Photoactivation of Methane by η^5-Cyclopentadienyl and Substituted η^5-Cyclopentadienyl Group 8 Metal Dicarbonyl Complexes, $[M(\eta^5\text{-}C_5R_5)(CO)_2]$ (M = Rh or Ir, R = H or Me), and Dicarbonyl(η^5-indenyl)iridium: A Matrix Isolation Study†

Antony J. Rest* and Ian Whitwell
Department of Chemistry, The University, Southampton SO9 5NH
William A. G. Graham,* James K. Hoyano, and Alexander D. McMaster
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Infrared spectroscopic evidence, including deuterium labelling, is presented to show that photolysis of $[M(\eta^5\text{-}C_5R_5)(CO)_2]$ (M = Rh or Ir, R = H or Me) complexes in CH_4 matrices at *ca.* 12 K leads primarily to $[M(\eta^5\text{-}C_5R_5)(CO)(Me)(H)]$ complexes. Comparative photolysis experiments in CH_4, Ar, and ^{13}CO-doped (5%) matrices provided evidence that the initial step is the loss of CO to form the 'naked' 16-electron species, $[M(\eta^5\text{-}C_5R_5)(CO)]$. Additional photoproducts in CH_4 matrices are tentatively assigned as the CH_4 complexes $[M(\eta^5\text{-}C_5R_5)(CO)\cdots CH_4]$. Cobalt analogues failed to activate CH_4 but did afford very weak bands which could possibly be assigned to the CH_4 complexes $[Co(\eta^5\text{-}C_5R_5)(CO)\cdots CH_4]$ (R = H or Me). The indenyl complex, $[Ir(\eta^5\text{-}C_9H_7)(CO)_2]$, behaves similarly to the cyclopentadienyl complexes. The mechanism of CH_4 activation in matrices in discussed and related to the activation of CH_4 in solution at ambient temperatures. The lack of CH_4 activation by Co analogues seems to be best rationalised on thermodynamic grounds.

Considerable interest has been generated by the recent discoveries[1-3] that saturated hydrocarbons can oxidatively add to a number of simple mononuclear organometallic complexes in homogeneous solutions to yield well characterised and frequently isolable hydrido(alkyl)metal complexes. A particularly exciting reaction is the photochemical activation of CH_4 by $[Ir(\eta^5\text{-}C_5R_5)(CO)_2]$ (R = H or Me) complexes in perfluorohexane as an inert solvent.[4] This work has indicated that the catalytic activation of C–H bonds in saturated alkanes, one of the most important goals for the petrochemicals industry, may be attainable under mild reaction conditions.

The favoured intermediates in the photochemical CH_4-activation reactions are the 16-electron species, $[Ir(\eta^5\text{-}C_5R_5)(CO)]$, formed by dissociative CO loss, but no direct evidence for such species has hitherto been presented. An alternative mechanism to CO loss might involve $\eta^5 \longrightarrow \eta^3$ ring slippage, *cf.* the formation of $[Co(\eta^3\text{-}C_5H_5)(CO)_3]$ on photolysis of $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ in CO matrices at *ca.* 12 K.[5] An analogous type of ring-slippage intermediate was proposed for the associative type substitution reactions of $[M(\eta^5\text{-}C_5R_5)(CO)_2]$ (M = Co or Rh, R = H or Me) complexes.[6,7]

In order to understand more about the mechanism of CH_4 photoactivation, a matrix isolation study of the photochemical reactions of the complexes $[M(\eta^5\text{-}C_5R_5)(CO)_2]$ (M = Co, Rh, or Ir; R = H or Me) together with $[Ir(\eta^5\text{-}C_9H_7)(CO)_2]$ (C_9H_7 = indenyl) in CH_4, CD_4, Ar, and 5% ^{13}CO-doped frozen gas matrices at *ca.* 12 K has been undertaken. A preliminary account of this work, which demonstrated CH_4 photoactivation even at 12 K, has been published.[8]

Experimental

Cryogenic temperatures (*ca.* 12 K) were obtained using a closed-cycle He refrigerator (Air Products and Chemicals Inc, Displex CS-202). Matrices containing $[M(\eta^5\text{-}C_5H_5)(CO)_2]$ (M = Co or Rh) complexes were prepared by making gas mixtures with excess matrix gas (*ca.* 1:2 000) on a vacuum line (standard manometric technique) and depositing the mixtures onto cooled CaF_2 or CsI windows using the pulsing method.[9] All other compounds, *i.e.* $[M(\eta^5\text{-}C_5Me_5)(CO)_2]$ (M = Co, Rh, or Ir), $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$, and $[Ir(\eta^5\text{-}C_9H_7)(CO)_2]$, were too involatile to make gas mixtures and so the vapours from samples held at constant temperatures were co-condensed with a vast excess of host matrix gases onto the cooled spectroscopic window of the cryostat. The spray-on temperatures (°C) for the various compounds were: $[Co(\eta^5\text{-}C_5Me_5)(CO)_2]$, 5; $[Rh(\eta^5\text{-}C_5Me_5)(CO)_2]$, 20; $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$, −10; $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$, 20; $[Ir(\eta^5\text{-}C_9H_7)(CO)_2]$, 30.

Infrared spectra (resolution *ca.* 1 cm^{-1}) were recorded on a Grubb–Parsons Spectromajor grating spectrometer and on a Nicolet 7199 Fourier-transform spectrometer (number of data points = 16 384; number of transform points = 32 768). The formation of new species was monitored primarily using the terminal CO stretching regions of the i.r. spectra. Bands in the metal–ring and ring deformation regions were comparatively weak and did not show changes which contributed useful information. Electronic absorption spectra were recorded using a Pye Unicam SP1800B spectrometer (resolution *ca.* 1 nm).

The photolysis source was a Philips HPK 125-W medium-pressure Hg arc lamp. Wavelength-selective photolysis was achieved by a combination of absorbing materials: filter A (λ < 280 nm and λ > 550 nm), quartz gas cell (pathlength 27 mm) containing Cl_2 (2 atm) plus a quartz gas cell (pathlength 27 mm) containing Br_2 (200 Torr); filter B (290 < λ < 370 nm and λ > 550 nm), quartz gas cell containing Br_2 (200 Torr) plus a Pyrex disc (thickness 2 mm); filter C (330 < λ < 390 nm), Corning glass filter number 5 874 (thickness 3 mm); filter D (λ > 370 nm), Corning glass filter number 3 060 (thickness 3 mm); filter E (λ > 290 nm), Pyrex disc (thickness 2 mm); filter F (λ < 370 nm and λ > 550 nm), quartz gas cell containing Br_2 (200 Torr).

Matrix gases (Ar and CH_4; Research Grade purity) were obtained from BOC Limited. The isotopically enriched gases CD_4 (99%) and ^{13}CO (99%) were obtained from MSD Isotopes and Amersham International, respectively. Metal complexes were prepared by reported procedures, $[M(\eta\text{-}C_5R_5)(CO)_2]$

---

† *Non-S.I. units employed:* atm = 101 325 Pa, Torr ≈ 133 Pa, cal = 4.184 J.

Table 1. Electronic absorption bands[a] for $[M(\eta^5\text{-}C_5R_5)(CO)_2]$ and $[Ir(\eta^5\text{-}C_9H_7)(CO)_2]$ complexes isolated at high dilution in Ar matrices at *ca.* 12 K, unless otherwise stated

Compound	$\lambda_{max.}$/nm[b]
$[Co(\eta^5\text{-}C_5H_5)(CO)_2]$[c]	230 (s), 245 (s), 293 (s), 339 (w)
$[Co(\eta^5\text{-}C_5Me_5)(CO)_2]$[d]	*ca.* 250 (s), 310 (s), 340 (m), 390 (w)
$[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$	218 (s), 280 (s)
$[Rh(\eta^5\text{-}C_5Me_5)(CO)_2]$	240 (s), 262 (sh), 305 (s)
$[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$	257 (s)
$[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$	219 (s), 280 (s)
$[Ir(\eta^5\text{-}C_9H_7)(CO)_2]$[d]	*ca.* 250 (s), 342 (m)

[a] Peaks at wavelengths shorter than 210 nm could not be reliably detected because of the background scattering by some matrices. [b] s = Strong, m = medium, w = weak, sh = shoulder. [c] CO matrix: data from D. J. Taylor, Ph.D. Thesis, University of Southampton, 1981. [d] CH_4 matrix.

(M = Rh, R = H[10a] or Me;[10b] M = Co, R = Me,[10c] M = Ir, R = H[10d] or Me[10b]), except for the new compound, $[Ir(\eta^5\text{-}C_9H_7)(CO)_2]$, the preparation and characterisation of which will be described elsewhere,[11] and $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ which was obtained from Strem Chemicals Inc, and purified by distillation prior to use.

Results

The photolysis of complexes in frozen gas matrices generally employed radiation similar in energy to that used in solution photochemical studies,[4] *i.e.* $290 < \lambda < 370$ nm (filter B). Higher energy photolyses were subsequently carried out with filters corresponding to the higher energy u.v. absorption bands of each complex (Table 1).

