

Preliminary communication

C–H AND Si–H ACTIVATION REACTIONS OF $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)\text{CO}$ IN LOW-TEMPERATURE MATRICES AND IN SOLUTION

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(Received May 9th, 1986)

Summary

C–H and Si–H activation is exhibited by $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)\text{CO}$ in low temperature matrices and in solution. C–H activation requires photochemical loss of C_2H_4 whilst Si–H activation takes place following both C_2H_4 and CO photo-dissociation. $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)$ and $(\eta^5\text{-C}_5\text{H}_5)\text{RhCO}$ have been isolated and characterised in low temperature matrices. The final product of photo-reaction with triethylsilane in solution is $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\text{SiEt}_3)\text{H}$.

The photochemical dissociation of a small ligand from a Cp^*M or CpM centre ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{M} = \text{Rh}, \text{Ir}$) has been shown previously to be an excellent way of producing a coordinatively unsaturated metal centre capable of oxidatively adding a carbon–hydrogen bond of a saturated alkane [1–3]. However, the intermediates involved in this type of reaction have remained elusive. A matrix isolation study of the photochemistry of $\text{CpM}(\text{CO})_2$ produced only small amounts of CpMCO , postulated as the intermediate in Graham's C–H activation system [3,4], presumably because of recombination of CpMCO and CO in the matrix cage.

In a recent study we demonstrated photochemical loss of C_2H_4 from $\text{CpRh}(\text{C}_2\text{H}_4)_2$ in low temperature matrices to produce the diamagnetic $\text{CpRh}(\text{C}_2\text{H}_4)$ fragment in reasonable yield [5,6]; $\text{CpRh}(\text{C}_2\text{H}_4)$ does not react with methane under these conditions. Irradiation of $\text{CpRh}(\text{C}_2\text{H}_4)_2$ in the presence of carbon monoxide in both low temperature matrices and in liquid xenon [7] produces $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$. In this paper I will present data to show that in situ formation of $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$ in low temperature methane matrices leads to efficient C–H activation. This realisation led to the synthesis and photochemical study of $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$ in low temperature matrices and in solution. This compound offers the interesting possibility of two competing photochemical pathways [8]: oxidative addition of Si–H bonds occurs following either CO or C_2H_4 loss, but oxidative addition of the methane C–H bond requires photodissociation of C_2H_4 .

Irradiation (60 min, λ 229 nm) of $\text{CpRh}(\text{C}_2\text{H}_4)_2$ in a 10% CO/90% CH_4 matrix leads to the production of one strong terminal $\nu(\text{CO})$ band at 1986 cm^{-1} ($\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$) together with two weaker bands at 2049 cm^{-1} ($\text{CpRh}(\text{CO})_2$) and

