77-8; 3-nitrophenol, 554-84-7; tris(3-chloropropyl)amine, 79189-90-5; acetic formic anhydride, 2258-42-6; diphosgene, 503-38-8.

Supplementary Material Available: Tables listing all bond distances and angles, anisotropic thermal parameters, and hydrogen positions and ORTEP plots of both molecular structures with the employed numbering scheme for 7·0.5CH$_2$Cl$_2$ and 8c·HCl·2.5CH$_2$Cl$_2$ (13 pages); tables of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

Mechanism of Homogeneous Hydrosilation of Alkenes by (η^5-Cyclopentadienyl)rhodium

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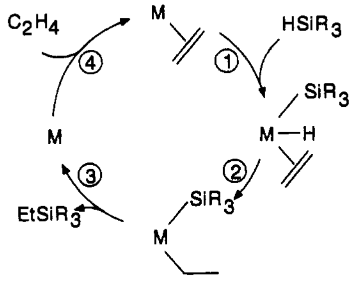
The mechanism of hydrosilation of ethene with R$_3$SiH catalyzed by (η^5-C$_5$H$_5$)Rh(C$_2$H$_4$)(SiR$_3$)H (principally with R = Et) has been studied by NMR and GC/MS methods. Comparison with related compounds indicates that activity is confined to this group of compounds at room temperature. The mercury test demonstrates that the reaction is homogeneous, in contrast to recent evidence on platinum catalysts. The reaction mechanism was investigated by deuterium labeling of either substrate and variation of alkene and trialkylsilane. These experiments demonstrated conclusively that (η^5-C$_5$H$_5$)Rh(C$_2$H$_4$)(SiR$_3$)H acts as a precursor to the catalytically active species but is not within the catalytic cycle. In consequence, the Chalk–Harrod mechanism cannot apply in this system. An alternative cycle is proposed which is initiated by a hydrogen shift to form (η^5-C$_5$H$_5$)Rh(C$_2$H$_5$)(SiR$_3$). The latter generates the hydrosilation products via oxidative addition of R$_3$SiH to form an intermediate containing two silicon atoms. The initial hydrogen shift is consistent with studies of intramolecular exchange and stoichiometric reactions of the starting material. The mechanism is equivalent to the one proposed by Wrighton and Seitz for hydrosilation catalyzed by cobalt carbonyls.

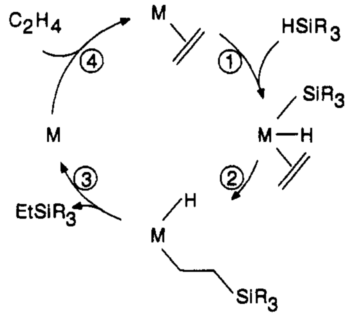
Introduction

Many recent reviews and papers, in common with their predecessors, explain the catalytic mechanism of hydrosilation by the Chalk–Harrod cycle or one of its variants.[1] In the first step of these mechanisms, a metal alkene complex is converted to a metal alkene silyl hydride complex.[2] It follows that a complex conforming to the latter description is unlikely to be isolable. In a communication published in 1985, we reported the characterization of CpRh(C$_2$H$_4$)(SiR$_3$)H (1) formed on photolysis of CpRh(C$_2$H$_4$)$_2$ in the presence of R$_3$SiH (R = Me, Et; Cp = η^5-C$_5$H$_5$; Cp* = η^5-C$_5$Me$_5$).[3] This molecule contains all the essential ligands for the key intermediate in the Chalk–Harrod mechanism of hydrosilation. Moreover, we showed that its formation is accompanied by hydrosilation and silation products. In subsequent work, we showed that 1 could be obtained in high yield without hydrosilation products by carrying out the photolysis at low temperature.[4] We also examined the stoichiometric reactivity of 1 toward ethene, trialkylsilanes, and other ligands under photochemical and thermal conditions.[5] We now report the catalytic reactivity of 1 toward alkenes and trialkylsilanes together. Isotopic labeling is used to probe the reaction mechanism and to show that hydrosilation in this case does not proceed via the Chalk–Harrod mechanism or variants involving silyl migration (Schemes I and II).

Scheme I. Chalk–Harrod Mechanism of Hydrosilation



Scheme II. Variant on Chalk–Harrod Mechanism for Hydrosilation with Silyl Migration



The Chalk–Harrod mechanism employs conventional oxidative-addition/reductive-elimination steps to explain hydrosilation (Scheme I).[1] Oxidative addition of R$_3$SiH to a metal alkene complex, usually with a d^8 configuration (step 1), is followed by migration of the hydride onto the

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(1) Speier, J. L. *Adv. Org. Chem.* **1979**, *17*, 407. Lukevics, E. *Russ. Chem. Revs.* (*Engl. Transl.*) **1977**, *46*, 264. Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989. Caseri, W.; Pregosin, P. S. *J. Organomet. Chem.* **1988**, *356*, 259. Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 8621.

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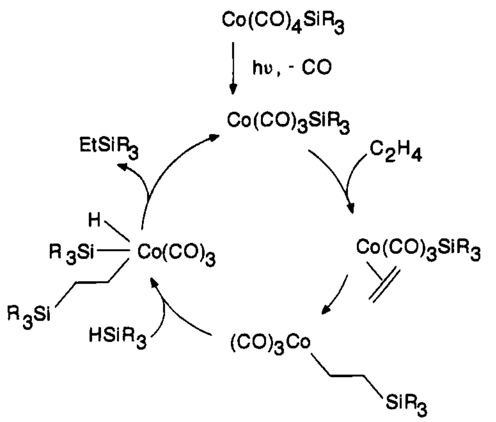
Scheme III. Seitz–Wrighton Mechanism for Hydrosilation



alkene (step 2). The resulting metal silyl alkyl undergoes reductive elimination by Si–C bond formation (step 3) to yield a 14-electron complex, which reacts with alkene to regenerate the d^8 metal alkene complex (step 4).

In the variant on the Chalk–Harrod mechanism (Scheme II), the silyl group migrates to the alkene (step 2) and the product is formed by C–H reductive elimination (step 3).[6]

This mechanism has well-established precedents for each step, whereas the reductive elimination of a Si–C bond is very uncommon. Seitz and Wrighton, who studied photochemical hydrosilation with $Co(CO)_4(SiMe_3)$, proposed a mechanism which incorporated steps 2 and 3 of the cycle in Scheme II but did not involve the formation of a metal ethene silyl hydride.[7a] Instead of building each unit onto the metal before the migration step, they proposed that a [1,3]-silyl shift preceded attack by trialkylsilane (Scheme III). Striking evidence for similar insertion of alkenes into metal–silicon bonds has been obtained recently.[7b]

Hydrosilation (eq 1) by rhodium and iron complexes is often accompanied by the formation of alkenylsilanes (eq 2),[8] referred to here as silation.

$$R_3SiH + H_2C{=}CH_2 \rightarrow CH_3{-}CH_2SiR_3 \quad \text{(hydrosilation)} \qquad (1)$$

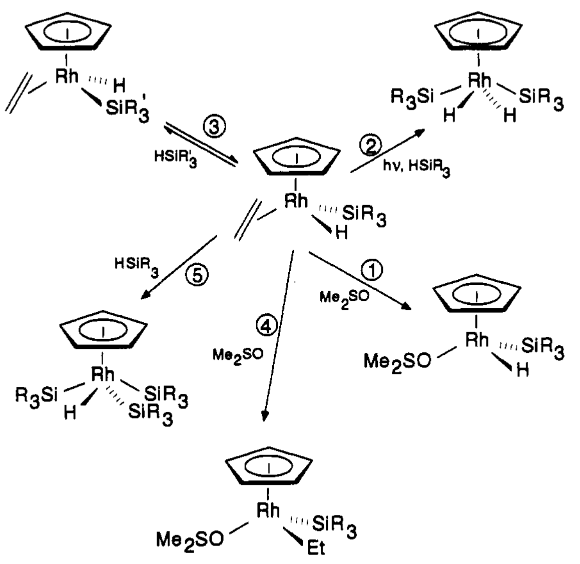
$$R_3SiH + 2H_2C{=}CH_2 \rightarrow CH_2{=}CHSiR_3 + C_2H_6 \qquad \text{(silation)} \quad (2)$$

The hydrogen released is usually consumed in hydrogenation of the alkene. Silation may be understood by silyl migration (Scheme II, step 2), followed by β-elimination and release of alkenylsilane. A number of detailed mechanisms have been proposed.[9] Our own studies also revealed silation products, but the mechanistic evidence was ambiguous. We will, therefore, concentrate our analysis on the hydrosilation products.