(*a*) *Photolysis of* $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ *in* CH_4, CD_4, Ar, *and* ^{13}CO*-doped Matrices.*—The i.r. spectrum (terminal CO stretching region) of $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ isolated at high dilution in a pure CH_4 matrix is shown in Figure 1(*a*). This spectrum shows two strong terminal CO stretching bands with weaker 'satellite' bands (marked with *) corresponding to the CO stretching modes of $[Ir(\eta^5\text{-}C_5Me_5)(^{12}CO)(^{13}CO)]$ present in natural abundance (Table 2); the spectrum is typical of all dicarbonyl spectra in this work. Extended photolysis (filter B) resulted in the production of a strong terminal CO stretching band at 1 991.3 cm^{-1}, a very weak band at 2 149.3 cm^{-1}, a band for 'free' CO and reduction in the intensities of the parent bands [Figure 1(*b*) and (*c*)]. Photolysis with high-energy light (filter F) afforded a second new terminal CO stretching band at 1 971.2 cm^{-1}, at the expense of the parent bands and the other new band at 1 991.3 cm^{-1}, together with an increase in the band for 'free' CO [Figure 1(*d*) and (*e*)].

The i.r. spectrum of $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ isolated at high dilution in a CD_4 matrix is shown in Figure 2(*a*). Extended photolysis (filter B) resulted in the production of a new terminal CO stretching band at 1 990.1 cm^{-1} together with a band for 'free' CO. No band was observed at 2 149.3 cm^{-1} but a weak band was detected at 1 548.2 cm^{-1} [Figure 2(*b*) and (*c*)]. Such a band shift is consistent with H/D exchange so that the band at 2 149.3 cm^{-1} in the CH_4 matrix experiment can be assigned as an Ir–H stretching mode (Table 2). The production of a second CO stretching band on higher energy photolysis is obscured by bands due to the CD_4 matrix.

Photolysis in Ar matrices failed to yield any major changes in the i.r. spectrum of $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ despite using a variety of filters over prolonged periods of time (12 h). However, photolysis using 5% ^{13}CO-doped Ar matrices resulted in some $^{12}CO/^{13}CO$ exchange, *cf.* previous results for $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$,[5] although the extent of exchange for Ir was less than for Co. In contrast to the Co complex, there was no evidence for $^{12}CO/^{13}CO$ exchange when $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ was photolysed in 5% ^{13}CO-doped CH_4 matrices.

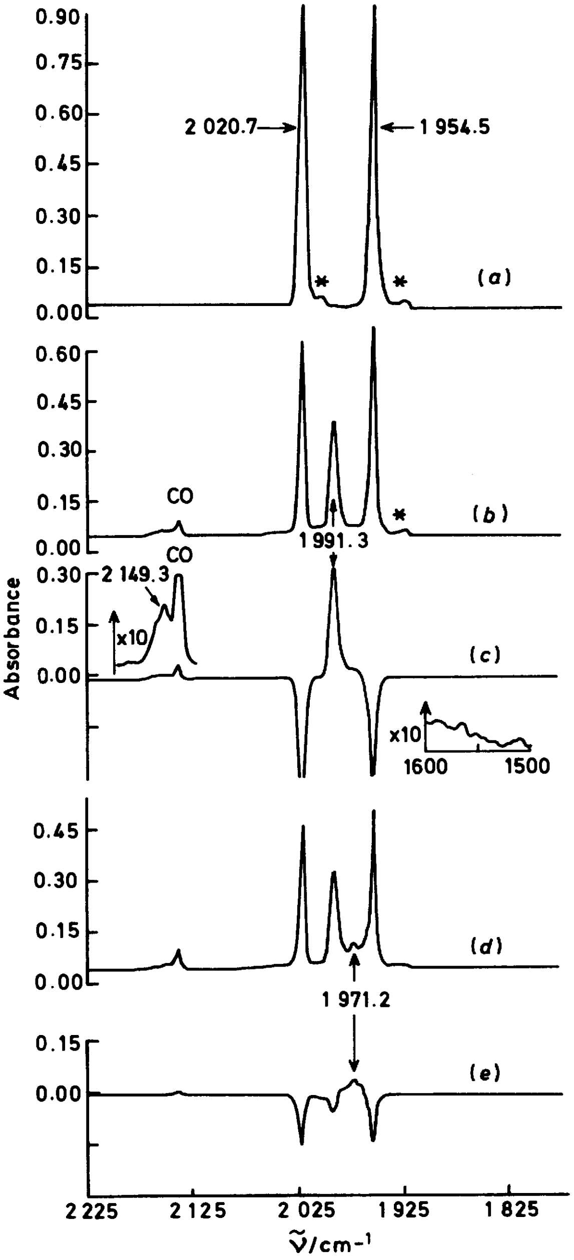


Figure 1. Infrared spectra (Nicolet 7199, 1 cm^{-1} resolution; as for Figures 2—7 and 9) from an experiment with $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ isolated at high dilution in a CH_4 matrix: (*a*) after deposition, (*b*) after irradiation for 88 h using filter B, (*c*) subtraction spectrum [(*b*) – (*a*)], (*d*) after irradiation for 3 h using filter F, (*e*) subtraction spectrum [(*d*) – (*c*)]. Bands marked (*) arise from $[Ir(\eta^5\text{-}C_5Me_5)(^{12}CO)(^{13}CO)]$ present in natural abundance

Comparison of the matrix isolation i.r. data (Table 2) with solution i.r. data[4] identified the major product species formed in CH_4 matrices as $[Ir(\eta^5\text{-}C_5Me_5)(CO)(Me)(H)]$ (ν_{IrH} = 2 149.3 and ν_{CO} = 1 991.3 cm^{-1}). The other new terminal CO stretching band at 1 971.2 cm^{-1} is more difficult to assign; it appears to be produced from $[Ir(\eta^5\text{-}C_5Me_5)(CO)(Me)(H)]$ and possibly

Table 2. Observed positions (cm^{-1}) of terminal CO stretching modes of $[M(\eta^5\text{-}C_5R_5)(CO)_2]$, $[Ir(\eta^5\text{-}C_9H_7)(CO)_2]$, and their photoproducts in Ar and CH_4 frozen gas matrices at *ca.* 12 K and n-hexane at 298 K

	M = Ir			M = Rh			M = Co		
Compound	Ar	CH_4	C_6H_{14}	Ar	CH_4	C_6H_{14}	Ar	CH_4	C_6H_{14}
$[M(\eta^5\text{-}C_5Me_5)(CO)_2]$	2 025.5	2 020.7[a]	2 019	2 031.1	2 028.2[a]	2 026	2 013.7	2 008.5	2 009
	1 959.0	1 954.5[a]	1 953	1 967.9	1 965.6[a]	1 964	1 953.3	1 947.9	1 949
$[M(\eta^5\text{-}C_5Me_5)(^{12}CO)(^{13}CO)]$	2 007.6	2 003.7	2 003	2 014.5	2 012.2[b]	2 011	1 997.9	1 992.9	1 994
	1 926.8	1 924.7	1 923	1 936.8	1 934.9[b]	1 935	1 922.6	1 917.2	1 918
$[M(\eta^5\text{-}C_5Me_5)(CO)(Me)(H)]$		1 991.3[c]	1 990[c]		2 008.7[d]				
$[M(\eta^5\text{-}C_5Me_5)(CO)]$									
$[M(\eta^5\text{-}C_5Me_5)(CO)\cdots CH_4]$[e]		1 971.2[f]			1 981.9[f]			1 962.8	
$[M(\eta^5\text{-}C_5H_5)(CO)_2]$	2 044.5	2 040.0[a,g]	2 041	2 053.0[g]	2 048.9[g]	2 049	2 034.9[g]	2 029.8[g]	2 031
	1 977.2	1 972.5[a,g]	1 974	1 988.8[g]	1 985.1[g]	1 986	1 973.8[g]	1 969.3[g]	1 971
$[M(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)]$	2 028.4	2 023.7	2 024	2 035.6	2 033.2	2 033	2 019.1	2 015.2	2 015
	1 945.9	1 941.6	1 943	1 958.2	1 954.4	1 955	1 942.8	1 939.7	1 940
$[M(\eta^5\text{-}C_5H_5)(CO)(Me)(H)]$		2 006.0[g,h]	2 009[h]		2 024.2[i]				
$[M(\eta^5\text{-}C_5H_5)(CO)]$	1 953.7			1 968.5[g]					
$[M(\eta^5\text{-}C_5H_5)(CO)\cdots CH_4]$[e]		1 984.8[f]			1 992.2			1 989.7	
$[M(\eta^5\text{-}C_9H_7)(CO)_2]$	2 044.2[g]	2 041.0[g]	2 041						
	1 983.7[g]	1 979.2[g]	1 980						
$[M(\eta^5\text{-}C_9H_7)(^{12}CO)(^{13}CO)]$	2 028.4	2 022.8	2 025						
	1 951.6	1 945.8	1 949						
$[M(\eta^5\text{-}C_9H_7)(CO)(Me)(H)]$		2 005.4[i]							

