# Regioselection and Enantioselection in Organolanthanide-Catalyzed Olefin Hydrosilylation. A Kinetic and Mechanistic Study

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*Received January 24, 1995*[⊗]

**Abstract:** This contribution describes a study of scope, regioselection, enantioselection, metal and ancillary ligand effects, and kinetics in the catalytic $PhSiH_3$ hydrosilylation of olefins using the organolanthanide precatalysts $Cp'_2LnCH(SiMe_3)_2$, $Me_2SiCp''_2LnCH(SiMe_3)_2$, and $Me_2SiCp''(R^*C_5H_4)LnCH(SiMe_3)_2$ ($Cp' = \eta^5$-$Me_5C_5$; $Cp'' = \eta^5$-$Me_4C_5$; Ln = lanthanide; $R^*$ = chiral auxillary). Sluggish catalyst initiation processes were first circumvented by hydrogenolysis of the $Ln-CH(SiMe_3)_2$ functionality. For α-olefins, hydrosilylation turnover frequency and selectivity for 2,1 addition regiochemistry are enhanced by openness of the metal ligation sphere ($Cp'_2Ln \rightarrow Me_2SiCp''_2$, $Me_2SiCp''(R^*C_5H_4)$) and increasing $Ln^{3+}$ ion radius. For styrenic olefins, complete 2,1 regioselectivity (Si delivery to the benzylic position), rate enhancement by *para* electron-releasing substituents, and turnover frequencies as high as 400 $h^{-1}$ (60 °C) are observed. For 1-hexene, 2,1 addition regioselectivities as high as 76% and turnover frequencies >1000 $h^{-1}$ (90 °C) are observed. For 2-phenyl-1-butene, (*R*)-$Me_2SiCp''$[(−)-menthyl Cp]$SmCH(SiMe_3)_2$ and (*S*)-$Me_2SiCp''$[(−)-menthylCp]$SmCH(SiMe_3)_2$ effect asymmetric hydrosilylation with ee values of 68% and 65%, respectively (25 °C). The former reaction obeys the rate law $v = k[Sm]^1[olefin]^0[PhSiH_3]^1$. $D_2O$ quenching of the reaction yields $PhCD(CH_3)(CH_2CH_3)$ and $PhSiH_2D$ as mechanistically informative products. The hydrosilylation of 1,5-hexadiene effected by $Cp'_2SmCH(SiMe_3)_2$ affords predominantly cyclopentyl$CH_2SiH_2Ph$, while $Me_2SiCp''_2SmCH(SiMe_3)_2$ and (*R*)-$Me_2SiCp''$[(−)-menthylCp]$SmCH(SiMe_3)_2$ also yield hydrosilylation products derived from 1,5-hexadiene skeletal rearrangement. The hydrosilylation mechanism is discussed in terms of a hydride/alkyl cycle involving rapid, exothermic olefin insertion into an Ln−H bond followed by turnover-limiting Si−H/Ln−alkyl transposition (delivery of the alkyl group to Si).

Olefin hydrosilylation processes form the basis for a large class of silicon−carbon bond-forming transformations of great importance in the production of organosilanes.[1] Of the effective homogeneous catalysts for olefin hydrosilylation, organolanthanides[2] offer a number of distinctive as well as potentially informative and useful characteristics.[3,4] These derive from the high electrophilicity of the metal centers, inaccessibility of conventional oxidative addition/reductive elimination sequences, relatively constrained/immobile yet tunable (e.g., coordinative unsaturation; asymmetry) ancillary ligation, and the possibility of coupling hydrosilylation to other organolanthanide-catalyzed transformations.

In regard to the mechanism of organolanthanide-catalyzed hydrosilylation, two pathways seem most reasonable on the basis of precedent and metal−ligand bond enthalpy considerations (Scheme 1).[5,6] Pathway A invokes exothermic (enthalpy data shown are for $L_nM = Cp'_2Sm$, $Cp' = \eta^5$-$Me_5C_5$)[6] olefin insertion into a metal−silyl bond, for which there is precedent in both early and late transition metal chemistry,[1a,6,7] followed by what is essentially a (less exothermic) protonolysis (σ bond metathesis) step, for which there is formal precedent.[2] Although pathway A is formally analogous to organolanthanide-catalyzed group 15 transformations such as hydroamination[8] and hydrophosphination,[9] the polarity of an Si−H bond is of course expected to be quite different from that of an N−H or P−H bond.[10] Pathway B invokes exothermic insertion of olefin into

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1995.

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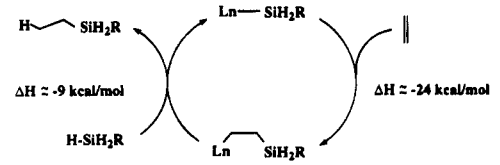
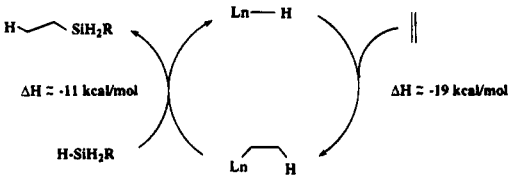
0002-7863/95/1517-7157$09.00/0 

**Scheme 1.** Possible Mechanistic Scenarios for Organolanthanide-Catalyzed Olefin Hydrosilylation

A. Metal Silyl/Alkyl Cycle




B. Metal Hydride/Alkyl Cycle




a lanthanide hydride bond, for which there is substantial precedent,[2,11,12] followed by an exothermic[5,6a] M−C/Si−H transposition (presumably $\sigma$-bond metathesis) process. The latter has precedent in M−C/B−H transpositions identified in organolanthanide-catalyzed olefin hydroboration.[13] Since the first step in pathway B is, as written, identical to that in mechanistically characterized achiral[11,14] and enantioselective[15] olefin hydrogenation mediated by this same class of catalysts, the potential for efficient chirality transfer is evident, and, as written, stereochemistry should be fixed at precisely the same juncture as in asymmetric hydrogenation.[15b] These issues and several interesting initial regiochemical observations prompted the present study of scope and mechanism for organolanthanide-catalyzed olefin hydrosilylation using a variety of olefinic substrates with both achiral and chiral organolanthanide catalysts containing a variety of lanthanide ions.

## Experimental Section

**Materials and Methods.** All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high vacuum ($10^{-5}$ torr) line, or in a nitrogen-filled Vacuum Atmospheres glovebox with a high-capacity recirculator (1−2 ppm of $O_2$). Argon (Matheson, prepurified) was purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents were distilled under nitrogen from sodium benzophenone ketyl. Hydrocarbon solvents (toluene, pentane, heptane) were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. Deuterated solvents were obtained from Cambridge Isotope Laboratories (all 99 atom % D) and were freeze−pump−thaw−degassed and dried over Na/K alloy. The prochiral olefin 2-phenyl-1-butene was prepared from propiophenone (Aldrich) via Wittig reaction with (methylene)triphenylphosphorane[16] and was freeze−pump−thaw−degassed, dried over Na/K alloy for 0.5 h, and vacuum transferred prior to use. The olefin 2-vinylanisole was prepared from *o*-anisaldehyde (Aldrich) in a similar fashion and purified by an identical procedure. Phenylsilane was obtained commercially (Aldrich, Petrach) and was freeze−pump−thaw−degassed, dried over Na/K alloy for 0.5 h, and vacuum transferred to a storage tube prior to use. Styrene was obtained commercially (Aldrich) and was washed with base (1.0 M NaOH), dried over $Na_2SO_4$−$K_2CO_3$, further dried over BaO, distilled three times from $CaH_2$, distilled onto $(Cp'_2SmH)_2$, and vacuum transferred from this solution prior to use. Other olefins for NMR scale hydrosilylation experiments were obtained from Aldrich, stirred over $CaH_2$ for 24 h, and vacuum transferred. Phenylsilane-$d_3$ was obtained by the reduction of phenyltrichlorosilane with $LiAlD_4$ according to literature procedures.[17] The organolanthanide catalysts/precatalysts $Cp'_2LnCHTMS_2$ (Ln = La, Nd, Sm, Lu; TMS = $SiMe_3$),[6b,11b] $Cp'_2YCHTMS_2$,[11c] $Me_2SiCp''_2SmCHTMS_2$ ($Cp'' = \eta^5$-$Me_4C_5$),[18] (*R*)-$Me_2SiCp''$[(−)-menthylCp]SmCHTMS$_2$ ((*R*)-Sm),[19a] and (*S*)-$Me_2SiCp''$[(−)-menthylCp]-SmCHTMS$_2$ ((*S*)-Sm)[19a] were prepared by published procedures.

**Physical and Analytical Measurements.** NMR spectra were recorded on either a Varian Gemini VXR 300 (FT, 300 MHz, $^1$H; 75 MHz, $^{13}$C), or a Varian XL-400 (FT, 400 MHz, $^1$H; 100 MHz, $^{13}$C; 61.4 MHz, $^2$H) instrument. Chemical shifts for $^1$H, $^{13}$C, and $^2$H are referenced to internal solvent resonances. NMR experiments on air-sensitive samples were conducted in either Teflon valve-sealed tubes (J. Young) or in screw-capped tubes fitted with septa (Wilmad). Optical activities were measured at 25 °C with an Optical Activity Ltd. AA-100 polarimeter (± 0.001°) using a 0.50 dm quartz cell. Concentrations reported with specific rotations are in units of g·(100 cm$^2$)$^{-1}$. Analytical gas chromatography was performed on a Varian Model 3700 gas chromatograph with FID detectors and a Hewlett-Packard 3390A digital recorder/integrator using a 20 ft, 0.125in. column with a 3.8% w/w SE-30 liquid phase on Chromosorb W support. GC/MS studies were conducted on a VG 70-250 SE instrument with 70 eV electron impact ionization. Elemental analyses were performed by G. D. Searle Corp., Skokie, IL.

**NMR Scale Catalytic Hydrosilylation Reactions.** In a typical experiment, a 5 mm NMR tube equipped with a Teflon valve was charged in the glovebox with precatalyst (0.005 mmol), $PhSiH_3$ (1.0 mmol), olefin (1.2 mmol), and 0.5 mL of benzene-$d_6$. The tube was closed, quickly removed from the glovebox, and maintained at −78 °C. Next, the NMR tube was degassed on the vacuum line, backfilled with $H_2$ (1 atm, 1.5−2.0 mL, 0.0067−0.0089 mmol) at −78 °C, and further maintained at −78 °C until NMR measurements were initiated. Meanwhile, the NMR probe was equilibrated to the desired experiment temperature (checked with a methanol or ethylene glycol standard) and the sample was quickly warmed to room temperature for ~8 s and then inserted into the probe. The progress of the reaction was monitored by $^1$H NMR spectroscopy, which showed that the initiation with hydrogen is essentially instantaneous and occurs with quantitative release of $CH_2(TMS)_2$. Any remaining small amounts of hydrogen are very rapidly consumed in hydrogenating small fractions of the olefinic substrate. Turnover frequencies for hydrosilylation ($N_t$) were calculated based on the time for 25% consumption of $PhSiH_3$. Product characterization data are given below where the compound numbering refers to entrees and rates in Table 1.

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**$PhHC(SiH_2Ph)CH_3$ (1).** $^1H$ NMR ($C_6D_6$, 400 MHz): $\delta$ 7.40−7.04 (m, 10H), 4.51 (m, 2H), 2.44 (m, 1H), 1.36 (d, $J$ = 7.6 Hz, 3H). $^{13}C$ NMR ($C_6D_6$, 100 MHz, APT): $\delta$ 145.06 ($C_q$), 136.39 (CH), 131.97 ($C_q$), 130.14 (CH), 129.11 (CH), 128.67 (CH), 126.96 (CH), 125.81 (CH), 26.0 ($CH_3$), 16.9 (CH). GC/MS (EI, 70 eV, relative intensity): *m/e* 212.1 (76.3), 134.0 (21.2), 105.0 (100), 107.0 (56.2). High resolution mass spectrum, calcd for $C_{14}H_{16}Si$: 212.1021. Found: 212.1017.

**$PhCH_2CH_2SiH_2Ph$ (2).** $^1H$ NMR ($C_6D_6$, 400 MHz): $\delta$ 7.40 (m, 2H), 7.30−6.92 (m, 8H), 4.40 (t, $J$ = 3.8 Hz, 2H), 2.57 (m, 2H), 1.05 (m, 2H). $^{13}C$ NMR ($C_6D_6$, 100 MHz, APT): $\delta$ 144.22 ($C_q$), 136.06 (CH), 135.50 (CH), 132.78 ($C_q$), 129.02 (CH), 128.59 (CH), 127.84 (CH), 126.50 (CH), 32.01 ($CH_2$), 13.05 ($CH_2$). GC/MS (EI,70 eV, relative intensity): *m/e* 212 (3.9), 134 (100), 105 (27.7), 91 (11.6). High resolution mass spectrum, calcd for $C_{14}H_{16}Si$: 212.1021. Found: 212.1017.

