Photochemistry of Carbonyl(η^5-cyclopentadienyl)dihydridoiridium in Frozen Gas Matrices at *ca.* 12 K: Infrared Evidence relating to C–H Activation

Peter E. Bloyce, Antony J. Rest,* and Ian Whitwell
Department of Chemistry, The University, Southampton SO9 5NH

Infrared spectroscopic evidence, including deuterium and ^{13}CO labelling, is presented to show that photolysis of [Ir(η^5-C_5H_5)(CO)H_2] in a methane matrix at *ca.* 12 K affords [Ir(η^5-C_5H_5)(CO)(CH_3)H] probably *via* initial reductive elimination of the hydride ligands as molecular H_2 to form [Ir(η^5-C_5H_5)(CO)], which is detected in argon matrices. Photolysis of [Ir(η^5-C_5H_5)(CO)H_2] in nitrogen and carbon monoxide matrices yields [Ir(η^5-C_5H_5)(CO)(N_2)] and [Ir(η^5-C_5H_5)$(CO)_2$], respectively. The lack of evidence for HCO$^\bullet$ in CO matrices and the lack of isotopic scrambling in mixed H/D isotope experiments, *e.g.* studies of [Ir(η^5-C_5H_5)(CO)H_2] in CD_4 and [Ir(η^5-C_5H_5)(CO)D_2] in CH_4 matrices, confirms that the initial photoprocess is H_2 ejection. Surprisingly, this ejection is reversible even at 12 K using long-wavelength irradiation. Mechanisms for C–H activation processes are discussed, *cf.* the observation that [Ir(η^5-C_5H_5)(^{12}CO)H_2] exchanges ^{13}CO for ^{12}CO *via* a thermal reaction in the gas phase at 298 K.

Transition-metal hydride complexes are an extremely important class of compounds in the field of homogeneous catalysis. A number of hydride complexes have been shown to be capable of activating C–H bonds in aromatic molecules and more recently in alkanes. Generally the reactions have been photochemically initiated and the complexes have two or more hydride ligands.[1–9] This has led to the proposal that the primary photoprocess in these complexes is reductive elimination of H_2, a reaction known to occur for a number of transition-metal dihydride complexes.[10–14]

Recently the photochemistry of [Ir(η^5-C_5H_5)(CO)H_2] (**1**) has been investigated in hydrocarbon solvents.[15] Photolysis in neopentane resulted in production of [Ir(η^5-C_5H_5)(CO)(CH_2CMe_3)H] (**2**), *i.e.* oxidative addition of an alkane C–H bond had occurred. The obvious interpretation was that an intermediate, [Ir(η^5-C_5H_5)(CO)] (**3**), was produced by H_2 loss and that it attacked the solvent forming (**2**). The dihydride complex (**1**) would, in this view, represent an alternative to [Ir(η^5-C_5H_5)$(CO)_2$] for generation of the intermediate (**3**). More details were sought by carrying out the reaction of the dideuterio complex [Ir(η^5-C_5H_5)(CO)D_2](**1D**) with unlabelled neopentane under the same conditions. Formation exclusively of D_2 and unlabelled (**2**) would have been consistent with (**3**) as the only intermediate in the reaction. In fact there was extensive and complex scrambling of the deuterium labels [equation (1)].

$$\begin{aligned}&[\mathrm{Ir}(\eta^5\text{-}C_5H_5)(CO)D_2] + CH_3CMe_3 \xrightarrow[>300\ \mathrm{nm}]{h\nu}\\ &[\mathrm{Ir}(\eta^5\text{-}C_5H_5)(CO)HD] + [\mathrm{Ir}(\eta^5\text{-}C_5H_5)(CO)H_2] +\\ &[\mathrm{Ir}(\eta^5\text{-}C_5H_5)(CO)(CH_2CMe_3)H] +\\ &[\mathrm{Ir}(\eta^5\text{-}C_5H_5)(CO)(CH_2CMe_3)D] +\\ &[\mathrm{Ir}(\eta^5\text{-}C_5H_5)(CO)(CHDCMe_3)H] +\\ &[\mathrm{Ir}(\eta^5\text{-}C_5H_5)(CO)(CHDCMe_3)D] + H_2 + HD + D_2 \quad (1)\end{aligned}$$

These results appeared to exclude initial D_2 loss and subsequent solvent activation by (**1**) as the *only* process involved. In the hope of gaining further insight into the processes involved, photolysis of complexes (**1**) and (**1D**) has been investigated in frozen gas matrices at *ca.* 12 K. These compounds are particularly amenable to matrix-isolation studies due to their extremely high volatility. A preliminary account of this work, including these solution results, has been published.[15a]

Experimental

Cryogenic temperatures (*ca.* 12 K) were obtained using a closed-cycle helium refrigerator (Air Products and Chemicals Inc., Displex CS-202). Matrices containing [Ir(η^5-C_5H_5)(CO)R_2] (R = H or D) complexes were prepared by making gas mixtures with excess of 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.[16]

Infrared spectra (resolution *ca.* 1 cm^{-1}) were recorded 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 Perkin-Elmer Lambda 7 spectrometer (resolution *ca.* 1 nm).

The photolysis source was a Philips HPK 125-W medium-pressure mercury arc lamp. Wavelength-selective photolysis was achieved by a combination of absorbing materials: filter A (λ <280 and >550 nm), quartz gas cell (pathlength 27 mm) containing Cl_2 (2 atm, *ca.* 2×10^5 Pa) plus a quartz gas cell (pathlength 27 mm) containing Br_2 (200 Torr, *ca.* 2.7×10^4 Pa); filter B (290 < λ < 370 and >550 nm), quartz gas cell containing Br_2 (200 Torr) plus a Pyrex disc (thickness 2 mm); filter C (240 < λ < 390 nm), Corning glass filter number 9863 (thickness 3 mm); filter D (λ >375 nm), Corning glass filter number 3060 (thickness 3 mm); filter E (λ >300 nm), soda glass disc (thickness 3 mm).

Matrix gases (Ar, N_2, CO, 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. The metal complexes were prepared[17] and generously donated by Professor W. A. G. Graham and Dr. J. K. Hoyano and were used without further purification.

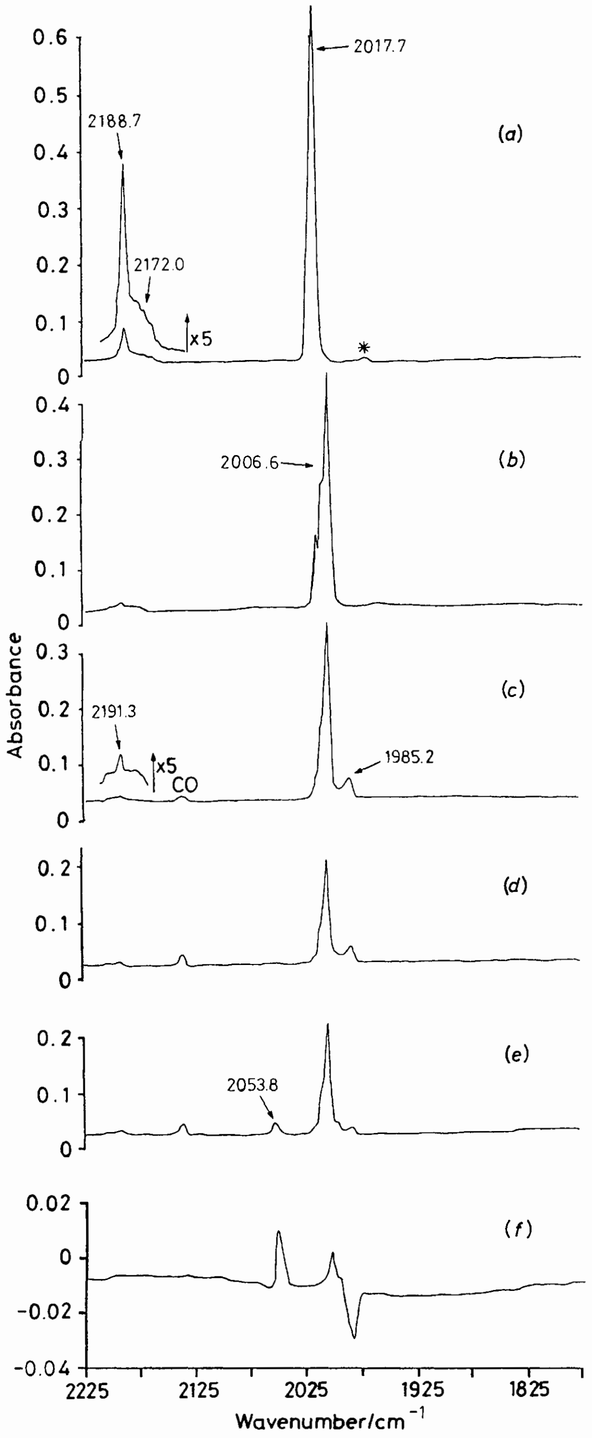
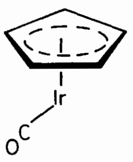


