Hz, 2 H), 7.05 (d = 1.5 Hz, 2 H), 7.12 (d = 1.5 Hz, 2 H). ^{29}Si NMR (C_6D_6): δ −30.39. MS:M^+ m/e 885. HR/MS: $M^+ - (CH_3)_2CH$ calc, m/e 841.6141; found, m/e 841.6000. Mp: 212–231 °C.

Synthesis of Tetrakis(2,4,6-triisopropylphenyl)-1,3-cyclodisiloxane (3). Disilene 1 was oxidized using the same procedure as for the synthesis of 5, except that a large excess of mCPBA was used. The conversion to 3 was quantitative.

Purification of 3 and 4 from a Mixture. A mixture of solid 3 and 4 from the oxidation of 1 was washed with ethanol until a small amount of the mixture had visibly dissolved. The volume of the ethanol was then reduced by boiling and eventually cooled to 0 °C for 2 weeks. If only a few crystals formed they were, sometimes, either pure 3 or pure 4. Small amounts of pure compounds were isolated in this way. However, this procedure was difficult to reproduce. Most often either crystallization did not occur or, if it did, it produced crystals of both 3 and 4. Gel permeation chromatography with toluene as the eluant afforded an additional 5 mg of pure 3 and 4 after recycling 25 times in toluene over 12 h.

X-ray Crystal Structure Data for 1,3-Disilaoxirane 3 ($C_{60}H_{92}O_2Si_2$). Colorless prisms were grown by the slow cooling of an ethanol solution of 3. The crystals were monoclinic and belonged to the space group $P2_1/c$ with a = 10.420 (2) Å, b = 15.184 (3) Å, c = 37.410 (7) Å, β = 95.02 (3)°, V = 5896 (2) Å^3, and d_{calcd} = 1.016 g/cm^3 for Z = 4. Data were collected at 113 K on a Siemens P3f diffractometer using Mo Kα radiation (λ = 0.710 73 Å). A total of 9889 reflections were collected with 9469 independent reflections (R_{int} = 4.05%) and 4580 observed reflections ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by full-matrix least-squares procedures, using SHELXTL-PLUS software. Hydrogen atoms were added at calculated positions. Final R indices: R = 7.81%, R_w = 7.56%.

X-ray Crystallography Data for Disilaoxirane 5 ($C_{60}H_{92}OSi_2$). Colorless prisms were grown by the slow cooling of an ethanol solution of 5. The crystals were triclinic and belonged to the space group $P1$ with a = 13.049 (4) Å, b = 13.607 (4) Å, c = 17.567 (5) Å, α = 88.69 (2)°, β = 85.38 (2)°, γ = 68.90 (2)°, V = 2900.5 (15) Å^3, and d_{calcd} = 1.014 g/cm^3 for Z = 2. Data were collected at 113 K on a Siemens P3f diffractometer using Cu Kα radiation (λ = 1.541 78 Å). A total of 8241 reflections were collected with 7815 independent reflections (R_{int} = 1.33%) and 6034 observed reflections ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by full-matrix least-squares procedures, using SHELXTL-PLUS software. Hydrogen atoms were added at calculated positions. Final R indices: R = 6.50%, R_w = 8.10%.

Acknowledgment. Research was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract AFOSR-89-0004, and the National Science Foundation, Grant CHE-8922737. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation thereon. We thank Yoshitaka Hamada for his assistance in carrying out the gel permeation chromatography and Lori LaPean and Tom Bedard for synthesis of trisilane.

Registry No. 1, 114057-47-5; 2, 138784-56-2; 3, 138435-81-1; 4, 121578-61-8; 5, 138784-57-3; 6, 74226-59-8; 7, 108202-50-2; 8, 114057-43-1; SiF_4, 7783-61-1; 1-bromo-2,4,6-triisopropylbenzene, 21524-34-5.

Supplementary Material Available: Tables of crystallographic data, atomic coordinates and anisotropic thermal parameters, and bond lengths and angles for 3 and 5 (23 pages); listings of observed and calculated structure factor amplitudes for 3 and 5 (62 pages). Ordering information is given on any current masthead page.

Group 4 Metallocene Olefin Hydrosilylation Catalysts

Michael R. Kesti and Robert M. Waymouth*

Department of Chemistry, Stanford University, Stanford, California 94305

Received July 18, 1991

The hydrosilylation of olefins such as styrene, 1-hexene, and 2-pentene with diphenylsilane can be carried out with catalysts generated from zirconocene dichloride and 2 equiv of butyllithium. Complete regioselectivity is observed as only terminal organosilicon products are produced (~90%). In the case of styrene, three major products are formed: phenethyldiphenylsilane, *trans*-1-phenyl-2-(diphenylsilyl)ethene, and ethylbenzene. The product distribution was found to be dependent on reagent concentrations: reactions run with excess diphenylsilane favored diphenylphenethylsilane; excess styrene favored *trans*-1-(diphenylsilyl)-2-phenylethene. Reactivity as a function of silane, olefin, and catalyst was examined. Secondary silanes are generally superior to primary and tertiary silanes for hydrosilylation. Silane coupling reactions compete with hydrosilylation with less sterically hindered silanes to produce oligomeric products. Sterically hindered silanes, such as triphenylsilane, react only at elevated temperature and yield vinylsilane as the major product. Extensive H/D exchange is observed in the hydrosilylation of styrene with Ph_2SiD_2. Stoichiometric reactions indicate that dibutylzirconocene reacts to form a zirconocene–butene complex at room temperature. The possibility of an "olefin first" mechanism is discussed.

Transition-metal-catalyzed olefin hydrosilylation is one of the most important methods for the preparation of organosilicon compounds.[1] The vast majority of hydrosilylation catalysts are derived from group 8 metals due to their exceptional catalytic activity. Because of the utility of these later-transition-metal catalysts, relatively little effort has been devoted to early-transition-metal hydrosilylation catalysts[2] despite the possibility that such catalysts might display improved chemo- or stereoselectivities. Recent results[3] revealed that early-transition-metal metallocenes are active catalyst precursors for olefin hydrosilylation. These results, combined with the recent

---

(1) For reviews on hydrosilylation see: (a) Speier, J. L. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1979; Vol. 2, p 407. (b) Ojima, I. In *Chem. Org. Silicon Cpds.*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 25, p 1479. (c) Harrod, J. F.; Chalk, A. J. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, p 673.

(2) (a) Hydrosilylation of ketones (Ti): Nakano, T.; Nagai, Y. *Chem. Lett.* 1988, 481. (b) Olefin hydrosilylation (Nd): Sakakura, T.; Lautenschlager, H. J.; Tanaka, L. *J. Chem. Soc., Chem. Commun.* 1991, *1*, 40. (Sc, Y): Watson, P. L.; Tebbe, F. N. U.S. Patent 4 965 386, 1990.

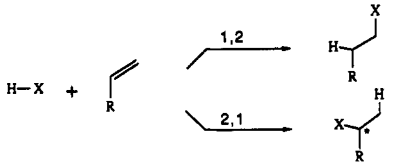
(3) (a) Harrod, J. F.; Yun, S. S. *Organometallics* 1987, *6*, 7, 1381–1387. (b) Harrod, J. F. In *Organometallic and Inorganic Polymers*; Zeldin, M., Allcock, H. R., Wynne, K. J., Eds.; American Chemical Society: Washington, DC, 1988; Chapter 7, p 89. (c) Harrod, J. F. *Polym. Prepr.* 1987, *28*, 403.

0276-7333/92/2311-1095$03.00/0 © 1992 American Chemical Society

availability of chiral metallocenes,[4] prompted us to investigate the scope of group 4 metal catalyzed olefin hydrosilylation to study the feasibility of these systems for enantioselective hydrosilylation. Herein we report our investigations on the chemo- and regioselectivity of group 4 metallocene catalysts for olefin hydrosilylation and present results which attest to the rich reaction chemistry of these systems.

The catalytic system is based on one developed by Harrod for the dehydrogenative coupling of primary silanes.[3] In the presence of olefins, hydrosilylation was found to compete with dehydrogenative oligomerization of silane to yield a mixture of hydrosilylation products and silane oligomers. To improve the chemoselectivity for hydrosilylation, we have investigated secondary silanes. Since the dehydrogenative coupling of secondary silanes is slow,[3,8b] we anticipated that the dehydrogenative oligomerization reactions observed in reactions with primary silanes would be minimized. In fact, we observe high chemoselectivity for hydrosilylation in the presence of secondary silanes.

A basic issue in hydrosilylation is the regiochemistry of Si–H addition. Different regioisomers have potentially different stereochemical features. For example, 1,2 (terminal) addition to linear olefins produces achiral products while 2,1 addition yields new stereocenters (eq 1).

