bond distance, coordination number, Debye–Waller factor (Δs^2), and threshold energy (ΔE_0). The EXAFS radial distribution functions obtained by Fourier transformation have not been corrected for phase shifts (β), and therefore show deviations from actual neighbor distances R in real space by 0.02 to 0.05 nm. The apparent distances $R' = R + \beta$ are indicated in the corresponding figures.

The ^{31}P **MAS-NMR spectra** were obtained on a Bruker CXP-300 instrument. Andrews type rotors were filled with ca. 200 mg of sample in the drybox and introduced into the NMR probe in a glovebag under flowing nitrogen. Dry nitrogen was used as a drive gas for the rotor to obtain spinning rates between 2 and 4 kHz. A 30° to 90° pulse with 10-s recycle time was used, depending on the T_1, to obtain quantitative spectra. H-decoupling time was 20–60 ms. Chemical shifts were referred to 85% H_3PO_4. No significant oxidation of the samples was observed during the NMR experiments. The solution $^{31}P\{^1H\}$ NMR spectra were recorded in mixtures of pentane or hexane with C_6D_6.

Electron Micrographs were taken on an Hitachi H600 from microtomed sections of 80–90-nm thickness. Samples were embedded in EPON 812 under exclusion of air.

Molecular modeling was done with Chem-X software developed and distributed by Chemical Design Ltd., Oxford, England, on a VAX 8650 computer. Bond lengths and angles from known crystal structures were used wherever possible. Unknown structure parameters were estimated from known structures. Most structures had their van der Waals energy minimized by an iterative process which allowed rotation about single bonds and translation and rotation of the guest molecule within the fixed zeolite supercage.

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Registry No. $Ni(CO)_3P(t\text{-}Bu)_3$, 22955-41-5; $Ni(CO)_3PMe_3$, 16406-99-8; $Ni(CO)_2(PMe_3)_2$, 16787-34-1; $Ni(CO)_3PPh_2(CHMe_2)$, 112320-39-5; $Ni(CO)_4$, 13463-39-3; $Ni(allyl)_2$, 12077-85-9; NiO, 1313-99-1; Ni, 7440-02-0.

Matrix Photochemistry of (η^5-Cyclopentadienyl)bis(ethene)rhodium and (η^5-Cyclopentadienyl)(ethene)carbonylrhodium: A Test-Bed for Intermediates in C–H Activation

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Abstract: The photochemical reactivities of $CpRh(C_2H_4)_2$ (**1**) and $CpRh(C_2H_4)CO$ (**2**) (Cp = η^5-C_5H_5) have been examined in low-temperature matrices with IR and UV/vis detection. Photodissociation of ethene from **1** in inert matrices (Ar or CH_4) yields the coordinatively unsaturated $CpRh(C_2H_4)$; the reaction is reversed by long-wavelength irradiation. The identity of $CpRh(C_2H_4)$ is demonstrated with ^{2}H labeling of ethene and cyclopentadienyl groups. The IR results support a "bent", ground-state geometry for $CpRh(C_2H_4)$. UV photolysis of **1** in CO matrices releases ethene and generates **2** and $CpRh(CO)_2$ sequentially. The corresponding reaction in nitrogen matrices leads to $CpRh(C_2H_4)(N_2)$. On photolysis of **1** in CO-doped methane matrices, $CpRh(CO)(CH_3)H$ is formed in addition to substitution products. Complex **2** undergoes loss of either CO, yielding $CpRh(C_2H_4)$, or of C_2H_4, yielding CpRhCO, on UV photolysis in argon matrices. These reactions are reversed by long-wavelength photolysis, but in more concentrated matrices $Cp_2Rh_2(CO)_2$ is formed as an additional product. In nitrogen matrices both $CpRh(C_2H_4)(N_2)$ and $CpRh(CO)(N_2)$ are generated. In methane matrices $CpRh(C_2H_4)$ is still detected on UV photolysis, but CpRhCO is replaced by the product of oxidative addition of methane, $CpRh(CO)(CH_3)H$. Long-wavelength photolysis removes $CpRh(C_2H_4)$ but increases conversion to the (methyl)hydride complex. These experiments demonstrate that oxidative addition of methane must proceed via CpRhCO. The role of CpRhL (L = C_2H_4, CO) intermediates in solution reactions is discussed.

Some of the most successful of recent C–H activation reactions are thought to involve the dissociation of a small molecule from organometallic rhodium and iridium complexes in the primary step. Photochemical reactions of (η^5-C_5R_5)MLH_2 and (η^5-C_5R_5)ML_2 and thermal reactions of (η^5-C_5R_5)ML(H)R′ species (R = H, Me; R′ = alkyl; L = CO, phosphine, etc.; M = Rh, Ir) with alkanes have recently been postulated to proceed through (η^5-C_5R_5)ML, 16-electron intermediates.[1,2] Such fragments have excited considerable theoretical interest because of their carbenoid character and because both triplet and singlet states are available to them.[3] Attempts have been made to calculate the (ring-centroid)ML angle of the fragment and its dependence on spin state and to define those factors that stabilize the singlet state relative to the triplet.[3] However, experimental observation of these fragments has been extremely limited.

Photochemical matrix-isolation experiments on $Cp^*Ir(CO)_2$ (Cp^* = η^5-C_5Me_5) failed to induce CO loss in inert matrices, probably because of in-cage recombination. This conclusion has been confirmed in detailed studies of (η^5-C_5R_5)$M(CO)_2$ by Rest

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and Whitwell.[4] Only $CpRh(CO)_2$ gave appreciable conversion to the $(\eta^5\text{-}C_5R_5)MCO$ fragment, and even here the yields were very low. On the other hand, all these rhodium and iridium carbonyl complexes reacted photochemically in methane matrices to form $(\eta^5\text{-}C_5R_5)M(CO)(Me)H$.[4] Earlier observations of higher yields of Cp_2W on photolysis of $Cp_2W(C_2H_4)$ than on photolysis of Cp_2WCO[5] suggested that we should investigate the photochemistry of an ethene complex as a source of a CpML fragment. In this way the cage effect might be circumvented.

$CpRh(ethene)_2$ (**1**) is readily sublimed without decomposition and has strongly bound ethene ligands. Early work showed that **1** is inert to substitution by alkenes even at 100 °C,[6] but that thermal substitution by alkenes and by some phosphines does occur at >115 °C and proceeds by a dissociative mechanism. Substitution by some other phosphines, notably PMe_3 and PF_3, proceeds much more rapidly and at lower temperatures, with a significant contribution from an associative mechanism. One reagent, SO_2, even reacts at −78 °C to form a substitution product; *t*-BuCP displaces the bound ethene at room temperature. Complex **1** has also been used to effect H/D exchange in aromatic hydrocarbons at higher temperatures. A dissociative mechanism is postulated.[6]

At the outset of this work, no photochemical reactions of **1** had been recorded. The NMR spectrum of $CpRh(C_2H_4)CO$ has been reported very briefly,[7] but no chemistry of this complex has been mentioned. In this study, we will demonstrate that irradiation of $CpRh(ethene)_2$ (**1**) and CpRh(ethene)CO (**2**) can lead to photodissociation of ethene in low-temperature matrices. When photolyzed in inert matrices, molecular "fragments" are formed that can be characterized even in the absence of ν_{CO} modes. Irradiation in reactive matrices can lead to nucleophilic substitution and, in some circumstances, to methane activation. This work is a part of an extensive study in which the photochemistry of these and related ethene complexes is being investigated in hydrocarbon solution and in liquid xenon solution, as well as in low-temperature matrices. These studies are complemented by laser flash photolysis experiments in solution. Brief reports on some parts of this work have been published.[8-10]

Experimental Section

General Comments. Rhodium trichloride hydrate was obtained by generous loan from Johnson Matthey and used without further purification. C_2D_4 (99.4 atom %) and CD_4 (99 atom %) were obtained from MSD isotopes. Other matrix gases were purchased from BOC (research grade; 99.999%). Carbon monoxide and ethene for syntheses were purchased from BOC and Fisons, respectively (CP grade). Thallium cyclopentadienide, methanol-d_1, 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 with standard Schlenk or high vacuum techniques.