**[1-(*p*-Methoxyphenyl)-1-ethyl](phenyl)silane (3).** $^1H$ NMR ($C_6D_6$, 400 MHz): $\delta$ 7.39 (d, $J$ = 6.4 Hz, 2H), 7.32−7.10 (m, 3H), 6.97 (d, $J$ = 6.8 Hz, 2H), 6.78 (d, $J$ = 6.6 Hz, 2H), 4.52 (m, 2H), 3.38 (s, 3H), 2.45 (m, 1H), 1.39 (d, $J$ = 7.2 Hz, 3H). $^{13}C$ NMR ($C_6D_6$, 100 MHz, APT): $\delta$ 157.86 ($C_q$), 136.35 (CH), 135.98 (CH), 131.76 ($C_q$), 130.00 ($C_q$), 128.27 (CH), 128.17 (CH), 114.26 (CH), 54.74 ($CH_3$), 24.51 ($CH_3$), 16.98 (CH). GC/MS (EI, 70 eV, relative intensity): *m/e* 242 (25.5), 227 (84.3), 135 (100). High resolution mass spectrum, calcd for $C_{15}H_{18}SiO$: 242.1127. Found: 242.1151.

**[1-(*p*-Fluorophenyl)-1-ethyl](phenyl)silane (4).** $^1H$ NMR ($C_6D_6$, 300 MHz): $\delta$ 7.28−7.02 (m, 9H), 4.36 (d, $J$ = 3.00 Hz, 2H), 2.29 (m, 1H), 1.23 (d, $J$ = 7.47 Hz, 3H). $^{13}C$ NMR (75 MHz, $C_6D_6$, APT): $\delta$ 161.27 ($C_q$, $J_{C-F}$ = 247 Hz), 140.28 (CH), 136.13 ($C_q$), 134.05 ($C_q$), 131.28 (CH), 130.07 (CH), 128.74 (CH), 128.22 (CH), 28.82 (CH), 16.59 ($CH_3$). GC/MS (70 eV, EI, relative intensity): *m/e* 230.1 (26.0), 123.1 (45.5), 122.0 (20.7), 107.0 (34.8), 104.0 (100). High resolution mass spectrum, calcd for $C_{14}H_{15}SiF$: 230.0927. Found: 230.0941.

**[1-(*o*-Methoxyphenyl)-1-ethyl](phenyl)silane (5).** $^1H$ NMR ($C_6D_6$, 300 MHz): $\delta$ 7.48 (m, 3H), 7.11(m, 4H), 6.92 (m, 1H), 6.54 (d, $J$ = 8.01 Hz, 1H), 4.58 (d, $J$ = 2.76 Hz, 2H), 3.28 (s, 3H), 3.18 (m, 1H), 1.43 (d, $J$ = 7.62 Hz, 3H). $^{13}C$ NMR ($C_6D_6$, 100 MHz, APT): $\delta$ 156.52 ($C_q$), 135.85 (CH), 132.74 ($C_q$), 132.40 ($C_q$), 129.70 (CH), 128.00 (CH), 127.15 (CH), 126.17 (CH), 121.06 (CH), 110.22 (CH), 54.63 ($CH_3$), 18.23 ($CH_3$), 15.94 (CH). GC/MS (70 eV, EI, relative intensity): *m/e* 242.3 (38.8), 227.3 (100), 211.2 (21.8), 135 (88.8). High resolution mass spectrum, calcd for $C_{15}H_{18}SiO$: 242.1127. Found: 242.1149.

**$PhMeC(SiH_2Ph)CH_3$ (6).** $^1H$ NMR ($C_6D_6$, 400 MHz): $\delta$ 7.40−7.05 (m, 10H), 4.50 (s, 2H), 1.41 (s, 6H). $^{13}C$ NMR ($C_6D_6$, 100 MHz, APT): $\delta$ 148.07 ($C_q$), 143.98 (CH), 136.72 (CH), 132.02 ($C_q$), 130.44 (CH), 128.03 (CH), 126.84 (CH), 126.25 (CH), 25.75 ($CH_3$), 24.56 ($C_q$). GC/MS (EI, 70 eV, relative intensity): *m/e* 226.1 (46.4), 119.1 (100), 91.0 (34.9). High resolution mass spectrum, calcd for $C_{15}H_{18}Si$: 226.1178. Found: 226.1181.

**$PhEtC(SiH_2Ph)CH_3$ (7).** $^1H$ NMR ($C_6D_6$, 400 MHz): $\delta$ 7.27−7.04 (m, 10H), 4.48 (m, 2H), 2.13 (m, 1H), 1.71 (m, 1H), 1.34 (s, 3H), 0.71 (t, $J$ = 7.3 Hz, 3H). Decoupled ($^1H$) at 0.71 ppm: $\delta$ 2.13 (d, $J$ = 13.4 Hz, 1H), 1.71 (d, $J$ = 13.9 Hz, 1H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 145.15, 136.01, 131.25, 129.64, 128.08, 127.59, 127.74, 124.65, 30.13, 30.03, 19.12, 7.67. GC/MS (EI, 70 eV, relative intensity): *m/e* 240.1 (66.0), 133.1 (99.5), 117.0 (19.8), 107.0 (22.0), 105.0 (25.6), 91 (100). High resolution mass spectrum, calcd for $C_{16}H_{20}Si$: 240.1334. Found: 240.1351.

**$Ph_2C(CH_3)SiH_2Ph$ (8).** $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ 7.22−6.95 (m, 15H), 4.87 (s, 2H), 1.69 (s, 3H). $^{13}C$ NMR (100 MHz, $C_6D_6$, APT): $\delta$ 147.6 ($C_q$), 136.64 (CH), 134.14 ($C_q$), 130.09 (CH), 130.05 (CH), 128.58 (CH), 127.98 (CH), 125.85 (CH), 37.79 ($C_q$), 25.76 ($CH_3$). GC/MS (70 eV, EI, relative intensity): *m/e* 288.5 (27.6), 182.4 (22.3), 181.4 (100), 180.4 (16.3), 166.4 (16.7), 165.3 (19.5), 103.2 (27.7), 77.1 (12.4). High resolution mass spectrum, calcd for $C_{20}H_{20}Si$: 288.1334. Found: 288.1331.

**[1-(2-Napthyl)-1-ethyl](phenyl)silane (9).** $^1H$ NMR ($C_6D_6$, 300 MHz): $\delta$ 7.62−7.10 (m, 12H), 4.56 (m, 2H), 2.55 (m, 1H), 1.41 (d, $J$ = 7.2 Hz, 3H). $^{13}C$ NMR ($C_6D_6$, 300 MHz, APT): $\delta$ 142.28 ($C_q$ ), 135.99 (CH), 134.39 ($C_q$), 132.24 ($C_q$), 131.41 ($C_q$), 130.04 (CH), 128.35 (CH), 128.24 (CH), 128.20 (CH), 128.15 (CH), 126.91 (CH), 126.17 (CH), 125.17 (CH), 125.00 (CH), 25.93 ($CH_3$), 16.45 (CH). GC/MS (70 eV, EI, relative intensity): *m/e* 262.1 (58.5), 184.2 (8.2), 155.1 (100), 128.1 (11.2), 107 (13.8). High resolution mass spectrum, calcd for $C_{18}H_{18}Si$: 262.1178. Found: 262.1159.

**(2-Hexyl)(phenyl)silane (10).** $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ 7.57−7.45 (m, 2H), 7.20−7.15 (m, 3H), 4.39 (m, 2H), 1.50 (m, 2H), 1.45−1.10 (m, 4H), 1.05 (m, 4H), 0.93−0.78 (m, 3H). $^{13}C$ NMR (100 MHz, $C_6D_6$, APT): $\delta$ 135.95 (CH), 132.30 ($C_q$), 129.79 (CH), 128.24 (CH), 33.53 ($CH_2$), 31.16 ($CH_2$), 23.10 ($CH_2$), 16.64 ($CH_3$), 16.33 (CH), 14.25 ($CH_3$). GC/MS (70 eV, EI, relative intensity): *m/e* 192.1 (9.5), 149.1 (18.2), 121.0 (19.0), 114.1 (71.3), 107.0 (100), 86.0 (31.6), 84.1 (31.2). High resolution mass spectrum, calcd for $C_{12}H_{20}Si$: 192.1334. Found: 192.1320. The structure of this compound was further confirmed by COSY and GPMBC (Gradient Pulsed Field Multiple-Bond HMQC) NMR experiments which rule out (3-hexyl)(phenyl)-silane, a possible product which could be formed from a $\pi$-allyl intermediate.

**(1-Hexyl)(phenyl)silane (11).** $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ 7.55−7.45 (m, 2H), 7.20−7.15 (m, 3H), 4.46 (t, 2H, $J$ = 3.9 Hz), 1.45−1.10 (m, 8H), 0.93−0.78 (m, 5H). $^{13}C$ NMR (100 MHz, $C_6D_6$, APT): $\delta$ 135.53 (CH), 134.80 ($C_q$), 128.25 (CH), 127.80 (CH), 32.93 ($CH_2$), 31.84 ($CH_2$), 25.43 ($CH_2$), 22.96 ($CH_2$), 14.34 ($CH_3$), 10.40 ($CH_2$). GC/MS (70 eV, EI, relative intensity): *m/e* 192.1 (3.5), 135.0 (5.6), 114.1 (72.1), 107.0 (100), 86.0 (85.4). High resolution mass spectrum, calcd for $C_{12}H_{20}Si$: 192.1334. Found: 192.1324.

**2-Cyclohexyl(1-ethyl)(phenyl)silane (12).** $^1H$ NMR (400 MHz, $C_6D_6$): $\delta$ 7.55−7.45 (m, 2H), 7.20−7.12 (m, 3H), 4.48 (t, $J$ = 3.6 Hz, 2H), 1.75−1.55 (m, 5H), 1.35−1.25 (m, 2H), 1.25−1.00 (m, 4H), 0.85−0.65 (m, 4H). $^{13}C$ NMR (100 MHz, $C_6D_6$, APT): $\delta$ 135.53 (CH of Ph), 132.89 ($C_q$ of Ph), 129.80 (CH of Ph), 128.30 (CH of Ph), 40.52 (CH), 33.14 ($CH_2$), 32.95 ($CH_2$), 27.07 ($CH_2$), 26.74 ($CH_2$), 7.49 ($CH_2$). GC/MS (70 eV, EI, relative intensity): *m/e* 218 (2.1), 189 (2.3), 140 (100), 110 (39.5), 107.0 (53.0), 81.0 (39.9). High resolution mass spectrum, calcd for $C_{14}H_{22}Si$: 218.1491. Found: 218.1467.

**[1-(2-Ethyl)butyl](phenyl)silane (13).** $^1H$ NMR ($C_6D_6$, 400 MHz): $\delta$ 7.50 (m, 2H), 7.15 (m, 3H), 4.51 (t, $J$ = 4.0 Hz, 2H), 1.44 (m, 1H), 0.98 (m, 4H), 0.90 (m, 2H), 0.81 (t, $J$ = 7.2 Hz, 6H). $^{13}C$ NMR ($C_6D_6$, 100 MHz): $\delta$ 135.51, 133.17, 129.72, 128.24, 38.04, 28.29, 14.73, 10.99. GC/MS (EI, 70 eV, relative intensity): *m/e* 192.1 (3.1), 163.0 (33.9), 114.0 (60.8), 107.0 (100), 85.0 (22.3). High resolution mass spectrum, calcd for $C_{12}H_{20}Si$: 192.1334. Found: 192.1338.

**$PhSiH_2CHTMS_2$ (14).** $PhSiH_2Br$ (2.06 g, 11 mmol)[19b] was added dropwise to a solution of $LiCHTMS_2$ (1.66 g, 10 mmol) in $Et_2O$ (200 mL) at room temperature, and the mixture was allowed to stir for 3 h. The solvent was then removed under high vacuum, and the residue was purified by flash chromatography (silicon gel) with pentane as the eluant to yield a colorless oil, 2.2 g (83%). $^1H$-NMR (400 MHz, $C_6D_6$): $\delta$ 7.55 (m, 2H), 7.15 (m, 3H), 4.65 (d, $J$ = 3.6 Hz, 2H), 0.11 (s, 18H), −0.55 (t, $J$ = 3.6 Hz, 1H,). $^{13}C$ NMR (100 MHz, $C_6D_6$, APT): $\delta$ 135.35 (CH), 134.83 ($C_q$), 129.66 (CH), 128.27 (CH), 1.83 (CH), −2.36 ($CH_3$). MS (70 eV, EI, relative intensity): *m/e* 266.0 (0.9), 265.0 (1.9), 251.0 (100), 249.0 (47.6), 188.0- (29.5). Anal. Calcd for $C_{13}H_{26}Si_3$: C, 58.65; H, 9.77. Found: C, 58.10; H, 9.75.

