Solution and Matrix Photochemistry of (η-Cyclopentadienyl)bis(ethene)rhodium

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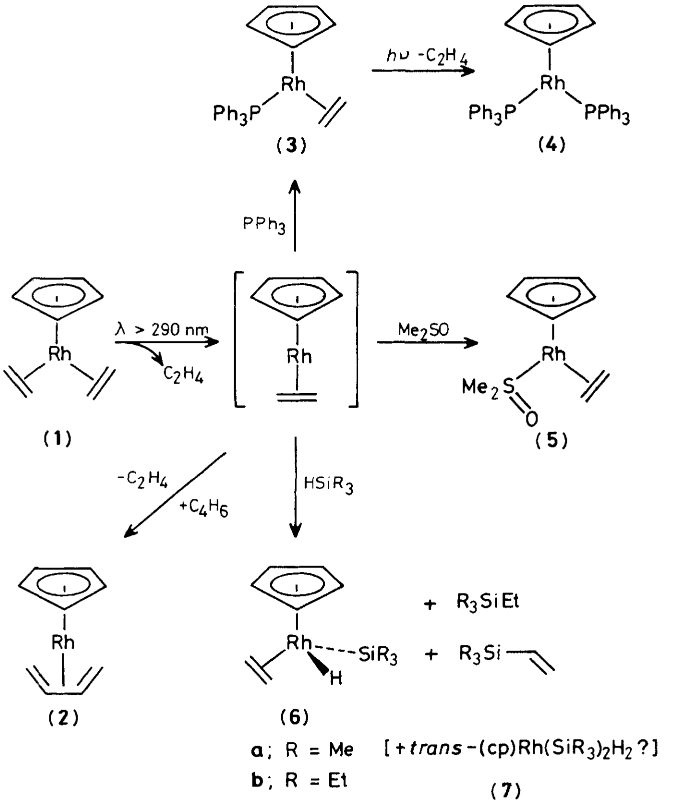
Solution photolysis of (η-C_5H_5)Rh(C_2H_4)$_2$ leads to substitution of ethene in the presence of donor ligands, and to oxidative addition with R_3SiH (R = Me or Et); photolysis in inert matrices causes reversible loss of ethene, but in reactive matrices substitution by N_2 and CO takes place.

The most potent of the recently discovered photochemical activators of alkane C–H bonds are (η-C_5R_5)M(CO)$_2$ and (η-C_5Me_5)MH_2(PMe_3) (R = Me or H; M = Rh or Ir).[1,2] Matrix isolation has proved an effective method of demonstrating methane activation by (η-C_5R_5)M(CO)$_2$, but the postulated intermediates, (η-C_5R_5)MCO, could not be detected convincingly.[1c] However, several lines of evidence point to (η-C_5R_5)ML intermediates in these reactions.[1—3] The mechanism of Rh-catalysed Si–H bond activation has also been examined in detail, leading to the postulation of such reactive intermediates as (η-C_5Me_5)Rh($SiEt_3$)(C_2H_4)H.[4] Indeed, [M](C_2H_4)(SiR_3)H complexes are usually postulated as intermediates in hydrosilation reactions, but have rarely, if ever, been observed.

Following successful matrix photolysis of (cp)$_2$W(C_2H_4) (cp = η-C_5H_5) to form the C–H activator, (cp)$_2$W,[5] we have examined the photochemistry of (cp)Rh(C_2H_4)$_2$ (**1**) in solution and in matrices. Although we lose the advantages associated with matrix-isolated metal carbonyls,[1c] the characteristic i.r. absorptions of C_2H_4 assist in product identification. Complex (**1**) undergoes thermal substitution by donor ligands such as PPh_3 and Me_2SO only above 115 °C;[6,7] at these temperatures it also activates arene C–H bonds.[8] We have discovered an extensive photochemistry of (**1**) and have used this to characterise stable complexes associated with hydrosilation and the first d^8 (cp)RhL intermediate.

Photolysis (λ >290 nm) of (**1**) at 25 °C in benzene or toluene the presence of donor ligands butadiene, PPh_3, and Me_2SO leads to substitution of one or both ethene ligands and formation of known complexes (**2**)—(**5**) (Scheme 1).†[7,9,10] On photolysis of (**1**) in the presence of Et_3SiH, hydrosilation products Et_4Si and CH_2=$CHSiEt_3$ (g.c.–mass spectrometric and n.m.r. identification), and two rhodium hydrides are formed. The major hydride product was identified as (cp)Rh($SiEt_3$)(C_2H_4)H (**6b**) by detailed n.m.r. studies (including 2D n.m.r.); the minor product is assigned provisionally to the Rh^V complex *trans*-(cp)Rh($SiEt_3$)$_2H_2$ (**7b**) [compare the established (η-C_5Me_5) analogue].[11] The proportion of (**7b**) increased with the ratio of Et_3SiH to (**1**). Use of Me_3SiH led to $EtSiMe_3$, CH_2=$CHSiMe_3$ and methyl analogues of the hydrides (**6a**) and (**7a**) (Scheme 1).†