Matrices for infrared experiments were deposted by the slow spray-on method onto a cesium iodide or cesium bromide spectroscopic window cooled to 20 K with cesium iodide outer windows. For UV/vis experiments all three windows were made of barium fluoride, thus giving near perfect UV/vis transmission and allowing the IR spectrum to be monitored to 1100 cm^{-1}. Noncondensable gases were passed through a spiral liquid nitrogen trap on the low-pressure side of the needle valve prior to deposition. The rate of deposition of matrix gas was followed with a Baratron capacitance gauge. The window was cooled by a closed cycle helium refrigerator (Air Products CS202) mounted via a double O-ring seal in the stainless steel vacuum shroud. The system was pumped to better than 5×10^{-6} mbar prior to cooling and achieved better than 5×10^{-7} mbar cold. The trolley supporting the entire setup is mounted on tracks with overhead services, so that it can be wheeled readily between spectrometers. The position of the sample in the spectrometers may be reproduced to within 1 mm with the aid of a pair of photosensors mounted on the vacuum shroud, which receive light from a reflecting cross inscribed on a black plate. One such plate is mounted on each spectrometer; one sensor monitors the vertical position, the other the horizontal position. The entire shroud may be adjusted in each of three orthogonal directions with the aid of an *x*-*y*-*z* mount. Matrices for magnetic circular dichroism (MCD) were deposted onto a lithium fluoride window cooled by a liquid helium cryostat, described elsewhere.[11]

Matrices were photolysed with either a Philips cadmium arc, type 91362E (principal emission wavelengths: 326.1 and 228.8 nm), or a Philips HPK medium-pressure mercury arc in conjunction with a water filter to remove heat (path length = 5 cm). Selective wavelength irradiation was achieved with cutoff filters, a Schott interference filter (λ_{max} = 436 nm, full-width at half-maximum, fwhm = 10 nm), and a $NiSO_4/CoSO_4$ chemical filter ($220 < \lambda < 340$ nm).

Infrared spectra were recorded on a Perkin-Elmer 580A spectrometer. UV/vis spectra were recorded on a Perkin-Elmer Lambda 7G spectrometer and MCD spectra on a Cary 61 dichograph. Mass spectra were recorded on a Kratos MS3074 spectrometer by the University of York service. NMR spectra were recorded on a Bruker WP80 with ^1H at 80 MHz and ^{13}C at 20.15 MHz. Chemical shifts are reported in ppm downfield of tetramethylsilane but were recorded relative to residual benzene-d_5 (^1H δ = 7.15) and benzene-d_6 (^{13}C δ = 128.0 ppm).

Typical Conditions for Matrix Formation. $CpRh(ethene)_2$ (1). Matrix gas (7.5 mmol) was deposited over 180 min onto a spectroscopic window at 20 K. $CpRh(ethene)_2$ was codeposited simultaneously from a glass sidearm cooled to 265–273 K. Spectra were recorded before and after periods of ultraviolet irradiation through a silica window of the vacuum shroud.

CpRh(ethene)(CO) (2). Matrix gas (4.0 mmol) was deposited over 60 min onto a spectroscopic window at 20 K. Complex **2** was codeposited from a sidearm cooled to 228–233 K.

Syntheses. Published methods were used for the syntheses of $[(C_2H_4)_2RhCl]_2$,[12] $[(OC)_2RhCl]_2$,[13] $[(OC)(C_2H_4)RhCl]_2$,[14] $(C_5H_5)Rh(C_2H_4)_2$ (**1a**),[15] sodium cyclopentadienide,[16] and deuteriated sodium cyclopentadienide.[17]

$[(C_2D_4)_2RhCl]_2$. Attempts to prepare $[(C_2D_4)_2RhCl]_2$ by Cramer's method,[12] but replacing the C_2H_4 by C_2D_4, failed, probably because acid catalyzed H/D exchange with the solvent occurred giving $[(C_2H_4)RhCl]_2$ as the major product. Instead, 0.8 g of rhodium trichloride hydrate (3.0×10^{-3} mol) was heated at 120 °C in a stream of dry argon on a glass sinter for 120 min to remove water of crystallization. The rhodium trichloride was dissolved in 1 cm^3 of D_2O and 13 cm^3 of methanol-d_1 (CH_3OD) was added in a 200-cm^3 round-bottomed flask. The flask was filled to 1 atm with C_2H_4 and stirred at room temperature for 16 h. The product begins to precipitate as orange microcrystals after approximately 1 h. The reaction mixture is filtered and the residues washed with 4 cm^3 of ice cold methanol; yield 0.21 g (36%).

$(C_5D_5)Rh(C_2H_4)_2$ (1b). $((C_2H_4)_2RhCl)_2$ (0.26 g, 6.7×10^{-4} mol) and 0.60 g of $Na(C_5D_5)$ (5.4×10^{-3} mol) were dissolved in tetrahydrofuran. The reaction mixture was refluxed under argon for 30 min and was stirred subsequently at room temperature for 16 h. It was then filtered and dried in vacuo. The product was sublimed out of the residues at room temperature and 6×10^{-4} mbar. Mass spectral analysis showed the ring to be 89% deuteriated; yield 0.19 g (55%).

$(C_5D_5)Rh(C_2D_4)_2$ (1c). This complex was prepared as for $(C_5D_5)Rh(C_2H_4)_2$ replacing $((C_2H_4)_2RhCl)_2$ with $((C_2D_4)_2RhCl)_2$. Mass spectral analysis showed the ring to be 91% deuteriated and the ethene ligands to be 89% deuteriated.

$(C_5H_5)Rh(C_2H_4)CO$ (2). $((C_2H_4)(CO)RhCl)_2$ (0.38 g, 9.8×10^{-4} mol) of was dissolved in hexane. Thallium cyclopentadienide (1.37 g, 5.7×10^{-3} mol) was added to the solution, and the mixture was stirred for

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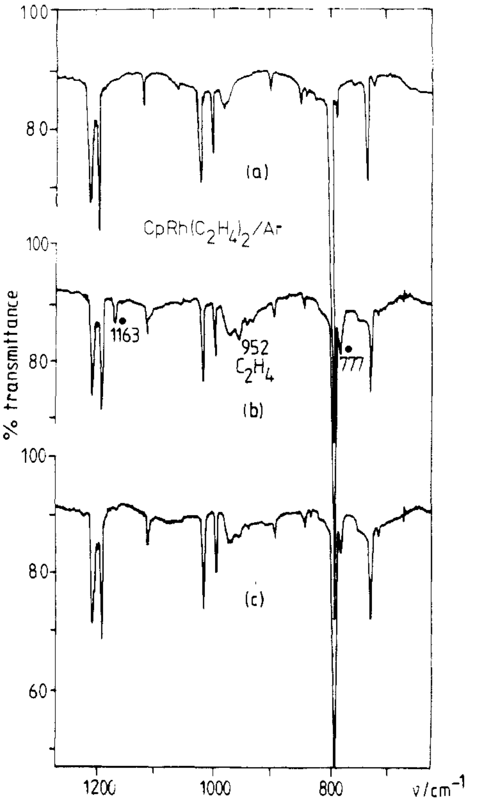

Figure 1. (a) Infrared spectrum of CpRh(C_2H_4)$_2$ (**1a**) in argon at 20 K (sublimation temperature, T_s = 273 K, deposition time, t_d = 130 min, 4.2 mmol of Ar); (b) after 900 min of irradiation with Cd arc (λ = 326, 229 nm) showing growth of bands of C_2H_4 and **3** (●); (c) after a further 150 min of irradiation at λ = 436 nm showing partial reversal of reaction.

