Photochemical Oxidative Addition Reactions of (η^5-Cyclopentadienyl)bis(ethene)rhodium with Dihydrogen and Trialkylsilanes: Formation and Isolation of Rhodium(III) and Rhodium(V) Hydrides

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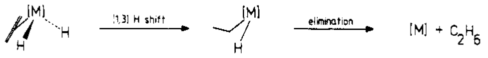
Photolysis of $CpRh(C_2H_4)_2$ (1; Cp = η^5-C_5H_5) in benzene or toluene in the presence of R_3SiH (R = Me, Et) yields $CpRh^{III}(C_2H_4)(SiEt_3)H$ (2), $CpRh^V(SiEt_3)_2(H)_2$ (3), ethane, and triethylsilane. By appropriate choice of conditions the reaction can be controlled to enable the isolation of either 2 or 3. The identifications of 2 and 3 are secured by multinuclear NMR. Photolysis of 1 in liquid xenon at 170 K under a 10-bar pressure of hydrogen yields $CpRh(C_2H_4)(H)_2$ (4). Complex 4 and several ^2H-substituted analogues are identified by FTIR spectroscopy. 4 may be converted to $CpRh(C_2H_4)(D)_2$ by photolysis under D_2. Ethane is generated in a slow thermal process subsequent to photolysis that may be followed by FTIR or NMR spectroscopy in liquid xenon. The dihydride 4 has not been detected by NMR when 1 is photolyzed in toluene solution or LXe under lower hydrogen pressures, even though ethane is generated.

Introduction

We recently reported preliminary evidence that $CpRh(C_2H_4)_2$ (1; (Cp = η^5-C_5H_5) is photosensitive, undergoing several reactions in low-temperature matrices, in benzene solution at room temperature, and in liquid xenon (LXe).[2-4] The intermediate $CpRh(C_2H_4)$ is formed in the primary step by photochemical elimination of ethene and has been observed by both matrix-isolation and laser flash photolysis in solution.[5] Both the substitution (e.g. by N_2)[3] and oxidative addition (e.g. of Et_3SiH)[2] reactions of 1 are consistent with the loss of ethene in the primary step. These compounds are labeled according to Chart I.

Bentz et al. have previously reported the reactions of $Cp^*Rh(C_2H_4)_2$ (Cp* = η^5-C_5Me_5) with silanes.[6] Here we report a study of the photochemical oxidative addition of trialkylsilanes and of H_2 to $CpRh(C_2H_4)_2$ including (i) the isolation of $CpRh^{III}(C_2H_4)(SiEt_3)H$ (**2a**), (ii) the isolation of a Rh^V species, $CpRh(SiEt_3)_2(H)_2$ (**3a**), produced by the photochemically initiated oxidative addition of a second molecule of Et_3SiH to 2, and the full characterization of **2a** and **3a** via ^1H, ^{13}C, ^{29}Si, and $^{103}Rh\{^1H\}$ NMR, and (iii) the production of $CpRh^{III}(C_2H_4)(H)_2$ (4) by the photochemical reaction of 1 with H_2 in LXe. This last reaction was made possible by the use of a high hydrogen overpressure combined with the low temperature of LXe, a method previously used to make several dihydrogen complexes.[7]

Both metal ethene dihydride and metal ethene trialkylsilyl hydride complexes should be able to eliminate a C_2 unit by a [1,3] H shift onto coordinated ethene (eq 1) followed by reductive elimination. Alternatively, tetraalkylsilane may be formed by silyl migration onto the coordinated ethene followed by reductive elimination of $R_3SiCH_2CH_2$–H (eq 2). Indeed, a metal alkene silyl hydride complex is the key intermediate in Chalk and Harrod's scheme for hydrosilation.[8] We show that the thermal reactions that occur after photolysis do generate elimination products. Ethane is formed after photolysis of 1 with H_2; both tetraethylsilane and ethane are formed after the photolysis of 1 with triethylsilane.



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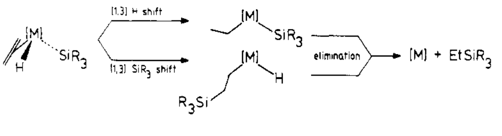
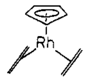
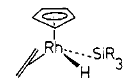


(2)

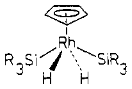
Chart I



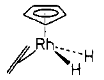
1a, $(C_5H_5)Rh(C_2H_4)_2$
b, $(C_5D_5)Rh(C_2H_4)_2$
c, $(C_5D_5)Rh(C_2D_4)_2$



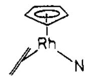
2a, R = Et
b, R = Me



3a, R = Et
b, R = Me



4aH, $(C_5H_5)Rh(C_2H_4)(H)_2$
4aD, $(C_5H_5)Rh(C_2H_4)(D)_2$
4bH, $(C_5D_5)Rh(C_2H_4)(H)_2$
4cH, $(C_5D_5)Rh(C_2D_4)(H)_2$



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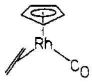

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† No reprints available.

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(9) The chemical shifts of ethane and ethene were checked against authentic samples in both $C_6D_5CD_3$ and LXe. The observed values are as follows: ethene, δ 5.24, ethane, δ 0.82 ($C_6D_5CD_3$); ethene, δ 5.58, ethane, δ 0.73, and H_2, δ 4.70, in LXe at 198 K.

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Table I. NMR Data for Rhodium Silyl Products in Benzene-d_6 at Ambient Temperature Recorded at 360 or 400 MHz[a]

