# Photochemistry of Dicarbonyl($\eta^5$-cyclopentadienyl)-methyl- and -ethyl-iron and -ruthenium Complexes in Solutions at −30 °C and in Frozen Gas Matrices at 12 K

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The photolysis reactions of $[M(CO)_2R(\eta^5\text{-}C_5H_5)]$ (M = Fe or Ru, R = Me or Et) complexes have been studied by a combination of solution (−30 °C) and matrix-isolation (12 K) techniques. In pentane solutions (−30 °C) photolysis of $[M(CO)_2Me(\eta^5\text{-}C_5H_5)]$ (M = Fe or Ru) alone yields the dimers $[\{M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$, whereas that of $[M(CO)_2Et(\eta^5\text{-}C_5H_5)]$ (M = Fe or Ru) leads to the known dimers, $[\{M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$, and the *new* dimer $[\{Ru(CO)(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}H)_2]$. Photolysis of $[M(CO)_2Me(\eta^5\text{-}C_5H_5)]$ (M = Fe or Ru) in pentane (−30 °C) in the presence of $C_2H_4$ results in the formation of the *new* complexes $[M(CO)(C_2H_4)Me(\eta^5\text{-}C_5H_5)]$. The ethyl complex $[Fe(CO)_2Et(\eta^5\text{-}C_5H_5)]$ reacts photochemically with $C_2H_4$ to produce $[Fe(CO)_2H(\eta^5\text{-}C_5H_5)]$, $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$, and the *new* dimer $[\{Fe(CO)(C_2H_4)(\eta^5\text{-}C_5H_5)\}_2]$, while the complex $[Ru(CO)_2Et(\eta^5\text{-}C_5H_5)]$ dealkylates to give only $[Ru(CO)_2H(\eta^5\text{-}C_5H_5)]$. In gas matrices (12 K) the trapping of $[Ru(^{12}CO)Me(\eta^5\text{-}C_5H_5)]$ and $[Ru(^{13}CO)Me(\eta^5\text{-}C_5H_5)]$ species provided direct evidence for the CO-dissociation pathway. The $[M(CO)Me(\eta^5\text{-}C_5H_5)]$ species readily recombined with ejected CO or reacted with $N_2$ or $C_2H_4$ to give the complexes $[Fe(CO)(C_2H_4)Me(\eta^5\text{-}C_5H_5)]$, $[Ru(CO)(N_2)Me(\eta^5\text{-}C_5H_5)]$, and $[Ru(CO)(C_2H_4)Me(\eta^5\text{-}C_5H_5)]$. Photolysis of $[M(CO)_2Et(\eta^5\text{-}C_5H_5)]$ (M = Fe or Ru) in $CH_4$ matrices afforded the β-elimination products $[M(CO)_2H(\eta^5\text{-}C_5H_5)]$ together with $[Ru(CO)(C_2H_4)H(\eta^5\text{-}C_5H_5)]$. The photolysis of $[Ru(CO)_2Et(\eta^5\text{-}C_5H_5)]$ in $N_2$ and $C_2H_4$-doped $CH_4$ matrices yielded $[Ru(CO)(N_2)H(\eta^5\text{-}C_5H_5)]$ and $[Ru(CO)(C_2H_4)H(\eta^5\text{-}C_5H_5)]$, respectively. Using $^{13}CO$-doped $CH_4$ matrices and energy-factored force-field fitting to investigate the possibility of competing reactions, it was found that the initial process was β elimination which was followed by CO exchange. Photolysis in CO matrices revealed the existence of a further pathway possibly involving ring-slippage products, *e.g.* $[Fe(CO)_3R(\eta^3\text{-}C_5H_5)]$ (R = Me or Et) and $[Ru(CO)_3H(\eta^3\text{-}C_5H_5)]$.

Although photo-induced carbonyl-substitution reactions of $[Fe(CO)_2Me(\eta^5\text{-}C_5H_5)]$ have been known for almost 20 years,[1] the first reported photolysis reactions of $[Fe(CO)_2R(\eta^5\text{-}C_5H_5)]$ (R = Me, Et, or Ph) complexes in solution in the absence of potential ligands appeared only in 1979.[2] In pentane or other non-co-ordinating solvents photolysis of $[Fe(CO)_2R(\eta^5\text{-}C_5H_5)]$ yields $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ as the sole metal-containing product. The photo-induced dissociation of one carbonyl ligand and the generation of a 16-electron species was assumed to be the first step in the reaction [equation (1)]. Support for this assumption came from the fact that two-electron ligands L, *e.g.*

$$[Fe(CO)_2R(\eta^5\text{-}C_5H_5)] \underset{\text{solvent}}{\overset{h\nu}{\rightleftharpoons}} [Fe(CO)R(\eta^5\text{-}C_5H_5)] + CO \quad (1)$$

$PR_3$, were able to stabilise these $[Fe(CO)R(\eta^5\text{-}C_5H_5)]$ fragments. The composition of the organic photoproducts, *i.e.* $CH_4$ (for R = Me), $C_2H_4$, $C_2H_6$, and $H_2$ (for R = Et), and $C_6H_6$ and $(C_6H_5)_2$ (for R = Ph), suggested a hydrogen-abstraction pathway for the methyl and phenyl complexes and a β-hydrogen elimination pathway for the ethyl complex. These results were confirmed recently.[3,4] The photolysis of $[Fe(CO)_2Me(\eta^5\text{-}C_5H_5)]$ in a CO matrix at 12 K, leading to $[Fe(CO)_3Me(\eta^3\text{-}C_5H_5)]$, revealed that ring slippage, *i.e.* $\eta^5\text{-} \rightarrow \eta^3\text{-}C_5H_5$, should also be considered as the basis for a reaction pathway.[5]

In order to obtain more details about the mechanisms of the photolysis of $[Fe(CO)_2R(\eta^5\text{-}C_5H_5)]$ (R = Me or Et) compounds experiments have been carried out on the ruthenium analogues $[Ru(CO)_2R(\eta^5\text{-}C_5H_5)]$ (R = Me or Et). Similar reactions with $[M(CO)_3R(\eta^5\text{-}C_5H_5)]$ (M = Mo or W; R = Me, Et, Pr$^n$, Pr$^i$, Bu$^n$, or Ph) complexes have demonstrated that the heavier homologues of a triad give more stable photolysis intermediates.[6] In this paper we report the photolysis of $[M(CO)_2R(\eta^5\text{-}C_5H_5)]$ compounds (M = Fe or Ru, R = Me or Et) with and without potential ligands, *e.g.* $N_2$, CO, and $C_2H_4$, in solution at −30 °C and in various matrices at 12 K.

## Experimental

The complexes to be studied $[Fe(CO)_2R(\eta^5\text{-}C_5H_5)]$ and $[Ru(CO)_2R(\eta^5\text{-}C_5H_5)]$ (R = Me or Et) were prepared according to the literature methods.[7–9]

(*i*) *Solution Studies.*—All experiments were carried out under nitrogen using Schlenk techniques. The solvents were water free and freshly distilled. For photolysis a high-pressure mercury lamp (Hanovia L, 450 W) was used. The Duran glass of the Schlenk tubes acted as a filter for u.v. light giving $\lambda > 300$ nm. The n.m.r. spectra were obtained on a JEOL FX90Q multi-nuclei Fourier-transform spectrometer, and the i.r. spectra on a Perkin-Elmer 297 instrument. For gas analysis a Packard 427 gas chromatograph, equipped with a Porapak Q column and a thermal conductivity detector was used. Photo-induced reactions of $[M(CO)_2R(\eta^5\text{-}C_5H_5)]$ complexes were performed at −30 °C in pentane. Gases, *e.g.* $C_2H_4$ and $N_2$, could be bubbled through the solutions during photolyses, and the courses of the reactions were monitored by i.r. spectroscopy. After photolysis the reaction mixtures were filtered over a frit covered with filter

**Table 1.** I.r. and n.m.r. spectroscopic data for $[M(CO)_2R(\eta^5-C_5H_5)]$ (M = Fe or Ru; R = Me, Et, or H) complexes and photochemically generated derivatives in solution studies

| Complex | I.r.[a] $\tilde{\nu}$(CO)/cm$^{-1}$ | $^1$H N.m.r.[b] | | | $^{13}$C N.m.r.[b] ($^1$H-decoupled) | | | | $\theta_c$/°C for n.m.r. spectra[c] |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta(C_5H_5)$ | $\delta$(H), $\delta(CH_3)$, or $\delta(C_2H_5)$ [$J$(H–H)/Hz] | $\delta(C_2H_4)$ [$J$(H–H)/Hz] | $\delta(C_5H_5)$ | $\delta$(alkyl) | $\delta(C_2H_4)$ | $\delta$(CO) | |
| $[Fe(CO)_2Me(\eta^5-C_5H_5)]$ | 2 008,<br>1 955 | 4.95 | 0.12 | | 86.3 | −23.6 | | 218.6 | r.t. |
| $[Fe(CO)_2Et(\eta^5-C_5H_5)]$ | 2 010,<br>1 952 | 4.87 | 1.52 (q),<br>2.22 (t) [7.7] | | 86.4 | −2.9,<br>22.5 | | 218.8 | r.t. |
| $[Fe(CO)_2H(\eta^5-C_5H_5)]$ | 2 022,<br>1 962 | 4.80 | −12.16 | | 82.8 | | | 216.6 | −30 |
| $[Fe(CO)(C_2H_4)Me(\eta^5-C_5H_5)]$ | 1 960 | 4.62 | 0.02 | 2.57,<br>2.04 | 86.1 | −15.8 | 43.3[d] | 225.8 | −30 |
| $[\{Fe(CO)(C_2H_4)(\eta^5-C_5H_5)\}_2]$ | 1 950s,<br>1 762s,[e,f]<br>1 989w,<br>1 735w | 4.80,<br>4.62[f] | | 2.73,<br>0.07 [12.3][f] | 90.0,<br>89.2,<br>89.0,<br>88.5[f] | | 45.1,<br>43.7[f] | 277.8,<br>213.5[f] | −60 |
| $[Ru(CO)_2Me(\eta^5-C_5H_5)]$ | 2 020,<br>1 959 | 5.38 | 0.31 | | 89.3 | −33.2 | | 203.3 | 0 |
| $[Ru(CO)_2Et(\eta^5-C_5H_5)]$ | 2 021,<br>1 960 | 5.39 | 1.85—1.15(m) | | 89.6 | −10.1,<br>24.4 | | 203.7 | 0 |
| $[Ru(CO)_2H(\eta^5-C_5H_5)$ | 2 032,<br>1 974 | 5.46 | −11.00 | | 86.3 | | | 202.1 | −30 |
| $[\{Ru(CO)(\eta^5-C_5H_5)\}_2(\mu-H)_2]$ | 1 901 | 5.22 | −17.33 | | 85.6[g] | | | 196.5[g] | −30 |
| $[Ru(CO)(C_2H_4)Me(\eta^5-C_5H_5)]$ | 1 960 | 5.21 | 0.62 | 2.43, 2.25 | 89.9 | −23.5 | 35.0[h] | 206.1 | −30 |

[a] In pentane solution; w = weak, s = strong. [b] In $[^2H_6]$acetone; δ values in p.p.m. t = Triplet, q = quartet, m = multiplet, br = broad. [c] r.t. = Room temperature. [d] At −90 °C, $\delta(C_2H_4)$ 48.3 and 37.2 p.p.m. [e] The number and the intensity of the signals is dependent upon the *cis/trans*-isomer ratio. [f] In tetrahydrofuran or $[^2H_8]$tetrahydrofuran solution. [g] In $[^2H_8]$toluene. [h] At −90 °C, $\delta(C_2H_4)$ 40.2 and 30.3 p.p.m.

pulp in the cases where only *one* product existed, or chromatographed on a silica column in other cases. The products from the different fractions were characterised by i.r., $^1$H, $^{13}$C n.m.r., and mass spectroscopy (m.s.). The i.r. and n.m.r. data of the starting materials and the products are given in Table 1.