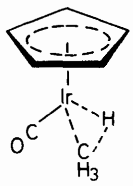
Figure 1. Infrared spectra (Nicolet 7199, resolution 1 cm^{-1}) from an experiment with [Ir(η^5-C_5H_5)(CO)H_2] isolated at high dilution in a methane matrix: (*a*) after deposition; (*b*) after 12 h of irradiation using filter B; (*c*) after 15 min of irradiation using filter A; (*d*) after a further period (30 min) of irradiation using filter A; (*e*) after further irradiation (60 min) using filter B; (*f*) subtraction spectrum [(*e*) − (*d*)]. The band marked * arises from [Ir(η^5-C_5H_5)(^{13}CO)H_2] present in natural abundance

Results

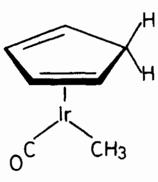
The electronic spectra of complex (**1**) isolated in gas matrices were almost featureless showing one strong band centred at approximately 230 nm. This band has not been assigned and no significant changes in the electronic spectra were detected during photolysis sequences.



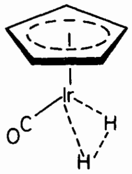
(**3**)



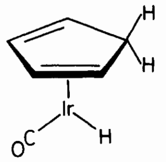
(**5**)



(**6**)



(**7**)



(**8**)

(*a*) *Photolysis of Complex* (**1**) *in Methane and Tetradeuteriomethane Matrices*.—The i.r. spectrum of complex (**1**) isolated at high dilution in a pure methane matrix is shown in Figure 1(*a*) (Table 1). Extended photolysis with filter B, *i.e.* irradiation wavelengths corresponding to solution reactions,[15] resulted in almost complete conversion of (**1**) into a new species with a strong matrix-split terminal CO-stretching band centred at 2 006.6 cm^{-1}, though no 'free' CO was produced [Figure 1(*b*)]. This new band can conclusively be assigned to [Ir(η^5-C_5H_5)(CO)(CH_3)H] (**4**) by comparison with previous solution[18] and matrix-isolation studies (ν_{CO} at 2 006.0 cm^{-1} in CH_4).[19] The very weak Ir–H stretching band of this species is seen on spectral subtraction at *ca.* 2 176 cm^{-1}. It is apparent that H_2 loss from (**1**) provides a much more efficient route to methane activation than previously observed for CO loss from [Ir(η^5-C_5H_5)$(CO)_2$]. Higher-energy photolysis with filter A resulted in partial destruction of the bands for complex (**4**) and the remaining [Ir(η^5-C_5H_5)(CO)H_2] together with the production of a new band at 1 985.2 cm^{-1} and some 'free' CO [Figure 1(*c*)]. Continued photolysis (filter A) caused decreases in all bands except that of 'free' CO, which increased [Figure 1(*d*)]. Subsequent photolysis (filter B) produced a decrease in the band at 1 985.2 cm^{-1} together with an increase in the band for (**4**) and the production of a new band at 2 053.8 cm^{-1} [Figure 1(*e*) and (*f*)].*

The band at 1 985.2 cm^{-1} corresponds exactly to the band previously observed on high-energy photolysis of [Ir(η^5-C_5H_5)$(CO)_2$] in methane matrices (ν_{CO} at 1 984.8 cm^{-1}).[19] In the present experiments it is clear that it is produced by secondary photolysis of (**4**). A likely possibility for the species responsible is the methane complex [Ir(η^5-C_5H_5)(CO)(η^2-CH_4)] (**5**). It has been suggested that a reasonable model compound for this complex is provided by [Ir(η^5-C_5H_5)(CO)(η^2-C_2H_4)], which has ν_{CO} at 1 980 cm^{-1} in a carbon monoxide matrix,[20] and has been extensively studied by Haddleton and Perutz.[20b] However, a diene isomer (**6**), where H has been transferred to the ring, as considered earlier,[19,21] cannot be excluded. Such ring-to-metal and metal-to-ring hydrogen

---

* Interestingly, in a repeat experiment carried out using a different but identically rated mercury lamp, similar band patterns resulted on photolysis, except that less 'free' CO was produced with filter A. When photolysis was then carried out with filter B the species absorbing at 2 053.8 cm^{-1} was still partially reconverted into (**4**). This suggests that the band at 2 053.8 cm^{-1} may arise from a species produced by initial loss of CO from (**4**) on high-energy photolysis.

Table 1. Observed positions (cm^{-1}) of terminal CO-stretching modes of $[Ir(\eta^5\text{-}C_5H_5)(CO)H_2]$, $[Ir(\eta^5\text{-}C_5H_5)(CO)D_2]$, and their photoproducts in CH_4, CD_4, N_2, and CO frozen gas matrices at *ca.* 12 K

Compound	CH_4	CD_4	N_2	CO
$[Ir(\eta^5\text{-}C_5H_5)(CO)H_2]^a$ (**1**)	2 017.7^{b,c}	2 017.1^d	2 022.1^e	2 018.8^f
$[Ir(\eta^5\text{-}C_5H_5)(^{13}CO)H_2]$	1 969.6	1 970.0	1 973.8	*g*
$[Ir(\eta^5\text{-}C_5H_5)(CO)D_2]^h$ (**1D**)	2 017.2^{b,i}			
$[Ir(\eta^5\text{-}C_5H_5)(^{13}CO)D_2]$	1 970.1			
$[Ir(\eta^5\text{-}C_5H_5)(CO)(CH_3)H]$ (**4**)	2 006.6^j			
$[Ir(\eta^5\text{-}C_5H_5)(^{13}CO)(CH_3)H]$	1 960.3			
$[Ir(\eta^5\text{-}C_5H_5)(CO)(\eta^2\text{-}CH_4)]^k$	1 985.2			
$[Ir(\eta^5\text{-}C_5H_5)(^{13}CO)(\eta^2\text{-}CH_4)]^k$	1 942.3			
$[Ir(\eta^5\text{-}C_5H_5)(CO)({=}CH_2)]^k$	2 053.8			
$[Ir(\eta^5\text{-}C_5H_5)(^{13}CO)({=}CH_2)]^k$	*ca.* 2 008			
$[Ir(\eta^5\text{-}C_5H_5)(CO)(CD_3)D]$		2 006.2^l		
$[Ir(\eta^5\text{-}C_5H_5)(CO)(\eta^2\text{-}H_2)]^k$			2 002.0	
$[Ir(\eta^5\text{-}C_5H_5)(CO)(N_2)]$			1 981.6^m	
$[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$				2 041.8 1 974.7
$[Ir(\sigma\text{-}C_5H_5)(CO)_4]$				2 117.5 2 049.4 2 029.8 *n*
$[\{Ir(\eta^5\text{-}C_5H_5)(CO)\}_2]$			1 939.7^b	

^{a} ν_{IrH} at 2 175.9 cm^{-1} in n-pentane. ^{b} Average position of matrix-split band. ^{c} ν_{IrH} at 2 188.7 and 2 172.0 cm^{-1}. ^{d} ν_{IrH} at 2 189.6 and 2 173.6 cm^{-1}. ^{e} ν_{IrH} at 2 193.1 and 2 174.2 cm^{-1}. ^{f} ν_{IrH} obscured by other peaks. ^{g} Obscured by $[Fe(CO)_5]$ impurity. ^{h} ν_{CO} at 2 018.2 cm^{-1} in n-pentane. ^{i} ν_{IrD} at 1 575.6 and 1 558.2 cm^{-1}. ^{j} ν_{IrH} obscured, ν_{CO} average position of matrix-split band; ν_{IrH} at 2 170 cm^{-1} and ν_{CO} at 2 009 cm^{-1} in n-hexane. ^{k} Tentative assignment. ^{l} ν_{IrD} at 1 565.6 cm^{-1}. ^{m} ν_{NN} at 2 161.4 cm^{-1}. ^{n} Band obscured.