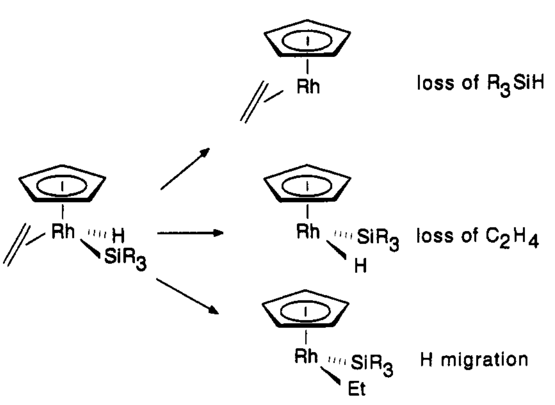
The stoichiometric reactions of 1 shown in Scheme IV proceed by the three pathways of Scheme V:[5]

(i) Ethene substitution is observed in the presence of Me_2SO (reaction 1). Ethene is also expelled photochemically, so that photolysis with excess R_3SiH yields the important Rh^V complexes $CpRh(SiR_3)_2(H)_2$ (reaction 2).

Scheme IV. Reactions of $CpRh(C_2H_4)(SiR_3)H$ (1)



Scheme V. Three Reaction Pathways of $CpRh(C_2H_4)(SiR_3)H$ (1)



(ii) Trialkylsilane may be eliminated leading to silane exchange in the presence of another trialkylsilane, R'_3SiH (reaction 3).

(iii) The hydride may migrate onto the ethene. This process leads to slow exchange between hydride and ethene protons in 1. It also gives rise to a second product in the reaction with Me_2SO, $CpRh(C_2H_5)(Me_2SO)(SiR_3)$ (reaction 4). The same hydride migration is postulated as the initiating step in the thermal reaction of 1 with excess R_3SiH, which generates $CpRh(SiR_3)_3H$ (4) (reaction 5) and subsequently $(C_5H_4SiR_3)Rh(SiR_3)_2(H)_2$. Notice that there is no evidence for slippage or loss of the ring in contrast to C_5Me_5 complexes.[10]

Very few other complexes are known with this combination of ethene, silyl, and hydride ligands. Maitlis et al. have generated the Cp* analogue of 1.[11] Tanke and Crabtree have recently reported the iridium complex $[(\text{triso})Ir(C_2H_4)(H)(SiPh_3)]$ [triso = $C\{Ph_2PO\}_3$], which proves much more thermally stable than 1.[12] This complex has been shown to be catalytically active in the hydrosilation of alkynes.

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There are many examples of rhodium complexes which catalyze the hydrosilation reaction, including $RhCl_3{\cdot}3H_2O$, $Rh(PPh_3)_3Cl$, $[Rh(COD)Cl]_2$,[13] $[Cp^*Rh]_2Cl_4$, $[Cp^*Rh]_2Cl_3H$, and $\{[Cp^*Rh]_2(OH)_3\}^+$.[14] More importantly for this work, $Cp^*Rh(C_2H_4)_2$ and $Cp^*Rh(SiEt_3)_2(H)_2$ prove to be hydrosilation catalysts with the Cp^*Rh^V complex being the less active of the two.[14] This list illustrates that initiation of the hydrosilation reaction is not confined to a single oxidation state of rhodium but spans the range Rh(I)–Rh(V).

The compounds under study here are numbered as follows:

1 $CpRh(C_2H_4)(SiR_3)H$

2 $CpRh(C_2H_4)_2$

3 $CpRh(SiR_3)_2(H)_2$

4 $CpRh(SiR_3)_3H$

5 $CpRh(C_2H_4)(CH_2{=}CHSiR_3)$

a R = Et

b R = Pr^i

c R = Bu^s

d R = Me

Experimental Section

General Methods and Chemicals. All syntheses and manipulations were carried out using standard Schlenk and high-vacuum-line techniques.[15] All the hydrosilation reactions were carried out in 5-mm NMR tubes (Wilmad 507-PP) and sealed in vacuo. Reactions were followed periodically by NMR spectroscopy; final observations were made by breaking open the tubes and injecting the solution into a GC/MS. Analysis of the rhodium-containing component was achieved by removing the volatiles and recording electron-impact mass spectra. Chemicals were obtained from the following sources: ethene from Mattheson, C_2D_4 from MSD (99 atom %), Et_3SiH from Fluka; Pr^i_3SiH, Me_2ClSiH, and $[(CH_3)_2CHCH_2]_3SiH$ from Aldrich. Silanes were used without further purification. Me_3SiH, Me_3SiD, and Et_3SiD were prepared by standard $LiAlH_4$ or $LiAlD_4$ reduction of the corresponding chloride, which was purchased from Aldrich. Toluene was obtained from Fisons (AR grade), dried prior to use over Na/benzophenone, and stored under argon. Rhodium trichloride trihydrate was a gift from Dow Corning and used without further purification. NMR solvents were stored over molecular sieves (3-Å) and handled under argon. Toluene-d_8 and cyclohexane-d_{12} were obtained from Goss Scientific.

Pyrex NMR tubes ($\lambda > 290$ nm) were irradiated with a Philips HPK medium-pressure mercury arc (125 W) or Applied Photophysics lamp (250 W) in conjunction with a water filter to remove heat (path length 5 cm). For low-temperature work, samples were irradiated in a partially silvered Pyrex Dewar, containing methanol as the coolant. Alternatively a stream of cold nitrogen was passed over the sample, which was held in an evacuated Pyrex jacket. The temperature was controlled by a Jeol controller.

Mass spectra were recorded on a Kratos MS3074 spectrometer by the University of York service. NMR spectra were recorded on Bruker WP80SY, AM360 (Edinburgh), and MSL300 (York) spectrometers. ^1H spectra were referenced to the peaks of the residual protio solvent: toluene, δ 2.1; cyclohexane-d_{12}, δ 1.38. ^{13}C spectra in toluene were referenced to solvent at δ 21.3. CH, CH_2, and CH_3 groups were distinguished using DEPT pulse sequences.

Synthesis of $CpRh(SiEt_3)(C_2H_4)H$ (1a). $CpRh(C_2H_4)_2$ (**2**) synthesized as previously[16] (0.5 g, 2.2×10^{-3} mol), 1.5 g of Et_3SiH (1.3×10^{-2} mol), and toluene-d_8 (1 cm^3) were placed in a 10-mm NMR tube, giving a solution 0.75 mol dm^{-3} in **2**. The contents were then degassed using several freeze–pump–cycles before the tube was sealed. The sample was irradiated at 213 K for 40 h until 60% conversion to **1a** was achieved, as indicated by ^1H NMR spectroscopy. The NMR tube was opened and the yellow solution eluted through an alumina column with hexane. The first 20-cm^3 fraction, which was enriched in **1a**, was transferred to a small Schlenk tube, and the solvent was removed under a stream of argon. The resulting yellow oil was sublimed (at 298 K) onto a cold finger (273 K) at a pressure of 4×10^{-4} mbar to remove $CpRh(C_2H_4)_2$. Further sublimation (at 298 K) onto a cold finger (at 77 K) yielded **1a** as a yellow oil contaminated with on average 10% **2**.

Preparation of $CpRh(SiEt_3)(C_2H_4)D$. Approximately 20 mg of $CpRh(C_2H_4)_2$ (9×10^{-5} mol), Et_3SiD (84 mg, 7×10^{-4} mol), and 0.5 cm^3 of toluene-d_8 were placed in a 5-mm NMR tube. The solution was degassed and the tube sealed. A ^1H NMR spectrum showed that the ratio of $CpRh(C_2H_4)_2$ to Et_3SiD was 1:8. The solution was irradiated for 4 h at 213 K. The ^1H NMR spectrum then recorded revealed 38% conversion to $CpRh(SiEt_3)(C_2H_4)D$.

Hydrosilation Reactions. The samples of **1a** used in the hydrosilation tests contained no more than 12% **2** and **3a** relative to **1a**. The samples used in the control experiments contained a 10-fold excess of Et_3SiH and ethene relative to the organometallic complex **2** or **3a**. The solvent was toluene unless otherwise stated.

