



in the ^{1}H NMR spectra at room temperature. This fluxional phenomenon is often observed for rare-earth metal complexes[6,12] and other transition-metal complexes.[15] The presence of Ln−S coordinative bonds is indicated by slight to apparent downfield

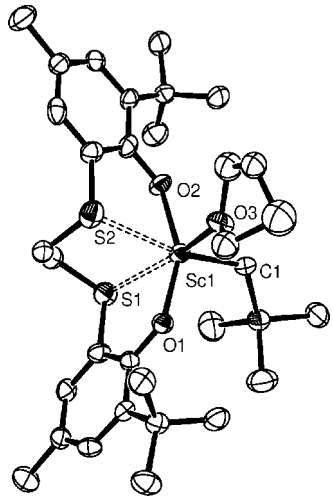


Figure 1. Molecular structure of [Sc(etbmp)(CH$_2$SiMe$_3$)(THF)] (**5**) (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc1−C1 = 2.206(4), Sc1−O1 = 2.003(4), Sc1−O2 = 1.985(3), Sc1−O3 = 2.136(3), Sc1−S1 = 2.711(2), Sc1−S2 = 2.860(3); O1−Sc1−O2 = 151.72(11), O3−Sc1−S1 = 159.12(9), C1−Sc1−S1 = 103.45(13), C1−Sc1−S2 = 168.32(11), O1−Sc1−O3 = 93.61(11), S1−Sc1−S2 = 79.80(9).

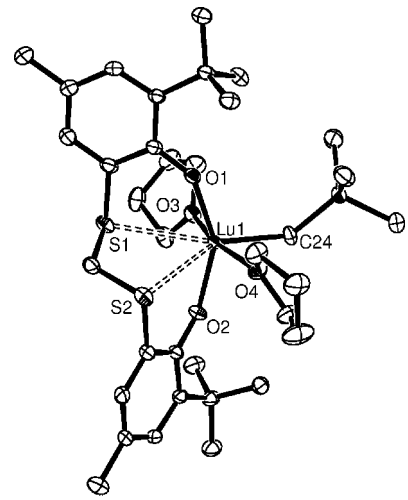


Figure 2. Molecular structure of [Lu(mtbmp)(CH$_2$SiMe$_3$)-(THF)$_2$]·2THF (**7**) (50% probability ellipsoids). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Lu1−C24 = 2.369(3), Lu1−O1 = 2.103(2), Lu1−O2 - 2.099(2), Lu1−O3 = 2.334(2), Lu1−O4 = 2.334(2), Lu1−S1 = 3.1671(1), Lu1−S2 = 3.110(1); O1−Lu1−O2 = 147.41(9), O3−Lu1−O4 = 166.54(8), S1−Lu1−S2 = 58.13(2), C24−Lu1−S2 = 149.45(8), C24−Lu1−S1 = 151.08(8).

Table 1. Selected ^{1}H and ^{13}C NMR Spectroscopic Data for Complexes 1−3, 5, and 7 in THF-d_8

			LnCH$_2$		LnC	
complex	Ln	L	δ (ppm) (multiplicity)	$^2J_{YH}$ (Hz)	δ (ppm) (multiplicity)	$^1J_{YC}$ (Hz)
1	Y	tbmp	−0.84 (d)	3.0	24.8 (d)	45.1
2	Y	etbmp	−0.94 (d)	3.0	21.8 (d)	41.6
3	Y	mtbmp	−0.85 (d)	3.5	24.5 (d)	44.2
5	Sc	etbmp	−0.11		34.8	
7	Lu	mtbmp	−0.95		29.2	

shifts of the SCH$_2$ protons in **2**, **3**, and **5**−**7** compared to those in the corresponding bis(phenol). The aforementioned fluxional behavior of the alkyl complexes in solution is thought to be due to a reversible THF or pyridine dissociation/coordination process that leads to a molecule with a higher symmetry. In the case of the 1,4-dithiabutanediyl-bridged (**2**, **5**, **6**) and 1,3-dithiapropanediyl-bridged (**3** and **7**) complexes the THF dissociation would result in a pseudo five-coordinate metal center with either C_2 (trigonal bipyramidal, *trans*-(O,O)) or C_s symmetry (square pyramidal, *cis*-(O,O)). This would render both phenyl moieties in the same ligand chemically equivalent, resulting in only one set of signals observed in the ^{1}H NMR spectra at room temperature. Selected ^{1}H and ^{13}C NMR data for the alkyl bis(phenolato) complexes are summarized in Table 1.

At room temperature the ^{1}H NMR spectra (in THF-d_8) of the 1,4-dithiabutanediyl-bridged yttrium (**2**, **6**) and scandium complexes (**5**) show symmetrical features and four ethylene bridge protons in the backbone of the bis(phenolato) ligand appear as a singlet at δ 2.75 (**2**) and 2.46 ppm (**6**) or as a very broad singlet at 2.67 ppm (**5**). In the case of the 1,3-dithiapropanediyl-bridged complexes **3** and **7** this resonance is shifted even more to low field (δ 4.02 ppm, **3**; δ 4.04 ppm, **7**). Variable-temperature ^{1}H NMR studies of **2** show that the fluxionality of the ethylene bridge is frozen out on the NMR time scale at −90 °C, where two broad signals at δ 2.31 and 3.23 ppm are displayed (Figure 3). In the case of the scandium analogue **5**, this fluxionality is frozen out on the NMR time scale at −20 °C, and at −80 °C the four ethylene bridge protons show a typical AA′BB′ pattern (doublets at δ 2.27 and 3.16 ppm) (Figure 4). The activation barrier at coalescence temperature $\Delta G_c^{\ddagger}$ was estimated to be 50.5 ± 0.8 ($\Delta\nu$ = 358.6 Hz, T_c = 268 K) for **5** and 41.3 ± 0.8 kJ mol^{-1} ($\Delta\nu$ = 446.2 Hz, T_c = 223 K) for **2**, compared to $\Delta G_c^{\ddagger}$ = 38.7 ± 0.8 kJ mol^{-1} ($\Delta\nu$ = 380.7 Hz, T_c = 208 K) for the lutetium analogue.[9]

The holmium alkyl complexes **9** and **10**, generated in situ, were found to react smoothly at room temperature with PhSiH$_3$ to form the corresponding hydride complexes [Ho(L)(μ-H)(THF)$_n$]$_2$ (L = tbmp, n = 3, **11**; L = etbmp, n = 2, **12**) (Scheme 2). Due to their relatively high solubility the hydride complexes were isolated in 33 and 42% yields, respectively. They are stable at −40 °C for several weeks. Although we have not succeeded in obtaining diffraction-quality crystals, the identity of both complexes was confirmed by means of elemental analysis. By analogy with the lutetium hydride [Lu(tbmp)(μ-H)(THF)$_2$]$_2$,[9] a dimeric structure should be expected.

The NMR investigations on the reaction of the yttrium alkyl complex **1** with PhSiH$_3$ showed the formation of the corresponding hydride **13**, as indicated by the presence of a triplet resonance at δ 7.07 ppm with $^1J_{YH}$ = 27.5 Hz. The triplet pattern of the resonance clearly indicates two equivalent yttrium centers in a dimeric yttrium hydride species.[4] The ^{1}H NMR spectrum shows a C_s-symmetric molecule with a singlet resonance for both Me and ^{t}Bu groups and two doublets for the aromatic protons. In contrast to the case for the lutetium analogue, all attempts to isolate the yttrium hydride **13** failed.

Bis(phenolato)-Bridged Complex. The reaction of 1,4-dithiabutanediylbis(6-*tert*-butyl-4-methylphenol) (etbmpH$_2$) with [Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$] in a 2:1 ratio resulted in formation of the bis(phenolato)-bridged complex [Lu$_2$(etbmp)$_3$(THF)$_2$] (**8**) (Scheme 2). This complex had also been found as a decomposition product of the previously reported lutetium hydrido complex [Lu(etbmp)(μ-H)(THF)]$_2$.[9] Diffraction-quality crystals of **8** were obtained upon storing a THF/pentane solution of the hydride at −40 °C over a period of several days. An X-ray diffraction analysis revealed that the compound **8** crystallized in a centrosymmetric space group as a racemate of homochiral dimers with C_2 symmetry.[16a] As shown in Figure 5, the lutetium atom adopts a seven-coordinate geometry that can best be described as a distorted pentagonal bipyramid, as indicated by the

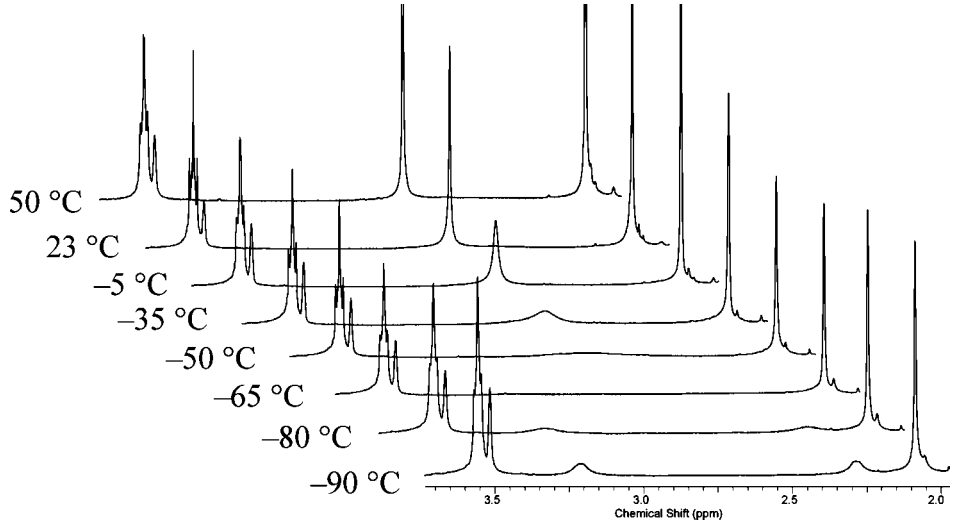


Figure 3. Variable-temperature ^{1}H NMR spectra of [Y(etbmp)(CH$_2$SiMe$_3$)(THF)$_n$] (**2**).