30 min. The solution was filtered and the solvent was removed from the filtrate in vacuo to leave a dark green oil. The product is contaminated at this stage with small amounts of CpRh(CO)$_2$ and a green impurity, possibly [CpRh(CO)]$_3$,[18] most of which can be removed by extracting with hexane, or by fractional sublimation (procedure due to Dr. M. Arthurs, private communication). The pure material is a thermally unstable volatile yellow oil that was characterized in solution. ^{1}H NMR δ 4.86 (d, 5 H, C_5H_5Rh, *J*(Rh–H) = 0.4 Hz), 2.52 (s, br, 4 H, RhC_2H_4). ^{13}C NMR δ 87.9 (d, C_5H_5Rh, *J*(Rh–C) = 3.8 Hz), 31.30 (d, RhC_2H_4, *J*(Rh–C) = 13.3 Hz). IR (hexane) 1988 (s) cm^{-1}.

Results

Photochemistry of 1 in Argon and Methane Matrices. The most intense infrared bands of **1a** in an argon matrix are at 1198, 1186 ($\nu_{CC} - \delta_{CH_2}$, ethene) and 784 cm^{-1} (δ_{CH}, C_5H_5, Figure 1a). These bands are shifted to 953, 945, and 590 cm^{-1} respectively on complete deuteriation (**1c**). Their assignments will be discussed in detail elsewhere. In the ultraviolet, **1** exhibits a prominent band at 220 nm with a weaker band at 266 nm, a shoulder at 306 nm, and a tail stretching into the visible. Irradiation (Cd arc) of **1a** in an argon matrix for 900 min leads to the appearance of new bands in the infrared spectrum and a 21% decrease in the intensity of the bands due to the starting material (Figure 1b). No free ethene is observed prior to photolysis, but its characteristic bands are seen in the matrix at 952 cm^{-1}, ν_7, and at 1441 cm^{-1}, ν_{12}, following irradiation.[19] A second product, **3a**, has absorptions at 1163 and 777 cm^{-1}. Figure 1c illustrates the effects on the IR spectrum of 150 min of irradiation at 436 nm (irradiation with λ >416 nm is equally suitable). All product bands decrease in intensity. The band of the product **3a** at 1163 cm^{-1} is no longer detectable in the spectrum; meanwhile the starting material bands return to approximately 87% of their original intensity. The band of free ethene decreases but does not disappear entirely from the spectrum. The products **3a** and C_2H_4 can be reformed on further UV irradiation (only 120 min). Annealing the matrix to approximately 40 K has no effect on the spectrum, indicating that the reaction is not thermally reversible at this temperature. One of the cadmium emission lines coincides with the most intense absorption of the starting material and causes more efficient conversion to products than UV radiation from a mercury arc. The lack of complete reversibility suggests that some dimeric or secondary photolysis product may be generated, but no IR bands have been detected for this product. When the matrix is diluted by reducing the sublimation temperature from 273 to 265 K, reversibility remains imperfect.

Similar experiments were carried out with UV/vis (200–800 nm) and IR detection (1000–4000 cm^{-1}) on the *same* matrix. When the sublimation temperature was 273 K, a product was observed on Cd arc photolysis with UV/vis bands at 250, 302, 366, and ca. 490 nm, together with the characteristic IR band of **3a**. However, on long-wavelength photolysis the UV/vis bands increased slightly, while the IR band disappeared. These UV bands are therefore assigned to the irreversible product (contrary to our initial assignment).[8] Using deposition from a sample at 265 K, we generated **3a** with much less interference from the irreversible product and showed reversible formation of an intense UV band at 269 nm with a shoulder at 294 nm and a broad, weak maximum at 420 nm. The spectra of these two products were separated most effectively by difference spectroscopy at the end of a sequence of deposition (i), Cd arc (ii), and λ = 436 nm (iii). Thus (iii) – (i) revealed the spectrum of the irreversible product and (ii) – (iii) the spectrum of the reversible product, in either case relative to lost precursor, **1**.

The reaction of **1a** in argon has also been followed by MCD spectroscopy. After 60 min of irradiation with the Cd arc a very weak MCD signal is detected. The intensity of the signal is temperature independent between 4.5 and 15 K, indicating the presence of diamagnetic species only.

Irradiation of **1b**, (C_5D_5)Rh(C_2H_4)$_2$, in an argon matrix results in the loss of starting material with the explusion of ethene, 952 cm^{-1}. A further new band in the spectrum is seen at 1162 cm^{-1} (**3b**), but no product band is observed at 777 cm^{-1}. The reaction can again be reversed by irradiation at 436 nm. Irradiation of **1c**, (C_5D_5)Rh(C_2D_4)$_2$, in an argon matrix results in the loss of starting material and release of C_2D_4 into the matrix (721 cm^{-1}).[20] Other product bands are observed at 1277 and 934 cm^{-1} (**3c**). Again the reaction is reversed by photolysis at longer wavelength. Table I summarizes the spectral properties of the products observed on photolysis of **1** in inert matrices.

Irradiation of **1a** in methane matrices results in very similar changes in the infrared spectrum to those observed in argon matrices, but the reaction proceeds in far higher yield (Figure 2). Irradiation for 240 min with the Cd arc results in a 45% decrease in starting material with the release of ethene, 952 cm^{-1}, and production of **3a** (Figure 2b, most intense bands at 1169 and 783 cm^{-1}, for further bands see Table I). Use of the Cd arc with a λ >280 nm filter shows that both of the major emission lines (229 and 326 nm) are photoactive. The reaction is reversed by photolysis at 436 nm (Figure 2c). The reaction was also monitored by simultaneous UV/vis and IR spectroscopy (Figure 3) on a dilute sample (sublimation temperature 265 K). The bands of **1a** recovered to >90% of their original intensity on photolysis at λ >416 nm (Figure 3c). The method using difference spectroscopy described above revealed UV bands of the reversible product **3a** at 262, 297, and ca. 399 nm and a small amount of irreversible product with bands at 296 and 372 nm (Figure 3b).

On irradiation of **1c** in methane, a band of free C_2D_4 (722 cm^{-1}) and two other product bands at 937 and 592 cm^{-1} are observed (Figure 4). The band at 592 cm^{-1} appears between two bands from **1c** and is detected as a loss of resolution of these bands.

