group 14 Sn or Pb atom increases the possibility of the transmetalation reaction as noted by the increasing amount of such reactions in the order EPh$_3$/LDA < EMe$_3$/LDA < EMe$_3$(EPh$_3$)/*n*-BuLi.

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Registry No. (η^5-C$_5$H$_4$GeMe$_3$)Fe(CO)$_2$Me, 118318-54-0; (η^5-C$_5$H$_4$GeMe$_3$)Mo(CO)$_3$Me, 118318-55-1; (η^5-C$_5$H$_4$GeMe$_3$)W(CO)$_3$Me, 118318-56-2; (η^5-C$_5$H$_4$GePh$_3$)Fe(CO)$_2$Me, 118318-57-3; (η^5-C$_5$H$_4$SnMe$_3$)Fe(CO)$_2$Me, 118318-58-4; (η^5-C$_5$H$_4$SnPh$_3$)Fe(CO)$_2$Me, 118318-59-5; (η^5-C$_5$H$_4$SnPh$_3$)Mo(CO)$_3$Me, 118334-33-1; (η^5-C$_5$H$_4$SnPh$_3$)W(CO)$_3$Me, 118318-60-8; (η^5-C$_5$H$_4$PbPh$_3$)Mo(CO)$_3$Me, 118318-61-9; (η^5-C$_5$H$_4$PbPh$_3$)W(CO)$_3$Me, 118318-62-0; (η^5-C$_5$H$_4$SnMe$_3$)Mo(CO)$_3$Me, 118318-63-1; (η^5-C$_5$H$_4$PbMe$_3$)Mo(CO)$_3$Me, 118318-64-2; (η^5-C$_5$H$_4$SnMe$_3$)W(CO)$_3$Me, 118318-65-3; (η^5-C$_5$H$_4$PbMe$_3$)W(CO)$_3$Me, 118318-66-4; (η^5-C$_5$H$_5$)Mo(CO)$_3$Me, 12082-25-6; (η^5-C$_5$H$_5$)W(CO)$_3$Me, 12082-27-8; (η^5-C$_5$H$_5$)Fe(CO)$_2$Me, 12080-06-7; (η^5-C$_5$H$_5$)Fe(CO)$_2$GeMe$_3$, 32054-63-0; (η^5-C$_5$H$_5$)Mo(CO)$_3$GeMe$_3$, 33306-91-1; (η^5-C$_5$H$_5$)W(CO)$_3$GeMe$_3$, 33306-93-3; (η^5-C$_5$H$_5$)Fe(CO)$_2$GePh$_3$, 32824-70-7; (η^5-C$_5$H$_5$)Fe(CO)$_2$SnMe$_3$, 12084-36-5; (η^5-C$_5$H$_5$)Fe(CO$_2$)SnPh$_3$, 12132-09-1; (η^5-C$_5$H$_5$)Mo(CO)$_3$SnPh$_3$, 12100-85-5; (η^5-C$_5$H$_5$)W(CO)$_3$SnPh$_3$, 12100-87-7; (η^5-C$_5$H$_5$)Mo(CO)$_3$PbPh$_3$, 12100-86-6; (η^5-C$_5$H$_5$)W(CO)$_2$PbPh$_3$, 12100-88-8; (η^5-C$_5$H$_5$)Mo(CO)$_3$SnMe$_3$, 12214-92-5; (η^5-C$_5$H$_5$)Mo(CO)$_3$PbMe$_3$, 12093-28-6; (η^5-C$_5$H$_5$)W(CO)$_3$SnMe$_3$, 12093-29-7; (η^5-C$_5$H$_5$)W(CO)$_3$PbMe$_3$, 79110-54-6; (η^5-C$_5$H$_5$)Fe(CO)$_2$PbPh$_3$, 12132-08-0.

Photochemical Substitution of Ethene and H/D Exchange in (η^5-Cyclopentadienyl)bis(ethene)rhodium

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Photolysis of CpRh(C$_2$H$_4$)$_2$ (Cp = η^5-C$_5$H$_5$; 1) in benzene or toluene solution in the presence of substrates, L, leads to the formation of substitution products CpRh(C$_2$H$_4$)L and CpRhL$_2$. When L = Me$_2$SO and CH$_3$CN, only monosubstituted products are observed, but for other ligands (Ph$_3$P, CO, Bu^{t}NC, alkenes) both mono- and disubstituted products are formed. With 1,3-butadiene as the entering ligand, CpRh(C$_2$H$_4$)(η^2-C$_4$H$_6$) is formed prior to CpRh(η^4-C$_4$H$_6$). Conversion of the η^2-butadiene to the η^4-butadiene complex can be achieved photochemically or thermally. When CO or Bu^{t}NC are the substrates, dinuclear complexes (CpRhL)$_2$(μ-L) are formed in addition to substitution products. The photolysis method effects (a) the introduction of ligands that otherwise substitute only above 100 °C (Ph$_3$P, Me$_2$SO, alkenes), (b) the formation of labile complexes which cannot be formed by thermal methods (cyclohexene, CH$_3$CN, η^2-butadiene), and (c) the formation of the new dinuclear complex [CpRh(Bu^{t}NC)]$_2$(μ-Bu^{t}NC). For the labile complexes photolysis at low temperature is employed, since the products decompose at or below room temperature. Evidence is presented for the formation of CpRh(C$_2$H$_4$)(η^2-toluene) on photolysis at 193 K in toluene solution. An alternative route to substitution products involves photochemical conversion of 1 in CH$_3$CN to CpRh(C$_2$H$_4$)(CH$_3$CN) at 253 K followed by addition of ligand. The photochemical reactions are consistent with the mechanism deduced from earlier flash photolysis and matrix isolation experiments in which CpRh(C$_2$H$_4$) and CpRh(C$_2$H$_4$)S (S = solvent) act as intermediates. Photolysis with a C$_2$D$_4$ atmosphere demonstrates the existence of an additional pathway which causes H/D exchange within the ethene ligand. This pathway probably involves a vinyl hydride isomer of 1 as an unstable intermediate. There is no evidence for H/D exchange with the solvent. The complexes CpRh(C$_2$H$_4$)L (L = Me$_2$SO, CH$_3$CN, CH$_2$=CHSiMe$_3$) have a substantially higher barrier to rotation about the rhodium–ethene bond than has been reported for other complexes of this type. The dinuclear photoproduct [CpRh(Bu^{t}NC)]$_2$(μ-Bu^{t}NC) exhibits two fluxional processes, first interconversion of two conformers by internal rotation about the CN bond of the bridging isonitrile ($\Delta G^\ddagger = 45.7 \pm 1.6$ kJ mol^{-1}) and second exchange of bridging and terminal isonitriles ($\Delta G^\ddagger = 61.8 \pm 0.8$ kJ mol^{-1}).

Introduction

In a pioneering series of studies, Cramer showed that CpRh(C$_2$H$_4$)$_2$ (Cp = η^5-C$_5$H$_5$; 1), an 18-electron complex, is inert to substitution by alkenes (no exchange with ethene after 5 h at 100 °C), whereas (acac)Rh(C$_2$H$_4$)$_2$ (acac = pentan-2,4-dionato) with a 16-electron configuration is substitution-labile (half-life at −50 °C for exchange of ethene, 10^{-2} s).[2] Closer examination of the rates of reaction with donor ligands shows that the reactions fall into several distinct groups. Alkenes and dienes, Ph$_3$E (E = P, As, Sb), and AsEt$_3$ displace ethene at about 115–130 °C; P(OR)$_3$ (R = Et, Ph, *o*-tolyl) and PR$'_3$ (R$'$ = Et, *n*-Bu) react rapidly at 100 °C; PMe$_3$ and phosphaalkynes react at room temperature; PF$_3$, SO$_2$, and C$_2$(CN)$_4$ react well below room temperature.[3,4] It was demonstrated from the independence of the rate on the concentration of the entering ligand that the slowest group reacted by a mechanism involving dissociation of ethene from 1. This dissociation has an activation energy of 130 kJ mol^{-1} in the gas phase. In contrast, the rates of the faster reactions were ligand dependent. At the most extreme, SO$_2$ and PF$_3$ were argued to react by an electrophilic mechanism, in which the rhodium complex acted as the nucleophile.

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In a further series of experiments Seiwell described the incorporation of deuterium into 1 on heating in C_6D_6 or other deuterated arenes at 130 °C.[5] The exchange was completely suppressed by addition of excess ethene. Significantly, these exchange reactions induced some decomposition of 1.

Photochemical syntheses of organometallics are becoming increasingly important among complexes containing no carbonyl ligands; notable examples include reductive elimination of H_2,[6,7] replacement of arenes,[8] and α-elimination from alkyls.[9] The possibility of displacing strongly bound alkenes by photolysis has been exploited, for instance, in the case of $Cp_2W(C_2H_4)$[6] and in Pt^{II} chemistry.[10] Other photochemical reactions of alkene complexes include the recently discovered isomerization to vinyl hydride complexes[11,12] and the coupling of two ethene groups to form butene and cyclobutane.[13]

Following our recent discovery of the photosensitivity of 1,[14] we have undertaken detailed studies of its reactions using preparative photochemical methods in solution in conjunction with NMR spectroscopy, photolysis in low-temperature matrices,[15] photolysis in liquid xenon solution,[16] and laser flash photolysis in solution.[17] In inert matrices we observed reversible photochemical displacement of ethene to form $CpRh(C_2H_4)$, but substitution occurred in matrices containing CO or N_2.[14,15] The resulting dinitrogen complex was also observed on photolysis in liquid xenon containing dissolved nitrogen (eq 1).[16]

$$CpRh(C_2H_4)_2 \rightarrow CpRh(C_2H_4)L + C_2H_4 \qquad (1)$$

$$L = CO, N_2$$

Photoinduced oxidative addition (eq 2) was observed with such substrates as H_2 in liquid xenon or with trialkylsilanes in arene solvents.[18] The reaction with trialkylsilanes (eq 2 and 3) could be controlled to yield either

$$CpRh(C_2H_4)_2 \rightarrow CpRh(C_2H_4)(E)H + C_2H_4 \qquad (2)$$

$$E = H, SiR_3$$

$$CpRh(C_2H_4)(SiR_3)H \rightarrow CpRh(SiR_3)_2(H)_2 \qquad (3)$$

$$R = Me, Et$$

$CpRh(C_2H_4)(SiR_3)H$ or $CpRh(SiR_3)_2H_2$ as the major product. Maitlis et al have carried out analogous reactions on $Cp^*Rh(C_2H_4)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with R_3SiH and R_3SnH.[19,20]