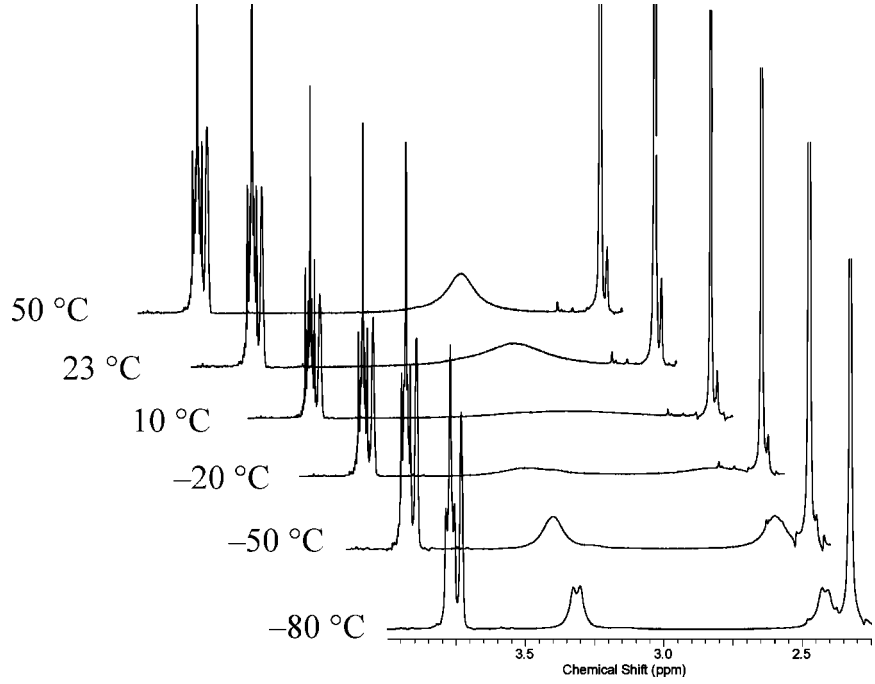


Figure 4. Variable-temperature ^{1}H NMR spectra of [Sc(etbmp)(CH_2SiMe_3)(THF)] (**5**).

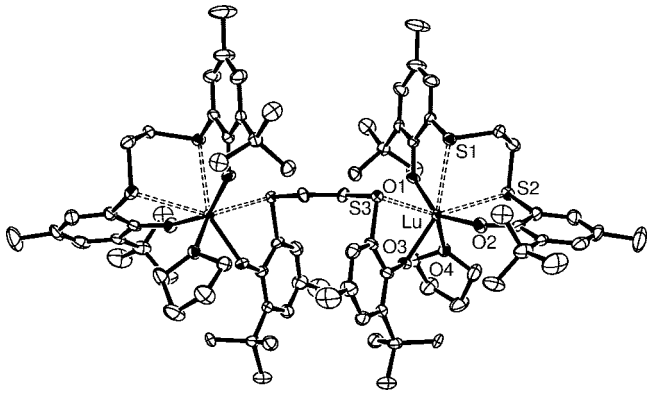


Figure 5. Molecular structure of $[Lu_2(etbmp)_3(THF)_2]\cdot 2C_5H_{10}$ (**8**) (ellipsoids with 50% probability). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Lu−O1 = 2.118(5), Lu−O2 = 2.122(5), Lu−O3 = 2.139(5), Lu−O4 = 2.316(5), Lu−S1 = 2.886(2), Lu−S2 = 2.923(2), Lu−S3 = 2.844(2); O1−Lu−O2 = 147.1(2), O4−Lu−S3 = 137.77(14), S1−Lu−S2 = 73.85(6), S2−Lu−S3 = 145.75(6), O3−Lu−O4 = 77.63(19).

corresponding angles O1−Lu−O2 = 147.1(2)°, S2−Lu−S3 = 145.75(6)°, S1−Lu−O3 = 141.46(14)°, and S1−Lu−O42 = 139.39(15)°.

Analogously to **7**, three Lu−S bond lengths of 2.886(2), 2.923(2), and 2.844(2) Å indicate the presence of coordinative bonds. The ^{1}H NMR spectrum of **8** shows at room temperature the equivalence of three ligand moieties, as indicated by the presence of only one set of signals. Thus, the ethylene bridge protons in the backbone appear as a singlet at δ 2.78 ppm. The structure of **8** is remarkably different from that reported for the lanthanum complex [La_2(xytbmp)$_3$] with a 1,2-xylylene-linked bis(phenolato) ligand, which reveals two unsymmetrically coordinated lanthanum centers and can be considered as consisting of the cationic fragment $[Ln(OSSO)]^+$ coordinated to the anionic fragment $[Ln(OSSO)_2]^-$.[16b]

Hydrosilylation of 1-Hexene. The yttrium complex **2** was tested as a precatalyst in the hydrosilylation of 1-hexene (Scheme 3), and the results are summarized in Table 2.

Three silanes, $PhSiH_3$, $^nBuSiH_3$, and Ph_2SiH_2, have been used for the hydrosilylation of 1-hexene. In all cases high conversion (91−100%) and selectivity (98−99%) toward the 1,2-addition product (Si added to the terminal position) were achieved. At 60 °C hydrosilylation with $PhSiH_3$ gave 91% of conversion after 4 h, whereas with $^nBuSiH_3$ and Ph_2SiH_2 nearly quantitative conversion was observed in ^{1}H NMR spectra after 19 h. Monitoring the hydrosilylation reaction with $PhSiH_3$ at 60 °C by ^{1}H NMR spectroscopy showed that, after 80% conversion within the first 2 h, a deactivation of the catalyst took place and no more than 91% conversion could be reached after the total reaction time of 4 h. The hydrosilylation of 1-hexene with a 10-fold excess of $PhSiH_3$ at room temperature showed a pseudo-first-order dependence with a rate constant of $k = (2.78 \pm 0.05) \times 10^{-2}$ min^{-1} (Figure 6).

The yttrium complex **2** was found to be more active than the scandium analogue **5** (Table 2, entries 2 and 4). This observation is in agreement with the literature data showing a correlation between the increasing ionic radius of Ln^{3+} and increasing rate (turnover frequency) of hydrosilylation.[3d,5a] Mechanistically, it is very likely that in the first step a silane reacts with the alkyl complex with formation of a reactive hydride species that is an active hydrosilylation catalyst. A monomeric d^0 metal hydride has been thought to be an active metal species in hydrosilylation reactions for several cyclopentadienyl-based early-transition-metal systems studied so far.[3b,d] This route is supported by formation of the yttrium hydride **13** and $PhSiH_2CH_2SiMe_3$ in the NMR reaction of **2** with $PhSiH_3$. Moreover, $PhSiH_2CH_2SiMe_3$ was also observed in the ^{1}H NMR spectra taken at the beginning of all hydrosilylation reactions, as indicated by the presence of two triplet resonances at δ −0.11 (CH_2Si) and 4.53 ppm (SiH_2) with $^3J_{HH}$ = 4.8 Hz. The proposed catalytic cycle is analogous to that proposed by Tilley and Gountchev for the hydrosilylation of olefins catalyzed by the bis(silylamido) yttrium hydride [Y(DADMB)(μ-H)(THF)]$_2$.[6] It involves a fast irreversible insertion of the olefin into the metal−hydrogen bond

Scheme 3

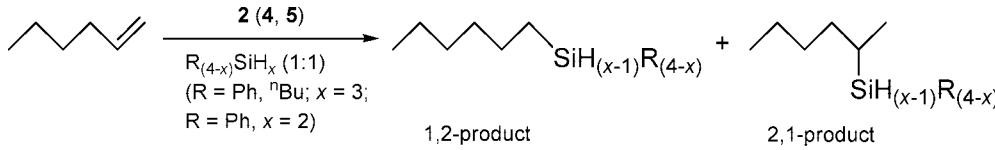


Table 2. Hydrosilylation of 1-Hexene Catalyzed by Scandium and Yttrium Bis(phenolato) Complexes[a]

						amt of regioisomer (%)	
entry	cat. (metal)	silane	T (°C)	t (h)	conversn (%)[b]	1,2[f]	2,1[f]
1	**2** (Y)	$PhSiH_3$	25	4.5	41.5	n.d.	n.d.
			25	24	85.5	n.d.	n.d.
			25	48	93	98	2
2	**2** (Y)	$PhSiH_3$	60	4	91[c]	99	1
3	**4** (Sc)	$PhSiH_3$	50	24	39	n.d.	n.d.
			50	65.5	66[d]	99	1
4	**5** (Sc)	$PhSiH_3$	60	43	60[e]	80	20
5	**2** (Y)	Ph_2SiH_2	50	19	99	99	<1
6	**2** (Y)	$^nBuSiH_3$	25	24	85	n.d.	n.d.
			25	57	96.5	>98.5	<1.5
7	**2** (Y)	$^nBuSiH_3$	50	19	100	>98.5	<1.5

[a] Reaction conditions: 0.0136 mmol (2.3 mol %) of **2**, 0.0160 mmol (2.7 mol %) of **4**, **5** in C_6D_6, substrate/precatalyst molar ratio of 40, silane/olefin ratio of 1.02−1.04. [b] Calculated by ^1H NMR spectroscopy. [c] Ca. 3% of unidentified side products. [d] The catalytic reaction was halted after about 66% consumption of 1-hexene. [e] The catalytic reaction was halted after about 60% consumption of 1-hexene. [f] The ratio of 1,2- and 2,1-regioisomers was calculated by integration of the SiH_2 resonances in the ^1H NMR spectra.