[a] Positions in CD_4: $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$, 2 020.6 and 1 953.6 cm^{-1}; $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$, 2 040.6 and 1 972.3 cm^{-1}; $[Rh(\eta^5\text{-}C_5Me_5)(CO)_2]$, 2 027.1 and 1 963.9 cm^{-1}. [b] $[Rh(\eta^5\text{-}C_5Me_5)(^{13}CO)_2]$, ν_{CO} at 1 979.3 and 1 918.4 cm^{-1} in 5% ^{13}CO-doped CH_4; *cf.* $[Rh(\eta^5\text{-}C_5Me_5)(CO)_2]$ (ν_{CO} at 2 027.4 and 1 964.2 cm^{-1}) and $[Rh(\eta^5\text{-}C_5Me_5)(^{12}CO)(^{13}CO)]$ (ν_{CO} at 2 010.5 and 1 933.7 cm^{-1}). [c] ν_{IrH} at 2 149.3 cm^{-1} in CH_4 and at 2 134 cm^{-1} in C_6H_{14}; $[Ir(\eta^5\text{-}C_5Me_5)(CO)(CD_3)(D)]$, ν_{CO} at 1 990.1 cm^{-1} and ν_{IrD} at 1 548.2 cm^{-1}. [d] ν_{RhH} not located; $[Rh(\eta^5\text{-}C_5Me_5)(CO)(CD_3)(D)]$, ν_{CO} at 2 006.3 cm^{-1} and ν_{RhD} not located. [e] Tentative assignment. [f] $[Ir(\eta^5\text{-}C_5Me_5)(CO)\cdots CD_4]$, ν_{CO} obscured in CD_4; $[Ir(\eta^5\text{-}C_5H_5)(CO)\cdots CD_4]$, ν_{CO} obscured in CD_4; $[Rh(\eta^5\text{-}C_5Me_5)(CO)\cdots CD_4]$, ν_{CO} at 1 979.3 cm^{-1} in CD_4. [g] Average position of matrix-split band. [h] ν_{IrH} at *ca.* 2 184 cm^{-1} in CH_4 and at 2 170 cm^{-1} in C_6H_{14}; $[Ir(\eta^5\text{-}C_5H_5)(CO)(CD_3)(D)]$, ν_{CO} at 2 006.4 cm^{-1} and ν_{IrD} at 1 564.5 cm^{-1}; $[Ir(\eta^5\text{-}C_5H_5)(^{13}CO)(Me)(H)]$, ν_{CO} at *ca.* 1 960 cm^{-1}. [i] ν_{MH} not located (M = Ir or Rh).

$[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ on high-energy photolysis. On the basis of matrix dilution and the lack of bridging CO stretching bands, it seems likely that the species responsible for this band is monomeric. An obvious candidate is the 'naked' 16-electron species $[Ir(\eta^5\text{-}C_5Me_5)(CO)]$. A comparison of the band position of this proposed monocarbonyl *versus* those for $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ and other related pairs, *e.g.* $[Fe(\eta^5\text{-}C_5H_5)(CO)(COMe)]$ (ν_{CO} at 1 947.5 cm^{-1}) *versus* $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COMe)]$ (ν_{CO} at 2 021.0 and 1 961.8 cm^{-1})[12] and [Rh(acac)(CO)] (acac = acetylacetonate; ν_{CO} at 2 002.9 cm^{-1}) *versus* $[Rh(acac)(CO)_2]$ (ν_{CO} at 2 086.0 and 2 019.5 cm^{-1}),[13] suggests that the band at 1 971.2 cm^{-1} is at too high a wavenumber to be consistent with $[Ir(\eta^5\text{-}C_5Me_5)(CO)]$. This conclusion is reinforced by the results for $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ and $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ in Ar matrices (see below). An alternative assignment is possibly a methane complex, *i.e.* $[Ir(\eta^5\text{-}C_5Me_5)(CO)\cdots CH_4]$. There are a number of precedents for such interactions: 'naked' $[Cr(CO)_5]$ *versus* $[Cr(CO)_5\cdots CH_4]$ (observed in the u.v.–visible spectra),[14] 'naked' $[Fe(CO)_4]$ *versus* $[Fe(CO)_4\cdots CH_4]$ (observed *via* the i.r. spectra).[15] More recently the interaction of CH_4 molecules with Fe atoms has led to CH_4 activation, equation (1).[16]

$$[Fe\cdots H\text{-}CH_3] \underset{\lambda\,>\,400\ \text{nm}}{\overset{280\,<\,\lambda\,<\,360\ \text{nm}}{\rightleftarrows}} [Fe(H)(Me)] \qquad (1)$$

On the basis of these precedents it seems at least possible that the band observed at 1 971.2 cm^{-1} in CH_4 matrices may correspond to the terminal CO stretching mode of the CH_4 complex, $[Ir(\eta^5\text{-}C_5Me_5)(CO)\cdots CH_4]$, formed either as an intermediate in C–H activation or by reductive elimination of CH_4 from $[Ir(\eta^5\text{-}C_5Me_5)(CO)(Me)(H)]$. Recent extended Hückel calculations on the $[Rh(\eta^5\text{-}C_5H_5)(CO)]$–$CH_4$ system support the idea that a CH_4 complex forms as an intermediate and subsequently goes on to yield a hydrido(methyl) product.[17] Additionally, the interaction of C–H bonds with 16-electron metal species is now well recognised from a number of structural and spectroscopic studies.[18] In the particular case under consideration it should be emphasised that there is no other spectroscopic evidence for a CH_4 complex and, therefore, other species/structures which could give rise to the 1 971.2 cm^{-1} band should not be ruled out.

(*b*) *Photolysis of* $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ *in* CH_4, CD_4, Ar, *and* ^{13}CO-*doped Matrices*.—The i.r. spectrum (terminal CO stretching region) of $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ isolated at high dilution in a pure CH_4 matrix is shown in Figure 3(*a*). Extended photolysis (filter B) resulted in the production of a strong terminal CO stretching band at 2 006.0 cm^{-1} (broadened by matrix splitting), a very weak band centred at *ca.* 2 184 cm^{-1}, and a band for 'free' CO while the parent bands decreased [Figure 3(*b*) and (*c*)]. Two very weak bands were also observed at 1 936.3 and 1 730.0 cm^{-1} and these may be assigned to a dimeric species (see below). On further photolysis (filter A) the parent bands were rapidly destroyed, the new band at 2 006.0 cm^{-1} increased slightly, more CO was produced and a new terminal CO stretching band grew in at 1 984.8 cm^{-1} [Figure 3(*d*)]. Further photolysis (filter E) with radiation similar to that used initially caused a decrease in the band at 1 984.8 cm^{-1} with a concomitant increase in the band at 2 006.0 cm^{-1} [Figure 3(*e*) and (*f*)]. A final period of irradiation with high-energy light (filter A) caused the parent bands and the band at 2 006.0 cm^{-1} to decrease while the band at 1 984.8 cm^{-1} and that for 'free' CO increased in intensity.

The i.r. spectrum of $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ isolated at high dilution in a CD_4 matrix is shown in Figure 4(*a*). Extended photolysis (filters B or A) resulted in the production of a strong terminal CO stretching band at 2 006.4 cm^{-1} together

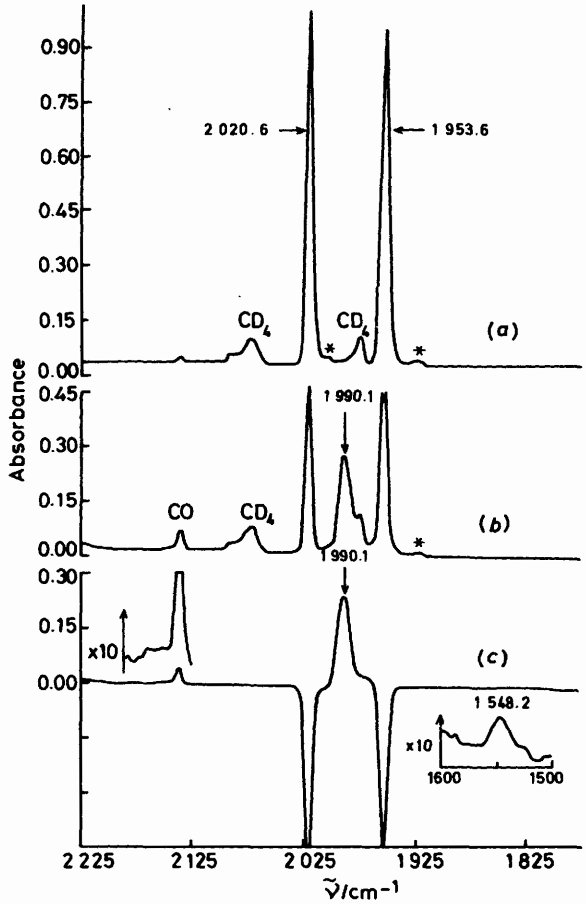


Figure 2. Infrared spectra from an experiment with $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ isolated at high dilution in a CD_4 matrix: (*a*) after deposition, (*b*) after irradiation for 76 h using filter B + 4 h using filter F, (*c*) subtraction spectrum [(*b*) − (*a*)]. Bands marked (*) arise from $[Ir(\eta^5\text{-}C_5Me_5)(^{12}CO)(^{13}CO)]$ present in natural abundance

with a band for 'free' CO but no band at 2 184 cm^{-1}. Instead a weak band was detected at 1 564.5 cm^{-1} [Figures 4(*b*) and (*c*)]. The 2 184 (CH_4)/1 564.5 cm^{-1} (CD_4) band shift is consistent with H/D exchange and enables the band at *ca.* 2 184 cm^{-1} in the CH_4 matrix to be assigned as an Ir–H stretching mode.

Photolysis (filter A, 16 h) in dilute Ar matrices[*] yielded a weak band at 1 953.7 cm^{-1}, a band for 'free' CO, and slight decreases in the parent bands. Long-wavelength photolysis (filter D) resulted in a slight decrease in the band at 1 953.7 cm^{-1} and the band for 'free' CO while the parent bands increased in intensity. In 5% ^{13}CO-doped CH_4 matrices photolysis (filter B or A) caused much less destruction of the parent complex than in CH_4 matrices. The principal products were a strong band at 2 006.0 cm^{-1} (*cf.* pure CH_4 matrices), incorporation of ^{13}CO to give $[Ir(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)]$, a new strong band at *ca.* 1 960 cm^{-1} corresponding to $[Ir(\eta^5\text{-}C_5H_5)(^{13}CO)(Me)(H)]$, but no band at 1 984.8 cm^{-1}.