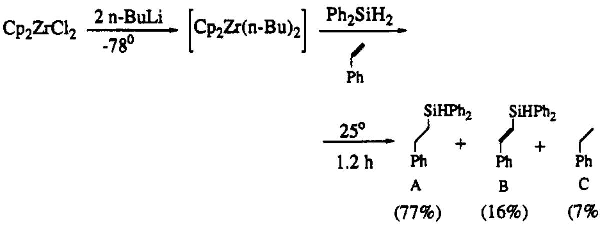


(1)

In general, terminal addition (1,2) of silane is observed in transition-metal-catalyzed olefin hydrosilylation.[1] Certain olefins such as styrene, however, exhibit a high selectivity for 2,1 addition, particularly with Pd catalysts.[5] On the basis of these results, we initially chose styrene as a substrate.

Results

Induction periods are often observed when dimethylzirconocene is employed as a catalyst precursor.[6] We have found that zirconocene derivatives generated from zirconocene dichloride and 2 equiv of butyllithium (by the method developed by Negishi[7]) are active catalyst precursors for the hydrosilylation of styrene with diphenylsilane (eq 2).[8,9]



(2)

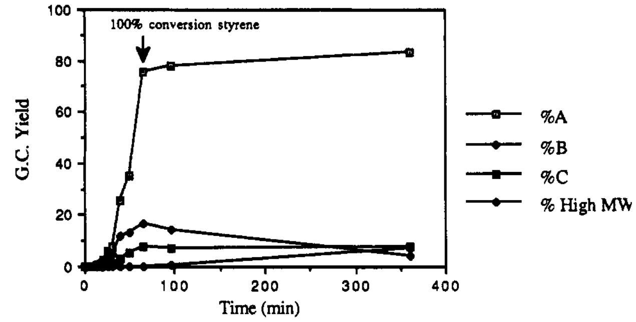
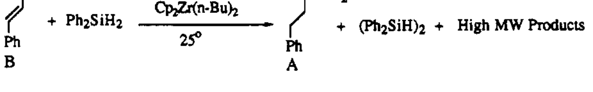


Figure 1. Hydrosilylation of styrene with diphenylsilane, reaction products versus time: (A) phenethyldiphenylsilane; (B) *trans*-1-phenyl-2-(diphenylsilyl)ethene; (C) ethylbenzene.

Addition of diphenylsilane and styrene to a preformed toluene solution of di-*n*-butylzirconocene (generated from zirconocene dichloride and *n*-BuLi at −78 °C) followed by warming to room temperature results in complete conversion of styrene and 93% conversion of diphenylsilane after 1.2 h (65 turnovers, turnover frequency ~1.44 min^{-1}). Three major products are formed: phenethyldiphenylsilane (A) (77%), *trans*-1-phenyl-2-(diphenylsilyl)ethene (B) (16%), and ethylbenzene (C) (7%). The regioselectivity is very high; only terminal silyl products are produced. In addition to the hydrosilylation, dehydrogenative silylation, and olefin hydrogenation products, traces of $(Ph_2SiH)_2$, butyldiphenylsilane, butane, and dihydrogen are also formed. The catalyst remained active for several days as repeated additions of silane and styrene were readily hydrosilylated (10 days, 6 additions, >450 turnovers). No appreciable change (slightly slower rates) in selectivity was observed in reactions run in diethyl ether or hexane in lieu of toluene.

The hydrosilylation of styrene with diphenylsilane in the presence of $Cp_2ZrCl_2/2BuLi$ was monitored by GC (Figure 1). Following complete conversion of styrene, a slow decrease in the concentration of vinylsilane B is observed while the concentration of alkylsilane A increases. Vinylsilane is completely consumed within 2 days, suggesting that it is slowly hydrogenated to alkylsilane A. The slow formation of higher molecular weight products is also detected during this time. These higher molecular weight products consist mainly of $(Ph_2SiH)_2$ along with traces of disilylalkyl compounds. The concentration of ethylbenzene C remained constant.

To investigate the reactivity of alkylsilane A and vinylsilane B under the reaction conditions, 1.0 equiv of vinylsilane B and 1.7 equiv of diphenylsilane were stirred in the presence of dibutylzirconocene at 25 °C for 40 h. Under these conditions, the vinylsilane was converted (>95%) to alkylsilane A in ~62% GC yield along with $(Ph_2SiH)_2$ and higher molecular weight products which were not characterized (eq 3).



(3)

In another control experiment, alkylsilane A was stirred in the presence of dibutylzirconocene for 39 h. No reaction

---

[4] (a) Wild, F. R. W. P.; Zsolnai, L.; Huttner, D. S.; Britzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233. (b) Wild, F. R. W. P.; Zsolnai, L.; Huttner, D. S.; Brintzinger, H. H. *Ibid.* **1985**, *288*, 63. (c) Collins, S.; Kuntz, B. A.; Hong, Y. *J. Org. Chem.* **1989**, *54*, 4154–4158. (d) Halterman, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1987**, *109*, 8105–8107. (e) Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D. *Organometallics* **1989**, *8*, 1707–1713. (f) Erker, G.; Van der Zeijden, A. A. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 512. (g) Couturier, S.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1980**, *195*, 291.

[5] Yamamoto, K.; Kiso, Y.; Ito, R.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1981**, *210*, 9.

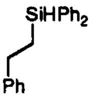
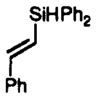
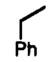
[6] Aitken, C.; Barry, J.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732.

[7] Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

[8] (a) Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, *8*, 1885. (b) Corey, J. Y.; Zhu, X. H.; Bedard, T. C.; Lange, L. D. *Organometallics* **1991**, *10*, 924. See also: (c) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564. (d) Kreutzer, K. A.; Fisher, R. A.; Davis, W. M.; Spaltenstein, E.; Buchwald, S. L. *Organometallics* **1991**, *10*, 4031.

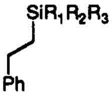
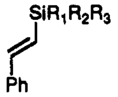
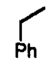
[9] Kesti, M. R.; Waymouth, R. M. *J. Organomet. Chem.* **1991**, *417*, C12–C15.

Table I. Effect of Different Reagent Concentrations on the Product Distribution for the Hydrosilylation of Styrene with Ph_2SiH_2[a]

				product distribution (%)[b]			
entry	$[Ph_2SiH_2]_i$	$[styrene]_i$	time (h)				$(Ph_2SiH)_2$
1	0.18	0.72	22	16	45	39	0
2	0.36	0.72	12	56	24	20	0
3	0.72	0.72	1.2	77	16	7	tr
4	1.44	0.72	6.5	81	11	7	1
5	0.72	2.88	22	15	69	16	0
6	0.72	1.44	6.5	52	29	16	0
7	0.72	0.36	12	88	tr	9	3

[a] Conditions: $[Cp_2ZrCl_2/BuLi]_i$ = 0.01 M, temp = 25 °C, 93–100% conversion of limiting reagent observed in each reaction. [b] Product distributions calculated by GC based on $[olefin]_i$.

Table II. Hydrosilylation of Styrene with Various Silanes[a]

						GC yield (%)[b]			
entry	silane	time (h)	temp (°C)	% conv silane	% conv styrene				other[c]
1	Ph_2SiH_2	1.2	25	93	100	77	16	7	0
		+3.8	25	95	100	81	10	8	1
2	$PhMeSiH_2$	5.0	25	93	100	82	4	8	6
3	Et_2SiH_2	3.0	25	27	35	10	16	9	1
4	$PhSiH_3$	2.7	18	94	100	80	0	10	10
5	Ph_3SiH	21.0	25	0	0	0	0	0	0
		+24.0	70	50[d]	100	0	49	51	0

[a] Conditions: $[Cp_2ZrCl_2/BuLi]_i$ = 0.01 M, $[styrene]_i$ = 0.72 M, $[silane]_i$ = 0.72 M. [b] Yields calculated by GC based on $[olefin]_i$. [c] $(Ph_2SiH)_2$ and other high-MW products. [d] Calculated by NMR.

Table III. Hydrosilylation of Various Olefins with Diphenylsilane[a]

						GC yield (%)[b]				
entry	olefin	time (h)	temp (°C)	% conv silane	% conv olefin	*n*-alkylsilane	(*E*)-vinylsilane	alkane	$(Ph_2SiH)_2$[c]	other
1	styrene	1.2	25	93	100	77	16	7	0	0
2	1-hexene	8	25	92	100	90	0	5	0	5[l]
3	1-octene	22	25	98	100	90	0	10	0	0
4	2-pentene[k]	8	25	93	100	90	0	10	0	0
5	(vinyl)TMS	8	25	95	100	85	0	9	2	5[e]
6	neohexene	19	25	<1	<1	<1	<1	<1	<1	0
		+3	60		25	0.5	12	13	1	0
		+14	60	96	100	17	13	48	34	21[f]
7	2-methyl-1-pentene	12	25	6	12	1[g]		8	7	3[h]
		+2	70	58	46	8[g]		26	46	8[h]
8	cyclohexene	24	25	15	13	1[g]		11	15	0
9	α-methylstyrene	8	25	65	70	19	15[i]	36	4	tr[j]
10[d]	α-methylstyrene	24	25	40	100	71	0	29	22	0

[a] Conditions (except entry 10): $[Cp_2ZrCl_2/BuLi]$ = 0.01 M, $[olefin]_i$ = 0.72 M, $[Ph_2SiH_2]_i$ = 0.72 M. [b] Yields calculated by GC based on $[olefin]_i$. [c] Yields based on $[Ph_2SiH_2]_i$. [d] Conditions: $[Cp_2ZrCl_2/2BuLi]$ = 0.01 M, $[olefin]_i$ = 0.18 M, $[Ph_2SiH_2]_i$ = 0.72 M. [e] $(Ph_2SiH)Ph_2SiCH_2CH_2(TMS)$. [f] $Ph_2SiHSiPh_2$(neohexyl) and *trans*-1-[(diphenylsilyl)diphenylsilyl]-2-*tert*-butylethene. [g] Combined yield of alkyl- and vinylsilane. [h] C_6H_{11} isomers. [i] One isomer by NMR; not characterized as *E* or *Z*. [j] 2-Phenyl-3-(diphenylsilyl)-1-propene. [k] 30/70 mixture of cis/trans isomers. [l] Unidentified silyl product.

was observed, suggesting that Si–C formation is not reversible under these conditions.