compound	nucleus	C_5H_5Rh	C_2H_4	SiR_3	RhH
$(C_5H_5)Rh(C_2H_4)$-$(SiEt_3)H$ (**2a**)	^1H	4.95 (t, J(Rh, H) = J(H,H) = 0.6, 5 H)	2.32 (br,[b] 4 H)	0.69 (Si$CH_2$$CH_3$, q, J(H,H) = 7.8, 6 H), 1.04 ($SiCH_2$$CH_3$, t, J(H,H) = 7.8, 9 H)	−14.85 (d, J(Rh,H) = 33.2, 1 H, ^2J(HSi) = 12.0)[c]
	$^{13}C\{^1H\}$	89.4 (d, J(Rh,C) = 3 [J(H,C) = 180]	31.7 (d, J(Rh,C) = 11 [J(H,C) = 160]	12.5 (s, $SiCH_2CH_3$) 10.3 (s, $SiCH_2CH_3$)	N/A
	$^{29}Si\{^1H\}$	N/A	N/A	41.6 (d, J(Rh,Si) = 22.2)	N/A
	^{103}Rh		N/A	N/A	−1492 (d, J(Rh,H) = 33)[c]
$(C_5H_5)Rh(SiEt_3)_2(H)_2$ (**3a**)	^1H	4.99 (q, J(Rh,H) = J(H,H) = 0.5, 5 H)	N/A	0.78 (Si$CH_2$$CH_3$, q, J(H,H) = 8.0, 12 H), 1.08 ($SiCH_2$$CH_3$, t, J(H,H) = 8.0, 18 H)	−14.16 (d, J(Rh,H) = 38.3, 2 H, ^2J(HSi) = 6.8)[c]
	$^{13}C\{^1H\}$	90.4 (d, J(Rh,C) = 3, [J(H,C) = 180])	N/A	14.36 (s, $SiCH_2CH)_3$,[c] 9.65 (s, $SiCH_2CH_3$)[c]	N/A
	^{103}Rh		N/A	N/A	−1931 (t, J(Rh,H) = 38.5)
	$^{29}Si\{^1H\}$	N/A	N/A	40.1 (d, J(Rh,Si) = 16.6)	N/A
$(C_5H_5)Rh(C_2H_4)$-$(SiMe_3)H$ (**2b**)	^1H	4.92 (t, J(Rh,H) = J(H,H) = 0.5, 5 H)	2.39 (br, 4 H)	0.11 (s, 9 H)	−14.84 (d, J(Rh,H) = 32, 1 H)
	$^{13}C\{^1H\}$	90.07 (d, J(Rh,C) = 2.8)	34.84 (d, J(Rh,C) = 12.8)	9.29	N/A
$(C_5H_5)Rh(SiMe_3)_2$-$(H)_2$ (**3b**)	^1H	not obsd	N/A	not obsd	−13.87 (d, J(Rh,H) = 40)

[a] Chemical shifts in δ; coupling constants in hertz. [b] In toluene at 213 K, this splits into separate components for each proton (δ 2.91, 2.68, 2.11, 1.65). [c] Recorded in toluene-d_8.

Experimental Section

General Comments. Rhodium trichloride trihydrate was the gift of Dow Corning and used without further purification. C_2D_4 (99.4 atom %) was obtained from MSD isotopes. Thallium cyclopentadienide, methanol-d_1, triethylsilane, and D_2O were purchased from Aldrich. Dicyclopentadiene (Lancaster Synthesis) was cracked immediately prior to use. Tetrahydrofuran, toluene, and hexane were distilled from sodium benzophenone ketyl under argon, and all solvents were degassed immediately prior to use. All syntheses were performed under an atmosphere of argon by using standard Schlenk or high vacuum techniques.

NMR tubes were irradiated with a Philips HPK medium-pressure mercury arc in conjunction with a water filter to remove heat (path length = 5 cm). For low-temperature work, samples were placed in a partially silvered Pyrex Dewar, containing methanol as the coolant.

Mass spectra were recorded on a Kratos MS3074 spectrometer by the University of York service. Analyses were carried out by Butterworth Laboratories Ltd. UV and IR spectra were recorded on Perkin-Elmer Lambda 7G and 580 spectrophotometers respectively. NMR spectra were recorded at York on a Bruker WP80 with ^1H at 80 MHz and ^{13}C at 20.15 MHz. High-field spectra were recorded at Nottingham (250 MHz), Edinburgh (360 MHz), and Sheffield (400 MHz). Hydrocarbon products were identified as follows: ethane and ethene by ^1H NMR and comparison with an authentic sample[9] and by Raman spectroscopy in the vapor phase in the NMR tube; tetraalkylsilanes, R_3SiEt (R = Me, Et), and vinyltrialkylsilanes, $CH_2{=}CHSiR_3$, by ^1H NMR including 2D measurements and comparison with authentic samples and GC/mass spectrometry. Chemical shifts are reported in parts per million downfield of tetramethylsilane but were recorded relative to residual benzene-d_5 (^1H δ 7.15), benzene-d_6 (^{13}C δ 128.0), and toluene-d_7 (^1H δ 2.15); ^{29}Si and ^{103}Rh chemical shifts are reported relative to external TMS (δ 0) and ^{103}Rh (3.16 MHz, δ 0), respectively.

The liquid xenon cell for use with FTIR has been described elsewhere.[7] The Xe, D_2, and H_2 were supplied by BOC and used without further purification. The IR spectra were recorded on a Nicolet MX-3600 interferometer (16K data points, 32K transform points, 2 cm^{-1} resolution). The use of LXe as a NMR solvent is currently being developed in Nottingham. A titanium valve with a Teflon bursting disk was fitted to a high-precision Pyrex NMR tube for this purpose. Experiments were carried out at 193 K with an overall pressure of 5 atm, 2 atm of which was the H_2 over pressure.[10]

Syntheses. $(C_5H_5)Rh(C_2H_4)(SiEt_3)H$ (2a). $CpRh(C_2H_4)_2$ (**1a**) (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 **1a**. The contents were then degassed by using several freeze–pump–thaw cycles before the tube was sealed. The sample was photolyzed at 213 K for 40 h until 60% conversion of **1a** to **2a** was achieved as indicated by ^1H NMR. The yellow solution was eluted through an alumina column with hexane. The first 200 cm^3 fraction, which was enriched in **2a**, was transferred to a small Schlenk tube where the solvent was removed under a stream of argon. The resulting yellow oil was sublimed (at 298 K) onto a cold finger (at 273 K) at a pressure of 6×10^{-4} mbar to remove **1a**. Further sublimation (at 298 K) onto a cold finger (at 77 K) yielded **2a** contaminated with ca. 10% **1a**. IR (Nujol mull): 2060 cm^{-1} [ν(Rh–H)]; UV (cyclohexane): maxima at 322 and 236 nm (intensity ratio 1:22) with a shoulder at 278 nm. NMR data appear in Table I and mass spectral data in Table II.