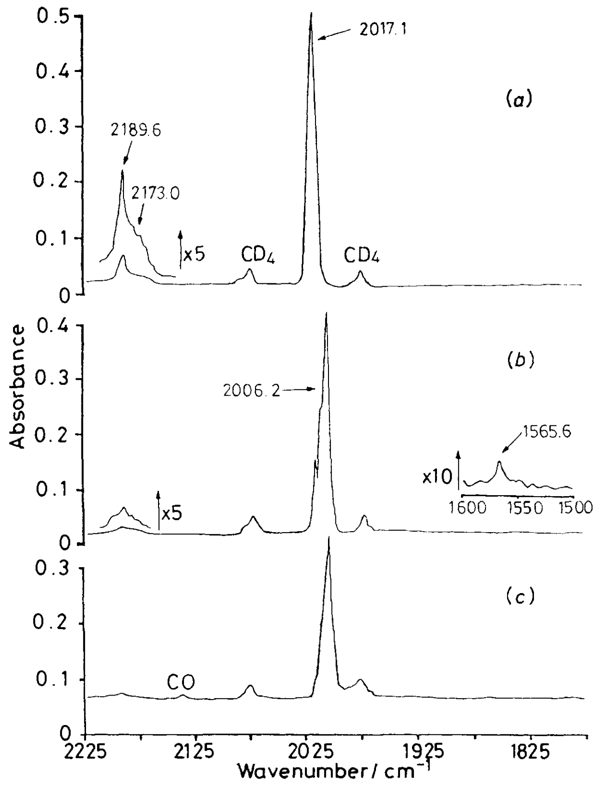


Figure 2. Infrared spectra (Nicolet 7199, resolution 1 cm^{-1}) from an experiment with $[Ir(\eta^5\text{-}C_5H_5)(CO)H_2]$ isolated at high dilution in a CD_4 matrix: (*a*) after deposition; (*b*) after 12 h of irradiation using filter B; (*c*) after 20 min of irradiation using filter A

migrations have been well documented for rhenium complexes[22] and would be consistent with the high-energy photolysis used in this work.

The i.r. spectrum of complex (**1**) isolated at high dilution in a CD_4 matrix is shown in Figure 2(*a*) (Table 1). Extended photolysis (filter B) resulted in almost complete conversion into a new species with a strong terminal CO-stretching band centred at 2 006.2 cm^{-1}. Once more no 'free' CO was produced, but a weak band was detected at 1 565.6 cm^{-1} [Figure 2(*b*)]. The new species can be assigned as $[Ir(\eta^5\text{-}C_5H_5)(CO)(CD_3)D]$ by comparison with data obtained on high-energy photolysis of $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ in CD_4 matrices (ν_{CO} at 2 006.4 and ν_{IrD} at 1 564.5 cm^{-1}).[21] Photolysis with filter A resulted in partial destruction of the bands for $[Ir(\eta^5\text{-}C_5H_5)(CO)(CD_3)D]$ and the remaining $[Ir(\eta^5\text{-}C_5H_5)(CO)H_2]$ together with a trace of 'free' CO [Figure (2*c*)]. The production of a second ν_{CO} band on higher-energy photolysis is probably obscured by bands due to the CD_4 matrix.

(*b*) *Photolysis of Complex* (**1**) *in Argon and* 5% ^{13}CO*-doped Argon Matrices.*—The i.r. spectrum (terminal CO-stretching region) of complex (**1**) isolated at high dilution in a pure argon matrix is shown in Figure 3(*a*) (Table 2). The spectrum shows one strong matrix-split terminal CO-stretching band centred at 2 021.6 cm^{-1} together with a band at 1 973.1 cm^{-1} (marked with an *) corresponding to the terminal ^{13}CO stretching mode of $[Ir(\eta^5\text{-}C_5H_5)(^{13}CO)H_2]$ present in natural abundance. Two weak broad matrix-split bands centred at 2 198.7 cm^{-1} are due to the IrH stretching modes of (**1**).[23] In n-pentane one broad IrH stretching band is observed at 2 176 cm^{-1}. Irradiation using filter B resulted in decreases in the parent bands together with the appearance of bands at 1 954.4 and 1 942.6 cm^{-1}, but no band for 'free' CO [Figure 3(*b*)]. Photolysis with filter C resulted in increases in these bands together with decreases in the parent bands and the appearance of a further weak new matrix-split band at 2 002.0 cm^{-1}. Higher-energy photolysis (filter A) resulted in increases in the matrix-split band at 1 954.4 cm^{-1} and the band at 2 002.0 cm^{-1}, while the parent bands decreased, the band at 1 942.6 cm^{-1} decreased slightly, and a trace of 'free' CO was produced [Figure 3(*c*)]. Photolysis at longer wavelengths (filter D) caused the band at 1 954.4 cm^{-1} to decrease significantly along with a smaller decrease in the weak band at 2 002.0 cm^{-1}, while the parent bands increased in

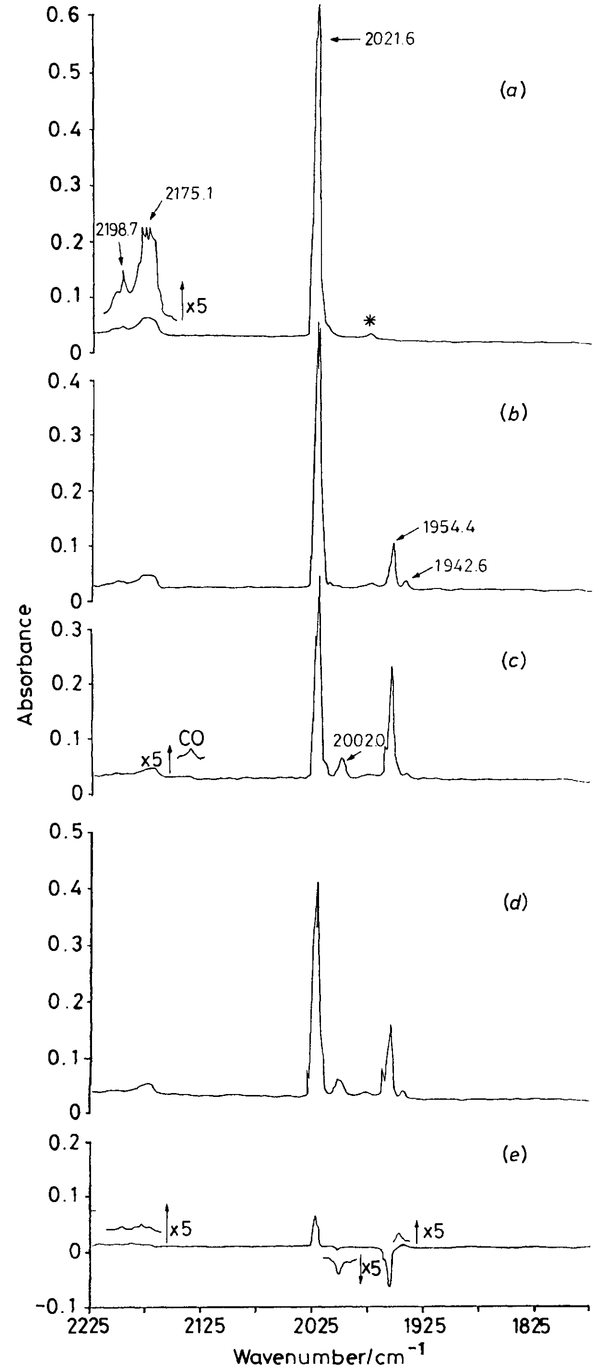
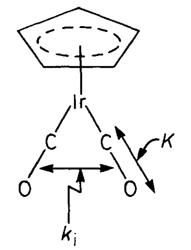


Figure 3. Infrared spectra (Nicolet 7199 resolution, 1 cm^{-1}) from an experiment with $[Ir(\eta^5-C_5H_5)(CO)H_2]$ isolated at high dilution in an argon matrix: (*a*) after deposition; (*b*) after 16 h of irradiation using filter B; (*c*) after 200 min of irradiation using filter C + 40 min of irradiation using filter A; (*d*) after 250 min of irradiation using filter D; (*e*) subtraction spectrum [(*d*) − (*c*)]. The band marked * arises from $[Ir(\eta^5-C_5H_5)(^{13}CO)H_2]$ present in natural abundance

Table 2. Observed and calculated positions (cm^{-1}) of terminal CO-stretching modes of complexes (**1**), (**1D**), and their photoproducts in pure argon and 5% ^{13}CO-doped argon frozen gas matrices at 12 K