In the present study we show that photochemical substitution of 1 provides a viable route to a number of $CpRh(C_2H_4)L$ and $CpRhL_2$ complexes, including some which could not be accessed by the conventional methods, viz., the reaction of dimers of the type $[L(C_2H_4)RhCl]_2$ or $(L_2RhCl)_2$ with NaCp or TlCp and the reaction of $(acac)RhL_2$ with LiCp.[21] In our studies of the photochemical reactivity of 1 toward ligands, we have concentrated on (i) those ligands belonging to the least reactive class in their thermal reactivity toward 1 (Me_2SO, CO, Ph_3P, Bu^tNC, alkenes, 1,3-butadiene) and (ii) labile ligands which can be introduced photochemically at low temperature but which cannot be introduced by thermal routes (e.g. some alkenes, CH_3CN). The CH_3CN complex may itself be used as a labile intermediate to synthesize $CpRh(C_2H_4)L$ (eq 4 and 5). This corresponds to the

$$CpRh(C_2H_4)_2 \xrightarrow[CH_3CN]{h\nu} CpRh(C_2H_4)CH_3CN + C_2H_4 \qquad (4)$$

$$CpRh(C_2H_4)CH_3CN \xrightarrow{L} CpRh(C_2H_4)L + CH_3CN \qquad (5)$$

standard procedures for substituting metal carbonyls via THF complexes followed by reaction with stronger ligands.[22] Most of these reactions have been monitored by NMR spectroscopy in situ, but several reactions have been scaled up. Infrared spectroscopy and UV spectroscopy prove useful occasionally, but the UV spectra of precursor and products are too similar to provide an effective means of following the reaction. (The UV/vis spectrum of 1 has been reported previously.[15,18]) We include some estimates of barriers to internal rotation of ethene ligands. We also report tests of H/D exchange using photochemical instead of thermal induction. Some of these results have been reported in a preliminary communication.[14]

Experimental Section

General Comments. Reactions were carried out under standard Schlenk conditions by using solvents distilled from sodium benzophenone ketyl. Sources of chemicals were as follows: TlCp, cyclohexene, acetonitrile, 1-pentene, and deuteriated solvents from Aldrich; *tert*-butyl isocyanide, vinyltrimethylsilane, and butadiene from Fluka; ethene from Mattheson, C_2D_4 from MSD (99 atom %). Rhodium trichloride was the gift of Dow Corning.

Photolysis of solutions sealed in vacuo in 5-mm NMR tubes (Pyrex, $\lambda > 285$ nm) was carried out with a water-filtered focussed Philips HPK 125 W medium-pressure Hg arc. When low temperatures were required, the tubes were placed in a Dewar of cooled methanol with an unsilvered stripe. For larger scale work the solution was placed in a photochemical reactor (volume 15 cm^3) with Schlenk connections, which fitted like a sleeve over the Pyrex cooling jacket of a standard Applied Photophysics reactor. This reactor could also be used with a more conventional sample

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tube (volume 80 cm^3) fitted with Schlenk connections.

NMR spectra were recorded on Bruker WP80, AM360, AM400, and MSL300 spectrometers. ^1H spectra were referenced to the peaks of residual protio solvent: benzene, δ 7.15; toluene, δ 2.10; acetonitrile, δ 2.0. ^{13}C spectra were referenced to solvent peaks: benzene, δ 128.0; toluene, δ 21.3; acetonitrile, δ 0.3. CH, CH_2, and CH_3 groups were distinguished by standard J-modulation, INEPT or DEPT pulse sequences.[23] ^{29}Si spectra were recorded with inverse-gated decoupling and referenced to external TMS. IR spectra were recorded on a Perkin-Elmer 580 grating spectrometer or a Mattson Sirius FTIR spectrometer. UV spectra were recorded at low temperature on a Perkin-Elmer Lambda 7G spectrometer with the aid of a cuvette cooled by gaseous nitrogen and held in a vacuum jacket fitted with quartz windows. Its temperature was controlled by a JEOL controller. Mass spectra were recorded on a Kratos MS3074 spectrometer. Microanalyses were performed by Butterworths Laboratories.

$CpRh(C_2H_4)_2$. $RhCl_3$ was converted to $[Rh(C_2H_4)_2Cl]_2$ by standard methods.[24] This was reacted with TlCp rather than the more usual NaCp (compare ref 21c). The resulting suspension was eluted through an alumina column with hexane. After the resulting yellow solution was pumped to dryness, the product was sublimed at 30 °C and 3×10^{-4} mbar onto an ice-cooled finger. This method allowed us to increase the yield to over 80%. NMR data of **1** are included in Table I for reference.

In a typical run for NMR spectroscopy, 30 mg of **1** was dissolved in dry, degassed benzene-d_6 or toluene-d_8, to which was added a 3- to 10-fold excess of ligand. The tube was sealed and photolyzed for 3–6 h. In one case (see below) the ethene was pumped away periodically in order to obtain higher conversion.

$CpRh(C_2H_4)(Me_2SO)$. **1** (0.2 g, 0.9 mmol) was dissolved in 80 cm^3 of toluene (AR grade) with 65 μL (0.9 mmol) of Me_2SO and irradiated in a Pyrex photochemical reactor for 240 min. After the mixture was pumped to dryness, the product **2** was recrystallized twice from toluene as long pale brown needles. IR (Nujol, cm^{-1}): 1315 (w), 1177 (m), 1173 (m), 1093 (s), 1080 (sh), 913 (m), 790 (m), 687 (m), 440 (m). Anal. Found (Calcd) C, 39.58 (39.42); H, 5.57 (5.47). Mass spectrum (*m/z*, relative intensity): 274 (25%, M^+), 246 (79%), 231 (43%), 168 (100%).

$CpRh(C_2H_4)(CH_3CN)$. **1** (0.14 g, 0.6 mmol) was photolyzed in 6 cm^3 of CH_3CN at about −20 °C in vacuo for 20 h. An intense red color develops under these conditions, but there is no precipitation if the sample is kept cold. Displacement reactions are carried out by warming these air-sensitive solutions to room temperature and adding ligand. After 30 min the sample is pumped down and redissolved in toluene-d_8 for NMR spectroscopy.

$CpRh(C_2H_4)(Bu^tNC)$. $[RhCl(C_2H_4)_2]_2$ (0.2 g, 0.5 mmol) was stirred in 20 cm^3 of THF; a solution of Bu^tNC (0.1 cm^3, 0.9 mmol) dissolved in 100 cm^3 of THF was added to the suspension. After the resultant dark solution had been stirred for 30 min, TlCp (0.27 g, 1.0 mmol) was added and the suspension was stirred for 30 min. The mixture was transferred to a short alumina column and eluted with THF to remove excess TlCp. An NMR spectrum obtained from this fraction before further purification shows that 93% of the rhodium-containing material is $CpRh(C_2H_4)(Bu^tNC)$. The solution was pumped to dryness and purified by fractional sublimation. Sublimation at room temperature and 10^{-3} mbar onto an ice-cooled finger for 30 min removes any of complex **1**. The residue was then sublimed again at 42 °C onto a cold finger at 77 K, yielding the desired product which is purified by resublimation at 30 °C. The resulting yellow air-sensitive solid consisted of $CpRh(C_2H_4)(Bu^tNC)$ in >99% purity according to ^1H NMR. Infrared (hexane, cm^{-1}): 2104, 2067. Infrared (Nujol, cm^{-1}): 2106 (b, s), 2065 (b, s), 1940 (w), 1256 (s), 1210 (s), 1166 (s), 1092 (b, s), 1015 (b, s), 792 (b, s), 773 (s) (abbreviations: s, strong; w, weak; b, broad). Anal. Found (Calcd): C, 51.82 (51.63); H, 6.48 (6.50); N, 5.28 (5.02). Mass spectrum (*m/z*): 279 (M^+, 17%), 251 ($M^+ - C_2H_4$, 24%), 195 ($CpRhH(CN)^+$, 100%), 168 ($CpRh^+$, 74%).

$[CpRh(Bu^tNC)]_2(\mu\text{-}Bu^tNC)$ and $CpRh(Bu^tNC)_2$. **1** (0.12 g, 0.54 mmol) was dissolved in 15 cm^3 of hexane with 160 μL (5.2 mmol) of Bu^tNC in the small photochemical reactor and photolyzed for 7 h. The solution was then transferred onto a 20-cm long alumina column. The column was eluted with toluene to remove mononuclear rhodium complexes and then with Et_2O. The yellow toluene fraction was collected and pumped to dryness. This crude product contained about 90% $CpRh(Bu^tNC)_2$ with the remaining 10% present as **1** and **7**. These impurities were removed by sublimation at 35 °C, yielding red $CpRh(Bu^tNC)_2$, (**8**). The red fraction from diethyl ether was collected and pumped to dryness. The resulting red solid was found to be $[CpRh(Bu^tNC)]_2(\mu\text{-}Bu^tNC)$ (**9**) with a purity >97% (by NMR). Infrared of **8** (hexane, cm^{-1}): 2108, 2073, 1982. Mass spectrum of **8** (*m/z*): 334 (M^+, 30%), 278 ($M^+ - C_4H_8$, 15%), 222 ($M^+ - C_8H_{16}$, 100%), 195 ($CpRh(H)CN^+$, 61%), 168 ($CpRh^+$, 20%). Infrared of **9** (hexane, cm^{-1}): 2106, 2064, 1970 (br sh), 1739, 1714. Mass spectrum of **9** (*m/z*): 585 (M^+, 16%), 502 ($M^+ - Bu^tNC$, 3%), 419 ($M^+ - (Bu^tNC)_2$, 5%), 334 ($CpRh(Bu^tNC)_2^+$, 12%), 234 (12%), 233 (82%), 222 (52%), 195 ($CpRhH(CN)^+$, 39%), 168 ($CpRh^+$, 27%).

$CpRh(C_2H_4)(CH_2{=}CHSiEt_3)$, Route via Reaction of 1 with Et_3SiH. **1** (0.2 g, 0.9 mmol) and 0.6 cm^3 of Et_3SiH were dissolved in 80 cm^3 of toluene in the large photochemical reactor. The solution was photolyzed for 1 h while ethene was bubbled through it. The solution was drained into a Schlenk tube and pumped to dryness. Residual starting material was sublimed out at room temperature. The residue was dissolved in toluene, transferred onto an alumina column, and eluted with toluene; the yellow fraction was collected. The solvent was removed in vacuo yielding a yellow oil containing 80% $CpRh(C_2H_4)(CH_2{=}CHSiEt_3)$ (**12**) and 20% **1**.

Reaction of $[(C_2H_4)_2RhCl]_2$ with $CH_2{=}CHSiMe_3$ and TlCp. The above dimer (0.05 g, 0.13 mmol) was stirred with 0.05 g (0.5 mmol) of vinyltrimethylsilane in 20 cm^3 of THF for 18 h. Thallium cyclopentadienide (0.7 g, 2.6 mmol) was added, and the resulting suspension was stirred for 30 min. After elution through a short alumina column with THF, the yellow fraction was collected and the solvent removed in vacuo. The resulting yellow oil contained 51% **1**, 29% $CpRh(C_2H_4)(CH_2{=}CHSiMe_3)$ (**10**), and 17% $CpRh(CH_2{=}CHSiMe_3)_2$ (**11**) by NMR integration.