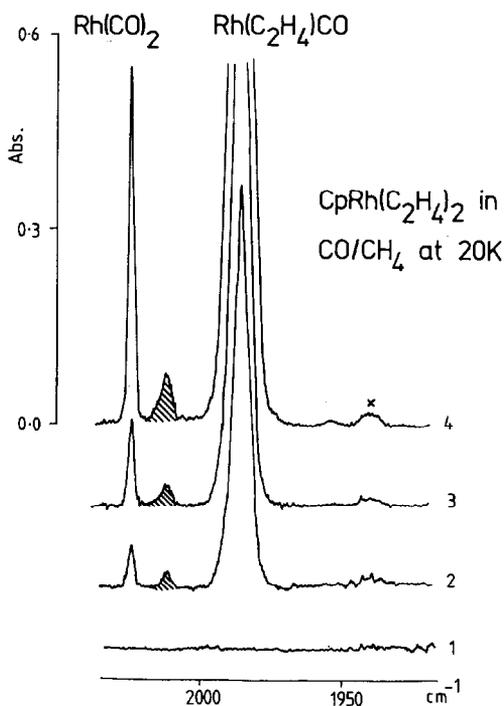


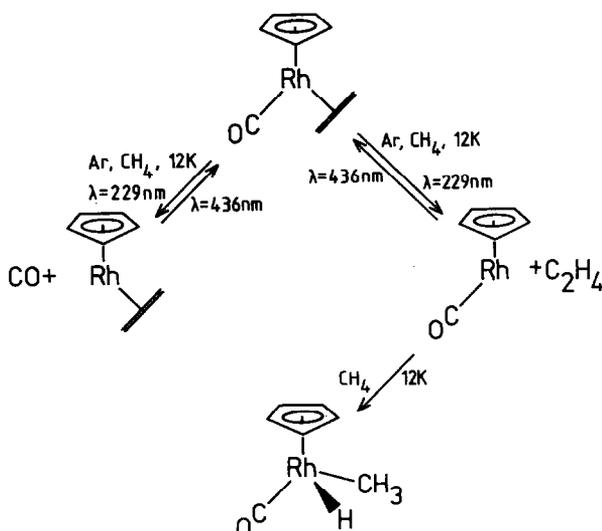
Fig. 1. Terminal $\nu(\text{CO})$ region of $\text{CpRh}(\text{C}_2\text{H}_4)_2$ in a solid 10% $\text{CO}/90\%$ CH_4 matrix at 20 K. Deposition conditions: sublimation temperature 273 K, 7.0 mmol gas mixture deposited in 160 min on to a CsI window at 20 K. (1) After deposition, (2) 65 min λ 229 nm photolysis, (3) 40 min, subsequent $\lambda > 370$ nm photolysis, (4) After a further 300 min, λ 229 nm photolysis. Shaded band, $\nu(\text{CO})$ of $\text{CpRh}(\text{CO})(\text{CH}_3)\text{H}$; x $\nu(^{13}\text{CO})$ of $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$. Spectra recorded on a PE580 spectrometer.

2023 cm^{-1} , $\text{CpRh}(\text{C}_2\text{H}_4)$ is seen at 1169 cm^{-1} . Subsequent irradiation at longer wavelength ($\lambda > 290\text{ nm}$) removes all $\text{CpRh}(\text{C}_2\text{H}_4)$ from the matrix and causes a big increase of $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$ and a smaller increase in the band due to $\text{CpRh}(\text{CO})_2$ (Fig. 1). (The remaining $\nu(\text{CO})$ band of $\text{CpRh}(\text{CO})_2$ is obscured by $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$.) There is little change in the band at 2023 cm^{-1} , but it increases after further short wavelength photolysis (180 min, λ 229 nm). The band at 2023 cm^{-1} is assigned as $\nu(\text{CO})$ of $\text{CpRh}(\text{CO})(\text{CH}_3)\text{H}$ by comparison with the literature [3]. The high proportion of $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$ relative to $\text{CpRh}(\text{CO})_2$ argues for $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$ as the precursor of the C–H activation product. These experiments suggested that the direct matrix isolation of $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$ would lead to effective C–H activation.

$\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$ was synthesised * from the reaction of $[(\text{C}_2\text{H}_4)(\text{CO})\text{RhCl}]_2$ and TiCp at room temperature [9,10] and may be sublimed at 233 K into a matrix **

* Spectroscopic data for $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$. NMR in benzene- d_6 : ^1H NMR at 80 MHz and 30°C , $\delta(\text{ppm})$ 2.52, broad singlet, $\text{Rh}(\text{C}_2\text{H}_4)$; 4.86, doublet, $J(\text{Rh}-\text{H}) = 0.4\text{ Hz}$, $\text{Rh}(\text{C}_5\text{H}_5)$. $^{13}\text{C}\{^1\text{H}\}$ NMR at 20.15 MHz and 30°C , $\delta(\text{ppm})$ 31.3, doublet, $J(\text{Rh}-\text{C})$ 13.2 Hz, $\text{Rh}(\text{C}_2\text{H}_4)$; 88.0, doublet, $J(\text{Rh}-\text{C})$ 3.8 Hz, $\text{Rh}(\text{C}_5\text{H}_5)$. IR in hexane solution, $\nu(\text{CO})$ 1988 cm^{-1} .

** IR data for $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$ in Ar matrix: 1997 vs, 1186m, 1184m, 1111w, 1017m, 988m, 952w, 790s, 554m, 524w cm^{-1} .



SCHEME 1

without detectable decomposition to C₂H₄ or CO. It exhibits a strong $\nu(\text{CO})$ band at high dilution in an argon matrix at 1997 cm⁻¹ (cf. 1990 cm⁻¹ in 5% CO/Ar matrix when generated in situ.) Irradiation of CpRh(C₂H₄)CO in argon (20 K) at λ 229 nm results in the appearance of a new terminal $\nu(\text{CO})$ band at 1969 cm⁻¹ which can be assigned as CpRhCO [4], and free ethene, 950 cm⁻¹. We also see a new band at 1163 cm⁻¹ assigned as $\delta(\text{CH})$ of CpRh(C₂H₄) [5], together with free CO, 2139 cm⁻¹. Irradiation at longer wavelength, λ 436 nm, results in the decrease of all product bands; photodissociation can be repeated by further irradiation at λ 299 nm (Scheme 1).