(*ii*) *Matrix Isolation Studies*.—Details of the 12 K cryostat, vacuum system, i.r. and u.v.–visible spectrometers, photolysis lamp, matrix gases and $^{13}$CO, and the manometric method of making dilute gas mixtures (1:2 000—1:5 000) for 'pulsed' deposition have been described previously.[5] Wavelength-selective photolysis was achieved by a combination of absorbing materials: filter A, $290 < \lambda < 370$ nm and $\lambda > 550$ nm, quartz gas cell (pathlength 25 mm) containing $Br_2$ gas (300 Torr, *ca.* $4 \times 10^4$ Pa) + Pyrex glass disc (thickness 2 mm); filter B, $270 < \lambda < 390$ nm, Corning blue filter (CS 7-54).

## Results

(*a*) *Photolysis of* $[M(CO)_2Me(\eta^5-C_5H_5)]$ (M = Fe *or* Ru) *Complexes in Pentane Solutions at* −30 °C *and in* $CH_4$, $^{13}$CO-*doped* $CH_4$, $N_2$, *and* CO *Matrices* at* 12 K.—The photolysis of the yellow complex $[Ru(CO)_2Me(\eta^5-C_5H_5)]$ in pentane at −30 °C proceeded much more slowly than for the iron analogue, *i.e.* after irradiation for 1 h only *ca.* 30% of the starting material had been converted into $[\{Ru(CO)_2(\eta^5-C_5H_5)\}_2]$. The main components of the photolysis gas were $CH_4$ and $C_2H_6$ (98:2) together with a trace of CO. These products are characteristic of the dealkylation reactions of transition-metal methyl complexes and are analogous to those found for $[Fe(CO)_2Me(\eta^5-C_5H_5)]$ in pentane.[2]

The i.r. spectrum of $[Ru(CO)_2Me(\eta^5-C_5H_5)]$ isolated at high dilution in a $CH_4$ matrix shows two strong absorption bands in the terminal CO-stretching region centred at 2 018.9 and 1 958.8 cm$^{-1}$ [Figure 1(*a*), Table 2]. Irradiation of the matrix with medium-energy u.v. radiation ($290 < \lambda < 370$ nm) produced a new band at 1 943.4 cm$^{-1}$ together with a band due to free CO at 2 138 cm$^{-1}$ [Figure 1(*b*)]. Annealing the matrix to a temperature (*ca.* 30 K) which allows the CO to diffuse in $CH_4$ caused reversal of the primary photolysis step [Figure 1(*c*)]. The ejection of CO in the primary photolysis step, the recombination on annealing, and the observation of a single new band in the terminal CO-stretching region suggest that the new species is $[Ru(CO)Me(\eta^5-C_5H_5)]$. This assignment was confirmed when $[Ru(CO)_2Me(\eta^5-C_5H_5)]$ was photolysed in a $^{13}$CO-doped (5%) $CH_4$ matrix. Initially rapid exchange occurred to produce $[Ru(^{12}CO)(^{13}CO)Me(\eta^5-C_5H_5)]$ and $[Ru(^{13}CO)_2Me(\eta^5-C_5H_5)]$ but then further bands assigned to $[Ru(^{12}CO)Me(\eta^5-C_5H_5)]$ and $[Ru(^{13}CO)Me(\eta^5-C_5H_5)]$ appeared. Satisfactory correspondence between observed and calculated band positions for the $^{13}$CO-enriched species was found (Table 3) using the energy-factored force-field approach.[10,11]

The reactivity of the 16-electron species $[Ru(CO)Me(\eta^5-C_5H_5)]$ was demonstrated by its reaction with $N_2$ and also $C_2H_4$ (see below). Irradiation of $[Ru(CO)_2Me(\eta^5-C_5H_5)]$ isolated at high dilution in a $N_2$ matrix [Figure 2(*a*)] produced new bands at 2 188.6, 2 152.5, and 1 968.2 cm$^{-1}$ together with a band due to free CO [Figure 2(*b*)]. Longer times of photolysis showed that the band at 2 152.5 cm$^{-1}$ grew independently of the pair at 2 188.6 and 1 968.2 cm$^{-1}$ which maintained a constant relative intensity. Bands in the 2 150—2 300 cm$^{-1}$ region are typical of ν(NN) for $N_2$ bonded to transition metals in matrix-isolation studies, *e.g.* $[Co(CO)(N_2)(\eta^5-C_5H_5)]$ [ν(NN) at 2 164.6 cm$^{-1}$].[12] The species with bands at 2 188.6 and 1 968.2 cm$^{-1}$ can, therefore, be assigned to $[Ru(CO)(N_2)Me(\eta^5-C_5H_5)]$ (Table 2).

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* Monitoring and analysing the effects of photolyses of matrices has been confined to observations in the CO-stretching region (2 200—1 800 cm$^{-1}$). While this is less than ideal, vibrations for other ligands, *e.g.* M–H, M–alkene, M–$C_5H_5$, are very much less intense than for CO ligands and are less well documented.

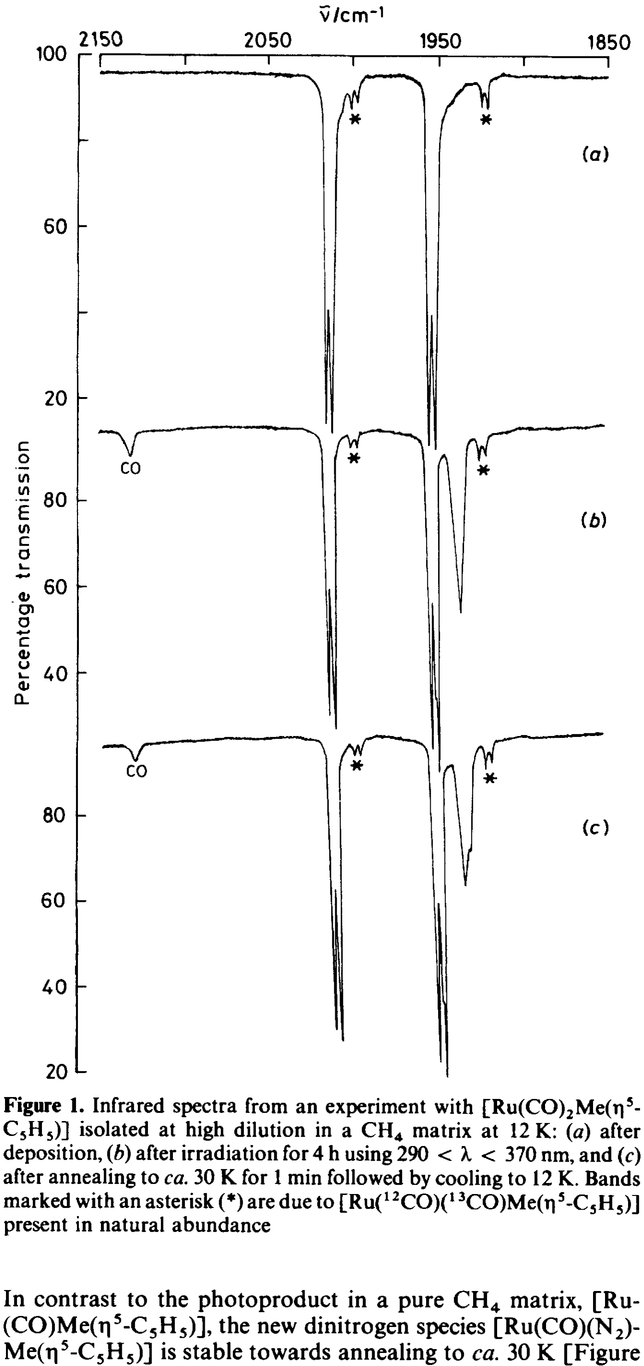


Figure 1. Infrared spectra from an experiment with $[Ru(CO)_2Me(\eta^5\text{-}C_5H_5)]$ isolated at high dilution in a $CH_4$ matrix at 12 K: (*a*) after deposition, (*b*) after irradiation for 4 h using 290 < λ < 370 nm, and (*c*) after annealing to *ca.* 30 K for 1 min followed by cooling to 12 K. Bands marked with an asterisk (*) are due to $[Ru(^{12}CO)(^{13}CO)Me(\eta^5\text{-}C_5H_5)]$ present in natural abundance