$CpRh(CH_2{=}CHSiMe_3)_2$ (11). **1** (30 mg, 0.13 mmol) and $CH_2{=}CHSiMe_3$ (15 mg, 0.14 mmol) were dissolved in 0.4 cm^3 toluene in a 5-mm NMR tube. The tube was sealed and photolyzed for 2 h, by which time a photostationary state had been reached. At this stage the major product was $CpRh(C_2H_4)(CH_2{=}CHSiMe_3)$ (**11**). The tube was opened under argon and more $CH_2{=}CHSiMe_3$ added, degassed, and resealed. Photolysis was resumed; after 2 h a new photostationary state was reached. After this process had been repeated twice more, NMR indicated that conversion to **11** exceeded 95%. The tube was opened and the solution transferred to a 10-cm long alumina column, which was eluted with hexane. The resulting yellow fraction was collected and concentrated. A fine yellow powder crystallized out at 178 K. NMR analysis showed that this material contained $CpRh(CH_2{=}CHSiMe_3)_2$ (**11**) in >99% purity. Mass spectrum (*m/z*): 368 (M^+), 268 ($M^+ - CH_2CHSiMe_3$), 240, 226, 168.

Results

When $CpRh(C_2H_4)_2$ (**1**), is photolyzed (λ > 285 nm) at room temperature in an arene or alkane solvent under 3 atm C_2H_4, the solution is entirely photostable. However, when photolysis is carried out in vacuo or under argon, a red-brown precipitate is formed. Although this precipitate may be redissolved in CH_3OH or CH_2Cl_2, we have not succeeded in characterizing it.

Substitution Reactions with Me_2SO, CH_3CN, Ph_3P, CO, and Bu^tNC. The reactions are summarized in Scheme I. When a solution of **1** in C_6D_6 is photolyzed (λ > 285 nm) in the presence of Me_2SO, C_2H_4 is released (^1H NMR δ = 5.25 ppm) and a new product is formed which is readily identified as $CpRh(C_2H_4)(Me_2SO)$ (**2**). In a sealed NMR tube a photostationary state is reached in which about 70% of **1** is converted to product (Figure 1). There is no evidence for formation of a disubstituted product. Since there was no published information about **2** other than the ^1H chemical shift of the Cp ring,[3b] we

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[23] Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon: Oxford, 1987.

[24] Cramer, R. *Inorg. Synth.* 1974, *15*, 14.

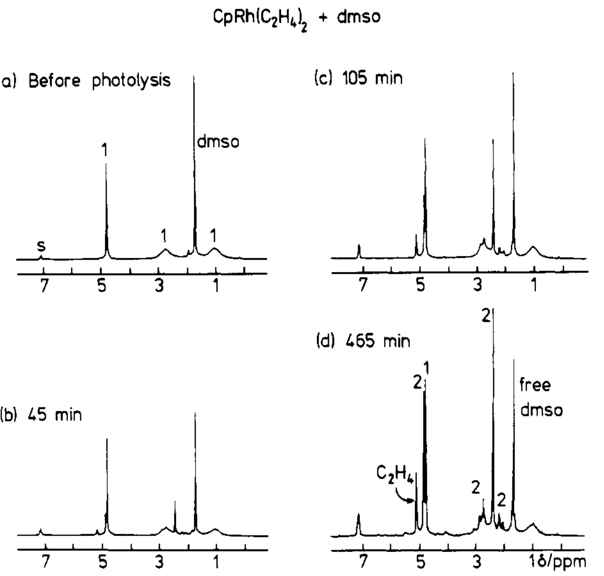
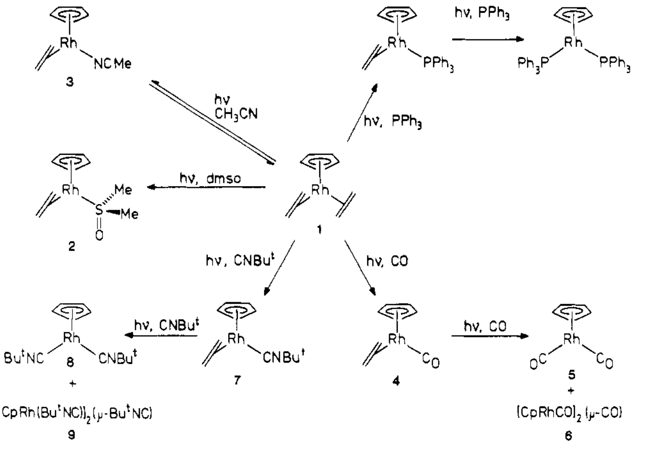


Figure 1. ^1H NMR spectra (80 MHz) showing the progressive conversion of 1 to $CpRh(C_2H_4)Me_2SO$ (2) and dissolved ethene on photolysis in the presence of DMSO: (a) spectrum before photolysis, (b) after 45 min, (c) after 105 min, (d) after 465 min photolysis.

Scheme I. Solution Photochemistry of $CpRh(C_2H_4)_2$ with η^1 Ligands



carried out the reaction on a preparative scale. NMR data appear in Table I; analytical and other spectroscopic data appear in the Experimental Section. The ^1H NMR spectrum at room temperature of the coordinated ethene shows the patterns expected for the A and M nuclei of a $[AM]_2X$ ($X = {}^{103}Rh$) multiplet in the low-temperature limit at both 80 and 400 MHz. The presence of two groups of C_2H_4 peaks and a rhodium-coupled doublet for coordinated Me_2SO establishes that the molecule possesses a plane of symmetry. The low-temperature limiting pattern taken with the small chemical shift difference between A and M protons (0.69 ppm) indicates that the barrier to internal rotation of the ethene is very high, indeed higher than in any of $CpRh(C_2H_4)L$ ($L = C_2H_4$, SO_2, CO, C_2F_4).[25,26] It is difficult to distinguish S- and O-bonded Me_2SO from the IR spectrum because there are several different fundamentals in the appropriate region. However, Fotheringham et al. showed recently that the ^{13}C NMR spectrum of Me_2SO complexes is a more reliable indicator.[27] Upfield shifts relative to free Me_2SO are indicative of O-bound complexes and downfield shifts indicative of S-bonded complexes. The present complex, 2, exhibits a particularly large downfield shift (15.0 ppm), showing that it is S-bonded as in Scheme I.

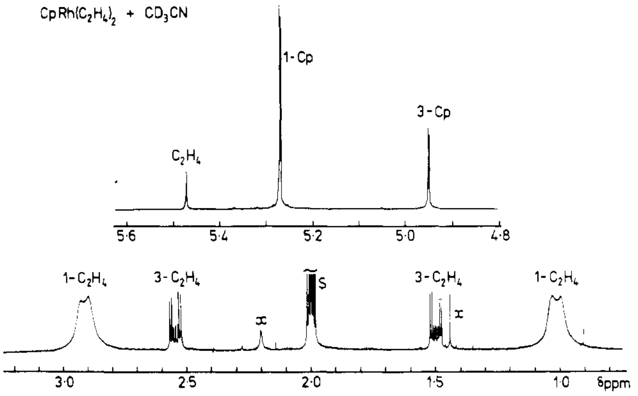


Figure 2. ^1H NMR spectrum (300 MHz) measured at 291 K after in situ photolysis of 1 in CD_3CN at 253 K, showing the presence of $CpRh(C_2H_4)(CD_3CN)$ (3): above, the spectrum in the region δ 4.8–5.6 showing the Rh-coupled doublets of 1 and 3 and dissolved ethene; below, the spectrum in the region δ 0.8–3.2 showing the protons of coordinated ethene of 1 and 3. Notice that the resonances of 1 are broadened by rotation about the Rh–ethene bond, while those of 3 show the low-temperature limiting pattern (S = solvent, x = impurity).

We examined the photochemical reaction of 1 with acetonitrile in two ways: as a solution of CH_3CN in toluene-d_8 and in pure CD_3CN. On photolysis of 1 in the presence of a 10-fold excess of CH_3CN in $C_6D_5CD_3$ at −40 °C, we observed 30% conversion to the red monosubstitution product $CpRh(C_2H_4)(CH_3CN)$ (3) ($\lambda_{max} = 453$ nm) with no evidence for disubstitution or decomposition. When photolyzed in pure CD_3CN, at −20 °C, we were able to increase the conversion of 1 to 3 to 70%. On warmup to room temperature, the complex reacted slowly to reform 1 ($k \simeq 5 \times 10^{-5}$ s^{-1}). (A minor decomposition product was not identified.) The ^1H NMR spectrum of 3 at 291 K still showed two sets of protons for coordinated ethene each with a typical $[AM]_2X$ low-temperature limiting pattern (Figure 2). The existence of equivalent pairs of protons shows that the molecule has a plane of symmetry. (Contrast $CpRh(C_2H_4)(SiR_3)H$ and $CpRh(C_2H_4)(CH_2{=}CHR)$ which show four inequivalent ethene protons in the low-temperature limit.) The photochemical reaction of 1 in neat CH_3CN may also be followed by IR spectroscopy. Difference spectra show loss of 1 (1201, 1189, 803 cm^{-1}), release of dissolved ethene (948 cm^{-1}), and formation of 3 with bands at 2265 (ν_{CN}), 1168 ($\nu_{CC} - \delta_{CH_2}$), and 780 cm^{-1} (δ_{Cp}). The difference spectrum closely resembles that obtained on conversion of 1 to $CpRh(C_2H_4)N_2$ in liquid xenon.[16] The shift of ν_{CN} to high frequency relative to CH_3CN and the NMR evidence of a plane of symmetry indicate that the CH_3CN group of 3 is coordinated end-on, unlike $Cp^*Ir(CO)(\eta^2\text{-}RCN)$.[29]

The photochemical reaction of 1 with Ph_3P leads to stepwise conversion to $CpRh(C_2H_4)(PPh_3)$ and $CpRh(PPh_3)_2$, identified by their ^1H and ^{13}C NMR spectra recorded previously.[30] However, the reaction is followed

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[27] Fotheringham, J. D.; Heath, G. A.; Lindsay, A. J.; Stephenson, T. A. *J. Chem. Res., Synop.* **1986**, 82.