The matrix photochemistry (λ >200 nm) of (**1**) also reveals substitution reactions. In N_2 matrices, one ethene is replaced forming the dinitrogen complex (**8**). Both ethene ligands may be substituted sequentially by CO in CO matrices; more control is obtained in 5% CO–Ar matrices. The products (**8**)—(**10**) and expelled ethene[12] are identified by i.r. spectro-



Scheme 1. Solution photochemistry of (cp)Rh(C_2H_4)$_2$.

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† Selected spectroscopic data for (**2**)—(**7**), not overlapping with published data. N.m.r. spectra were recorded at 400 MHz (^{1}H). The JMOD method for ^{13}C n.m.r. studies is described in ref. 15. (**2**): n.m.r. ^{13}C (JMOD, C_6D_6): δ 87.8 (d, *J* 2.9 Hz, C_5H_5), 77.5 (d, *J* 7.5 Hz, CH_2*CH*), and 33.5 (d, *J* 16.3 Hz, *CH*$_2$CH).

(**3**): n.m.r. $^{31}P\{^1H\}$ (C_6D_6): δ 59.4 (d, *J* 210 Hz).

(**4**): n.m.r. $^{31}P\{^1H\}$ (C_6D_6): δ 57.3 (d, *J* 222 Hz).

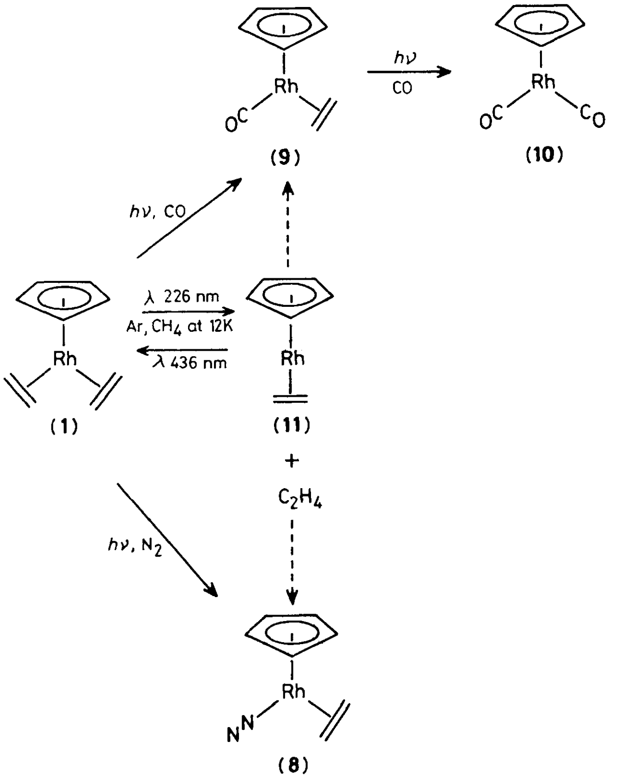
(**5**): n.m.r. ^{1}H ($C_6D_5CD_3$): δ 4.85 (d, 5H, *J* 0.8 Hz, C_5H_5), 2.85 ($[AM]_2X$ multiplet, 2H, C_2H_4), 2.42 (s, 6H, Me), and 2.16 ($[AM]_2X$ multiplet, 2H, C_2H_4); ^{13}C (JMOD, $C_6D_5CD_3$): δ 86.5 (d, *J* 3.3 Hz, C_5H_5), 56.6 (s, Me), and 32.9 (d, *J* 15.8 Hz, C_2H_4); i.r. (Nujol) ν 1315(w), 1177(m), 1173(m), 1097(s), 1080(sh), 913(m), 790(m), and 687(m) cm^{-1}; mass spec. *m*/*z*: 274 (25%, M^+), 246 (79%, $M^+-C_2H_4$), 231 (43%, $M^+-C_3H_7$), and 168 (100%, $M^+-C_4H_{10}SO$). Satisfactory microanalyses were obtained.

(**6a**): n.m.r. ^{1}H ($C_6D_5CD_3$): δ 4.92 (t, 5H, *J* 0.5 Hz, C_5H_5), 2.39 (br., 4H; sharpens at 353 K and 80 MHz to δ 2.21, d, *J* 2.1 Hz, C_2H_4), 0.29 (s, 9H, Me), and −14.84 (d, 1H, *J* 32 Hz, RhH); ^{13}C (JMOD, $C_6D_5CD_3$): δ 90.1 (d, *J* 2.8 Hz, C_5H_5) and 34.8 (d, *J* 12.8 Hz, C_2H_4).