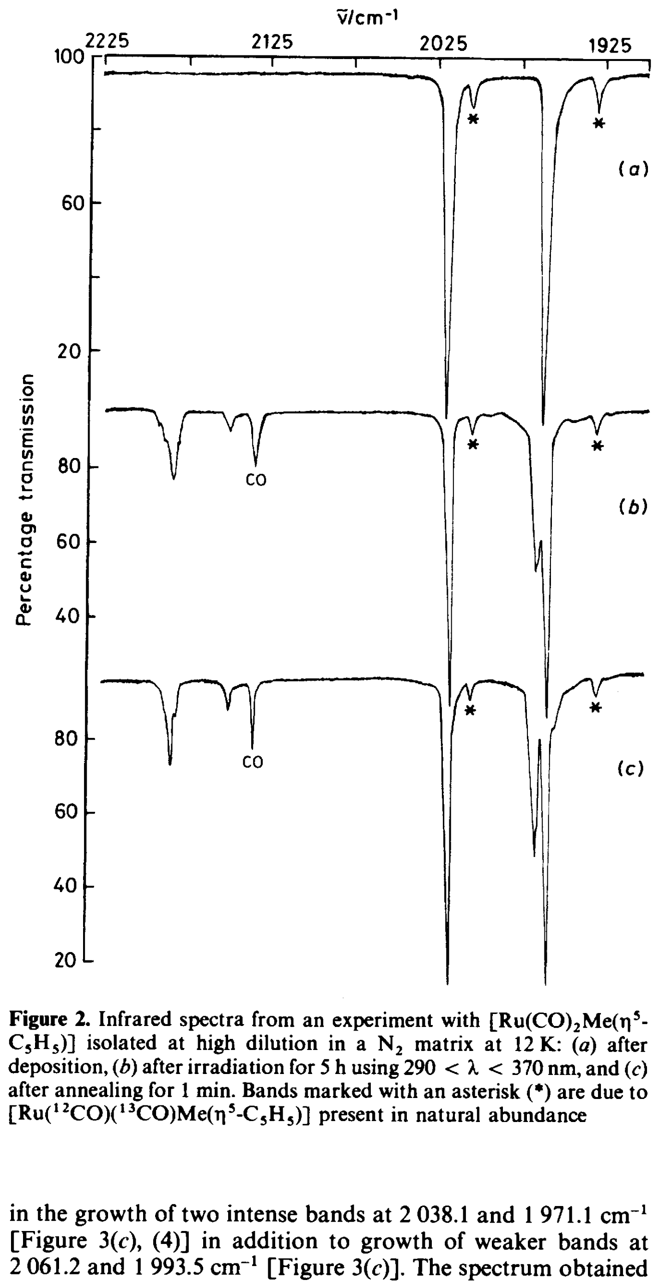


Figure 2. Infrared spectra from an experiment with $[Ru(CO)_2Me(\eta^5\text{-}C_5H_5)]$ isolated at high dilution in a $N_2$ matrix at 12 K: (*a*) after deposition, (*b*) after irradiation for 5 h using 290 < λ < 370 nm, and (*c*) after annealing for 1 min. Bands marked with an asterisk (*) are due to $[Ru(^{12}CO)(^{13}CO)Me(\eta^5\text{-}C_5H_5)]$ present in natural abundance

In contrast to the photoproduct in a pure $CH_4$ matrix, $[Ru(CO)Me(\eta^5\text{-}C_5H_5)]$, the new dinitrogen species $[Ru(CO)(N_2)Me(\eta^5\text{-}C_5H_5)]$ is stable towards annealing to *ca.* 30 K [Figure 2(*c*)]. In the same way that $^{13}CO$ from the matrix exchanges progressively with bound $^{12}CO$ ligands in $[Ru(^{12}CO)_2Me(\eta^5\text{-}C_5H_5)]$, it is likely that $N_2$ could behave similarly, *i.e.* the band at 2 152.5 cm$^{-1}$ may be assigned to the bis(dinitrogen) complex $[Ru(N_2)_2Me(\eta^5\text{-}C_5H_5)]$ for which the second NN stretching band may be weak or obscured by the band at 2 188.6 cm$^{-1}$. The photo-induced reaction of $[Ru(CO)_2Me(\eta^5\text{-}C_5H_5)]$ and $N_2$ in pentane at −30 °C resulted in the formation of a brown precipitate but so far it has proved impossible to characterise the product.

The i.r. spectrum of $[Ru(CO)_2Me(\eta^5\text{-}C_5H_5)]$ isolated at high dilution in a CO matrix at 12 K shows broader bands at 2 020.7 and 1 962.4 cm$^{-1}$ [Figure 3(*a*)] than for $CH_4$ matrices [Figure 1(*a*)]. On irradiation (290 < λ < 370 and λ > 550 nm) the bands of the starting material decreased in intensity and a number of new bands appeared [Figure 3(*b*), (1)—(3)]. Photolysis with higher-energy light (270 < λ < 390 nm) resulted in the growth of two intense bands at 2 038.1 and 1 971.1 cm$^{-1}$ [Figure 3(*c*), (4)] in addition to growth of weaker bands at 2 061.2 and 1 993.5 cm$^{-1}$ [Figure 3(*c*)]. The spectrum obtained after further irradiation [Figure 3(*d*)] showed a significant increase in the bands at 2 038.1, 1 993.5, and 1 971.1 cm$^{-1}$ and, of these, the bands at 2 038.1 and 1 971.1 cm$^{-1}$ increase together with constant relative intensities. On the basis that a co-ordinatively expanded species has been observed for the iron analogue which shows ring slippage, *i.e.* $[Fe(CO)_3Me(\eta^3\text{-}C_5H_5)]$ [ν(CO) at 2 050.3, 1 982.7, and 1 975.1 cm$^{-1}$],[5] and that even a $\eta^5\text{-}C_5H_5$ ligand can be replaced by CO ligands in matrix-isolation experiments, *e.g.* $[Ni(NO)(\eta^5\text{-}C_5H_5)] \xrightarrow{h\nu,\ CO} [Ni(CO)_2(\eta^5\text{-}C_5H_5)] \longrightarrow [Ni(CO)_4]$,[13] it seems likely that species such as $[Ru(CO)_3Me(\eta^3\text{-}C_5H_5)]$, $[Ru(CO)_4Me(\sigma\text{-}C_5H_5)]$, and ultimately $[Ru(CO)_5]$ could be produced. Support for this proposal is afforded by the observation of $[Mo(CO)_6]$ and $[W(CO)_6]$ on photolysis of $[M(CO)_3R(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, R = Me or Et) complexes in poly(vinylchloride) (pvc) film matrixes at 12 K.[14] Additionally, $[ReH(\eta^5\text{-}C_5H_5)_2]$ is known to undergo metal-to-ring hydrogen transfer on photolysis at 12 K,[15] and tricarbonyl($\eta^4$-5,5-dimethylcyclopentadiene)iron is known to show ring-to-metal methyl migration.[4] Definitive identification of these species *via* $^{13}CO$-

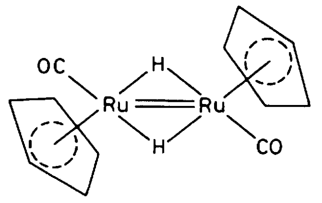
**Table 2.** I.r. band positions (cm$^{-1}$) observed in the CO-stretching region for $[\mathrm{M(CO)_2R}(\eta^5\text{-}\mathrm{C_5H_5})]$ (M = Fe or Ru, R = Me or Et) complexes and their photoproducts in various gas matrices at 12 K

| Complex | $CH_4$ | $N_2$ | 5% $C_2H_4$-doped $CH_4$ | CO |
|---|---|---|---|---|
| $[\mathrm{Fe(CO)_2Me}(\eta^5\text{-}\mathrm{C_5H_5})]$[a] | [b] 2 014.2<br>2 010.3 | [b] 2 017.0<br>2 015.4 | 2 011.2 | [b] 2 015.4<br>2 013.1 |
|  | [b] 1 958.6<br>1 954.3 | [b] 1 963.4<br>1 961.0 | 1 955.7 | 1 961.0 |
| $[\mathrm{Fe(CO)_2Et}(\eta^5\text{-}\mathrm{C_5H_5})]$ | [b] 2 007.3<br>2 003.5 | 2 009.6 | 2.003.7 | 2.008.3 |
|  | [b] 1 952.1<br>1 947.8 | 1 955.0 | 1 947.1 | 1 952.5 |
| $[\mathrm{Ru(CO)_2Me}(\eta^5\text{-}\mathrm{C_5H_5})]$ | [b] 2 020.1<br>2 016.7 | 2 024.0 | 2.016.5 | 2 020.7 |
|  | [b] 1 960.2<br>1 956.4 | 1 966.7 | 1 956.6 | 1 962.4 |
| $[\mathrm{Ru(CO)_2Et}(\eta^5\text{-}\mathrm{C_5H_5})]$ | [b] 2 018.1<br>2 015.2 | 2 019.8 | 2 010.8 | 2 018.2 |
|  | [b] 1 956.4<br>1 952.6 | 1 959.2 | 1 949.7 | 1 957.0 |
| $[\mathrm{Fe(CO)(C_2H_4)Me}(\eta^5\text{-}\mathrm{C_5H_5})]$ |  |  | 1 957.1 |  |
| $[\mathrm{Fe(CO)_2H}(\eta^5\text{-}\mathrm{C_5H_5})]$ | 2 017.6 | 2 021.8 | 2 018.8 | 2 020.8 |
|  | 1 958.5 | 1 964.1 | 1 957.5 | 1 957.5 |
| $[\mathrm{Fe(CO)_3Me}(\eta^3\text{-}\mathrm{C_5H_5})]$[a] |  |  |  | 2 050.3 |
|  |  |  |  | 1 982.7 |
|  |  |  |  | 1 975.1 |
| $[\mathrm{Fe(CO)_3Et}(\eta^3\text{-}\mathrm{C_5H_5})]$ |  |  |  | 2 046.0 |
|  |  |  |  | 1 978.7 |
|  |  |  |  | 1 969.3 |
| $[\mathrm{Ru(CO)Me}(\eta^5\text{-}\mathrm{C_5H_5})]$ | 1 943.4 |  | 1 941.7 |  |
| $[\mathrm{Ru(CO)(N_2)Me}(\eta^5\text{-}\mathrm{C_5H_5})]$[c] |  | 1 968.2 |  |  |
| $[\mathrm{Ru(CO)(C_2H_4)Me}(\eta^5\text{-}\mathrm{C_5H_5})]$ |  |  | 1 956.6[d] |  |
| $[\mathrm{Ru(CO)_2H}(\eta^5\text{-}\mathrm{C_5H_5})]$ | 2 029.2 | 2 033.2 | 2 024.7 | 2 032.4 |
|  | 1 967.5 | 1 971.4 | 1 961.2 | 1 971.2 |
| $[\mathrm{Ru(CO)(N_2)H}(\eta^5\text{-}\mathrm{C_5H_5})]$[e] |  | 1 979.8 |  |  |
| $[\mathrm{Ru(CO)(C_2H_4)H}(\eta^5\text{-}\mathrm{C_5H_5})]$ | 1 960.3 | 1 967.2 | 1 954.1 | 1 966.3 |
| $[\mathrm{Ru(CO)_3Me}(\eta^3\text{-}\mathrm{C_5H_5})]$ |  |  |  | 2 061.2 |
|  |  |  |  | [f] |
| $[\mathrm{Ru(CO)_3Et}(\eta^3\text{-}\mathrm{C_5H_5})]$ |  |  |  | 2 059.2 |
|  |  |  |  | 1 980.5 |
| $[\mathrm{Ru(CO)_3H}(\eta^3\text{-}\mathrm{C_5H_5})]$ |  |  |  | 2 068.8 |
|  |  |  |  | 1 983.4 |

[a] Data from ref. 5. [b] These bands arise from a single species with matrix splitting unless otherwise stated. [c] ν(NN) at 2 188.6 cm$^{-1}$ for $[\mathrm{Ru(CO)(N_2)Me}(\eta^5\text{-}\mathrm{C_5H_5})]$ and at 2 152.5 cm$^{-1}$ for $[\mathrm{Ru(N_2)_2Me}(\eta^5\text{-}\mathrm{C_5H_5})]$. [d] Obscured initially by lower band of $[\mathrm{Ru(CO)_2Me}(\eta^5\text{-}\mathrm{C_5H_5})]$. [e] ν(NN) at 2194.8 cm$^{-1}$ for $[\mathrm{Ru(CO)(N_2)H}(\eta^5\text{-}\mathrm{C_5H_5})]$ and at 2155.2 cm$^{-1}$ for $[\mathrm{Ru(N_2)_2H}(\eta^5\text{-}\mathrm{C_5H_5})]$. [f] Band obscured by other photoproducts.

labelling experiments seems unlikely because of the number of possible products and their overlapping band patterns.