**Preparative Scale Hydrosilylation of Styrene.** In the glovebox, 61 mg (0.10 mmol) of $Me_2SiCp''_2SmCH(SiMe_3)_2$, 2.16 g (20 mmol) of $PhSiH_3$, 2.08 g (20 mmol) of styrene, and 10 mL of benzene were added to a storage tube equipped with J-Young valve. The mixture was then allowed to stir at room temperature for 48 h. The solvent was removed by distillation, and the resulting residue was purified by flash chromatography (silicon gel) with pentane as the eluant to a yield colorless oil, 4.6 g (96%). NMR and mass spectral parameters are identical to those reported above. Anal. Calcd for $C_{14}H_{16}Si$: C, 79.25; H, 7.55. Found: C, 79.39; H, 7.60.

**Typical NMR Scale Asymmetric Hydrosilylation.** In a glovebox, a solution of (*R*)-$Me_2SiCp''$[(−)-menthylCp]$SmCH(SiMe_3)_2$ ((*R*)-Sm) (ca. 10 mg, 0.015 mmol), 2-phenyl-1-butene (240 mg, 1.82 mmol), phenylsilane (200 mg, 1.84 mmol), and 0.7 mL of benzene-$d_6$ was loaded into an NMR tube equipped with a Teflon valve. The tube was then sealed and the reaction monitored by $^1H$ NMR.

**Preparative Scale Asymmetric Hydrosilylation. (*R*)-(−)-(2-Phenyl-2-butyl)(phenyl)silane ((−)-15).** A 15-mL round-bottom reaction flask equipped with a magnetic stir bar was loaded in the glovebox with a premixed solution of 0.035 g (0.051 mmol) of (*R*)-$Me_2SiCp''$[(−)-menthyl-Cp]$SmCH(SiMe_3)_2$ ((*R*)-Sm), 1.32 g (10 mmol)

of 2-phenyl-1-butene, 1.10 g (10 mmol) of phenylsilane, and 2 mL of pentane. The resulting clear, orange solution was stirred under argon for 48 h at 25 °C. To this solution was next added, in the glovebox, a mixture of pentane (5 mL) and dry, degassed silica gel (2 g). The ensuing heterogeneous solution was then filtered and the volatiles removed on the rotary evaporator to afford 2.11 g (88%) of (−)-(2-phenyl-2-butyl)(phenyl)silane ((−)-**15**) as a viscous, high boiling, colorless oil. NMR spectral parameters are identical to those for **7**, $[\alpha]^{25}_D = -19.2°$ ($c$ = 1.0 in 95% EtOH, $l$ = 0.5).

**Preparative Scale Asymmetric Hydrosilylation. (*S*)-(+)-(2-Phenyl-2-butyl)(phenyl) silane ((+)-15).** A 15-mL round-bottom reaction flask, equipped with a magnetic stir bar, was loaded in the glovebox with a premixed solution of 0.035 g (0.051 mmol) of 70/30 (*S*)/(*R*)-$Me_2SiCp''$[(−)-menthylCp]SmCH($SiMe_3$)$_2$ (70/30 (*S*)/(*R*)-Sm), 1.32 g (10 mmol) of 2-phenyl-1-butene, 1.10 g (10 mmol) of phenylsilane, (**2**), and 2 mL of pentane. The resulting clear, orange solution was stirred under argon for 48 h at 25 °C. To this solution was next added, in the glovebox, a mixture of pentane (5 mL) and dry, degassed silica gel (2 g). The ensuing heterogeneous solution was then filtered and the volatiles removed on the rotary evaporator to afford 2.19 g (91%) of (+)-(2-phenyl-2-butyl)(phenyl)silane ((+)-**15**) as a viscous, high boiling, colorless oil. NMR spectral parameters are identical to those for **7**, $[\alpha]^{25}_D = +18.3°$ ($c$ = 1.08 in 95% EtOH, $l$ = 0.5).

**(*R*)-(−)-(1-Deuterio-2-phenyl-2-butyl)(phenyl)silane-$d_2$ ((-)-16).** A 15-mL round-bottom reaction flask, equipped with a magnetic stir bar, was loaded in the glovebox with a premixed solution of 35 mg (0.051 mmol) of (*R*)-$Me_2SiCp''$[(−)-menthylCp]SmCH($SiMe_3$)$_2$ ((*R*)-Sm), 1.32 g (10 mmol) of 2-phenyl-1-butene (**1**), 1.10 g (10 mmol) of phenylsilane-$d_3$, and 2 mL of pentane. The resulting clear, orange solution was stirred under argon for 48 h at 25 °C. To this solution was next added, in the glovebox, a mixture of pentane (5 mL) and dry, degassed silica gel (2 g). The ensuing heterogeneous mixture was then filtered and the volatiles removed by rotary evaporation to afford 2.0 g (84%) of (−)-1-deuterio-2-phenyl-2-butyl)(phenyl)silane ((−)-**16**) as a viscous, high boiling, colorless oil. $^1$H NMR ($C_6D_6$): $\delta$ 7.27 (dd, $J$ = 7.8 Hz, 2 H), 7.18−7.04 (m, 8 H), 2.13 (m, 1 H), 1.71 (m, 1 H), 1.34 (s, 2 H), 0.71 (t, $J$ = 7.3 Hz, 3 H). $^2$H NMR ($C_6D_6$): $\delta$ 4.48, 1.34. $^{13}$C NMR ($C_6D_6$): $\delta$ 145.3, 136.5, 131.5, 130.0, 128.6, 127.9, 127.2, 125.1, 30.2 (two overlapped resonances), 19.9 (t, 1:1:1 relative intensities), 7.9.

**Determination of Enantiomeric Excesses in the Asymmetric Hydrosilation of 2-Phenyl-1-butene with Phenylsilane Using Chiral Catalysts (*R*)-Sm and 70/30(*S*)/(*R*)-Sm. Conversion of (*S*)-(+)-(2-phenyl-2-butyl)(phenyl)silane ((+)-15) to Known (+)-2-Phenyl-2-butanol ((+)-17).** The enantiomeric purity of the final silane products was determined using a 3-step procedure.

**Step 1.** The optical rotations of the purified hydrosilylation products were measured ($c$ = 1.0 95% EtOH, $l$ = 0.5 dm).

**Step 2.** The product (+)-(2-phenyl-2-butyl)(phenyl)silane ((+)-**15**)-was converted to the tertiary alcohol (+)-2-phenyl-2-butanol ((+)-**17**), for which the optical rotation is known, by oxidative cleavage of the carbon−silicon bond (see procedure below). This protodesilylation/oxidation is known to proceed with 100% retention of configuration at the chiral carbon center.[20]

**Step 3.** The optical rotation of the alcohol obtained was measured ($c$ = 1.3 EtOH, $l$ = 0.5 dm) and compared to that of the pure alcohol.[21] The enantiomeric excess of the hydrosilylation reaction was obtained from this result.

**(+)-2-Phenyl-2-butanol ((+)-17).** A 100-mL 3-neck flask with an addition funnel and reflux condenser was charged with (+)-(2-phenyl-2-butyl)(phenyl)silane ((+)-**15**) (2.0 g, 3.34 mmol) and $CF_3COOH$ (5.0 g, 42 mmol). The resulting solution was heated to 50 °C and allowed to stir at this temperature for 5 h. The volatiles were then removed by rotary evaporation. MeOH (0.67 g, 21 mmol) and $KHF_2$ (1.17 g, 15 mmol) were then added to the residual mixture, and the resulting solution was stirred at 50 °C for another 5 h. With stirring, 0.61 g (20 mmol) of $NaHCO_3$, 1.5 g (45 mmol) of a 30% $H_2O_2$ solution, 20 mL of MeOH, and 20 mL of THF were then added. The mixture was refluxed for 48 h and white insoluble solids were observed. This heterogeneous mixture was then quenched with a dilute solution of $NaHSO_3$ (20 mL) at 0 °C, extracted with diethyl ether, and dried over $K_2CO_3$−$Na_2SO_4$. Evaporation of the volatiles afforded a white solid that was further purified by column chromatography on silica gel (eluent diethyl ether/pentane 1:10 v/v). Yield: 0.25 g (1.66 mmol, 50%) of (+)-2-phenyl-2-butanol ((+)-**17**) as a clear colorless liquid. $[\alpha]^{25}_D$ = + 10.5° ($c$ = 1.3 in EtOH, $l$ = 0.5). $^1$H NMR ($CDCl_3$): $\delta$ 7.45 (d, 2H), 7.35 (t, 2H), 7.25 (t, 1H), 1.84 (m, 3H), 1.55 (s, 3H), 0.8 (t, 3H). $^{13}$C NMR ($CDCl_3$): $\delta$ 147.7, 128.0, 126.4, 124.8, 74.9, 36.6, 29.5, 8.3.

**$D_2O$ Hydrosilylation Quenching Experiments.** A 10-mL J-Young storage tube was loaded in the glovebox with 70 mg (0.10 mmol) of (*R*)-$Me_2SiCp''$[(−)-menthylCp]SmCH$TMS_2$, 397 mg (3.00 mmol) of 2-phenyl-1-butene, and 320 mg (2.96 mmol) of phenylsilane. The reaction mixture was vigorously stirred for 15 min, and the dark yellow solution quenched under a strong Ar purge with ca. 5 drops (~250 mg, 14 mmol) of degassed $D_2O$. To this quenched solution was added a small amount of silica gel to adsorb the catalyst hydrolysis products. Next, the heterogeneous mixture was extracted with pentane (3 × 5 mL) and the extracts combined, dried over $Na_2SO_4$, and concentrated to a pale yellow liquid. The liquid was placed in an NMR tube and diluted to 1 mL with ~50 $\mu$L of $C_6D_6$ (internal standard) and with pentane. The mixture was then analyzed by $^2$H NMR.

**In Situ NMR Studies of the Initiation Process for 2-Phenyl-1-butene Asymmetric Hydrosilylation with Phenylsilane.** In the glovebox, 20 mg of (*R*)-Sm (0.042 mmol, 0.076 M), 49 mg (0.454 mmol, 0.825 M) of $PhSiH_3$, and 106 mg (0.803 mmol, 1.460 M) of 2-phenyl-1-butene were charged successively into a 5 mm J-Young NMR tube equipped with a Teflon valve (previously flamed in vacuo), and ca. 0.4 mL of benzene-$d_6$ was then added to bring the total volume of the solution to 0.55 mL. The tube was closed, quickly removed from the glovebox, and maintained at −78 °C until NMR measurements began. Quick warming and insertion into the NMR probe that had been previously equilibrated to 50 ± 0.4 °C (checked with ethylene glycol) initiated the reaction. Data were acquired using four scans per time interval with a long pulse delay to prevent saturation of the signal. The concentrations of the products were calculated based on the integrals of corresponding resonances using the total concentrations of [$PhSiH_3$] and [$PhEtMeCSiH_2Ph$] derived from their integrals as an internal standard. This sum remains constant throughout the reaction and equals the initial concentration of $PhSiH_3$ ($t$ = 0). $PhSiH_3$ was completely consumed in about 50 min with the clean formation of hydrosilylated product **7** and with only trace amounts (~0.1%) of hydrogenated product observed. About 16% of the precatalyst (*R*)-Sm was consumed during this time interval.

**In Situ NMR Studies of the Initiation Process for the Dehydrogenative Polymerization of Phenylsilane.** A 5-mm J-Young NMR tube (previously flamed in vacuo) was loaded in the glovebox with (*R*)-Sm (3.5 mg, 0.005 mmol) and $PhSiH_3$ (13 mg, 0.122 mmol) in benzene-$d_6$ (1 mL). The NMR tube was then closed, quickly removed from the glovebox, and maintained at −78 °C until the NMR measurements were initiated. Quick warming and insertion into the NMR probe (21 ± 0.4 °C) initiated the reaction, and data were then acquired using four scans per time interval and with a long pulse delay to avoid saturation of the signal. In about 90 min the (*R*)-Sm was almost completely consumed, and only the dimer ($PhSiH_2$−$SiH_2Ph$) ($\delta$ 4.49 p) and a small amount of trimer ($PhSiH_2$−$SiHPh$−$SiH_2Ph$) ($\delta$ 4.60 p) were observed in the $^1$H NMR analysis, even if reaction was prolonged an additional 40 min. The concentrations of the products were calculated based on the integrals of corresponding resonances using the total concentrations of [$PhSiH_3$] and [$PhSiH_2SiH_2Ph$] and [$PhSiH_2SiHPhSiH_2Ph$] derived from their integrals as the internal standard. This sum remains constant and equals the initial concentration of $PhSiH_3$ ($t$ = 0).