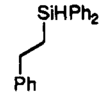
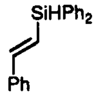
To increase selectivity for alkylsilane, a series of experiments was carried out to study the effects of different reagent concentrations on the product distribution (Table I). Selectivity for alkylsilane increases as $[Ph_2SiH_2]/[styrene]$ increases. The selectivity for hydrogenation of styrene to ethylbenzene generally increases with vinylsilane selectivity.

Results from the hydrosilylation of styrene with various silanes are summarized in Table II. Reaction with (methylphenyl)silane gave a product distribution similar to that of diphenylsilane. However, a greater amount of higher molecular weight products, such as silane dimer and doubly silylated olefins, are produced with (methylphenyl)silane. Only 27% of diethylsilane was consumed after 3 h; in this case, there was a slight selectivity for the vinylsilane *trans*-1-(diethylsilyl)-2-phenylethene (16%) over the alkylsilane diethylphenethylsilane (10%).

Phenethylphenylsilane (~80%) and higher molecular weight products (~10%) were produced during the reaction of phenylsilane and styrene. The branching ratio between hydrosilylation and hydrogenation of styrene is similar (90/10) to that observed for diphenylsilane and (methylphenyl)silane. Triphenylsilane did not react with styrene at 25 °C. At 70 °C, however, 100% conversion of styrene is observed to produce the vinylsilane 1-phenyl-2-(triphenylsilyl)ethene and ethylbenzene (1/1 ratio).

Aliphatic olefins such as 1-hexene, 2-pentene, 1-octene, and trimethylvinylsilane are readily hydrosilylated to

Table IV. Effect of Different Catalyst Precursors on Reactivity and Product Distribution[a]

						GC yield (%)[b]			
entry	catalyst precursor	time (h)	temp (°C)	% conv silane	% conv styrene				other
1	$Cp_2ZrCl_2/2BuLi$	1.2	25	93	100	77	16	7	0
2		0.9	70	99	100	80	tr	8	10[c]
3	$Cp_2Zr(CH_3)_2$	15.5	25	tr	tr	tr	tr	tr	0
		+2.0	70	92	100	81	10	9	0
4	$Cp_2HfCl_2/2BuLi$	13.0	25	5	5	1	4	1	0
		+6.0	70	57	93	13	44	34	3[d]
5	$Cp_2TiCl_2/2BuLi$	2.8	25	60	100	18	46	34	0
6	$Cp^*_2ZrCl_2/2BuLi$	2.0	25	0	0	0	0	0	0
		+2.0	70	3	10	0.2	3	5	2[d]

[a] Conditions: [catalyst precursor]$_i$ = 0.01 M, [styrene]$_i$ = 0.72 M, [Ph_2SiH_2]$_i$ = 0.72 M. [b] Yields calculated by GC based on [styrene]$_i$. [c] $(Ph_2SiH)_2$ and higher MW products. [d] Unidentified silyl product. Cp* = pentamethylcyclopentadienyl.

produce terminal silyl products in ~90% yield (Table III). In contrast to styrene, no vinylsilane products are detected during the reaction of 2-pentene. Approximately 10% of the olefin is hydrogenated in each case. Monitoring results indicate that *cis*-2-pentene is preferentially hydrosilylated over *trans*-2-pentene.

Cyclohexene yields only traces of silylated products.[10] The reaction is slow as less than 15% of cyclohexene is consumed after 24 h. Major products are $(Ph_2SiH)_2$ and cyclohexane. In a competition experiment, in which 5 equiv of cyclohexene and 1 equiv of styrene were mixed with 1 equiv of Ph_2SiH_2, cyclohexene remained unchanged and did not affect styrene hydrosilylation. 2-Methyl-1-pentene exhibits reactivity similar to that of cyclohexene as only traces of silylated products are formed; the major products are 2-methylpentane and $(Ph_2SiH)_2$. Elevated temperatures (70 °C) did not improve the selectivity for hydrosilylation.

Hydrosilylation of α-methylstyrene yielded the alkylsilane 1-methyl-1-phenyl-2-(diphenylsilyl)ethane (19%), the vinylsilane 1-methyl-1-phenyl-2-(diphenylsilyl)ethene (15%), and isopropylbenzene (36%). Selectivity for hydrosilylation was achieved at lower olefin concentration (entry 10). Monitoring by GC/MS revealed the formation of the vinylsilane product along with traces of the allylsilane diphenyl(2-phenylallyl)silane during the reaction.

In contrast to trimethylvinylsilane, 3,3-dimethyl-1-butene (neohexene) was not hydrosilylated at room temperature. At 60 °C, however, complete conversion of neohexene was observed. Initially, the vinylsilane *trans*-1-(diphenylsilyl)-2-*tert*-butylethene and neohexane are the exclusive reaction products. Upon further reaction, however, the alkylsilane neohexyldiphenylsilane (via hydrogenation of the vinylsilane), $(Ph_2SiH)_2$, and higher molecular weight disilylneohexa(e)nes are produced.

Phenylacetylene, benzaldehyde, and acetophenone did not undergo hydrosilylation under these conditions, even at elevated temperature (70 °C).

Other group 4 metallocenes were found to be active catalysts for the hydrosilylation of styrene with diphenylsilane (Table IV). Comparison experiments indicate that $Cp_2ZrCl_2/2BuLi$ is a more active catalyst precursor than Cp_2ZrMe_2 (Table IV). Only traces of reaction products were detected after 15.5 h at room temperature when Cp_2ZrMe_2 was employed as the catalyst precursor. The reaction could be initiated, however, by heating the reaction mixture to 70 °C; complete conversion of styrene was observed after 2 h at 70 °C. $Cp_2HfCl_2/2BuLi$ is inactive at room temperature but is active at 70 °C. The selectivity is in favor of vinylsilane B (44%) and hydrogenated olefin (32%) over alkylsilane A (13%). $Cp_2TiCl_2/2BuLi$ is active at room temperature; it exhibits selectivities similar to that of $Cp_2HfCl_2/2BuLi$. In contrast to the $Cp_2ZrCl_2/2BuLi$ and $Cp_2HfCl_2/2BuLi$ catalyst precursors, formation of butyldiphenylsilane is not detected when $Cp_2TiCl_2/2BuLi$ is the catalyst precursor. $Cp^*_2ZrCl_2/2BuLi$ (Cp* = pentamethylcyclopentadienyl) gave only traces of hydrosilylation products, even at elevated temperature (70 °C).

Deuterium Scrambling. Extensive deuterium scrambling was observed when styrene was hydrosilylated with Ph_2SiD_2. In this experiment, Ph_2SiD_2 and styrene were added at 0 °C to a dibutylzirconocene solution which had been generated at −78 °C. After 24% conversion of styrene, the reaction was quenched and the products and reactants were isolated and analyzed by ^1H NMR. The isolated diphenylsilane consisted of 46% Ph_2SiH_2, 42% Ph_2SiHD, and 12% Ph_2SiD_2. Each of the three olefinic H(D) sites of the unreacted styrene contained 39–43% deuterium incorporation. The hydrogen/deuterium distribution in alkylsilane A and vinylsilane B was also determined (see the Experimental Section). Ethylbenzene and butyldiphenylsilane were not isolated. A H/D mass balance analysis using the percentages calculated by NMR was within experimental error.

Reaction of neohexene and Ph_2SiD_2 in the presence of $Cp_2ZrCl_2/2BuLi$ for 3.8 h (25 °C) resulted in only 3% incorporation of H into Ph_2SiD_2 (0% conversion neohexene). However, when the reaction was run at 50 °C for 2 h, 22% incorporation of H into Ph_2SiD_2 was observed by ^1H NMR (10% conversion neohexene).

Studies of Catalyst Precursor. Butyldiphenylsilane and butane are produced in trace amounts during hydrosilylation reactions catalyzed by $Cp_2ZrCl_2/2BuLi$. The formation of these products presumably results from the reaction of the catalyst precursor, dibutylzirconocene, with silane and/or olefin during the initial stages of reaction. Preliminary mechanistic investigations have been carried out in an attempt to elucidate the processes involved in forming the active catalytic species.