Compound	5% ^{13}CO–Ar	Ar	Calculated
$[Ir(\eta^5-C_5H_5)(^{12}C^{16}O)H_2]$	2 019.8[a]	2 021.6[b,c]	
$[Ir(\eta^5-C_5H_5)(^{13}C^{16}O)H_2]$	1 971.4	1 973.1	1 974.9[d]
$[Ir(\eta^5-C_5H_5)(^{13}C^{18}O)H_2]$	1 928.4		1 925.1[d]
$[Ir(\eta^5-C_5H_5)(^{12}C^{16}O)D_2]$	2 019.2[e]	2 021.2[b,f]	
$[Ir(\eta^2-C_5H_5)(^{13}C^{16}O)D_2]$	1 973.8	1 973.4	1 974.3[g]
$[Ir(\eta^5-C_5H_5)(^{13}C^{18}O)D_2]$	1 925.6		1 924.5[g]
$[Ir(\eta^5-C_5H_5)(^{12}C^{16}O)_2]$		2 044.5[h]	2 044.3[i]
		1 977.2[h]	1 975.8[i]
$[Ir(\eta^5-C_5H_5)(^{12}C^{16}O)(^{13}CO^{16}O)]$	2 026.8	2 028.2[h]	2 028.3[i]
	1 945.7	1 946.1[h]	1 947.2[i]
$[Ir(\eta^5-C_5H_5)(^{13}C^{16}O)_2]$	1 995.1		1 998.9[i]
	1 930.2		1 931.9[i]
$[Ir(\eta^5-C_5H_5)(^{12}C^{16}O)]$	1 953.8	1 954.4	
$[Ir(\eta^5-C_5H_5)(^{13}C^{16}O)]$	*ca.* 1 912		1 910.0[j]
$[Ir(\eta^5-C_5H_5)(CO)(\eta^2-H_2)]$[k]		2 002.0	
$[Ir(\eta^2-C_5H_5)(CO)(\eta^2-D_2)]$[k]		2 002.5	

[a] ν_{IrH} at 2 170.4 cm^{-1}. [b] Average position of matrix-split band. [c] ν_{IrH} at 2 198.7 and 2 175.1 cm^{-1} (matrix split). [d] Calculated from the CO-stretching frequency of $[Ir(\eta^5-C_5H_5)(^{12}C^{16}O)H_2]$ in 5% ^{13}CO-doped Ar, assuming no coupling of the CO vibration with other molecular vibrations. [e] ν_{IrD} at 1 582.6 and 1 559.4 cm^{-1}. [f] ν_{IrD} at 1 584.2 and 1 561.3 cm^{-1}. [g] Calculated from the CO-stretching frequency of $[Ir(\eta^5-C_5H_5)(^{12}C^{16}O)D_2]$ with 5% ^{13}CO-doped Ar, assuming no coupling of the CO vibration with other molecular vibrations. [h] Data from ref. 19. [i] Calculated using refined stretching parameters (K = 1 632.8 nm cm^{-1}, k_i = 55.6 nm^{-1}, as defined in the diagram below) obtained from the CO-stretching frequencies of $[Ir(\eta^5-C_5H_5)(^{12}C^{16}O)_2]$ and $[Ir(\eta^5-C_5H_5)(^{12}C^{16}O)(^{13}C^{16}O)]$ in Ar.



[j] Calculated from the CO-stretching frequency of $[Ir(\eta^5-C_5H_5)(^{12}C^{16}O)]$ in 5% ^{13}CO-doped Ar, assuming no coupling of the CO vibration with other molecular vibrations. [k] Tentative assignment.

intensity [Figures 3(*d*) and (*e*)]. Surprisingly annealing the matrix to *ca.* 30 K produced no significant changes in the i.r. spectrum.

The three bands produced all behaved differently following photolysis at a variety of wavelengths of irradiation and hence are likely to be due to three different species. The most likely assignment of the major product band in the argon matrix, at 1 954.4 cm^{-1}, is to the monocarbonyl species $[Ir(\eta^5-C_5H_5)(CO)]$ (**3**), produced by photochemical H_2 elimination. This assignment is supported by the observed reversal to the parent complex on long-wavelength photolysis, analogous to the recombination of $[Fe(CO)_4]$ with H_2 in argon matrices[12] and more recently in low-temperature pentane solutions,[24] and the recent observations of the reactions of H_2 with $[Co(CO)_3H]$[25] and $[Co(CO)_3(CH_3)]$[26] in hydrogen–argon matrices, *i.e.* oxidative addition of H_2. This band is also in excellent agreement with the band assigned to (**3**) produced on photolysis of $[Ir(\eta^5-C_5H_5)(CO)_2]$ in argon matrices (ν_{CO} at 1 953.7 cm^{-1}).[19,21]

Assignments for the weaker bands at 1 942.6 and 2 002.0 cm^{-1} are more speculative. One possibility for the weak band at 1 942.6 cm^{-1} is that it corresponds to the bands seen previously at 1 940.4 (in argon matrices)[18] or 1 936.5 cm^{-1} (in nitrogen matrices)[21] which had been tentatively ascribed to the dimer $[\{Ir(\eta^5-C_5H_5)(CO)\}_2]$.

The species giving rise to the band at 2 002.0 cm^{-1} may be the H_2 analogue of (**5**), *i.e.* (**7**). Both are seen to form on high-energy photolysis and decrease in intensity during low-energy photolysis. The decrease in ν_{CO} upon substitution of H by CH_3

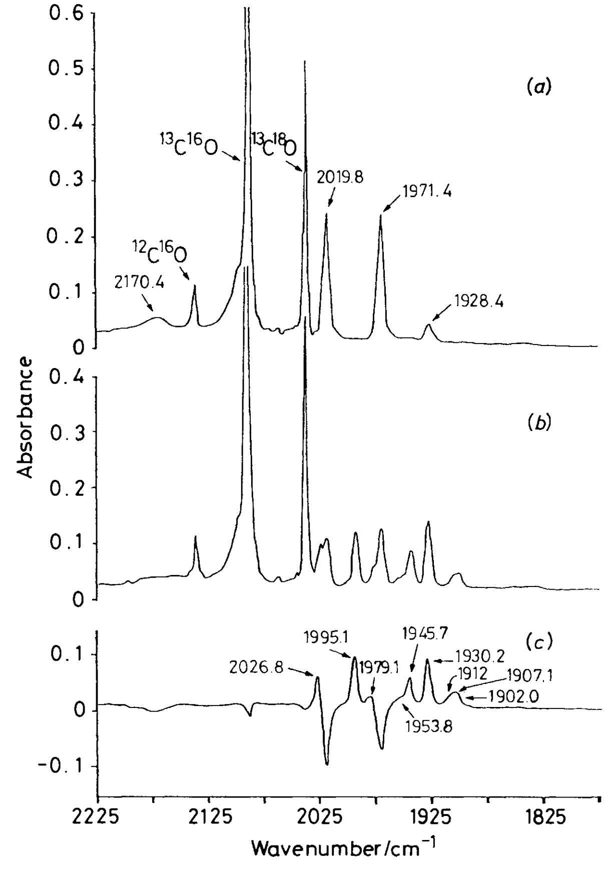


Figure 4. Infrared spectra (Nicolet 7199 resolution, 1 cm^{-1}) from an experiment with [Ir(η^5-C_5H_5)(^{12}CO)H_2] isolated at high dilution in a 5% ^{13}CO-doped argon matrix: (*a*) after deposition; (*b*) after 20 min of irradiation using filter A; (*c*) subtraction spectrum [(*b*) − (*a*)]

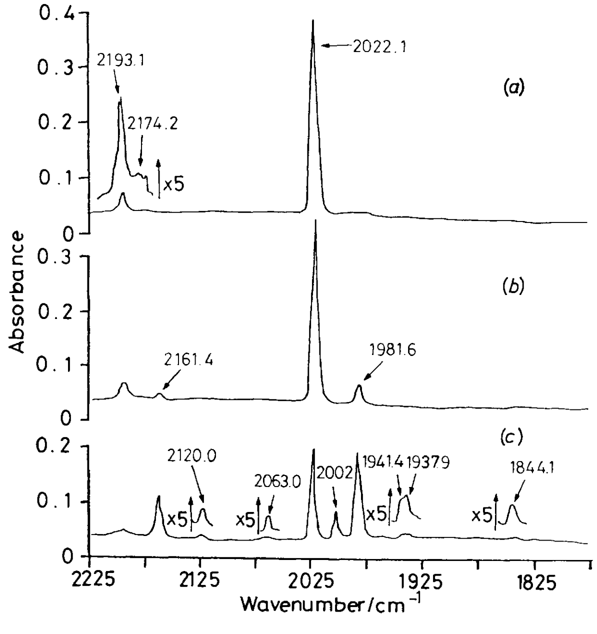


Figure 5. Infrared spectra (Nicolet 7199 resolution, 1 cm^{-1}) from an experiment with [Ir(η^5-C_5H_5)(CO)H_2] isolated at high dilution in a pure nitrogen matrix: (*a*) after deposition; (*b*) after 65 min of irradiation using filter B; (*c*) after 30 min of irradiation using filter A

[*i.e.* from (**7**) to (**5**)] is appropriate, and, moreover, the decrease in ν_{CO} in moving from parent dihydride (**1**) to the proposed η^2-H_2 complex (**7**) is consistent with shifts observed for a series of η^2-H_2 complexes and their equilibrium dihydride isomers.[27] On the basis of these arguments, complex (**7**) seems to be the species most likely to be responsible for the band at 2 002.0 cm^{-1} in argon matrices; however, the diene isomer, (**8**), of the parent cannot be excluded, *cf.* (**6**) as an alternative to (**5**).