**Kinetic Studies of the Asymmetric Hydrosilylation of 2-Phenyl-1-butene with Phenylsilane.** In a typical experiment, a 5-mm NMR

(20) Oxidation of this type of carbon−silicon bond is known to proceed with retention of configuration. For examples of this transformation see: (a) Colvin, E. W. in ref 1c, Vol. 7, Chapter 4.3. (b) Tamao, K. in *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Harwood: Chichester, 1985; Chapter 21. (c) Fleming, I. in ref 20c, Chapter 18. (d) Tamao; K. Ishida, N. *J. Organomet. Chem.* **1984**, *269*, C37-C39. (e) Tamao, K.; Tanaka, T.; Nakajima, T.; Sumiya, R.; Arai, H.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 3377−3380 and references therein. (f) Tamao, K.; Maeda, K.; Tanaka, T.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 6955−6957. (g) Tamao, K.; Maeda, K.; Yamaguchi, T.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4984−4985.

(21) (a) Based upon $[\alpha]^{25}_D = +16.1°$ for (*R*)-(+)-2-phenyl-2-butanol ($c$ = 1.3, EtOH).[21b,c] (b) Johnson, C. R.; Stark, C. J., Jr. *J. Org. Chem.* **1982**, *47*, 1193−1196. (c) Sakuraba, H.; Ushiki, S. *Tetrahedron Lett.* **1990**, *31*, 5349−5352.

tube with a Teflon valve (previously flamed in vacuo) was charged in the glovebox with (*R*)-Sm (2.0−20.0 mg, 0.0029−0.0290 mmol), $PhSiH_3$ (59 mg, 0.54 mmol), and 2-phenyl-1-butene (92−552 mg, 0.70−4.18 mmol). Benzene-$d_6$ was then added to bring the total volume of the solution to 1.0 mL. The tube was closed, quickly removed from the glovebox, and maintained at −78 °C. On the vacuum line, the NMR tube was then degassed and back-filled with $H_2$ (1 atm, 1.5−2.0 mL, 0.067−0.0089 mmol) at −78 °C, and further maintained at −78 °C until kinetic measurements were initiated. Meanwhile, the NMR probe was equilibrated to 50 ± 0.4 °C (checked with an ethylene glycol standard), the sample was quickly warmed up with shaking for ~8 s and inserted into the probe, and an initial spectrum was recorded. Data were acquired using four scans per time interval with a long pulse delay (10 s) to prevent saturation of the signal. The kinetics were monitored by the disappearance of the silane resonance (δ 4.22 p) over 3 to 4 half-lives. The concentration of $PhSiH_3$ at time *t* was determined from the area of the $^1$H-normalized integrals of silane standardized to the total area of resonances of silane and hydrosilylated product (δ 4.48). This sum remains constant and equals the initial concentration of silane (*t* = 0) during the entire reaction process. All the data collected could be convincingly fit (*R* = 0.986−0.998) by least squares to eq 1, where

$$\ln C = mt + \ln C_0 \qquad (1)$$

$C_0$ is the initial concentration of silane. Since the reaction was initiated with hydrogen, the hydrogenolysis of the precatalyst is essentially instantaneous during warming and shaking of the reaction solution. The initial spectrum recorded immediately after shaking shows the precatalyst to be totally consumed and a quantitative amount of $CH_2TMS_2$ to be released. The small, residual amounts of hydrogen present are very rapidly consumed in the hydrogenation of 2-phenyl-1-butene.

**Typical NMR Scale Catalytic Cyclohydrosilylation of 1,5-Hexadiene.** In the glovebox, a 5-mm NMR tube equipped with a Teflon valve was charged with precatalyst (0.005 mmol), $PhSiH_3$ (73 mg, 0.68 mmol), and 1,5-hexadiene (57 mg, 0.70 mmol). Benzene-$d_6$ was then added to bring the total volume of the solution to 1.0 mL. The tube was then closed, quickly removed from the glovebox, and the ensuing reaction was monitored by $^1$H NMR at 21 ± 0.4 °C. Data were acquired using four scans per time interval with a long pulse delay (10 s) to avoid saturation of the signal. The kinetics were monitored by the change of the corresponding product resonance. The concentration of the product at time *t* was determined from the area of the $^1$H-normalized integrals of product standardized to the total area of silane and hydrosilylated product resonances (δ 4.45 for **19** and **20**; δ 4.49 for **18**). This sum remains constant and equals the initial concentration of silane (*t* = 0) during the entire reaction process. The hydrosilylation processes were typically completed in a few hours as indicated by the disappearance of silane resonance in $^1$H NMR. However, the small residual quantity of 1,5-hexadiene undergoes very slow isomerization (>30 days), yielding a number of products with 3-methyl-1,4-pentadiene being the predominant one. Products **19** and **20** can also be produced by the hydrosilylation of 3-methyl-1,4-pentadiene with 1 equiv of $PhSiH_3$ using $Cp'_2YCHTMS_2$ as a precatalyst in $C_6D_6$. The yields of the product are 52% for **19** and 22% for **20**, with 24% of the 3-methyl-1,4-pentadiene remaining unconverted.

**(Cyclopentylmethyl)(phenyl)silane (18).** $^1$H NMR ($C_6D_6$, 400 MHz): δ 7.48 (m, 3H), 7.14 (m, 2H), 4.49 (t, *J* = 5.2 Hz, 2H), 1.90−0.60 (m, 9H). $^{13}$C NMR ($C_6D_6$, 100 MHz, APT): δ 136.22 (CH), 133.77 ($C_q$), 130.43 (CH), 128.89 (CH), 37.95 (CH), 36.43 ($CH_2$), 26.03 ($CH_2$), 17.92 ($CH_2$). GC/MS (EI, 70 eV, relative intensity): *m/e* 190.0 (4.2), 112.0 (100), 107.0 (53.8), 84.0 (43.6), 81.0 (33.4), 67.0 (20.4). High resolution mass spectrum, calcd for $C_{12}H_{18}Si$: 190.1178. Found: 190.1184.

**[1-(3-Methyl-4-pentenyl)](phenyl)silane (19).** $^1$H NMR (300 MHz, $C_6D_6$): δ 7.50 (m, 2H), 7.16 (m, 3H), 5.53 (m, 1H), 4.92 (m, 2H), 4.45 (t, *J* = 3.6 Hz, 2H), 1.95 (m, 1H), 1.40−1.10 (m, 4H), 0.88 (d, *J* = 6.9 Hz, 3H). $^{13}$C-NMR (100 MHz, $C_6D_6$, APT): δ 144.0 (CH), 135.40 (CH), 132.75 ($C_q$), 129.74 (CH), 127.68 (CH), 113.4 ($CH_2$), 40.85 (CH), 32.22 ($CH_2$), 19.90 ($CH_3$), 10.51 ($CH_2$). GC/MS (70 eV, EI, relative intensity): *m/e* 190.0 (55.6), 134.0 (19.3), 132.9 (11.8), 121.0 (14.0), 120.0 (25.4), 112.1 (100), 107.0 (42.8), 106.0 (20.3), 104.9 (53.9), 97.0 (52.9), 84.0 (37.6). High resolution mass spectrum, calcd for $C_{12}H_{18}Si$: 190.1178. Found: 190.1153.

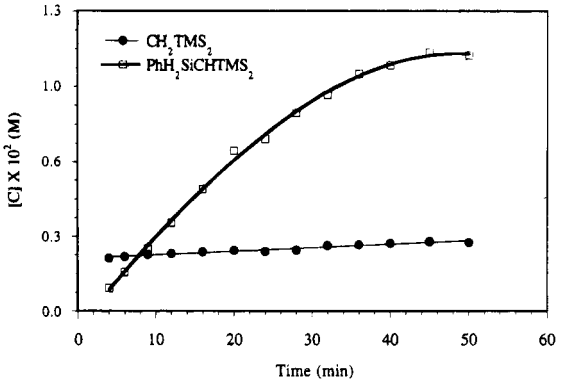



**Figure 1.** Kinetic profile for $-CHTMS_2$ product formation in the reaction of (*R*)-$Me_2SiCp''$[(−)-menthylCp]SmCHTMS$_2$ ((*R*)-Sm; 0.076 M) with $PhSiH_3$ (0.825 M) in the presence of 2-phenyl-1-butene (1.460 M). Solvent: benzene-$d_6$. Temperature: 50 °C. Levelling-off of product formation occurs at complete consumption of $PhSiH_3$.

**3-Methyl-1,5-pentylbis(phenylsilane) (20):** $^1$H NMR (300 MHz, $C_6D_6$): δ 7.48 (m, 4H), 7.10 (m, 6H), 4.45 (t, *J* = 3.6 Hz, 4H), 1.85 (m, 1H), 1.45−1.15 (m, 4H), 0.85−0.65 (m, 4H), 0.70 (d, *J* = 6.0 Hz, 3H). $^{13}$C NMR (100 M, $C_6D_6$, APT): δ 135.44 (CH), 132.71 ($C_q$), 129.73 (CH), 128.23 (CH), 37.85 (CH), 31.69 ($CH_2$), 18.71 ($CH_3$), 7.37 ($CH_2$). GC/MS (70 eV, EI, relative intensity): *m/e* 298.2 (0.6), 220.0 (49.1), 189.1 (61.1), 183.1 (22.4), 161.1 (27.9), 142.1 (44.2), 111.1 (29.8), 107.1 (100). High resolution mass spectrum, calcd for $C_{12}H_{20}Si_2$: 220.1104. Found: 220.1095 (the molecular ion peak was too weak for accurate HRMS under the conditions applied, thus the major fragment (*m/e* 220), which represents loss of benzene, was used instead).

## Results

The goal of this investigation was to examine the scope, regioselectivity, lanthanide ion sensitivity, ancillary ligand sensitivity, enantioselectivity, kinetics, and mechanism of organolanthanide-catalyzed olefin hydrosilylation. Relevant to, and contemporary with, this work are preliminary reports from Tanaka et al.[3d] that $Cp'_2NdR$ complexes (R = $CHTMS_2$, H, Cl; TMS = $SiMe_3$) mediate the hydrosilylation ($PhSiH_3$, *n*-$C_6H_{13}SiH_3$, $PhMeSiH_2$) of 1-decene and styrene (80 °C, 2 days) with high (~100% 1,2 addition—Si delivered to the terminal position) and moderate (69−82% 2,1 addition) selectivity, respectively, and from Molander and Julius[3e] that $Cp'_2YCHTMS_2$ mediates the hydrosilylation ($PhSiH_3$) of a variety of aliphatic olefins with high selectivity for 1,2 addition. In complementary work, we focused on catalyst variation for several informative classes of olefins with the hydrosilylation agent ($PhSiH_3$) held constant along with the issues outlined above. Initial in situ NMR experiments indicated that the first transformation to understand, as a prelude to all other studies, was the process by which the organolanthanide precatalyst is transformed into active catalyst.