(*b*) *Photolysis of* $[\mathrm{M(CO)_2Et}(\eta^5\text{-}\mathrm{C_5H_5})]$ (M = Fe *or* Ru) *Complexes in Pentane Solutions at* −30 °C *and in* $CH_4$, $^{13}CO$- *doped* $CH_4$, $N_2$, *and* CO *Matrices at* 12 K.—The photolysis of $[\mathrm{Ru(CO)_2Et}(\eta^5\text{-}\mathrm{C_5H_5})]$ in pentane proceeded more rapidly than that of the corresponding methyl derivative. The photoreaction was dependent on the concentration and temperature of the solution, *i.e.* more dilute solutions and progressively higher temperatures (−30 to +20 °C) accelerated the rate of dealkylation. During the course of the reaction the appearance of two new i.r.-active terminal CO-stretching bands was observed [Figure 4; ν(CO) at 2 032 and 1 974 cm$^{-1}$]. Upon further irradiation the yellow solution due to the starting material and the primary photoproduct, assigned as $[\mathrm{Ru(CO)_2H}(\eta^5\text{-}\mathrm{C_5H_5})]$, gradually changed to violet. Simultaneously with the colour change the appearance of a new CO band at 1 901 cm$^{-1}$ was noted. The deep violet reaction product was found to be a mixture of $[\mathrm{Ru(CO)_2H}(\eta^5\text{-}\mathrm{C_5H_5})]$ and $[\{\mathrm{Ru(CO)}(\eta^5\text{-}\mathrm{C_5H_5})\}_2(\mu\text{-}\mathrm{H})_2]$, by i.r. and n.m.r. spectroscopy (Table 1). The upfield signal (δ −17.33) in the $^1H$ n.m.r. spectrum of the latter compound is typical of a bridging hydrogen ligand in a dinuclear complex that contains a Ru–Ru double bond (**1**). A similar dimeric osmium complex, $[\{\mathrm{Os(CO)}(\eta^5\text{-}\mathrm{C_5H_5})\}_2(\mu\text{-}\mathrm{H})_2]$, has recently been reported.[16] Initially $C_2H_4$ is the dominant component of the photolysis gas together with a little $C_2H_6$, but gradually the amount of CO increases as the colour of the solution changes to violet and at the end of the reaction it is the main gaseous product.



(**1**)

The i.r. spectrum of $[\mathrm{Fe(CO)_2Et}(\eta^5\text{-}\mathrm{C_5H_5})]$ isolated at high dilution in a $CH_4$ matrix at 12 K showed two intense terminal CO stretching bands centred at 2 005.8 and 1 949.2 cm$^{-1}$ (Table 2).

**Table 3.** Observed and calculated[a] positions (cm$^{-1}$) of the terminal CO-stretching bands of $^{13}$CO-enriched [M(CO)$_2$R($\eta^5$-C$_5$H$_5$)] (M = Fe or Ru, R = Me or Et) complexes and their photoproducts in mixed $^{13}$CO–CH$_4$ (1:20) matrices at 12 K

| Complex | Point group | ν(CO) | Bands: Observed | Bands: Calc. |
|---|---|---|---|---|
| [Fe($^{12}$CO)$_2$Et($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | 2 003.8 | 2 003.1 |
| | | $A''$ | 1 946.3 | 1 946.0 |
| [Fe($^{12}$CO)($^{13}$CO)Et($\eta^5$-C$_5$H$_5$)] | $C_1$ | $A$ | 1.987.5 | 1 988.4 |
| | | $A$ | 1 916.6 | 1 916.8 |
| [Fe($^{13}$CO)$_2$Et($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | 1 957.7 | 1 958.6 |
| | | $A''$ | 1 902.2 | 1 902.7 |
| [Ru($^{12}$CO)$_2$Me($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | 2 016.7 | 2 016.7 |
| | | $A''$ | 1 956.3 | 1 956.3 |
| [Ru($^{12}$CO)($^{13}$CO)Me-($\eta^5$-C$_5$H$_5$)] | $C_1$ | $A$ | 2 011.7 | 2 011.6 |
| | | $A$ | 1 927.0 | 1 927.3 |
| [Ru($^{13}$CO)$_2$Me($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | 1 971.0 | 1 971.9 |
| | | $A''$ | 1 912.1 | 1 912.8 |
| [Ru($^{12}$CO)$_2$Et($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | 2 013.5 | 2 013.5 |
| | | $A''$ | 1 952.4 | 1 952.4 |
| [Ru($^{12}$CO)($^{13}$CO)Et-($\eta^5$-C$_5$H$_5$)] | $C_1$ | $A$ | *b* | 1 998.4 |
| | | $A$ | | 1 923.5 |
| [Ru($^{13}$CO)$_2$Et($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | *b* | 1 968.8 |
| | | $A''$ | | 1 909.0 |
| [Fe($^{12}$CO)$_2$H($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | 2 018.1 | 2 018.4 |
| | | $A''$ | 1 958.7 | 1 958.2 |
| [Fe($^{12}$CO)($^{13}$CO)H($\eta^5$-C$_5$H$_5$)] | $C_1$ | $A$ | 2 003.8 | 2 003.3 |
| | | $A$ | 1 928.4 | 1 929.2 |
| [Fe($^{13}$CO)$_2$H($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | 1 972.7 | 1 973.5 |
| | | $A''$ | 1 915.0 | 1 914.7 |
| [Ru($^{12}$CO)Me($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | 1 940.7 | 1 940.7 |
| [Ru($^{13}$CO)Me($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | 1 895.8 | 1 896.6 |
| [Ru($^{12}$CO)$_2$H($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | 2 027.6 | 2 027.7 |
| | | $A''$ | 1 965.7 | 1 965.7 |
| [Ru($^{12}$CO)($^{13}$CO)H-($\eta^5$-C$_5$H$_5$)] | $C_1$ | $A$ | 2 012.5 | 2 012.3 |
| | | $A$ | 1 936.1 | 1 936.6 |
| [Ru($^{13}$CO)$_2$H($\eta^5$-C$_5$H$_5$)] | $C_s$ | $A'$ | 1 981.0 | 1 981.6 |
| | | $A''$ | 1 920.8 | 1 921.0 |
| [Ru($^{12}$CO)(C$_2$H$_4$)H($\eta^5$-C$_5$H$_5$)] | $C_1$ | $A$ | 1 958.7 | 1 958.7 |
| [Ru($^{13}$CO)(C$_2$H$_4$)H($\eta^5$-C$_5$H$_5$)] | $C_1$ | $A$ | *b* | 1 914.2 |

[a] Refined energy-factored CO-stretching and interaction force constants (N m$^{-1}$) are: [Fe(CO)$_2$Me($\eta^5$-C$_5$H$_5$)], $K$ = 1 539.7 and $k_i$ = 44.3;[5] [Fe(CO)$_2$Et($\eta^5$-C$_5$H$_5$)], $K$ = 1 575.4 and $k_i$ = 45.6; [Ru(CO)$_2$-Me($\eta^5$-C$_5$H$_5$)], $K$ = 1 594.7 and $k_i$ = 48.5; [Ru(CO)$_2$Et($\eta^5$-C$_5$H$_5$)], $K$ = 1 589.0 and $k_i$ = 49.0; [Fe(CO)$_2$H($\eta^5$-C$_5$H$_5$)], $K$ = 1 597.5 and $k_i$ = 48.3; [Ru(CO)Me($\eta^5$-C$_5$H$_5$)], $K$ = 1 520.9; [Ru(CO)$_2$H($\eta^5$-C$_5$-H$_5$)], $K$ = 1 611.0 and $k_i$ = 50.0. [b] Enrichment competing with other photoprocesses which dominate in the course of the long photolysis times needed to produce these bands.

Irradiation of the matrix with medium-energy u.v. light (290 < λ < 370 nm) led to the generation of two new bands at 2 017.6 and 1 958.5 cm$^{-1}$. Since these two bands continued to grow with the same relative intensity ratio they must arise from a species with two terminal carbonyl ligands. Such a species is [Fe(CO)$_2$H-($\eta^5$-C$_5$H$_5$)], *i.e.* β elimination has taken place. This is in agreement with the findings of Kaslauskas and Wrighton,[3] who photolysed [Fe(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] in glasses and paraffin-wax matrices at 77 K, and Gerhartz *et al.*[4] who photolysed [Fe(CO)$_2$-Et($\eta^5$-C$_5$H$_5$)] in Ar at 10 K. When the experiment was repeated with a $^{13}$CO-doped CH$_4$ matrix, initial irradiation generated new bands which may be assigned to the species [Fe($^{12}$CO)$_2$H-($\eta^5$-C$_5$H$_5$)] and [Fe($^{12}$CO)($^{13}$CO)Et($\eta^5$-C$_5$H$_5$)], *i.e.* there is a competition between exchange and elimination. Prolonged photolysis resulted in bands which are attributed to complexes [Fe($^{13}$CO)$_2$Et($\eta^5$-C$_5$H$_5$)], [Fe($^{12}$CO)($^{13}$CO)H($\eta^5$-C$_5$H$_5$)], and [Fe($^{13}$CO)$_2$H($\eta^5$-C$_5$H$_5$)] on the basis of the satisfactory correspondence between the observed and calculated band positions produced by energy-factored force-field fitting (Table 3). Surprisingly, irradiation of [Fe(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] in N$_2$ and C$_2$H$_4$-doped CH$_4$ matrices resulted in the exclusive formation of [Fe(CO)$_2$H($\eta^5$-C$_5$H$_5$)]. This is in contrast to the formation of new N$_2$ and C$_2$H$_4$ complexes for the ruthenium analogue (see below).