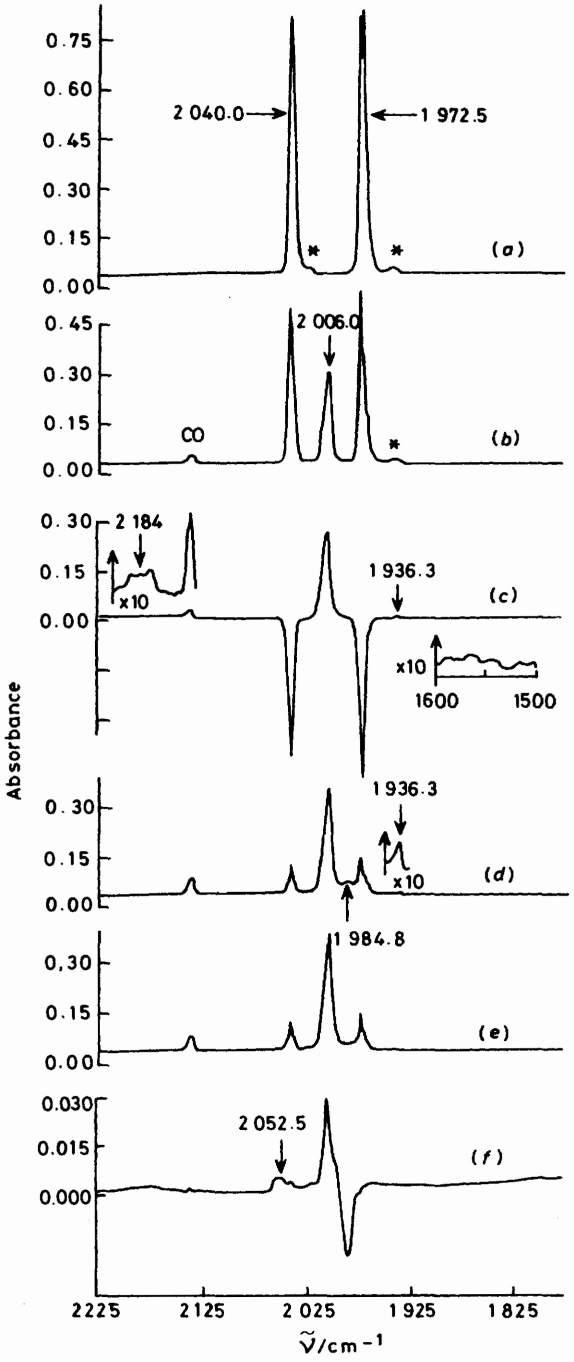


Figure 3. Infrared spectra from an experiment with $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ isolated at high dilution in a CH_4 matrix: (*a*) after deposition, (*b*) after irradiation for 19 h using filter B, (*c*) subtraction spectrum [(*b*) − (*a*)], (*d*) after irradiation for 55 min using filter A, (*e*) after irradiation for 95 min using filter E, (*f*) subtraction spectrum [(*e*) − (*d*)] (note: absorbance scale × 10). Bands marked (*) arise from $[Ir(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)]$ present in natural abundance

Comparison of the matrix isolation i.r. data with the solution i.r. data[4] identified the major photoproduct in CH_4 matrices as $[Ir(\eta^5\text{-}C_5H_5)(CO)(Me)(H)]$ (ν_{IrH} = 2 184 cm^{-1}; ν_{CO} = 2 006.0 cm^{-1}). The band at 1 984.8 cm^{-1} behaves similarly to that at 1 971.2 cm^{-1} in the $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$–$CH_4$ experiments. A CH_4 complex, $[Ir(\eta^5\text{-}C_5H_5)(CO)\cdots CH_4]$, is one possibility which could account for the observed reversal to $[Ir(\eta^5\text{-}C_5H_5)(CO)(Me)(H)]$ on longer wavelength photolysis though other isomeric species cannot be ruled out.

---

[*] When more concentrated matrices were photolysed weak bands were detected at 1 941.3 and 1 745.6 cm^{-1}; these bands correspond to species which could be photochemically interconverted. It is proposed that these species are the as yet unknown dimers $[\{Ir(\eta^5\text{-}C_5H_5)(CO)\}_2]$ and $[\{Ir(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CO)_2]$, respectively (see below for $[\{Rh(\eta^5\text{-}C_5Me_5)(CO)\}_2]$ and $[\{Rh(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}CO)_2]$).

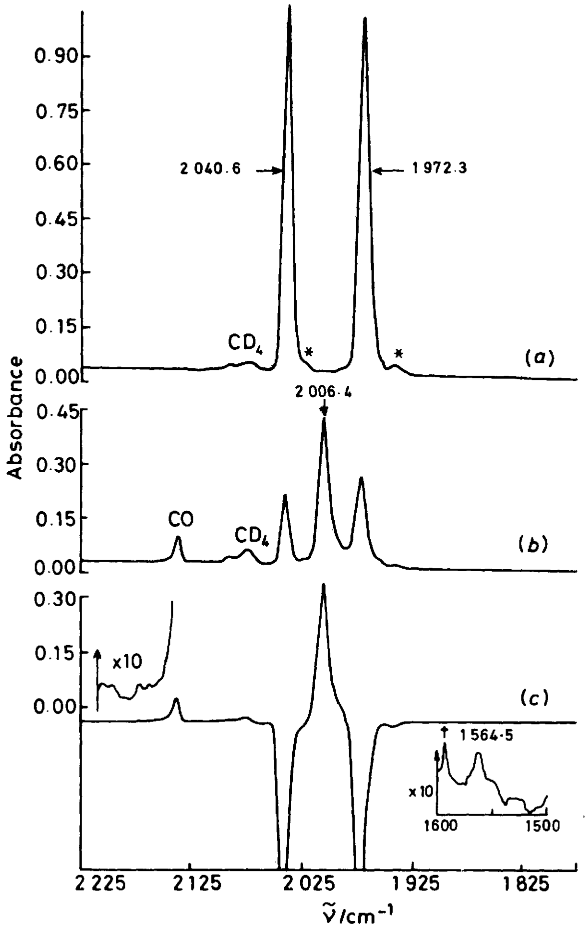


Figure 4. Infrared spectra from an experiment with $[Ir(\eta^5-C_5H_5)(CO)_2]$ isolated at high dilution in a CD_4 matrix: (*a*) after deposition, (*b*) after irradiation for 20 h using filter B + 2 h using filter A, (*c*) subtraction spectrum [(*b*) − (*a*)]. The band marked (†) arises from matrix-isolated water and the bands marked (*) arise from $[Ir(\eta^5-C_5H_5)(^{12}CO)(^{13}CO)]$ present in natural abundance

The band at 1 953.7 cm^{-1} in Ar matrices is at a position consistent with the assignment to the 'naked' 16-electron species $[Ir(\eta^5-C_5H_5)(CO)]$. The band position also agrees well with a band assigned to $[Ir(\eta^5-C_5H_5)(CO)]$ (ν_{CO} = 1 954.4 cm^{-1}) produced on photolysis of $[Ir(\eta^5-C_5H_5)(CO)(H)_2]$ in Ar matrices.[19]

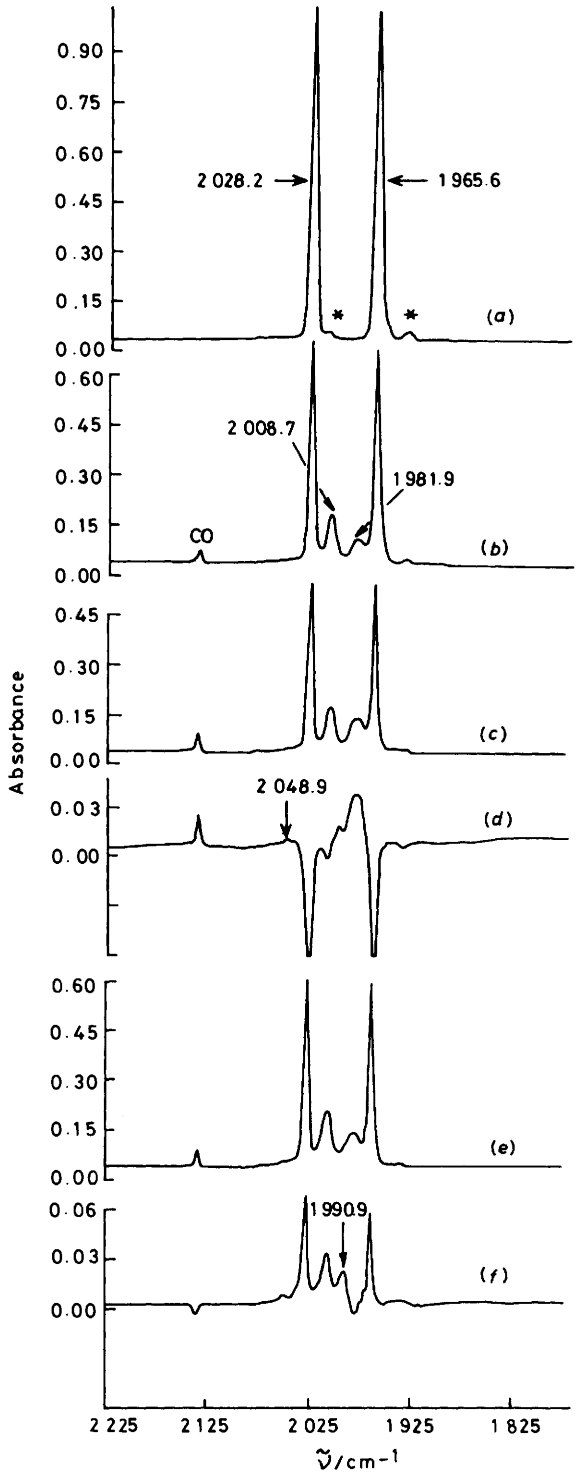
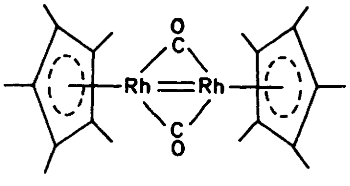
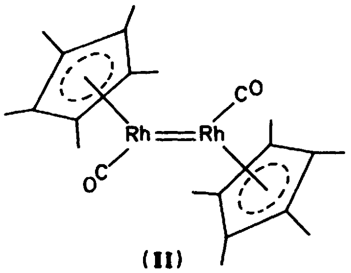