Hydrosilation of C_2H_4 and Et_3SiD by 1a. Sample 1. A tube was prepared which was shown by NMR spectroscopy to contain a 1:10:10 **1a**:Et_3SiD:C_2H_4 ratio. Hydrosilation proceeded as expected. GC/MS analysis of the products on completion of the reaction revealed the following [*m*/*z* (relative intensity, ion)]: $CH_2{=}CHSiEt_3$, 143 (0.8%, M + 1), 142 (3.5%, M^+), 114 (46%), 113 (82%), 85 (100%) (retention time 5.43 min, 9% D_1); Et_4Si, 145 (9.3%), 144 (8.1%), 116 (51%), 115 (83.7%), 88 (46.5%), 87 (100%) (retention time 5.97 min, 50% D_1); $Et_3SiCH_2CH_2SiEt_3$, 260 (2.6%), 259 (9.3%), 258 (11.3%) (retention time 18.12 min.)

Sample 2. The **1a**:Et_3SiD:C_2H_4 ratio in solution was 1.7:7:1. GC/MS analysis of the products on completion of the reaction revealed the following [*m*/*z* (relative intensity, ion)]: $CH_2{=}CHSiEt_3$, 143 (1.5%, M + 1), 142 (1.5%, M^+), 115 (19.5%), 114 (48.5%), 113 (51%), 86 (44%), 85 (100%) (retention time 5.3 min, 46% D_1); Et_4Si, 146 (3%), 145 (8.4%), 144 (2.3%) (retention time 5.83 min, 18% deuteration of new C_2H_5 group).

Hydrosilation of C_2D_4 and Et_3SiH by 1a. Sample 1. A sample was prepared in which the ratio of **1a**:Et_3SiD in solution was 1:1; an over-pressure of C_2D_4 was then added. GC/MS analysis of the products revealed the following [*m*/*z* (relative intensity, ion)]: $CH_2{=}CHSiEt_3$, 146 (0.2%, D_3), 145 (4.0%, D_2), 144 (1.9%, D_1), 143 (0.8%, D_0) (retention time 5.3 min, 58% D_3); Et_4Si, 149 (4.7%, D_5), 148 (9.5%, D_4), 147 (5.7%, D_3), 146 (4.3%, D_2), 145 (3.3%, D_1), 144 (6.2%, D_0) (retention time 5.75 min, counts 1708); Et_4Si, 149 (2.0%, D_5), 148 (4.2%, D_4) (retention time 5.68 min, counts 2774). Combination of these two Et_4Si fractions yielded an average deuteration level for the ethyl group formed in the hydrosilation process of 74%.

Sample 2. A sample was prepared in which the ratio of **1a**:Et_3SiD in solution was 1:5; a 10-fold excess of C_2D_4 was then added. GC/MS analysis of the products revealed the following [*m*/*z* (relative intensity, ion)]: $CH_2{=}CHSiEt_3$, 88 (100%, D_3), 87 (29.7%, D_2), 86 (22.7, D_1), 85 (11.4%, D_0) (retention time 5.3 min, 62% D_3, overall deuteration 78%); Et_4Si, 149 (7.8%, D_5), 148 (9.8%, D_4), 147 (0%, D_3), 146 (0%, D_2), 145 (3.3%, D_1), 144 (0%, D_0) (retention time 5.75 min, new ethyl group 50% D_4 with overall deuteration of 74%.

Synthesis of $CpRh(C_2H_4)(SiPr^i_3)H$ (1b). $CpRh(C_2H_4)_2$ (**2**) (0.22 g, 1×10^{-3} mol) and 0.54 cm^3 of Pr^i_3SiH (2.6×10^{-3} mol) were placed in a small ampule with a Young's ptfe stopcock, giving a solution 1.85 mol dm^{-3} in **2**. The contents were degassed and placed under an argon atmosphere. After 23 h of photolysis at 298 K ($\lambda > 365$ nm), an aliquot was removed. A ^1H NMR spectrum revealed 74% conversion of **2** to $CpRh(C_2H_4)(SiPr^i_3)H$ (**1b**) (54%) and $CpRh(SiPr^i_3)_2(H)_2$ (**3b**) (20%). The solution was

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[15] In common with most authors, we carried out our experiments in the absence of air, since the compounds under study are air-sensitive. Occasionally, air has been found to enhance hydrosilation as with Wilkinson's catalyst (Dickers, H. M.; Haszeldine, R. N.; Malkin, L. S.; Mather, A. M.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1980**, 308). Comments on the role of air have been made in ref 14.

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Table I. NMR Parameters of Selected Hydrosilation Products in Toluene-d_8 at 296 K and 300 MHz (δ/ppm; Multiplicity, J/Hz)

compd	nucleus	SiR_3	CH	CH_2	CH_3
Et_4Si	^1H			0.49 (q, 8)	0.97 (t, 8.0)
	$^{13}C\{^1H\}$			2.97	7.29
	$^{29}Si\{^1H\}$	0.35			
$CH_2{=}CHSiEt_3$	^1H	0.56 (q, 8), 0.99 (t, 8)	5.66 (dd, 20.8, 6.0)	6.06 (m, 20.8, 25), 6.0 (m, 25, 6)	
	$^{13}C\{^1H\}$	4.78 (CH_2), 7.75 (CH_3)			
Me_3SiEt	^1H	−0.024		0.45 (q, 8)	0.94 (t, 8)
	$^{13}C\{^1H\}$	−0.8		8.9	9.47
	$^{29}Si\{^1H\}$	2.49			
$CH_2{=}CHSiMe_3$	$^{13}C\{^1H\}$	−1.57	131.1	140.1	
	$^{29}Si\{^1H\}$	−5.93			
$Me_2ClSiEt$	^1H	0.19 (s)		0.58 (q, 8)	0.90 (t, 8)
	$^{13}C\{^1H\}$	1.76		11.94	7.52
C_2H_6	^1H				0.83 (s)
C_2H_4	^1H				5.29 (s)

Table II. Mass Spectral Data for Selected Hydrosilation Products (Electron Energy 70 eV)

	intensity/% at m/z																				
	186	184	158	156	144	143	142	141	129	127	115	113	101	99	87	85	83	73	71	59	57
Et_4Si					6						75				100					47	
Et_4Si^a					6						70				100					49	
$CH_2{=}CHSiEt_3$							2					89				100					41
$CH_2{=}CHSiEt_3{}^a$							2					68				100					37
$CH_3CH_2CH_2SiEt_3$			4						47		14		17		100					41	
$CH_3CH{=}CHSiEt_3$				15						100				82					32		
$EtSiPr^i_3$	12					100					30		61				34	62		32	
$CH_2{=}CHSiPr^i_3$		17						100				29		53		26			21	13	

[a] Authentic sample from Fluka; other measurements on hydrosilation products.

then transferred to a Schlenk tube and pumped to dryness; the resulting oil was sublimed from ice onto a finger (77 K). The sublimate was shown to contain **2** and **1b** in the ratio 7.6:1 by ^1H NMR spectroscopy; **3b** failed to sublime under these conditions. The residue was then dissolved in acetone and the solution cooled to 253 K, at which point pale yellow crystals formed. The mother liquor was decanted and a ^1H NMR spectrum of the crystals recorded. This showed that they contained **1b** and **3b** in the ratio 4:1. The liquor was then pumped to dryness and the residue dissolved in methylcyclohexane. At 203 K white crystals formed which were shown to contain 98.5% $CpRh(C_2H_4)(SiPr^i_3)H$ (**1b**), 0.5% $CpRh(C_2H_4)_2$ (**2**), and 1% $CpRh(SiPr^i_3)_2(H)_2$ (**3b**) by ^1H NMR spectroscopy.

Synthesis of $CpRh(SiPr^i_3)_2(H)_2$ (3b). $CpRh(C_2H_4)_2$ (**2**) (0.18 g, 8×10^{-4} mol), 2.5 cm³ of Pr^i_3SiH (1.93 g, 1.2×10^{-2} mol), and toluene (2.5 cm³) were placed in an ampule and degassed. The sample was irradiated ($\lambda > 290$ nm) for 24 h at 298 K. The resulting yellow solution was pumped to dryness, the solid was dissolved in toluene, and the solution was passed through a 5 cm long Celite column; this had no visible effect. The sample was then pumped to dryness and the residue dissolved in methylcyclohexane. On cooling of the solution to 203 K white crystals formed. The mother liquor was decanted, and the crystals were dissolved in toluene. After elution through a 5 cm long alumina column a pale yellow fraction was obtained. The toluene was removed under vacuum and the off-white residue dissolved in acetone. White crystals formed on cooling the solution to 253 K.