Table II. Mass Spectral Data for 2a and 3a

$CpRh(C_2H_4)(SiEt_3)H$ (**2a**)			$CpRh(SiEt_3)_2(H)_2$ (**3a**)		
m/z	%	fragment	m/z	%	fragment
			371	1.4	$M^+ - C_2H_5$
312	4	M^+	369	2.4	$M^+ - C_2H_7$
284	46	$M^+ - C_2H_4$	341	10	$M^+ - C_4H_9$
282	13	$M^+ - C_2H_6$	311	7	$M^+ - C_6H_{17}$
254	100	$M^+ - C_4H_{10}$	296	93	$M^+ - SiC_5H_{16}$
252	38	$M^+ - C_4H_{12}$	284	28	$M^+ - HSiEt_3$
226	44	$M^+ - C_6H_{14}$ or $- C_4H_{10}Si$	226	45	$M^+ - C_8H_{26}Si$
196	60	$M^+ - HSiEt_3 = CpRh(C_2H_4)^+$	196	100	$CpRhSi^+$ or $CpRh(C_2H_4)$
168	41	$CpRh^+$	168	17	$CpRh^+$

$(C_5H_5)Rh(SiEt_3)_2(H)_2$ (3a). $CpRh(C_2H_4)_2$ (**1a**) (0.1 g, 4×10^{-4} mol), 0.4 cm^3 of Et_3SiH (5×10^{-3} mol), and benzene (10 cm^3, 10^{-1} mol) were placed in a cylindrical photochemical reactor giving a solution 0.04 mol dm^{-3} in **1a**. The solution was irradiated with filtered UV light with $\lambda > 290$ nm for 120 min, transferred to a Schlenk under Ar, and reduced in volume to ca. 2 cm^3. The residue was then eluted with hexane through an alumina column of 5-cm length giving a pale yellow solution containing **3a** (95%) and **2a** (5%) according to ^1H NMR. To remove **2a**, CCl_4 was added, and after 5 min the light brown residue was eluted through an alumina column. ^1H NMR indicated **3a** was essentially the only species present in the eluant. The solvent was removed in vacuo, and the resulting yellow oil was sublimed at 50 °C to yield a white crystalline solid (mp 29–30 °C). IR (toluene solution): 2062 cm^{-1} [ν(Rh–H)]. IR (liquid film); 2950 (s), 2930 (m), 2906 (m), 2871 (s), 2060 (w), 1456 (w), 1418 (w), 1261 (m), 1095 (m, broad), 1018 (sh), 1005 (s), 804 (s), 747 (w), 721 (m), 693 (w) cm^{-1}. UV (cyclohexane): maximum at 226 nm with shoulder at 254 nm. Anal. Found (Calcd): C, 50.95 (50.98); H, 9.27 (9.31). NMR data are presented in Table I and mass spectral data in Table II.

The syntheses of **1a**, **1b**, and **1c** are described elsewhere.[4]

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[10] Gregory, M. F. Ph.D. Thesis, Nottingham 1985.

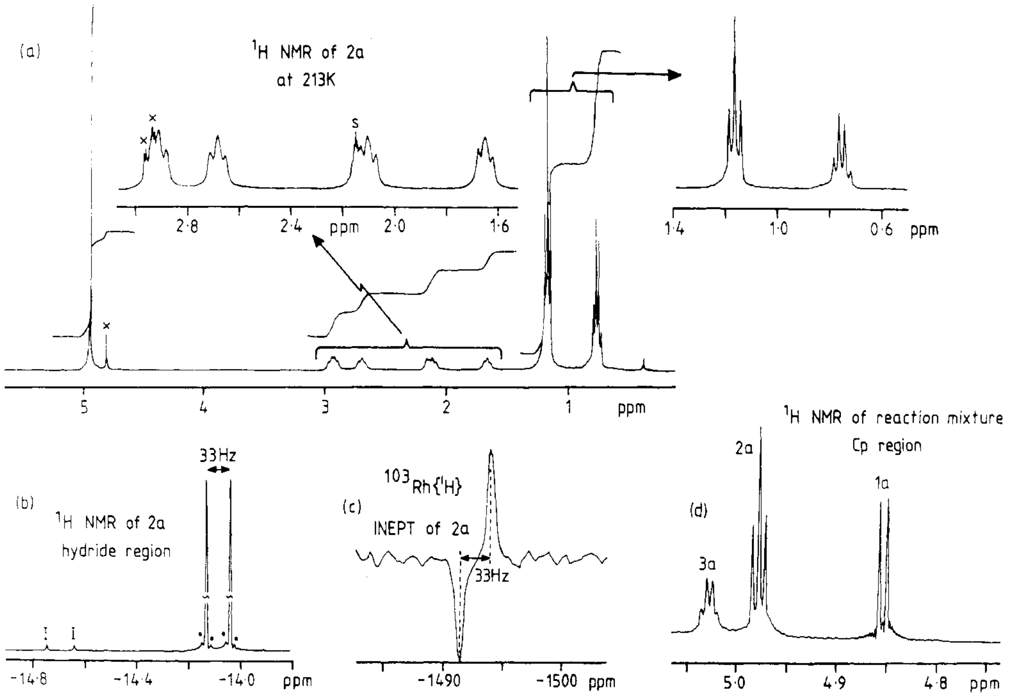

Figure 1. (a-c) NMR spectra of purified $CpRh(C_2H_4)(SiEt_3)(H)$ (**2a**) in toluene-d_8. (a) ^1H spectra of the region δ 0–6 recorded at 213 K and 360 MHz. The resonances marked (×) are due to residual $CpRh(C_2H_4)_2$ (8%). The individual inequivalent alkene and ethyl protons are shown in the expanded inserts. (b) ^1H spectrum of the hydride region. The ^{29}Si satellites are indicated (●). The hydride protons of the impurity **3a** (1.5%) are marked (I). (c) $^{103}Rh\{^1H\}$ INEPT spectrum of **2a** recorded at 12.64 MHz in toluene solution at 297 K; the resonance appears as a doublet with J_{RhH} = 33 Hz with phase −1,+1. (d) In situ ^1H NMR from reaction of **1** with Et_3SiH at 80 MHz showing the cyclopentadienyl protons of **1a**, **2a**, and **3a**. In each case there is coupling of ca. 0.5 Hz to ^{103}Rh. The resonances of **2a** and **3a** show additional coupling to the hydridic protons.

Results

Photochemical Reaction of 1 with R_3SiH (R = Me, Et). Complex **1** shows absorption maxima in the ultraviolet with a long tail extending into the visible part of the spectrum (in cyclohexane λ_{max} = 235 and 279 nm; extinction coefficients = 2.7×10^4 and 3.3×10^3 $dm^3\ mol^{-1}\ cm^{-1}$, respectively; in the tail at 450 nm, ϵ = 18 $dm^3\ mol^{-1}\ cm^{-1}$). Photolysis was carried out in Pyrex tubes ($\lambda > 285$ nm), thereby irradiating into the tail of the absorption. Loss of **1** and generation of products could be followed specifically by NMR but not by UV spectroscopy. The photochemical reaction of **1** with R_3SiH in C_6D_6 in an NMR tube at room temperature results in formation of hydrosilation products and two rhodium hydrides, **2** and **3**. The relative concentrations of **2** and **3** depend on the photolysis time, the initial concentration of **1**, and the proportion of R_3SiH. The most effective method of *isolating* **2a** (R = Et) proves to be photolysis of a concentrated solution of **1** in toluene at 213 K in the presence of a large excess of Et_3SiH. In situ ^1H NMR shows 90% conversion to **2a** is achievable by photolysis, but the purification is hampered by decomposition of **2a** when solutions are pumped down. Nevertheless, we have isolated a yellow oil containing 90% **2a**, ~8% **1a**, and ~2% **3a**.