Irradiation of **1a** in a CD_4 matrix results in new bands at 1169 and 783 cm^{-1} with ethene at 953 cm^{-1}. The use of labeled methane as the host has no effect on the product absorptions. The pho-

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Table I. IR and UV/Vis Spectra of Photolysis Products of $CpRh(ethene)_2$ in Inert Matrices

precursor/matrix						
$(C_5H_5)Rh(C_2H_4)_2$, **1a**			$(C_5D_5)Rh(C_2H_4)_2$, **1b**	$(C_5D_5)Rh(C_2D_4)_2$, **1c**		
Ar	CH_4	CD_4	Ar	Ar	CH_4	assignment
			IR, $\bar{\nu}$/cm^{-1}			
1441	–	–	–	–	–	ν_{12}, C_2H_4
–	–	–	–	1277	–	**3**
1163	1169	1169	1162	934	937	$\nu_{CC} - \delta_{CH_2}$, **3**
–	1009	–	–	–	–	**3**
–	972[a]	–	–	–	–	**3**
952	954	953	952	721	722	ν_7, C_2H_4
–	940 935 932	–	–	–	–	ν_7, C_2H_4, perturbed
777[a]	784	783	–	–	592[a]	δ_{Cp}, **3**
			UV/Vis, λ/nm			
269	262		–	–	–	**3**
295	297 sh		–	–	–	**3**
ca 420	ca 400		–	–	–	**3**
250	–		–	–	–	irreversible product
302	296		–	–	–	irreversible product
366	372		–	–	–	irreversible product
490	–		–	–	–	irreversible product

[a] Overlaps with precursor.

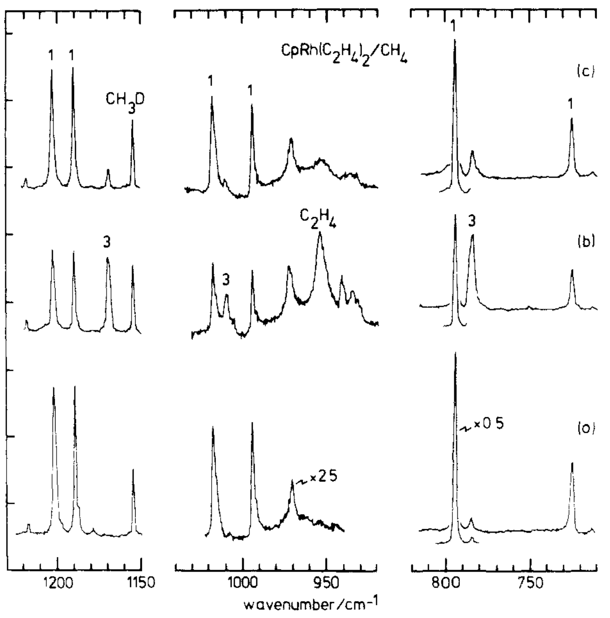

Figure 2. (a) IR spectra of **1a** in methane matrix at 20 K (T_s = 265 K, t_d = 180 min, 6.5 mmol of CH_4); (b) after 240 min of irradiation with the Cd arc showing bands of free C_2H_4 and of **3**; and (c) after 120 min of irradiation at λ >416 nm showing reversal of reaction.

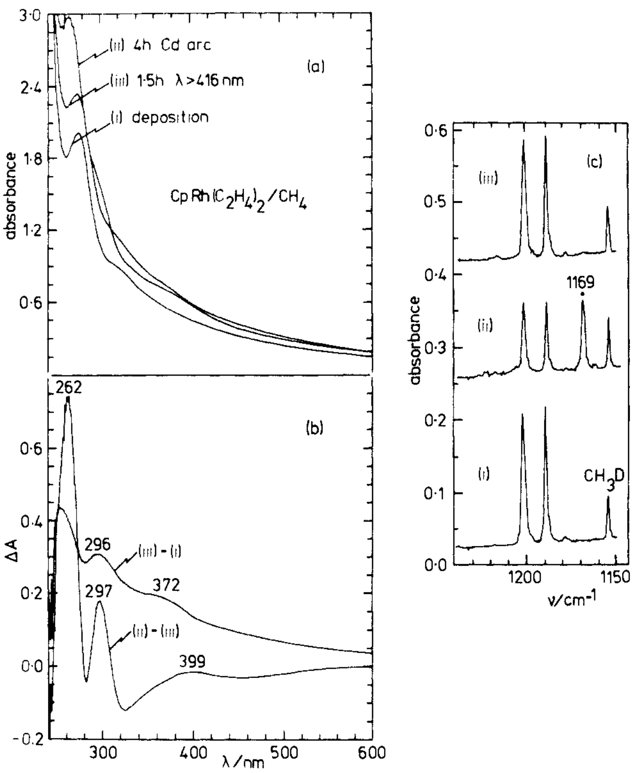

Figure 3. UV/vis (a) and IR (c) spectra of **1a** in methane matrix at 20 K measured on the same sample (T_s = 265 K, t_d = 130 min, 4.3 mmol of argon) (i) after deposition, (ii) after 240 min of Cd arc photolysis, (iii) after 90 min of further photolysis λ >416 nm; (b) difference spectrum (ii) − (iii) giving the spectrum of the reversible product, **3**, and difference spectrum (iii) − (i) giving the spectrum of the irreversible product.

toproduct cannot, therefore, be formed by a reaction of an organometallic fragment with methane.

These experiments demonstrate the conversion of **1** into three photoproducts: one organometallic species, **3**, and some ethene are generated reversibly, a second organometallic species, detected only in the UV, and further ethene are generated irreversibly. The quantum yield for the reaction is low and is dependent on the host matrix. The organometallic product is identical in both CH_4 and CD_4 and the bands are shifted only marginally from their positions in argon, indicating that oxidative addition of methane does not occur. Specific solvation by methane remains a possibility. The reversible production of ethene demonstrates that the product, **3**, must be assigned as the co-ordinatively unsaturated CpRh(ethene) rather than an isomer of **1**. It has been demonstrated previously that long-wavelength irradiation of a co-ordinatively unsaturated metal fragment produced in a low-temperature matrix often leads to reversal of the original photodissociation.[21] The band from **3a** at 1163 cm^{-1} shifts by only 1 cm^{-3} on ring deuteriation (**3b**), but by a factor of 1.24 on complete deuteriation (**3c**), showing it to be a mode of co-ordinated ethene. (If the vibrational mode was from a pure CH movement then we would expect a shift by a factor of approximately 1.3–1.4 on deuteriation.) The observed shift shows that this vibration contains a significant contribution from CC vibration and should be assigned as (ν_{CC} - δ_{CH_2}). The most intense absorption from **3a** (777 cm^{-1} in argon) shifts by a characteristic factor of 1.32 on deuteriation and is assigned as a CH deformation of the cyclopentadienyl ring.

The evidence for the assignment of the irreversible product is less conclusive. The sharpness of the IR bands of **1** (fwhm 1.5–3

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[21] Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

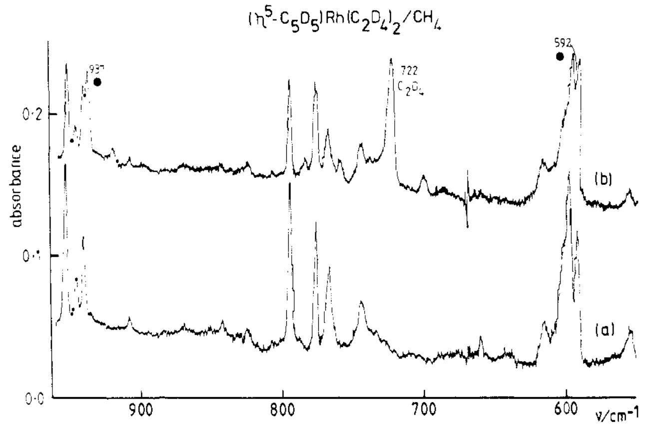
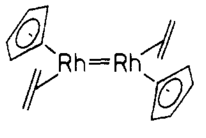
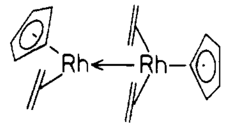


Figure 4. (a) IR spectrum of $(C_5D_5)Rh(C_2D_4)_2$ (**1c**) in CH_4 matrix at 18 K (T_s = 273 K, t_d = 240 min); (b) after 1020 min of Cd arc photolysis showing growth of **3c** (●) and C_2D_4.