Spectral data for $CpRh(SiPr^i_3)(C_2H_4)H$ (**1b**) are as follows. IR (hexane): 2077 cm^{-1} [ν(Rh–H)]. The UV spectrum of **1b** recorded in pentane showed a single maximum at 233 nm ($\epsilon = 1.5 \times 10^4$ dm³ mol^{-1} cm^{-1}). NMR data at 296 K (300 MHz, chemical shifts δ/ppm, coupling constants/Hz): ^1H, 5.03 (t, 5 H, $J_{RhH} = J_{HH} = 0.6$, C_5H_5), 2.28 (d, $J_{RhH} = 6$, 4 H, C_2H_4), 1.13 and 1.11 (complex, 21 H, $SiPr^i_3$), −14.85 (d with satellites, $J_{RhH} = 31.6$, $^2J_{SiH} = 15.6$, 1 H, RhH); $^{13}C\{^1H\}$, 89.6 (d, $J_{RhC} = 3$, C_5H_5), 31.5 (d, $J_{RhC} = 12$, C_2H_4), 21.9 (s, $SiCH(CH_3)_2$), 19.3 (d, $J_{RhC} = 1$, $SiCH(CH_3)_2$); $^{29}Si\{^1H\}$, 49.28 (d, $J_{SiRh} = 25.6$). Mass spectral data for **1b** [m/z (%, fragment)]: 354 (1%, $M^+ = CpRh(SiPr^i_3)(C_2H_4)H^+$ [mass(exptl) − mass(calcd) = −1.0 millimass units], 326 (10.3%, $M^+ - C_2H_4$), 309 (80%, $M^+ - C_3H_9$) 196 (54%, $CpRhSi^+$), 168 (100%, $CpRh^+$).

Spectral data for $CpRh(SiPr^i_3)_2(H)_2$ (**3b**) are as follows. NMR spectra recorded at 296 K and 300 MHz in toluene-d_8 (chemical shifts δ/ppm, coupling constants/Hz): ^1H, 5.24 (q, 5 H, $J_{RhH} = J_{HH} = 0.5$, C_5H_5), 1.15 and 1.14 (complex, 42 H, $SiPr^i_3$), −14.46 (d with satellites, $J_{RhH} = 35.5$, $^2J_{SiH} = 6.26$, 1 H, RhH); $^{13}C\{^1H\}$, 90.4 (d, $J_{RhC} = 2.6$, C_5H_5), 21.7 (s, $SiCH(CH_3)_2$), 20.9 (s, $SiCH(CH_3)_2$); $^{29}Si\{^1H\}$, 52.2 (d, $J_{SiRh} = 18.3$). Mass spectral data for **3b** [m/z (%, fragment)]: 441 (8%, $M^+ - C_3H_7$), 326 (22%, $M^+ - Pr^i_3SiH$), 282 (100%), 237 (4.8%), 196 (56%, $CpRhSi^+$), 168 (19%, $CpRh^+$).

Results

(1) Hydrosilation by $CpRh(C_2H_4)(SiR_3)H$. Photolysis of $CpRh(C_2H_4)_2$ (**2**) in the presence of Et_3SiH leads to the production of $CpRh(C_2H_4)(SiEt_3)H$ (**1a**). This reaction involves the liberation of ethene, which is detected in the ^1H NMR spectrum at δ 5.29 when the photolysis is carried out at 213 K. When the photolysis is carried out at room temperature, $CpRh(SiEt_3)_2(H)_2$ (**3a**) is formed in addition to **1a** and the liberated ethene is hydrosilated yielding Et_4Si together with the silation product $CH_2{=}CHSiEt_3$. The products were detected in situ by ^1H NMR spectroscopy including 2D-COSY where necessary, and their identities were checked against authentic samples (Table I). Ethane could also be detected in the vapor above the solvent by Raman spectroscopy (2956, 2900 cm^{-1}). No hydrogen was detected by either method. On completion of the reaction, the contents of the tubes were analyzed by GC/MS (Table II).

In order to determine the active species in our system, a series of control reactions were undertaken. These demonstrated that neither freshly sublimed $CpRh(C_2H_4)_2$ (**2**) nor $CpRh(SiEt_3)_2(H)_2$ (**3a**) catalyzed the hydrosilation of ethene by Et_3SiH at 298 K in the dark. In addition $CpRh(C_2H_4)_2$ (**2**) failed to react with Et_3SiH at 298 K. In 1987, Brown-Wensley showed that **2** catalyzed the hydrosilation of 1-hexene by Et_2SiH_2 at 18 °C.[17] However, we did not investigate Et_2SiH_2 as a substrate.

In the light of our control experiments which excluded **2** and **3a** as catalysts, it seemed likely that CpRh-

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[17] Brown-Wensley, K. A. *Organometallics* 1987, *6*, 1590.

Table III. Distribution of Hydrosilation Products as a Function of 1a, Ethene, and Et_3SiH[a]

precursor ratios				products/%	
1a	C_2H_4	Et_3SiH	C_2H_4/Et_3SiH	Et_4Si	$CH_2{=}CHSiEt_3$
1	0.7	6.5	0.1	100	0
1	10	10	1	46	54
1	4	3	1.3	20	80

[a] The values are determined by NMR integrals relative to [1a].

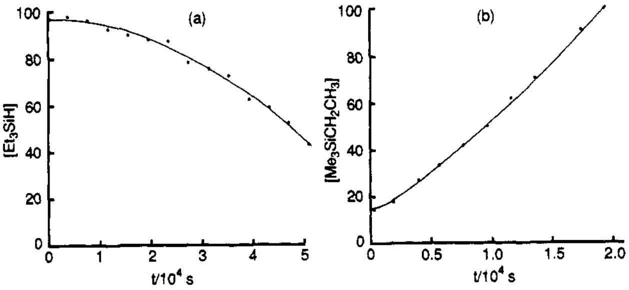

Figure 1. (a) Plot of intensity of Si-H resonance of Et_3SiH during hydrosilation of C_2H_4 with Et_3SiH catalyzed by 1. A smooth curve has been drawn through the experimental points. (b) Plot of the methyl resonance of Me_3SiEt during the hydrosilation of Me_3SiH and C_2H_4 by 1. Notice that 0.4 turnovers of Me_3SiEt were formed before measurements commenced.

Table IV. Summary of the NMR Data Obtained during Hydrosilation with 1a, Et_3SiH, and C_2D_4

	% Rh species			Et_3SiH[b]	absolute area
time/day	1a	5[a]	2	left	of Rh-H in 1a
4	95	2	3	5	1.41
7	90	6	4	4.6	1.47
15	85	5	10	3.1	1.41

[a] $CpRh(C_2H_{4-z}D_z)(CH_xD_{2-x}{=}CH_yD_{1-y}SiEt_3)$, at least two distinct isotopomers. [b] Relative to [1a].

$(C_2H_4)(SiEt_3)H$ (**1a**) was involved in the hydrosilation process.

In a series of experiments, **1a** was generated by photolysis of **2** in the presence of Et_3SiH at 213 K until 90% conversion to **1a** was obtained. The resulting complex was then warmed to 300 K in order to allow **1a** to catalyze the hydrosilation of ethene/silane mixtures in various ratios (see Table III). ^1H NMR spectroscopy was used to measure the percentage of vinylsilane formed. The proportion of the unsaturated silation product was observed to increase rapidly as the ratio of alkene to Et_3SiH was increased. A control experiment in which **2** was irradiated in the presence of $Me_3SiSiMe_3$ at 300 K failed to generate any CpRh products, implying that there is neither reaction with CH_3 groups bound to silicon nor with Si–Si bonds.