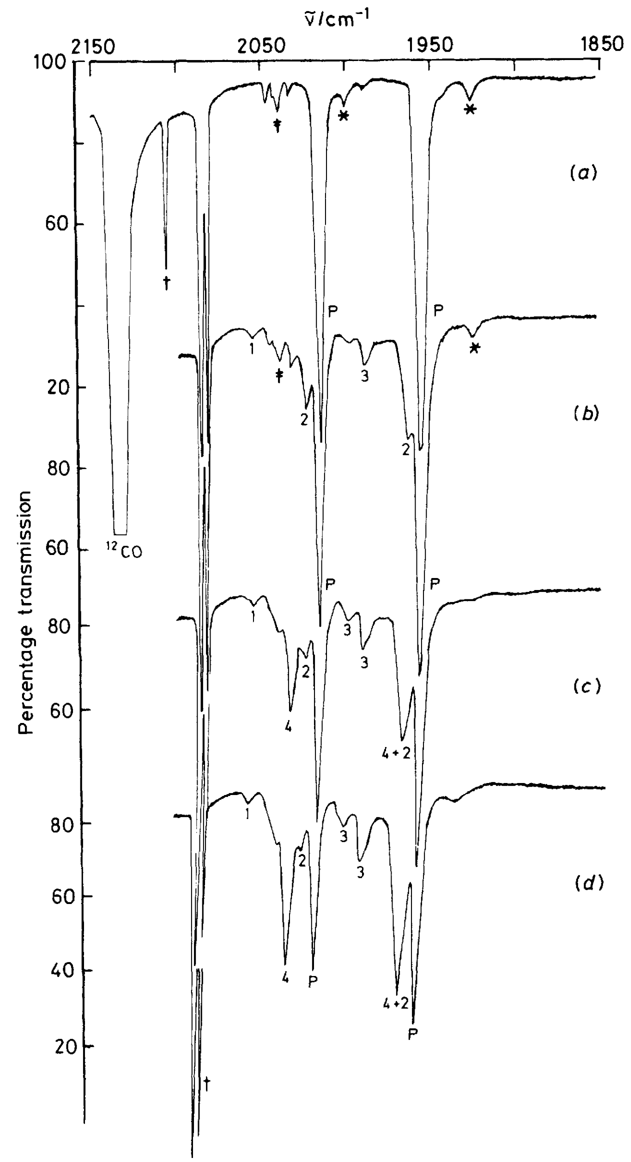


**Figure 3.** Infrared spectra from an experiment with [Ru(CO)$_2$Me($\eta^5$-C$_5$H$_5$)] (bands marked P) isolated at high dilution in a CO matrix at 12 K: (*a*) after deposition, (*b*) after photolysis for 100 min using 290 < λ < 370 and λ > 550 nm radiation, (*c*) after photolysis for 50 min with 270 < λ < 390 nm, and (*d*) after photolysis for another 100 min using the same radiation. Bands marked with an asterisk (*) are due to [Ru($^{12}$CO)($^{13}$CO)Me($\eta^5$-C$_5$H$_5$)] present in natural abundance, those marked with a dagger (†) to other isotopically substituted CO molecules, and those marked with a double dagger (‡) to a trace impurity. Bands (1)—(4) are derived from photoproducts (see text)

Photolysis (290 < λ < 370 nm) of [Fe(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] in pure CO matrices (Figure 5) resulted in the observation of new CO bands at 2 046.0, 2 020.8, 1 978.7, 1 969.3, and 1 957.5 cm$^{-1}$ [Figure 5(*b*)]. The bands at 2 020.8 and 1 957.5 cm$^{-1}$ [bands (1)] are assigned to the known hydrido-complex [Fe(CO)$_2$H($\eta^5$-C$_5$H$_5$)] by analogy with the behaviour of [Fe(CO)$_2$Et($\eta^5$-

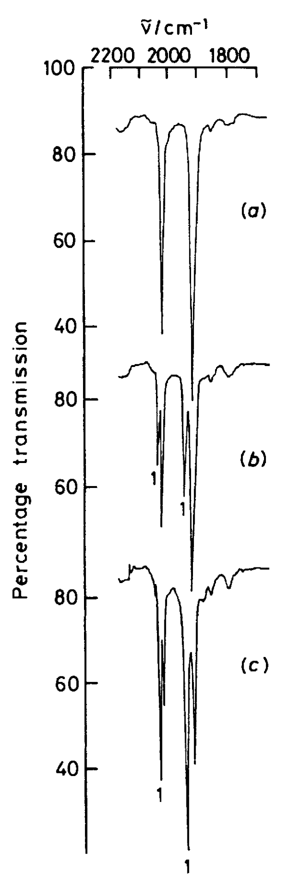


**Figure 4.** Infrared spectra from an experiment with [Ru(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] in pentane in an i.r. solution cell at 20 °C: (*a*) initial spectrum, (*b*) after photolysis for 150 min ($\lambda$ > 300 nm), and (*c*) after photolysis for another 120 min. Bands (1) are derived from [Ru(CO)$_2$H($\eta^5$-C$_5$H$_5$)]

C$_5$H$_5$)] in CH$_4$, N$_2$, and C$_2$H$_4$-doped matrices. The other three bands [bands (2); 2 046.0, 1 978.7, and 1 969.3 cm$^{-1}$] show a clear similarity to the bands of [Fe(CO)$_3$Me($\eta^3$-C$_5$H$_5$)] (2 050.3, 1 982.7, and 1 975.1 cm$^{-1}$; Table 2).[5] Bearing in mind that the ordering of the CO bands for [Fe(CO)$_2$R($\eta^5$-C$_5$H$_5$)] (R = H, Me, or Et) complexes is H > Me > Et and that the new product bands are at lower wavenumbers than those of [Fe(CO)$_3$Me($\eta^3$-C$_5$H$_5$)], the new photoproduct may probably be assigned as [Fe(CO)$_3$Et($\eta^3$-C$_5$H$_5$)]. Such an assignment reveals the possibility that in CO matrices ring slippage ($\eta^5 \longrightarrow \eta^3$) may compete with $\beta$ elimination (see above, $^{13}$CO exchange). Prolonged photolysis with higher-energy u.v. light ($270 < \lambda < 390$ nm) produced further new bands [bands (3)] at 2 035.2, 2 005.5, and 1 992.8 cm$^{-1}$ [Figures 5(*c*) and (*d*)], *cf.* the additional bands observed on photolysis of [Ru(CO)$_2$-Me($\eta^5$-C$_5$H$_5$)] in CO matrices (see above). Significantly, no bands were seen for HCO, MeCO, and EtCO radicals in contrast to the photoreactions of [M(CO)$_3$H($\eta^5$-C$_5$H$_5$)] (M = Mo or W) complexes in CO matrices which generate the HCO radical.[17]

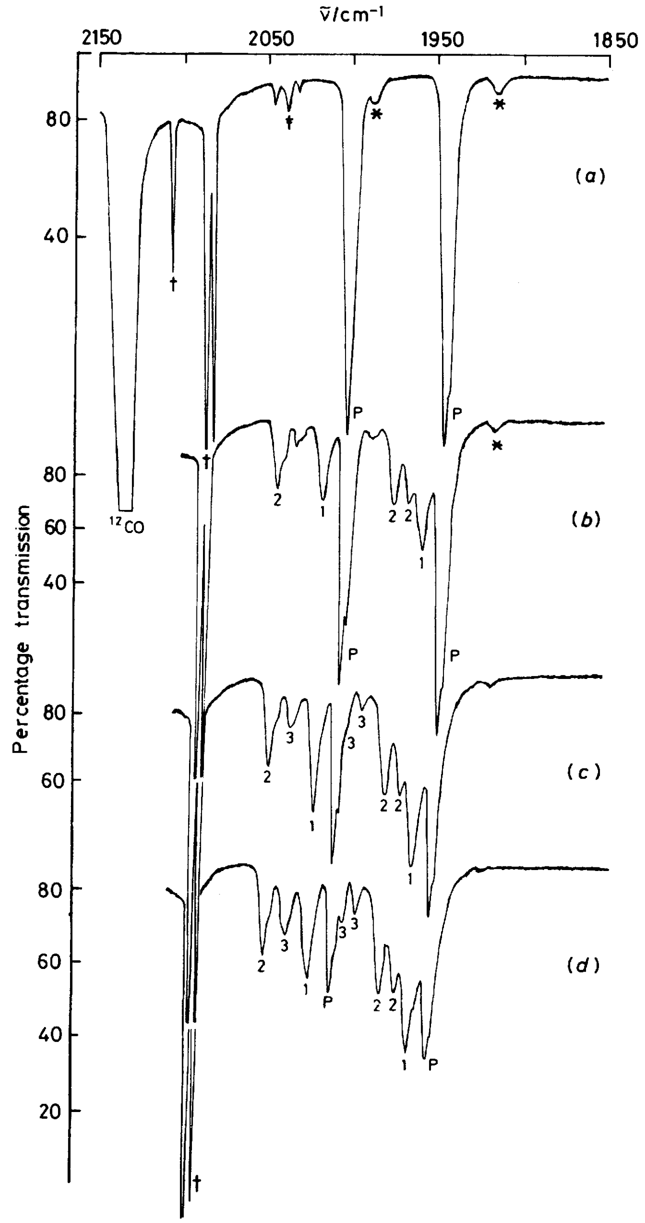


**Figure 5.** Infrared spectra from an experiment with [Fe(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] (bands marked P) isolated at high dilution in a CO matrix at 12 K: (*a*) after deposition, (*b*) after photolysis for 4 h using $290 < \lambda < 370$ nm, (*c*) after photolysis for 50 min with $270 < \lambda < 390$ nm, and (*d*) after photolysis for another 60 min with $270 < \lambda < 390$ nm. Bands marked with an asterisk (*) are due to [Fe($^{12}$CO)($^{13}$CO)Et($\eta^5$-C$_5$H$_5$)] present in natural abundance, those marked with a dagger (†) to other isotopically substituted CO molecules, and those marked with a double dagger (‡) to a trace impurity. Bands (1)—(3) are derived from photoproducts (see text)

The i.r. spectrum of [Ru(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] isolated at high dilution in a CH$_4$ matrix [Figure 6(*a*)] showed the same doublet splitting seen previously for [M(CO)$_2$Me($\eta^5$-C$_5$H$_5$)] (M = Fe or Ru) complexes in CH$_4$ matrices. A period of photolysis (45 min, $290 < \lambda < 370$ nm) led to the observation of three new bands at 2 029.2, 1 967.5, and 1 960.3 cm$^{-1}$ [Figure 6(*b*)] in addition to a band due to free CO. Continued photolysis with the same energy source showed that these three bands arise from two different species [Figure 6(*c*)]. Since the relative intensity ratio of the first two bands remained constant throughout the experiment, these [bands (1)] originate from the same species, [Ru(CO)$_2$H($\eta^5$-C$_5$H$_5$)]. The single CO-stretching band at 1 960.3 cm$^{-1}$ [band (2)] probably arises from a monocarbonyl product since free CO is also observed. Comparison of the band position for [Ru(CO)Me($\eta^5$-C$_5$H$_5$)] with those of [Ru(CO)$_2$Me($\eta^5$-C$_5$H$_5$)] (Table 2) results in the prediction that a band for [Ru(CO)Et($\eta^5$-C$_5$H$_5$)] should occur at *ca.* 1 938 cm$^{-1}$, which is at considerably lower wavenumber than that observed (1 960.3 cm$^{-1}$). An alternative candidate is [Ru(CO)(C$_2$H$_4$)H($\eta^5$-C$_5$H$_5$)] and this assignment was proved