Complex **2a** is identified as $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)(SiEt_3)H$ by ^1H, ^{13}C, ^{29}Si, and ^{103}Rh NMR (Table I and Figure 1) and mass spectra (Table II). The protons of the coordinated ethene are all inequivalent at low temperature; all four multiplets have been located and their connectivity verified by decoupling experiments. At 213 K saturation transfer is observed, indicating that the ethene ligand is still rotating slowly. On warming the signals of **2** coalesce at 240 K (operating frequency = 80 MHz) with the onset of rapid internal rotation about the rhodium–ethene bond. The corresponding coalescence temperature of **1** is above room temperature.

Two types of three-center bonding involving 3-center [M](C–H) or 3-center [M]–Si–H linkages are possible in a trialkylsilyl ethene hydride complex. Ethene hydride complexes are often found to be unstable with respect to agostic structures that have characteristically low values of J_{CH} when compared to hydrocarbons; $[Co(\eta^5\text{-}C_5Me_5)(C_2H_4)(\eta^2\text{-}C_2H_4\text{-}\mu\text{-}H)]BF_4$ is such an example.[11] However, measurement of J_{CH} for the ethene carbon of **2a** showed the value to be normal for sp^2-hybridized CH bonds (J_{CH} = 160 Hz). A three-center [M](Si–H) bond would be expected to have a Si–H coupling constant of between 60 and 70 Hz.[6] The hydride protons of **2a** appear as a doublet at (J_{RhH} = 33.2 Hz) with ^{29}Si satellites (Figure 1b). The intensities of the satellites are consistent with the presence of one $SiEt_3$ group per hydridic proton; the coupling constant is low ($^2J_{SiH}$ = 12 Hz) as expected for normal two-center bonds. The Cp resonance appears as a triplet with $^2J_{RhH}$ = $^3J_{HH}$ = 0.6 Hz (Figure 1d). The $^{103}Rh\{^1H\}$ spectrum measured by using the INEPT enhancement method on a concentrated solution shows an out-of-phase doublet with separation of 33 Hz in agreement with the value of $^1J_{RhH}$ obtained by ^1H NMR (Figure 1c).

When a concentrated solution of **1a** and Et_3SiH is photolyzed at 298 K, **2a** is generated as the principal rhodium product; ethane and tetraethylsilane are also produced. Conversely, when **2a** is generated at 213 K, neither hydrosilation products nor ethane are observed but they are obtained when the sample is warmed to 298 K. Vinyltriethylsilane is also produced as a minor product but is formed in more substantial quantities in the presence of excess ethene.

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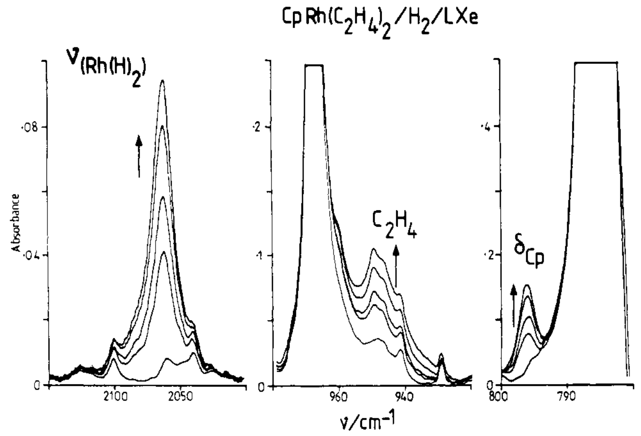

Figure 2. IR spectra showing the formation of **4aH** and free C_2H_4 during the photolysis of 1 in LXe under 10 atm of H_2 at 173 K. The traces were recorded before photolysis and after 90-s, 155-s, 275-s, and 395-s broad-band UV irradiation. The arrows indicate absorptions growing in. Unlabeled bands are due to unreacted **1a**.

Complex **3a** may be *isolated* as a white crystalline solid by photolyzing a dilute benzene solution of **1a** with a 12-fold excess of Et_3SiH at room temperature. The product has been examined by NMR. ^1H, ^{103}Rh, and ^{13}C spectra indicate that **3a** is the dihydride CpRh(H)$_2$(SiEt$_3$)$_2$. For this type of complex there are again two possible types of three-center bonding, involving either [M](Si–H) or [M](H–H) linkages. The hydride resonance appears as a doublet (J_{RhH} = 38.3 Hz) with ^{29}Si satellites. The intensity of the satellites (approximately 9.5% of the overall hydride integration) is consistent with coupling to two $SiEt_3$ groups. The low value of the J_{SiH} (6.8 Hz) argues for a two-bond coupling rather than a three-center [M](Si–H) interaction. The relaxation time, T_1, is long (3 s), indicating the absence of H···H interactions.[12] The $^{103}Rh\{^1H\}$ INEPT spectrum shows an out-of-phase doublet with a chemical shift of δ −1931.3. Since the intensity pattern of the signal for a triplet should be −1,0,+1 with this pulse sequence, the peak separation should be twice $^1J_{RhH}$. The observed separation is 77 Hz compared to the expected value of 2 × 38.3 = 76.6 Hz. The ^{103}Rh resonance is approximately 450 ppm to higher field than the corresponding resonance of **2a**. Nevertheless, the ^{103}Rh chemical shifts of CpRh(alkene)$_2$ and CpRh(diene) complexes span an even larger range, from −348 to −2057 ppm.[13] The Cp resonance appears as a quartet (0.4-Hz splitting) which is consistent with equal coupling to rhodium and two hydridic protons (Figure 1d). Table I also lists partial NMR data for **2b** and **3b** (R = Me).