A series of stoichiometric reactions was performed in which dibutylzirconocene was allowed to react in both the absence and presence of silane and/or olefin. In each experiment, a dibutylzirconocene solution was generated at −78 °C by addition of 2 equiv of BuLi to a toluene solution of Cp_2ZrCl_2 (~250 mg). The reactions were monitored by GC (−10 °C) by removal of 0.1-mL aliquots

---

[10] Corey has carried out similar studies with cyclic olefins with similar results. Corey, J. Y. Personal communication. Results presented at the 199th National Meeting of the American Chemical Society, Boston, April 1990; ORG 308.

from the reaction vessel head space.

In the absence of silane or olefin, a bright yellow dibutylzirconocene solution (-78 °C) was allowed to warm to room temperature. The solution turned dark brown within 30 min. Butane evolved over the 70 min in which the reaction was monitored. Trace amounts of 1-butene and *cis*- and *trans*-2-butene were also detected. Addition of 5.6 equiv of styrene to this solution after 70 min resulted in 1-butene evolution. Evolution of 1-butene continued throughout the next 96 min in which the reaction was monitored (butene/butane = 0.38). The evolution of 1-butene upon addition of styrene at room temperature suggests the intermediacy of a zirconocene-butene complex which can subsequently undergo olefin/olefin exchange with styrene.[11] In contrast to the above experiment, only trace amounts of 1-butene evolved when 3.3 equiv of diphenylsilane was added to a dibutylzirconocene solution which had been allowed to warm to room temperature. Butyldiphenylsilane was produced in quantitative yield (GC).

Addition of 5.6 equiv of styrene and 3.5 equiv of diphenylsilane to another dibutylzirconocene solution which had been warmed to room temperature resulted in the evolution of butane and 1-butene. The amount of 1-butene evolved was less (butene/butane = 0.14) than that evolved in the experiment where only styrene was added. Excess styrene was used in this experiment to facilitate the detection of butene. Finally, 3.5 equiv of styrene and 3.5 equiv of diphenylsilane were added to a dibutylzirconocene solution at -78 °C. Butane evolved as the solution warmed to room temperature, but only traces of 1-butene were detected. Diphenylbutylsilane was produced in 81% yield (GC).

Additional experiments using *n*-hexyl Grignard in lieu of *n*-BuLi were done in an attempt to quantify the amount of hexane and hexene produced during reactions with dihexylzirconocene and to detect displacement of hexene by silane. A 2.2-equiv portion of diphenylsilane was added to a dihexylzirconocene solution at 0 °C and slowly warmed to room temperature. The reaction solution was monitored eight times over 26 min. Each aliquot was filtered through alumina prior to injection onto the GC column; reaction of dihexylzirconocene with alumina produced 2 equiv of hexane (protonation of zirconocene-hexene by alumina to hexane is also possible; however, uncoordinated hexene can be detected). No hexene was detected by GC; the amount of hexane observed decreased from 2.0 to 1.3 equiv during the course of reaction, and 0.7 equiv of hexyldiphenylsilane was produced.

A dihexylzirconocene solution was generated at -78 °C and allowed to warm to room temperature; after 2 h, 1.7 equiv of hexane and only 0.06 equiv of hexene were detected by GC. A 13-equiv portion of styrene was added to the reaction mixture. After 3.5 h, the reaction mixture consisted of 1.3 equiv of hexane, 0.6 equiv of 1-hexene, 0.3 equiv of ethylbenzene, and 12.6 equiv of styrene; no higher MW products were detected by GC. A 5.1-equiv portion of diphenylsilane was then added to this solution (5 h following styrene addition). The system was catalytically active: after 70 min, 0.0 equiv of 1-hexene, 1.3 equiv of hexane, 0.74 equiv of hexyldiphenylsilane, 2.5 equiv of ethylbenzene, and styrene hydrosilylation products (not quantified) were detected.

Discussion

Hydrosilylation of Styrene. Dibutylzirconocene readily catalyzes the hydrosilylation of styrene at room temperature to yield *terminal* alkylsilanes and *trans*-vinylsilanes. In addition, ethylbenzene and dihydrogen are produced. Monitoring results show the product distribution to be time-dependent as vinylsilane is slowly hydrogenated to alkylsilane in the presence of excess diphenylsilane (with concomitant dimerization of silane). Rapid hydrogen/deuterium exchange is observed in both silane and styrene. The reaction is air-sensitive, and control experiments indicate Si-C bond formation is irreversible.

The chemoselectivity between alkyl- and vinylsilane can be controlled by altering the reaction conditions: selectivity for alkylsilane increases as $[Ph_2SiH_2]/[\text{styrene}]$ increases; selectivity for vinylsilane increases as $[Ph_2SiH_2]/[\text{styrene}]$ decreases. Alkyl/vinylsilane selectivity is sensitive to the steric bulk of the silane. For example, reaction with phenylsilane produces only alkylsilane while the more sterically hindered triphenylsilane yields exclusively vinylsilane (Table II, entries 4 and 5).

Secondary silanes are generally superior to primary and tertiary silanes for hydrosilylation. Silane coupling reactions compete with hydrosilylation with less sterically hindered silanes to produce oligomeric products. Sterically hindered silanes, such as triphenylsilane, react only at elevated temperature and yield vinylsilane as the major product.

The branching ratio between styrene hydrogenation versus styrene silylation is also dependent on reaction conditions. In general, selectivity for hydrogenation increases with selectivity for vinylsilane. The ratio of ethylbenzene/vinylsilane is almost always less than 1, except when triphenylsilane is employed as the silane (1/1 ratio).

$Cp_2ZrCl_2/2BuLi$ is a better catalyst precursor for styrene hydrosilylation than Cp_2ZrMe_2, $Cp_2TiCl_2/2BuLi$, and $Cp_2HfCl_2/2BuLi$ (Table IV). Both the Hf and Ti derivatives yield vinylsilane and ethylbenzene as the major reaction products. Unlike the Zr and Ti metallocenes, dibutylhafnocene is inactive at room temperature—presumably due to the stability of dialkylhafnocene at room temperature.

Hydrosilylation of Various Olefins. The hydrosilylation reactions are sensitive to the nature of the olefin (Table III). Linear, aliphatic olefins readily react to yield terminal alkylsilanes. Internal olefins such as 2-pentene also produce terminal alkylsilanes; presumably olefin isomerization occurs before hydrosilylation.[12] Internal olefins which cannot isomerize to terminal olefins are not hydrosilylated but are slowly hydrogenated (with concomitant dimerization of silane).[10] Selectivity for hydrosilylation decreases as the steric bulk and substitution of the olefin increases. For example, α-methylstyrene is less reactive than styrene, and 2-methyl-1-pentene yields only traces of silylated products. Substitution away from the olefin also affects hydrosilylation: no vinylsilane products are detected during the hydrosilylation of linear, aliphatic olefins, while neohexene yields exclusively the vinylsilane product (before subsequent hydrogenation to the alkylsilane by silane).

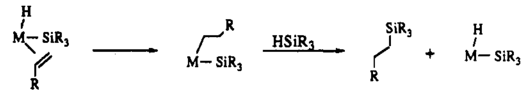
There is an apparent electronic affect on olefin reactivity. For example, aryl olefins are more reactive than aliphatic olefins: α-methylstyrene yields silylated products while 2-methyl-1-pentene does not, and trimethylvinyl-

---

[11] Buchwald and Negishi have examined the decomposition of dibutylzirconocene in the presence of phosphines and observed similar olefin/olefin exchange reactions. (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (b) Negishi, E.; Swanson, D. R.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1254.

[12] Bank, H. M.; Saam, J. C.; Speier, J. L. *J. Org. Chem.* **1964**, *29*, 792.

Scheme I. "Chalk-Harrod" Mechanism for Alkylsilane Formation



silane is readily hydrosilated at room temperature while neohexene is not.

Catalyst Precursor. The results from the stoichiometric reactions suggest that dibutylzirconocene, generated at –78 °C, undergoes an elimination process when warmed to room temperature which extrudes butane to form a zirconocene–butene complex. Buchwald and Negishi have observed a similar "non-dissociative mechanism" for dialkylzirconocenes in the presence of phosphines.[11]

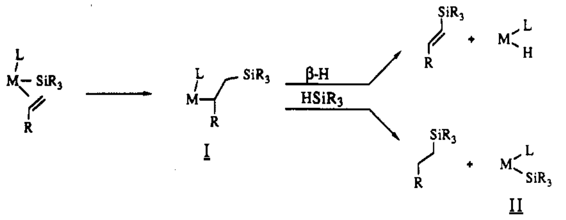
Addition of styrene to a dibutylzirconocene solution (generated at –78 °C and subsequently warmed to room temperature) results in 1-butene evolution which suggests olefin exchange occurs with styrene. Addition of Ph_2SiH_2 to a similar dibutylzirconocene solution yields butyldiphenylsilane in quantitative yield; no 1-butene could be detected (similar results were seen in the reaction of dihexylzirconocene and Ph_2SiH_2). These experiments suggest that 1-butene is not displaced from the metal by Ph_2SiH_2 but is removed via hydrosilylation.[13]

Addition of a mixture of diphenylsilane and styrene to a dibutylzirconocene solution at room temperature resulted in 1-butene evolution while no 1-butene was detected when the addition was done at –78 °C. This result suggests the selectivity between butene/styrene exchange and butene hydrosilylation may be temperature dependent; however, additional experiments are needed to fully clarify this result.