The i.r. spectrum obtained after making a mixture of complex (**1**) with 5% ^{13}CO-doped Ar and depositing onto the cooled window is shown in Figure 4(*a*). The bands at 2 019.8, 1 971.4, and 1 928.4 cm^{-1} correspond to the terminal CO-stretching modes of [Ir(η^5-C_5H_5)($^{12}C^{16}O$)H_2], [Ir(η^5- C_5H_5)($^{13}C^{16}O$)-H_2], and [Ir(η^5-C_5H_5)($^{13}C^{18}O$)H_2], respectively (Table 2), while the broad band centred at 2 170.4 cm^{-1} corresponds to the overlapping IrH stretching modes of each complex. Exchange between $^{13}C^{16}O$ and $^{13}C^{18}O$ and the parent complex has clearly occurred in the gas phase prior to deposition, an observation also made for solutions of (**1**) in the presence of ^{13}CO.[15b] Photolysis with filter A led to the production of new bands at 2 026.8, 1 995.1, 1 979.1, 1 945.7, 1 930.2, 1 907.1, 1 902.0, and possibly 1 953.8 cm^{-1}, at the expense of the parent bands [Figures 4(*b*) and (*c*)]. The observed new bands can be explained in terms of the parent complexes losing H_2 on photolysis and the resulting monocarbonyl fragments {mainly [Ir(η^5-C_5H_5)($^{12}C^{16}O$)] and [Ir(η^5-C_5H_5)($^{13}C^{16}O$)]} reacting with $^{13}C^{16}O$ and $^{13}C^{18}O$. Hence, the new bands can mainly be assigned to dicarbonyls as shown in Table 2. The weak band at 1 953.8 cm^{-1} may be assigned to [Ir(η^5-C_5H_5)($^{12}C^{16}O$)], while the corresponding band for [Ir(η^5-C_5H_5)($^{13}C^{16}O$)] may be the shoulder at approximately 1 912 cm^{-1} on the band at 1 907.1 cm^{-1}. It was not possible to tell whether the band at 2 002.0 cm^{-1} in pure argon matrices was present in this experiment due to overlapping bands in this region.

(*c*) *Photolysis of Complex* (**1**) *in a* 10% CH_4-*doped Argon Matrix at* 12 K.—Photolysis of complex (**1**) isolated in a 10% CH_4-doped argon matrix (filter B) produced slow conversion of the parent into [Ir(η^5-C_5H_5)(CO)(CH_3)H], which speeded up when filter A was used. With this same filter, bands were produced corresponding to the bands at 2 002.0 cm^{-1} in argon matrices and 1 985.2 cm^{-1} in methane matrices, together with a weak band at 1 955.0 cm^{-1} for [Ir(η^5-C_5H_5)(CO)] and a trace of 'free' CO. However, it was not possible to show stepwise conversion of [Ir(η^5-C_5H_5)(CO)] into the species proposed to be [Ir(η^5-C_5H_5)(CO)(η^2-CH_4)] or to [Ir(η^5-C_5H_5)(CO)(CH_3)H] on longer-wavelength photolysis. However, on annealing the matrix to *ca.* 30 K the resulting i.r. band increases and decreases were consistent with a thermal conversion of [Ir(η^5-C_5H_5)(CO)] into [Ir(η^5-C_5H_5)(CO)-(CH_3)H].

(*d*) *Photolysis of Complex* (**1**) *in Nitrogen Matrices at* 12 K.—The i.r. spectrum of complex (**1**) isolated at high dilution in a pure nitrogen matrix is shown in Figure 5(*a*) (Table 1). Photolysis with filter B resulted in decreases in the parent bands and the production of new bands at 2 161.4 and 1 981.6 cm^{-1} [Figure 5(*b*)]. These bands agree very closely with those previously assigned to [Ir(η^5-C_5H_5)(CO)(N_2)] (ν_{NN} at 2 161.0 cm^{-1} and ν_{CO} at 1 981.0 cm^{-1} in nitrogen matrices).[21] Higher-energy photolysis (filter A) resulted in further conversion into this dinitrogen complex together with the production of a new strong band at 2 002.0 cm^{-1} and weak bands at 2 120.0, 1 963.0, 1 941.4, 1 937.9, and 1 844.1 cm^{-1} [Figure 5(*c*)]. The band at 2 120.0 cm^{-1} may correspond to a bis(nitrogen) species, [Ir(η^5-C_5H_5)(N_2)$_2$]. The bands at 1 941.4 and 1 937.9 cm^{-1} probably arise from a matrix splitting and could correspond to the dimer

$[\{Ir(\eta^5\text{-}C_5H_5)(CO)\}_2]$ which was also thought to be produced from $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ in nitrogen matrices (ν_{CO} at 1 936.5 cm^{-1}).[21] The band at 1 844.1 cm^{-1} may correspond to another dimeric species possibly containing N_2, but this assignment is tentative due to the extreme weakness of the band. The band observed at 2 002.0 cm^{-1} in this experiment behaves similarly to the band observed at the same position in argon matrices and so is presumably due to the same photoproduct.

(*e*) *Photolysis of Complex* (**1**) *in* ^{12}CO *and* ^{12}CO–^{13}CO *Mixed Matrices.*—The i.r. spectrum (Table 1) obtained after making up a mixture of complex (**1**) with ^{12}CO and depositing onto the cold window showed a strong band at 2 018.8 cm^{-1} for the terminal CO-stretching mode of (**1**) together with two weak bands at 2 041.8 and 1 974.7 cm^{-1} corresponding to a small quantity of $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ which probably has been produced by thermal reaction in the blacked-out gas bulb. Other peaks were obscured by CO matrix bands and a small quantity of $[Fe(CO)_5]$, an impurity derived from CO reacting with the wall of the cylinder in which it is stored. Low-energy photolysis had little effect, but photolysis with filter B produced increases in the bands for $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ together with the production of new bands at 2 117.5, 2 049.4, and 2 029.8 cm^{-1} at the expense of the bands of (**1**). Photolysis with filter C resulted in further destruction of (**1**) together with decreases in the three new bands and large increases in the bands for $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$. Photolysis with filter E caused a destruction of the dicarbonyl together with an increase in the bands at 2 117.5, 2 049.4, and 2 029.8 cm^{-1} and, apparently, in the terminal CO-stretching band of the parent dihydride.

The results obtained can be explained in terms of the dihydride losing H_2 on high-energy photolysis and picking up CO, thus forming $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ which is itself photoreactive. The bands at 2 117.5, 2 049.4, and 2 029.8 cm^{-1} correspond very closely with bands previously assigned to $[Ir(\sigma\text{-}C_5H_5)(CO)_4]$ (ν_{CO} at 2 117.7, 2 049.3, 2 029.6, and 2 018.2 cm^{-1});[19,21] the band at 2 018.2 cm^{-1} would be obscured by the terminal CO-stretching band of (**1**). Hence it is proposed that once $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ has formed from (**1**), subsequent reactions are the same as for $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ isolated in CO matrices, *i.e.* long-wavelength photolysis causes conversion of $[Ir(\eta^5\text{-}C_5H_5)(CO)_2]$ into $[Ir(\sigma\text{-}C_5H_5)(CO)_4]$, while high-energy photolysis reverses this reaction. It is interesting that long-wavelength photolysis had no effect on (**1**). Also it is significant that no i.r. band for the HCO radical (ν_{CO} at 1 860 cm^{-1})[28–31] was produced in this experiment, even on high-energy photolysis. This indicates that homolytic cleavage of an Ir–H bond is not a major photoprocess for (**1**). Hence, i.r. bands produced on photolysis in other matrices, *e.g.* the band at 2 002.0 cm^{-1} in argon and nitrogen matrices, are probably not due to radical species.

In an attempt to confirm the structure and geometry of the species thought to be $[Ir(\sigma\text{-}C_5H_5)(CO)_4]$, complex (**1**) was photolysed in ^{13}CO–^{12}CO (60:40 and 40:60%) mixed matrices. In this way it was hoped that all of the isotopically different complexes of $[Ir(\sigma\text{-}C_5H_5)(CO)_4]$ could be produced and their i.r. frequencies measured and matched with calculated values using the energy-factored force-field fitting procedure. Unfortunately, due to the presence of $[Fe(CO)_5]$* and the extensive overlap of i.r. bands it was not possible to obtain all the band positions required to construct a reliable force field.