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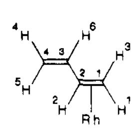
Table I. NMR Data for CpRh(C$_2$H$_4$)L and CpRhL$_2$ and for C$_2$H$_4$ (δ/ppm, *J*/Hz)

compound	nucleus; solvent; temp[a]	C$_5$H$_5$Rh	C$_2$H$_4$	L
C$_2$H$_4$	^{1}H; bz		5.25	
	^{1}H; tol		5.27	
	^{1}H; ac		5.47	
	^{13}C{^{1}H}; bz		122.8	
	^{13}C{^{1}H}; tol		123.7	
	^{13}C{^{1}H}; ac			
CpRh(C$_2$H$_4$)$_2$ (1)	^{1}H; bz	4.83 (d, *J*(Rh,H) = 0.8, 5 H)	2.87 (br, 4 H) 1.10 (br, 4 H)	
	^{1}H; tol	4.71 (d, *J*(Rh,H) = 0.7, 5 H)	2.78 (br, 4 H) 0.99 (br, 4 H)	
CpRh(C$_2$H$_4$)$_2$		5.36 (d, *J*(Rh,H) = 0.7, 5 H)	2.97 ([AM]$_2$X pattern, 4 H) 1.08 ([AM]$_2$X pattern, 4 H)	
	^{13}C{^{1}H}; bz	87.9 (d, *J*(Rh,C) = 4.0)	37.0 (d, *J*(Rh,C) = 14.1)	
	^{13}C{^{1}H}; tol	88.2 (d, *J*(Rh,C) = 3.9)	37.3 (d, *J*(Rh,C) = 13.5)	
	^{13}C{^{1}H}; ac; 253 K	87.7 (d, *J*(Rh,C) = 4.0)	35.7 (d, *J*(Rh,C) = 13.7)	
CpRh(C$_2$H$_4$)(Me$_2$SO) (**2**)	^{1}H; tol	4.85 (d, *J*(Rh,H) = 0.8, 5 H)	2.85 ([AM]$_2$X pattern, 2 H) 2.16 ([AM]$_2$X pattern, 2 H)	2.42 (d, *J*(Rh,H) = 0.4, 6 H)
	^{13}C{^{1}H}; tol	86.5 (d, *J*(Rh,C) = 3.3)	32.9 (d, *J*(Rh,C) = 15.8)	56.6 (d, *J*(Rh,C) = 1.8 Hz)
CpRh(C$_2$H$_4$)(MeCN) (**3**)	^{1}H; tol; 233 K	4.92 (d, *J*(Rh,H) = 0.8, 5 H)	2.85 ([AM]$_2$X pattern, 2 H) 1.77 ([AM]2X pattern, 2H)	1.10 (d, *J*(Rh,H) = 0.6, 3 H)
	^{1}H; ac; 253 K	4.93 (d, *J*(Rh,H) = 0.8, 5 H)	2.60 ([AM]$_2$X pattern, 2 H) 1.54 ([AM]$_2$X pattern, 2 H)	
	^{13}C; tol; 233 K	81.7 (d, *J*(Rh,C) = 5.0)	27.9 (d, *J*(Rh,C) = 15.6)	118.3 (d, *J*(Rh,C) = 10.0, CH$_3$*C*N) 2.6 (s, *C*H$_3$CN)
	^{13}C; ac; 253 K	81.7 (d, *J*(Rh,C) = 5.0)	27.2 (d, *J*(Rh,C) = 15.7)	
CpRh(C$_2$H$_4$)(Ph$_3$P)	^{31}P{^{1}H}; bz			59.4 (d, *J*(Rh,P) = 210)
CpRh(PPh$_3$)$_2$	^{31}P{^{1}H}; bz			57.3 (d, *J*(Rh,P) = 222)
CpRh(C$_2$H$_4$)(Bu^{t}NC) (**7**)	^{1}H; tol	5.20 (d, *J*(Rh,H) = 0.8, 5 H)	2.96 (br, d, 2 H) 2.17 (br, d, 2 H)	0.91 (s, 9 H)
	^{13}C{^{1}H}; tol	86.7 (d, *J*(Rh,C) = 3.4)	28.4 (d, *J*(Rh,C) = 14.7)	155.6 (d, *J*(Rh,C) = 78.6, *C*NCMe$_3$) 56.4 (d, *J*(Rh,C) = 0.6, CN*C*Me$_3$) 31.7 (s, CNC*Me*$_3$)
CpRh(Bu^{t}NC)$_2$ (**8**)	^{1}H; tol	5.42 (d, *J*(Rh,H) = 0.7, 5 H)		1.13 (s, 18 H)
	^{13}C{^{1}H}; tol	85.8 (d, *J*(Rh,C) = 3.2)		162.1 (d, *J*(Rh,C) = 80.3, *C*NCMe$_3$) 56.8 (d, *J*(Rh,C) = 0.9, CN*C*Me$_3$) 31.9 (s, CNC*Me*$_3$)
CpRh(C$_2$H$_4$)(CH$_2$=CHSiMe$_3$) (**10**)	^{1}H; tol	4.90 (d, *J*(Rh,H) = 0.6, 5 H)	$\left.\begin{matrix}2.83\\2.75\end{matrix}\right\}$ (ABMX multiplet, 1 H each) 1.67 (ddd, *J*(H,H) = 11.3, 8.3, 1.9, 1 H) 0.37 (ddd, *J*(H,H) = 12.1, 8.5, 1.4, 1 H)	2.92 (m, overlaps disubst) 2.12 (ddd, *J*(H,H) = 10, 2, *J*(Rh,H) = 1, overlaps solvent) −0.14 (ddd, *J*(H,H) = 14, 11, *J*(Rh,H) = 1, 1 H) 0.095 (s, 9 H, Si*Me*$_3$)
	^{13}C{^{1}H}; tol	88.2 (overlaps 1)	34.8 (d, *J*(Rh,C) = 12.6) 40.7 (d, *J*(Rh,C) = 13.5)	52.1 (d, *J*(Rh,C) = 13.8, *C*H) 39.7 (d, *J*(Rh,C) = 13.1, *C*H$_2$) 1.2 (s, *C*H$_3$)
	^{29}Si{^{1}H}; tol			0.64 (s)
CpRh(C$_2$H$_4$)(CH$_2$=CHSiEt$_3$) (**12**)	^{1}H; tol	4.91 (d, *J*(Rh,H) = 0.7, 5 H)	2.83 (m, *J*(H,H) = 12.1, 10.7, 2.2, 1 H) 2.79 (m, *J*(H,H) = 13.1, 10.7, 2.7, *J*(Rh,H) = 0.5, 1 H) 1.67 (ddd, *J*(H,H) = 13.1, 10.7, 2.2, 1 H) 0.38 (ddd, *J*(H,H) = 12.1, 10.7, 2.8, 1 H)	2.92 (ddd, *J*(H,H) = 14.3, 2.1, *J*(Rh,H) = 1.0, 1 H) 2.16 (ddd, *J*(H,H) = 11.1, 2.1, *J*(Rh,H) = 1.0, 1 H) −0.21 (ddd, *J*(H,H) = 14.3, 11.1, *J*(Rh,H) = 1.1, 1 H) 0.56 (q, *J*(H,H) = 8.0, CH$_2$ 6 H) 0.53 (q, *J*(H,H) = 8.0, CH$_2$ 1.08 (t, *J*(H,H) = 8.0, CH$_3$, 9 H)
	^{13}C{^{1}H}; tol	88.4 (d, *J*(Rh,C) = 1.8)	41.6 (d, *J*(Rh,C) = 13.2) 35.3 (d, *J*(Rh,C) = 13.0)	47.6 (d, *J*(Rh,C) = 14.3, *C*H(SiEt$_3$)=CH$_2$) 40.8 (d, *J*(Rh,C) = 13.7, CH(SiEt$_3$)=*C*H$_2$) 9.0 (s, Si(CH$_2$*C*H$_3$)$_3$) 6.1 (s, Si(*C*H$_2$CH$_3$)$_3$)
CpRh(CH$_2$=CHSiMe$_3$)$_2$ (**11a**; conformer A[b])	^{1}H; tol	4.99 (d, *J*(Rh,H) = 0.6, 5 H)		2.81 (ddd, *J*(H,H) = 14.0, 2.0, *J*(Rh,H) = 0.8, 2 H) 2.22 (ddd, *J*(H,H) = 11.1, 1.9, *J*(Rh,H) = 0.8, 2 H) −0.4 (ddd, *J*(H,H) = 14.0, 11.1, *J*(Rh,H) = 1.2, 2 H) 0.091 (s, 18 H, SiMe$_3$)
	^{13}C{^{1}H}; tol	88.3 (overlaps 1)		53.5 (d, *J*(Rh,C) = 13.1, CH$_2$) 40.7 (d, *J*(Rh,C) = 13.2, CH) 1.32 (s, SiMe$_3$)
	^{29}Si{^{1}H}; tol			1.06 (s)

Table I (Continued)

compound	nucleus; solvent; temp[a]	C_5H_5Rh	C_2H_4	L
$CpRh(CH_2{=}CHSiMe_3)_2$ (**11b**; conformer B[b])	^1H; tol	5.03 (d, J(Rh,H) = 0.6, 5 H)		2.90 (ddd, J(H,H) = 14.2, 2 J(Rh,H) = 0.8, 2 H) 1.52 (ddd, J(H,H) = 11.0, 2, J(Rh,H) = 0.6, 2 H) 0.68 (ddd, J(H,H) = 14.2, 11.0, J(Rh,H) = 1.3, 2 H) 0.11 (s, 18 H, $SiMe_3$)
	$^{13}C\{^1H\}$; tol	88.3 (overlap 1)		50.3 (d, J(Rh,C) = 15.7, CH) 43.9 (d, J(Rh,C) = 13.1, CH_2) 1.5 (s, $SiMe_3$)
	$^{29}Si\{^1H\}$; tol			1.76 (s)
$CpRh(C_2H_4)$(cyclohexene) (**14**)	^1H; tol; 208 K	4.75 (s, 5 H)	2.96 ($[AM]_2X$ pattern, 2 H)	2.34 (br, 4 H, $CH_2\alpha$)
			1.03 ($[AM]_2X$ pattern, 2 H)	2.18 (br, 2 H, (CH)) 1.33 (br, 4 H, $CH_2\beta$)
	$^{13}C\{^1H\}$; tol; 243 K	90.8 (d, J(Rh,C) = 2.3)	38.8 (d, J(Rh,C) = 13.8)	62.8 (d, J(RhC) = 13.3, CH) 32.3 (s, $CH_2\alpha$) 23.6 (s, $CH_2\beta$)
$CpRh(cyclohexene)_2$ (**15**)	^1H; tol; 208 K	4.84 (s)		2.29 (br, CH) 2.02 (br, $CH_2\alpha$) 1.33 (br, $CH_2\beta$)
	$^{13}C\{^1H\}$; tol; 243 K	93.4 (d, J(Rh,C) = 3.3)		63.5 (d, J(Rh,C) = 13.8, CH) 32.3 (s, $CH_2\alpha$) 23.7 (s, $CH_2\beta$)
$CpRh(C_2H_4)$(1-pentene) (**16**)	$^{13}C\{^1H\}$; tol	89.1 (s)	38.7 (d, J(Rh,C) = 15)	38.4 (d, J(Rh,C) = 13, $CH_2{=}CH$)
			35.7 (d, J(Rh,C) = 14)	67.9 (d, J(Rh,C) = 14, $CH_2{=}CH$) 45.6 (s, $CH_2CH_2CH_3$) 27.6 (s, $CH_2CH_2CH_3$) 15.1 (s, $CH_2CH_2CH_3$)
$CpRh(C_2H_4)(\eta^2\text{-}C_4H_6)$ (17)	^1H; tol; 250 K	4.72 (d, J(Rh,H) = 0.6, 5 H)	3.00 (ddd, J(H,H) = 11.6, 9.1, 2, 1 H)	5.45 (dt, J(H,H) = 16.9, 10, 10, 1 H, H^6)
			2.81 (ddd, J(H,H) = 11.6, 8.5, 2, 1 H)	5.16 (dd, J(H,H) = 16.9, 2, 1 H, H^5)
			1.57 (ddd, J(H,H) = 12.3, 8.5, 2, 1 H)	4.77 (dd, J(H,H) = 10, 2, 1 H, H^4)
			0.77 (ddd, J(H,H) = 12.3, 9.1, 2, 1 H)	2.81 (dd, J(H,H) = 9, 2, 1 H, H^3)
				2.19 (m, J(H,H) = 10, 9, 7.5, J(Rh,H) = 2, 1 H, H^2) 1.47 (dd, J(H,H) = 7.5, 2, 1 H, H^1)
	$^{13}C\{^1H\}$; tol; 250 K	89.6 (d, J(Rh,C) = 3.8)	39.3 (d, J(Rh,C) = 13.4)	146.9 (s, C^3)
			37.2 (d, J(Rh,C) = 13.4)	107.9 (s, C^4) 64.8 (d, J(Rh,C) = 12.6, C^2) 37.7 (d, J(Rh,C) = 13.9, C^1)

[a] All spectra measured at 296 K unless otherwise stated. Abbreviations: bz, benzene; tol, toluene; ac, acetonitrile. [b] The two conformers are assigned arbitrarily.

most conveniently by ^{31}P NMR (data are given in Table I).