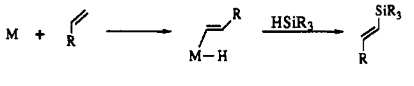
The intermediacy of zirconacyclopentanes which would result from reversible olefin coupling reactions is also possible.[14] However, no products resulting from olefin coupling reactions were detected by GC.

Mechanistic Implications. Although the formation of vinylsilane, the "dehydrogenative silylation" of olefins, is a common feature of hydrosilylation reactions catalyzed by later transition metals,[15,16] it has not been previously reported for early-transition-metal catalysts. Characteristic features of dehydrogenative silylation reactions catalyzed by later transition metals include competitive alkyl- and vinylsilane formation which is dependent upon reagent concentrations, temperature, silane, and rapid H/D exchange. We observe many of these features in zirconium-catalyzed hydrosilylation. In addition, we observe the dehydrogenative coupling of silane and the cohydrogenation of olefins.

Scheme II. Possible Mechanism for Alkyl- and Vinylsilane Formation



Scheme III. Possible Mechanism for Vinylsilane Formation via Activation of Olefin C–H



For later-transition-metal catalysts, the Chalk–Harrod mechanism[1] (Scheme I) has been postulated for olefin hydrosilylation in which the key step is reductive elimination of alkylsilane.[17] The Chalk–Harrod mechanism, however, does not account for vinylsilane formation; mechanisms involving olefin insertion into a M–Si bond are often postulated.[15] Examples of olefin insertion into M–Si bonds have been demonstrated for Fe,[18] Co,[15c] Hf, and Zr[19] complexes. Vinylsilane formation has been proposed to proceed via olefin insertion into the M–Si bond of a (silyl)(olefin)(L)metal intermediate to give intermediate I which can undergo β-H elimination to yield vinylsilane and the metal hydride (Scheme II); I could also yield alkylsilane via reductive elimination (L = H) or reaction with silane. Ligand L has been suggested to be H, SiR_3, or alkyl.[15]

An additional mechanistic possibility is the formation of a metal–vinyl intermediate via activation of an olefinic C–H bond which can react with silane to yield vinylsilane (Scheme III).

An oxidative addition/reductive elimination sequence is a common feature of mechanisms proposed for later-transition-metal-catalyzed reactions. For early-transition-metal d^0 systems, however, oxidative addition/reductive elimination is rare;[20] mechanisms based on "σ-bond metathesis" are more commonly invoked.[21] Early-transition-metal d^0 complexes have been shown to undergo a number of σ-bond metathesis reactions with silanes; Tilley has reported such reactions involving M–H, M–Si, Si–Si, and H–H bonds.[22] Similar reactions for d^0 M–H and M–C

---

[13] Pt–olefin complexes extrude olefin in the presence of silanes to form Pt–silyl complexes. Auburn, M.; Ciriano, M.; Howard, J. A. K.; Murray, M.; Pugh, N. J.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 659.

[14] Swanson, D. R.; Roussett, C. J.; Negishi, E.; Takahashi, T.; Seki, T.; Saburi, M.; Uchida, Y. *J. Org. Chem.* **1989**, *54*, 3521.

[15] Vinylsilane formation based on olefin insertion into M–Si: (a) Seitz, F.; Wrighton, M. S.; *Angew Chem., Int. Ed. Engl.* **1988**, *2*, 289. (b) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366. (c) Reichel, C. L.; Wrighton, M. S. *Inorg. Chem.* **1980**, *19*, 3858. (d) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345. (e) Ojima, I.; Fuchimaka, T.; Yatabe, M. *J. Organomet. Chem.* **1984**, *260*, 335. (f) Millan, A.; Fernandez, M.; Bentz, P.; Maitlis, P. M. *J. Mol. Catal.* **1984**, *26*, 89. (g) Millan, A.; Towns, E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 673. (h) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389. (i) Cornish, A. J.; Lappert, M. F. *J. Organomet. Chem.* **1984**, *271*, 153. (j) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467. (k) Seki, Y.; Takeshita, K.; Kawamoto, K. *J. Organomet. Chem.* **1989**, *369*, 117. (l) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 3890. (m) Marciniec, B. *J. Organomet. Chem.* **1983**, *253*, 349. (n) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415.

[16] References which report vinylsilane formation but do not propose mechanisms: (a) Caseri, W.; Pregosin, P. S. *J. Organomet. Chem.* **1988**, *356*, 259. (b) Oro, L. A.; Fernandez, M. J.; Estervuelas, M. A.; Jimenez, M. S. *J. Mol. Catal.* **1986**, *37*, 151.

[17] Few reductive eliminations of alkylsilanes are known. Blakeney, A. J.; Gladysz, J. A. *Inorg. Chim. Acta* **1980**, *53*, 225.

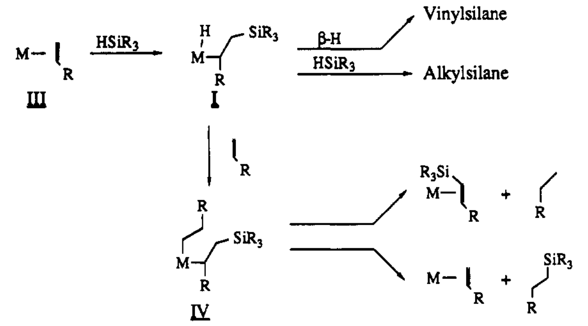
[18] (a) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345. (b) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366.

[19] For Zr and Hf, Tilley has demonstrated ethylene insertion into $Cp^*Cl_2M(Si(SiMe)_3)$ and $CpCp^*M[Si(SiMe_3)_3]Cl$; the reaction was slow and light-catalyzed. Ethylene did not insert into $Cp_2ZrClSi(SiMe_3)_3$. Arnold, J.; Engeler, M. P.; Eisner, F. H.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 2284.

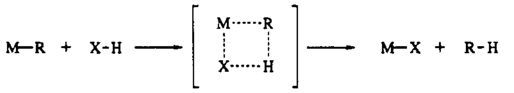
[20] Schwartz has studied the reductive elimination of zirconocene alkyl hydrides in the presence of phosphines. Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.

[21] σ-Bond metathesis references for C–H/M–H: (a) Thompson, M. E.; Baxter, Steven M.; Bulls, R. A.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981. (c) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (d) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40. (e) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425.

Scheme IV. Postulated "Olefin First" Mechanism



bonds have been described, and mechanistic studies[21a] suggest that they proceed through concerted, four-center transition states (eq 4). On the basis of these precedents, it is likely that early-transition-metal-catalyzed olefin hydrosilylation occurs via similar σ-bond metathesis reactions.

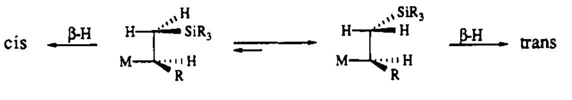


(4)

In zirconium-catalyzed hydrosilylation, alkylsilane and vinylsilane formation may result via a common intermediate such as I. β-H elimination would yield vinylsilane, and σ-bond metathesis of I with silane would produce alkylsilane and metal silyl II (Scheme II). The observed dependence of alkyl- versus vinylsilane selectivity on reagent concentration is consistent with the intermediacy of I since the product selectivity should depend on silane concentration.

The dependence of the product ratio on the size of the silane is also consistent with intermediate I since the rate of σ-bond metathesis should be sensitive to the size of the silane[22c] while β-H should be less so. Such a steric effect is in fact observed: phenylsilane produces only alkylsilanes while the more sterically hindered triphenylsilane gives exclusively vinylsilane (Table II, entries 4 and 5). With bulkier olefins β-H elimination should be favored relative to reaction with silane; α-methylstyrene shows a higher selectivity for vinylsilane compared to styrene (Table III, entry 9). In addition, traces of the allylsilane 2-phenyl-3-(diphenylsilyl)-1-propene are observed during α-methylstyrene hydrosilylation. This result is consistent with an intermediate such as I which can yield two β-H elimination products.

The selectivity for *trans*-vinylsilane could be explained by a preference for the threo conformer in the transition state for β-H elimination from I (eq 5).