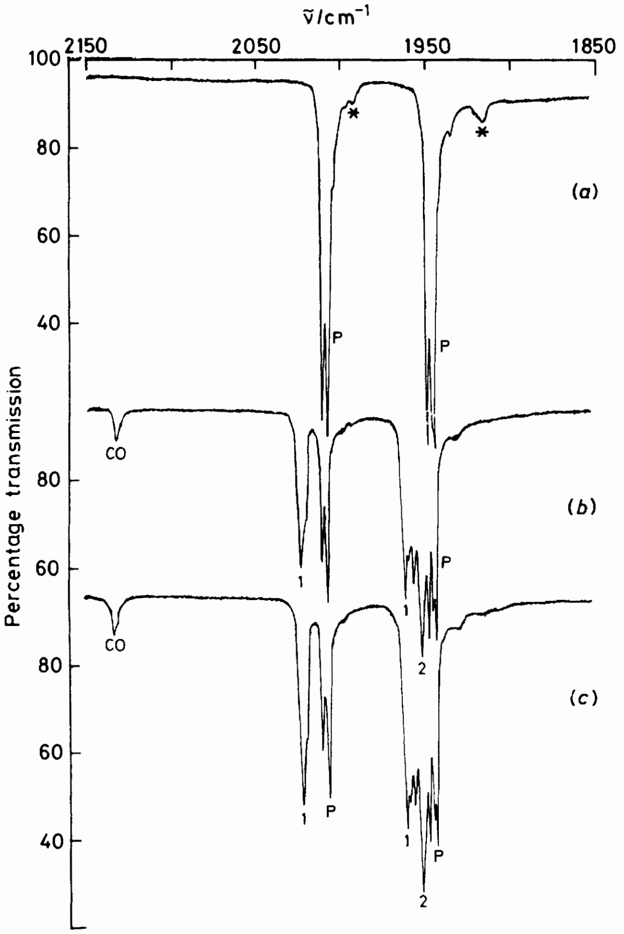


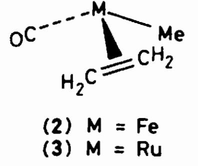
**Figure 6.** Infrared spectra from an experiment with [Ru(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] (bands marked P) isolated at high dilution in a CH$_4$ matrix at 12 K: (*a*) after deposition, (*b*) after photolysis for 45 min using 290 < $\lambda$ < 370 nm, and (*c*) after photolysis for 20 min using the same filter. Bands marked with an asterisk (*) are due to [Ru($^{12}$CO)($^{13}$CO)-Et($\eta^5$-C$_5$H$_5$)] present in natural abundance. Bands (1) and (2) are derived from photoproducts (see text)

correct when [Ru(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] was photolysed in a C$_2$H$_4$-doped CH$_4$ matrix (see below). The product with the single band at 1960.3 cm$^{-1}$ [band (2)] was formed in high yield in addition to [Ru(CO)$_2$H($\eta^5$-C$_5$H$_5$)]. To attempt to provide further information about reaction pathways, [Ru(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] was photolysed in a $^{13}$CO-doped CH$_4$ matrix. Initial products were [Ru($^{12}$CO)$_2$H($\eta^5$-C$_5$H$_5$)] and [Ru($^{12}$CO)-(C$_2$H$_4$)H($\eta^5$-C$_5$H$_5$)] and, additionally, a band due to free $^{12}$CO. Prolonged photolysis with the same source (290 < $\lambda$ < 370 nm) resulted in the growth of bands which are assigned to [Ru($^{12}$CO)($^{13}$CO)H($\eta^5$-C$_5$H$_5$)] and [Ru($^{13}$CO)$_2$H($\eta^5$-C$_5$H$_5$)] on the basis of the satisfactory agreement between the observed and calculated bands using an energy-factored force-field treatment (Table 3). Significantly, *no* bands were observed for [Ru($^{12}$CO)$_{2-n}$($^{13}$CO)$_n$Et($\eta^5$-C$_5$H$_5$)] ($n$ = 0—2) or [Ru($^{13}$CO)(C$_2$H$_4$)H($\eta^5$-C$_5$H$_5$)].

Photolysis of [Ru(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] in a N$_2$ matrix with medium-energy u.v. radiation (290 < $\lambda$ < 370 nm) led to the production of new photoproduct bands at 2 194.8, 2 033.2, 1 979.8, 1 971.4, and 1 967.2 cm$^{-1}$ in addition to the band of free CO. Further irradiation resulted in the growth of all the new bands at the expense of the parent complex. The two bands at 2 033.2 and 1 971.4 cm$^{-1}$ are at similar positions to those obtained when [Ru(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] is photolysed in CH$_4$ matrices (Table 2) and can be assigned to [Ru(CO)$_2$H($\eta^5$-C$_5$H$_5$)]. Similarly the single band at 1 967.2 cm$^{-1}$ may be assigned to [Ru(CO)(C$_2$H$_4$)H($\eta^5$-C$_5$H$_5$)]. The remaining bands at 2 194.8 and 1 979.8 cm$^{-1}$ are typical of terminal v(NN) and v(CO) bands respectively, so that the new photoproduct may be identified as [Ru(CO)(N$_2$)H($\eta^5$-C$_5$H$_5$)], *cf.* [Ru(CO)(N$_2$)-Me($\eta^5$-C$_5$H$_5$)]. Prolonged photolysis (290 < $\lambda$ < 370 nm) led to the growth of a further weak band at 2 155.2 cm$^{-1}$ which probably arises from [Ru(N$_2$)$_2$H($\eta^5$-C$_5$H$_5$)], *cf.* [Ru(N$_2$)$_2$Me-($\eta^5$-C$_5$H$_5$)] (Table 2).

Photolysis (290 < $\lambda$ < 370 nm) of [Ru(CO)$_2$Et($\eta^5$-C$_5$H$_5$)] isolated at high dilution in a CO matrix resulted in the initial growth of three new bands at 2 032.4, 1 971.2, and 1 966.3 cm$^{-1}$, which may be assigned to the species [Ru(CO)$_2$H($\eta^5$-C$_5$H$_5$)] and [Ru(CO)(C$_2$H$_4$)H($\eta^5$-C$_5$H$_5$)] (Table 2). Prolonged irradiation with the same source generated two further bands at 2 059.2 and 1 980.5 cm$^{-1}$ which grew with constant relative intensities and hence arise from a single species. By analogy with the band positions for [Fe(CO)$_3$Me($\eta^3$-C$_5$H$_5$)] (Table 2), the new bands can probably be assigned to the species [Ru(CO)$_3$-Et($\eta^3$-C$_5$H$_5$)]. Upon further photolysis with higher-energy u.v. light (270 < $\lambda$ < 390 nm) some further new bands appear at 2 068.8 and 1 983.4 cm$^{-1}$ at the expense of the bands due to [Ru(CO)$_2$H($\eta^5$-C$_5$H$_5$)] which decrease. A comparison of the relative band positions for [Ru(CO)$_2$R($\eta^5$-C$_5$H$_5$)] (R = H, Me, or Et) complexes gives an order H > Me > Et so that having assigned the Me and Et ring-slippage products it seems likely that the higher-wavenumber bands for this new product can be assigned to [Ru(CO)$_3$H($\eta^3$-C$_5$H$_5$)], though the ethylene complex [Ru(CO)$_2$(C$_2$H$_4$)H($\eta^3$-C$_5$H$_5$)] cannot be ruled out. Further weak bands at 2 041.5, 2 003.5, and 1 993.5 cm$^{-1}$ were also observed but a definitive assignment of these seems improbable {see above for [Ru(CO)$_2$Me($\eta^5$-C$_5$H$_5$)]}.

(*c*) *Photo-induced Reactions of* [M(CO)$_2$Me($\eta^5$-C$_5$H$_5$)] (M = Fe *or* Ru) *Complexes with* C$_2$H$_4$ *in Pentane Solutions at* $-30$ °C *and in* C$_2$H$_4$*-doped* CH$_4$ *Matrices at* 12 K.—The photo-induced reactions of [M(CO)$_2$Me($\eta^5$-C$_5$H$_5$)] (M = Fe or Ru) complexes in the presence of C$_2$H$_4$ result in the formation of the mono-substitution products [M(CO)(C$_2$H$_4$)Me($\eta^5$-C$_5$H$_5$)]. The reaction of C$_2$H$_4$ with the iron complex is *ca.* four times faster than with the ruthenium analogue. No other products could be detected. The iron–olefin product is particularly temperature sensitive and it decomposes above $-30$ °C. The $^1$H and $^{13}$C n.m.r. spectra of the [M(CO)(C$_2$H$_4$)Me($\eta^5$-C$_5$H$_5$)] complexes show temperature-dependent olefin proton and carbon signals analogous to the behaviour shown by [Fe(CO)(SnR$_3$)(C$_2$H$_4$)($\eta^5$-C$_5$H$_5$)] and [Fe(CO)(SnR$_3$)(C$_2$H$_4$)($\eta^5$-C$_9$H$_7$)] complexes (R = Me or Ph, C$_9$H$_7$ = indenyl).[18] The energy barrier for rotation of C$_2$H$_4$ around the metal–olefin bond axis in complexes (**2**) and (**3**) ($\Delta G^\ddagger$ = 41.3 and 34.6 kJ mol$^{-1}$, respectively) is comparatively low and probably indicates weak M$\rightarrow$C$_2$H$_4$ back donation. The modest shielding of the olefinic carbon signals ($\delta$ = 43.3 and 35.0 p.p.m.) is another indication of weak back donation. By way of contrast, the complexes *trans*-[W(CO)$_2$(C$_2$H$_4$)Me($\eta^5$-C$_5$H$_5$)] and *trans*-[W(CO)$_2$(C$_2$H$_4$)Me($\eta^5$-C$_9$H$_7$)] exhibit more strongly shielded olefinic carbon signals ($\delta$ = 21.0 p.p.m.; [$^2$H$_8$]toluene) and higher barriers for olefin rotation ($\Delta G^\ddagger$ =

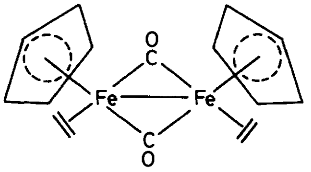


(**2**) M = Fe
(**3**) M = Ru

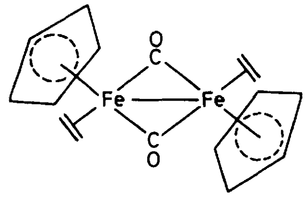
60.1 and 62.2 kJ mol$^{-1}$, respectively).[19] In addition the presence of $^{183}$W–$^{13}$C coupling [$J$(W–C) = 12 Hz] indicates distinct *s* character in the metal–olefin bond and consequently a contribution from a metallocyclic structure to the metal–olefin bonding.