cm^{-1}, Figure 1a) indicates good isolation. Nevertheless, the effect of dilution, our experience with **2** (see below), and the intense UV/vis product bands suggest a dimer such as D1 or D2. Complex D1 may be compared to $[CpRhCO]_2$,[22] while D2 has precedent in complexes such as $[Cp^*(CO)_2IrW(CO)_5]$ with donor-acceptor metal–metal bonds.[23]



D1



D2

Photochemistry of 1 in Nitrogen and Carbon Monoxide Matrices. Irradiation of **1a** in a nitrogen matrix for 3 min at λ >200 nm produces an intense band in the infrared spectrum at 2178 cm^{-1}. Further photolysis increases the intensity of this band until after 60 min it is the most intense band in the spectrum and approximately 25% of **1a** is lost. Ethene is released into the matrix (948 cm^{-1}) and there is a weak product absorption at 1185 cm^{-1}. Irradiation of **1a** in a mixed 60% $^{14}N_2$:40% $^{15}N_2$ matrix causes a 40% loss of **1a** and produces two intense product bands at 2178 and 2107 cm^{-1} (Figure 5). A weak band at 1185 cm^{-1} is again present and ethene is seen at 948 cm^{-1}. These results demonstrate that photolysis generates the dinitrogen complex $CpRh(C_2H_4)N_2$ (**4**), with an intense ν_{NN} mode at 2178 cm^{-1}. The isotopic shift of 72 cm^{-1} compares very well with that calculated for an isolated NN oscillator: 73 cm^{-1}. The weak band at 1185 cm^{-1} can be assigned to (ν_{CC} - δ_{CH_2}) of **4**; the expected Cp mode of the product is probably hidden under the 785-cm^{-1} absorption of **1a**. The substitution reaction does not proceed to the bis(dinitrogen) species. There is no evidence for the production of **3a**, suggesting that it reacts rapidly with nitrogen to give **4**.

Irradiation of **1a** in a carbon monoxide matrix for 6 min at λ >200 nm produces two terminal ν_{CO} bands at 2050 and 1989 cm^{-1} (Figure 6) with a small amount of free ethene in the matrix, 953 cm^{-1}. After 16 min of photolysis, the loss of starting matrial is ca. 44% and a large amount of free ethene is released into the matrix, so ν_{12} is now detectable at 1438 cm^{-1} (Figure 7). The intensity ratio of the ν_{CO} bands changes from 1:3.6 to 1:1.8 (Figure 6b,c). A weak product absorption is observed at 1195 cm^{-1} and the resolution of the bands around 795 cm^{-1} is lost due to underlying product bands. Four new bands are seen at low frequency: 575, 556, 525, and 499 cm^{-1} (Figure 7). After a further 80 min of photolysis, loss of **1** is ca. 80% and both ν_{CO} bands have an absorbance exceeding one.

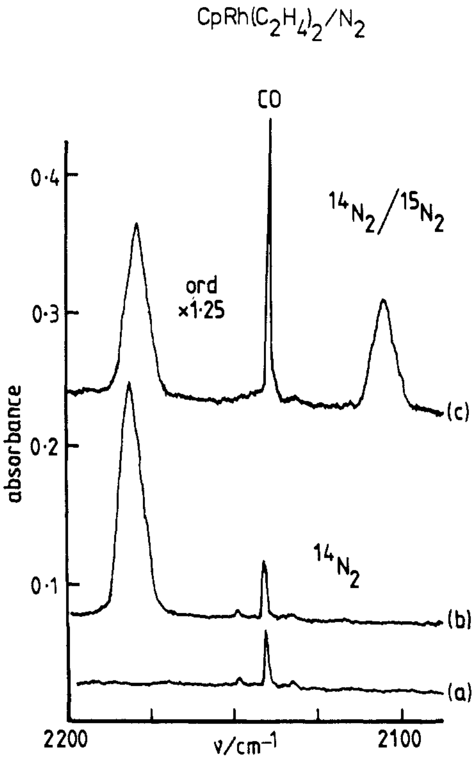


Figure 5. (a) IR spectrum in the NN stretching region of **1a** in N_2 matrix at 20 K (T_s = 273 K, t_d = 180 min, 6.4 mmol of N_2), the band at 2140 cm^{-1} is due to CO impurity; (b) after 9 min of photolysis with water-filtered Hg arc showing production of **4** (at this stage 17% of **1** has reacted); (c) spectrum after 10 min of photolysis of **1a** in a $^{14}N_2/^{15}N_2$ (60:40) matrix, showing $\nu_{^{14}N^{14}N}$ and $\nu_{^{15}N^{15}N}$ of **4** and its labeled counterpart.

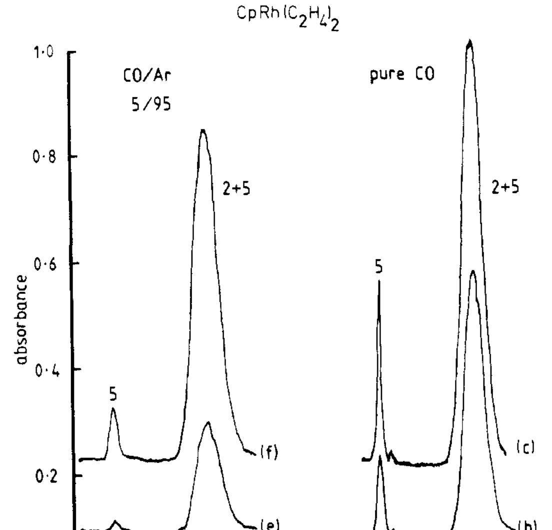


Figure 6. (a) IR spectrum in the CO-stretching region of **1a** in CO matrix at 20 K (T_s = 269 K, t_d = 170 min, 8.2 mmol of CO); (b) after 6 min of irradiation with water-filtered Hg arc showing ν_{CO} bands of **2** and **5**; (c) after a further 5 min of photolysis; (d) spectrum before photolysis of **1a** in CO/Ar (5:95) matrix at 20 K (T_s = 269 K, t_d = 170 min, 6.6 mmol of gas mixture); (e) after 3 min of photolysis; (f) after a further 5 min of photolysis. Notice the changing intensity ratio of the two product bands.

Irradiation of **1a** for 3 min in a dilute CO/Ar matrix (5% CO:95% Ar) generates one intense terminal ν_{CO} band at 1989 cm^{-1} with a weaker band at 2048 cm^{-1} (intensity ratio of 2048:1989 cm^{-1} bands = 1:12); a band at 553 cm^{-1} also appears on photolysis. On irradiation for a further 5 min, all product bands increase in intensity but the intensity ratio of the two ν_{CO} bands changes to 1:6.5 (Figure 6e,f). The different relative intensities of the two

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[22] Anderson, F. R.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 112.

[23] Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Organometallics* **1985**, *4*, 250.

Table II. IR Data for the Photoproducts of **1a** in Matrices Containing CO or N_2, ν/cm^{-1}

matrix			matrix			
$^{14}N_2$	$^{14}N_2/^{15}N_2$	assignment	CO	CO/Ar	CO/CH_4	assignment
2178	2179	$\nu_{^{14}N^{14}N}$, **4**	2050 s	2048 w	2049 s	ν_{CO}, **5**
	2107	$\nu_{^{15}N^{15}N}$, **4**			2024 w	ν_{CO}, **7**
1185 sh	1185 sh	$\nu_{CC} - \delta_{CH_2}$, **4**	1989 vs	1989 vs	1986 vs	ν_{CO}, **2** + **5**
948	948	ν_7, C_2H_4	1438			ν_{12}, C_2H_4
			1195			$\nu_{CC} - \delta_{CH_2}$, **2**
			953		943	ν_7, C_2H_4
			798[a]			δ_{Cp}, **2**
			575			δ_{MCO}, **5**
			556	553		δ_{MCO}, **2**
			525			δ_{MCO}, **5**
			499			δ_{MCO}, **5**

[a] Overlaps with precursor bands.