(5)

At this point it is difficult to surmise the nature of the other ligand L in intermediate I or the process or processes by which I is formed. Likely candidates for ligand L are H or SiR_3. Olefin insertion into a Zr–Si bond is the most obvious possibility for the formation of I; however, studies by the Tilley group suggest that such reactions are slow.[19] Another possibility is that olefin hydrosilylation with group 4 metallocenes proceeds by an "olefin first" mechanism whereby I is formed via the reaction of the olefin adduct III[23] with silane (Scheme IV). The observation that zirconium–butene adducts react with diphenylsilane to yield butyldiphenylsilane directly provides some support for this proposal.[8c,d] Intermediate I (L = H) could then undergo β-H elimination to yield vinylsilane[24] and MH_2 or react with another 1 equiv of silane to afford alkylsilane and $MHSiR_3$.[25] Alternatively, I (L = H) could react with olefin to form dialkylzirconocene IV (Scheme IV).[26] As discussed earlier, dialkylzirconocenes containing β-hydrogens undergo an elimination process whereby the alkane is liberated to form a zirconocene–olefin complex.[11] Depending on the affinity of each alkyl ligand to form alkane or alkene, such an elimination process would yield either vinylsilane and hydrogenated olefin, or alkylsilane and olefin adduct III.

The rapid (much faster than hydrosilylation) H/D exchange observed during the hydrosilylation of styrene with Ph_2SiD_2 suggests the presence of metal hydride species. Facile σ-bond metathesis reactions between M–H and Si–D would account for the rapid exchange of Si–H(D). The scrambling of the styrene hydrogens could result via a concomitant, reversible insertion/β-H elimination of styrene into M–D; both 1,2 and 2,1 insertion of styrene must occur by this route in order to explain the statistical incorporation of D into each of the styrene olefinic H(D) sites.[8d,16a] Similar H/D scrambling was observed during the hydrozirconation of styrene with Cp_2ZrDCl and was attributed to the presence of trace amounts of Cp_2ZrH_2.[27]

Conclusion

Catalysts derived from Cp_2ZrCl_2/2BuLi are active for the hydrosilylation of olefins. The formation of vinylsilane during the hydrosilylation of styrene, the rapid H/D exchange, and olefin isomerization of 2-pentene attest to the complexity of this catalytic system. The regioselectivity for terminal addition and the high selectivity for vinylsilane formation with 1,1-disubstituted olefins indicate that careful choice of olefin substrate will be required to develop practical enantioselective olefin hydrosilylation catalysts with group 4 metallocenes.

At this point it is difficult to propose a unified mechanism which explains all of the experimental results. An "olefin first" mechanism was proposed that is consistent with the experimental results.

Experimental Section

All manipulations involving air-sensitive compounds were carried out under nitrogen either in a glovebox or using standard Schlenk techniques. All solvents were distilled under nitrogen prior to use: toluene, benzene, and ether from sodium/benzophenone and pentane from $LiAlH_4$. Olefins were distilled from CaH_2 and degassed; 2-pentene was used as a 30/70 mixture of cis/trans isomers. Butyllithium (Aldrich; 1.6 M) was titrated[28] and its purity confirmed by NMR.[29] The metallocene dichlorides

---

[22] Si σ-bond metathesis references: (a) Tilley, T. D.; Woo, H. G. *Polym. Prepr.* **1990**, *31*, 228. (b) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043. (c) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 3757. (d) Roddick, D. M.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 324. (e) Campion, B. K.; Falk, T.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049.

[23] The olefin adduct may also be viewed as a metallacyclopropane.

[24] Olefin exchange with unreacted olefin would regenerate olefin adduct III.

[25] Attempts to generate $Cp_2ZrHSiR_3$ complexes directly and study their reactivity with olefins have so far proven unsuccessful; displacement of $HSiR_3$ from $Cp_2Zr(H)SiR_3$ by olefin would regenerate the olefin adduct III to complete the "olefin-first" catalytic cycle.

[26] A similar intermediate has been proposed for Rh catalysts. Millan, A.; Fernandez, M.; Bentz, P.; Maitlis, P. M. *J. Mol. Cat.* **1984**, *26*, 89.

[27] Nelson, J. E.; Bercaw, J. E.; Labinger, J. A. *Organometallics* **1989**, *8*, 2484.

[28] Two methods were used to standardize BuLi solutions: (a) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447. (b) titration with diphenylacetic acid: Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 10, 1879.

[29] Urwin, J. R.; Reed, P. J. *J. Organomet. Chem.* **1968**, *15*, 1.

were used as received (Cp_2ZrCl_2, Boulder Scientific; $Cp^*_2ZrCl_2$, Cp_2TiCl_2, Cp_2HfCl_2, Aldrich). Silanes (Petrarch) were either used as received or prepared from the reduction of the corresponding dichlorides with $LiAlH_4$ and distilled from CaH_2. All compounds were greater than 95% pure by GC analysis. GC analyses were obtained on a Hewlett-Packard 5890 chromatograph equipped with an SE 54 column (5% phenylmethylsilicone, 95% methylsilicone, 0.33 μm × 0.2 mm × 25 m). GC response factors were determined for each compound[30] in order to calculate GC yields. GC/MS data were obtained on an identical HP 5890 chromatograph connected to a Hewlett-Packard 5970 mass-selective detector. ^1H, ^{13}C, and attached proton test (APT) NMR spectra were recorded on Varian Gemini 200, Gemini 300, and XL 400-MHz spectrometers. Elemental analyses were performed by Microlabs, UC Berkeley.

General Hydrosilylation Procedure. The hydrosilylation reactions were done under a variety of conditions; see Tables I–IV for specific reaction conditions. Reactions were not optimized for isolated yields. The following description for the hydrosilylation of styrene with diphenylsilane with $Cp_2ZrCl_2/2BuLi$ is representative.

In the drybox, a 25-mL Schlenk tube was charged with 24 mg of Cp_2ZrCl_2 (0.082 mmol, 0.01M), 4.78 mL of toluene, and 1 mL of benzene (internal standard). The solution was placed in the drybox freezer (−30 °C). After equilibration, 2 equiv of 1.63 M BuLi was added. The solution was moved to the bench and placed in a dry ice/acetone bath (−78 °C) for 30 min and then in an ice bath (0 °C) for 30 min. A bright yellow solution resulted which slowly turned orange at 0 °C. A 1-mL portion of diphenylsilane (5.4 mmol, 0.72 M) and 0.62 mL of styrene (5.4 mmol, 0.72 M) were added, and the solution was allowed to warm to room temperature. Aliquots (0.25–0.5 mL) were removed for GC analysis at convenient intervals to monitor the reaction; each aliquot was passed through a short column of alumina with diethyl ether as the eluant. Upon warming, the solution turned orange and evolution of gas was observed (^1H NMR analysis of a C_6D_6 solution which had been aerated with 10 mL of gas from the reaction vessel head space revealed the presence of dihydrogen (s, σ 4.46) and butane). At 25 min after addition of styrene and diphenylsilane, the solution was a very dark brown-orange color. This color persisted until 65 min when the solution turned a darker brown color. The reaction was quenched by addition of alumina, water, or air to the reaction mixture. [Note: dioxygen has been observed to act as a cocatalyst in Pt-catalyzed hydrosilylation reactions, leading to colloidal Pt.[31] No such affect was observed in Zr-catalyzed hydrosilylations; addition of 5 mL of dry air will quench a Zr catalyzed reaction.] The catalyst was removed via filtration of the reaction mixture through a column of alumina (diethyl ether as the eluant). The solvents were removed under vacuum and products distilled under reduced pressure. Products were identified by GC/MS, coinjection of known compounds onto the GC or ^1H, ^{13}C, and APT NMR, and/or elemental analysis.

Phenethyldiphenylsilane: bp 95 °C (0.02 mmHg); ^1H NMR (C_6D_6) (400 MHz) δ 1.38 (m, 2 H), 2.68 (m, 2 H), 5.05 (t, 1 H, $^3J_{HH}$ = 3.68 Hz, $^1J_{SiH}$ = 192 Hz), 6.9–7.2 (m, 11 H), 7.5 (m, 4 H); ^{13}C NMR (C_6D_6) (200 MHz) δ 14.0, 30.25, 125.8, 128.0, 128.2, 128.5, 129.8, 134.0, 135.3, 144.5; partial GC/MS data, *m/e* (relative intensity) 289 (8), M^+ = 288 (0.003), 287 (0.002), 286 (0.001), 211 (0.12), 210 (0.61), 184 (0.39), 183 (1.0), 182 (0.22), 191 (0.39), 133 (0.14), 132 (0.94), 106 (0.18), 105 (0.83), 104 (0.016), 103 (0.15), 79 (0.22), 78 (0.13), 77 (0.18). Anal. Calcd for $C_{20}H_{20}Si$: C, 83.33; H, 6.99. Found: C, 83.55; H, 7.00.