(**6b**): n.m.r. ^{1}H (C_6D_6): δ 4.95 (t, 5H, *J* 0.6 Hz, C_5H_5), 2.32 (br., 4H; sharpens at 80 MHz to 2.28, d, *J* 1.7 Hz, C_2H_4), 1.04 (t, 9H, *J* 7.8 Hz, $SiCH_2$*CH*$_3$), 0.69 (q, 6H, *J* 7.8 Hz, Si*CH*$_2CH_3$), and −14.87 (d, 1H, *J* 33.2 Hz, RhH); ^{13}C (JMOD, C_6D_6): δ 89.4 (d, *J* 3 Hz, C_5H_5) and 31.7 (d, *J* 11 Hz, C_2H_4, J_{CH} 160 Hz); ^{29}Si(JMOD, C_6D_6): δ 41.6 p.p.m. (d, *J* 22.2 Hz, RhSi); mass spec. *m*/*z*: 312 (4%, M^+), 284 (46%, $M^+-C_2H_4$), 282 (13%, $M^+-C_2H_6$), 254 (100%, $M^+-C_4H_{10}$), 252 (38%, $M^+-C_4H_{12}$), 226 (44%, $M^+-C_6H_{14}$), 196 (60%, $M^+-C_8H_{20}$ and $M^+-SiC_6H_{16}$), and 168 (41%, M^+ $-SiC_8H_{20}$).

(**7a**): n.m.r. ^{1}H ($C_6D_5CD_3$): δ 4.89 (s, 5H, C_5H_5), 0.09 (s, 18H, CH_3), and −13.87 (d, 2H, *J* 40 Hz, RhH_2).

(**7b**): n.m.r. ^{1}H (C_6D_6): δ 4.99 (s, 5H, C_5H_5), 1.05 (t, 18H, *J* 7.7 Hz, CH_2*CH*$_3$), 0.78 (q, 12H, *J* 7.7 Hz, *CH*$_2CH_3$), and −14.16 (d, 2H, *J* 38.3 Hz, RhH_2); ^{13}C (JMOD, C_6D_6): δ 90.5 (br. s, C_5H_5), 14.47 (s, CH_2), and 9.75 (s, Me).



Scheme 2. Matrix photochemistry of (cp)Rh(C$_2$H$_4$)$_2$.

scopy (Scheme 2).‡ Photolysis of (**1**) in Ar or CH$_4$ matrices [most effectively with λ 228.8 nm, coinciding with the most intense absorption of (**1**) at 231 nm], leads to limited yields of ethene and a product (**11**) with a new band in the CH deformation region of co-ordinated ethene, a new cp mode, and a u.v. absorption to long wavelength of the absorptions of (**1**) (Figure 1).‡ As with many co-ordinatively unsaturated metal carbonyls,[13] the reaction is reversed by irradiation into the tail of this band (λ 436 nm). Photolysis of (η-C$_5$D$_5$)Rh(C$_2$D$_4$)$_2$[8] in a CH$_4$ matrix gave C$_2$D$_4$ and shifted bands assigned to [^{2}H$_9$]-(**11**).‡ The reversible photoproduction of ethene demonstrates that (**11**) must be assigned as the co-ordinatively unsaturated (cp)Rh(C$_2$H$_4$) (Scheme 2), rather than an isomer of (**1**). Dimerisation can be excluded both from the reversibility of the reaction and the dilution of the matrix.

These experiments demonstrate: (i) the photo-sensitivity of (cp)Rh(C$_2$H$_4$)$_2$ and the synthetic utility of photolysis for substitution of a strongly bound ethene ligand; (ii) the oxidative addition of SiH bonds leading to hydrosilation products and (**6**), an analogue of the postulated intermediate in hydrosilation reactions of (η-C$_5$Me$_5$)Rh complexes[4]§ (see also the addition of R$_3$SiH to co-ordinatively unsaturated metal carbonyls);[14] (iii) reversible formation of co-ordinatively unsaturated d^8 (cp)Rh(C$_2$H$_4$) in inert matrices.