Photochemical substitution of ethene in 1 by CO was followed by IR spectroscopy. Like the reaction with Ph_3P, there was sequential substitution giving $CpRh(C_2H_4)CO$ (**4**) and $CpRh(CO)_2$ (**5**). However, even at an early stage, there was appreciable conversion to $(CpRhCO)_2(\mu\text{-}CO)$ (**6**), easily recognized by the ν_{CO} band of the bridging carbonyl (Figure 3).[31] Toward the end of the reaction, the contribution to the spectrum from the monosubstitution product becomes insignificant. The formation of **6** is readily understood from the photosensitivity both of $CpRh(C_2H_4)CO$ and $CpRh(CO)_2$.[15,32] A more detailed study of the photochemistry of **4**, **5**, and **6** will be reported shortly.

Irradiation of a solution of 1 in the presence of Bu^tNC follows a similar pattern to substitution by CO, with progressive conversion to mono- and disubstituted products and a dinuclear complex characterized by NMR, mass, and IR spectroscopy. The products may be separated by a combination of chromatography and sublimation.

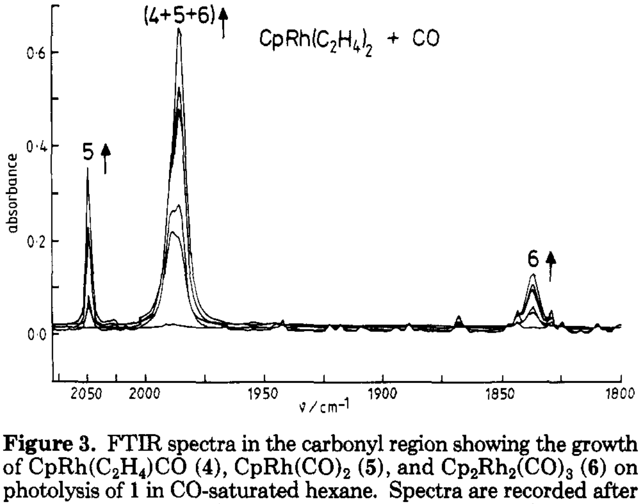


Figure 3. FTIR spectra in the carbonyl region showing the growth of $CpRh(C_2H_4)CO$ (**4**), $CpRh(CO)_2$ (**5**), and $Cp_2Rh_2(CO)_3$ (**6**) on photolysis of **1** in CO-saturated hexane. Spectra are recorded after 0, 21, 32, 62, 72, and 120 min photolysis of a stock solution.

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Table II. NMR Spectra of $Cp_2Rh_2(Bu^tNC)_3$ in Toluene-d_8 (δ/ppm; J/Hz)

nucleus; temp, K	Cp	Bu^tNC terminal	Bu^tNC bridging
^1H; 350	5.36 (m, $[AX_5]_2$) $J(Rh,H) = 0.4$ $J(Rh,Rh) = 4.3$	1.29 (br)	
$^{13}C\{^1H\}$; 350	88.6 (m, ABX) $J(Rh^1,C) + J(Rh^2,C) = 3.5$	32.6 (s, CNC*Me*) 57.4 (s, CN*C*Me_3)	
^1H; 263	5.48 (s, 10 H)	1.04 (s, 18 H)	1.65 (s, 9 H)
^{13}C; 263	88.3 (s)	31.8 (s, CNCMe_3) 56.5 (s, CN*C*Me_3) 153.5 (d, *C*NCMe_3) $J(Rh,C) = 84.6$	32.3 (s, CNCMe_3) 58.1 (s, CN*C*Me_3) 208.2 (t, *C*NCMe_3) $J(Rh,C) = 41.6$
^1H; 184	5.70 (s) 5.64 (s)	0.98 (s) 0.89 (s)	1.78 (s)
$^{13}C\{^1H\}$; 184	88.6 (s) 88.0 (s)	31.3 (s, CNCMe_3) 56.30 (s, CN*C*Me_3) 56.16 (s) 149.7 (d, *C*NCMe_3) $J(Rh,C) = 77.7$ 148.3 (d) $J(Rh,C) = 88.4$	32.1 (CNCMe_3) 58.3 (CN*C*Me_3) 210 (br, *C*NCMe_3)

$CpRh(C_2H_4)(Bu^tNC)$ (**7**) may also be made by reaction of $[RhCl(C_2H_4)_2]_2$ with a substoichiometric amount of Bu^tNC followed by reaction with TlCp (see Experimental Section). The yellow monosubstituted complex is readily sublimed. Its ^1H NMR spectrum at room temperature resembles that of **1**: the pair of resonances due to coordinated ethene coalesce at 323 ± 4 K at 80 MHz, yielding a barrier to internal rotation of the coordinated ethene of 66.1 ± 1.0 kJ mol^{-1} (derived from T_c and $\Delta\nu$). The NMR spectrum of **7** at 224 K shows the $[AM]_2X$ low-temperature limiting pattern for coordinated ethene indicating that the molecule has a plane of symmetry like **2**. The IR spectra of **7** and $CpRh(Bu^tNC)_2$ (**8**) show bands in the 2110–1980 cm^{-1} region characteristic of linear terminally coordinated isonitrile.[28] However, for reasons as yet unclear, they each show more than the expected number of bands.

The dinuclear product formed on photolysis of **1** with Bu^tNC proves to be $[CpRh(Bu^tNC)]_2(\mu\text{-}Bu^tNC)$ (**9**), exactly analogous to the indenyl complex[33a] $[(\eta^5\text{-indenyl})Rh(Bu^tNC)]_2(\mu\text{-}Bu^tNC)$, and the cyclopentadienyl carbonyl complex **6**. The new dinuclear complex shows two-stage fluxional behavior in its ^1H and ^{13}C NMR spectra (Table II, Figures 4 and 5). At low temperature (184 K), there are two equally intense, closely spaced ^1H resonances each for the Cp protons and for the terminal isonitrile protons, but one slightly broadened resonance for the bridging isonitrile. In the ^{13}C spectrum of **9** we see two resonances for the Cp carbons, 0.5 ppm apart. Two further resonances assigned to the methyl carbons of the bridging and terminal isonitriles are detected at around 30 ppm. There are two resonances each for the RhCN*C* and Rh*C*NC carbons of the *terminal* isonitriles. The resonance of the bridging Rh*C*NC carbon is broadened and shifted substantially to high frequency compared to the corresponding resonance of the terminal isonitrile. This chemical shift is consistent with that in the pentamethylcyclopentadienyl complex $[Cp^*Rh]_2(\mu\text{-}Bu^tNC)_2$ characterized previously.[33b]

When the sample is warmed, the pair of Cp resonances coalesce at 215 ± 4 K (300 MHz). From this temperature and the corresponding coalescence temperatures of the cyclopentadienyl carbons and the terminal isonitrile protons, we have three independent estimates of the barrier to this first rearrangement yielding an average $\Delta G^{\ddagger}$ of 45.7 ± 1.6 kJ mol^{-1}. On warming further, the resonances sharpen until 263 K. At this temperature, the resonances of bridging and terminal isonitrile protons are sharp and integrate satisfactorily in the ratio 1:2. The corresponding ^{13}C spectrum shows a doublet for the terminal RhCNC carbons ($J(Rh,C) = 85$ Hz) and a triplet for the bridging Rh*C*NC carbons ($J(Rh,C) = 42$ Hz). The maintenance of rhodium coupling to both Rh nuclei demonstrates that the first fluxional process is intramolecular.

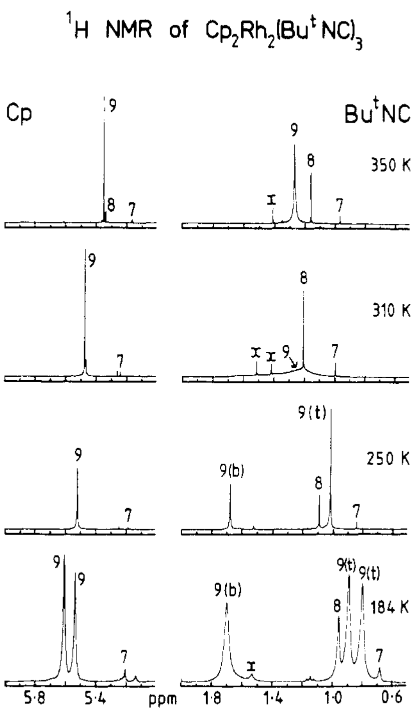

Figure 4. Temperature dependence of the ^1H NMR spectrum of $Cp_2Rh_2(Bu^tNC)_3$ (**9**) in toluene-d_8 at 300 MHz. The sample contains small amounts of the mononuclear complexes **7** and **8**. The peaks in the Bu^tNC methyl region are labeled **9(b)** (bridging) and **9(t)** (terminal). All spectra are normalized to the same maximum peak height. Notice the presence of two sets of terminal methyl and Cp resonances at 184 K, which sharpen to single peaks by 250 K. Bridging and terminal methyl resonances broaden, reaching coalescence at 310 K (broad methyl peak just above base line). By 350 K the resonance has narrowed to a single conspicuous peak (x = impurity).