**In Situ NMR Studies of the Initiation Process for 2-Phenyl-1-Butene Asymmetric Hydrosilylation with Phenylsilane.** Initial studies of hydrosilylation processes using either $Cp'_2LnCHTMS_2$ or analogous lanthanide hydrocarbyl precatalysts revealed a brief induction period before full catalytic activity was attained. Thus, in situ $^1$H NMR studies were carried out of the reaction of (*R*)-$Me_2SiCp''$[(−)-menthylCp]SmCHTMS$_2$ ((*R*)-Sm) with $PhSiH_3$ in the presence and absence of 2-phenyl-1-butene. In the presence of olefin at 50 °C in benzene-$d_6$, the spectra (see Figure 1) reveal the presence of trace amounts of $CH_2TMS_2$, which increases slowly and linearly with time until *t* = 50 min, at which point $PhSiH_3$ has been completely consumed. This pathway represents a small amount of material, extrapolating to ~2.6% of the available (*R*)-Sm at *t* = 0. This *t* = 0 quantity seems most reasonably ascribable to traces of adventitious protonic reagents (eq 2), while the small additional increments formed as the reaction proceeds may arise from

$$L_nSmCHTMS_2 \xrightarrow{-OH} L_nSmO^- + CH_2TMS_2 \quad (2)$$

either hydrogenolysis (eq 3) or silanolysis (eq 4).[22] The

$$L_nSmCHTMS_2 \xrightarrow{H_2} L_nSmH + CH_2TMS_2 \quad (3)$$

$$L_nSmCHTMS_2 \xrightarrow{PhSiH_3} L_nSmSiH_2Ph + CH_2TMS_2 \quad (4)$$

detection of trace quantities of 2-phenylbutane (~0.1% of the available olefin) and the evidence that (*R*)-Sm is an active precatalyst for 2-phenyl-1-butene hydrogenation ($N_t \approx 5000\ h^{-1}$ under these conditions)[15b] argues that some quantities of $H_2$ are available. Likewise, $D_2O$ quenching studies at the beginning of the hydrosilylation process, revealing small amounts of $PhSiH_2D$ in the $^2H$ NMR, further implicate the presence of $L_n$-$SmSiH_2Ph$ functionalities (vide infra). As will be elaborated upon further in the Discussion Section, these pathways are relatively minor in the initiation process (and catalytic chemistry), and the major pathway produces $PhH_2SiCHTMS_2$ (**14**), which was identified by independent synthesis and characterization (see Experimental Section for details). This product increases rapidly as initiation proceeds, with production finally leveling off when the $PhSiH_3$ is exhausted via the hydrosilylation process (Figure 1). At this point, only ca. 48% of the (*R*)-Sm precatalyst has been consumed. This observation has two important ramifications. First, Ln-C/Si-H transposition processes as in Scheme 1B and eq 5 are clearly a major pathway

$$L_nSmCHTMS_2 \xrightarrow{PhSiH_3} L_nSmH + PhH_2SiCHTMS_2 \quad (5)$$

for hydrosilylation and warrant additional scrutiny (vide infra). Secondly, the sluggishness of the silane + lanthanide hydrocarbyl initiation process renders any hydrosilylation rate information derived from lanthanide−$CHTMS_2$ catalyst precursors unreliable.

The above results prompted studies of initiation using (*R*)-Sm and $PhSiH_3$ in the absence of olefin. In this case, only traces of $PhH_2SiCHTMS_2$ are produced (Figure 2). The formation of $CH_2TMS_2$ dominates, and the time dependence suggests an autocatalytic process (Figure 2). The only detectable catalytic reaction is the dehydrogenative coupling of $PhSiH_3$[22,23] (Scheme 2) which, under the present conditions, yields largely dimeric and trimeric products (eq 6).

$$PhSiH_3 \xrightarrow{catalyst} PhSiH_2SiH_2Ph + PhSiH_2SiHPhSiH_2Ph + H_2 \quad (6)$$

Importantly, $L_nLn-H$ species are both the direct product of $L_nLnCHTMS_2$ hydrogenolysis (which is generally very rapid, Scheme 3)[11,15] and key participants in catalytic cycles for dehydrogenative silane polymerization.[22,23] Thus, the coupling of Schemes 2 and 3 explains the observed autocatalytic behavior (polymerization produces $H_2$ which in turn produces more catalyst—Tilley has recently reported a similar organolanthanide-mediated process[24] ) and also argues (as subsequently verified by experiment) that addition of stoichiometric or near-stoichiometric quantities of $H_2$ is an effective means to rapidly initiate catalytic hydrosilylation, in turn arguing (vide infra) that $L_n$-Ln−H species are active intermediates in this catalytic cycle.

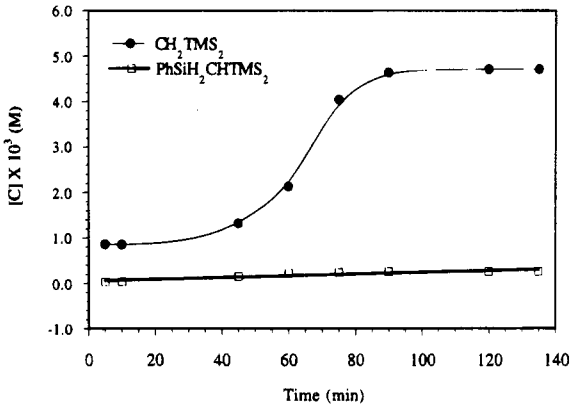
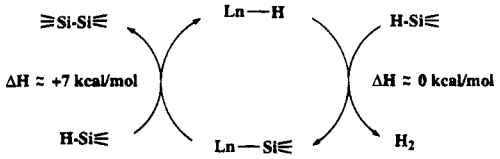
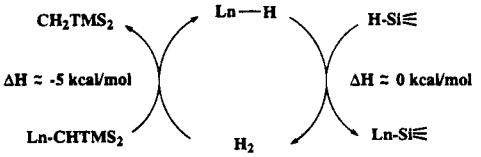



**Figure 2.** Kinetic profile for -$CHTMS_2$ product formation in the reaction of (*R*)-$Me_2SiCp''$[(−)-menthylCp]$SmCHTMS_2$ ((*R*)-Sm; 0.076 M) with $PhSiH_3$ (0.825 M). Solvent: benzene-$d_6$. Temperature: 21 °C. Levelling-off of product formation occurs at complete consumption of $PhSiH_3$.

**Scheme 2.** Mechanism of Organolanthanide-Catalyzed Dehydrogenative Silane Coupling




**Scheme 3.** Cycle for Hydrogenolysis of Lanthanide-Carbon Bonds with the Formation of Lanthanide-Silyl Bonds




**Hydrosilylation of Styrenic and Related Olefins. Ancillary Ligand, Metal, and Substituent Effects.** Table 1 presents results bearing on the hydrosilylation of a variety of styrenic olefins. All reactions employed $L_nLnCHTMS_2$ precatalysts which were rapidly consumed (verified by $^1H$ NMR) by the addition of $H_2$ as an initiator. Products were characterized by standard analytical techniques. A number of unusual trends are evident. In regard to regiochemistry, proper choice of organolanthanide catalyst effects an unprecedented[1] *2,1 addition to styrenic substrates with complete regiospecificity*. That is, the silyl functionality is delivered exclusively to the internal (branched) phenethyl position. In regard to metal ion size effects, Table 1 shows that increasing $Ln^{3+}$ ionic radius[25] correlates with both increasing hydrosilylation turnover frequency and 2,1 regioselectivity (entry 1). Furthermore, opening the metal coordination sphere by connecting the ancillary ligands ($Cp'_2Ln \rightarrow Me_2SiCp''_2Ln$ or $Me_2SiCp''(R*Cp)$)[18,19a] effects a further enhancement in both turnover frequency and regioselectivity (entries 1, 5, 6). Thus, the $Me_2SiCp''_2Sm$-based catalysts are ca. 15× more active for styrene hydrosilylation. In addition, the $Me_2SiCp''_2Sm$-based catalyst effects the regioselective hydrosilylation of sterically encumbered α-substituted styrenes (entries 6 and 7) while the corresponding $Cp'_2Sm$-based catalyst does not. In entry 5, the $Cp'_2Sm$-based catalyst mediates

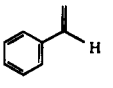
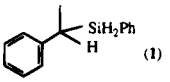
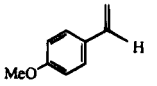
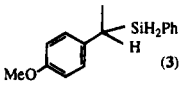
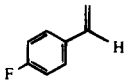
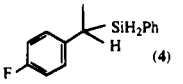
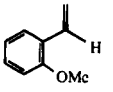
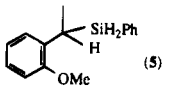
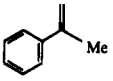
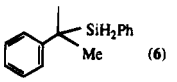
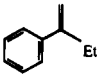
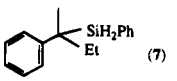
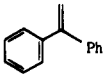
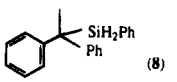
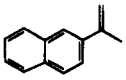
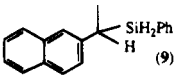
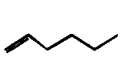
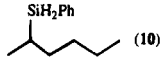
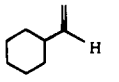
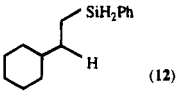
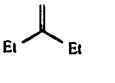
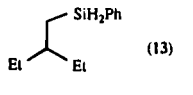
(22) (a) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543−2545. (b) Watson, P. L.; Tebbe, F. N. U.S. Patent 4,965,386 (1990).

(23) (a) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22−29 and references therein. (b) Corey, J. Y.; Huhmann, J. L.; Zhu, X.-H. *Organometallics* **1993**, *12*, 1121−1130 and references therein. (c) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047−7055. (d) Harrod, J. F. In *Inorganic and Organometallic Polymers with Special Properties;* Lain, R. M., Ed.; Kluwer Academic Publishers: Amsterdam, 1991; Chapter 14 and references therein. (e) Kobayashi, T.; Sakakura, T.; Hayashi, T.; Yumura, M.; Tanaka, M. *Chem. Lett.* **1992**, 1157−1160.

(24) Tilley, T. D. International Conference on Coordination Chemistry, Kyoto, Japan, July 25−29, 1994.

(25) Shannon, R. E. *Acta Crystallogr.* **1976**, *A32*, 751−760.

**Table 1.** Organolanthanide-Catalyzed Hydrosilylation of Alkenes with $PhSiH_3$[a]

| Entry | Substrate | Product | Precatalyst[b] | $N_t$, $h^{-1}$ (°C)[c,d] | Yield (%)[e] | Regioselect.(%) (2,1-addn.) |
|---|---|---|---|---|---|---|
| 1. |  |  (1) | $Cp'_2LuR$ | 25 (60) | 5.5 | 5.8 |
| | | | $Cp'_2SmR$ | 1.6 (23) | 71 | 74 |
| | | | | 28 (60) | 78 | 82 |
| | | | $Cp'_2NdR$ | 30 (60) | 84 | 90 |
| | | | $Cp'_2LaR$ | 75 (60) | 88 | 96 |
| | | | $Me_2SiCp''_2SmR$ | 25 (23) | 98 | >99 |
| | | | | 400 (60) | 98 | >99 |
| 2. |  |  (3) | $Me_2SiCp''_2SmR$ | 50 (23) | 98 | >99 |
| 3. |  |  (4) | $Me_2SiCp''_2SmR$ | 10 (23) | 80[f] | >99 |
| 4. |  |  (5) | $Me_2SiCp''_2SmR$ | 45 (23) | 98 | >99 |
| 5. |  |  (6) | $Cp'_2SmR$ | | none[g] | |
| | | | $Me_2SiCp''_2SmR$ | 12 (23) | 85[h] | >99 |
| 6. |  |  (7) | $Cp'_2SmR$ | | none[i] | |
| | | | $Me_2SiCp''_2SmR$ | 10 (23) | 98[j] | >99 |
| | | | | 400 (60) | 98 | >99 |
| | | | (*R*) - SmR | 50 (23) | 98 | >98 (68% ee) |
| | | | (*S*) - SmR[k] | 50 (23) | 98 | >98 (65% ee) |
| 7. |  |  (8) | $Me_2SiCp''_2SmR$ | 10 (60) | 92 | >99 |
| 8. |  |  (9) | $Me_2SiCp''_2SmR$ | 12 (23) | 96 | >99 |
| 9. |  |  (10) | $Cp'_2SmR$ | 4 (23) | 5.0 | 5.2 |
| | | | $Me_2SiCp''_2SmR$ | > 1000 (90)[l] | 49 | 51 |
| | | | | 400 (60) | 64 | 67 |
| | | | | 120 (23) | 74 | 76 |
| | | | | 35 (0)[l] | 63 | 64 |
| | | | | 12 (-30)[l] | 59 | 61 |
| 10. |  |  (12) | $Me_2SiCp''_2SmR$ | 10 (23) | 96 | 0[m] |
| 11. |  |  (13) | $Cp'_2SmR$ | 1.2 (60) | 98 | 0[m] |
| | | | $Me_2SiCp''_2SmR$ | 10 (60) | 98 | 0[m] |

[a] Reactions were carried out in $C_6D_6$ (unless otherwise indicated) and initiated with a small amount of $H_2$ with a typical substrate/precatalyst molar ratio of 200, and a silane/olefin ratio of 1.2. [b] R = $CH(TMS)_2$. [c] Turnover frequency ($N_t$) was measured in $C_6D_6$ unless otherwise indicated. [d] $N_t$ was calculated based on the time required for 25% of the substrate to be consumed. [e] Yield was estimated based on GC analysis and the integration of $^1$H-NMR spectra. [f] The catalytic reaction was stopped after about 82% consumption of the substrates. [g] Only hydrogenated product was observed over 30 days at 60 °C. [h] About 10% hydrogenated product was also produced. [i] No reaction was observed over 30 days at 60 °C. [j] NMR scale and scale-up reaction. [k] 70:30 (*S*):(*R*) precatalyst mixture. [l] toluene-$d_8$ was used as the solvent and $N_t$ was measured in toluene-$d_8$. [m] 1,2-Addition product was formed exclusively.