In a $C_2H_4$-doped (5%) $CH_4$ matrix photolysis of [Ru(CO)$_2$Me($\eta^5$-$C_5H_5$)] produced new bands at 1 956.6 and 1 941.7 cm$^{-1}$ in addition to a band due to free CO. The band at 1 941.7 cm$^{-1}$ corresponds to the 16-electron species [Ru(CO)Me($\eta^5$-$C_5H_5$)] (Table 2). On the basis of the similarity of the new band at 1 956.6 cm$^{-1}$ with the CO-stretching band of [Ru(CO)($C_2H_4$)Me($\eta^5$-$C_5H_5$)] in solution [$\nu$(CO) at 1 960 cm$^{-1}$], it seems reasonable to assign the other new band to [Ru(CO)($C_2H_4$)Me($\eta^5$-$C_5H_5$)]. Similarly [Fe(CO)$_2$Me($\eta^5$-$C_5H_5$)] gave [Fe(CO)($C_2H_4$)Me($\eta^5$-$C_5H_5$)] [$\nu$(CO) at 1 957.1 (matrix) and at 1 960 cm$^{-1}$(solution)] but no band was observed for [Fe(CO)Me($\eta^5$-$C_5H_5$)].

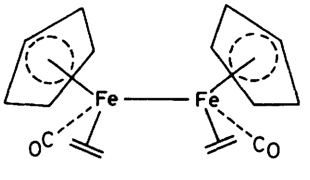
(*d*) *Photo-induced Reactions of* [M(CO)$_2$Et($\eta^5$-$C_5H_5$)] (M = Fe *or* Ru) *Complexes with* $C_2H_4$ *in Pentane Solutions at* −30 °C *and in* $C_2H_4$*-doped* $CH_4$ *Matrices at* 12 K.—The photo-induced reaction of [Fe(CO)$_2$Et($\eta^5$-$C_5H_5$)] and ethylene in pentane solution at −30 °C resulted in a fast colour change from yellow to green and simultaneously a dark green precipitate was formed. The i.r. spectrum of the solution indicated the formation of the hydrido-complex [Fe(CO)$_2$H($\eta^5$-$C_5H_5$)] [$\nu$(CO) at 2 022 and 1 962 cm$^{-1}$]. Two new weak bands in the region of bridging carbonyl ligands [$\nu$(CO) at 1 788 and 1 770 cm$^{-1}$] also indicated the formation of the dimer [{Fe(CO)$_2$($\eta^5$-$C_5H_5$)}$_2$]. After 45 min of photolysis the dark green suspension was chromatographed (silica column). Elution (−30 °C) with toluene yielded a little [{Fe(CO)$_2$($\eta^5$-$C_5H_5$)}$_2$] while elution (− 30 °C) with diethyl ether gave a major green fraction (*ca.* 80%) that showed four CO bands in the i.r. spectrum [$\nu$(CO) at 1 990, 1 947, 1 776, and 1 759 cm$^{-1}$; diethyl ether]. The mass spectrum indicated a molecular peak at $m/e$ = 354 that could * be due to the *new* dimeric species [{Fe(CO)($C_2H_4$)($\eta^5$-$C_5H_5$)}$_2$]. The $^1$H n.m.r. spectrum of the green product contains five separate $C_5H_5$ resonances with different intensities (4.91, 4.77, 4.58, 4.50, and 4.44 p.p.m.; [$^2H_8$]tetrahydrofuran]) at −20 °C. At 20 °C broad signals without splittings are observed for the $C_2H_4$ protons between 3 and 0 p.p.m. Upon cooling to −20 °C there are two intense signals (2.72 and 0.13 p.p.m.) with other smaller unstructured broad signals in the 3—0 p.p.m. region. At −80 °C, however, there are only two signals (2.73 and 0.07 p.p.m.) which are split into two doublets [$J$(CH–H) = 12.3 Hz]. The $^{13}$C n.m.r. spectrum ($^1$H-decoupled) of the green product shows four $C_5H_5$ resonances (90.0, 89.2, 89.0, and 88.5 p.p.m.; [$^2H_8$]tetrahydrofuran) at −20 °C with relative intensities (2:9:8:2) that are comparable with the $C_5H_5$ signals in the $^1$H n.m.r. spectrum. At −20 °C two signals [$\delta$ = 45.1 and 43.7 p.p.m.; $^1J$(C–H) = 179 Hz] may be assigned to two differently shielded $C_2H_4$ ligands and these signals remained unchanged upon cooling to −80 °C. Two signals were observed ($\delta$ = 277.8 and 213.5 p.p.m.) in the CO-ligand region and these may be assigned to bridging and terminal CO ligands respectively. The ethylene dimer [{Fe(CO)($C_2H_4$)($\eta^5$-$C_5H_5$)}$_2$] may be considered to exist in four forms, (**4**)—(**7**), that can undergo rapid intramolecular bridge–terminal carbonyl interconversions and *cis–trans* isomerisation, while intramolecular rotation of the $C_2H_4$ ligands should not be overlooked. Of the four forms, which are indicated by the four $^{13}$C resonances assigned to $C_5H_5$ ligands, it is proposed that (**5**) and (**7**) are dominant, by analogy with the detailed $^{13}$C n.m.r. study of [{Fe(CO)$_2$($\eta^5$-$C_5H_5$)}$_2$].[20] The i.r. spectrum of [{Fe(CO)($C_2H_4$)($\eta^5$-$C_5H_5$)}$_2$] shows two main bands in the CO-stretching region (1 950 and 1 762 cm$^{-1}$; tetrahydrofuran) with approximately equal intensity. These bands may be assigned to the terminal and bridging CO ligands of (**7**) and (**5**), respectively, present in *ca.* 1:1 ratio (see above).



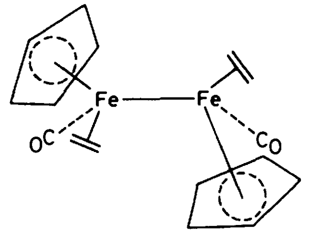
(**4**)



(**5**)



(**6**)



(**7**)

The photolysis of [Ru(CO)$_2$Et($\eta^5$-$C_5H_5$)] in pentane in the presence of $C_2H_4$ at −30 °C did not yield the dimer [{Ru(CO)($C_2H_4$)($\eta^5$-$C_5H_5$)}$_2$], as found for Fe. The only product isolated was the yellow hydride [Ru(CO)$_2$H($\eta^5$-$C_5H_5$)] together with a small amount of unidentified brown precipitate that did not show any CO bands in the i.r. spectrum.

Irradiation of [Fe(CO)$_2$Et($\eta^5$-$C_5H_5$)] in $C_2H_4$-doped $CH_4$ matrices did not lead to the formation of [Fe(CO)($C_2H_4$)H($\eta^5$-$C_5H_5$)] or [Fe(CO)($C_2H_4$)H($\eta^5$-$C_5H_5$)] but only to [Fe(CO)$_2$H($\eta^5$-$C_5H_5$)]. However, photolysis of [Ru(CO)$_2$Et($\eta^5$-$C_5H_5$)] in a $C_2H_4$-doped $CH_4$ matrix afforded a new band at 1 954.1 cm$^{-1}$ which may be assigned to [Ru(CO)($C_2H_4$)H($\eta^5$-$C_5H_5$)] by comparison with the photolysis product from [Ru(CO)$_2$Et($\eta^5$-$C_5H_5$)] in non-co-ordinating matrices (see above, Table 2).

## Discussion

The photoreactions of [M(CO)$_2$R($\eta^5$-$C_5H_5$)] (M = Fe or Ru, R = Me or Et) complexes studied in pentane solutions (−30 °C) and in gas matrices (12 K) are summarised in Tables 4 and 5 respectively.

The mechanisms of the photoreactions of these complexes in alkanes in the absence and presence of potential ligands have been proposed to involve the dissociative loss of CO as the primary process following near-u.v. excitation.[1–3] Support for a dissociative mechanism comes from quantum-yield measurements on photosubstitution reactions which showed no dependence on the incoming ligand and its concentration. For such a dissociative mechanism it has been proposed that the reactive intermediates are the 16-electron [M(CO)R($\eta^5$-$C_5H_5$)] species.

Photolysis of [Ru(CO)$_2$Me($\eta^5$-$C_5H_5$)] in an alkane matrix at 77 K[3] provided the first evidence for the co-ordinatively unsaturated species [Ru(CO)Me($\eta^5$-$C_5H_5$)]. Confirmation of this result is afforded by the work in gas matrices and in particular by the observation of bands for [Ru($^{12}$CO)Me($\eta^5$-$C_5H_5$)] and [Ru($^{13}$CO)Me($\eta^5$-$C_5H_5$)] in $^{13}$CO-doped matrices (Table 3). Previous failures[4,5] to trap the species [Fe(CO)Me($\eta^5$-$C_5H_5$)] even at *ca.* 10 K must reflect the higher

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* In the field desorption mass spectrum there are also peaks at $m/e$ = 539, 538, and 537 that have not yet been explained.