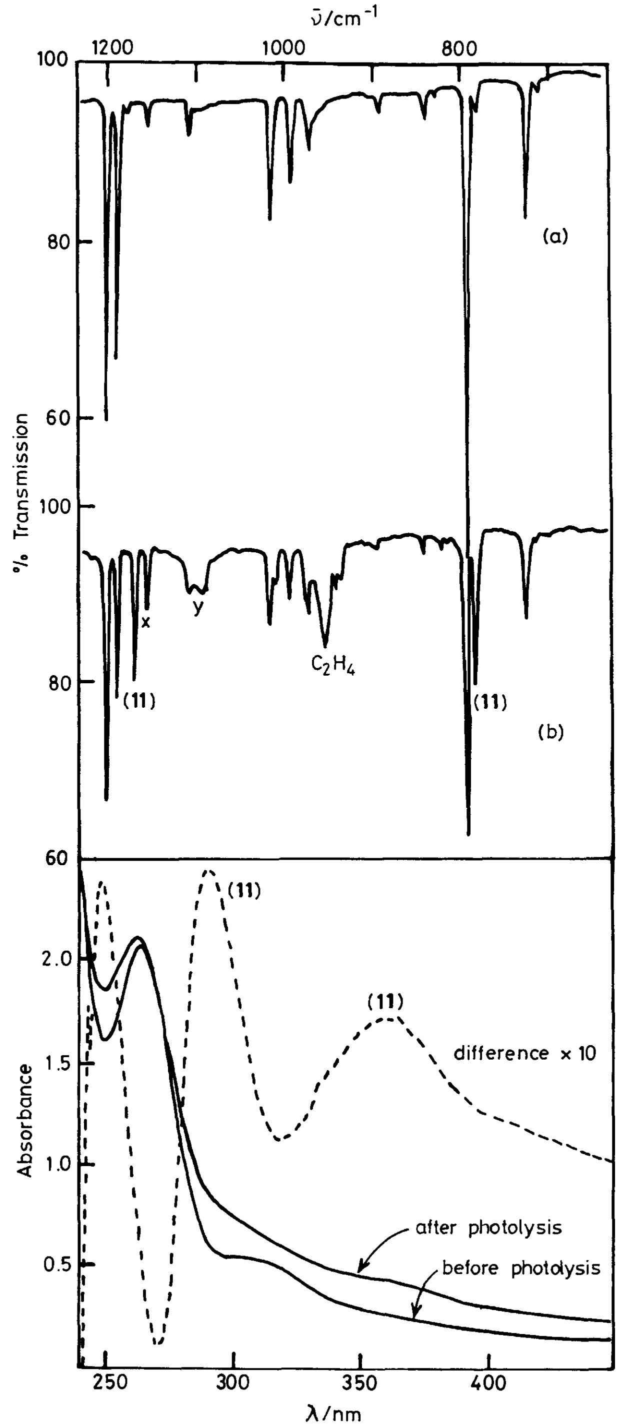


Figure 1. Above. (a) I.r. spectrum of (**1**) in CH$_4$ matrix at 16 K (180 min deposition, sublimation temperature 273 K, 5.3 mmol CH$_4$); (b) i.r. spectrum at 12 K of sample obtained by alternate deposition of (**1**) with CH$_4$ and Cd arc (λ 228.8 nm) photolysis showing product bands due to (**11**) and C$_2$H$_4$ (3 periods alternating 60 min deposition and 60 min photolysis followed by 300 min photolysis, x = CH$_3$D, y = impurity on outer window). Below. U.v. spectrum of (**1**) in Ar matrix at 12 K before and after 1140 min Cd arc photolysis. The broken line shows the difference spectrum with ×10 ordinate expansion, peaks due to (**11**), troughs due to (**1**).

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‡ Matrix spectroscopic data for (**8**)—(**11**). (**8**) i.r., ^{14}N$_2$ matrix, ν 2180 cm^{-1} [ν(NN)]; ^{14}N$_2$/^{15}N$_2$ (3/2) matrix, ν 2180 and 2107 cm^{-1} [ν(^{14}N^{14}N), ν(^{15}N^{15}N)]. (**9**): i.r., CO matrix, ν 1989 and 556 cm^{-1}. (**10**): i.r., CO matrix, ν 2050, 1989, 575, 526, and 499 cm^{-1}. (**11**): i.r., Ar matrix, ν 1163 and 777 cm^{-1}; u.v., Ar matrix, λ 249, 292, and 363 nm; i.r., CH$_4$ matrix, ν 1169, 1009(?), and 783 cm^{-1}; u.v., CH$_4$ matrix, λ 300 and 372 nm. [^{2}H$_9$]-(**11**): i.r., CH$_4$ matrix, ν 937 and 592 cm^{-1}.

§ P. M. Maitlis informs us that he has synthesised the C$_5$Me$_5$ analogue of (**6**) by photolysis of (η-C$_5$Me$_5$)Rh(C$_2$H$_4$)$_2$: see accompanying communication.

This complex is presumed to be an intermediate in the other photo-reactions of (**1**) (Schemes 1, 2) and has been postulated as an intermediate in the thermal reactions of (**1**).[6—8] It is closely related to the hypothetical C–H activating intermediates, *e.g.* (cp)RhCO.[1—3] We note the absence of evidence for CH_4 activation by (**1**) as might have been observed, *e.g. via* ν(Rh–H).

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