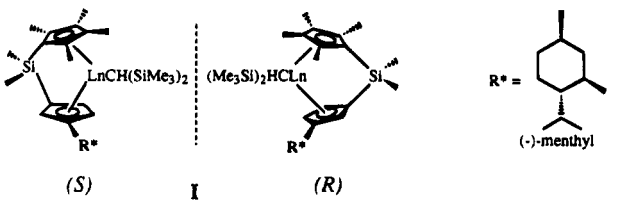
slow hydrogenation of the olefin, with the $H_2$ derived from competing dehydrogenative $PhSiH_3$ oligomerization[22,23] (silane dimers and trimers were observed in the $^1$H NMR). Some olefin hydrogenation is also observed in the $Me_2SiCp_2''Sm$-mediated process (entry 5).

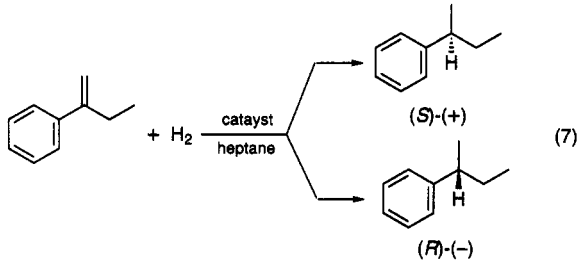
In regard to the nature of the styrenic substrate, Table 1 reveals that the rate of styrene hydrosilylation is depressed by strongly $\sigma$-electron-withdrawing *para* substituents (F)[26] and is slightly accelerated by more $\pi$-electron-releasing *para* substituents ($OCH_3$).[26] Styrene substitution at the α position has little

influence on the rate (entry 1 vs 5 and 6) unless the substituent is extremely large (entry 1 vs 7). Efforts to "steer" the regiochemistry to 1,2 addition with an *ortho* Lewis base substituent capable of interacting with a proximate, acidic lanthanide center have no obvious effect (entry 4).

Considerably different behavior is observed in the hydrosilylation of non-styrenic olefins. Again, a large enhancement in rate is observed for $Cp'_2Sm$- vs $Me_2SiCp''_2Sm$-based catalysts (entry 9). In the case of α-olefins, the selectivity for 2,1 addition can be driven as high as 76% (also unprecedented[1]) with the $Me_2SiCp''_2Sm$-based catalyst. Variation of temperature has only a minor influence on selectivity. For sterically encumbered 1-substituted and 1,1′-disubstituted olefins, the $Me_2SiCp''_2Sm$-based catalyst effects far more rapid hydrosilylation than the $Cp'_2Sm$-based analogues (entrees 10,11). In both cases, the regiochemistry of addition is exclusively 1,2.

**Enantioselective Hydrosilylation of 2-Phenyl-1-butene.** The chiral organolanthanide precatalysts (*R*)-$Me_2SiCp''$[(−)-menthyl Cp]SmCHTMS$_2$ ((*R*)-Sm) and (*S*)-$Me_2SiCp''$[(−)-menthylCp]SmCHTMS$_2$ ((*S*)-Sm) (**I**) mediate the enantioselective hydrogenation of 2-phenyl-1-butene (eq 7) with turnover frequencies on the order 9000 and 19000 $h^{-1}$, respectively, under non-mass transfer-limited conditions (rapid agitation)[14c] at 25 °C and 1.0 atm of $H_2$ pressure.[15] Under these conditions,




(7)

observed ee values are 16% ((*R*) product) for the enantiopure (*R*)-Sm catalyst and 80% ((*S*) product) for the 70% enantiopure (*S*)-Sm catalyst. Kinetic and enantioselectivity studies with catalyst mixtures (e.g., 1:1 (*R*) + (*S*)) give results differing little from numerical averages of the results for the enantiopure catalysts (chirality transfer does not involve a multimolecular species). With $D_2$, 2-phenylbutane-*1,2-d*$_2$ is the exclusive reduction product and $k_{H_2}/k_{D_2}$ values of 2.3(2) and 2.1(2) are observed for the above (*R*) and (*S*) catalysts, respectively. The kinetics of the hydrogenation obey eq 8

$$v = k[\mathrm{Sm}]^{1/2}[\mathrm{olefin}]^0[\mathrm{H_2}]^1 \qquad (8)$$

over a wide range of concentrations.[15] Under mass transfer-limited conditions (slower stirring) at 25 °C, there is some erosion of enantioselectivity to 8% ee ((*R*) product) for (*R*)-Sm and 64% ee ((*S*) product) for 70% enantiopure (*S*)-Sm. Lowering the temperature yields higher ee values for both catalysts: 27% ee ((*R*) product) at −30 °C for (*R*)-Sm and 96% ee ((*S*) product) at −80 °C for 70% enantiopure (*S*)-Sm. The derived

(26) (a) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, 1984; Part A, pp 179−190. (b) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; Chapter 9.

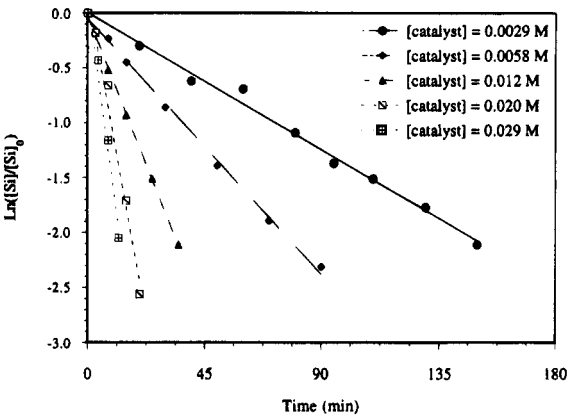
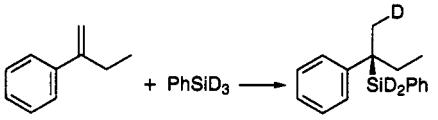



**Figure 3.** Kinetic plots for the catalytic $PhSiH_3$ hydrosilylation of 2-phenyl-1-butene as a function of the indicated (*R*)-$Me_2SiCp''$[(−)-menthylCp]SmCHTMS$_2$ ((*R*)-Sm) precatalyst concentrations. Initial [$PhSiH_3$] = 0.543 M; [olefin] = 4.182 M. The lines represent least-squares fits to the data points.

$\Delta\Delta H^{\ddagger}$ values are 0.8(1) and 1.6(7) kcal/mol, respectively, and $\Delta\Delta S^{\ddagger}$ values are 1.4(2) and 1.3(6) eu, respectively.

At room temperature in aliphatic solvents, 2-phenyl-1-butene undergoes (*R*)-Sm, (*S*)-Sm-mediated hydrosilylation by $PhSiH_3$ with exclusive (≥99%) 2,1 addition and with $N_t \sim 50$ $h^{-1}$. Enantioselection proceeds with 68% ee ((*R*) product) and 65% ee ((*S*) product) for the (*R*)-Sm and (*S*)-Sm catalysts (70% enantiopure), respectively (Table 1, entry 6). Product absolute configuration and % ee were determined by protodesilylation and oxidative cleavage (with retention)[20] to the known 2-phenyl-2-butanol (see Experimental Section for details).[21] Deuterosilylation with $PhSiD_3$ mediated by (*R*)-Sm under the above conditions yields exclusively the 1-deuterio addition product (eq 9).




(9)

Kinetic studies of $H_2$-initiated 2-phenyl-1-butene hydrosilylation with $PhSiH_3$ were conducted by $^1H$ NMR at 50 °C (a more convenient temperature) in $C_6D_6$ using (*R*)-Sm as the catalyst (see Experimental Section for details). A series of experiments was first conducted in which the catalyst concentration was varied from 0.0029 to 0.029 M with [olefin] and [silane] in large excess and held constant. The olefin concentration was maintained in 8-fold excess over the silane concentration while the decrease in [$PhSiH_3$] was monitored. This relationship approaches pseudo zero order in olefin concentration and suppresses dehydrogenative silane polymerization processes.[22] The latter are evidenced by the readily detected appearance of $PhSiH_2SiH_2Ph$ and $PhC(CH_3)CH_2CH_3$ product resonances in the $^1H$ NMR and are particularly acute when the $PhSiH_3$ concentration is held in excess over that of olefin. It is likely that the excess olefin captures Sm-H species which would otherwise mediate Si−Si bond formation (Scheme 2). The variable catalyst concentration experiments yield good first-order plots for $PhSiH_3$ decay (Figure 3). In regard to reaction order in catalyst concentration, a van't Hoff treatment yields an order of 1.1(1) in catalyst (Figure 4). Studies were then carried out in which the catalyst concentration was held constant and the $PhSiH_3$ concentration monitored while the olefin concentration was varied over a 6-fold range (while always under approximately pseudo-zero-order conditions in olefin). Again, $PhSiH_3$ decay follows first-order behavior (Figure 5) while, within experimental uncertainty, the observed rate constant is

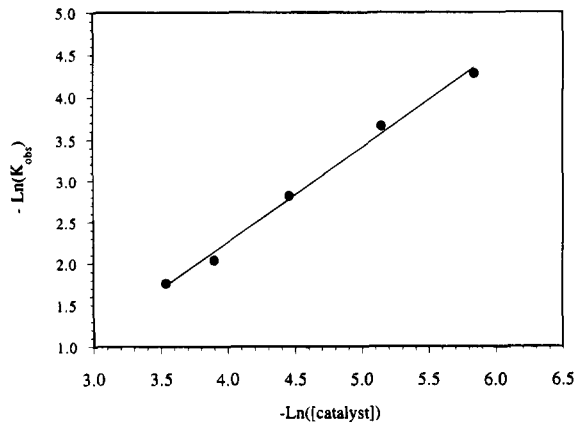



**Figure 4.** Dependence of the observed rate constants for the hydrosilylation process in Figure 3 on the catalyst concentration. The line represents a least-squares fit to the data points.

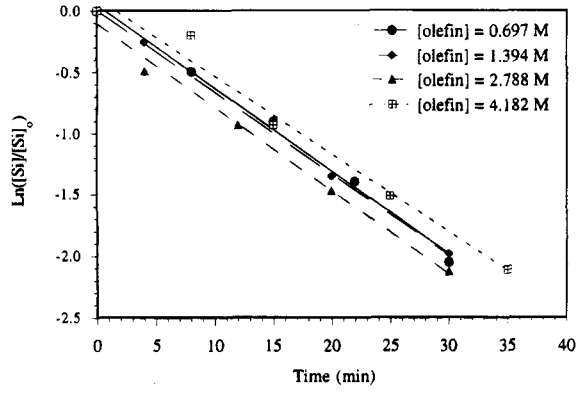



**Figure 5.** Kinetic plots for the catalytic $PhSiH_3$ hydrosilylation of 2-phenyl-1-butene for constant silane (0.543 M) and (*R*)-$Me_2SiCp''$-[(−)-menthylCp]$SmCHTMS_2$ ((*R*)-Sm) precatalyst concentration (0.012 M) over the indicated range of olefin concentrations. The lines represent least-squares fits to the data points.

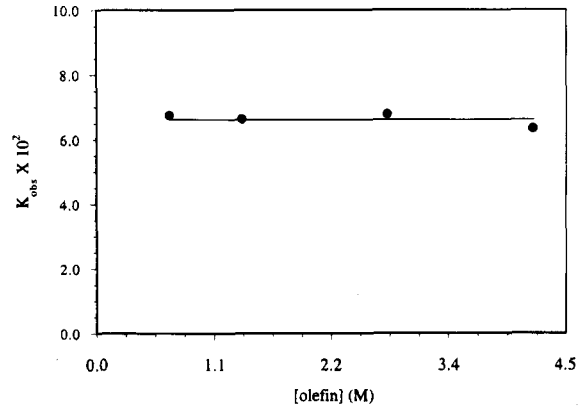



**Figure 6.** Dependence of the observed rate constants for the hydrosilylation process in Figure 5 on the olefin concentration. The line represents a least-squares fit to the data points.

insensitive to the olefin concentration (Figures 5 and 6). These results yield the rate law of eq 10 with $k = 0.17(2)\ M^{-1}\ s^{-1}$.

$$v = k[Sm]^1[olefin]^0[PhSiH_3]^1 \qquad (10)$$

**$D_2O$ Quenching of Asymmetric Hydrosilylation.** In an effort to intercept and identify possible catalytic intermediates and to observe other species that might be present during the (*R*)-Sm-mediated addition of $PhSiH_3$ to 2-phenyl-1-butene, degassed $D_2O$ was added to a reaction during catalytic turnover (the reaction had not been initiated with $H_2$). The organics produced in this process were isolated and examined by $^2H$ NMR (see Experimental Section for details). In addition to signals associated with straightforward deuterolysis products $CHDTMS_2$ and $Me_2SiCp''D$[(−)-menthylCpD] (eq 11), the

$$Me_2SiCp''[(-)\text{-menthylCp})]SmCHTMS_2 \xrightarrow{D_2O} Me_2SiCp''D[(-)\text{-menthylCpD}] + CHDTMS_2 + \text{"}Sm(OD)_3\text{"} \qquad (11)$$

species $PhCD(CH_3)(CH_2CH_3)$ and $PhSiH_2D$ were also detected in approximately comparable quantities. These can best be explained in terms of the deuterolysis processes portrayed in eqs 12 and 13. Importantly, there is no evidence among the

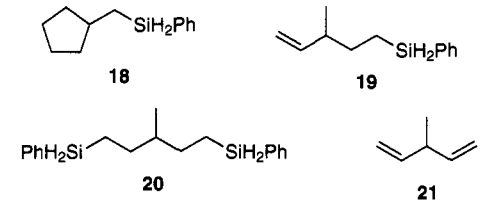
$$L_nSmSiH_2Ph \xrightarrow{D_2O} L_nD_2 + PhSiH_2D + \text{"}Sm(OD)_3\text{"} \qquad (12)$$

$$L_nSmCPh(CH_3)(CH_2CH_3) \xrightarrow{D_2O} L_nD_2 + PhCD(CH_3)(CH_2CH_3) + \text{"}Sm(OD)_3\text{"} \qquad (13)$$

products for either $PhSiH_2CH_2CD(Ph)(CH_2CH_3)$ or $PhSiH_2C(Ph)(CH_2CH_3)CH_2D$, which might arise from the interception of silaalkyl organolanthanides as invoked in Scheme 1A.