Photochemical Reaction of CpRh(ethene)$_2$ with Hydrogen/Deuterium in Liquid Xenon. FTIR spectroscopy of a saturated solution of CpRh(C_2H_4)$_2$ (**1a**) in liquid xenon at 173 K under a high H_2 pressure (10 bar) reveals progressive photochemical conversion to dissolved ethene[14] and another product, **4aH**, with a prominent band at 2062 cm^{-1} (see Figure 2 and Table III). In these and subsequent experiments further weak product bands at 2173 and 1990 cm^{-1} were usually generated. They are readily assigned to CpRh(C_2H_4)N_2 and CpRh(C_2H_4)CO formed by photochemical reaction with trace impurities in the xenon.[3] When the experiments were repeated by using D_2 instead of H_2, C_2H_4 was again generated upon photolysis. The bands of the other product, **4aD**, were shifted (Figure 3), with a feature at 1489 cm^{-1} replacing the band at 2062 cm^{-1}.

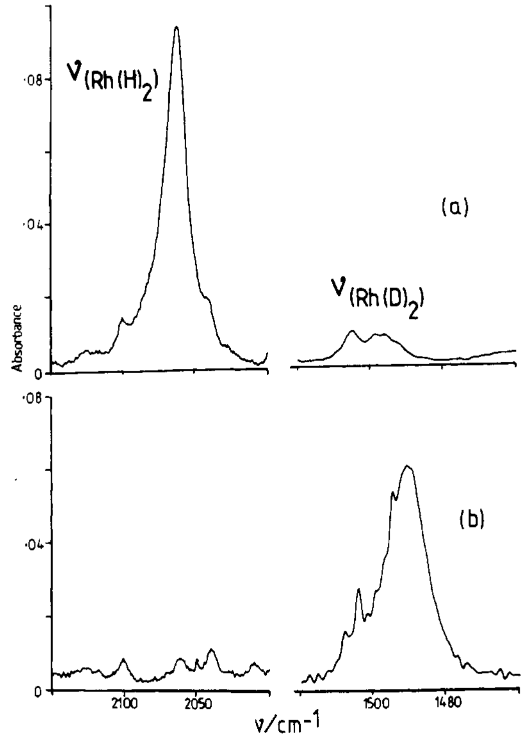

Figure 3. IR spectra showing the ν(Rh(H)$_2$) and ν(Rh(D)$_2$) regions for both **4aH** (a) and **4aD** (b) in LXe at 173 K. Figure 3b is obtained by an interactive computer subtraction of the spectrum of the parent complex **1a**.

Table III. Wavenumbers (cm^{-1}) of the IR Bands of Photolysis Products of the Reaction of 1 with Hydrogen in LXe at 173 K

(C_5H_5)Rh(C_2H_4)$_2$				(C_5D_5)Rh-(C_2H_4)$_2$,[a]		(C_5D_5)Rh-(C_2D_4)$_2$,[b]	
1a + H_2		1a + D_2		1b + H_2		1c + H_2	
3090	C_2H_4	3091	C_2H_4			2321 w	C_2D_4
3006	**4aH**	3061	**4aD**			2187 w	**4cH**
2997	C_2H_4	2993	C_2H_4			2192	C_2D_4
		2977	**4aD**	2975	**4bH**		
2172 w	**5**	2173 w	**5**	2173 w	**5**	2172 w	**5**
		1990 w	**6**	1991 w	**6**		
2062	**4aH**			2062	**4bH**	2063	**4cH**
		1489	**4aD**				
1437	C_2H_4	1435	C_2H_4	1436	C_2H_4	1072 br	C_2D_4
1430	**4aH**	1429 sh	**4aD**	1216 sh	**4bH**	980	**4cH**
1208	**4aH**	1208	**4aD**	1207	**4bH**	948	**4cH**
		1086		1162	**4bH**		
		1044					
		1010					
948 br	C_2H_4	948 br, s	C_2H_4	946 br	C_2H_4	718	C_2D_4
796	**4aH**	794 s	**4aD**	782	**4bH**	782	**4cH**
776	**4aH**			774	**4bH**	755	**4cH**
758	**4aH**			754	**4bH**		
714	**4aH**	718 s	**4aD**				
520		555		418			
400		410		407			

[a] Containing ca. 90% atom D on the ring. [b] D/H approximately 90%.

On replacing **1a** by (η^5-C_5D_5)Rh(C_2H_4)$_2$ (**1b**) and photolyzing for 420 s under a H_2 atmosphere in liquid xenon, we detected free C_2H_4 together with bands corresponding to the deuteriated analogue of **4aH**, assigned as **4bH**

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[12] Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *Ibid.* **1986**, *108*, 2294. Crabtree, R. H.; Lavin, M.; Bonneviot, L. *Ibid.* **1986**, *108*, 4032. Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661.

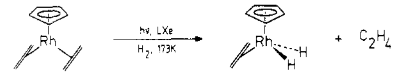
[13] Benn, R.; Rufinska, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861. Maurer, M.; Rieker, S.; Schollbach, M.; Schwenk, A.; Egolf, T.; von Philipsborn, W. *Helv. Chim. Acta* **1982**, 26.

[14] C_2H_4 dissolved directly in liquid xenon absorbs at 3092 m, 2978 m, 1881 w, 1437 m, and 947 s cm^{-1}. All the bands are broadened by rotational effects. Dissolved hydrogen gives broad rotational transitions at 585 cm^{-1}; the corresponding band of D_2 is at 527 cm^{-1}.

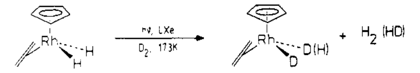
(Table III). The region near 580 cm^{-1} in which ν(CD) modes of the C_5D_5 ring are expected is obscured by the rotational band of dissolved H_2. Hydrogen was then vented and the cell repressurised with D_2 (9.5 bar). Subsequent irradiation (420 s) results in further loss of ethene, loss of the **4bH** product band at 2062 cm^{-1}, and gain of a new band at 1489 cm^{-1}.

The corresponding experiment in which (η^5-C_5D_5)Rh(C_2D_4)$_2$ (**1c**) is photolyzed under a H_2 atmosphere generates product bands due to free C_2D_4 and bands of the deuteriated species **4cH** (Table III). Although one of the bands of **4cH** is almost coincident with a band of C_2H_4, it can be distinguished readily by its sharpness (948 cm^{-1}).