Figure 5. Infrared spectra from an experiment with $[Rh(\eta^5-C_5Me_5)(CO)_2]$ isolated at high dilution in a CH_4 matrix: (*a*) after deposition, (*b*) after irradiation for 120 min using filter A, (*c*) after irradiation for a further 120 min using filter A + 200 min using filter B, (*d*) subtraction spectrum [(*c*) − (*b*)] (note: absorbance scale × 5), (*e*) after irradiation for 245 min using filter D, (*f*) subtraction spectrum [(*e*) − (*c*)] (note: absorbance scale × 5). Bands marked (*) arise from $[Rh(\eta^5-C_5Me_5)(^{12}CO)(^{13}CO)]$ present in natural abundance

(*c*) *Photolysis of* $[Rh(\eta^5-C_5Me_5)(CO)_2]$ *in* CH_4, CD_4, Ar, *and* ^{13}*CO-doped Matrices.*—The i.r. spectrum (terminal CO stretching region) of $[Rh(\eta^5-C_5Me_5)(CO)_2]$ isolated at high dilution in a CH_4 matrix is shown in Figure 5(*a*). Initial photolysis (filter B, 120 min) afforded reductions in the parent bands, a new terminal CO stretching band at 2 008.7 cm^{-1} and a band for 'free' CO. When filter A was used in the initial photolysis an additional band (1 981.9 cm^{-1}) was obtained [Figure 5(*b*)]. Further photolysis (filter A or B) produced an increase in the band at 1 981.9 cm^{-1} at the expense of the parent bands and the band at 2 008.7 cm^{-1} [Figure 5(*c*)]; a subtraction revealed another weak band at 2 048.9 cm^{-1} [Figure 5(*d*)]. Longer wavelength photolysis (filter D) resulted in a decrease in the bands at 1 981.9 cm^{-1} and for 'free' CO while the bands at 2 048.9 and 2 008.7 cm^{-1} and the parent bands all increased [Figure 5(*e*)]. A subtraction revealed a further possible new band at 1 990.9 cm^{-1}, although this could be a matrix splitting of the band at 1 981.9 cm^{-1} [Figure 5(*f*)]. When photolyses were carried out in CD_4 matrices two strong terminal CO stretching bands were observed at 2 006.3



(I)



(II)

and 1 979.3 cm^{-1} (*cf.* the CH_4 matrix bands at 2 008.7 and 1 981.9 cm^{-1}) but no band attributable to a Rh–D stretching mode could be detected. The very weak band observed at 2 048.9 cm^{-1} in CH_4 matrices was also observed in CD_4 matrices although it was partially overlapped by a CD_4 band.

In Ar matrices very little effect was observed on photolysis with a variety of filters. On extended photolysis with high-energy radiation (filter A) very weak bands appeared at 1 745.0 and 1 943.0 cm^{-1}. In 5% ^{13}CO-doped CH_4 matrices the major photoreduction was ^{13}CO substitution resulting in the formation of bands corresponding to $[Rh(\eta^5\text{-}C_5Me_5)(^{12}CO)(^{13}CO)]$ and $[Rh(\eta^5\text{-}C_5Me_5)(^{13}CO)_2]$ (Table 2).

The similarity of the band patterns for $[Rh(\eta^5\text{-}C_5Me_5)(CO)_2]$ and its photolysis products to those for $[Ir(\eta^5\text{-}C_5R_5)(CO)_2]$ (R = H or Me) complexes and their photolysis products suggests that similar photoproducts are formed: $[Rh(\eta^5\text{-}C_5Me_5)(CO)(Me)(H)]$ (ν_{CO} = 2 008.7 cm^{-1}), although no Rh–H or Rh–D stretching modes could be detected; $[Rh(\eta^5\text{-}C_5Me_5)(CO)\cdots CH_4]$ (ν_{CO} = 1 981.9 cm^{-1}), which seems plausible on the basis of reversal to $[Rh(\eta^5\text{-}C_5Me_5)(CO)_2]$ and $[Rh(\eta^5\text{-}C_5Me_5)(CO)(Me)(H)]$.

The bands at 1 745.0 and 1 943.0 cm^{-1} may be assigned to the known bridged dimer $[\{Rh(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}CO)_2]$ [(**I**); ν_{CO} at 1 725 cm^{-1} in CH_2Cl_2][20] and, more tentatively, the non-bridged dimer $[\{Rh(\eta^5\text{-}C_5Me_5)(CO)\}_2]$ (**II**), *cf.* the results for $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ in more concentrated Ar matrices. Support for the presence of (**I**) was afforded by the electronic spectrum after photolysis where a strong new band was observed at 565 nm which agrees well with the band for (**I**) at 582 nm in CH_2Cl_2 solution.[21] It has, however, proved impossible so far to identify the species responsible for the weak bands at 2 048.9 and 1 990.9 cm^{-1}.

(*d*) *Photolysis of* $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ *in* CH_4 *and* Ar *Matrices*.—The i.r. spectra (terminal CO stretching region) from an experiment with $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ isolated at high dilution in a CH_4 matrix are shown in Figure 6. The bands are sharper because the complex is volatile enough to enable a high-dilution gas mixture to be prepared and deposited in pulses[9] onto the cooled spectroscopic window. Photolysis (filter B) led to the production of a matrix-split CO stretching band at 2 024.2 cm^{-1} and a band for 'free' CO at the expense of the parent bands [Figure 6(*b*)]. Subsequent photolysis with high-energy radiation (filter A) afforded a rapid decrease in the parent bands, a slight increase in the bands at 2 024.2 cm^{-1} and for 'free' CO, and a new band at 1 992.2 cm^{-1} [Figure 6(*c*)]. Photolysis with radiation similar to that used initially (filter E) caused the bands at 1 992.2 cm^{-1} and for 'free' CO to decrease with concomitant increases in the bands at 2 024.2 cm^{-1} and those due to the parent complex [Figure 6(*d*) and (*e*)].

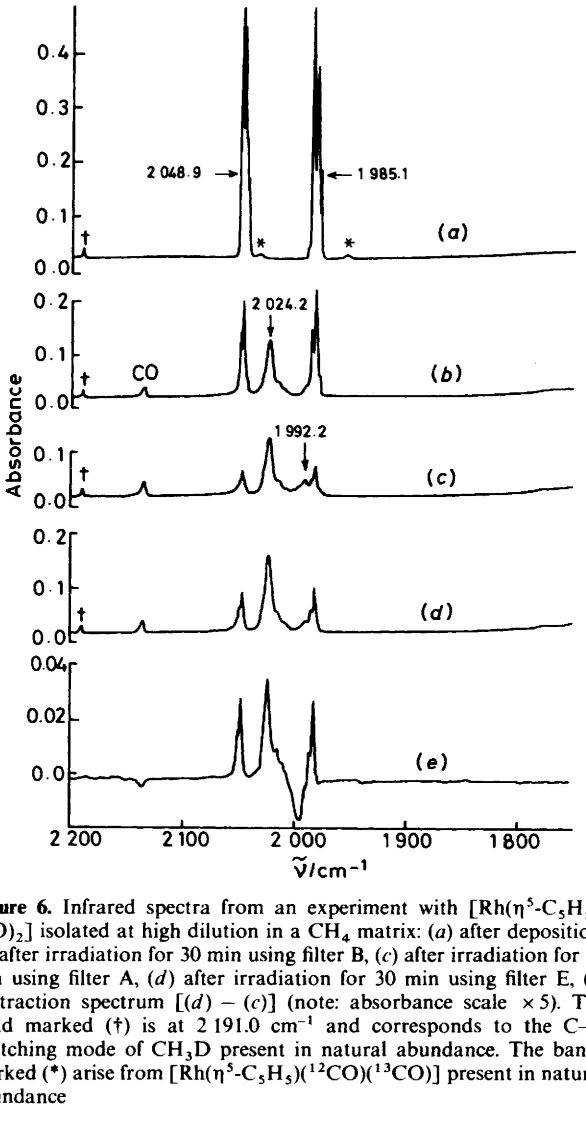


Figure 6. Infrared spectra from an experiment with $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ isolated at high dilution in a CH_4 matrix: (*a*) after deposition, (*b*) after irradiation for 30 min using filter B, (*c*) after irradiation for 25 min using filter A, (*d*) after irradiation for 30 min using filter E, (*e*) subtraction spectrum [(*d*) – (*c*)] (note: absorbance scale × 5). The band marked (†) is at 2 191.0 cm^{-1} and corresponds to the C–D stretching mode of CH_3D present in natural abundance. The bands marked (*) arise from $[Rh(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)]$ present in natural abundance

The i.r. spectra (terminal and bridging CO stretching regions) and electronic spectra from an experiment with $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ isolated at high dilution in an Ar matrix are shown in Figures 7 and 8, respectively. Photolysis with high-energy radiation (filter A) resulted in decreases in the parent bands together with the production of new bands at 1 968.5 (matrix split), 1 792.7 cm^{-1}, and for 'free' CO [Figure 7(*b*)] while in the electronic spectrum new bands were observed at 330 and 550 nm [Figure 8(*b*)]. Photolysis with mid-u.v. radiation (filter C) corresponding to the band at 330 nm partially reconverted the band at 1 968.5 cm^{-1} to the parent complex along with a small decrease in the band for 'free' CO but with no change in the band at 1 792.7 cm^{-1} [Figure 7(*c*) and (*d*)].