**Cyclohydrosilylation of 1,5-Hexadiene.** The high reactivity of lanthanide-carbon $\sigma$ bonds with respect to olefin insertion in the present systems,[11] coupled with the great kinetic advantage of the intramolecular variants of such processes,[8] suggests another probe of Scheme 1A vs Scheme 1B pathways. In principle, a hydride/alkyl cycle should yield products arising from silane/alkyl transposition subsequent to alkene insertive cyclization (Scheme 4). Depending upon 1,2 or 2,1 diene insertion regiochemistry, silanes of structure **A** or more strained **B**, respectively, can be formed. In contrast, a silyl/alkyl cycle should afford products of structure **C** or again **B** depending upon whether olefin insertion into the lanthanide−silyl linkage occurs with 1,2 or 2,1 regiochemistry (Scheme 4).

Hexadiene experiments were carried out under standard hydrosilylation conditions using $Cp'_2SmCHTMS_2$, $Me_2SiCp''_2SmCHTMS_2$, and (*R*)-Sm as precatalysts. Products were characterized by standard analytical techniques as well as by independent synthesis of authentic samples (see Experimental Section for details). Interestingly, four major products are produced (**18**−**20**, and 1,5-hexadiene isomerization products -- predominantly **21**), with the distribution depending upon catalyst and reaction time. Product distributions for completed reactions are given in Table 2. In the case of $Cp'_2SmCHTMS_2$, the




predominant product is **18** (general structure **A** in Scheme 4), with only small amounts of **19** and **20** detected.[27] However, in the case of $Me_2SiCp''_2SmCHTMS_2$ and (*R*)-Sm as precatalysts, substantial quantities of **19** and **20** are produced, with in situ $^1H$ NMR monitoring (Figure 7) indicating that **19** and **20** do not arise from **18** but via a separate process involving skeletal rearrangement of 1,5-hexadiene—vide infra. Importantly, no products of general structure **C** (Scheme 4) are observed, arguing against the silyl/alkyl hydrosilylation pathway.

(27) The hydrosilylation of 1,5-hexadiene with $PhSiH_3$ catalyzed by $Cp'_2LuCH_3$ has been reported in a patent.[22b] A cyclopentamethylsilane of structure **A** is obtained in "essentially quantitative yield".

**Scheme 4.** Posible Scenarios for Organolanthanide-Catalyzed 1,5-Hexadiene Hydrosilylation

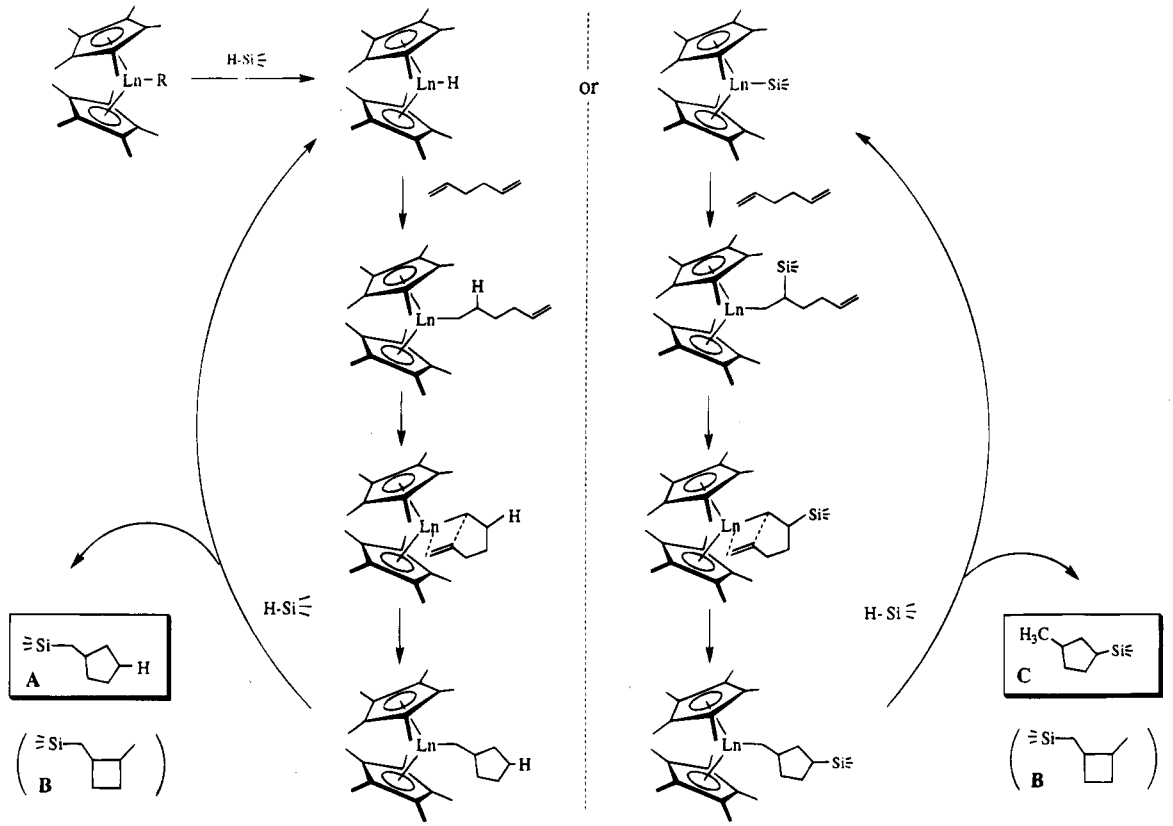



**Table 2.** Product Distribution (%) for the Organolanthanide-Catalyzed Hydrosilylation of 1,5-Hexadiene with Phenylsilane

| precatalyst[a] | 18 | 19 | 20 | 21[b] |
|---|---|---|---|---|
| $Cp'_2SmR$ | 90 | 6 | 1 | 1 |
| $Me_2SiCp''_2SmR$ | 50 | 32 | 8 | 7 |
| (*R*)-$Me_2SiCp''$[(−)-menthylCp]SmR | 51 | 31 | 7 | 7 |

[a] R = $CHTMS_2$. [b] And other 1,5-hexadiene isomerization products.

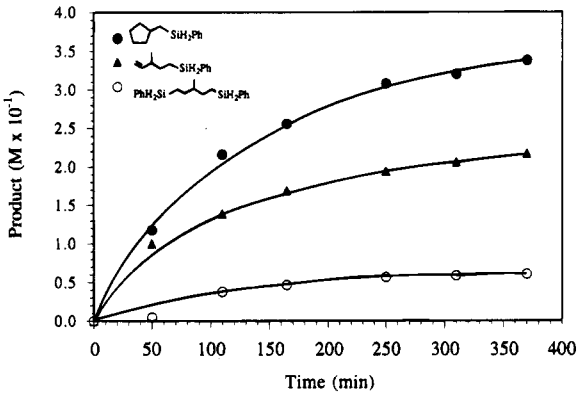
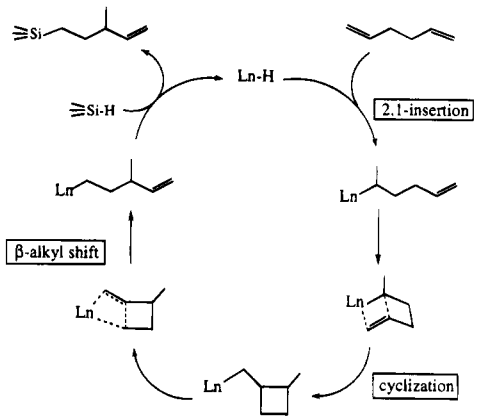



**Figure 7.** Kinetic profile for product formation in the $PhSiH_3$ hydrosilylation of 1,5-hexadiene using (*R*)-$Me_2SiCp''$[(−)-menthylCp]-$SmCHTMS_2$ ((*R*)-Sm) as the precatalyst.

The origin of products **19** and **20** can be rationalized on the basis of the foregoing discussion and known diene chemistry for electrophilic metal centers of this type. As evident in entry 9, Table 1, $Cp'_2SmCHTMS_2$-mediated α-olefin hydrosilylation (and presumably net Sm−C bond formation—vide infra) occurs in a 1,2 addition pattern. However, the large proportion of 2,1 addition products (Table 1, entry 9) observed for the more "open" catalysts argues that 2,1 addition predominates for these catalysts. Scheme 5 elaborates a pathway by which sequential 2,1 insertion, insertive cyclization, β-alkyl shift processes, and

**Scheme 5.** Possible Pathway for Formation of Hydrosilylated 3-Methyl-1,4-pentadiene Skeletal Rearrangement Products




Ln−C/Si−H transposition can effect the conversion of 1,5-hexadiene to **19**. Such a transformation finds precedent in organoscandium-catalyzed olefin rearrangements elucidated by Bercaw[28] as well as in examples of organolanthanide-catalyzed β-alkyl shift and cyclization processes.[11d,29] In the present case, the absence of detectable/intercepted cyclobutylmethylsilanes suggests that the intramolecular β-alkyl shift/ring-opening process must be considerably more rapid in these organolanthanide coordination spheres than silane/alkyl transposition. Subsequent hydrosilylation of **19** would yield **20** while β-H elimination rather than Ln−C/Si−H transposition in Scheme 5 would yield **21**. Hydrosilylation of a commercial sample of 3-methyl-1,4-pentadiene with $PhSiH_3$ (1:1 ratio) using $Cp'_2$-$YCHTMS_2$ as the precatalyst (the use of a smaller metal ion

(28) (a) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74−84. (b) Bunel, E. E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976−978.

(29) Yang, X.; Seyam, A. M.; Fu, P.-F.; Marks, T. J. *Macromolecules* **1994**, *27*, 4625−4626.

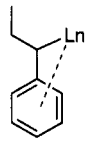
was anticipated to suppress rapid skeletal rearrangements) yielded compounds **19** (52%) and **20** (22%) along with the stoichiometrically expected quantity of unreacted **21** (24%).

## Discussion

The present study significantly broadens what is known about the scope and mechanism of organolanthanide-catalyzed olefin hydrosilylation. In the ensuing discussion we focus on phenomenology and conclusions relating to the scope and mechanism of this process.

**Reaction Scope**. In regard to scope, it is seen that variation of lanthanide size and ancillary ligation can effect considerable tunability of hydrosilylation rate and regiochemistry. In particular, larger lanthanide ions and more "open" metal coordination environments afford higher turnover frequencies and enhanced regiospecificity. The tendency of larger ions and more open coordination spheres to accelerate organo-f-element catalyzed olefin transformations has been noted before (hydrogenation,[11,14,15,18,30] polymerization,[11a,b,18] hydroamination,[8] hydrophosphination[9]), and in a number of cases this effect is associated with catalytic cycles involving turnover-limiting olefin insertion.