These experiments demonstrate that the photolysis of 1 under hydrogen causes dissociation of ethene. The other product 4 has bands that are consistent with the $\nu(Rh(H)_2)$ (2062 cm^{-1}) and $\nu(Rh(D)_2)$ (1489 cm^{-1}) stretching modes [$\nu((H)_2)/\nu((D)_2)$ = 1.385] of a rhodium dihydride. We also note that the Rh–H stretching frequency of **2a** appears at 2060 cm^{-1} (Nujol mull) in the IR, which is only 2 cm^{-1} lower than the value for **4aH**. The presence of a single product band at 1208 cm^{-1} on photolysis of **1a** and **1b** is characteristic of one coordinated ethene [ν(C=C)–δ(CH_2)] in the photoproduct. This band shifts downward in **4cH** which contains C_2D_4. The intense bands at ca. 795 cm^{-1} of **4aH** and **4aD** are characteristic of a Cp ring δ(CH) mode. Thus the organometallic photoproduct 4 has the vibrational characteristics of a cyclopentadienylmetal hydride ethene complex and may be assigned as CpRh(C_2H_4)(H)$_2$ and its D-labeled counterparts, produced by the oxidative addition of H_2 (or D_2) according to eq 3. The dihydride 4 is stable indefinitely in LXe at 173 K under H_2 pressure. The experiments in which hydrogen gas was replaced by deuterium also demonstrate that the dihydride can be converted photochemically to the dideuteride (eq 4) or possibly the hydride deuteride. Production of CpRh(C_2H_4)HD would not be easily detectable by IR since the spectrum would probably be a superposition of the spectrum of the dihydride **4aH** and the dideuteride **4aD**.[15]



(3)



(4)

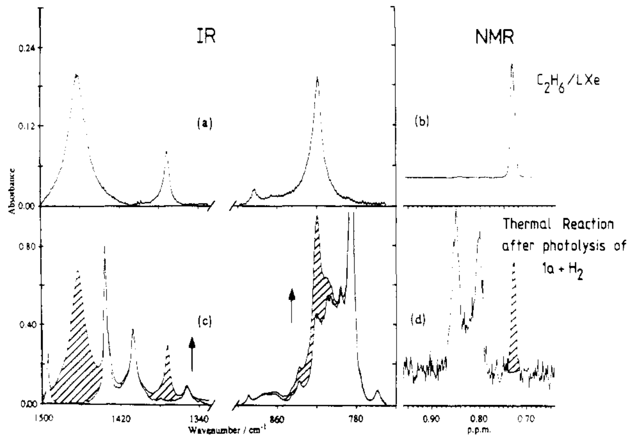


Figure 4. IR and NMR spectra in LXe from different experiments showing the coincidence of absorptions and resonances of an authentic sample of ethane with the thermal product shaded. (a) IR spectrum of an authentic sample of ethane at 183 K. (b) ^{1}H NMR spectrum of ethane at 193 K. (c) IR spectra recorded at 183 K directly after photolysis of **1a** with H_2 and 330 min later. Unshaded bands in the IR are due to **1a** and **4aH**. (d) ^{1}H NMR spectrum recorded 24 h after photolysis at 193 K. The spectrum shows resonances of the thermal product (0.73 ppm) and coordinated ethene in **1a** (0.82 ppm).

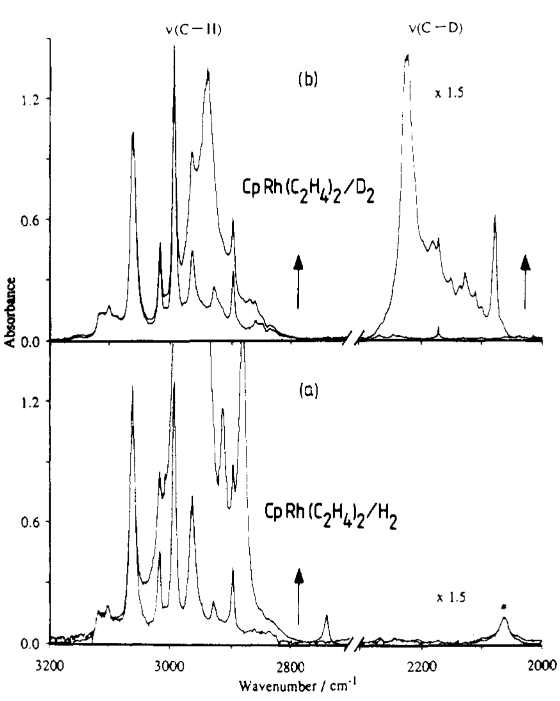

Thermal Reaction following Photolysis

Figure 5. IR spectra in LXe at 173 K showing the isotopic shift of deuteriated hydrogenation products. (a) The growth of bands due to ethane in the C–H stretching region arising from thermal reaction following photolysis **1a** with H_2. The asterisk (*) indicates the Rh–(H)$_2$ stretch of **4aH**. (b) Spectrum obtained following similar thermal reaction after photolysis under D_2. Note the absence of the hydride stretch and the presence of both ν(CH) and ν(CD) modes of isotopically enriched ethane.

Thermal Reactions of the Photoproducts of 1 with Hydrogen/Deuterium. When a solution of **1a** in LXe under 10 bar of H_2 was photolyzed, to generate **4a** and ethene, and then left in the dark for 17 h, growth of a new species in solution is observed. This product shows bands in the C–H stretching region and elsewhere of absorbance $\gg$2 (Table IV) while the $\nu(Rh(H)_2)$ band of **4a** is unaffected (Figures 4 and 5). Similar experiments with different isotopic combinations show that this thermal product has intense bands in both the ν(C–H) and the ν(C–D) regions when H_2 was replaced by D_2 or when coordinated C_2H_4 was replaced by C_2D_4 (Table IV and Figure 5). The thermal product of these reactions was shown to be ethane and its isotopically substituted counterparts ($C_2D_nH_{6-n}$) by comparison with an authentic sample of C_2H_6 dissolved in LXe. No further ethene production is observed. As a control experiment we left a solution of **1a** in LXe under 10 bar of H_2 to stand without any photolysis. No ethane or hydride is generated.

We have examined the photochemical reaction of CpRh(ethene)$_2$ with hydrogen in three further ways. When photolyzed in an argon matrix in the presence of 10% H_2, no products were observed other than those found in a pure argon matrix.[4] When a solution of **1a** in $C_6D_5CD_3$ was

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[15] Girling, R.; Grebenik, P.; Perutz, R. N. *Inorg. Chem.* **1986**, *25*, 31. The symmetric and antisymmetric stretching modes of metal dihydrides are virtually coincident, implying that the stretch–stretch interaction force constant is very low. In addition, the coupling between the ν(MH) and ν(MD) modes (both of which belong to the same representation) is very weak in such complexes. As a result metal hydride deuteride complexes have their fundamentals almost coincident with the corresponding $M(H)_2$ and $M(D)_2$ molecules.