The rate of disappearance of the Si–H resonance of free R_3SiH was followed in two separate reactions by ^1H NMR spectroscopy on samples containing **1a**, R_3SiH (R = Me, Et), and C_2H_4. In the first tube (R = Et) the consumption of Et_3SiH was followed for only 1.5 turnovers of Et_3SiH, but the rate of reaction was found to increase over the period of observation (Figure 1a). The maximum rate of hydrosilation is ca. 0.2 turnover h^{-1}. (Notice that this rate is very slow compared to good catalysts, which give ca. 10^2–10^3 turnovers h^{-1} but which are usually employed at 40–60 °C.)[1,14] In the second tube, **1a** was allowed to catalyze the hydrosilation of C_2H_4 with Me_3SiH yielding $EtSiMe_3$. An increase in reaction rate with time was again observed (Figure 1b). After 2.7 turnovers with respect to **1a** only 2% of the expected silane exchange complex $CpRh(C_2H_4)(SiMe_3)H$ (**1d**) was detected. These experiments reveal that there is no induction period without product formation but that the kinetics are complex.

Work by Crabtree et al. and later by Whitesides et al. demonstrated that colloidal mercury acts as an inhibitor of heterogeneous catalysis.[18] Lewis and Lewis used this technique to demonstrate conclusively that colloid formation is the key step in the hydrosilation reactions of $Pt(COD)_2$ and $Pt(COD)Cl_2$ and Speier's catalyst.[19] In order to test the homogeneity of the hydrosilation reaction catalyzed by $CpRh(C_2H_4)(SiEt_3)H$ (**1a**), two samples were prepared containing **1a**, C_2H_4, and Et_3SiH; to one sample a small amount of distilled mercury was added. After 12 h of agitation in the absence of light no Et_3SiH remained in either sample, indicating that the catalytic process is homogeneous.

(2) Isotopic Labeling Studies. (a) Intramolecular H/D Exchange in 1a. In our earlier studies, we showed that $CpRh(C_2H_4)(SiEt_3)H$ (**1a**) is a classical complex exhibiting neither 3-center Rh–Si–H nor Rh–C–H interactions. Nevertheless, it remains likely that it will exhibit intramolecular exchange between ethene and hydride protons. In order to test whether the hydride ligand in the complex $CpRh(C_2H_4)(SiEt_3)H$ (**1a**) undergoes a [1,3]-H shift onto the coordinated ethene, selectively deuterated isotopomers of **1a** were prepared by photolysis of $CpRh(C_2H_4)_2$ with Et_3SiD or $(C_5D_5)Rh(C_2D_4)_2$ with Et_3SiH at 213 K. The isotopically labeled samples of **1a** were then warmed to 286 K, and the change in the area of the hydride resonance was monitored over a period of 6 h. The integration of the hydride was observed to grow over this period for the sample of $CpRh(C_2H_4)(SiEt_3)D$ and fall for $(C_5D_5)Rh(C_2D_4)(SiEt_3)H$ consistent with a reversible [1,3]-D/H shift between hydride and ethene. Analysis of the integral data obtained for $CpRh(C_2H_4)(SiEt_3)D$ at 286 K yielded an initial rate constant of 8×10^{-5} s^{-1} for the hydride migration, corresponding to a half-life of 8 h. In the following experiments we test for participation of **1** in the hydrosilation cycle by isotopic labeling.

(b) Hydrosilation with C_2D_4. The effect on hydrosilation of employing C_2D_4 in place of C_2H_4 was examined by sealing an NMR tube containing **1a** and Et_3SiH in the ratio 1:1 under 3 atm of C_2D_4. After 7 days, 5% of $CpRh(C_2H_4)(SiEt_3)H$ (**1a**) had been converted into the complex $CpRh(C_2H_4)(CH_2{=}CHSiEt_3)$ (**5**).[15] The isotopic purity of this complex was not established. GC/MS analysis of the volatile residue revealed that the trace of Et_3SiH remaining was 40% D_1. The unsaturated silation product, vinyltriethylsilane, was made up of the isotopomers D_1–D_3 in the ratio 13:28:59. The saturated hydrosilation product, Et_4Si, was detected in two sequential scans. The weighted average of the two scans shows that the Et_4Si produced was 25% D_5, 53% D_4, 6% D_3, 5% D_2, 4% D_1, and 7% D_0, with an overall deuteration level of 74%.

Mass spectral analysis of the less volatile residue yielded fragments at m/z ratios 196 and 197 of intensity 106 and 8 units characteristic of $[CpRh(C_2H_4)]^+$. Since the same ratio in an authentic sample of pure ^1H $CpRh(C_2H_4)(SiEt_3)H$ (**1a**) was 106:6, the residual **1a** is <2% D_1 after 1 turnover. No fragments with m/z values between 197 and 200 were observed.

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(18) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855. Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

(19) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.

Table V. Summary of the NMR Data Obtained during Hydrosilation with 1a, Et_3SiD, and C_2H_4

time/day	1a	mol ratio of $Et_3SiCH{=}CH_2$ wrt 1a	mol ratio of Et_3Si-H wrt 1a	% D of exchangeable protons of 1a
1	1	1.9	1.2	54
5	1	3.7	3.0	53
8	1	8.7	1.1	57

A similar experiment was conducted with a sample containing a **1a**:C_2D_4:Et_3SiH ratio of 1:10:5. The sample was examined by ^1H NMR spectroscopy after 4, 7, and 15 days at room temperature (Table IV).

GC/MS analysis revealed that the isotopic distribution of the vinyltriethylsilane was 62% D_3, 17% D_2, 14% D_1, and 7% D_0. The saturated hydrosilation product Et_4Si was made up of the isotopomers D_5, D_4, and D_1 in the ratio 33:50:17 consistent with 74% deuteration of the new ethyl group. Mass spectral analysis of the less volatile component revealed that the ratio of the m/z values 196 and 197 was 68:19. Thus, a D_0 to D_1 isotopomer ratio of 4:1 for **1a** was indicated after 2 turnovers.

When the experiment was repeated with initial proportions of **1a** to Et_3SiH of 1:110 and an excess of C_2D_4, and followed for 100 turnovers of Et_3SiH, the extent of deuteration of the residual **1a** increased. The isotopomers D_0, D_1, D_2, and D_3 were now detected in the ratio 70:15:8:2 for the $CpRh(C_2H_4)^+$ fragment, but there was no D_4 peak. In **1a** there are 5 exchangeable hydrogens; to a first approximation they were still only 9% deuterated after 100 turnovers.

(c) Hydrosilation and Intermolecular Exchange with Et_3SiD. The effect on hydrosilation of employing Et_3SiD instead of Et_3SiH was examined at various ratios **1a**:C_2H_4:Et_3SiD ratios. An NMR tube containing $CpRh(C_2H_4)(SiEt_3)H$ (**1a**), C_2H_4, and Et_3SiD in the ratio 1:7:17.5 was prepared, and ^1H NMR spectra were recorded after 1, 3, and 8 days (Table V). After 1 day at room temperature the decrease in the intensity of the hydride resonance of **1a** revealed that the isotopomer $CpRh(C_2H_4)(SiEt_3)D$ (**1aD**) was produced. The amount of **1a** converted into **1aD** remained roughly constant, at 54 ± 3% (compared to the statistical limit of 78%), during the experiment. Over the same period the integral of the free Si–H resonance of Et_3SiH relative to that of **1a** changed from 1.9 through 3.0 (after 3 days) to 1.1.

As indicated earlier, ethane is generated during the production of $Et_3SiCH{=}CH_2$. In this experiment two resonances in the ^1H NMR spectrum at 0.83 and 0.82 ppm were detected due to C_2H_6 and $C_2H_{6-x}D_x$. The relative intensity of these two resonances inverted over the reaction period, and in the final spectrum their intensity was 2:1.

Three further samples were prepared containing (i) **1a**, Et_3SiD; (ii) **1a**, Et_3SiH, C_2D_4; and (iii) **1a**, Et_3SiD, C_2H_4 with an initial 14-fold excess of silane relative to **1a** and a 5.5-fold excess of ethene. The solvent used in these experiments was cyclohexane-d_{12}. The three samples were followed concurrently over 15 days. In the system containing Et_3SiD and C_2H_4 the amount of free Et_3SiH was observed to increase before finally reaching a plateau. The loss of Et_3SiH in sample ii showed similar characteristics. In the control experiment the growth of free Et_3SiH was observed to follow the same initial curve as that of the Et_3SiD/C_2H_4 system but failed to level out in a similar fashion. The process of Si–D/Si–H exchange is, therefore, not enhanced by the presence of ethene in solution. At the end of the reaction the deuteration of hydride position in **1a** was larger in the Et_3SiD/C_2H_4 system than the Et_3SiH/C_2D_4 system implying that exchange is incomplete.