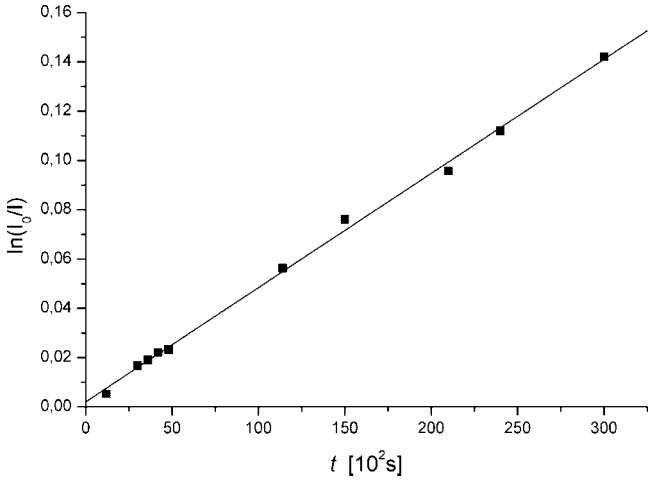
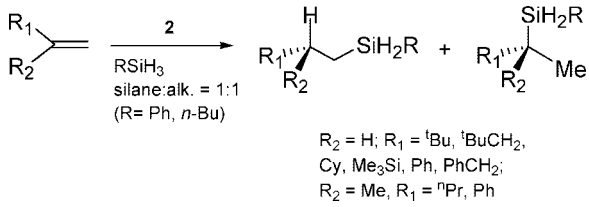


Figure 6. Pseudo-first-order plot for the disappearance of 1-hexene catalyzed by **2** (25 °C, C_6D_6).

Scheme 4



to give an alkyl species, which then reacts with a silane to give a silylated product and to regenerate the hydride. The insertion of 1-hexene into the metal−hydrogen bond with formation of an *n*-hexyl complex has been observed for [Lu(etbmp)(μ-H)(THF)]$_2$ in C_6D_6.[17a]

Hydrosilylation of Monoolefins. We have investigated a wide range of aliphatic and aromatic olefins in hydrosilylation reactions with $PhSiH_3$ and $^nBuSiH_3$ catalyzed by complex **2** (Scheme 4), and the results of these experiments are collected in Table 3.

As has been noted for other lanthanide and yttrium hydrosilylation catalysts,[3–6] both 1,2- and 2,1-additions of a silane to a double bond are observed and the selectivity is governed by steric and electronic factors of both catalyst and substrate. Thus, in the case of aliphatic terminal olefins formation of anti-Markovnikov (1,2-addition) products with high selectivity (92−99%) has been observed (Table 3, entries 2−5). Surprisingly, 3,3-dimethylbut-1-ene did not undergo hydrosilylation at 25 °C (entry 1). The reaction of trimethylvinylsilane with $PhSiH_3$ in the presence of **2** led to the corresponding 1,2-addition product with only 85% selectivity (entry 7). In contrast to the case for the aliphatic olefins, styrene was hydrosilylated with $PhSiH_3$, giving the secondary addition product (1-phenethyl)phenylsilane with 97% selectivity (entry 8). With $^nBuSiH_3$ no hydrosilylation of styrene was observed (entry 9), presumably due to steric effects of the bulkier ^{n}Bu group. The secondary regioselectivity for styrene, also observed for other lanthanide and yttrium hydrosilylation catalysts,[3d,4e,5,6] has been rationalized in terms of η^n coordination between the Lewis acidic/electrophilic metal center and the π-electron system of styrene, directing the insertion reaction toward the α-phenylalkyl intermediate. This stabilization of a rare-earth metal by an aromatic ring has been commonly observed in other benzyl and arene complexes.[3d,4e,18] The interactions between yttrium and the phenyl ring are also indicated by the deep yellow color of the hydrosilylation reaction mixture. Moreover, a lutetium hydride complex with a bis(phenolato) ligand, [Lu(etbmp)(μ-H)(THF)]$_2$, was found to react regioselectively with styrene to yield the 2-phenylethyl complex [Lu(etbmp)(CH(Ph)CH$_3$)(THF)].[9] This strong preference of

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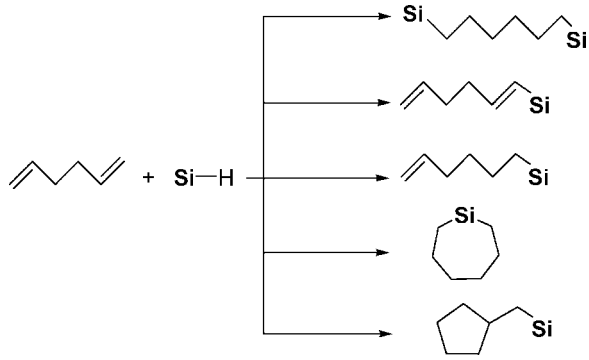
Table 3. Hydrosilylation of Alkenes Catalyzed by the Yttrium Bis(phenolato) Complex 2[a]

entry	alkene	silane	T (°C)	t (h)	%-conv[b]	1,2- (%)[d]	2,1- (%)[d]
1	^{t}BuCH=CH$_2$	PhSiH$_3$	25	24	0		
2	^{t}BuCH=CH$_2$	PhSiH$_3$	50	20	75.5	n.d.	n.d.
			50	63	93	>99	<1
3	^{t}BuCH=CH$_2$	^{n}BuSiH$_3$	50	21	73		
			50	39	89		
			50	54	92	98.5	1.5
4	^{t}BuCH$_2$CH=CH$_2$	PhSiH$_3$	50	37	88	92	8
5	^{n}PrC(Me)=CH$_2$	PhSiH$_3$	60	20	72	n.d.	n.d.
			60	41	85	99	<1
6	CyCH=CH$_2$	PhSiH$_3$	50	21	99	>99	<1
7	Me$_3$SiCH=CH$_2$	PhSiH$_3$	50	21	99	85	15
8	PhCH=CH$_2$	PhSiH$_3$	50	19	75	3	97
			50	35	94.5[c]		
9	PhCH=CH$_2$	^{n}BuSiH$_3$	50	120	0		
10	Ph$_2$C=CH$_2$	PhSiH$_3$	50	21	0		
11	PhC(Me)=CH$_2$	PhSiH$_3$	60	20	8	100	
12	PhCH$_2$CH=CH$_2$	PhSiH$_3$	50	20	99	93.5	6.5
13	PhCH$_2$CH=CH$_2$	^{n}BuSiH$_3$	50	69	91	95	5

[a] Reaction conditions: 0.0136 mmol (2.3 mol %) of **2** in C_6D_6, substrate/precatalyst molar ratio of 40, silane/olefin ratio of 1.02−1.04. [b] Calculated by ^{1}H NMR spectroscopy. [c] 5−10% of another byproduct was also formed. [d] The ratio of 1,2- and 2,1-regioisomers was calculated by integration of the resonances in the ^{1}H NMR spectra.