***trans*-1-Phenyl-2-(diphenylsilyl)ethene**: obtained as a 10/1 mixture with phenethyldiphenylsilane during the hydrosilylation of 8 equiv of styrene and 1 equiv of diphenylsilane in the presence of $Cp_2TiCl_2/2BuLi$; bp 95 °C (0.02 mmHg); ^1H NMR (C_6D_6) (400 MHz) δ 7.8–7.0 (m, 16 H), 6.66 (dd, 1 H, $^3J_{HH}$ = 3.12 Hz, $^3J_{HH}$ = 18.99 Hz), 5.50 (d, 2 H, $^3J_{HH}$ = 3.12 Hz, $^1J_{SiH}$ = 200 Hz); ^{13}C NMR (C_6D_6) (200 MHz) δ 121.77, 127.75, 128.0, 128.58, 130.03, 133.95, 135.94, 138.17, 149.7; partial GC/MS data, *m/e* (relative intensity) M^+ = 286 (0.68), $M^+ - {}^\bullet Ph$ = 209 (0.18), $M^+ - {}^\bullet C_6H_6$ = 208 (072), 181 (0.79), 181 (1.0).

Butyldiphenylsilane: isolated during stoichiometric reactions; ^1H NMR ($CDCl_3$) (400 MHz) δ 7.6–7.25 (m, 10 H), 4.85 (t, 1 H, J = 3.70 Hz), 1.5–1.05 (m, 6 H), 0.87 (t, 3 H, $^3J_{HH}$ = 6.97 Hz); partial GC/MS data, *m/e* (relative intensity), M^+ = 240 (0.03), $M^+ - {}^\bullet Bu$ = 183 (1.0).

$(Ph_2SiH)_2$: mp 78 °C (lit.[32] mp 78–80 °C); ^1H NMR ($CDCl_3$) (400 MHz) δ 7.5–7.2 (m, 20 H), 5.19 (s, 2 H); partial GC/MS data, *m/e* (relative intensity), M^+ = 366 (0.04), $M^+ - {}^\bullet C_6H_6$ = 288 (0.012), $Ph_3Si^\bullet$ = 259 (1.0), 183 (0.21).

Methylphenethylphenylsilane: ^1H NMR ($CDCl_3$) (300 MHz) δ 7.5–7.2 (m, 10 H), 4.40 (m, 1 H), 2.70 (t, 2 H, $^3J_{HH}$ = 8.61 Hz), 1.20 (m, 2 H), 0.34 (d, 3 H, $^3J_{HH}$ = 3.79 Hz); partial GC/MS data, *m/e* (relative intensity) M^+ = 226 (0.002), $M^+ - {}^\bullet CH_3$ = 211 (0.03), 183 (1.0), $M^+ - {}^\bullet Ph$ = 149 (0.12), 147 (0.38), 133 (0.28), $PhMeSiH^\bullet$ = 121 (1.0). Anal. Calcd for $C_{15}H_{18}Si$: C, 79.58; H, 8.01. Found: C, 79.22; H, 8.41.

***trans*-1-(Methylphenylsilyl)-2-phenylethene**: obtained as a 1/2 mixture with methylphenethylphenylsilane during the hydrosilylation of 3 equiv of styrene with 1 equiv of phenylmethylsilane in the presence of $Cp_2ZrCl_2/2BuLi$; ~19% yield; ^1H NMR ($CDCl_3$) (300 MHz) δ 7.6–7.2 (m, 10 H), 7.05 (d, 1 H, $^3J_{HH}$ = 19.17 Hz), 6.56 (dd, 1 H, $^3J_{HH}$ = 19.17 Hz, $^3J_{HH}$ = 2.93 Hz), 4.73 (m, 1 H), 0.507 (d, 3 H, $^3J_{HH}$ = 3.84 Hz); partial GC/MS data, *m/e* (relative intensity) M^+ = 224 (0.55), $M^+ - {}^\bullet CH_3$ = 209 (0.74), 210 (0.17), $M^+ - {}^\bullet C_6H_6$ = 146 (.91), 145 (0.33), 131 (0.4), 121 (0.28), 120 (0.66), 106 (0.14), 105 (1.0), 104 (0.12), 103 (0.12).

Diethylphenethylsilane: obtained as a 1/1.6 mixture with 1-(diethylsilyl)-2-phenylethene; ~6% yield; ^1H NMR ($CDCl_3$) (400 MHz) δ 7.5–7.1 (m, 5 H), 3.70 (m, 1 H), 2.68 (m, 2 H), ~1.0 (2 H), 0.99 (t, 6 H), 0.62 (m, 4 H); partial GC/MS data, *m/e* (relative intensity) M^+ = 192 (0.022), $M^+ - {}^\bullet CH_2CH_3$ = 163 (1.0).

***trans*-1-(Diethylsilyl)-2-phenylethene**: obtained as a 1.6/1 mixture with diethylphenethylsilane; ~8% yield; ^1H NMR ($CDCl_3$) (400 MHz) δ 7.5–7.1 (m, 5 H), 7.01 (d, 1 H, $^3J_{HH}$ = 19.23 Hz), 6.43 (dd, 1 H, $^3J_{HH}$ = 19.19 Hz, $^3J_{HH}$ = 3.39 Hz), 4.00 (m, 1 H), 1.03 (t, 6 H), 0.73 (m, 4 H); partial GC/MS data, *m/e* (relative intensity) M^+ = 190 (0.019), $M^+ - {}^\bullet CH_2CH_3$ = 161 (1.0).

Phenethylphenylsilane: obtained as an 8/1 mixture with $(PhSiH_2)PhSiHCH_2CH_2Ph$; ^1H NMR ($CDCl_3$) (400 MHz) δ 7.67 (m, 2 H), 7.52–7.22 (m, 8 H), 4.43 (t, 2 H, $^3J_{HH}$ = 3.66 Hz), 2.87 (m, 2 H), 1.40 (m, 2 H); ^{13}C NMR ($CDCl_3$) (200 MHz) δ 144.13, 135.39, 129.78, 128.49, 128.17, 128.02, 127.96, 125.92, 30.92, 11.87; partial GC/MS data, *m/e* (relative intensity) M^+ = 212 (0.010), $M^+ - C_6H_6$ = 134 (1.0), 133 (0.39).

$(PhSiH_2)PhSiHCH_2CH_2Ph$: obtained as a 1/8 mixture with phenethylphenylsilane; ^1H NMR ($CDCl_3$) (400 MHz) δ 2.80 (m, 2 H), 1.33 (m, 2 H), other proton signals masked by phenethylphenylsilane; ^{13}C NMR ($CDCl_3$) (200 MHz) δ 134.85, 132.25, 30.34, 13.68, other ^{13}C signals masked by phenethylphenylsilane; partial GC/MS data, *m/e* (relative intensity) $M^+ - {}^\bullet Ph$ = 238 (0.08), $M^+ - {}^\bullet SiPh_2H$ = 211 (1.0), ${}^\bullet PhSiH_2$ = 107 (0.88).

1-Phenyl-2-(triphenylsilyl)ethene: purified by sublimation (120 °C, 0.060 mmHg); characterized by ^1H, ^{13}C, and APT NMR and GC/MS; data agreed with literature values.[33] Anal. Calcd for $C_{15}H_{18}Si$: C, 86.14; H, 6.12. Found: C, 85.76; H, 6.40.

***n*-Hexyldiphenylsilane**: 72% isolated yield; ^1H NMR ($CDCl_3$) (200 MHz) δ 7.55 (m, 4 H), 7.33 (m, 6 H), 4.87 (t, 1 H, $^3J_{HH}$ = 3.8 Hz, $^1J_{SiH}$ = 192 Hz), 1.5–1.1 (m, 10 H), 0.88 (t, 3 H); ^{13}C NMR ($CDCl_3$) (200 MHz) δ 129.6, 128.08, 32.75, 31.33, 24.22, 22.42, 13.93, 11.97; partial GC/MS data, *m/e* (relative intensity) M^+ = 268 (0.001), $M^+ - {}^\bullet C_6H6$ = 190 (0.20), 184 (0.18), 183 (1.0), 181 (0.24), 105 (0.59), 106 (0.12), 97 (0.11), 84 (0.16). Anal. Calcd for $C_{17}H_{22}Si$: C, 80.53; H, 9.01. Found: C, 80.26; H, 9.33. An additional product of identical molecular weight (GC/MS) was observed in ~5% GC yield.

***n*-Octyldiphenylsilane**: 52% isolated yield; bp 109 °C (0.14 mmHg); ^1H NMR (C_6D_6) (400 MHz) δ 7.55 (m, 4 H), 7.15 (m, 6 H), 5.10 (t, 1 H, J = 3.97 Hz), 1.5–1.1 (m, 14 H), 0.86 (t, 3 H, $^3J_{HH}$

---

(30) Response factors (*F*) were calculated by analyzing a series of standard solutions and fitting the data (linear regression) to the following equation: [(moles of compound)/(moles of reference)] = [(% area compound)/% area reference)]*F*. Unisolated products were assigned response factors corresponding to compounds of similar molecular weight.

(31) Lewis, L. N.; Uriarte, R. J. *Organometallics* **1990**, *9*, 621.

(32) Bazant, V.; Vaclav, C.; Rathousky, J. *Organosilicon Compounds*; Academic: New York, 1965; Vol. 2, Part 2, p 324.

(33) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101.