Irradiation of CpRh(C₂H₄)CO in a methane matrix at 20 K, λ 229 nm, results in a new band at 1169 cm⁻¹, again assignable to CpRh(C₂H₄), a new terminal $\nu(\text{CO})$ band, 2022 cm⁻¹, and bands due to free ethene (954 cm⁻¹) and free CO (2139 cm⁻¹). Prolonged photolysis at 229 nm causes an increase in all products, irradiation at λ 436 nm results in a decrease of the band at 1169 cm⁻¹ with no effect on the $\nu(\text{CO})$ band at 2022 cm⁻¹ (Fig. 2). The band at 2022 cm⁻¹ is assigned to CpRh(CO)(CH₃)H by comparison with published data [3] (Scheme 1).

Irradiation of a benzene solution of CpRh(C₂H₄)(CO), $\lambda > 290$ nm, in a sealed NMR tube in the presence of triethylsilane results in the competitive loss of CO and C₂H₄ and formation of CpRh(C₂H₄)(SiEt₃)H [5] and CpRh(CO)(SiEt₃)H* (Fig. 3). Initial irradiation for 75 min produces the two silyl rhodium hydrides and free ethene in solution, monitored by ¹H NMR at 80 MHz. On prolonged photolysis

* Spectroscopic data for CpRh(CO)(SiEt₃)H. NMR in benzene-*d*₆: ¹H NMR at 360 MHz and 25°C, $\delta(\text{ppm})$ -12.18, doublet, $J(\text{Rh}-\text{H})$ 33.8 Hz, RhH; 0.84, quartet, J 7.7 Hz, CH₂CH₃; 1.07, triplet, J 7.8 Hz, CH₂CH₃; 4.99, singlet, C₅H₅. ¹³C{¹H} at 90.6 MHz and 30°C, $\delta(\text{ppm})$ 9.2, singlet, CH₂CH₃; 13.0, singlet, CH₂CH₃; 89.2, singlet, C₅H₅; 191.5, doublet, $J(\text{Rh}-\text{C})$ 80 Hz, RhCO. IR in hexane solution, $\nu(\text{CO})$ 2012 cm⁻¹. Mass spec: m/z 312 (28%, M⁺), 284 (47%), 283 (32%), 255 (35%), 254 (100%), 253 (27%), 252 (32%), 226 (47%), 224 (27%), 196 (81%) and 168 (45%).

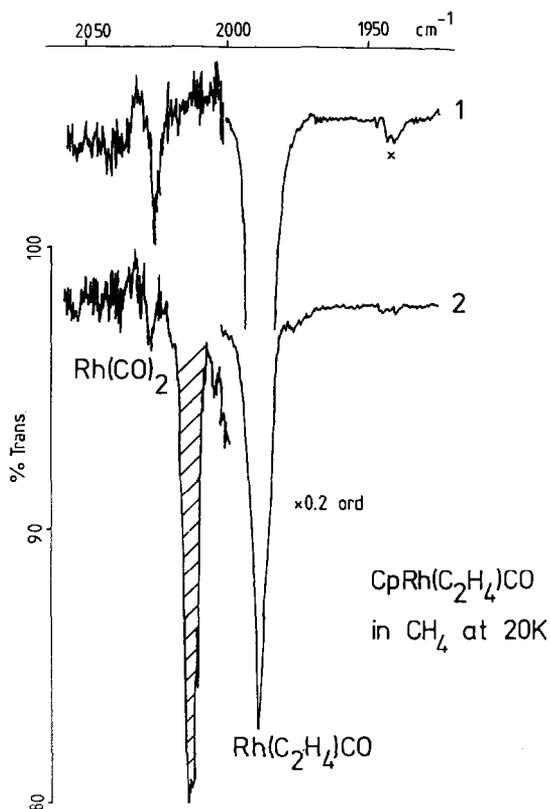


Fig. 2. Terminal $\nu(\text{CO})$ region of $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$ in a solid methane matrix at 20 K. Deposition conditions: sublimation temperature 233 K, 4.2 mmol CH_4 deposited in 55 min onto a CsI window at 20 K. (1) After deposition, (2) 980 min, λ 229 nm photolysis. Shaded band, $\nu(\text{CO})$ of $\text{CpRh}(\text{CO})(\text{CH}_3)\text{H}$.