Scheme 5



styrene for a secondary insertion into a metal−hydride bond has been previously reported.[19] Both the extension of an alkyl chain in the case of allylbenzene (entries 12 and 13) and the lack of an aromatic ring in vinylcyclohexane (entry 6) result in formation of 1,2-addition products with the silicon added to the less hindered side. In the case of α-methylstyrene steric effects presumably prevent interactions between yttrium and the aromatic ring and the addition of PhSiH$_3$ to the double bond, as indicated by low conversion (8%) and high selectivity toward 1,2-addition product (99%) (Table 3, entry 11). Furthermore, no reaction with 1,1-diphenylethylene and *trans*-1,2-diphenylethene was observed (entry 10). The lack of reactivity toward *trans*-1,2-diphenylethene has also been reported for the bis(silylamido) yttrium hydride [Y(DADMB)(μ-H)(THF)]$_2$.[6]

Hydrosilylation of 1,5-Hexadiene. The possible products of hydrosilylation of 1,5-hexadiene are summarized in Scheme 5. Group 8 metal catalysts are generally known to yield predominantly linear products such as 5-hexenylsilane, 1,5-hexadienylsilane, and 1,6-bis(silyl)hexane or silacycloheptane, depending on the diene/silane ratio and the types of silanes and catalysts.[20] In contrast, hydrosilylation catalyzed by rare-earth metals generally proceeds via intramolecular carbon−carbon bond formation, yielding (silylmethyl)cyclopentane.[3c–e,4c,5,8a]

The dimeric hydrido complex [Y(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$N^{t}Bu)(μ-H)(THF)]$_2$ with a linked amido−cyclopentadienyl ligand was found to catalyze the hydrosilylation of 1,5-hexadiene with PhSiH$_3$ (1:1 ratio) to give a mixture of both linear and cyclic products as well as oligomers.[4d] The metallocene samarium alkyl complex [Sm(η^5-C$_5$Me$_5$)$_2${CH(SiMe$_3$)$_2$}] was reported to yield predominantly (phenylsilylmethyl)cyclopentane, whereas in the case of [Sm{(η^5-C$_5$Me$_4$)$_2$SiMe$_2$}{CH(SiMe$_3$)$_2$}] and (*R*)-[Sm{(η^5-C$_5$Me$_4$)}{(−)-menthylC$_5$H$_3$}SiMe$_2${CH(SiMe$_3$)$_2$}] ca. 30% of linear products arising from a process involving skeletal rearrangement of 1,5-hexadiene was observed.[3d] On the other hand, hydrosilylation of 1,6-heptadiene with PhSiH$_3$ catalyzed by the permethylyttrocene complex [Y(η^5-C$_5$Me$_5$)$_2$-{CH(SiMe$_3$)$_2$}] resulted in the formation of 1,7-bis(phenylsilyl)heptane.[3b] Hydrosilylation of 1,5-hexadiene with PhSiH$_3$ ([Y]:[silane]:[diene] = 1:82:40) at 50 °C catalyzed by **2** led predominantly to 1,6-bis(phenylsilyl)hexane in ca. 90% yield with ca. 10% of (phenylsilylmethyl)cyclopentane, as shown by ^{1}H and ^{13}C NMR spectroscopy. Surprisingly, the analogous hydrosilylation with ^{n}BuSiH$_3$ resulted in reversed selectivity, yielding 84% of the cyclic product (Scheme 6). The proposed mechanism for hydrosilylation of 1,5-hexadiene catalyzed by **2** is presented in Scheme 7.

Analogously to the hydrosilylation of monoolefins, it is likely that the reaction of **2** with RSiH$_3$ initiates the catalytic cycle with concomitant generation of the yttrium hydride. The anti-Markovnikov addition of the hydride to 1,5-hexadiene leads to the intermediate yttrium 5-hexenyl complex, which further reacts via two competing reaction pathways, **A** and **B**. In the case of PhSiH$_3$ pathway **A** is favored, yielding the linear product **A1**. The ring closure pathway (**A2**) to give silacycloheptane was not observed. In contrast to the reaction with PhSiH$_3$, intramolecular insertion of the yttrium 5-hexenyl complex leads to the yttrium methylcyclopentyl complex in the presence of ^{n}BuSiH$_3$, which undergoes intermolecular σ-bond metathesis with ^{n}BuSiH$_3$ to yield (silylmethyl)cyclopentane. This distinctly different reactivity of PhSiH$_3$ and ^{n}BuSiH$_3$ can be rationalized by the slower attack on the 1-hexenyl yttrium species by the bulkier ^{n}BuSiH$_3$. In addition, intramolecular (labile) coordination of the dangling double bond at the Lewis acidic yttrium center may play a role.[17c]

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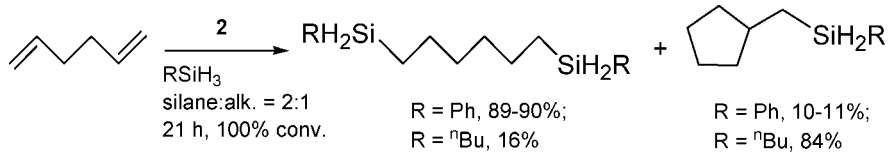
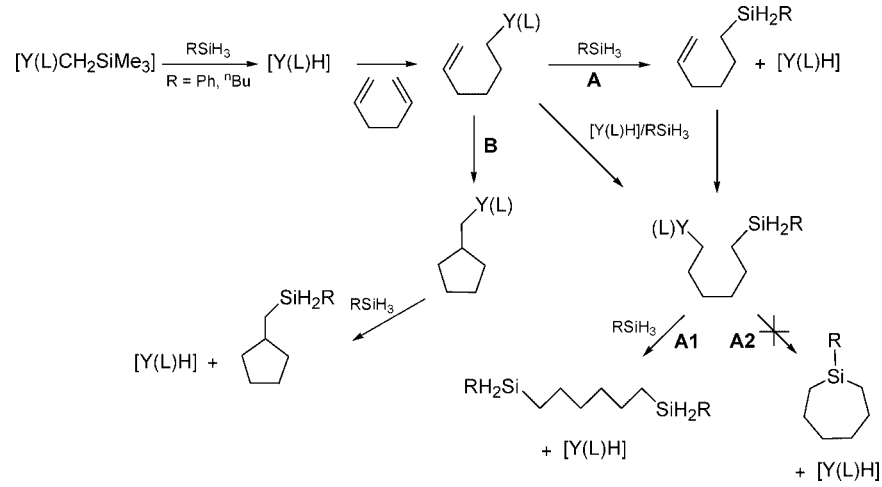
Scheme 6



Scheme 7



Conclusion

Following our initial studies on the lutetium (trimethylsilyl)-methyl and hydrido complexes with tridentate [OSO]-type and tetradentate [OSSO]-type bis(phenolato) ligands,[9] we have now extended this chemistry to other rare-earth metals. The reaction of the alkyl complexes with phenylsilane leads to the formation of the corresponding hydrido complexes, which could be isolated for lutetium[9] and holmium. The catalytic activity of the scandium and yttrium complexes has been explored in the hydrosilylation of a variety of aliphatic and aromatic monoolefins and 1,5-hexadiene. The hydrosilylation reaction is proposed to occur via the mechanism generally accepted for d^0 systems, involving fast olefin insertion into a metal−hydride bond, followed by a slow σ-bond metathesis reaction with a silane. The yttrium complex was found to be more active than the scandium analogue. The bis(phenolate) complexes with an [OSO]-/[OSSO]-type framework exhibits a high regioselective preference for terminal (1,2) addition in the case of aliphatic monoolefins and a high preference for internal (2,1) addition with styrene. The selectivity toward secondary addition in the hydrosilylation of styrene using phenylsilane is remarkably higher than that reported for the lanthanum amido complex $[La\{N(SiHMe_2)_2\}_2\{CH(PPh_2NSiMe_3)_2\}]$[5b,c] and an yttrium alkyl complex bearing a bis(silylamido) ligand, [Y(DADMB)-Me(THF)$_2$],[6] and is comparable with the selectivity of $[La\{N(SiMe_3)_2\}_3]$.[5a] The steric characteristics of both olefin and silane substituents were found to influence the reactivity. The yttrium catalyst is sufficiently reactive to allow a secondary silane (Ph_2SiH_2) to be used in the hydrosilylation of 1-hexene. An intriguing influence of the nature of a silane on the addition reaction pathway has been observed for 1,5-hexadiene. With phenylsilane the linear product is formed with high selectivity, whereas with *n*-butylsilane formation of the cyclic product is observed. This may reflect the fact that the rate constant for the hydrosilylation of the 5-hexenyl intermediate is significantly decreased for the bulkier *n*-butylsilane.

Experimental Section

General Procedures. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. THF, *n*-pentane, and C_6D_6 were distilled under argon from sodium/benzophenone ketyl prior to use. $PhSiH_3$ and $^nBuSiH_3$ were dried over sodium. The following compounds were prepared according to published procedures: $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Sc, Y, Ho),[21] 2,2′-thiobis(6-*tert*-butyl-4-methylphenol) (tbmpH$_2$).[22] 1,3-Dithiapropanediylbis(6-*tert*-butyl-4-methylphenol) (mtbmpH$_2$) and 1,4-dithiabutanediylbis(6-*tert*-butyl-4-methylphenol) (etbmpH$_2$) were synthesized according to a modification of the methods reported in the literature.[23] All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded on a Varian Mercury 200 BB (^{1}H, 200.0 MHz), Varian Unity 500 (^{1}H, 499.6 MHz; ^{13}C, 125.6 MHz), or Bruker DRX 400 spectrometer (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz) at 25 °C unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. Elemental analyses were performed by the Microanalytical Laboratory of this department. In some cases the results were not satisfactory and the best values from repeated runs were given. In the context of organometallic rare-earth metal compounds, this difficulty was also observed by other groups and may be ascribed to the formation of inert carbides.[24] Metal analyses were performed by complexometric titration.[25] The sample (15−30 mg) was dissolved in THF (2 mL) or acetonitrile (2 mL) and titrated with a 0.005 M aqueous solution of EDTA using xylenol orange as indicator and a 1 M ammonium

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(25) Das, B.; Shome, S. C. *Anal. Chim. Acta* **1971**, *56*, 483.

acetate buffer solution (20 mL). The GC/MS(EI) experiments were run on a Varian VF-5ms spectrometer.