Table VI. Change in the Unsaturated Organic Derivatives Present in Solution during the Analysis of Hydrosilation of Propene and Triethylsilane by 1a

time/day	catalyst 1a	alkene $CH_2{=}CHCH_3$	unsaturated hydrosilation products[a]		
			E	*Z*	allyl
1	1	2.2	1.6	0.2	0.1
2.5	1	1.5	1.8		
4	1	1.2	1.7	0.3	0.2
10	1	0.3	1.6	0.2	0.2

[a] The values are determined by NMR integrals relative to [**1a**].

The deuterium label of Et_3SiD is transferred into the ethene and hydride ligands of **1a** by simple reductive elimination of Et_3SiH, oxidative addition of Et_3SiD, and subsequent [1,3]-H shifts between the ethene and hydride protons.

A similar experiment was performed with a **1a**:C_2H_4:Et_3SiD ratio of 1:10:10. After 6 days at room temperature, 2% of the $CpRh(C_2H_4)(SiEt_3)H$ (**1a**) present originally was converted into $CpRh(C_2H_4)(CH_2{=}CHSiEt_3)$ (**5**). Again the initial ethane resonance at 0.82 ppm was soon exceeded by the isotopomer at 0.83 ppm. Subsequent analysis of the volatiles by GC/MS indicated that the vinyltriethylsilane produced was 9% D_1 and the tetraethylsilane 50% D_1. A group of peaks at m/z = 258, 259, and 260 in the ratio of 64:28:8 was detected, which corresponds to the molecular ions of $Et_3SiC_2H_4SiEt_3$ and its D_1 and D_2 isotopomers. The formation of the latter implies that **1** also catalyzes the hydrosilation of $(CH_2{=}CH)SiEt_3$, albeit slowly.

A sample with an initial **1a**:C_2H_4:Et_3SiD ratio in solution of 1.7:1:7 was allowed to react in the same way. After hydrosilation was complete, GC/MS analysis of the volatiles revealed that the vinyltriethylsilane produced was 46% D_1 and the tetraethylsilane was 69% D_1 and 11% D_2. Little ethane and vinyltriethylsilane were produced because of the small proportion of ethene. These experiments show that the percentage deuteration of the hydrosilation products increases in line with the ratio of Et_3SiD/C_2H_4.

(3) Hydrosilation of Propene by 1a. The progress of hydrosilation was followed in a sample containing **1a**, Et_3SiH, and $CH_2{=}CHCH_3$ in the initial ratio 1:13:6. NMR spectroscopy indicated that both saturated and unsaturated hydrosilation products were produced in a ratio of 5:1. The only change in the Rh-based species was the production of a new Cp resonance in the ^1H NMR spectrum at 5.26 ppm. The chemical shift of this product is identical to that of $CpRh(SiEt_3)_3H$. No new rhodium(III) hydride resonances were detected. Thus, neither rhodium propene nor rhodium allyl complexes are formed. Three new sets of resonances were detected in the region 1.47–1.72 ppm (Table VI). The major component, probably the *E* isomer of the alkenylsilane $CH(Me){=}CHSiEt_3$, had couplings of 6.1 and 1.7 Hz (1.72 ppm). The minor products were assigned to the *Z* isomer (1.67 ppm, J_{HH} = 6.8 and 1.5 Hz) and the isomerized allyl species $CH_2{=}CHCH_2SiEt_3$ (1.47 ppm, ddd, J_{HH} = 2.4, 1.3, and 0.9 Hz). The predominance of the *E* isomer and the detection of the allyl product are both consistent with earlier observations.[8]

After 10 days, the volatile component was analyzed by GC/MS. The organic products $CH_3CH_2CH_2SiEt_3$, $C_3H_5SiEt_3$ (*Z*/*E*-$CH(Me){=}CHSiEt_3$ and allyl), and Et_4Si were detected. The unsaturated products were present in small proportions and not distinguished by this method.

(4) Cross-Silane Reactions. In this series of experi-

Table VII. Change in the Rhodium Product Distribution Observed during Hydrosilation of C_2H_4 with Pr^i_3SiH Catalyzed by 1a

	% compd remaining						
			$CpRh(C_2H_4)(CH_2CHR)$				
time/day	1a	1b	2 (R = H)	5a (R = $SiEt_3$)	5b (R = $SiPr^i_3$)	Pr^i_3SiH remaining[a]	conversion of 1a/%
0	85		15			3.5	0
1	82		18			3.5	3
11	64	13	20	3		3.2	25
25	57	16	21	6			33
66	42	22	22	8	6	2.7	51
104	29	21	31	10	9		66

[a] Relative to [1a] present initially.

ments $CpRh(C_2H_4)(SiR_3)H$ was reacted with C_2H_4 and a "cross"-silane, R'_3SiH ($R \neq R'$). The previous reactions have shown that the presence of **1a** is necessary for hydrosilation under the conditions employed. However, essentially no evidence for the involvement of the ethene ligand was obtained, since hydrosilation of C_2D_4 or $CH_2{=}CHCH_3$ failed to produce significant amounts of the expected Rh(III) complexes $CpRh(C_2D_4)(SiEt_3)H$ or $CpRh(CH_2{=}CHCH_3)(SiEt_3)H$. In order to test whether **1a** was indeed changed by hydrosilation, a series of experiments in which ethene was hydrosilated by the different silanes Me_3SiH, Me_2ClSiH, and Pr^i_3SiH was carried out. However, by its very nature this comparison has several drawbacks. The rate of the hydrosilation reaction is strongly influenced by the substituents on the silane.[13] This effect manifests itself quite clearly in the differing reactivities shown by $CpRh(C_2H_4)(SiR_3)H$ (**1**) toward R'_3SiH.[5]

The hydrosilation of C_2H_4 with Me_3SiH catalyzed by **1a** has already been outlined. After 7 days only 12% of the **1a** present originally was consumed. Although hydrosilation proceeded moderately rapidly, only 2% of the catalyst **1a** was converted into $CpRh(C_2H_4)(SiMe_3)H$ (**1d**) after 2.7 turnovers. A more conclusive indication of the difference in rate of the two exchange pathways was obtained from the reaction of **1a** with a 4-fold excess of Me_3SiH. In this reaction after 7 days at 298 K, 25% of the **1a** present originally was converted into **1d**.

In addition, a sample containing **1a**, $ClMe_2SiH$, and ethene was prepared. After 2 h at room temperature, a ^1H NMR spectrum showed that the hydrosilation reaction was already complete and that 3.6 turnovers of $Me_2Si(Cl)Et$ were generated on the basis of the amount of **1a**. No new rhodium products were obtained.

A sample containing **1a**, C_2H_4, and the less reactive silane, Pr^i_3SiH, in the ratio 1:4:3.5 was prepared. Slow hydrosilation was indicated by the fall in the characteristic Si–H resonance of Pr^i_3SiH at δ 3.55. After 60 days, the turnover was 1.8 units with a total of 0.5 units of vinylsilanes being formed (both $CH_2{=}CHSiEt_3$ and $CH_2{=}CHSiPr^i_3$). The GC/MS of the organic products confirmed that Et_4Si, $CH_2{=}CHSiEt_3$, $CH_2{=}CHSiPr^i_3$, and $CH_3CH_2SiPr^i_3$ were formed. During this reaction **1a** was converted into **1b** and the Rh(I) complexes $CpRh(C_2H_4)(C_2H_3R)$ (R = H, $SiEt_3$, $SiPr^i_3$) (Table VII).

A control experiment was undertaken at the same time in order to examine the competing silane exchange reaction. A sample containing **1a** and Pr^i_3SiH in the ratio 1:7 was made up. This ratio approximates to the total initial ethene and silane excess in the hydrosilation experiment. Only two products were formed, namely **1b** and **3b**, in this reaction. The ratio of **1b** to **3b** in the control sample was 2:1 after 104 days, the overall conversion of **1a** into these two species being 55%. In contrast, no **3b** was produced in the hydrosilation experiment. Belt showed by laser flash photolysis of **2** that the fragment $CpRh(C_2H_4)$ reacts 36 times faster with Et_3SiH than C_2H_4.[20] We have since shown that the first-order rate constants, k_{obs}, obtained for the reaction of Et_3SiH and Pr^i_3SiH with $CpRh(C_2H_4)$ are identical. If this intermediate were formed, it would react with R_3SiH (R = Et, Pr^i) in preference to ethene. Instead we found that the ratio of Rh(III)/Rh(I) products generated during the hydrosilation of Pr^i_3SiH and C_2H_4 in the presence of **1a** was 0.6:1. The ratio cannot, therefore, be explained by simple reductive elimination of silane from **1a** to form the reactive species $CpRh(C_2H_4)$. By inference, the silyl group of $CpRh(C_2H_4)(SiEt_3)H$ takes part in hydrosilation.