At higher temperatures, the proton resonances of the isonitrile methyls broaden again: this time the resonances of the bridging protons coalesce with those of the terminal protons. From the coalescence temperature (310 ± 4 K), we calculate a barrier of 61.8 ± 0.8 kJ mol^{-1} for terminal–bridge exchange. These figures are expressed so as to include the correction for the 1:2 ratio of bridging to terminal Bu^tNC groups.[34] Above 310 K the resonances sharpen again until the fine structure associated with the rhodium couplings to the Cp proton and carbon resonances is resolved. From these couplings we derive a Rh–Rh coupling constant of 4.3 Hz. Although these observations prove that the Cp_2Rh_2 unit remains intact during the rearrangement, the large chemical shift difference between the resonances of the RhCNC carbons of the bridging and terminal isonitriles (56 ppm) prevents any demonstration of intramolecularity with respect to the isonitrile ligands.

The IR spectrum of **9** in solution shows two major bands and a broad shoulder for the terminal ν(CN) modes and two distinct bands at 1739 and 1714 cm^{-1} for the bridging

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[33] (a) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648. (b) Jones, W. D.; Feher, W. J. *Organometallics* **1983**, *2*, 687.

[34] Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961.

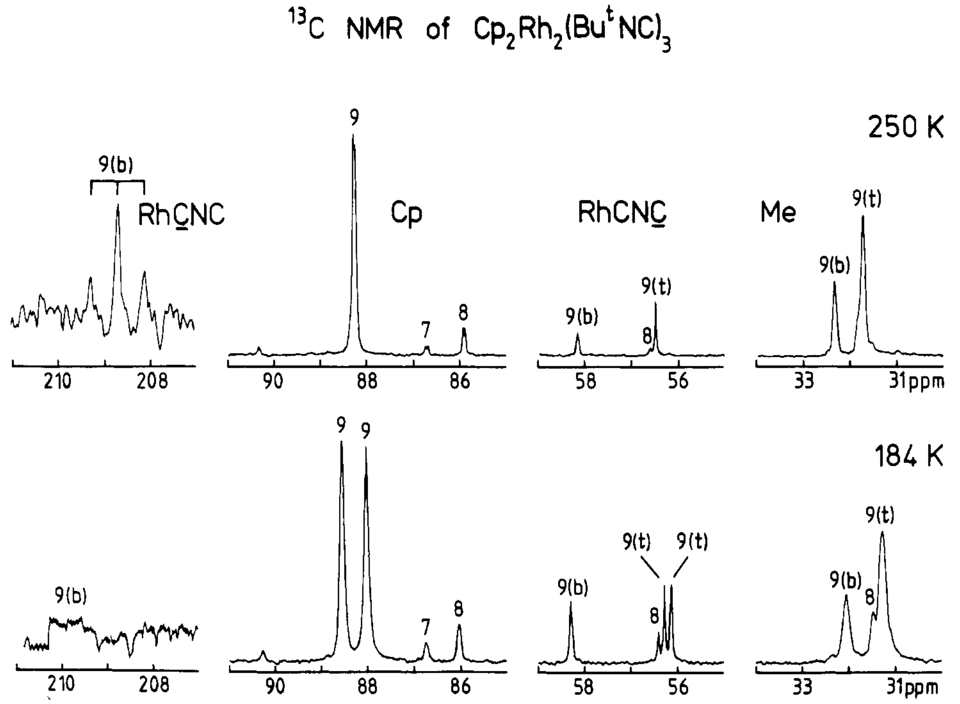
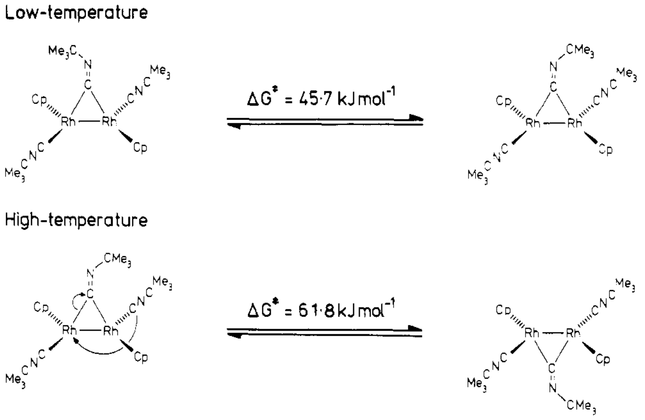


Figure 5. Temperature dependence of the ^{13}C NMR spectrum of $Cp_2Rh_2(Bu^tNC)_3$ (9) in toluene-d_8. The peaks are labeled as in Figure 4. The spectrum at 184 K shows the two sets of Cp and terminal isonitrile resonances, the latter via the quaternary carbons of the Bu^t group. The quaternary isonitrile carbon of the bridging ligand is broad. At 250 K the spectrum has simplified to give single resonances for the Cp carbons and the carbons of the terminal ligand. Notice the rhodium coupling to the resonance of the quaternary bridging carbon.

ν(CN) modes. A change of solvent from hexane to THF barely affected the position of the bands but did increase the intensity of the bridging modes relative to the terminal modes. These spectra suggest that at least two isomers of **9** are present in solution.

Bridging isonitrile complexes typically adopt an imino-type structure with a bent RNC linkage.[35a] There are two types of process which we have considered for the low-temperature rearrangement: (i) cis–trans exchange or (ii) exchange between conformers. If we were observing cis–trans isomerization, we would have an explanation of the two bridging bands in the IR spectrum, but we would have expected a substantial change in the relative intensity of the two bridging modes in the IR on changing the solvent polarity. We also have to reconcile this theory with the lack of evidence for cis and trans isomers of **6**. Moreover, a cis isomer of the Bu^tNC complex **9** would suffer from considerable steric strain. The alternative of an inversion at nitrogen interchanging two degenerate conformers (Scheme II) can explain the presence of two sets of terminal isonitrile and Cp resonances but only one bridging isonitrile resonance. The barrier to interconversion also accords well with those measured by Adams and Cotton for bridging MeNC groups.[35a] However, this hypothesis leaves no clear explanation of the IR spectra. Earlier work on $CpRu(CNBu^t)_2I$ has shown a similar phenomenon in the IR spectrum. The crystal structure of this complex shows two nonequivalent isonitrile groups with significant distortions from linearity. The extra IR bands are postulated to arise from multiple conformations of the Bu^tNC ligands.[35b] The indenyl analogue of **9** also shows anomalies in its IR spectrum.[33a] It is likely that conformational equilibria with very low barriers between conformers cause the complications in the IR spectra of **9**, but a more detailed theory must await crystallographic evidence.

Scheme II. Fluxional Behavior of $Cp_2Rh_2(Bu^tNC)_3$



The high-temperature fluxional process exchanges bridge and terminal isonitrile groups of **9**. The mechanism of this rearrangement is probably similar to that for bridge–terminal carbonyl exchange in **6** and related compounds in which pairwise exchange occurs through a trans-oriented pathway.[36] The corresponding process has also been reported for the indenyl analogue.[33a]

Alkenes and Butadiene. The photosubstitution reactions of **1** with alkenes and butadiene are summarized in Scheme III. Photolysis in the presence of vinyltrialkylsilanes (alkyl = methyl or ethyl) yields stable mono- and disubstituted products in proportions which can be controlled by choice of substrate concentration. We have also formed mixtures of $CpRh(C_2H_4)(CH_2{=}CHSiMe_3)$ (**10**) and $CpRh(CH_2{=}CHSiMe_3)_2$ (**11**) by reaction of $[(C_2H_4)RhCl]_2$ with $CH_2CHSiMe_3$ followed by reaction with TlCp.[21] However, a more effective synthesis of the related

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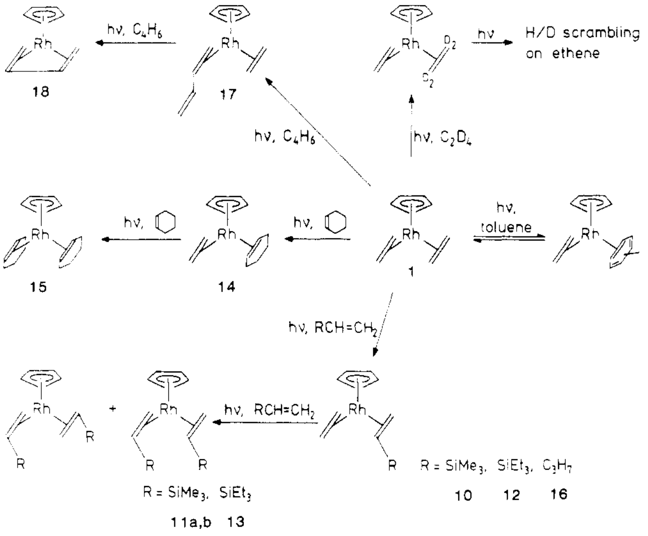
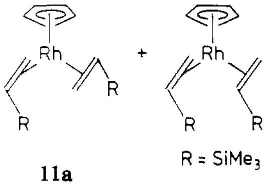
[35] (a) Adams, R. D.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 249. (b) Boeyens, J. C. A.; Coville, N. V.; Soldenhoff, K. *S. Afr. J. Chem.* **1984**, *37*, 153.

[36] Evans, J.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W.; Norton, J. R. *J. Chem. Soc., Dalton Trans.* **1978**, 961.

Scheme III. Solution Photochemistry of $CpRh(C_2H_4)_2$ with Alkenes, Dienes, and Arenes



complex $CpRh(C_2H_4)(CH_2{=}CHSiEt_3)$ (**12**) was found by photolysis of **1** with Et_3SiH under an ethene purge, a method which gives only a trace of the disubstituted product.[18b] In the monosubstituted products, all ethene protons are inequivalent and fully resolved, showing that there is a high barrier to internal rotation of the ethene. Nevertheless, the observation of saturation transfer during decoupling experiments indicates that rotation is occurring on a slower time scale. Although, a molecule of this type can have two isomers in the limit of slow internal rotation,[37] only one is observed, suggesting that steric hindrance keeps the $SiMe_3$ group pointing away from the ring (Scheme III). The disubstituted product **11** occurs in two distinct isomers which we assign as **11a** and **11b**. These isomers cannot be interconverted by internal rotation about the metal–alkene bond. Such isomerism was documented in detail by Cramer for $CpRh(CH_2{=}CHF)_2$.[37] Although six isomers are possible in the low-temperature limit, the steric bulk of the $SiMe_3$ groups restricts us to the two isomers with the $SiMe_3$ groups pointing away from the Cp ring. Complex **11** has been mentioned previously,[38] but its only recorded characteristic, its ^{29}Si spectrum, differs from our measurements.



11a

11b

Since the photosubstitution products of **1** with cyclohexene decomposed at room temperature releasing cyclohexene, the reaction was carried out at −20 °C. The monosubstituted complex **14** was the major product and showed ethene resonances with very similar chemical shifts to those of **1**. The disubstituted product **15** was detected but was formed only in about 20% of the yield of the monosubstituted product. The lability of these complexes dissuaded us from attempting isolation.