(*f*) *Photolysis of* $[Ir(\eta^5\text{-}C_5H_5)(CO)D_2]$ (**1D**) *in Argon and Methane Matrices.*—The i.r. spectrum of complex (**1D**) isolated at high dilution in an argon matrix (Table 2) showed one strong matrix-split terminal CO-stretching band at 2 021.2 cm^{-1}. Elsewhere the spectrum showed a broad band centred at 1 561.3 cm^{-1} which may correspond to the symmetric IrD stretching mode of (**1D**) and a weaker peak at 1 584.2 cm^{-1} which may arise from the antisymmetric mode. Photolysis (filter B) produced the monocarbonyl species (**3**) (ν_{CO} at 1 954.7 cm^{-1}). Further photolysis (filter C) continued to produce (**3**) along with a very weak band at 2 002.5 cm^{-1}. Low-energy photolysis (filter D) resulted in photochemical reversal to the parent (**1D**) at the expense of both the i.r. band due to (**3**) and the other new band at 2 002.5 cm^{-1}.

It is apparent that complex (**3**) has been produced *via* photochemical reductive elimination of D_2 from (**1D**). The band at 2 002.5 cm^{-1} is in agreement with one seen at similar wavenumbers on photolysis of (**1**) in argon matrices. Possible identities of that species have been discussed earlier; the band seen here is likely to be due to a similar species, perhaps a deuterium complex or a diene product of metal to ring D transfer.

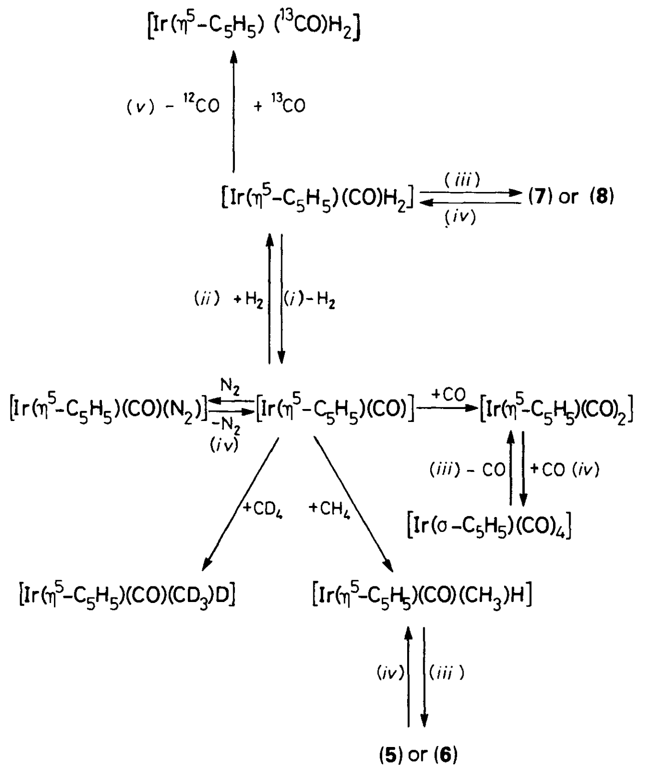
Photolysis (filter B) of complex (**1D**) in a pure methane matrix (Table 1) resulted in almost complete conversion into a new species with a strong matrix-split terminal CO-stretching band at 2 006.2 cm^{-1} along with a weak band at 2 176.0 cm^{-1}, though no 'free' CO was produced. These new bands can be assigned to $[Ir(\eta^5\text{-}C_5H_5)(CO)(CH_3)H]$ by comparison with data obtained on photolysis of (**1**) in methane matrices. In this experiment a weak band was observed at 2 176.0 cm^{-1} which probably corresponds to the IrH stretching mode of $[Ir(\eta^5\text{-}C_5H_5)(CO)(CH_3)H]$ (ν_{IrH} at 2 175 cm^{-1} in C_6F_{14}).[18]

Photolysis with filter A resulted in partial destruction of the bands for $[Ir(\eta^5\text{-}C_5H_5)(CO)(CH_3)H]$ and the remaining parent, together with the production of a new band at 1 985.6 cm^{-1} and a trace of 'free' CO. Subsequent photolysis with filter B produced a decrease in the band at 1 985.6 cm^{-1} together with an increase in the band for $[Ir(\eta^5\text{-}C_5H_5)(CO)(CH_3)H]$ and the production of a new band at 2 053.8 cm^{-1}. The two new bands at 2 053.8 and 1 985.6 cm^{-1} are produced by the same photolyses as two bands seen at the same frequencies when complex (**1**) was photolysed in methane matrices and are presumably due to the same two species. Possible identities have already been discussed, and as they are produced when both the dihydride and dideuteride complexes are photolysed in methane matrices this supports their assignments as intermediary species produced on secondary photolysis of $[Ir(\eta^5\text{-}C_5H_5)(CO)(CH_3)H]$.

(*g*) *Photolysis of* ^{13}CO*-enriched* $[Ir(\eta^5\text{-}C_5H_5)(CO)D_2]$ (**1D**) *in Methane Matrices.*—This experiment was carried out in an attempt simply to confirm that the tentatively assigned bands at 2 053.8 and 1 985.6 cm^{-1} are indeed carbonyl-stretching modes. The i.r. spectrum of ^{13}CO-enriched $[Ir(\eta^5\text{-}C_5H_5)(CO)D_2]$ isolated in a pure methane matrix showed two fairly strong terminal CO-stretching bands at 2 017.2 and 1 970.1 cm^{-1} due respectively to $[Ir(\eta^5\text{-}C_5H_5)(CO)D_2]$ and $[Ir(\eta^5\text{-}C_5H_5)(^{13}CO)D_2]$. On photolysis (filter B) bands for $[Ir(\eta^5\text{-}C_5H_5)(^{12}CO)(CH_3)H]$ and $[Ir(\eta^5\text{-}C_5H_5)(^{13}CO)(CH_3)H]$ were seen at 2 006.6 and 1 960.3 cm^{-1} respectively (Table 1). Photolysis with filter A resulted in partial destruction of both these and the remaining parent bands, together with the production of the band at 1 985.2 and another at 1 942.3 cm^{-1}, which is probably due to the ^{13}CO isotope of the species absorbing at 1 985.2 cm^{-1}. Subsequent photolysis (filter B) produced a decrease in both these bands together with an increase in the bands for both the ^{12}CO and ^{13}CO isotopomers of $[[Ir(\eta^5\text{-}C_5H_5)(CO)(CH_3)H]$ and the production of two new weak bands, one seen previously at 2 053.8 cm^{-1} on photolysis of the ^{12}CO isotopomer of $[Ir(\eta^5\text{-}C_5H_5)(CO)D_2]$ in methane matrices and a second, thought to be the ^{13}CO equivalent of

---

* Older cylinders were fabricated from steel but newer cylinders are fabricated from aluminium and do not show this problem.



Scheme. (*i*) $h\nu$, $\lambda < 320$nm; (*ii*) $h\nu$, $\lambda > 350$ nm; (*iii*) $h\nu$, $\lambda < 280$ nm; (*iv*) $h\nu$, $\lambda > 300$ nm; (*v*) heat, in the gas phase

this, at *ca.* 2 008 cm^{-1}. This experiment therefore proved that the bands at 2 053.8 and 1 985.6 cm^{-1} were due to carbonyl-stretching modes but as yet the definite identify the species giving rise to them is not clear (see Discussion).

Discussion

The proposed photochemical and thermal reaction pathways observed for complex (**1**) in frozen gas matrices, or before deposition in the gas phase, are summarised in the Scheme.

The results presented here show clearly that photolysis of (**1**) in methane matrices at 12 K leads to the formation of the hydridomethyl complex $[Ir(\eta^5-C_5H_5)(CO)(CH_3)H]$, *i.e.* methane activation has occurred.

In argon matrices the observation of $[Ir(\eta^5-C_5H_5)(CO)]$ suggests that C–H activation is likely to be occurring *via* concerted reductive elimination of H_2 followed by oxidative addition of a C–H bond. This mechanism is supported by the observation of $[Ir(\eta^5-C_5H_5)(CO)(N_2)]$ in nitrogen matrices, and further supported by the observations of $[Ir(\eta^5-C_5H_5)(CO)]$ and $[Ir(\eta^5-C_5H_5)(CO)(CH_3)H]$ in the matrix photochemistry of $[Ir(\eta^5-C_5H_5)(CO)_2]$.[19] However, a study of quantum yields for the photochemistry of $[Ir(\eta^5-C_5H_5)(CO)_2]$ in hydrocarbon solution at ambient temperatures concluded that the data were more consistent with a hapticity change ($\eta^5 \longrightarrow \eta^3$) than with the CO ejection mechanism.[32] It is possible that the time-resolved laser flash-photolysis experiments[32] will resolve the differences between gas-matrix and solution quantum yield mechanisms.