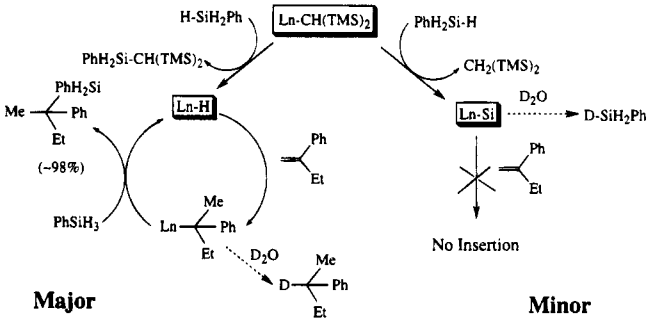
The regiochemical course of the present hydrosilylation processes is also noteworthy. Such a bias toward 2,1 additions is not a general characteristic of homogeneous transition metal hydrosilylation catalysts.[1,4,31] For a simple α-olefin such as 1-hexene, we find that 2,1 regioselectivity can be driven to as high as 76%, while return to 1,2 addition regiochemistry is observed for more sterically encumbered olefins such as vinylcyclohexene and 2-ethyl-1-butene. The metal ion size and ancillary ligand effects on regiochemistry are likely to have a major steric component while lanthanide-induced positive polarization of the evolving carbon skeleton may be better stabilized at internal carbon positions. Nevertheless, the marked 2,1 regiochemistries observed for *all* styrenic olefins[1,32] suggest important factors other than steric are operative as do the aryl substituent effects on hydrosilylation rates which, from the rate law, must operate subsequent to olefin insertion (electron-withdrawing groups retard; electron-releasing groups accelerate). An appealing possibility to explain these regiochemical preferences and electronic kinetic effects invokes interaction of the electrophilic lanthanide center with the arene $\pi$ system (**II**).




**II**

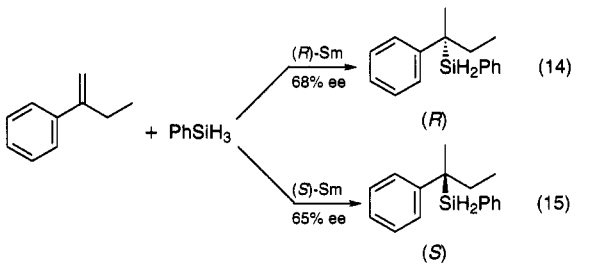
There is considerable precedent for such $\eta^n$-benzylic structures in organo-f-element chemistry.[15b,33] They should be favored by sterically more open metal coordination spheres. Delivery of the lanthanide ion to the styrene benzylic position is of course in accord with a metal hydride/alkyl hydrosilylation pathway (Scheme 1A), for which this study provides much other support (vide infra).

**Scheme 6.** Mechanistic Scenarios for Organolanthanide-Catalyzed Hydrosilylation




Rate ~ $[Ln]^1[Silane]^1[Olefin]^0$

In regard to stereochemistry, the chiral organolanthanide precatalysts (*R*)-$Me_2SiCp''$[(−)-methylCp]$SmCHTMS_2$ and (*S*)-$Me_2SiCp''$[(−)-menthylCp]$SmCHTMS_2$ (70% enantiopure) effect the hydrosilylation of 2-phenyl-1-butene with relatively high enantioselectivity (eq 14 and 15).




The sense of this chirality transfer exactly mirrors the analogous hydrogenation systems:[15] (*R*) catalyst affords predominantly (*R*) product; (*S*) catalyst affords predominantly (*S*) product; however, the magnitudes of chirality transfer differ significantly for the two catalytic systems. Thus, for 2-phenyl-1-butene hydrogenation, ee ((*S*)-Sm) = 80% >> ee ((*R*)-Sm) = 16% (compare to eqs 14 and 15). The present efficiencies of chirality transfer are high compared to what has previously been reported for styrenes (50% ee for the addition of $HSiCl_3$ catalyzed by (*S*)-PPFA-$PdCl_2$)[32,34] but are lower than the best results for $HSiCl_3$ addition to other α-olefins catalyzed by MOP-$[PdCl(\eta^3\text{-}C_3H_5)]_2$.[31,34]

**Reaction Mechanism**. In regard to reaction pathway, the results of the present study favor a hydride/alkyl sequence (Schemes 1B and 6) over a silyl/alkyl sequence (Scheme 1A) as the principal hydrosilylation pathway. Scheme 1B invokes initial, exothermic olefin insertion in a Ln−H bond. There is ample precedent for such processes, and they can be expected, for the present ancillary ligation, to be very rapid.[11,14,15] Indeed, the zero-order kinetics in [olefin] of the 2-phenyl-1-butene + $PhSiH_3$ addition mediated by (*R*)-Sm are consistent with rapid, operationally irreversible olefin insertion into the Sm−H bond. With reference to Scheme 1A, there is no precedent for rapid olefin insertions into Ln−Si bonds,[1a,6,7] and olefins such as

(30) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828−1838.

(31) To our knowledge, only MOP-$[PdCl(\eta^3\text{-}C_3H_5)]_2$ catalyzes the hydrosilylation ($HSiCl_3$) of unfunctionalized α-olefins with comparable (or in some cases higher) regioselectivity and by what is doubtless a different mechanism: Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887−9888. MOP = 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl.

(32) To our knowledge, regiospecific 2,1 addition to styrenes has only been observed for Ni[32a]- and Pd[32b,c]-based homogeneous catalysts, although the poor regioselectivity of the Spier catalyst can be improved by addition of $Ph_3P$ or pyridine.[32d] (a) Svoboda, P.; Sedlymayer, P.; Hetflejs, J. *Collect Czech. Chem. Commun.* **1973**, *38*, 1783−1785 (using $[Ni(CO)(\eta^5\text{-}C_3H_5)]_2$). (b) Yamamoto, K.; Hayashi, T.; Kumada, M. *J. Am. Chem. Soc.* **1971**, *93*, 5301−5302 (using (*S*)-PPFA-$PdCl_2$; PPFA = 1-(diphenylphosphino)-1′-(1-(dimethylamino)ethyl)ferrocene). (c) Hayashi, T.; Tamao, K.; Katsuro, Y.; Nakae, I.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 1871−1874. (d) Capka, M.; Svoboda, P.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3830−3833.

(33) (a) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219−223. (b) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 4692−4695.

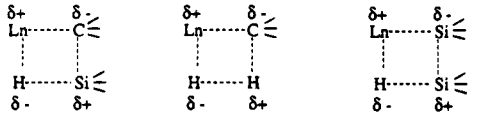
(34) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994 pp 124−131.

2-phenyl-1-butene would appear to offer significant steric impediments. Also in support of Scheme 1B is the similarity between the (*R*)-Sm-mediated hydrosilylation and hydrogenation of 2-phenyl-1-butene. The kinetics of both processes are zero-order in olefin and, with the stereochemistry likely fixed in this step, it is not surprising that both processes transfer the same net sense of chirality (but not the same magnitude—vide infra).

Although the $D_2O$ quenching experiments do not differentiate catalytic intermediates or resting states from other non-participating species which may be present (e.g., "dead ends"), they do provide an assay of the lanthanide−element bonds that are present in the reaction mixture. The results of these experiments are consistent with Scheme 1B in that 2-phenylbutane-2-$d_1$ is detected, indicating interception of a benzylic lanthanide complex formed via olefin insertion into a Ln-H bond (cf., **II** and Scheme 6). The other significant quenching product is $PhSiH_2D$, indicative of a $Sm\text{-}SiH_2Ph$ functionality (eq 12) which presumably arises in a bimolecular protonolytic process as observed during initiation (cf., eq 4) and Figure 1[35]). The presence of this species could be taken as evidence for the operation of Scheme 1A in hydrosilylation, however it is also noteworthy that $\beta$-deuteroalkylsilanes, another possible intermediate/resting state of Scheme 1A, are not observed in this experiment.

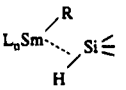
The results of the 1,5-hexadiene hydrosilylation experiment strongly favor a hydride/alkyl cycle since Ln−H olefin insertion would yield an olefinic alkyl which would be expected to undergo subsequent cyclization (Scheme 4). Importantly, the observed cyclopentylmethylsilane product is inconsistent with the expectations of Scheme 1A (Scheme 4). The other products of the 1,5-hexadiene experiments are shown to arise from diene skeletal rearrangements occurring prior to hydrosilylation.

The second step in proposed Scheme 1B is a Si−H/Ln−C transposition, presumably of the heterolytic, four-center $\sigma$ bond metathesis type (**III**).




This process is turnover-limiting for the (*R*)-Sm-mediated 2-phenyl-1-butene hydrosilylation, in congruence with the analogous hydrogenation process,[15] which presumably proceeds via an analogous transition state (**IV**).[36] Transition states similar to **III** have been invoked previously in organolanthanide-catalyzed dehydrogenative silane coupling processes (**V** and Scheme 2).[22a,23] The aforementioned styrene substituent kinetic effects (more $\pi$ electron-releasing groups accelerate the hydrosilylation rate) would appear to be in accord with the depicted charge demands in **III**. In agreement with this picture, a previous study showed that electron-releasing substituents (e.g., $NMe_2$) accelerate Th−C bond hydrogenolysis in complexes such as $Cp'_2Th(OR)(p\text{-}C_6H_4X)$.[37] In regard to stereochemistry, it is not unreasonable that **III** (and **IV**) should be traversed with retention of configuration at the carbon center.[15]

Despite the aforementioned mechanistic parallels, the catalytic hydrogenation and hydrosilylation cycles differ in two respects. First, the rate law for hydrogenation is *one-half order* in [Sm][15] (eq 8) while that for hydrosilylation is *first-order* (eq 10). Second, while the predominant sense of chirality transfer is the same for the two cycles, hydrogenation occurs with both high (80% ee, (*S*)-Sm) and low (16% ee, (*R*)-Sm) net chirality transfer, while the corresponding hydrosilylation parameters are 65% and 68%, respectively. The hydrogenation rate law was rationalized in terms of a dimer (e.g., a $\mu^2$-dialkyl or a $\mu^2$-hydridoalkyl) which was in rapid preequilibrium with a hydrogenolytically reactive monomer. It is reasonable that stereochemistry is fixed in the insertion step which produces this species, with the differing magnitudes of chirality transfer reflecting the diastereomeric nature of the catalysts. For asymmetric hydrogenation, it was shown that stereochemical integrity is only erroded (and only slightly) in $H_2$-starved (mass transport-limited) regimes, presumably via competing $\beta$-H elimination/readdition sequences.[15] The reason no intermediate dimer is detected in the asymmetric hydrosilylation cycle may also explain the differences in chirality transfer vis-à-vis asymmetric hydrogenation. We suggest that the relatively high concentrations and Lewis basicity of $PhSiH_3$ may result in weak complexation (e.g., **VI**) capable of inducing/preserving dissociation of dimeric species and thereby influencing the stereochemistry of olefin insertion. While a number of $\eta^2$-silane complexes have been structurally characterized,[7a,38] we are aware of none for $d^0$ metals or lanthanides, although transitory lanthanide $\eta^2$-$H_2$ and hydrocarbon complexes can be detected by NMR in solution.[39] Note that **VI** is a plausible precursor to transition state **III**.



VI

## Conclusions

Suitable selection of metal ion and ancillary ligands affords organolanthanide catalysts which effect a diverse variety of regio- and enantioselective olefin hydrosilylations. Large ions and open coordination spheres favor unusual 2,1 additions, especially for styrenic olefins. The probable mechanism of this transformation resembles that of the analogous olefin hydrogenation process, with rapid olefin insertion into a Ln−H bond, followed by turnover-limiting Si−H/Ln−C transposition. One interesting ramification of this pathway is that diverse sequences of transformations can be effected at the lanthanide center (e.g., insertion, cyclization, ring opening) and the resulting altered organic structure then transferred to silicon in a final step. The scope and exploitation of such processes is currently under investigation.

**Acknowledgment.** We thank NSF for support of this research under Grant CHE9104112. P. F. and L.B. thank Dow-Corning and Rhône-Poulenc, respectively, for fellowships.

JA950246H

(35) (a) Intramolecular metalation/elimination of $CH_2TMS_2$ to yield an $M(\eta^6\text{-}CH_2C_5Me_4)$ species[2,11d,35b,c] which subsequently reacts with $PhSiH_3$ cannot be excluded with the data at hand. (b) Booy, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 3246−3252 and references therein. (c) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232−241 and references therein.

(36) For relevant theoretical work, see: Folga, E.; Ziegler, T.; Fan, L. *New. J. Chem.* **1991**, *15*, 741−748 and references therein.

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(38) (a) Luo, X.-L.; Kubas, G. J.; Bryan, J. C.; Burns, C. J.; Unkefer, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 10312−10313 and references therein. (b) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151−187 and references therein. (c) Spaltenstein, E.; Palma, P.; Kreutzer, K. A.; Willoughby, C. A.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 10308−10309.

(39) Nolan, S. P.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8538−8540.