[Y(tbmp)(CH$_2$SiMe$_3$)(THF)$_n$] (1; n = 1, 2). To a solution of [Y(CH$_2$SiMe$_3$)$_3$(THF)$_{2.4}$] (0.219 g, 0.418 mmol) in pentane (3 mL) was added a solution of thiobis(6-*tert*-butyl-4-methylphenol) (tbmpH$_2$; 0.150 g, 0.418 mmol) in pentane (2 mL) at room temperature with stirring. Within 1 h a pale yellowish precipitate formed. The supernatant was decanted, and the precipitate was washed with pentane and dried. **1** was isolated as an off-white powder upon recrystallization from THF/pentane (0.100 g, 35% for n = 2). ^{1}H NMR (400.1 MHz, THF-d_8): δ −0.84 (d, $^2J_{YH}$ = 3.0 Hz, 2H, YCH_2), −0.03 (s, 9H, SiMe$_3$), 1.38 (s, 18H, CMe$_3$), 1.77 (m, β-H, THF), 2.12 (s, 6H, Me), 3.62 (m, α-H, THF), 6.84 (d, $^4J_{HH}$ = 2.3 Hz, 2H, 3-C$_6$H$_2$), 7.20 (d, $^4J_{HH}$ = 2.3 Hz, 2H, 5-C$_6$H$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): δ 4.6 (SiMe$_3$), 20.8 (Me), 24.8 (d, $^1J_{YC}$ = 45.1 Hz, Y*C*H$_2$), 26.4 (THF), 30.2 (C*Me*$_3$), 35.8 (*C*Me$_3$), 68.2 (THF), 124.0 (4-C$_6$H$_2$), 126.6 (2-C$_6$H$_2$), 129.4 (3-C$_6$H$_2$), 133.9 (5-C$_6$H$_2$), 137.8 (6-C$_6$H$_2$), 166.0 (d, $^2J_{YC}$ = 3.5 Hz, 1-C$_6$H$_2$). Anal. Calcd for C$_{34}$H$_{55}$O$_4$SSiY (n = 2) (676.86): Y, 13.13. Found: Y, 12.84.

[Y(etbmp)(CH$_2$SiMe$_3$)(THF)$_n$] (2; n = 1, 2). A solution of [Y(CH$_2$SiMe$_3$)$_3$(THF)$_3$] (0.200 g, 0.353 mmol) in pentane (3 mL) was added dropwise to a solution of 1,4-dithiabutanediylbis(6-*tert*-butyl-4-methylphenol) (etbmpH$_2$; 0.148 g, 0.353 mmol) in THF (1 mL). The reaction mixture was stirred at room temperature for 2 h, and then pentane (2 mL) was added. Upon storage overnight at −40 °C a white precipitate of **2** formed. The supernatant was decanted, and the precipitate was washed with pentane and dried (0.185 g, 71% for n = 2). ^{1}H NMR (400.1 MHz, THF-d_8): δ −0.94 (d, $^2J_{YH}$ = 3.0 Hz, 2H, YCH_2), −0.08 (s, 9H, SiMe$_3$), 1.44 (s, 18H, CMe$_3$), 1.77 (m, β-H, THF), 2.13 (s, 6H, Me), 2.75 (s, 4H, SCH$_2$), 3.62 (m, α-H, THF), 6.92 (m, 4H, 3-/5-C$_6$H$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): δ 4.8 (SiMe$_3$), 20.7 (Me), 21.8 (d, $^1J_{YC}$ = 41.6 Hz, Y*C*H$_2$), 26.4 (THF), 30.2 (C*Me*$_3$), 35.7 (*C*Me$_3$), 36.7 (SCH$_2$), 68.2 (THF), 119.8 (2-C$_6$H$_2$), 124.6 (4-C$_6$H$_2$), 129.2, 132.3 (3-/5-C$_6$H$_2$), 138.3 (6-C$_6$H$_2$), 166.6 (d, $^2J_{YC}$ = 3.5 Hz, 1-C$_6$H$_2$). Anal. Calcd for C$_{36}$H$_{59}$O$_4$S$_2$SiY (n = 2) (736.98): C, 58.67; H, 8.07; Y, 12.06. Found: C, 58.46; H, 7.70; Y, 11.82.

[Y(mtbmp)(CH$_2$SiMe$_3$)(THF)] (3). A solution of [Y(CH$_2$SiMe$_3$)$_3$(THF)$_3$] (0.200 g, 0.353 mmol) in pentane (3 mL) was added dropwise to 1,3-dithiapropanediylbis(6-*tert*-butyl-4-methylphenol) (mtbmpH$_2$; 0.143 g, 0.353 mmol) in THF (0.5 mL). The reaction mixture was stirred at room temperature for 1 h, and then pentane (2 mL) was added. Upon storage overnight at −40 °C a white precipitate of **3** formed. The supernatant was decanted, and the precipitate was washed with pentane and dried (0.152 g, 66%). ^{1}H NMR (400.1 MHz, THF-d_8): δ −0.85 (d, $^2J_{YH}$ = 3.5 Hz, 2H, YCH_2), −0.04 (s, 9H, SiMe$_3$), 1.48 (s, 18H, CMe$_3$), 1.77 (m, 4H, β-H, THF), 2.14 (s, 6H, Me), 3.62 (m, 4H, α-H, THF), 4.02 (s, 2H, SCH$_2$), 6.98 (m, 4H, 3-/5-C$_6$H$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): δ 4.5 (SiMe$_3$), 20.6 (Me), 24.5 (d, $^1J_{YC}$ = 44.2 Hz, Y*C*H$_2$), 26.4 (THF), 30.4 (C*Me*$_3$), 35.9 (*C*Me$_3$), 50.1 (SCH$_2$), 68.2 (THF), 124.2 (2-C$_6$H$_2$), 124.8 (4-C$_6$H$_2$), 130.5, 134.4 (3-/5-C$_6$H$_2$), 138.7 (6-C$_6$H$_2$), 165.6 (d, $^2J_{YC}$ = 3.5 Hz, 1-C$_6$H$_2$). Anal. Calcd for C$_{31}$H$_{49}$O$_3$S$_2$SiY (650.85): C, 57.21; H, 7.59; Y, 13.66. Found: C, 57.14; H, 8.11; Y, 13.52.

[Sc(tbmp)(CH$_2$SiMe$_3$)(THF)$_n$] (4; n = 1, 2). To a solution of [Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (0.100 g, 0.222 mmol) in pentane (3 mL) was added a solution of thiobis(6-*tert*-butyl-4-methylphenol) (tbmpH$_2$; 0.080 g, 0.222 mmol) in THF (0.5 mL) at room temperature with stirring. After 1 h of stirring solvents were removed in vacuo and pentane was added (3 mL). Upon storage overnight at −40 °C a yellowish precipitate of **4** formed. The supernatant was decanted, and the precipitate was washed with pentane and dried (0.05 g, 36% for n = 2). ^{1}H NMR (400.1 MHz, THF-d_8): δ −0.29 (s, 2H, ScCH_2), −0.03 (s, 9H, SiMe$_3$), 1.39 (s, 18H, CMe$_3$), 1.77 (m, β-H, THF), 2.10 (s, 6H, Me), 3.62 (m, α-H, THF), 6.85 (m, 2H, 3-C$_6$H$_2$), 7.08 (m, 2H, 5-C$_6$H$_2$). ^{1}H NMR (400.1 MHz, C$_6$D$_6$): δ 0.05 (s, 2H, ScCH_2), 0.53 (s, 9H, SiMe$_3$), 1.19 (br s, 4H, THF), 1.66 (s, 18H, CMe$_3$), 2.11 (s, 6H, Me), 3.72 (br s, 4H, α-H, THF), 7.10 (d, $^4J_{HH}$ = 2.3 Hz, 2H, 3-C$_6$H$_2$), 7.20 (m, 2H, 5-C$_6$H$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): δ 4.1 (SiMe$_3$), 20.8 (Me), 26.4 (THF), 30.1 (C*Me*$_3$), 35.8 (*C*Me$_3$), 68.2 (THF), 124.8 (4-C$_6$H$_2$), 127.2 (2-C$_6$H$_2$), 129.8 (3-C$_6$H$_2$), 133.4 (5-C$_6$H$_2$), 137.9 (6-C$_6$H$_2$), 165.6 (1-C$_6$H$_2$); the Sc*C*H$_2$ resonance was not observed. Anal. Calcd for C$_{34}$H$_{55}$O$_4$SScSi (n = 2) (632.92): Sc, 7.10. Found: Sc, 7.50.