Table IV. Wavenumbers (cm^{-1}) of IR Bands of Products of Thermal Reactions of Photoproducts of 1 with H_2 in LXe at 173 K[a]

after photolysis				
1a + H_2	1a + D_2	1b + D_2	1c + H_2	C_2H_6[b]
2978				2974
		2960	2968	
2939	2940	2938	2938	2940
2915				2913
2884				
2881			2880	2880
2738				2738
	2223	2222	2216	
	2182	2181		
			2175	
			2150	
	2137	2139	2138	
	2128	2129	2123	
	2110	2110		
	2078	2078		
1463			1462	1463
			1383	
1372			1372	1372
			1296	
820			817	820

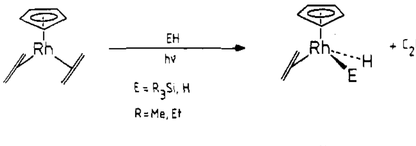
[a] Only intense bands are listed. [b] Authentic sample of ethane in LXe at 183 K.

photolyzed in the presence of 1 bar of H_2 at 213 K, a red-brown precipitate formed, as is observed when no substrate is present and ethene and ethane were generated.[9] When a saturated solution of **1a** in LXe at 180 K was photolyzed in an NMR tube with 2 bar of H_2, some precipitation took place. The ^1H NMR spectra recorded showed steady growth of ethane subsequent to photolysis and some ethene (C_2H_4:C_2H_6 = 1:3) relative to dissolved **1a** (Figure 4).[9] A signal due to **4a** was not detected in these experiments.

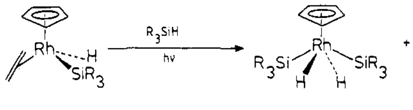
If we make the qualitative assumption that the coordinated ethene bands at around 1200 cm^{-1} have similar extinction coefficients, then the ratio of [**1a**]:[**4a**] observed in the IR experiments was of the order 20:1. Considering the signal-to-noise ratios achieved in the ^1H NMR experiments, we can state that the ratio of [**1a**]:[**4a**] must exceed 150:1. However, the NMR and IR studies differ in several respects. In the NMR experiments the H_2 over pressure was considerably lower (2 bar instead of 10 bar), the solution may have warmed during transfer to the probe and it was not stirred. Decomposition products were also observed. Any of these differences could account for the failure to dectect **4**.

Discussion

The experiments described above establish photoinduced oxidative addition reactions of CpRh(C_2H_4)$_2$ (eq 5). When E = SiR_3, a further ethene ligand may dissociate yielding the first $CpRh^V$ complexes (eq 6).



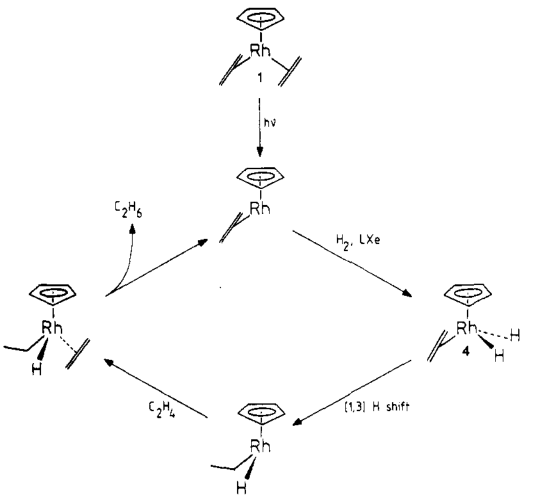
(5)



(6)

There is strong evidence in each of the cases **2**, **3**, and **4** against three-center [Rh](E-H) (E = H, C, Si) interactions. There are at least two modes of 3-center bonding that might have been expected for **2** and **3** involving [M](H-H), [M](C-H), or [M](Si-H) links. Three-center bonding, [M](H-H) and [M](Si-H), has been confined so far to d^6 metal fragments with the notable exception of the carbonyl nitrosyl dihydrogen complexes.[16a] Relevant examples include (CO)$_4$Cr(tr-cyo)(H_2) (tr-cyo = *trans*-cyclooctene)[16b] and Cp*(CO)$_2$Mn-H···SiHPh$_2$.[17] However, agostic [M]-C-H interactions also occur with d^8 fragments.[11] In the present case, the relevant fragments for **2** and **4** have d^8 configurations, whereas the fragment for **3** has a d^6 configuration.

Scheme I



According to the Chalk-Harrod mechanism of hydrosilation, the ethene trialkylsilyl hydride complex **2** is expected to eliminate ethyltrialkylsilane. Indeed it is a surprise to find that it is an isolable volatile oil. Nevertheless both ethane and tetraethylsilane are produced during its synthesis at room temperature. These materials are not obtained when the synthesis is carried out at 213 K, as is consistent with a thermally controlled reaction of **2a**. The properties of **2** as a hydrosilation catalyst will be discussed in detail elsewhere.

The dihydride complex **4** is expected to be capable of eliminating ethane via a [1,3] hydrogen shift, ethene attack, and reductive elimination (Scheme I). The first step in such a mechanism, reaction of **4** with ethene to form CpRh(C_2H_4)(C_2H_5)(H), has precedent from the reactions of (η^5-C_5R_5)$_2$Nb(C_2H_4)H with C_2H_4 or with other donor ligands.[18] We have indeed demonstrated thermal production of ethane following generation of **4** in LXe. However, the intensity of **4** remains unchanged while ethane is released. In the NMR experiments in LXe ethane is also released, this time together with ethene, yet the hydride **4** could not be detected (see results). The production of ethane in both the NMR tube and the IR cell indicates that this reaction is independent of the materials used in constructing the cell. However, we are unable to decide conclusively at this stage whether **4** is the source of ethane or whether it is formed from another photoproduct. In further experiments, we will examine the reactivity of **4** toward C_2H_4 and CO.

Complexes of Rh^V are extremely rare, the best characterized being Cp*Rh(H)$_2$(SiR$_3$)$_2$.[19] The similarity of the

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[16] (a) Gadd, G. E.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2547. (b) Jackson, S. A.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J.; Burdett, J. K.; Grevels, F.-W. *J. Chem. Soc., Chem. Commun.* **1987**, 678.

[17] Schubert, U.; Ackermann, K.; Worle, B. *J. Am. Chem. Soc.* **1982**, *104*, 7378. Schubert, U.; Scholz, G.; Muller, J.; Ackermann, K.; Worle, B. *J. Organomet. Chem.* **1986**, *306*, 303.