**Table 4.** Summary of photoproducts formed in solution reactions at −30 °C

| Starting complex | Solvent | Products |
|---|---|---|
| $[M(CO)_2Me(\eta^5\text{-}C_5H_5)]$<br>(M = Fe or Ru) | Pentane | $[\{M(CO)_2(\eta^5\text{-}C_5H_5)\}_2] + CH_4$ |
| | $C_2H_4$–pentane | $[M(CO)(C_2H_4)Me(\eta^5\text{-}C_5H_5)]$ |
| $[Fe(CO)_2Et(\eta^5\text{-}C_5H_5)]$ | Pentane | $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2] + C_2H_4 + C_2H_6 + H_2$ |
| | $C_2H_4$–pentane | $[Fe(CO)_2H(\eta^5\text{-}C_5H_5)] + [\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2] + [\{Fe(CO)(C_2H_4)(\eta^5\text{-}C_5H_5)\}_2]$ |
| $[Ru(CO)_2Et(\eta^5\text{-}C_5H_5)]$ | Pentane | $[Ru(CO)_2H(\eta^5\text{-}C_5H_5)] + [\{Ru(CO)(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}H)_2] + C_2H_4 + CO$ |
| | $C_2H_4$–pentane | $[Ru(CO)_2H(\eta^5\text{-}C_5H_5)]$ |

**Table 5.** Summary of photoproducts formed in matrices at 12 K

| Starting complex | Matrix | Products |
|---|---|---|
| $[Fe(CO)_2Me(\eta^5\text{-}C_5H_5)]$ | 5% $^{13}CO$-doped $CH_4$ | $[Fe(^{12}CO)_{2\text{-}n}(^{13}CO)_nMe(\eta^5\text{-}C_5H_5)]$ |
| | 5% $C_2H_4$-doped $CH_4$ | $[Fe(CO)(C_2H_4)Me(\eta^5\text{-}C_5H_5)]$ |
| $[Ru(CO)_2Me(\eta^5\text{-}C_5H_5)]$ | $CH_4$ | $[Ru(CO)Me(\eta^5\text{-}C_5H_5)]$ |
| | 5% $^{13}CO$-doped $CH_4$ | $[Ru(^{12}CO)_{2\text{-}n}(^{13}CO)_nMe(\eta^5\text{-}C_5H_5)] + [Ru(^{13}CO)Me(\eta^5\text{-}C_5H_5)]$ |
| | $N_2$ | $[Ru(CO)(N_2)Me(\eta^5\text{-}C_5H_5)]$ |
| | 5% $C_2H_4$-doped $CH_4$ | $[Ru(CO)(C_2H_4)Me(\eta^5\text{-}C_5H_5)]$ |
| $[Fe(CO)_2Et(\eta^5\text{-}C_5H_5)]$ | $CH_4$ and $N_2$ | $[Fe(CO)_2H(\eta^5\text{-}C_5H_5)]$ |
| | 5% $^{13}CO$-doped $CH_4$ | $[Fe(^{12}CO)_{2\text{-}n}(^{13}CO)_nEt(\eta^5\text{-}C_5H_5)] + [Fe(^{12}CO)_{2\text{-}n}(^{13}CO)_nH(\eta^5\text{-}C_5H_5)]$ |
| | CO | $[Fe(CO)_3Et(\eta^3\text{-}C_5H_5)]$ |
| $[Ru(CO)_2Et(\eta^5\text{-}C_5H_5)]$ | $CH_4$ | $[Ru(CO)(C_2H_4)H(\eta^5\text{-}C_5H_5)] + [Ru(CO)_2H(\eta^5\text{-}C_5H_5)]$ |
| | 5% $^{13}CO$-doped $CH_4$ | $[Ru(^{12}CO)_{2\text{-}n}(^{13}CO)_nH(\eta^5\text{-}C_5H_5)] + [Ru(^{12}CO)(C_2H_4)H(\eta^5\text{-}C_5H_5)]$ |
| | $N_2$ | $[Ru(CO)(N_2)H(\eta^5\text{-}C_5H_5)] + [Ru(CO)(C_2H_4)H(\eta^5\text{-}C_5H_5)] + [Ru(CO)_2H(\eta^5\text{-}C_5H_5)]$ |
| | 5% $C_2H_4$-doped $CH_4$ | $[Ru(CO)(C_2H_4)H(\eta^5\text{-}C_5H_5)] + [Ru(CO)_2H(\eta^5\text{-}C_5H_5)]$ |
| | CO | $[Ru(CO)(C_2H_4)H(\eta^5\text{-}C_5H_5)] + [Ru(CO)_2H(\eta^5\text{-}C_5H_5)] + [Ru(CO)_3H(\eta^3\text{-}C_5H_5)] + [Ru(CO)_3Et(\eta^3\text{-}C_5H_5)]$ |

reactivity/lower activation-energy barrier of the iron species towards recombination with the ejected CO ligand. In solution the 16-electron fragments $[M(CO)Me(\eta^5\text{-}C_5H_5)]$ presumably attack unreacted parent molecules to yield the dimers $[\{M(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$.

For the ethyl complexes the co-ordinative unsaturation in the $[M(CO)Et(\eta^5\text{-}C_5H_5)]$ species can be satisfied by β elimination to afford $[M(CO)(C_2H_4)H(\eta^5\text{-}C_5H_5)]$ complexes which may undergo CO substitution to give the carbonyl hydrides $[M(CO)_2H(\eta^5\text{-}C_5H_5)]$. Not surprisingly, no evidence could be found for the 16-electron species $[M(CO)Et(\eta^5\text{-}C_5H_5)]$ in gas matrices, but the ruthenium complex gave $[Ru(CO)(C_2H_4)H(\eta^5\text{-}C_5H_5)]$ at *ca.* 12 and 77 K [3] in addition to $[Ru(CO)_2H(\eta^5\text{-}C_5H_5)]$, whereas the iron complex gave only $[Fe(CO)_2H(\eta^5\text{-}C_5H_5)]$ under the same conditions.[3,4] An indication of the subtle differences between Fe and Ru in the matter of β elimination was provided by experiments involving $^{13}CO$-doped matrices. For the iron complex two $^{13}CO$-enriched products, $[Fe(^{12}CO)_{2\text{-}n}(^{13}CO)_nH(\eta^5\text{-}C_5H_5)]$ and $[Fe(^{12}CO)_{2-n}(^{13}CO)_nEt(\eta^5\text{-}C_5H_5)]$, were observed whereas for the ruthenium complex the only enriched product was $[Ru(^{12}CO)_{2\text{-}n}(^{13}CO)_nH(\eta^5\text{-}C_5H_5)]$. Differences were also apparent in the solution photoreactions, *e.g.* the iron complex gave $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$[2] whereas the ruthenium analogue gave $[Ru(CO)_2H(\eta^5\text{-}C_5H_5)]$ and the *new* dimer $[\{Ru(CO)(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}H)_2]$. Although an intermediate ethylene hydrido-complex of the type $[Ru(CO)(C_2H_4)H(\eta^5\text{-}C_5H_5)]$ could not be detected in solution, support for the participation of such a species is afforded by the conversion of $[Ru(PPh_3)_2Et(\eta^5\text{-}C_5H_5)]$ into $[Ru(PPh_3)(C_2H_4)H(\eta^5\text{-}C_5H_5)]$ and subsequently into $[Ru(PPh_3)_2H(\eta^5\text{-}C_5H_5)]$ in solution at 80 °C.[21]

The photo-induced reactions of $[M(CO)_2Me(\eta^5\text{-}C_5H_5)]$ (M = Fe or Ru) complexes in pentane in the presence of $C_2H_4$ result in the formation of $[M(CO)(C_2H_4)Me(\eta^5\text{-}C_5H_5)]$ complexes which represent the *first* examples of olefin alkyl derivatives of Fe and Ru. Similar $C_2H_4$–CO exchange was observed in doped matrices at 12 K. Differences between Fe and Ru also emerge when $[M(CO)_2Et(\eta^5\text{-}C_5H_5)]$ complexes are photolysed in the presence of $C_2H_4$. For example, in solution the metal-containing products for Fe are $[Fe(CO)_2H(\eta^5\text{-}C_5H_5)]$, $[\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$, and the *new* dimer $[\{Fe(CO)(C_2H_4)(\eta^5\text{-}C_5H_5)\}_2]$, whereas for Ru the only product is $[Ru(CO)_2H(\eta^5\text{-}C_5H_5)]$, while in matrices the products are $[Fe(CO)_2H(\eta^5\text{-}C_5H_5)]$ as opposed to $[Ru(CO)_2H(\eta^5\text{-}C_5H_5)]$ and $[Ru(CO)(C_2H_4)H(\eta^5\text{-}C_5H_5)]$. Differences between iron and ruthenium species were also underlined in respect of dinitrogen complexes, *i.e.* detection of $[Ru(CO)(N_2)Me(\eta^5\text{-}C_5H_5)]$ and $[Ru(CO)(N_2)H(\eta^5\text{-}C_5H_5)]$ in $N_2$ matrices but no analogous iron complexes.

The photolysis of $[Fe(CO)_2Me(\eta^5\text{-}C_5H_5)]$ in CO matrices to give the ring-slippage product $[Fe(CO)_3Me(\eta^3\text{-}C_5H_5)]$ was taken to indicate that the associative mechanism for CO exchange and substitution should not be ruled out.[5] Other such $\eta^5 \rightarrow \eta^3$ products have been tentatively identified on photolysis of $[M(CO)_2R(\eta^5\text{-}C_5H_5)]$ (M = Fe or Ru, R = Me or Et) complexes in CO matrices. The identification of $[Fe(CO)_3Et(\eta^3\text{-}C_5H_5)]$, $[Ru(CO)_3Et(\eta^3\text{-}C_5H_5)]$, and $[Ru(CO)_3H(\eta^3\text{-}C_5H_5)]$ species suggests that the ring-slippage process may compete with CO ejection and β elimination.

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## References

1 P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, 1966, **5**, 1177.
2 H. G. Alt, M. Herberhold, M. D. Rausch, and B. H. Edwards, *Z. Naturforsch., Teil B*, 1979, **34**, 1070.

3 R. J. Kazlauskas and M. S. Wrighton, *Organometallics*, 1982, **1**, 602.

4 W. Gerhartz, G. Ellerhorst, P. Dahler, and P. Eilbracht, *Liebigs Ann. Chem.*, 1980, 1296.

5 D. J. Fettes, R. Narayanaswamy, and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 1982, 2311.

6 K. A. Mahmoud, A. J. Rest, H. G. Alt, M. E. Eichner, and B. M. Jansen, *J. Chem. Soc., Dalton Trans.*, 1984, 175.

7 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **3**, 104.

8 T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 1968, 2158.

9 A. P. Humphries and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1975, 1710.

10 P. S. Braterman, 'Metal Carbonyl Spectra,' Academic Press, London, 1975.

11 D. J. Taylor, Ph.D. Thesis, University of Southampton, 1981.

12 O. Crichton, A. J. Rest, and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1980, 167.

13 O. Crichton and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 1977, 981.

14 R. H. Hooker and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 1984, 761.

15 J. Chetwynd-Talbot, P. Grebenik, and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, 1981, 452; J. Chetwynd-Talbot, P. Grebenik, R. N. Perutz, and M. H. A. Powell, *Inorg. Chem.*, 1983, **22**, 1675.

16 J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 3722; J. K. Hoyano, C. J. May, and W. A. G. Graham, *Inorg. Chem.*, 1982, **21**, 2095.

17 K. A. Mahmoud, A. J. Rest, and H. G. Alt, *J. Organomet. Chem.*, 1983, **246**, C37; *J. Chem. Soc., Dalton Trans.*, 1984, 187.

18 J. W. Faller, B. V. Johnson, and C. D. Schaeffer, jun., *J. Am. Chem. Soc.*, 1976, **98**, 1395.

19 C. G. Kreiter, K. Nist, and H. G. Alt, *Chem. Ber.*, 1981, **114**, 1845.

20 O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Am. Chem. Soc.*, 1976, **98**, 5817.

21 H. Lehmkuhl, J. Grundke, R. Benn, G. Schroth, and R. Mynott, *J. Organomet. Chem.*, 1981, **217**, C5; H. Lehmkuhl, J. Grundke, and R. Mynott, *Chem. Ber.*, 1983, **116**, 159.

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