The similarities of the band patterns to those seen previously suggests the following assignments (Table 2): $[Rh(\eta^5\text{-}C_5H_5)(CO)(Me)(H)]$ (ν_{CO} = 2 024.2 cm^{-1}) although no Rh–H stretching mode could be detected; $[Rh(\eta^5\text{-}C_5H_5)(CO)\cdots CH_4]$ (ν_{CO} = 1 992.2 cm^{-1}); $[Rh(\eta^5\text{-}C_5H_5)(CO)]$ (ν_{CO} = 1 968.5 cm^{-1}); $[\{Rh(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CO)_2]$ (ν_{CO} = 1 792.7 cm^{-1}, $\lambda_{max.}$ = 330 and 550 nm). Support for the assignment of the band at

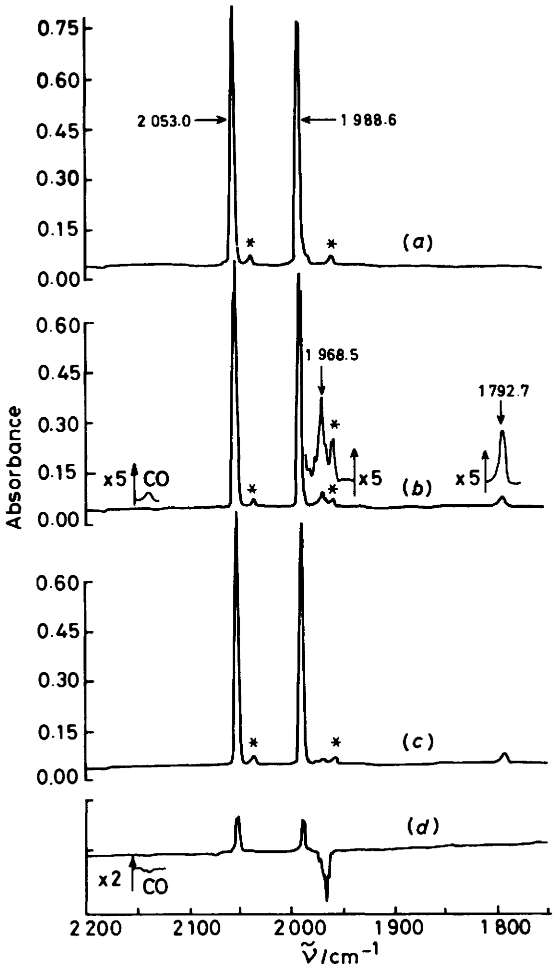


Figure 7. Infrared spectra from an experiment with [Rh(η^5-C_5H_5)(CO)$_2$] isolated at high dilution in an Ar matrix: (*a*) after deposition, (*b*) after irradiation for 110 min using filter A, (*c*) after irradiation for 30 min using filter C, (*d*) subtraction spectrum [(*c*) – (*b*)] (note: absorbance scale ×5). The bands marked (*) arise from [Rh(η^5-C_5H_5)(^{12}CO)(^{13}CO)] present in natural abundance

2 024.2 cm^{-1} to a hydrido(methyl) complex is provided by the observation of a CO stretching band at 2 013 cm^{-1} in experiments where [Rh(η^5-C_5H_5)(CO)$_2$] was photolysed at 77 K in a methylcyclohexane glass. In this experiment the product was assigned as [Rh(η^5-C_5H_5)(CO)($C_6H_{10}CH_3$)(H)].[22] A second product in this work was assigned as [{Rh(η^5-C_5H_5)}$_2$(μ-CO)$_2$] (ν_{CO} = 1 778 cm^{-1})[22] (*cf.* the band in Ar matrices at 1 792.7 cm^{-1}). This product [structure (I)] was also formed efficiently on photolysis of [Rh_2(η^5-C_5H_5)$_2$(CO)$_3$] in glasses at 77 K.[22]

(*e*) *Photolysis of* [Co(η^5-C_5Me_5)(CO)$_2$] *in* CH_4 *and* Ar *Matrices*.—Photolysis (filter A) of [Co(η^5-C_5Me_5)(CO)$_2$] isolated at high dilution in CH_4 matrices led to the production of a weak band at 1 962.8 cm^{-1} and a trace of 'free' CO at the expense of the parent bands. Further photolysis with longer wavelength radiation (filter D) generated a shoulder on the band at 1 962.8 cm^{-1} but extended photolysis with a wide range of filters failed to produce further changes. In Ar matrices there was a similar lack of photoproducts except perhaps for a trace of 'free' CO.

The results for [Co(η^5-C_5Me_5)(CO)$_2$] are dramatically different from those of Rh and Ir analogues, which activate CH_4, but are consistent with those for [Co(η^5-C_5H_5)(CO)$_2$] obtained previously[5] and in this work (see below). The identification of the species responsible for the band at 1 962.8 cm^{-1} band is difficult because of its lack of further reactivity after its formation. The band position is consistent with a methane complex [Co(η^5-C_5Me_5)(CO)···CH_4] by analogy with Rh (ν_{CO} = 1 981.9 cm^{-1}) and Ir (ν_{CO} = 1 971.2 cm^{-1}) analogues. Another possibility is the non-bridged dimer [{Co(η^5-C_5Me_5)(CO)}$_2$] by analogy with Rh [(II), ν_{CO} = 1 943.0 cm^{-1}] and Ir (ν_{CO} = 1 941.3 cm^{-1}) analogues. In assessing these possibilities it should be borne in mind that CH_4 complexes are generally reactive while Co forms bridged rather than non-bridged dimers, *e.g.* [{Co(CO)$_3$}$_2$(μ-CO)$_2$] and [{Co(η^5-C_5H_5)}$_2$(μ-CO)$_2$] (see below). On balance, the relative intensity of the band is probably too strong for a dimeric product and thus the tentative assignment is to [Co(η^5-C_5Me_5)(CO) ··· CH_4] [see (*a*) above].

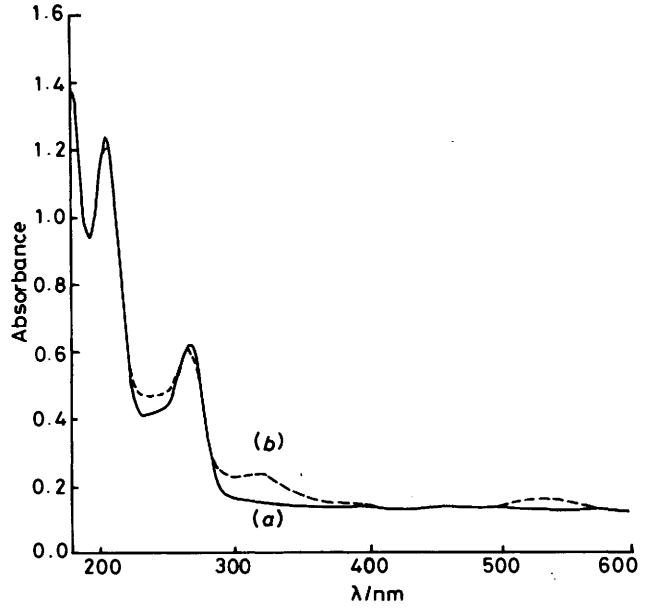


Figure 8. Electronic absorption spectra (Pye Unicam SP1800B) from an experiment with [Rh(η^5-C_5H_5)(CO)$_2$] isolated at high dilution in an Ar matrix: (*a*) after deposition, (*b*) after irradiation for 60 min using filter A + 60 min using filter C

(*f*) *Photolysis of* [Co(η^5-C_5H_5)(CO)$_2$] *in* CH_4 *and* Ar *Matrices*.—The photolysis (filter A) of [Co(η^5-C_5H_5)(CO)$_2$] isolated at high dilution in CH_4 matrices led to the production of a weak band at 1 989.7 cm^{-1}, a weak band for 'free' CO and a weak band at 1 792.1 cm^{-1}, which can be attributed to the previously observed dimer [{Co(η^5-C_5H_5)}$_2$(μ-CO)$_2$] (ν_{CO} = 1 798.9 cm^{-1} in a N_2 matrix[5] and at 1 798 cm^{-1} in high-boiling light petroleum[23]). The band at 1 989.7 cm^{-1} showed no changes on subsequent photolysis with a variety of filters but disappeared on annealing the matrices to *ca.* 30 K; the dimer band remained unchanged. In Ar matrices photolysis resulted in a trace of 'free' CO and a weak band corresponding to [{Co(η^5-C_5H_5)}$_2$(μ-CO)$_2$].