[18] Doherty, M. N.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

NMR parameters suggest that **3** has a transoid structure too. Ruiz et al. have recently reported the synthesis of the tin analogues $Cp^*Rh(H)_2(SnR_3)_2$ and the silyl trihydride $Cp^*Rh(H)_3(SiR_3)$.[20,21] The stability of the Cp analogue **3** makes it evident that the higher oxidation state can be achieved without the more strongly donating (η^5-C_5Me_5) ligands.[22] Schubert et al. have demonstrated for a series of Mn complexes that oxidative addition can be favored either by increasing the electron density available to the metal center by the use of electron-donating ligands or by incorporating electron-withdrawing groups on the silane.[17] Therefore, should the stability of the higher oxidation state be marginal, we might expect to observe three-center [M](Si–H) bonding, but this is absent. One mechanism for preserving electroneutrality in such Rh^V complexes has been proposed by Rabaa et al. in the context of oxidative addition of silanes to other d^6 and d^8 fragments. They find theoretical evidence that a negative charge on the hydridic hydrogen is partially balanced by a positive charge on the silyl group.[23] If this principle is applicable more generally, the way should be open to synthesizing a variety of $CpRh^V$(silyl) hydrides and perhaps, even, alkyl hydrides. Moreover, the presence of equilibria between Cp^*Rh^{III} and Cp^*Rh^V complexes suggests that mechanisms involving Rh^V intermediates should be considered in oxidative addition mechanisms, e.g. for C–H or Si–H activations both with CpRh and Cp*Rh complexes.

Conclusions

We have demonstrated that **1** undergoes photochemically initiated oxidative addition of both a silicon hydride producing **2** and hydrogen producing **4**. We have isolated **2**, an intermediate of the type postulated by Chalk and Harrod in hydrosilation. A Rh^V species, **3**, has also been isolated by the photochemical oxidative addition of a second molecule of Et_3SiH to **2**. The stability of Rh^V complexes[9] of the type $Cp^*Rh^V(SiR_3)_2(H)_2$ and the Ir^V complexes,[21] such as $Cp^*Ir(CH_3)_4$, has been previously attributed to the special properties of the Cp* ligand.[22] Our experiments show that this ligand is not necessary for isolation of Rh^V complexes. We have also found evidence that **2** and **4** undergo thermal rearrangement to eliminate the saturated products ethyltrialkylsilane and ethane.

Acknowledgment. We are grateful to the SERC NMR service (Edinburgh), I. Marshall (Nottingham), and Dr. B. Mann (Sheffield) for providing high-quality NMR spectra and J. M. Whalley for technical assistance. We also acknowledge the support of SERC, The Royal Society, the EEC, Nicolet Instruments Ltd, Dow Corning, ICI New Science Group, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also appreciate helpful discussions with Dr. M. A. Healy and Prof. P. Maitlis and Prof. J. J. Turner.

Registry No. **1a**, 12211-95-9; **1b**, 112680-96-3; **1c**, 112680-97-4; **2a**, 102744-67-2; **2b**, 102744-69-4; **3a**, 102744-68-3; **3b**, 102986-79-8; **4aH**, 112680-97-4; **4aD**, 113748-33-7; **4bH**, 113748-34-8; **4cH**, 113748-35-9; Et_3SiH, 617-86-7; Me_3SiH, 993-07-7.

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(19) Fernandez, M. J.; Bailey, P. M.; Bentz, P. O.; Ricci, J. S.; Koetzle, T.; Maitlis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 5458.

(20) Ruiz, J.; Spencer, C. M.; Mann, B. E.; Taylor, B. F.; Maitlis, P. M. *J. Organomet. Chem.* **1987**, *325*, 253.

(21) Ruiz, J.; Mann, B. E.; Spencer, C. M.; Taylor, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 1963.

(22) Isobe, K.; Vazquez de Migel, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 929. Dudeney, N.; Kirchner, O. N.; Green, J. C.; Maitlis, P. M. *Ibid.* **1984**, 1877.

(23) Rabaa, H.; Saillard, J.-Y.; Schubert, U. *J. Organomet. Chem.* **1987**, *330*, 397.

Syntheses and Reactions of η^5-(Dimethylboryl)cyclopentadienyl Cobalt and Rhodium Derivatives. Site-Specific Binding of Unsaturated Amines

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Syntheses and reactions of (η^5-(py·Me_2B)C_5H_4]ML_2 complexes (M = Rh or Co; py = pyridine; C_5H_4 = η^5-cyclopentadienyl) are described. Treatment of $[(CO)_2RhCl]_2$ with $C_5H_5(BMe_2{\cdot}py)$ or $(Me_3Si)C_5H_4(BMe_2{\cdot}py)$ affords [η^5-(py·Me_2B)C_5H_4]$Rh(CO)_2$ (**2**) in 24 and 60% yields, respectively. Reaction of $(py{\cdot}BMe_2)C_5H_5$ with $Co_2(CO)_8$ provides [η^5-(py·Me_2B)C_5H_4]$Co(CO)_2$ (**4**) in 40% yield. Substitution of **2** with triphenylphosphine affords [η^5-(py·Me_2B)C_5H_4]$Rh(CO)(PPh_3)$. Complex **4** is converted sequentially to [η^5-(py·Me_2B)C_5H_4]$Co(CO)I_2$ and [η^5-(py·Me_2B)C_5H_4]$Co(PPh_3)I_2$ in high yield. Pyridine exchanges at the boron centers of both **2** and **4** are rapid on NMR time scales at ambient temperatures. The cooperative binding properties of the transition-metal and boron centers are described in the context of chelations of dimethylallylamine ($Me_2NCH_2CH{=}CH_2$) to form [η^5-(Me_2B)C_5H_4]Co(η^3-$Me_2NCH_2CH{=}CH_2$)(CO) and [η^5-(Me_2B)C_5H_4]Co(η^3-$Me_2NCH_2CH{=}CH_2$)(PPh_3) (**9**). The corresponding rhodium chelates cannot be prepared. Chelate **9** undergoes a photochemically mediated reaction at elevated temperatures with diphenylacetylene to afford a chelated butadiene complex, [η^5-(Me_2B)C_5H_4]Co[η^5-$R_2NCH_2CH{=}CHC(Ph){=}C(Ph)H$].

Introduction

We recently began exploring new strategies for binding polyfunctional organic substrates within transition-metal coordination spheres. Our earliest efforts focussing on the use of phosphinite ester linkages to bind unsaturated alcohols under aprotic conditions met with only limited success. Despite the development of mild and highly stereoselective syntheses of phosphinite ester chelates (cf.