There was no evidence that complex (**1**) could lose CO on photolysis in matrices. However, such a process cannot be completely ruled out since in argon matrices the conversion of (**1**) into $[Ir(\eta^5-C_5H_5)H_2]$ and free CO might be subject to a very rapid recombination reaction, as was suggested for $[Ir(\eta^5-C_5H_5)(CO)]$ and CO.[19,21] Also it has recently been reported that $[Re(\eta^5-C_5H_5)(PPh_3)_2H_2]$ loses a phosphine ligand in preference to H_2 upon photolysis.[33] There is some evidence that on high-energy photolysis $[Ir(\eta^5-C_5H_5)(CO)(CH_3)H]$ might be subject to CO loss and that the resulting species on longer-wavelength photolysis might form a species associated with the unassigned band at 2 053.8 cm^{-1} in methane matrices. A possible series of reactions which might give rise to a new carbonyl-containing product with a terminal CO-stretching frequency greater than that for $[Ir(\eta^5-C_5H_5)(CO)(CH_3)H]$ are shown in equations (2)—(5). The methylene species also shown

$$[Ir(\eta^5-C_5H_5)(CO)(CH_3)H] \longrightarrow [Ir(\eta^5-C_5H_5)(CH_3)H] + CO \quad (2)$$

$$[Ir(\eta^5-C_5H_5)(CH_3)H] \longrightarrow [Ir(\eta^5-C_5H_5)({=}CH_2)H_2] \quad (3)$$

$$[Ir(\eta^5-C_5H_5)({=}CH_2)H_2] \longrightarrow [Ir(\eta^5-C_5H_5)(CH_2)] + H_2 \quad (4)$$

$$[Ir(\eta^5-C_5H_5)({=}CH_2)] + CO \longrightarrow [Ir(\eta^5-C_5H_5)(CO)({=}CH_2)] \quad (5)$$

as the product in equation (5) might also be expected to have been produced in experiments with $[Ir(\eta^5-C_5H_5)(CO)_2]$ in methane matrices, and indeed a very weak band was detected at 2 052.5 cm^{-1} in those experiments.[21] Production of a methylene hydride species in frozen gas matrices has previously been observed for $[Cr(\eta^5-C_5H_5)(CO)_3(CH_3)]$.[34] An alternative proposal involving metal-to-ring transfer[22] is given in equation (6).

$$\begin{tikzcd}[Ir(\eta^5-C_5H_5)(CO)(CH_3)H] \arrow[r, shift left, "\text{filter A}"] & {[Ir(\eta^4-C_5H_6)(CO)(CH_3)]} \arrow[l, shift left, "\text{filter B}"] \arrow[d, "+CH_4"', "\text{filter B}"] \\ & {[Ir(\eta^4-C_5H_6)(CO)(CH_3)_2H]} \end{tikzcd} \quad (6)$$

Photochemical reactions in CO matrices showed no evidence that complex (**1**) could undergo an associative reaction to give a detectable species such as $[Ir(\eta^3-C_5H_5)(CO)_2H_2]$, although the possible production of this in the gas phase at room temperature is discussed shortly. Reactions in CO matrices were only observed when photolysis was carried out with radiation corresponding to $\lambda < 320$ nm, and it is known from the results in argon matrices that H_2 loss occurs under these conditions. Hence, formation of $[Ir(\eta^5-C_5H_5)(CO)_2]$ in CO matrices can be explained in terms of reductive elimination of H_2 from (**1**) as the primary photoprocess.

When photolysis is carried out in matrices with radiation similar in energy to that used in solution[15] photochemical reactions of complex (**1**) and its dideuterio isotope (**1D**), *i.e.* $290 < \lambda < 350$ nm (filter B) in matrix experiments, *cf.* $\lambda > 300$ nm in solution experiments, the only primary photoprocess observed appears to be reductive elimination of H_2 or D_2. It seems reasonable to suppose that this mechanism operates in solution as well, although the H/D scrambling results [equation (1)] appear to exclude initial D_2 or H_2 loss and subsequent solvent activation as the only process involved. Moreover, solution studies[15b] showed that when $[Ir(\eta^5-C_5H_5)(CO)(CH_2CMe_3)H]$ was irradiated in neopentane in the presence of D_2 no deuterium incorporation had occurred, *i.e.* deuterium incorporation must arise from (**1D**) undergoing other photoreactions in addition to the reductive elimination of D_2.

To account for H/D scrambling in solution at 298 K it is necessary to invoke intermediates which incorporate H, D, and R ($R = CH_2CMe_3$) as ligands so that H/D exchange can precede reductive elimination. Three *a priori* possibilities are outlined in equations (7)—(9). The first possibility [equation

$$(\mathbf{1D}) \xrightarrow[-\mathrm{CO}]{h\nu} [\mathrm{Ir}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{D_2}] \xrightarrow{\mathrm{RH}} [\mathrm{Ir}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{D_2(H)R}] \xrightarrow[\mathrm{HD\ or\ D_2}]{-\mathrm{RH,RD}} \xrightarrow{+\mathrm{CO}} \quad (7)$$

$$(\mathbf{1D}) \xrightarrow{h\nu} [\mathrm{Ir}(\eta^3\text{-}\mathrm{C_5H_5})(\mathrm{CO})\mathrm{D_2}] \xrightarrow{\mathrm{RH}} [\mathrm{Ir}(\eta^3\text{-}\mathrm{C_5H_5})(\mathrm{CO})\mathrm{D_2(H)R}] \xrightarrow[\mathrm{HD\ or\ D_2}]{-\mathrm{RH,RD}} \quad (8)$$
$$\text{and } \eta^3 \rightarrow \eta^5$$

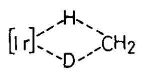
$$(\mathbf{1D}) \xrightarrow{h\nu} [\mathrm{Ir}(\eta^4\text{-}\mathrm{C_5H_5D})(\mathrm{CO})\mathrm{D}] \xrightarrow{\mathrm{RH}} [\mathrm{Ir}(\eta^4\text{-}\mathrm{C_5H_5D})(\mathrm{CO})\mathrm{D(H)R}] \xrightarrow[\mathrm{or\ HD}]{-\mathrm{RH,RD}} \quad (9)$$

(7)] involves ejection and later return of CO, with an iridium(V) intermediate related to known stable Ir(η^5-C_5H_5) complexes, *e.g.* [Ir(η^5-C_5Me_5)H_4][35] and [Ir(η^5-C_5Me_5)Me_4].[36,37] The matrix experiments show that on irradiation at the wavelengths used in solution experiments no 'free' CO is produced. This tends to exclude the possible formation of the first *a priori* intermediate [Ir(η^5-C_5H_5)D_2], going on to form [Ir(η^5-C_5H_5)D_2H(R)], and hence the first possibility is unlikely.

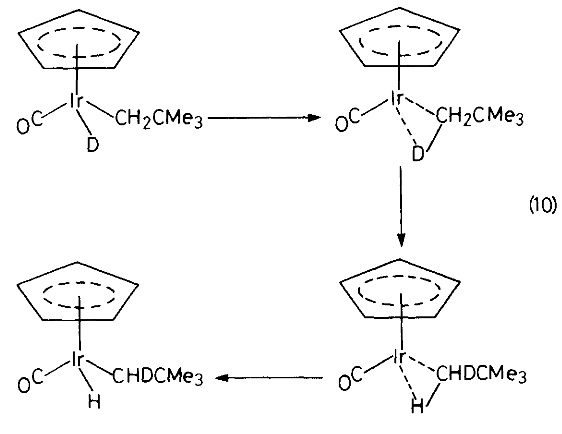
The second possibility [equation (8)] visualises a ring hapticity change, while the third possibility [equation (9)] entails a metal-to-ring deuterium transfer. Both result in the necessary involvement of co-ordinatively unsaturated intermediates. These possible transient species have not been positively identified in the gas matrices, but species produced by metal-to-ring H or D transfer have been postulated as possible matrix-isolated photoproducts. Metal-to-ring H/D transfer in conjunction with the reductive elimination of H_2/D_2 could account for all the products observed on photolysis of complex (**1D**) in neopentane [equation (1)] except for those with deuteriated neopentyl methylene groups.