In a further test of the role of the silane, **1d** was allowed to catalyze the hydrosilation of ethene by $[(CH_3)_2CHCH_2]_3SiH$. A sample containing $CpRh(C_2H_4)(SiMe_3)H$ (**1d**), C_2H_4, and $[(CH_3)_2CHCH_2]_3SiH$ in the ratio 1:4:29 was prepared. After 7 days at room temperature, 30% of the **1d** present originally was converted into $CpRh(C_2H_4)(SiBu^s_3)H$ (**1c**). At this stage the free Si–H resonance was reduced by an amount which corresponded to 4.2 turnovers of silane. In a control experiment in which a 7-fold excess of $[(CH_3)_2CHCH_2]_3SiH$ was present, only 10% of the **1d** present originally was converted into **1c** after 9 days.

Discussion

The three reaction pathways of **1** (Scheme V) form the basis of our analysis of the hydrosilation mechanism. We also take account of the demonstrated ability of **1** to form Rh^V complexes. An additional step essential to our argument is silyl migration onto coordinated ethene. This step has not been observed in stoichiometric reactions of these rhodium complexes but has been established by Wrighton et al. for iron and cobalt complexes.[7,21]

Lewis and Lewis have shown that Speier's catalyst requires formation of colloidal platinum for hydrosilation.[19] Our tests with **1** in the presence of mercury provide good evidence that the reactions of **1** are homogeneous. We have also tested a number of other related complexes for catalytic activity under similar conditions and have established that catalytic activity is confined to **1**. We infer that **1** is directly involved in catalysis, although not necessarily within the catalytic cycle.

Addition of ethene and Et_3SiH to a solution containing $CpRh(C_2H_4)(SiEt_3)H$ (**1a**) resulted in the formation of the conventional hydrosilation product Et_4Si and the unsaturated product $CH_2{=}CHSiEt_3$. For mass balance, ethane is produced alongside the unsaturated product. The proportion of vinylsilane was observed to increase as the ratio of C_2H_4 to Et_3SiH increased. The same trend was

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(20) Belt, S. B. D. Phil. Thesis, University of York, 1989.

(21) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366.

observed when $Cp^*Rh(C_2H_4)_2$ was used as a hydrosilation catalyst by Maitlis et al.[14]

On addition of Et_3SiH and C_2D_4 to $CpRh(C_2H_4)(SiEt_3)H$ (**1a**) hydrosilation proceeded as before. Both the new ethyl and vinyl groups of the hydrosilation products were ~75% deuterated. H/D scrambling within the hydrosilation products was observed. Notably, there was very little deuteration of $CpRh(C_2H_4)(SiEt_3)H$ (**1a**) even after 100 turnovers of C_2D_4. However, in the presence of the unsaturated hydrosilation product $CH_2{=}CHSiEt_3$ traces of $CpRh(C_2H_4)(CH_2{=}CHSiEt_3)$ (**5a**) were formed during the reaction.

On examining the hydrosilation of Et_3SiD and C_2H_4 by $CpRh(C_2H_4)(SiEt_3)H$ (**1a**) incorporation of the deuterium label into **1a** was observed and free Et_3SiH was detected. The rate of production of Et_3SiH in the exchange reaction involving **1a** and Et_3SiD alone was observed to follow the same initial growth characteristics. The extent of deuteration of both the hydrosilation and silation products was observed to increase as the ratio of Et_3SiD to C_2H_4 increased. The observation of such exchange between the Si–D and C–H of the alkene is not uncommon.[22]

When $CpRh(C_2H_4)(SiEt_3)H$ (**1a**) catalyzed the hydrosilation of propene, three unsaturated products were obtained besides the saturated product, $Et_3SiCH_2CH_2CH_3$. These were identified as *Z*- and *E*-$CH(SiEt_3){=}CH(CH_3)$ and the allyl isomer $CH_2{=}CHCH_2SiEt_3$. The *E* isomer was favored as expected.[8] Again no new Rh(III) complexes were observed.

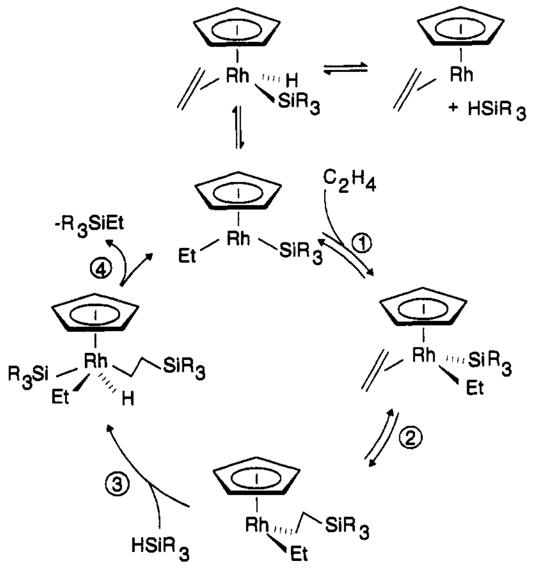
The cross-silane reactions indicate that the original silyl function is consumed during the hydrosilation process. The evidence for this process was obtained from the reactions of **1a** with ethene and Pr^i_3SiH or **1d** with $[(CH_3)_2CHCH_2]_3SiH$, where the expected Rh(III) products **1b** and **1c** are formed during hydrosilation. When the hydrosilation is very fast as with $Me_2(Cl)SiH$, no new Rh(III) products are detected.

The mechanisms of Chalk and Harrod (Scheme I) and the variant with silyl migration (Scheme II) replace the ethene and silane ligands of **1** once for every turnover of the cycle. The isotopic labeling experiments presented above show conclusively that the ethene ligand is not replaced during hydrosilation so excluding both these mechanisms. It is harder to show whether the silane is replaced once per cycle. Upon hydrosilation of Me_3SiH and C_2H_4 by $CpRh(C_2H_4)(SiEt_3)H$ (**1a**) very little of the silane in **1a** is replaced in the reaction, but it is replaced in the much slower reaction with Pr^i_3SiH. A more detailed explanation of these results is given below, when an alternative cycle has been presented.

A satisfactory cycle cannot involve the formation of $CpRh(C_2H_4)$, since this would be inconsistent with the ratio of the Rh(III) to Rh(I) products generated during the hydrosilation of Pr^i_3SiH and C_2H_4 in the presence of **1a**. We require, therefore, a mechanism in which the coordinated ethene ligand behaves as a spectator ligand during hydrosilation but, nevertheless, one which does not involve $CpRh(C_2H_4)$.

An alternative mechanism based on a *two-silicon cycle* is illustrated in Scheme VI. This satisfies the requirements that (i) $CpRh(C_2H_4)(SiR_3)H$ is not involved directly in the cycle, (ii) $CpRh(C_2H_4)$ is not formed during hydrosilation, and (iii) the integrity of the original ethene ligand is retained.[23]

Scheme VI. Two-Silicon Cycle for Hydrosilation



The cycle is initiated by a [1,3]-H shift forming $CpRh(SiEt_3)(C_2H_5)$. Ethene attack on this d^6 16-electron fragment yields $CpRh(C_2H_4)(SiR_3)(Et)$, which must then undergo a [1,3]-silyl shift. This process leads to the generation of the new intermediate $CpRh(CH_2CH_2SiEt_3)Et$. Addition of Et_3SiH to this species would generate a complex containing *two silicon* atoms, $CpRh(CH_2CH_2SiEt_3)Et(SiEt_3)H$. This species, formally with Rh in oxidation state V, but possibly containing a RhSiH or RhCH 3-center bond,[5] could then eliminate the conventional hydrosilation product Et_4Si and re-form the original intermediate, $CpRh(SiEt_3)Et$. The initial [1,3]-H shift is fully consistent with the H/D exchange reactions of $CpRh(C_2H_4)(SiEt_3)D$ and the formation of $CpRh(Me_2SO)(SiEt_3)(Et)$ rather than $CpRh(Me_2SO)(CH_2CH_2SiEt_3)H$, the corresponding [1,3]-silyl shift product. The generation of the complex $CpRh(CH_2CH_2SiEt_3)Et(SiEt_3)H$ is consistent with our demonstrations that compounds of the type $CpRh(SiR_3)_3H$ and $CpRh(SiR_3)_2H_2$ are accessible at room temperature. However, an alkyl hydride would be expected to be far less stable than these silyl hydrides and hence active in the catalytic cycle.