[Sc(etbmp)(CH$_2$SiMe$_3$)(THF)] (5). A solution of [Sc(CH$_2$SiMe$_3$)$_3$(THF)$_3$] (0.100 g, 0.222 mmol) in pentane (3 mL) was added dropwise to a suspension of 1,4-dithiabutanediylbis(6-*tert*-butyl-4-methylphenol) (etbmpH$_2$; 0.093 g, 0.222 mmol) in pentane (1 mL). After a while a colorless solution formed that was stirred at room temperature for 2 h. Upon storage of the solution overnight at −40 °C colorless crystals of **5** formed that were filtered, washed with pentane, and dried (0.085 g, 62%). ^{1}H NMR (400.1 MHz, THF-d_8): δ −0.17 (s, 9H, SiMe$_3$), −0.11 (br s, 2H, ScCH_2), 1.47 (s, 18H, CMe$_3$), 1.77 (m, 4H, β-H, THF), 2.16 (s, 6H, Me), 2.67 (v br, 4H, SCH$_2$), 3.62 (m, 4H, α-H, THF), 6.98 (m, 4H, 3-/5-C$_6$H$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): δ 3.6 (SiMe$_3$), 20.8 (Me), 26.4 (THF), 29.9 (C*Me*$_3$), 34.8 (br, Sc*C*H$_2$), 35.7 (*C*Me$_3$), 37.5 (SCH$_2$), 68.2 (THF), 118.6 (2-C$_6$H$_2$), 126.2 (4-C$_6$H$_2$), 130.3, 132.4 (3-/5-C$_6$H$_2$), 138.0 (6-C$_6$H$_2$), 167.1 (1-C$_6$H$_2$). Anal. Calcd for C$_{32}$H$_{51}$O$_3$S$_2$ScSi (620.93): C, 61.90; H, 8.28; Sc, 7.24. Found: C, 62.46; H, 8.10; Sc, 7.90.

[Y(etbmp)(CH$_2$SiMe$_3$)(NC$_5$H$_5$)$_n$] (6; n = 1, 2). Pyridine (0.030 g, 30 μL, 0.375 mmol) was slowly added to a suspension of **2** (0.070 g, 0.095 mmol) in pentane (3 mL). The reaction mixture was stirred for 1 h at room temperature until the suspension turned pink. Upon storage of the suspension overnight at −40 °C **6** was isolated as a pink powder (0.04 g, 56% for n = 2). ^{1}H NMR (400.1 MHz, C$_6$D$_6$): δ −0.26 (d, $^2J_{YH}$ = 3.2 Hz, 2H, YCH_2), 0.17 (s, 9H, SiMe$_3$), 1.83 (s, 18H, CMe$_3$), 2.16 (s, 6H, Me), 2.46 (s, 4H, SCH$_2$), 6.54 (m, 4H, 3-/5-H, py), 6.76 ("t", 2H, 4-H, py), 6.92 (m, 2H, 3-/5-C$_6$H$_2$), 7.25 (m, 2H, 3-/5-C$_6$H$_2$), 8.89 (br s, 4H, 2-/6-H, py). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): δ 4.8 (SiMe$_3$), 20.8 (Me), 22.0 (d, $^1J_{YC}$ = 41.6 Hz, Y*C*H$_2$), 30.2 (C*Me*$_3$), 35.7 (*C*Me$_3$), 36.7 (SCH$_2$), 119.8 (2-C$_6$H$_2$), 124.3 (3-/5-C, py), 124.6 (4-C$_6$H$_2$), 129.3, 132.3 (3-/5-C$_6$H$_2$), 136.3 (4-C, py), 138.3 (6-C$_6$H$_2$), 150.7 (2-/6-C, py), 166.6 (d, $^2J_{YC}$ = 3.5 Hz, 1-C$_6$H$_2$). Anal. Calcd for C$_{38}$H$_{53}$N$_2$O$_2$S$_2$SiY (n = 2) (750.97): C, 60.78; H, 7.11; N, 3.73; Y, 11.84. Found: C, 58.34; H, 7.03; N, 3.38; Y, 11.71.

[Lu(mtbmp)(CH$_2$SiMe$_3$)(THF)$_n$] (7; n = 1, 2). A solution of [Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (0.200 g, 0.344 mmol) in pentane (3 mL) was added dropwise to 1,3-dithiapropanediylbis(6-*tert*-butyl-4-methylphenol) (mtbmpH$_2$; 0.139 g, 0.344 mmol) in pentane (1 mL). The reaction mixture was stirred at room temperature for 2 h. Within that time a white precipitate of **7** formed. Upon storage overnight at −40 °C the supernatant was decanted and the precipitate was washed with pentane and dried (0.171 g, 61% for n = 2). ^{1}H NMR (400.1 MHz, THF-d_8): δ −0.95 (s, 2H, LuCH_2), −0.03 (s, 9H, SiMe$_3$), 1.48 (s, 18H, CMe$_3$), 1.77 (m, β-H, THF), 2.14 (s, 6H, Me), 3.62 (m, α-H, THF), 4.04 (s, 2H, SCH$_2$), 6.98 (m, 4H, 3-/5-C$_6$H$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): δ 4.6 (SiMe$_3$), 20.6 (Me), 26.4 (THF), 29.2 (Lu*C*H$_2$), 30.6 (C*Me*$_3$), 35.9 (*C*Me$_3$), 49.5 (SCH$_2$), 68.2 (THF), 123.9 (2-C$_6$H$_2$), 124.8 (4-C$_6$H$_2$), 130.4, 134.5 (3-/5-C$_6$H$_2$), 139.2 (6-C$_6$H$_2$), 166.3 (1-C$_6$H$_2$). Anal. Calcd for C$_{35}$H$_{57}$LuO$_4$S$_2$Si (n = 2) (809.02): C, 51.96; H, 7.10; Lu, 21.63. Found: C, 51.55; H, 7.59; Lu, 21.61.

[Lu$_2$(etbmp)$_3$(THF)$_2$] (8). A solution of [Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (0.100 g, 0.172 mmol) in pentane (3 mL) was added dropwise to 1,4-dithiabutanediylbis(6-*tert*-butyl-4-methylphenol) (etbmpH$_2$; 0.151 g, 0.361 mmol) in THF (0.3 mL) at room temperature with stirring. The reaction mixture was stirred at room temperature for 3 h. Upon storage overnight at −40 °C a white precipitate of **8** formed. The supernatant was decanted, and the precipitate was washed with

pentane and dried (0.075 g, 50%). Single crystals of **8** suitable for X-ray diffraction studies were obtained in a decomposition reaction of the hydrido complex [Lu(etbmp)(μ-H)(THF)]$_2$[9] in THF/pentane solution at −40 °C. ^{1}H NMR (400.1 MHz, THF-d_8): δ 1.37 (s, 3 × 18H, CMe_3), 1.77 (m, 2 × 4H, β-H, THF), 2.19 (s, 3 × 6H, Me), 2.78 (s, 3 × 4H, SCH_2), 3.62 (m, 2 × 4H, α-H, THF), 7.06 (m, 3 × 4H, 3-/5-C_6H_2). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): δ 20.7 (Me), 26.4 (THF), 29.9 (CMe_3), 35.6 (CMe_3), 36.5 (SCH_2), 68.2 (THF), 119.5 (2-C_6H_2), 129.3 (4-C_6H_2), 129.9, 134.5 (3-/5-C_6H_2), 136.7 (6-C_6H_2), 154.8 (1-C_6H_2). Anal. Calcd for $C_{80}H_{112}Lu_2O_8S_6$ (1744.10): C, 55.09; H, 6.47; Lu, 20.06. Found: C, 55.31; H, 6.72; Lu, 19.79.

[Ho(tbmp)(CH_2SiMe_3)(THF)$_2$] (9). A solution of [Ho(CH_2SiMe_3)$_3$(THF)$_2$] (0.165 g, 0.289 mmol) in pentane (5 mL) was added dropwise to a solution of thiobis(6-*tert*-butyl-4-methylphenol) (tbmpH$_2$; 0.104 g, 0.289 mmol) in pentane (5 mL) at room temperature with stirring. The resulting yellow-orange solution was stirred for 1 h, and upon storage overnight at −40 °C a yellow precipitate of **9** formed. The supernatant was decanted, and the precipitate was washed with pentane and dried (0.085 g, 39%). Anal. Calcd for $C_{34}H_{55}HoO_4SSi$ (752.89): C, 54.24; H, 7.36; Ho, 21.91. Found: C, 55.03; H, 6.87; Ho, 21.84.

[Ho(etbmp)(CH_2SiMe_3)(THF)] (10). A solution of [Ho(CH_2SiMe_3)$_3$(THF)$_2$] (0.165 g, 0.289 mmol) in pentane (3 mL) was added dropwise to a suspension of 1,4-dithiabutanediylbis(6-*tert*-butyl-4-methylphenol) (etbmpH$_2$; 0.121 g, 0.289 mmol) in pentane (3 mL) at room temperature with stirring. The resulting pink solution was stirred for 1 h, and upon storage overnight at −40 °C a pink precipitate of **10** formed. The supernatant was decanted, and the precipitate was washed with pentane and dried (0.104 g, 48%). Anal. Calcd for $C_{32}H_{51}HoO_3S_2Si$ (740.90): C, 51.88; H, 6.94; Ho, 22.26. Found: C, 53.16; H, 6.70; Ho, 22.06.