The corresponding reaction of **1** with 1-pentene yields substitution products and the expected alkene isomerization products *trans*- and *cis*-2-pentene. The isomerization of the 1-pentene proceeds catalytically, generating a 5:4:1 mixture of 1-pentene–*trans*-2-pentene–*cis*-2-pentene after 20 h photolysis. The monosubstitution product with 1-pentene, **16**, has been positively identified in the reaction mixture (see below), but several further substitution products are also present.

Photolysis in the presence of 1,3-butadiene at 233 K yields a mixture of the well-known $CpRh(\eta^4\text{-}C_4H_6)$[38] (**18**) and a new product identified as $CpRh(C_2H_4)(\eta^2\text{-}C_4H_6)$ (**17**). At −45 °C all C_2H_4 protons in the monosubstitution product are inequivalent and are fully resolved, but at room temperature, they are broadened by internal rotation. Through selective decoupling and 2D-COSY experiments we have identified all of the protons of the η^2-butadiene unit (Table I). This complex is converted to $CpRh(\eta^4\text{-}C_4H_6)$ (**18**) on warming or on further photolysis.

Low-Temperature Photolysis in Toluene. When **1** is irradiated in toluene at room temperature in the absence of other ligands, precipitation is observed as usual (see above). However, when the reaction is carried out at −60 °C, a wine-colored solution is formed instead with no precipitation. On warmup, the color reverts to the usual yellow of **1**. Examination of the UV spectrum at low temperature shows the development of bands at 507 (w) and 339 ± 2 (s) nm. The more intense band is remarkably close to that observed for the transient benzene solvate of $CpRh(C_2H_4)$ by flash photolysis at room temperature (λ_{max} = 345 ± 5 nm). Proton NMR of such solutions at 198 K shows that the conversion to product is very low. We have succeeded, nevertheless, in observing free ethene together with the Cp resonance (δ 4.26) and a possible resonance of coordinated ethene (δ −0.28) in the photoproduct. Both product resonances are broad at 198 K and broaden to the point of extinction on warming to 213 K. Considering the resemblance of the UV spectrum to that of the flash photolysis product and the lack of evidence for C–H activation (see below), we consider that this species is most likely to be $CpRh(C_2H_4)(\eta^2\text{-toluene})$ rather than $CpRh(C_2H_4)(C_6H_4CH_3)H$. We associate the broadening of the NMR spectra with solvent exchange and/or hopping of the metal around the ring.

Reaction with C_2D_4. We mentioned earlier that **1** is completely stable to photolysis under a C_2H_4 atmosphere. Following the discovery of the substitution reactions described above, we anticipated that reaction with C_2D_4 would lead to simple exchange of C_2H_4 for C_2D_4. On photolysis of **1** in toluene-d_8 at 300 K under 5 bar C_2D_4 (i.e. $[C_2D_4]:[1] = 3.6$), the NMR spectrum shows a 25% reduction in the integration of the ethene protons over 6 h photolysis. At the same time, release of ethene is observed. Initially, the photodissociated ethene appears as a singlet characteristic of C_2H_4, but as photolysis proceeds, extra bands appear slightly to high field of the ethene resonance. Broad-band deuterium decoupling simplifies the structure on these bands (Figure 6a) and shows that several isotopomers of deuterium-labeled ethene are present. The vapor above the NMR sample was collected and examined by FTIR spectroscopy. All possible isotopomers of $C_2H_{4-x}D_x$ could be positively identified by their Q branches in the 1000–700 cm^{-1} region (Figure 6b).[40] The mass spectrum of the involatile residue containing the rhodium-based products shows that deuteration of **1** has

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[37] Cramer, R.; Reddy, G. S. *Inorg. Chem.* **1973**, *12*, 346.

[38] Pannell, K. H.; Bassindale, A. R.; Fitch, J. W. *J. Organomet. Chem.* **1981**, *209*, C65.

[39] Porri, L.; Lionetti, A.; Allegra, G.; Immirzi, A. *J. Chem. Soc., Chem. Commun.* **1965**, 336.

[40] Crawford, B. L.; Lancaster, J. E.; Inskeep, R. G. *J. Chem. Phys.* **1953**, *21*, 678. Duncan, J. L.; McKean, D. C.; Mallinson, P. D. *J. Mol. Spectrosc.* **1973**, *45*, 221.

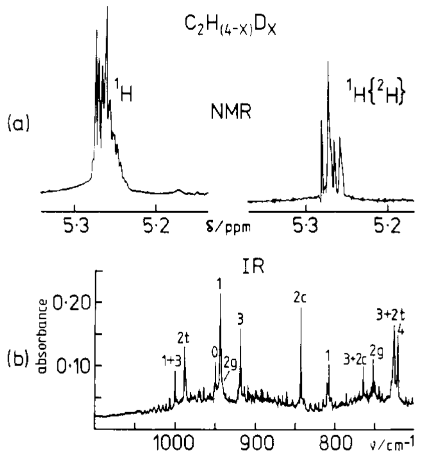


Figure 6. (a) ^1H NMR spectra (360 MHz, 213 K) of dissolved ethene obtained after 33 h photolysis of a solution of 1 in toluene-d_8 with 3 atm of C_2D_4: left, normal spectrum; right, spectrum with broad-band deuterium decoupling. The various bands are due to the different isotopomers of $C_2H_{4-x}D_x$ (x = 0–3). (b) FTIR spectrum of the vapor above the photolysate showing the Q branches of all the isotopomers of $C_2H_{4-x}D_x$ (x = 0–4). The numbering indicates the value of x (t, trans; c, cis; g, gem).

Table III. Molecular Ion Distribution of Residue of Deuterium-Labeled 1 Obtained after Photolysis of $CpRh(C_2H_4)_2$ with C_2D_4

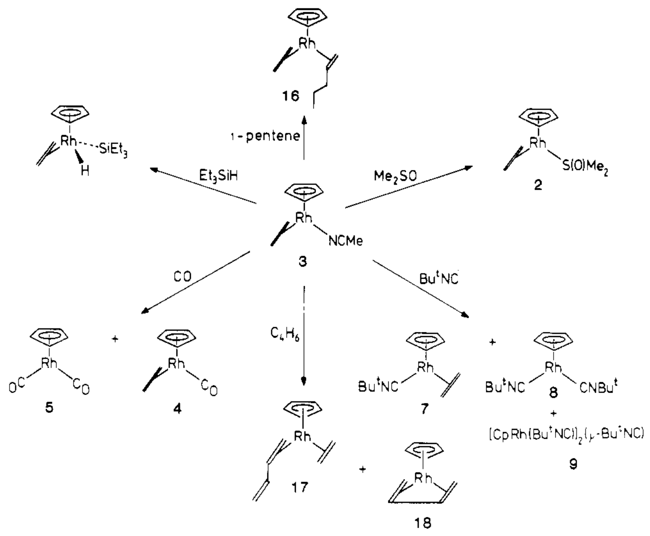
m/z	counts	ion distributn	%[a]	
232	378	H_5D_8	5	
231	147	H_6D_7	2	
230	85	H_7D_6	0	
229	286	H_8D_5	2	
228	2251	H_9D_4	31	M^+
227	442	$H_{10}D_3$	6	
226	192	$H_{11}D_2$	2	
225	687	$H_{12}D_1$	5	
224	3348	H_{13}	47	
200	506	H_5D_4	22	
199	105	H_6D_3	5	
198	39	H_7D_2	1	M^+ − ethene
197	208	H_8D_1	3	
196	1596	H_9	69	
169	881	H_4D	3	M^+ − (ethene)$_2$
168	8523	H_5	97	

[a] The ion distribution is presented as a percentage of the overall counts for (i) M^+, (ii) M^+ − ethene, and (iii) M^+ − (ethene)$_2$. The distribution is corrected for ^{13}C-labeled ions present in natural abundance and in case (iii) for hydrogen capture products.

occurred. The isotope pattern of the parent ions indicates that the dominant species present are $CpRh(C_2H_4)_2$ and $CpRh(C_2H_4)(C_2D_4)$, but significant amounts of isotopomers containing partially deuteriated ethene are also detected (Table III). Examination of the $CpRh^+$ peak suggests that there has been slight formation of $(C_5H_4D)Rh$ species (about 3%), but no double-labeled cyclopentadienyl groups are present. The overall deuterium content as measured by mass spectrometry is 27% in satisfactory agreement with the value obtained by NMR integration.[41] A control experiment to check whether the deuterium comes from the solvent is described below.

Tests for H/D Exchange with Solvent. The early Du Pont experiments[5] on H/D exchange led us to attempt further tests for exchange between solvent deuterium and 1 or solvent deuterium and added solute. In these experiments, the NMR tube was sealed with a capillary containing $(CH_3)_4Si$, which served as a standard.[42] Prolonged photolysis could be carried out of solutions of 1 in the presence of a C_2H_4 atmosphere without decomposition. These experiments showed no exchange of 1 or of added ferrocene with C_6D_6 solvent. A more critical test was provided by photolysis in vacuo, but again no exchange could be detected. (In this case the photolysis causes precipitation of a decomposition product, see above.)

Scheme IV. Thermal Displacement Reactions of $CpRh(C_2H_4)MeCN$



Displacement Reactions of $CpRh(C_2H_4)(CH_3CN)$. The ability to form a $CpRh(C_2H_4)S$ (S = solvent) complex provides a potential route to avoid the complications of disubstitution and of ligand isomerization (e.g. of 1-pentene). For this reason we carried out a number of test experiments in which we generated $CpRh(C_2H_4)(CH_3CN)$ (**3**) at low temperatures to which we added another ligand on warmup to room temperature. The results are summarized in Scheme IV. (i) Reaction with Me_2SO proceeded quantitatively to $CpRh(C_2H_4)(Me_2SO)$ (**2**). (ii) Reaction with 1-pentene gave $CpRh(C_2H_4)$(1-pentene) (**16**) in >95% conversion with no evidence for ligand isomerization within the limits of NMR detection. (iii) Reaction with Et_3SiH gave quantitative conversion to $CpRh(C_2H_4)(SiEt_3)H$. However, it should be noted that this complex reacts very slowly with excess Et_3SiH, so these solutions are not stable indefinitely at room temperature. (iv) Reaction with CO gave both $CpRh(C_2H_4)CO$ (**4**) and $CpRh(CO)_2$ (**5**) in an approximately 1:1 ratio. Addition of CO to **4** showed that the dicarbonyl was not formed by secondary displacement of ethene in **4**. (v) Reaction with Bu^tNC gave **7**, **8**, and **9**, but far less of the dinuclear product was generated than by photolysis. (vi) Displacement of CH_3CN by butadiene at room temperature gave $CpRh(C_2H_4)(\eta^2\text{-}C_4H_6)$ (**17**) and $CpRh(\eta^4\text{-}C_4H_6)$ (**18**) in an initial proportion of ca. 3:1, but the $\eta^2\text{-}C_4H_6$ complex continues to react thermally to form the $\eta^4\text{-}C_4H_6$ complex under these conditions.