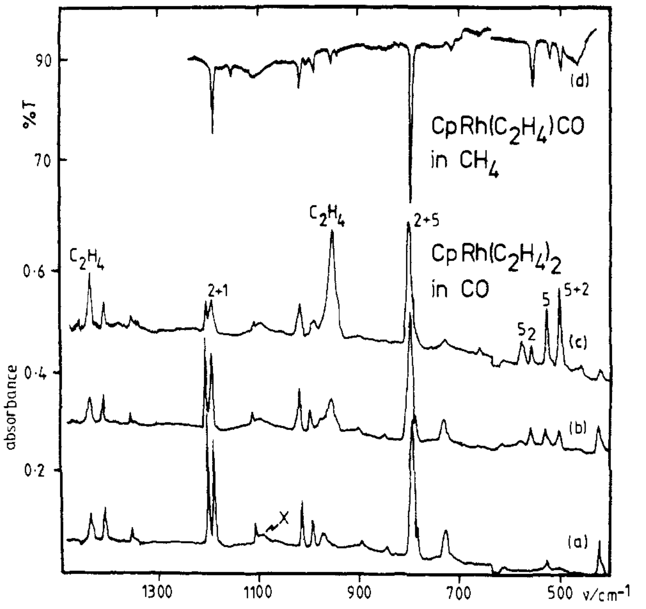


Figure 7. (a) IR spectrum of **1** in CO matrix (conditions as in Figure 5); (b) after 11 min of Hg arc photolysis; (c) after annealing to 38 K, recooling followed by a further 93 min of photolysis showing growth of bands of **2**, **5**, and C_2H_4; (d) spectrum of **2** deposited directly into a CH_4 matrix (T_s = 249 K, t_d = 55 min, 4.2 mmol of CH_4).

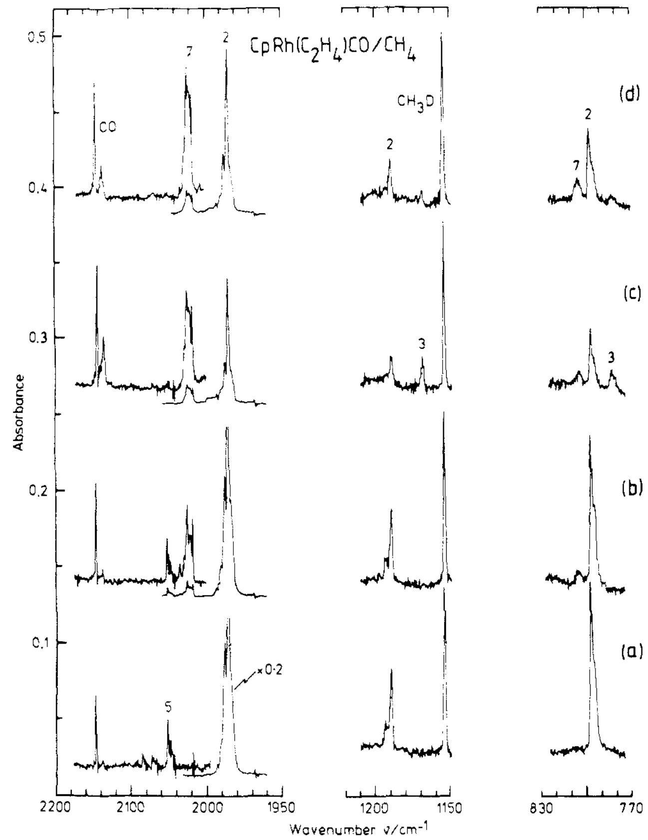


Figure 8. (a) IR spectrum of **2** in CH_4 matrix at 12 K (T_s = 228–232 K, t_d = 210 min, 6.9 mmol of CH_4); (b) after 240 min of irradiation at λ >365 nm showing bands of **7**; (c) after a further 420 min of irradiation with Cd arc showing growth of **7** and appearance of bands of **3**; (d) after 300 min of irradiation at λ >416 nm showing further growth of **7** and loss of **3**.

ν_{CO} bands between the two experiments indicate the presence of two distinct products.

Rest has shown that $CpRh(CO)_2$ has two equally intense bands at 2049 and 1985 cm^{-1} in an argon matrix.[4] The band at 2048 cm^{-1} in our experiment and an equal contribution to the band at 1989 cm^{-1} can, therefore, be assigned to $CpRh(CO)_2$ (**5**). The use of a more dilute matrix allows more control over the reaction and the dominant product becomes the monocarbonyl CpRh(ethene)(CO), **2**, ν_{CO} = 1989 cm^{-1} (cf. 1996 cm^{-1} for **2** matrix isolated in argon, see later). The changes in relative intensity induced by diluting the matrix show that this reaction is a sequential substitution of ethene by carbon monoxide. The low-frequency bands are assigned on the basis of their behavior in the dilute matrix (Table II) and by comparison with the matrix spectrum of **2** deposited directly (Figure 7).

It is to be expected that the conversion of **2** into **5** proceeds via the CpRh(CO) (**6**) intermediate. This fragment has been shown previously to activate methane under these conditions, but it has been observed only in very small yields in an inert matrix.[4] Irradiation of **1a** in a 10% CO:90% CH_4 matrix for 60 min with the Cd arc leads to the production of one strong terminal ν_{CO} band at 1986 cm^{-1}, **2**, together with two weaker bands at 2049 cm^{-1}, **5**, and 2023 cm^{-1}. Complex **3** is seen at 1169 cm^{-1} and ethene at 943 cm^{-1}. Subsequent irradiation at longer wavelength (λ >290 nm) removes all **3** and causes a substantial increase of **2**. There is little change in the band at 2023 cm^{-1}, but it increases after further short wavelength photolysis. The new band at 2023 cm^{-1} is assigned to ν_{CO} of $CpRh(CO)(CH_3)H$ (**7**), by comparison with the value quoted by Rest (2024 cm^{-1}).[4]

Scheme I summarizes the reactions of **1** in low-temperature matrices.

Photochemistry of 2. The photochemistry of **1** presented above suggested that irradiation of matrix-isolated **2** might provide an efficient way of characterizing **6**. The infrared spectrum of **2** in low-temperature matrices exhibits one intense split ν_{CO} band with its most intense component at 1997 cm^{-1} (argon, Figure 8a). In all experiments the matrix was contaminated with small amounts of the dicarbonyl, **5**, CO and traces of ethene. The low-frequency region of the spectrum has two bands of medium intensity at 1183 and 789 cm^{-1} (also complicated by matrix splittings) and δ_{MCO} modes at 554 and 524 cm^{-1} (Figure 7). The UV/vis spectrum of **2** in an argon matrix has λ_{max} at 220 nm with a shoulder at 269 nm which tails well into the visible.