These results are essentially consistent with the previous study[5] except for the detection of the weak band at 1 989.7 cm^{-1}; this may result from using a Fourier-transform i.r. spectrometer in the present work. The lack of reactivity in Ar and CH_4 matrices was demonstrated previously to be apparent rather than real because of facile ^{13}CO substitution in ^{13}CO doped matrices.[5] Perhaps therefore, the weak new band (1 989.7 cm^{-1})

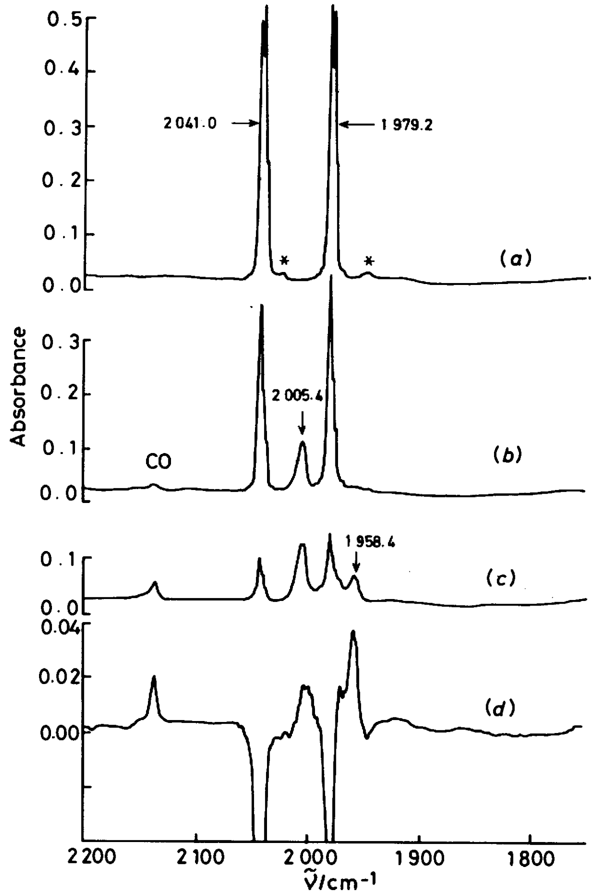
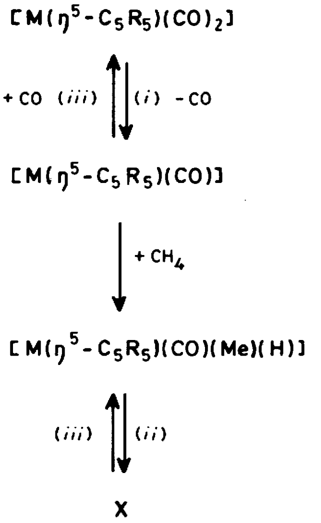


Figure 9. Infrared spectra from an experiment with $[Ir(\eta^5-C_9H_7)(CO)_2]$ isolated at high dilution in a CH_4 matrix: (*a*) after deposition, (*b*) after irradiation for 33 h using filter B + 3 h using filter A, (*c*) after irradiation for a further 20 h using filter A, (*d*) subtraction spectrum [(*c*) − (*b*)] (note: absorbance scale × 5). Bands marked (*) arise from $[Ir(\eta^5-C_9H_7)(^{12}CO)(^{13}CO)]$ present in natural abundance

corresponds to a CH_4 complex, $[Co(\eta^5-C_5H_5)(CO) \cdots CH_4]$ present in a trace amount.

(*g*) *Photolysis of* $[Ir(\eta^5-C_9H_7)(CO)_2]$ *in* CH_4 *and* Ar *Matrices.*—Infrared spectra (terminal stretching region) from an experiment with $[Ir(\eta^5-C_9H_7)(CO)_2]$ isolated at high dilution in a CH_4 matrix are shown in Figure 9. Extended photolysis (filter B, 33 h) caused some decreases in the parent bands, the appearance of a weak band at 2 005.4 cm^{-1} and a trace of 'free' CO. Photolysis with higher energy radiation (filter A) initially promoted the same photoreaction [Figure 9(*b*)] but on longer photolysis a new band was observed to grow at 1 958.4 cm^{-1} at the expense of the parent complex and the species with the band at 2 005.4 cm^{-1} [Figure 9(*c*)]. A subtraction revealed another band (*ca.* 1 970 cm^{-1}) which had been partially obscured by a parent band [Figure 9(*d*)]. In Ar matrices no new bands were observed despite using a variety of filters.

The band at 2 005.4 cm^{-1} appears analogous to bands for other $[M(\eta^5-C_5R_5)(CO)(Me)(H)]$ (M = Rh or Ir, R = H or Me) complexes (Table 2) and hence it may be assigned to the species $[Ir(\eta^5-C_9H_7)(CO)(Me)(H)]$. The new bands at *ca.* 1 970 and 1 958.4 cm^{-1} are probably due to monomeric species because of the high dilutions used and presumably arise from some interaction with CH_4 since they were not detected in Ar matrices. The band at *ca.* 1 970 cm^{-1} may correspond to an analogous species to those formed on high-energy photolysis in $[Ir(\eta^5-C_5R_5)(CO)_2]$–$CH_4$ experiments, *i.e.* $[Ir(\eta^5-C_9H_7)(CO) \cdots CH_4]$. The lower wavenumber band at 1 958.4 cm^{-1} could arise from the 'naked' 16-electron species $[Ir(\eta^5-C_9H_7)(CO)]$, arising because of higher quantum yields in CH_4 matrices compared to Ar matrices, but is more likely to be due to some other photoproduct which is isomeric with $[Ir(\eta^5-C_9H_7)(CO)(Me)(H)]$ because it arises in CH_4 matrices.

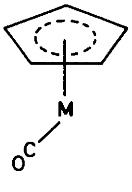


Scheme. M = Rh or Ir, R = H or Me; see text for the identity of X. (*i*) *hν* (λ < 320 nm), (*ii*) *hν′* (λ < 280 nm), (*iii*) *hν″* (λ > 300 nm)

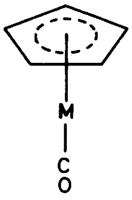
Discussion

A possible path for C–H photoactivation is shown in the generalised Scheme; spectroscopic evidence for $[M(\eta^5-C_5R_5)(CO)]$ species was not obtained in all cases. The results show clearly that the photolysis of $[Ir(\eta^5-C_5R_5)(CO)_2]$ (R = H or Me) complexes in CH_4 matrices leads to the formation of the hydrido(methyl)complexes $[Ir(\eta^5-C_5R_5)(CO)(Me)(H)]$ corresponding to the solution photochemical products.[4] There is also good evidence that photolysis of analogous Rh complexes in CH_4 matrices affords hydrido(methyl) complexes, $[Rh(\eta^5-C_5R_5)(CO)(Me)(H)]$ (R = H or Me), although such complexes have not been isolated from solution photochemical reactions,[24] presumably due to their thermal instability. This is consistent with the fact that the complexes $[Rh(\eta^5-C_5Me_5)(PMe_3)(R)(H)]$ (R = alkyl) are unstable above *ca.* −20 °C.[3,25] There is also some evidence that $[Ir(\eta^5-C_9H_7)(CO)_2]$ is capable of oxidatively adding CH_4 in matrices at 12 K although no products could be isolated on photolysis of this complex in a variety of hydrocarbon solvents.[26]

In Ar matrices the observation of $[M(\eta^5-C_5R_5)(CO)]$ (M = Rh or Ir, R = H or Me) species suggests that C–H photoactivation may be occurring *via* ejection of CO as the primary photoprocess. This is not surprising since CO loss is a pervasive feature of the photochemistry of metal carbonyl complexes.[27] It seems likely that CO loss may be occurring for all complexes studied and that the failure to observe such monocarbonyl fragments may be due to facile recombination with CO in the matrix cage, *e.g.* the recombination of $[Ni(CO)_n]$ (*n* = 1—3) fragments with CO on annealing matrices to 15, 20, and 30 K.[28,29] Further evidence for CO ejection is provided by ^{13}CO substitution using ^{13}CO-doped matrices. Interestingly, the extent of ^{13}CO incorporation (Co ≫ Rh > Ir) is the reverse of C–H activation; in ^{13}CO-doped CH_4 matrices the Ir complexes



(III)



(IV)

show a preference for C–H activation whereas the Rh complexes favour substitution.

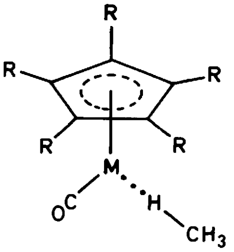
Recent extended Hückel calculations showed that the 16-electron d^8 intermediates [M(η^5-C_5H_5)(L)] (M = Co, Rh, or Ir), especially for L = CO, might exist in singlet states thus avoiding spin-imposed high activation energies of formation.[30] It was also shown that the more likely geometry of such singlet species would be the bent structure (**III**) rather than the C_{5v} linear structure (**IV**). A bent geometry might allow more facile recombination with CO in matrices than the linear structure.