Discussion

The results described in this paper show that $CpRh(C_2H_4)_2$ undergoes a variety of photochemical reactions generating products of the type $CpRh(C_2H_4)L$ by substitution of coordinated ethene. The monosubstitution products are liable to further photochemical reaction to form $CpRhL_2$ except in the cases of Me_2SO and CH_3CN (Schemes I and III). For some of these ligands alternative

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[41] We have also observed similar H/D exchange on photolysis of solutions of 1 in C_6D_6 under a C_2D_4 atmosphere.

[42] Grebenik, P. D.; Green, M. L. H.; Izquierdo, A.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Dalton Trans.* 1987, 9.

routes are available via high-temperature reaction or other methods, but the photochemical method is particularly valuable for incorporation of weak ligands such as cyclohexene, η^2-butadiene, and CH_3CN. We expected that the synthetic problems of obtaining both substitution products would be avoided by formation of **3** followed by displacement (Scheme IV, eq 4 and 5). Although this method proved a success in preventing disubstitution and ligand isomerization with 1-pentene, it did not prevent the formation of disubstituted products with the carbonyl and isonitrile complexes. The alternative of careful control of reaction conditions for direct photolysis seems more promising as we demonstrated previously for the reaction with Et_3SiH.[18]

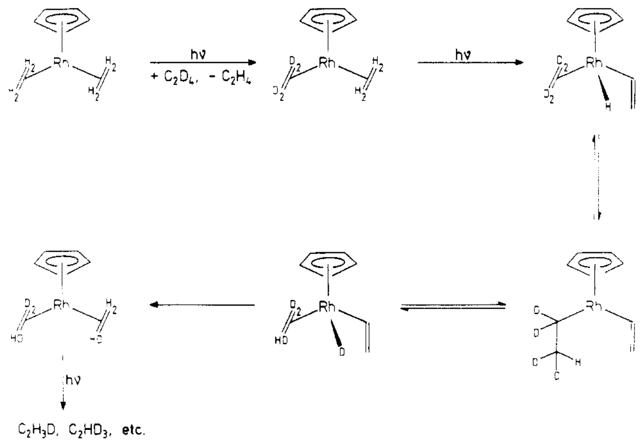
The electronic structure of $CpRh(C_2H_4)_2$ (**1**) is only partially understood. Photoelectron spectra indicate that the HOMO is metal–ethene bonding.[43] It is likely that the LUMO is metal–ethene antibonding and that photolysis causes labilization of ethene via population of the LUMO.

The mechanism of some of these reactions has already been investigated in detail by matrix isolation and laser flash photolysis. Matrix isolation allowed us to observe the IR and UV spectra of the $CpRh(C_2H_4)$ intermediate.[15] Flash photolysis of **1** in cyclohexane revealed two transient intermediates, both of which were shown to be involved in product formation.[17] The first intermediate has a microsecond lifetime and is argued to be an unsolvated state of $CpRh(C_2H_4)$. It is the major source of product at high concentrations of entering ligand. The second intermediates has a millisecond lifetime and decays via saturation kinetics with a strong solvent dependence. This species $CpRh(C_2H_4)S$ (S = solvent) becomes more important as a source of product at low ligand concentrations. Its lifetime is prolonged about 300-fold in benzene compared to cyclohexane. In the present study we have used arene solvents for most reactions, although a few (e.g. with Bu^tNC) have been carried out in alkanes or in CH_3CN. We have shown that the solvent complex with toluene, presumably $CpRh(C_2H_4)(\eta^2\text{-toluene})$, is stable at −60 °C and that the solvent complex with CH_3CN has a half-life of several hours at room temperature. Evidence for η^2-arene intermediates is growing.[44-46] Jones et al. have implicated such an intermediate in arene activation by $Cp^*Rh(PMe_3)H_2$. Detailed NMR spectra have been obtained for $[Os(NH_3)_5(\eta^2\text{-benzene})]^{2+}$[44] and for $Cp^*Re(CO)_2(\eta^2\text{-benzene})$, a long-lived photochemical intermediate.[45] Lee and Brintzinger previously described the formation of CpCoCO at −78 °C in toluene.[47] Considering the reactivity of such 16-electron intermediates, it seems likely that this is $CpCoCO(\eta^2\text{-toluene})$.

Our studies of the photochemistry of **1** provide ample evidence for the importance of the back reaction of $CpRh(C_2H_4)$ or $CpRh(C_2H_4)S$ with ethene to re-form **1**. In several reactions we observe photostationary states. For instance, with $CH_2{=}CHSiMe_3$ as the added ligand we demonstrated that the position of the photoequilibrium could be shifted by pumping out the dissolved ethene. Both $CpRh(C_2H_4)(CH_3CN)$ (**3**) and $CpRh(C_2H_4)(\eta^2\text{-toluene})$ react with ethene on warming.

One reaction among those described in this paper stands out as an indicator that this dissociative mechanism does not operate alone, namely, the H/D exchange between dissolved and coordinated ethene. Such exchange appears to require the formation of an ethene hydride complex followed by reversible 1,3-hydrogen shifts between metal and ligand. The observation of photoinduced isomerization of the corresponding iridium complex to an ethene vinyl hydride complex[12] offers a plausible mechanism for the current results (Scheme V). The lack of evidence for $CpRh(C_2H_4)(C_2H_3)H$ in the matrix experiments or for vinyl-containing products in the substitution reactions indicates that this pathway has a much lower quantum yield than the dissociative pathway and that the vinyl hydride complexes are much less stable that their iridium congeners. Other examples of isomerization of ethene complexes to vinyl hydride complexes and evidence for vinylic activation of alkenes have been accumulating recently.[11,48]

Scheme V. Mechanism of Photochemical H/D Exchange of $CpRh(C_2H_4)_2$ with C_2D_4



The catalytic isomerization of 1-pentene is observed only under photochemical conditions. It may proceed either by the η^3-allyl hydride mechanism[49] or via formation of the vinyl hydride isomer $CpRh(C_2H_3)(H)(\eta^2\text{-1-pentene})$.

These experiments have involved extensive tests for C–H activation by $CpRh(C_2H_4)$ and $CpRh(C_2H_4)S$ (S = solvent). Neither in these tests nor in the reactions in methane matrices is there any evidence for activation of arene or alkyl C–H bonds. The thermal H/D exchange reported by Seiwell[5] may therefore involve a step with high activation energy, which is not accessible under our conditions. Alternatively, it may involve the decomposition product which is likely to be more soluble at higher temperature.

The NMR data give some additional information concerning the barriers to internal rotation about the metal–ethene bond.[26] For all the complexes of the type $CpRh(C_2H_4)L$, the chemical shift difference between the ethene protons is smaller than in **1**. Those with L = Me_2SO, CH_3CN, and $CH_2{=}CHSiEt_3$ exhibit room temperature spectra in which the ethene resonances correspond to the low-temperature limit. These compounds must have a substantially higher barrier to ethene rotation than that of **1** probably because their ligands do not compete appreciably with ethene for π-electron density from the metal. When L = Bu^tNC, the barrier is reduced to a value very close to that of **1**, suggesting substantial π-bonding to the isonitrile.

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(44) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. Harmon, W. D.; Taube, H. *Ibid.* **1987**, *109*, 1883.

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The dinuclear isonitrile complex **9** is synthesized most effectively by photolysis. Like other isonitrile complexes, it exhibits an intramolecular rearrangement corresponding to inversion of the bridging nitrogen. At higher temperatures, bridge–terminal exchange is observed but with a barrier about 20 kJ mol^{-1} higher than for the corresponding carbonyl complex **6**.[36] All the isonitrile complexes exhibit more ν(CN) bands in the IR than expected—the conformational (or Fermi resonance) effects underlying these features are not understood.

Conclusions

$CpRh(C_2H_4)_2$ is susceptible to a range of photochemical substitution reactions. The advantage of working at low temperature is valuable for the synthesis of labile complexes and for the identification of solvento complexes, which play a significant role in the reaction mechanism. Most of the products are derived by simple substitution of ethene, but additional dinuclear products are formed with CO and $\mathrm{Bu^tNC}$. The latter (**9**) shows two-stage fluxional behavior. The presence of an alternative pathway to substitution is demonstrated by photolysis in the presence of C_2D_4 which effects H/D exchange within the ligand, probably via a vinyl hydride mechanism.

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Reactions of Gas-Phase Iron(I) Ions with Neutral Allenes. Degenerate Double-Bond Isomerization versus Competitive Activation of Vinylic and Allenylic C–C Bonds

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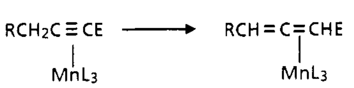
The study of a large set of labeled allenes (4,5-nonadiene and isomeric 1,2-, 2,3-, and 3,4-octadienes) provides a quite detailed insight in the chemistry of bare Fe^+ with these hydrocarbons in the gas phase. General features are the following: (i) Oxidative addition of a carbon–hydrogen bond to the metal ion is not associated with the rate-limiting step. This is more likely to correspond with the elimination of C_2H_4, as demonstrated in the case of, for example, Fe(4,5-nonadiene)$^+$. (ii) The tendency of isomerization processes (presumably via multiple hydrogen migrations) is much more pronounced for Fe(allene)$^+$ complexes than isomeric Fe(alkyne)$^+$ counterparts. The position of the C=C=C unit seems to affect the extent of isomerization preceding unimolecular dissociations of the Fe^+ complexes. The most complex pattern, which involves up to four(!) hydrogen shifts from one alkyl chain across the Fe^+-complexed C=C=C unit to the other, is observed for 1,2- and 2,3-octadienes. (iii) Highly specific processes are demonstrated for Fe(3,4-octadiene)$^+$. Data are reported which are in keeping with the operation of an unprecedented degenerate isomerization. This process may question the conventional view that both vinylic and allylic C–C bond cleavages are operative in competition for Fe(allene)$^+$ complexes. Labeling experiments are mandatory for an understanding of the reaction pathways.

It is well established[1] that the isomerization process allenes ⇄ alkynes, which for the first time was described a century ago by Favorskii,[2] can be accomplished under quite a variety of conditions including base catalysis or enzymatic, thermal, or electrochemical activation. Although it is known that both the substrate and the actual conditions used affect the rates of isomerization and the extent to which the equilibrium may be shifted from the C≡C to the C=C=C system or vice versa, the understanding of the various factors is far from being complete.

In recent years it was demonstrated[3] that transition-metal complexes (in particular those containing MnL_3 fragments) mediate the *irreversible* isomerization of substituted acetylenes (E denotes an electron-withdrawing substituent) to allenes (eq 1).



$$\underset{MnL_3}{RCH_2C\equiv CE} \longrightarrow \underset{MnL_3}{RCH=C=CHE} \qquad (1)$$

Of particular interest, in quite a different context, are the reactions of allenes with *bare transition-metal ions*, like Fe^+, as these studies provide some insight into the elementary steps of the activation of C–H and C–C bonds. Indeed, this topic has emerged as a most fascinating and promising one over the last decade.[4] Moreover, a comparison of the gas-phase chemistry of complexes of unli-

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