Irradiation of **2** in an argon matrix for 900 min with the Cd arc (Table III) results in a 40–50% loss of starting material and the appearance of new bands at 2139 cm^{-1} (free CO), 1970 cm^{-1},

Scheme I. Matrix Photochemistry of $CpRh(C_2H_4)_2$

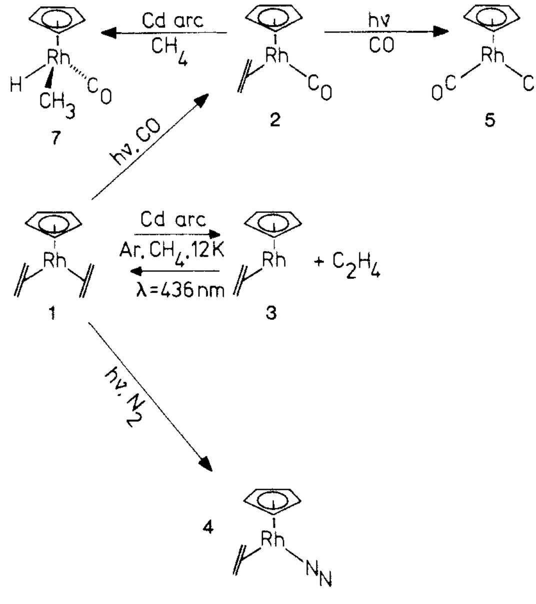


Table III. IR Data for Matrix Photoproducts of **2**, $\bar{\nu}$/cm^{-1}

matrix			
Ar	CH_4	N_2	assignment
–	–	2208	ν_{NN}, **8**
–	–	2178	ν_{NN}, **4**
2139	2137	2140	CO
–	2025 2021 2018	–	ν_{CO}, **7**
1976^a	–	–	unassigned
1970	–	–	ν_{CO}, **6**
1965 sh			
1791^a	–	1787	ν_{CO}, $[CpRh]_2(\mu_2\text{-}CO)_2$
–	–	1186	$\nu_{CC} - \delta_{CH_2}$, **4**
1163	1169	–	$\nu_{CC} - \delta_{CH_2}$, **3**
952	954	948	ν_7, C_2H_4
–	805	–	δ_{Cp}, **7**
–	–	794 792	δ_{Cp}, **4**
777	783	–	δ_{Cp}, **3**

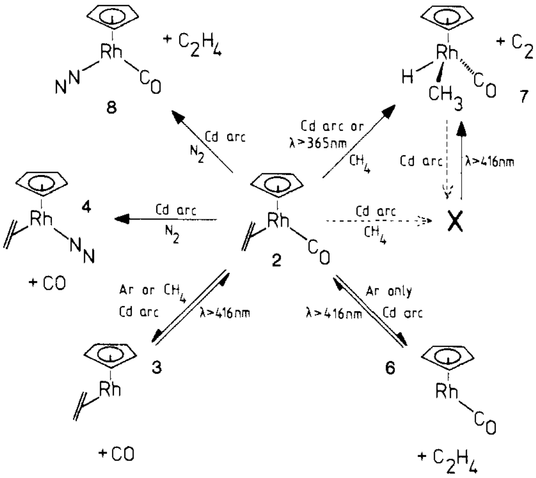
^{a} Observed in concentrated matrices only.

1163 cm^{-1} ($\nu_{CC} - \delta_{CH_2}$ of **3**), and 952 cm^{-1} (free ethene). The exact degree of conversion is hard to estimate because there are considerable changes in the matrix splittings of the precursor bands on photolysis. Irradiation at longer wavelength, λ >416 nm, results in a substantial decrease in all product bands and an increase in bands of **2**. Photodissociation can be repeated by further UV irradiation. When the matrix is more concentrated, further product bands are observed at 1791 and 1976 cm^{-1}.

Rest has reported the ν_{CO} band of CpRhCO (**6**) at 1968 cm^{-1} when formed by irradiation of **5** in an argon matrix. Our product band at 1970 cm^{-1} may be assigned to **6**. However, the source of **6** in our experiment must be **2** since the bands of impurity **5** are weak and do not change in intensity, whereas those of **2** change reversibly. Thus UV photolysis of **2** in solid argon causes reversible loss of either CO or C_2H_4 to form **3** or **6**, respectively. Wrighton has reported that the photolysis of $Cp_2Rh_2(CO)_3$ in low-temperature organic glasses results in rapid loss of carbon monoxide to produce the doubly bridged product with ν_{CO} at 1778 cm^{-1}.[22] The band observed in concentrated matrices at 1791 cm^{-1} is assigned as ν_{CO} of the bridging carbonyl of this dimerization product. This product was also observed at 1793 cm^{-1} on photolysis of **5** in Ar matrices.[4] We have confirmed the assignment to $[CpRh]_2(\mu\text{-}CO)_2$ by photolysis of $Cp_2Rh_2(CO)_3$ in Ar matrices. A similar postulate was made by Rest for $[(\eta^5\text{-}C_5Me_5)Rh(CO)]_2$.[4]

Irradiation of **2** in a methane matrix for 240 min with λ >365 nm (Figure 8b) causes formation of ethene (954 cm^{-1}) and a new terminal ν_{CO} band at 2025 cm^{-1} (with matrix splittings). At this stage, the trace of **5** is unaffected. The band at 2025 cm^{-1} is assigned to the (methyl)hydride complex **7** by comparison with earlier experiments in which it was formed from **1** in CO/CH_4 matrices (see below). After 420 min of further photolysis with the Cd arc, the precursor, **2**, decreases to ca. 35% of its original intensity, all **5** disappears, ethene and **7** increase, and in addition, CO (2139 cm^{-1}) and **3** (1169 cm^{-1}) are formed (Figure 8c). A final stage of long-wavelength photolysis (λ >416 nm) removes most of **3**, reduces CO, but causes growth of precursor, **2**, and of the 2025-cm^{-1} band (Figure 8d). Further experiments were performed in which photolysis with the Cd arc and λ >416 nm was alternated. This sequence demonstrated growth of **2** and **7** and decay of **3** after long-wavelength photolysis, alternating with decay of **2** and **7** but growth of **3** after short-wavelength photolysis. The implication is that **2**, **3**, and **7** are all involved in photostationary states. There is no evidence for any dimeric species.

Scheme II. Matrix Photochemistry of $CpRh(C_2H_4)CO$



Although we can generate **7** in the virtual absence of **5** (absorbance of **7** >12 times absorbance of **5**), like Rest et al. we have not identified any ν_{RhH} mode for **7**. Metal–hydride stretching modes are often much weaker than ν_{CO} modes, so the absence of ν_{RhH} should not be taken as evidence against the assignment. Rest et al. have succeeded in identifying ν_{IrH} modes in related iridium complexes.[4] They have also examined isotopic effects on ν_{CO} by use of CD_4 matrices for several closely related molecules and have found slight but significant shifts. In common with them, we consider the assignment of **7** to $CpRh(CO)(CH_3)H$ to be reliable.

Complex **7** must be formed by photochemical loss of ethene from **2**, followed by rapid reaction with the matrix. This can be achieved selectively with irradiation at λ >365 nm. The immediate source of **7** formed on longer wavelength photolysis (λ >416 nm) is not **2**, however, since initial photolysis at this wavelength is ineffective. The identity of this intermediate, X, is unknown; no alternative carbonyl source for **7** could be identified.