The addition of R_3SiH to $CpRh(Et)(CH_2CH_2SiR_3)$ must be stereoselective, since no ethane is detected in the absence of vinyltrialkylsilane; i.e. ethane formation is characteristic of silation not hydrosilation. The hydride and ethyl ligands cannot therefore be cis to one another. Although hydrosilation is commonly stereoselective, too little is known of this type of reaction to identify the basis of the selectivity.

Scheme VI, therefore, provides a likely hydrosilation cycle for the production of the saturated hydrosilation

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[22] Ryan, J. W.; Speier, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 895.

[23] In this cycle hydrosilation proceeds via the formation of $CpRh(C_2H_4)(SiEt_3)Et$ (Scheme VI). On photolysis of $CpRh(C_2H_4)_2$ (**2**) at 213 K in the presence of Me_3SiH the primary product was $CpRh(C_2H_4)(SiMe_3)H$ (**1d**), but on warming, the new rhodium products $CpRh(C_2H_4)(SiMe_3)_2$ and $CpRh(SiMe_3)_3H$ (**4d**) were formed along with Me_3SiEt. It is important to note that while $CpRh(C_2H_4)(SiEt_3)Et$ has not been detected, $CpRh(C_2H_4)(SiMe_3)_2$ proved to be stable. Under the conditions in which $CpRh(C_2H_4)(SiMe_3)_2$ was obtained, $CpRh(C_2H_4)(SiMe_3)Et$ is likely to have been formed, since both originate from the same intermediate, namely $CpRh(Et)(SiMe_3)$. The failure to detect this product signifies that either (i) elimination of Me_3SiEt occurs or (ii) a [1,3]-silyl shift into the coordinated ethene forms a new intermediate, $CpRh(Et)(CH_2CH_2SiEt_3)$. There is no evidence that $CpRh(C_2H_4)(SiMe_3)_2$ reductively eliminates $Me_3SiSiMe_3$ at room temperature, supporting the proposal that $CpRh(SiEt_3)(C_2H_4)Et$ does not eliminate $EtSiEt_3$ directly.

product R_3SiEt by $CpRh(C_2H_4)(SiR_3)H$ which satisfies the principal observations. If this mechanism operates, we would expect the production of a new Rh(III) complex when $CpRh(C_2H_4)(SiEt_3)H$ catalyzes the hydrosilation of R'_3SiH ($R' \neq Et$) and C_2H_4. The rate of formation of such products would depend on the rate of the back-reaction connecting 1 to the cycle. Although such new Rh(III) complexes are observed, they could also originate from a simple silane exchange process based on the reductive elimination of the initial silane. The failure to detect significant exchange when the cross-silane is more reactive than the original silane is consistent with the failure to regenerate $CpRh(C_2H_4)(SiR_3)H$ in the cycle. It is understandable if the rate of reaction of 1 within the cycle exceeds the rate of the back-reaction external to the cycle. All the steps in the proposed cycle are consistent with the need for retention of the original configuration at silicon throughout the hydrosilation process.[24] Significantly, if $(CO)_3Co$ is replaced by CpRh(Et) in Wrighton's scheme for hydrosilation (Scheme III), then the cycle obtained is identical to that presented in Scheme VI.[7a] Since the ethyl group acts as a bystander, we predict that other sources of $CpRh(SiR_3)X$ (X = alkyl, silyl, etc.) should be active hydrosilation catalysts. Experimental tests of this prediction will be undertaken.

Conclusions

Scheme VI is supported by the following evidence: (i) the lack of isotopic exchange during hydrosilation of C_2D_4 with Et_3SiH, catalyzed by **1a**; (ii) the replacement of the $SiEt_3$ group of **1a** by $SiPr^i_3$, when C_2H_4 is hydrosilated by $HSiPr^i_3$ in the presence of **1a**; (iii) the accessibility of complexes formally in the Rh(V) oxidation state; (iv) the intramolecular hydrogen-exchange reactions of 1; (v) the fact that $CpRh(C_2H_4)(SiR_3)H$ is isolable makes it implausible that it is the key intermediate in the cycle; (vi) the stoichiometric reactions of 1, especially with Me_2SO, match the steps of the cycle.

It is likely that Scheme VI is only a description of the main pathway of reaction, since our observations require additional processes that account for the unsaturated products formed in the presence of excess alkene. Quantitative kinetic analysis of this system is under consideration at the present time.

In conclusion, the Chalk-Harrod hydrosilation cycle does not operate for $CpRh(C_2H_4)(SiR_3)H$. The mechanism illustrated in Scheme VI, in which the coordinated alkene behaves as a spectator ligand, is supported by numerous observations. This reaction cycle involves the generation of a Rh(V) intermediate and fails to re-form $CpRh(C_2H_4)(SiR_3)H$ directly.

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Registry No. **1a**, 102744-67-2; **1b**, 137203-36-2; **2**, 12211-95-9; **3a**, 102744-68-3; **3b**, 137259-27-9; **5a**, 118869-81-1; $CpRh(SiEt_3)(C_2H_4)D$, 137203-35-1; Et_3SiH, 617-86-7; C_2H_4, 74-85-1; Et_3SiD, 1631-33-0; C_2D_4, 683-73-8; Et_4Si, 631-36-7; $Et_3SiCH_2CH_2SiEt_3$, 2295-15-0; Me_3SiEt, 3439-38-1; $CH_2{=}CHSiMe_3$, 754-05-2; $Me_2ClSiEt$, 6917-76-6; $CH_3CH_2CH_2SiEt_3$, 994-44-5; $CH_3CH{=}CHSiEt_3$, 3931-84-8; (*E*)-$CH_3CH{=}CHSiEt_3$, 83053-45-6; (*Z*)-$CH_3CH{=}CHSiEt_3$, 83053-46-7; $EtSiPr^i_3$, 56568-90-2; $CH_2{=}CHSiPr^i_3$, 121675-48-7; Pr^i_3SiH, 6485-79-6; $CH_2{=}CHCH_3$, 115-07-1.

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Synthesis and Spectroscopic and Structural Characterization of $PhB[P(Mes)BMes_2]_2$: A Boron-Phosphorus Analogue of the Pentadienyl Cation

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The synthesis and spectroscopic (^1H, ^{11}B, and ^{31}P NMR) and X-ray structural characterization of the bis(borylphosphino)arylborane $PhB[P(Mes)BMes_2]_2$ are described. Its structure is composed of an array of planar coordinated boron and phosphorus atoms with a mean B-P distance of 1.864 (15) Å. These features suggest significant delocalization of the phosphorus lone pairs throughout the B_3P_2 skeleton. The dynamic behavior of $PhB[P(Mes)BMes_2]_2$ in solution was examined by variable-temperature ^1H NMR (-99 to +152 °C). These studies indicated that the $\Delta G^{\ddagger}$ rotation for B-P π-bonds is about 17-18 kcal mol^{-1}. Crystal data with Cu Kα (λ = 1.54178 Å) at 130 K: a = 22.052 (7) Å, b = 15.662 (8) Å, c = 41.107 (7) Å, orthorhombic, space group $Pna2_1$ (33), Z = 8 (2 molecules per asymmetric unit), R = 0.105.

Introduction

Much of the impetus in the study of boron-nitrogen compounds[1] comes from their isoelectronic relationship to the corresponding carbon species. Thus, borazine[2] and aminoboranes[1] of the type $R_2BNR'_2$ (where R and R' = alkyl, aryl, halogens, etc.) have been recognized for many years as the inorganic analogues of benzene and ethylene. The chemistry of the corresponding compounds with boron bonded to P, As, Sb, or Bi has just recently begun to attract attention.[3,4] Thus, the X-ray crystal structures of

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