[Ho(tbmp)(μ-H)(THF)$_3$]$_2$ (11). A solution of [Ho(CH_2SiMe_3)$_3$(THF)$_2$] (0.215 g, 0.376 mmol) in pentane (2 mL) was added dropwise to a solution of thiobis(6-*tert*-butyl-4-methylphenol) (tbmpH$_2$; 0.134 g, 0.374 mmol) in pentane (3 mL) at room temperature with stirring. After 10 min an orange-pink suspension was observed. After 30 min $PhSiH_3$ was added (0.26 mL, 2.08 mmol) and the reaction mixture was stirred for a further 2 h. Upon storage overnight at −40 °C a pink precipitate of **11** formed. The supernatant was decanted, and the precipitate was washed with a small amount of pentane and dried (0.092 g, 33%). Anal. Calcd for $C_{34}H_{53}HoO_5S$ (738.79): C, 55.28; H, 7.23; Ho, 22.32. Found: C, 55.10; H, 7.36; Ho, 21.79.

[Ho(etbmp)(μ-H)(THF)$_2$]$_2$ (12). A solution of [Ho(CH_2SiMe_3)$_3$(THF)$_2$] (0.250 g, 0.438 mmol) in pentane (5 mL) was added dropwise to 1,4-dithiabutanediylbis(6-*tert*-butyl-4-methylphenol) (etbmpH$_2$; 0.183 g, 0.437 mmol) in pentane (5 mL) at room temperature with stirring. After 30 min $PhSiH_3$ was added (0.3 mL, 2.43 mmol) and the reaction mixture was stirred for a further 1 h. A pink precipitate started to deposit after a few minutes. Upon storage overnight at −40 °C the supernatant was decanted and the precipitate of **12** was washed with a small amount of pentane and dried (0.135 g, 42%). Anal. Calcd for $C_{32}H_{49}HoO_4S_2$ (726.80): C, 52.88; H, 6.79; Ho, 22.69. Found: C, 52.26; H, 6.85; Ho, 22.04.

Reaction of [Y(tbmp)(CH_2SiMe_3)(THF)] (1) with $PhSiH_3$. $PhSiH_3$ (20 μL, 160 μmol) was added at room temperature to a solution of **1** (0.025 g, 43 μmol) in C_6D_6. The reaction was monitored by NMR spectroscopy. The ^{1}H NMR spectrum after 15 min showed, besides other products, the formation of the hydrido complex **13**. ^{1}H NMR (400.1 MHz, C_6D_6): δ 1.36 (s, 18H, CMe_3), 1.75 (br s, 4H, β-H, THF), 2.10 (s, 6H, Me), 3.61 (br s, 4H, α-H, THF), 6.80 (br s, 2H, 3-C_6H_2), 7.07 (t, $^1J_{YH}$ = 27.5 Hz, 1H, YHY), 7.15 (d, $^4J_{HH}$ = 2.4 Hz, 2H, 5-C_6H_2); other products ($PhSiH_2CH_2SiMe_3$) and educts ($PhSiH_3$):, 0.03 (s, 9H, $SiMe_3$), 0.12 (t, $^3J_{HH}$ = 4.6 Hz, 2H, $SiCH_2Si$), 4.15 (s, 3H, SiH_3), 4.35 (t, $^3J_{HH}$ = 4.6 Hz, 2H, SiH_2), 7.32, 7.56 (m, Ph).

Typical Hydrosilylation Procedure. In a glovebox a precatalyst (**2**, 0.0136 mmol; **4/5**, 0.0160 mmol) and C_6D_6 (0.6 mL) were introduced into a J. Young NMR tube equipped with a Teflon screw cap, and then silane (0.558 mmol) and the appropriate alkene or diene (0.544 mmol) were added by microsyringe. The tube was shaken vigorously, and the homogeneous reaction mixture was maintained at 25, 50, or 60 °C using a water bath. The reaction was monitored by ^{1}H and ^{13}C NMR spectroscopy. The ratio of Markovnikov and anti-Markovnikov regioisomers was calculated by integration of the appropriate signals (in most cases SiH_2) in the ^{1}H NMR spectra. In the case of kinetic studies on the disappearance of 1-hexene with time a 10-fold excess of $PhSiH_3$ was used and the ^{1}H NMR spectra were recorded at 23 °C at regular 10 min intervals for 10 h.

NMR Data of Selected Hydrosilylation Products. 1-Hexylphenylsilane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.75−0.81 (m, 2H, CH_2Si), 0.83 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3), 1.07−1.29 (m, 6H, CH_2), 1.30−1.43 (m, 2H, CH_2), 4.46 (t, $^3J_{HH}$ = 3.7 Hz, 2H, SiH_2), 7.09−7.17 (m, 3H, Ph), 7.44−7.51 (m, 2H, Ph). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 10.4 (CH_2Si), 14.3 (CH_3), 22.9 (CH_2), 25.4 (CH_2), 31.8 (CH_2), 32.9 (CH_2), 128.3 (*m*-C, Ph), 129.8 (*p*-C, Ph), 132.9 (*i*-C, Ph), 135.5 (*o*-C, Ph).

1-Butyl-1-hexylsilane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.57−0.71 (m, 4H, CH_2Si), 0.87 (t, $^3J_{HH}$ = 7.0 Hz, CH_3), 0.90 (t, $^3J_{HH}$ = 7.0 Hz, CH_3), 1.16−1.47 (m, 12H, CH_2), 5.10 (qn, $^3J_{HH}$ = 3.7 Hz, 2H, SiH_2). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 9.2 (CH_2Si), 9.5 (CH_2Si), 14.0 (CH_3), 14.3 (CH_3), 23.0 (CH_2), 25.9 (CH_2), 26.3 (CH_2), 28.1 (CH_2), 31.9 (CH_2), 33.0 (CH_2).

(3,3-Dimethyl-1-butyl)phenylsilane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.70−0.76 (m, 2H, CH_2Si), 0.77 (s, 9H, CH_3), 1.23−1.30 (m, 2H, CH_2), 4.46 (t, $^3J_{HH}$ = 3.7 Hz, 2H, SiH_2). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 4.8 (CH_2Si), 28.8 (CH_3), 31.3 (C), 39.4 (CH_2), 128.3 (*m*-C, Ph), 129.8 (*p*-C, Ph), 132.8 (*i*-C, Ph), 135.5 (*o*-C, Ph).

1-Butyl(3,3-dimethyl-1-butyl)silane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.53−0.60 (m, 2H, CH_2Si), 0.60−0.67 (m, 2H, CH_2Si), 0.85 (s, 9H, CH_3), 0.87 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_2CH_3), 1.24−1.30 (m, 2H, CCH_2), 1.30−1.40 (m, 4H, CH_2), 3.91 (qn, $^3J_{HH}$ = 3.7 Hz, 2H, SiH_2). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 3.9 (*t*-$BuCH_2CH_2Si$), 9.1 (CH_2Si), 14.0 (CH_2CH_3), 26.3 (CH_2), 28.0 (CH_2), 28.9 (CH_3), 31.3 (C), 40.0 (CH_2C).

(4,4-Dimethyl-1-pentyl)phenylsilane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.75−0.79 (m, 2H, CH_2Si), 0.79 (s, 9H, CH_3), 1.13−1.21 (m, 2H, CH_2), 1.32−1.42 (m, 2H, CH_2), 4.48 (t, $^3J_{HH}$ = 3.8 Hz, 2H, SiH_2), 7.11−7.16 (m, 3H, Ph), 7.45−7.52 (m, 2H, Ph). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 11.1 (CH_2Si), 20.4 (CH_2), 29.5 (CH_3), 30.5 (C), 47.9 (CH_2), 128.3 (*m*-C, Ph), 129.8 (*p*-C, Ph), 132.8 (*i*-C, Ph), 135.5 (*o*-C, Ph).

(4,4-Dimethyl-2-pentyl)phenylsilane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 1.05−1.09 (m, 4H, CH_3 + CH), 4.36−4.42 (m, 2H, SiH_2); other signals could not be assigned due to overlapping. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 12.0 (CH), 19.2 (CH_3), 29.8 (CMe_3), 47.2 (CH_2), 128.4 (*m*-C, Ph), 130.1 (*p*-C, Ph), 132.6 (*i*-C, Ph), 135.2 (*o*-C, Ph); C resonance could not be assigned.

2-Cyclohexyl-1-(phenylsilyl)ethane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.66−0.83 (m, 4H, CH_2Si + CH_2), 0.99−1.20 (m, 5H, CH + 2 × CH_2), 1.22−1.32 (m, 2H, CH_2), 1.54−1.67 (m, 4H, CH_2), 4.46 (t, $^3J_{HH}$ = 3.8 Hz, 2H, SiH_2), 7.10−7.17 (m, 3H, Ph), 7.44−7.53 (m, 2H, Ph). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 7.5 (CH_2Si), 26.7 (CH_2), 27.0 (CH_2), 32.9 (CH_2), 33.1 (CH_2), 40.5 (CH), 128.3 (*m*-C, Ph), 129.8 (*p*-C, Ph), 132.9 (*i*-C, Ph), 135.5 (*o*-C, Ph).