= 6.96 Hz); partial GC/MS data, *m/e* (relative intensity) M^+ = 296 (0.002), $M^+ - {}^\bullet C_6H6$ = 219 (0.02), 218 (0.07), 184 (0.18), 183 (1.0), 181 (0.24), 140 (0.26), $^\bullet$Oct = 112 (0.20), 107 (0.19), 106 (0.13), 105 (0.60). Anal. Calcd for $C_{17}H_{22}Si$: C, 81.01; H, 9.52. Found: C, 80.79, H, 9.53.

***n*-Pentyldiphenylsilane**: 69% isolated yield; bp 80 °C (0.07 mmHg); ^1H NMR ($CDCl_3$) (200 MHz) δ 7.57 (m, 4 H), 7.35 (m, 6 H), 4.87 (t, 1 H, $^3J_{HH}$ = 3.67 Hz, $^1J_{SiH}$ = 194 Hz), 1.08–1.55 (m, 8 H), 0.852 (t, 3 H); ^{13}C NMR ($CDCl_3$) (200 MHz) 135.3, 134.8, 129.6, 128.1, 35.3, 23.9, 22.1, 13.8, 11.9; partial GC/MS data, *m/e* (relative intensity) M^+ = 254 (0.003), 184 (0.18), 183 (1.0), 182 (0.71), 181 (0.24), 176 (0.36), 148 (0.17), 107 (0.13), 105 (0.60). Anal. Calcd for $C_{17}H_{22}Si$: C, 80.25; H, 8.72. Found: C, 80.18; H, 8.68.

1-(Trimethylsilyl)-2-(diphenylsilyl)ethane: obtained as a 17/1 mixture with $(Ph_2SiH)Ph_2SiCH_2CH_2(TMS)$; 81% yield; ^1H NMR ($CDCl_3$) (400 MHz) δ 7.57 (m, 2 H), 7.39 (m, 6 H), 4.83 (t, 1 H, $^3J_{HH}$ = 3.63 Hz), 1.06 (dt, 2 H), 0.56 (m, 2 H), 0.013 (s, 9 H); partial GC/MS data, *m/e* (relative intensity) M^+ = 284 (0.082), $M^+ - CH_3$ = 269 (0.16), 210 (0.16), 183 (0.91), $^\bullet SiMe_3$ = 73 (1.0).

Neohexyldiphenylsilane: obtained as a 1.3/1 mixture with 1-(diphenylsilyl)-2-*tert*-butylethene; ~11% yield; ^1H NMR ($CDCl_3$) (200 MHz) δ 7.55–7.20 (m, 10 H), 4.83 (t, 1 H, $^3J_{HH}$ = 3.62 Hz), 1.33 (m, 2 H), 1.05 (m, 2 H), 0.87 (s, 9 H); ^{13}C NMR ($CDCl_3$) (200 MHz) δ 135.9–128.1 (4 phenyl carbons), 38.18, 31.15, 28.77, 6.25; partial GC/MS data, *m/e* (relative intensity) M^+ = 268 (0.015), $M^+ - {}^\bullet C_6H_6$ = 190 (0.21), 184 (0.18), 183 (1.0), 105 (0.21).

***trans*-1-(Diphenylsilyl)-2-*tert*-butylethene**: obtained as a 1/1.3 mixture with neohexyldiphenylsilane; ~8% isolated yield; ^1H NMR ($CDCl_3$) (200 MHz) δ 7.55–7.20 (m, 10 H), 6.35 (d, 1 H, $^3J_{HH}$ = 19.35 Hz), 5.83 (dd, 1 H, $^3J_{HH}$ = 18.91 Hz, $^3J_{HH}$ = 3.52 Hz), 5.10 (d, 1 H, $^3J_{HH}$ = 3.34 Hz), 1.04 (s, 9 H); ^{13}C NMR ($CDCl_3$) (200 MHz) δ 135.9–128.1 (4 phenyl carbons), 164.2, 115.4, 35.62, 28.61; partial GC/MS data, *m/e* (relative intensity) M^+ = 266 (0.183), 224 (0.248), 210 (0.11), $M^+ - {}^\bullet C(CH_3)_3$ = 209 (0.41), 196 (0.20), 184 (0.20), 183 (1.0), 182 (0.55), 181 (66).

$Ph_2SiHSiPh_2$(neohexyl): obtained as a mixture with 1-[(diphenylsilyl)diphenylsilyl]-2-*tert*-butylethene and $(Ph_2SiH)_2$; ^1H NMR ($CDCl_3$) (400 MHz) δ 7.5–7.2 (m, 10 H), 5.18 (s, 1 H), 1.24 (m, 2 H), 1.16 (m, 2 H), 0.76 (s, 9 H); partial GC/MS data, *m/e* (relative intensity): M^+ = 450 (0.026), $^\bullet(Ph_2SiH)_2$ = 366 (0.016), 365 (0.049), $M^+ - {}^\bullet SiPh_2$ = 267 (0.24), 259 (0.30), 193 (1.0), 105 (0.13).

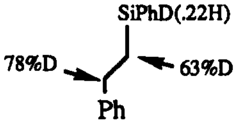
***trans*-1-[(diphenylsilyl)diphenylsilyl]-2-*tert*-butylethene**: obtained as a mixture with $Ph_2SiHSiPh_2$(neohexyl) and $(Ph_2SiH)_2$; ^1H NMR ($CDCl_3$) (400 MHz) δ 7.5–7.2 (m, 10 H), 6.14 (d, 1 H, $^3J_{HH}$ = 20 Hz), 5.86 (d, 1 H, $^3J_{HH}$ = 20 Hz), 5.14 (d, 1 H, $^3J_{HH}$ = 4.21 Hz), 0.97 (s, 9 H); partial GC/MS data, *m/e* (relative intensity) $M^+ - {}^\bullet Ph$ = 391 (0.08), 267 (0.28), 266 (1.0), 259 (0.36), 183 (0.56).

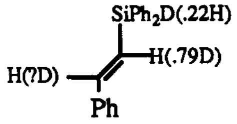
Cyclohexyldiphenylsilane: partial GC/MS data, *m/e* (relative intensity) M^+ = 266 (0.10), 267 (0.03), 189 (0.05), $M^+ - {}^\bullet Ph$ = 188 (0.27), 184 (0.22), 183 (1.0), 106 (0.12), 105 (0.28), 82 (0.02).

1-Methyl-1-phenyl-2-(diphenylsilyl)ethane: data from entry 10, Table III; 27% isolated yield; ^1H NMR ($CDCl_3$) (200 MHz) δ 7.5–7.1 (m, 15 H), 4.78 (t, 1 H, $^3J_{HH}$ = 3.95 Hz), 2.95 (m, 1 H), 1.54 (m, 2 H), 1.30 (d, 3 H, $^3J_{HH}$ = 6.87 Hz); ^{13}C NMR ($CDCl_3$) (200 MHz) δ 135.25, 129.63, 128.46, 128.08, 126.72, 126.04, 36.04, 25.00, 22.38; partial GC/MS data, *m/e* (relative intensity) M^+ = 302 (0.003), $M^+ - CH_3$ = 287 (0.008), $M^+ - {}^\bullet Ph$ = 225 (0.17), 224 (0.75), 184 (0.21), 183 (1.0), 182 (0.24), 181 (0.34), 147 (0.11), 146 (0.71), 145 (0.11), 105 (0.59).

1-Methyl-1-phenyl-2-(diphenylsilyl)ethene: data from entry 9, Table III; obtained as a 0.8/1 mixture with 1-methyl-1-phenyl-2-(diphenylsilyl)ethane; ^1H NMR ($CDCl_3$) (400 MHz) δ 7.63–7.15 (m, 15 H), 6.24 (d, 1 H, J = 4.88 Hz), 5.39 (d, 1 H, $^3J_{HH}$ = 4.89 Hz); partial GC/MS data, *m/e* (relative intensity) M^+ = 300 (0.55), $M^+ - CH_3$ = 285 (0.05), $M^+ - {}^\bullet Ph$ = 223 (0.26), 222 (1.0), 221 (0.23), 207 (0.32), 183 (0.52), 182 (0.40), 181 (0.91), 180 (0.22), 145 (0.16), 144 (0.42), 105 (0.68).

Hydrosilylation of Styrene with Ph_2SiD_2. Separate ^1H NMR signals were obtained for Ph_2SiH_2 and Ph_2SiHD.[34] H/D percentages for $Ph_2SiH(D)$ and styrene were calculated by comparison of the integral regions of the appropriate proton signals with the ortho phenyl protons (internal standard). The H/D incorporation into the hydrosilylation products was determined by ^1H NMR (one of the olefinic hydrogens was obscured by the signals due to the phenyl hydrogens):





Acknowledgment. We gratefully acknowledge partial support from the NSF-MRL Program through the Center for Materials Research at Stanford University and the Department of Education for a GAANN Fellowship for M.R.K.

---

(34) Liepins, E.; Gevorgyan, V.; Lukevics, E. *J. Magn. Reson.* **1989**, *85*, 170.