In CD_4 matrices the photolysis of complex (**1**) showed no evidence for H/D scrambling, *i.e.* only [Ir(η^5-C_5H_5)(CO)(CD_3)D] was produced and no [Ir(η^5-C_5H_5)(CO)(CD_3)H] was observed. Also when (**1D**) was photolysed in methane matrices only [Ir(η^5-C_5H_5)(CO)(CH_3)H] was observed and no evidence was found for [Ir(η^5-C_5H_5)(CO)(CH_3)D]. However, the activation energy for H/D scrambling in any of the proposed intermediates is likely to be substantial and the process would not be expected at 12 K.

Formation in solution of products with deuteriated neopentyl groups is reasonable in view of the intramolecular exchange observed in [Ir(η^5-C_5Me_5)(PMe_3)D(R)] (R = CH_3 or cyclohexyl).[37] A possible 'σ complex' was invoked (see below).



Disregarding the speculative geometric details, the idea of a photochemically generated 'methane-type complex' could account for the scrambling of deuterium into the methylene protons [equation (10)]. Another point should be made regarding any scrambling mechanisms leading to Ir–CHDCMe$_3$. It cannot happen *via* reductive elimination of CH_2DCMe_3 and its subsequent reactions because the dilution effect in the solution experiments was too great. The entry of D into methylene in the quantity observed[15] (*ca.* 25%) most likely requires an intramolecular process.



(10)

The exchange of ^{12}CO and ^{13}CO in complexes (**1**) and (**1D**) in the blacked-out gas bulb must be a thermal reaction. It might have been expected[38] that thermal loss of H_2 from (**1**) would have occurred giving rise to large quantities of [Ir(η^5-C_5H_5)(^{12}CO)(^{13}CO)]. In fact, for the 5% ^{13}CO-doped argon mixture no dicarbonyls were observed, while for the pure ^{12}CO and ^{13}CO–^{12}CO mixtures only weak dicarbonyl bands were observed on depositing onto the cold window. These observations suggest that, though the thermal loss of H_2 from complex (**1**) may account for the small quantities of dicarbonyl produced, it does not provide the major pathway mechanism for ^{12}CO–^{13}CO exchange in (**1**) and (**1D**) in the gas phase at 298 K. Alternative pathways might involve CO loss or an associative ring slippage [equation (11)] as has been proposed[39] for the thermal CO-substitution reactions of [Rh(η^5-C_5Me_5)$(CO)_2$] and [Co(η^5-C_5Me_5)$(CO)_2$].

$$\begin{tikzcd}
{[\mathrm{Ir}(\eta^5\text{-}\mathrm{C_5H_5})({}^{12}\mathrm{CO})\mathrm{H_2}]} \arrow[dr, shift left, "\pm{}^{13}\mathrm{CO}"] & \\
& {[\mathrm{Ir}(\eta^3\text{-}\mathrm{C_5H_5})({}^{12}\mathrm{CO})({}^{13}\mathrm{CO})\mathrm{H_2}]} \arrow[ul, shift left, "\mathrm{Heat}"] \arrow[d, shift right, "\pm{}^{12}\mathrm{CO}"'] \\
& {[\mathrm{Ir}(\eta^5\text{-}\mathrm{C_5H_5})({}^{13}\mathrm{CO})\mathrm{H_2}]} \arrow[u, shift right, "\mathrm{Heat}"'] & (11)
\end{tikzcd}$$

Acknowledgements

We thank the S.E.R.C. and British Gas for Studentships (to P. E. B. and I. W.) respectively and for support (to A. J. R.). We thank Professor W. A. G. Graham and Dr. J. K. Hoyano for discussions, helpful suggestions, and for kindly providing samples of [Ir(η^5-C_5H_5)(CO)H_2] and [Ir(η^5-C_5H_5)(CO)D_2]. We also thank the referees for helpful comments.

References

1 C. Gianotti and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1972, 1114; M. L. H. Green, *Pure Appl. Chem.*, 1978, **50**, 27.
2 P. D. Grebenik, M. L. H. Green, and A. J. Izquierdo, *J. Chem. Soc., Chem. Commun.*, 1981, 186.
3 M. G. Bradley, D. A. Roberts, and G. L. Geoffroy, *J. Am. Chem. Soc.*, 1981, **103**, 379.
4 A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1982, **104**, 352; *ibid.*, 1983, **105**, 3929.
5 M. J. Wax, J. M. Stryker, J. M. Buchanan, C. A. Kovac, and R. G. Bergman, *J. Am. Chem. Soc.*, 1984, **106**, 1121.
6 R. A. Periana and R. G. Bergman, *Organometallics*, 1984, **3**, 508.
7 W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, 1982, **104**, 4240; *ibid.*, 1984, **106**, 1650.
8 W. D. Jones and F. J. Feher, *Organometallics*, 1983, **2**, 562.
9 M. V. Baker and L. D. Field, *J. Am. Chem. Soc.*, 1987, **109**, 2825.
10 G. L. Geoffroy and M. G. Bradley, *Inorg. Chem.*, 1977, **16**, 744; *J. Organomet. Chem.*, 1977, **134**, C27; *Inorg. Chem.*, 1978, **17**, 2410.
11 G. L. Geoffroy and R. Pierantozzi, *J. Am. Chem. Soc.*, 1976, **98**, 8054.
12 R. L. Sweany, *J. Am. Chem. Soc.*, 1981, **103**, 2410.
13 J. Chetwynd-Talbot, P. D. Grebenik, and R. N. Perutz, *Inorg. Chem.*, 1982, **21**, 3647.
14 R. N. Perutz and J. C. Sciano, *J. Chem. Soc., Chem. Commun.*, 1984, 457.

15 (*a*) P. E. Bloyce, A. J. Rest, I. Whitwell, W. A. G. Graham, and R. Holmes-Smith, *J. Chem. Soc., Chem. Commun.*, 1988, 846; (*b*) W. A. G. Graham and R. Holmes-Smith, unpublished work.

16 M. M. Rochkind, *Spectrochim. Acta, Part A*, 1971, **27**, 547.

17 W. A. G. Graham and J. K. Hoyano, unpublished work.

18 J. K. Hoyano, A. D. McMaster, and W. A. G. Graham, *J. Am. Chem. Soc.*, 1983, **105**, 7190.

19 I. Whitwell, A. J. Rest, W. A. G. Graham, J. K. Hoyano, and A. D. McMaster, *J. Chem. Soc., Chem. Commun.*, 1984, 624; *J. Chem. Soc., Dalton Trans.*, 1987, 1181.

20 (*a*) A. J. Rest and I. Whitwell, unpublished work; (*b*) D. M. Haddleton and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, 1986, 1734.

21 I. Whitwell, Ph.D. Thesis, University of Southampton, 1986.

22 W. D. Jones and J. A. Maguire, *Organometallics*, 1987, **6**, 1301.

23 R. B. Girling, P. Grebenik, and R. N. Perutz, *Inorg. Chem.*, 1986, **25**, 31.

24 P. J. Krusic, D. J. Jones, and D. C. Roe, *Organometallics*, 1986, **5**, 456.

25 R. L. Sweany, *J. Am. Chem. Soc.*, 1982, **104**, 3739.

26 R. L. Sweany and F. N. Russell, *Organometallics*, 1988, **7**, 719.

27 G. J. Kubas, C. J. Unkefer, B. I. Swanson, and E. Fukishima, *J. Am. Chem. Soc.*, 1986, **108**, 7000.

28 R. L. Sweany, *Inorg. Chem.*, 1980, **19**, 3512.

29 R. L. Sweany, *Inorg. Chem.*, 1982, **21**, 752.

30 S. P. Church, M. Poliakoff, J. A. Timney, and J. J. Turner, *J. Am. Chem. Soc.*, 1981, **103**, 7515.

31 K. A. Mahmoud, A. J. Rest, and H. G. Alt, *J. Chem. Soc., Dalton Trans.*, 1984, 187.

32 D. E. Marx and A. J. Lees, *Inorg. Chem.*, 1988, **27**, 1121.

33 W. D. Jones and J. A. Maguire, *Organometallics*, 1986, **5**, 590.

34 K. A. Mahmoud, A. J. Rest, and H. G. Alt, *J. Chem. Soc., Chem. Commun.*, 1983, 1011.

35 T. M. Filbert and R. G. Bergman, *Organometallics*, 1983, **2**, 1458.

36 K. Isobe, A. Vasquez de Miguel, A. Nutton, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1984, 929.

37 J. M. Buchanan, J. M. Stryker, and R. G. Bergman, *J. Am. Chem. Soc.*, 1986, **108**, 1537.

38 J. R. Shapley, P. C. Adair, R. J. Lawson, and C. G. Pierpont, *Inorg. Chem.*, 1982, **21**, 1701.

39 M. E. Rerek and F. Basolo, *Organometallics*, 1983, **2**, 372.

Received 18*th April* 1989; *Paper* 9/01620A