The identity of the unassigned species (X in the Scheme) formed on high-energy photolysis of [M(η^5-C_5R_5)(CO)(Me)(H)] complexes remains uncertain. Four likely possibilities would seem to be: (*i*) a CH_4 complex, *i.e.* [M(η^5-C_5R_5)(CO) $\cdots$ CH_4] (**V**), (*ii*) a monocarbonyl formed by metal to ring H transfer (**VI**), (*iii*) a dicarbonyl species (**VII**) formed from (**VI**) by the recapture of ejected CO, (*iv*) a radical species formed by homolytic cleavage of M–H or M–Me bonds. Of these possibilities there are precedents for metal to ring H transfer[31,32] but such complexes as (**VI**) could not be formed for the Co complexes, which do not activate CH_4, while the capture of CO in the formation of (**VII**) seems unlikely under forcing irradiation conditions (high-energy photolysis) because there would be insufficient CO present. If there was a M–H cleavage the reversibility of the formation of X would be impossible since H atoms are known to diffuse freely in gas matrices[33] while Me$^\bullet$ radicals would remain trapped in the cage and be subject to facile back reactions such that the metal species would not exist for long enough to be trapped and observed by i.r. spectroscopy. On balance, the reversibility seems to favour structure (**V**) for X.

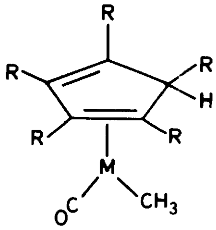
In contrast to the positive evidence for a CO loss process leading to C–H activation, there is no direct evidence so far for an associative pathway being involved in C–H activation. The indenyl complex, [Ir(η^5-C_9H_7)$(CO)_2$], was expected to favour an associative pathway because of the equilibrium [equation (2)] which creates a site for C–H activation to yield (**VIII**). In practice the indenyl complex behaved analogously to the cyclopentadienyl complexes forming [Ir(η^5-C_9H_7)(CO)(Me)(H)] and, therefore, it appears that the associative pathway is not favoured.

The formation of hydrido(methyl) complexes may be considered to arise in two ways. One possibility is that there is sufficient energy available from the photons absorbed by [M(η^5-C_5R_5)$(CO)_2$] complexes both to eject CO and to overcome the conversion barrier from a CH_4 complex (**V**) to [M(η^5-C_5R_5)(CO)(Me)(H)]. An alternative possibility is that a second photon is required. Assuming that the dissociation energy of a Rh–CO bond is *ca.* 30 kcal mol^{-1} and the kinetic barrier to hydrido(methyl) complex formation from a CH_4 complex is 20 kcal mol^{-1} (estimated from Figure 7 of ref. 17), there should be sufficient energy from a '90-kcal photon' (λ = 320 nm, filter B) for a single-photon process to be possible. In solution reactions there will be additional thermal energy to supplement the photochemical energy.

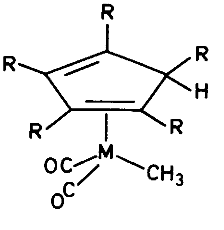
The failure of Co to yield hydrido(methyl) complexes even at 12 K may be attributed to steric and/or thermodynamic factors.



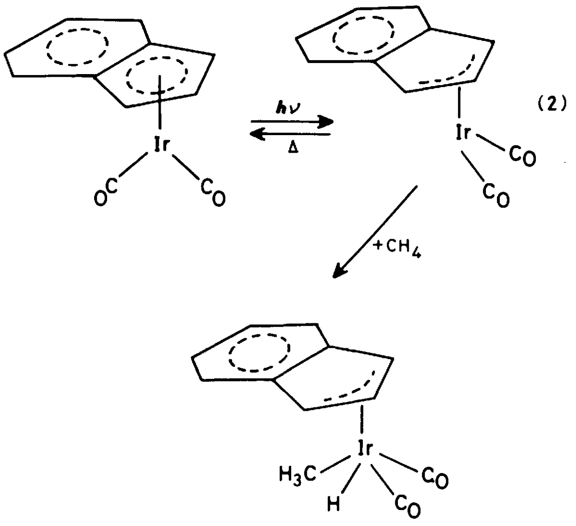
(V)



(VI)



(VII)



(2)

(VIII)

Since weak bands are observed in CH_4 matrices, the steric explanation seems unlikely. This is supported by the known stability of other alkyl complexes, *e.g.* [Co(η^5-C_5R_5)(PPh_3)$(Me)_2$] (R = H or Me),[34] which contain bulkier ligands than those in [Co(η^5-C_5R_5)(CO)(Me)(H)]. In the absence of extended Hückel calculations for the [Co(η^5-C_5R_5)(CO)]–CH_4 systems, taking average dissociation energies for M–H and M–Me bonds as 60 and 30 kcal mol^{-1} for first-row transition metals[35] together with the dissociation energy for a C–H bond in CH_4 as 105 kcal mol^{-1},[36] the conversion of [Co(η^5-C_5H_5)(CO) $\cdots$ CH_4] to [Co(η^5-C_5H_5)(CO)(Me)(H)] would appear to be an endothermic process. For second- and third-row transition metals the M–H and M–Me bonds are stronger and thus the conversion may be an exothermic process. An additional factor for Co could be some photophysical process which could depopulate the photoreactive state or provide a preferred deactivation pathway for the initial excited state. Such a process has been found for [Co(η^5-C_5H_5)$(CO)_2$] which has been shown to luminesce in frozen gas matrices.[37] Without knowing whether the Rh and Ir analogues also luminesce it is difficult to assess the importance of the radiative decay pathway for the Co complexes.

Acknowledgements

The Southampton group thanks the S.E.R.C. for support (to A. J. R.) and British Gas for a Scholarship (to I. W.). The Edmonton group thanks the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support. We are grateful to Professor M. Wrighton for informing us of work in his laboratory on C–H activation in low-temperature glasses prior to publication.

References

1 J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 3723.
2 A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1982, **104**, 352; 1983, **105**, 3929.
3 W. D. Jones and F. J. Feher, *Organometallics*, 1983, **2**, 562; *J. Am. Chem. Soc.*, 1984, **106**, 1650.
4 J. K. Hoyano, A. D. McMaster, and W. A. G. Graham, *J. Am. Chem. Soc.*, 1983, **105**, 7190.
5 O. Crichton, A. J. Rest, and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1980, 167.
6 F. Basolo, *Coord. Chem. Rev.*, 1982, **43**, 7.
7 M. E. Rerek and F. Basolo, *Organometallics*, 1983, **2**, 372.
8 A. J. Rest, I. Whitwell, W. A. G. Graham, J. K. Hoyano, and A. D. McMaster, *J. Chem. Soc., Chem. Commun.*, 1984, 624.
9 M. M. Rochkind, *Spectrochim Acta, Part A*, 1971, **27**, 547.
10 (*a*) E. O. Fischer and K. Bittler, *Z. Naturforsch., Teil B*, 1961, **16**, 225; (*b*) J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970; (*c*) L. R. Byers and L. F. Dahl, *Inorg. Chem.*, 1980, **19**, 277; (*d*) E. O. Fischer and K. S. Brenner, *Z. Naturforsch., Teil B*, 1962, **17**, 774.
11 W. A. G. Graham, J. K. Hoyano, and A. D. McMaster, unpublished work.
12 D. J. Fettes, R. Narayanaswamy, and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 1981, 2311.
13 A. M. F. Brouwers, A. Oskam, R. Narayanaswamy, and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 1982, 1777.
14 R. N. Perutz and J. J. Turner, *J. Am. Chem. Soc.*, 1975, **97**, 4791.
15 M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1974, 2276.
16 Z. H. Kafafi, R. H. Hauge, and J. L. Margrave, *J. Am. Chem. Soc.*, 1985, **107**, 6134.
17 J.-Y. Saillard and R. Hoffmann, *J. Am. Chem. Soc.*, 1984, **106**, 2006.
18 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395.
19 I. Whitwell, Ph.D. Thesis, University of Southampton, 1986.
20 W. A. Herrmann, J. Plank, C. Bauer, M. L. Ziegler, E. Guggolz, and R. Alt, *Z. Anorg. Allg. Chem.*, 1982, **487**, 85.
21 A. Nutton and P. M. Maitlis, *J. Organomet. Chem.*, 1979, **166**, C21.
22 F. R. Anderson and M. S. Wrighton, *Inorg. Chem.*, 1986, **25**, 112.
23 W.-S. Lee and H. H. Brintzinger, *J. Organomet. Chem.*, 1977, **127**, 87.
24 W. A. G. Graham and J. K. Hoyano, unpublished work.
25 R. A. Periana and R. G. Bergman, *Organometallics*, 1984, **3**, 508.
26 W. A. G. Graham and R. Holmes-Smith, unpublished work.
27 G. L. Geoffroy and M. S. Wrighton, 'Organometallic Photochemistry,' Academic Press, New York, 1979; R. B. Hitam, K. A. Mahmoud, and A. J. Rest, *Coord. Chem. Rev.*, 1984, **55**, 1.
28 A. J. Rest and J. J. Turner, *Chem. Commun.*, 1969, 1026.
29 R. L. DeKock, *Inorg. Chem.*, 1971, **10**, 1205.
30 P. Hofmann and M. Padmanabhan, *Organometallics*, 1983, **2**, 1273.
31 J. Chetwynd-Talbot, P. Grebenik, R. N. Perutz, and M. H. A. Powell, *Inorg. Chem.*, 1983, **22**, 1675.
32 J. Müller, H. Menig, and P. V. Rinze, *J. Organomet. Chem.*, 1979, **181**, 387.
33 B. Meyer, 'Low Temperature Spectroscopy,' Elsevier, New York, 1971.
34 A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1981, **103**, 2488.
35 J. Halpern, *Acc. Chem. Res.*, 1982, **15**, 238.
36 M. H. Baghal-Vayjooee, A. J. Colussi, and S. W. Benson, *J. Am. Chem. Soc.*, 1978, **100**, 3214.
37 R. Narayanaswamy, A. J. Rest, and D. J. Taylor, unpublished work.

Received 29*th July* 1986; *Paper* 6/1730