1-(Phenylsilyl)-2-(trimethylsilyl)ethane. ^{1}H NMR (400.1 MHz, C_6D_6): δ −0.07 (s, 9H, CH_3), 0.48−0.55 (m, 2H, H_2SiCH_2), 0.71−0.79 (m, 2H, CH_2SiMe_3), 4.51 (t, $^3J_{HH}$ = 3.7 Hz, 2H, SiH_2), 7.14−7.18 (m, 3H, Ph), 7.49−7.54 (m, 2H, Ph). ^{13}C{^{1}H} NMR

Table 4. Experimental Data for the Crystal Structure Determination of the Complexes 5, 7·2THF, and 8·2C$_5$H$_{10}$

	5	**7**·2THF	**8**·2C$_5$H$_{10}$
empirical formula	$C_{32}H_{51}O_3S_2ScSi$	$C_{43}H_{71}LuO_6S_2Si$	$C_{45}H_{68}LuO_4S_3$
M_r	620.90	951.18	944.20
cryst size/mm	0.18 × 0.18 × 0.08	0.48 × 0.42 × 0.16	0.13 × 0.12 × 0.04
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/c$	$C2/c$
a/Å	10.604(17)	13.4712(12)	13.2096(13)
b/Å	17.30(2)	27.631(3)	26.185(3)
c/Å	38.19(5)	13.4928(12)	27.025(3)
β/deg	90	114.6650(10)	96.358(2)
U/Å^3	7006(17)	4564.2(7)	9290.3(17)
Z	8	4	8
D_c/g cm^{-3}	1.177	1.384	1.350
μ(Mo Kα)/mm^{-1}	0.392	2.323	2.298
F(000)	2672	1976	3911
T/K	130(2)	110(2)	130(2)
θ range/deg	2.13−26.41	2.22−30.86	2.17−28.34
no. of rflns collected	79 142	67 539	33 675
no. of rflns obsd ($I > 2\sigma(I)$)	3498	11 617	8871
no. of indep rflns (R_{int})	7187 (0.1969)	13 463 (0.0390)	11 464 (0.0907)
no. of data/restraints/params	7187/6/356	13 463/96/478	11 464/5/453
GOF	1.007	1.093	1.161
final *R* indices R1,[a] wR2[b] (obsd data)	0.0705, 0.1091	0.0364, 0.0948	0.0762, 0.1516
final *R* indices R1, wR2 (all data)	0.1459, 0.1260	0.0452, 0.1001	0.1031, 0.1623
largest *e*(max), *e*(min)/e Å^{-3}	0.447, −0.332	2.222, −1.016	1.744, −3.013

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

(100.6 MHz, C_6D_6): δ −2.1 (CH_3), 3.0 (CH_2SiMe_3), 10.8 (H_2SiCH_2), 128.3 (*m*-C, Ph), 129.8 (*p*-C, Ph), 133.0 (*i*-C, Ph), 135.5 (*o*-C, Ph).

1-(Phenylsilyl)-1-(trimethylsilyl)ethane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.01 (s, 9H, CH_3), 0.09−0.16 (m, 1H, CH), 1.05 (d, $^3J_{HH}$ = 7.5 Hz, 3H, CH_3), 4.41−4.45 (m, 1H, SiH), 4.56−4.59 (m, 1H, SiH), 7.14−7.18 (m, 3H, Ph), 7.49−7.54 (m, 2H, Ph). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ −1.8 (CH_3), 2.4 (CH), 10.7 (CH_3CH), 128.3 (*m*-C, Ph), 129.7 (*p*-C, Ph), 133.2 (*i*-C, Ph), 135.8 (*o*-C, Ph).

1-Phenyl-1-(phenylsilyl)ethane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 1.30 (d, $^3J_{HH}$ = 7.5 Hz, 3H, CH_3), 2.34−2.42 (m, 1H, CH), 4.44 (m, 2H, SiH_2), 6.95−6.99 (m, 2H, Ph), 7.02−7.13 (m, 6H, Ph), 7.28−7.31 (m, 2H, Ph). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 16.5 (CH_3), 25.6 (CH), 125.4 (Ph), 127.4 (Ph), 128.1 (Ph), 128.7 (Ph), 130.0 (Ph), 131.6 (*i*-C, Ph), 136.0 (Ph), 144.6 (*i*-C, Ph).

3-Phenyl-1-(phenylsilyl)propane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.72−0.78 (m, 2H, CH_2Si), 1.58−1.66 (m, 2H, CH_2), 2.44 (t, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 4.42 (t, $^3J_{HH}$ = 3.6 Hz, 2H, SiH_2), 6.94−6.98 (m, 2H, Ph), 7.00−7.15 (m, 6H, Ph), 7.40−7.44 (m, 2H, Ph). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 9.9 (CH_2Si), 27.3 (CH_2), 39.2 (CH_2), 126.1 (Ph), 128.3 (Ph), 128.6 (Ph), 128.8 (Ph), 129.8 (Ph), 132.6 (*i*-C, Ph), 135.5 (Ph), 142.2 (*i*-C, Ph).

3-Phenyl-2-(phenylsilyl)propane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.92 (d, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3), 1.27−1.33 (m, 1H, CH), 2.33−2.39 (m, 1H, CH_AH_BCH), 2.77−2.82 (m, 1H, CH_AH_BCH), 4.34−4.40 (m, 2H, SiH_2); Ph resonances were not found due to overlapping. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 15.7 (CH_3), 18.8 (CHSi), 39.7 (CH_2), 126.2 (Ph), 128.5 (Ph), 129.2 (Ph), 131.9 (*i*-C, Ph), 135.2 (Ph), 141.6 (*i*-C, Ph); other two Ph signals were not found.

3-Phenyl-1-(butylsilyl)propane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.46−0.54 (m, 2 × 2H, CH_2Si), 0.77 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3), 1.19−1.27 (m, 2 × 2H, CH_2), 1.53−1.61 (m, 2H, CH_2), 2.44 (t, $^3J_{HH}$ = 7.6 Hz, 2H, $PhCH_2$), 3.80 (qn, $^3J_{HH}$ = 3.7 Hz, 2H, SiH_2), 6.96−7.02 (m, 3H, Ph), 7.06−7.11 (m, 2H, Ph). ^{13}C{^{1}H} (100.6 MHz, C_6D_6): δ 9.07 (CH_2Si), 9.11 (CH_2Si), 13.9 (CH_3), 26.2 (CH_3CH_2), 27.8 (CH_2), 28.0 (CH_2), 39.4 ($PhCH_2$), 126.1 (*p*-C, Ph), 128.6/128.8 (*o*/*m*-C, Ph), 142.4 (*i*-C, Ph).

1,6-Bis(phenylsilyl)hexane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.76 (m, 4H, CH_2Si), 1.14−1.20 (m, 4H, CH_2), 1.24−1.36 (m, 4H, CH_2), 4.45 (t, $^3J_{HH}$ = 3.6 Hz, 4H, SiH_2), 7.11−7.17 (m, 6H, *m*-/*p*-H), 7.43−7.51 (m, 4H, *o*-H). ^{13}C{^{1}H} (100.6 MHz, C_6D_6): δ 10.3 (CH_2Si), 25.3 (CH_2), 32.7 (CH_2), 128.3 (*m*-C, Ph), 129.8 (*p*-C, Ph), 132.8 (*i*-C, Ph), 135.5 (*o*-C, Ph). MS *m*/*z* (rel. int.): 220.2 (M-C_6H_6, 30), 142 (M−2 × C_6H_6, 100), 114 (56), 111 (22), 107 ($PhSiH_2$, 98), 106 (27), 105 (43), 85 (20).

(Phenylsilylmethyl)cyclopentane. ^{1}H NMR (400.1 MHz, C_6D_6): δ 0.88 (dt, *J* = 7.3 Hz, 3.8 Hz, 2H, CH_2Si), 0.99−1.05 (m, 2H, CH_2), 1.33−1.55 (m, 4H, CH_2), 1.66−1.86 (m, 3H, CH+CH_2), 4.47 (t, $^3J_{HH}$ = 3.8 Hz, 2H, SiH_2), 7.11−7.17 (m, Ph), 7.43−7.51 (m, Ph). ^{13}C{^{1}H} (100.6 MHz, C_6D_6): δ 17.2 (CH_2Si), 25.4 (CH_2), 35.7 (CH_2), 37.2 (CH), 128.4 (*m*-C, Ph), 129.7 (*p*-C, Ph), 133.1 (*i*-C, Ph), 135.5 (*o*-C, Ph).

X-ray Crystal Structure Determination. Relevant crystallographic data are summarized in Table 4. The X-ray diffraction data of the complexes **5**, **7**, and **8** were collected on a Bruker AXS diffractometer with a CCD area detector with Mo Kα radiation (graphite monochromator, λ = 0.710 73 Å) using λ scans. The SMART program package was used for the data collection and unit cell determination; processing of the raw frame data was performed using SAINT.[26] The structures were solved by direct methods using the SHELXS-97 program[27] and refined against F^2 using all reflections with the SHELXL-97 software.[28] The hydrogen atoms were placed in calculated positions. The twist disorder of the coordinated THF molecule in **5** was modeled to a split occupancy of 0.53/0.47. All carbon atoms in the molecule of THF were treated as isotropic in refinement. Two pentane molecules in the structure of **8** were solved as isotropic in refinement.

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Supporting Information Available: Text and tables giving X-ray crystal data and additional NMR data and CIF files giving full crystallographic data for **5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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