Irradiation of **2** in a nitrogen matrix for 145 min with the Cd arc causes 30% loss of **2** and produces two ν_{NN} bands at 2008 and 2178 cm^{-1} together with free carbon monoxide at 2140 cm^{-1}. The band at 2178 cm^{-1} is assigned to the ν_{NN} of **4** formed following loss of carbon monoxide from **2**. The band at 2208 cm^{-1} is assigned to ν_{NN} of $CpRh(CO)N_2$, **8**, by comparison with the results of Rest and Whitwell.[4] The ν_{CO} band of **8** is reported to be at 1993 cm^{-1} in a nitrogen matrix and is obscured by ν_{CO} of **2** (1992.5 cm^{-1}). In a dilute matrix, conversion to products exceeds 80%, with a strong preference for CO loss over C_2H_4 loss. Thus, the ν_{NN} band of **4** is 24 times more intense than that of **8**. Prolonged irradiation results in the formation of the $Cp_2Rh_2(CO)_2$ dimer seen at 1787 cm^{-1}. The dimer band is significantly more intense in concentrated matrices.

Scheme II shows the reactions of **2** in low-temperature matrices and Table III the infrared data of the products.

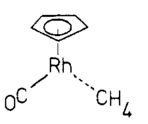
Discussion

Photochemical Pathways. The primary photoprocess on irradiation of **1** is the dissociation of ethene. This reaction is reversed by irradiation at longer wavelength coinciding with weak absorptions of the organometallic photoproduct in the near-UV. The loss of ethene from both **1** and **2** and carbon monoxide from **2** has been shown to be reversible by irradiation of the photogenerated organometallic fragments. This is characteristic of coordinatively unsaturated species in matrices. In more concentrated matrices, dimers are formed irreversibly. In the case of **1**, the dimer has not been identified conclusively but may have structure D1 or D2; the established carbonyl dimer $[CpRh(CO)]_2$ is formed from **2**. Dissociation of ethene is not the only pathway available on photoexcitation of a metal–ethene complex. Kafafi has reported that irradiation of $Fe(C_2H_4)$ in low-temperature matrices results in an insertion to give the vinyl hydride $HFe(C_2H_3)$.[24] Irradiation of $CpIr(C_2H_4)_2$ in either low-temperature matrices or solution also results in insertion to give a vinyl hydride compound;[25] similar insertions have been observed in other complexes recently.[26] However, on photolysis of $CpRh(C_2H_4)_2$ we have never observed any evidence for a $\nu_{C=C}$ mode, characteristic of a (vinyl) hydride.

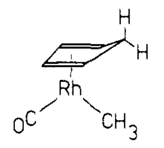
Ultraviolet photoelectron spectroscopy has shown that the HOMO of **1** has high ethene π-bonding character, in agreement with EHMO calculations.[27] If we assume, as is likely, that the LUMO is metal–alkene antibonding, a simple one-electron model predicts that HOMO to LUMO excitation will result in a considerable weakening of the metal–ethene bond and dissociation. In practice the LUMO may be populated via higher states and internal conversion. This excitation process is similar to that occurring on irradiation of carbonyls, population of the σ-antibonding orbital being of most importance in promoting carbonyl dissociation.

Substitution reactions with carbon monoxide and nitrogen demonstrate the possible synthetic applications of photolytic substitution of a strongly bound ethene ligand. The formation of **7** from **1** in a CO-doped methane matrix is more efficient than the direct reaction with **5**. Thus the replacement of an ethene ligand can be more useful than that of a carbonyl ligand. The rapid photochemical reaction with CO suggests that the quantum yield for loss of C_2H_4 from **1** may be as high as for many metal carbonyls. However, the effective yield in argon and, to a lesser extent, in methane is reduced by in-cage recombination.

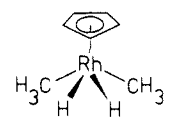
Irradiation of **2** results in competitive ethene and carbon monoxide loss as the primary processes, and thus produces a mixture of products. However, loss of ethene has been shown to predominate in solution.[8] Photolysis in argon occurs under conditions where $CpRh(CO)_2$ shows negligible reaction. Photolysis in methane results in the formation of **7**, instead of **6**. These results taken together with those from the irradiation in inert matrices demonstrate that CpRhCO is an intermediate in this C–H activation reaction. This dissociative pathway accords with a considerable body of kinetic evidence.[1] Significantly, the oxidative addition can be stimulated selectively with $\lambda > 365$ nm. When photolyzed with the Cd arc followed by $\lambda > 416$ nm, the conversion to **7** increases in both steps, although no other carbonyls are detected. Subsequent Cd arc photolysis reduces the intensity of **7** again. These reactions suggest a photoinduced equilibrium between $CpRh(CO)(CH_3)H$ and another product X, as in Scheme II. We have considered three possibilities for X as shown below, a CH_4 complex,[21] a metal–ring hydrogen migration,[28] and a Rh(V) complex.[8,29] There is a precedent for each, but we cannot distinguish them at present. The most likely is a diene complex, b, its ν_{CO} band overlapping with that of **2**. Our spectra do not support Rest's assignment of a band at 1992 cm^{-1} to a methane complex.[4]



a



b



c

Structure of 3. CpRhL is a carbenoid fragment that could be bent or linear at rhodium, singlet or triplet. At the C_{5v} extreme, available to CpRhCO but not $CpRh(C_2H_4)$, it *must* be a triplet since it has a doubly degenerate HOMO occupied by two electrons. If the (ring-centroid)ML angle is reduced, the symmetry is also reduced and the degeneracy of the HOMO is lifted. In consequence, if the molecule has a bent geometry, it could adopt either a singlet or a triplet ground state, depending on the energy separation between the molecular orbitals. Unfortunately, EHMO calculations on the CpRhCO fragment designed to calculate the spin ground state have been contradictory.[3a,b] Calculations have not been performed for $CpRh(C_2H_4)$.

The temperature independence of the MCD signal of an argon matrix containing **3** strongly suggests that it exists in a singlet ground state. (Notice that the isolobal methylene molecule adopts a bent triplet ground state (angle = 136°) with an excited singlet state with a bond angle of 102°.[30]) Like **3**, $CpRh(ethene)N_2$ has two intense bands in the 1200–700-cm^{-1} region of the spectrum, at 1180 and 781 cm^{-1} in liquid xenon.[10] CpRh(ethene)CO also has two intense bands in this region. The similarity of the infrared spectra suggests that the symmetry of the three species is identical. Thus irradiation of **1** in inert matrices causes photodissociation of ethene to give **3** which probably exists in a bent, singlet ground state. There is no experimental evidence yet for the structure of CpRhCO.

A sterically uncongested center promotes C–H activation.[2] The difference in reactivity toward hydrocarbons between the two fragments **3** and **6** could arise from the greater steric demands of an ethene ligand compared to a carbonyl, which could prevent the approach of a saturated C–H bond, but the ability of phosphine-substituted CpRhL intermediates to activate C–H bonds suggests that electronic factors are also important. The differences in the electronic structures of the two fragments are not yet understood.

Role of $CpRh(C_2H_4)$ in Solution Reactions of 1. The photochemical reactions of **1** in room temperature and liquid xenon solutions have also been studied extensively. A brief account of some of this work has already been published.[8,10] The primary photoprocess in all reactions studied to date has been dissociation of an ethene ligand. We have also identified **3** in solution by laser flash photolysis.[10] The thermal reactions of **1** have been studied extensively by Cramer, who postulates **3** as an intermediate, for instance, in the substitution of ethene by other alkenes.[6] Although some thermal substitutions take place associatively, we have no evidence for associative photochemical reactions. Similar solution photochemical reactions have been observed for $(\eta^5\text{-}C_5Me_5)Rh(C_2H_4)_2$.[31]

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Registry No. 1a, 12211-95-9; **1b**, 112680-96-3; **1c**, 112680-97-4; **2**, 88411-46-5; $((C_2D_4)_2RhCl)_2$, 112680-98-5; $((C_2H_4)_2RhCl)_2$, 12081-16-2; $((C_2H_4)(CO)RhCl)_2$, 12306-60-4.

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