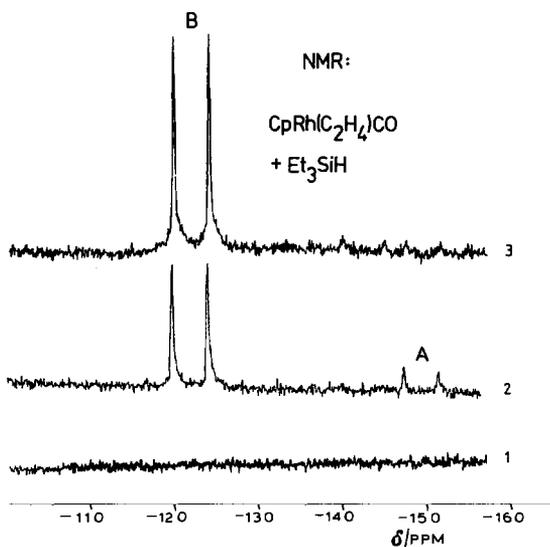
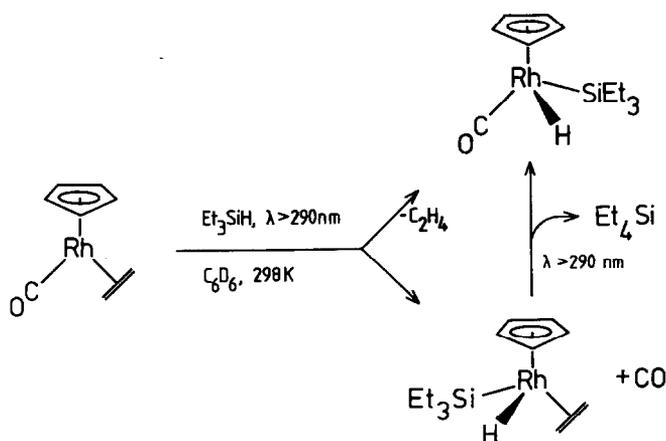


Fig. 3. Hydride region of the ^1H NMR spectrum (80 MHz) from the reactions between $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$ and Et_3SiH in C_6D_6 solution at 300 K. (1) Before irradiation (2) 75 min irradiation $\lambda > 290$ nm showing production of $\text{CpRh}(\text{CO})(\text{SiEt}_3)\text{H}$ (B), and $\text{CpRh}(\text{C}_2\text{H}_4)(\text{SiEt}_3)\text{H}$ (A). (3) After 300 min irradiation $\lambda > 290$ nm. Only $\text{CpRh}(\text{CO})(\text{SiEt}_3)\text{H}$ is now present.



SCHEME 2

(300 min) $\text{CpRh}(\text{C}_2\text{H}_4)(\text{SiEt}_3)\text{H}$ disappears and we have complete conversion to $\text{CpRh}(\text{CO})(\text{SiEt}_3)\text{H}$. The reaction products also include the hydrosilation product Et_4Si (Scheme 2). Earlier attempts at synthesising $\text{CpRh}(\text{CO})(\text{SiR}_3)\text{H}$ by photolysis of $\text{CpRh}(\text{CO})_2$ succeeded only for $\text{R} = \text{Ph}, \text{PhCH}_2$ [11].

These experiments demonstrate the competitive loss of CO and C_2H_4 from $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$ in low temperature matrices and in solution. This has led to new routes for the reversible formation of $\text{CpRh}(\text{C}_2\text{H}_4)$ and CpRhCO in low temperature inert matrices. The formation of $\text{CpRh}(\text{CO})(\text{CH}_3)\text{H}$ and absence of CpRhCO in methane matrices provides further evidence that the CpML fragment is the major intermediate in the C-H activation reactions of this type of complex. Competitive loss of C_2H_4 and CO also occurs in solution. However, upon prolonged photolysis there is 100% conversion to a single product demonstrating the synthetic utility of the photochemistry of $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$. This study has reaffirmed the detection of free ethene by its infrared absorptions in low-temperature matrices, despite the IR inactivity of the $\nu(\text{C}=\text{C})$ mode [5,7], and by its NMR spectrum in solution. It is also useful to note the similarity in the IR spectra of $\text{CpRh}(\text{C}_2\text{H}_4)\text{CO}$, $\text{CpRh}(\text{C}_2\text{H}_4)\text{N}_2$ [7] and $\text{CpRh}(\text{C}_2\text{H}_4)$. All show two relatively intense bands, $\delta(\text{CH})$ at $\sim 1200\text{ cm}^{-1}$ and a Cp ring mode at $\sim 800\text{ cm}^{-1}$, suggesting that the symmetry of the $\text{CpRh}(\text{C}_2\text{H}_4)$ in all three species is identical. Thus the bent structure is probably retained for the coordinatively unsaturated $\text{CpRh}(\text{C}_2\text{H}_4)$ following expulsion of either CO or C_2H_4 (Scheme 1).

Acknowledgements. I thank Dr. R.N. Perutz for useful discussions and help with this work, Dr. M. Arthurs for his advice, the SERC High-field NMR service, Johnson Matthey for the loan of rhodium salts and Professor R.E. Hester for the loan of a PE 580 IR spectrometer.

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