Photochemistry of Pyridine-, 3-Bromopyridine-, and Hydrogen sulphide-pentacarbonyltungsten in Frozen Gas Matrices at 10 K. Infrared Spectroscopic Evidence for *Reversible* Detachment of Bulky Ligands

By **Terence M. McHugh, Antony J. Rest,**[*] **and John R. Sodeau,** Department of Chemistry, The University, Southampton SO9 5NH

Infrared spectroscopic evidence is presented to show, for the *first* time, that photodetachment of bulky ligands with relatively high molecular weights can take place in gas matrices at 10 K. Ultraviolet photolysis of [W(CO)$_5$L] [L = pyridine (py), 3-bromopyridine, or hydrogen sulphide] isolated at high dilution in methane and argon matrices produces new i.r. absorptions associated with [W(CO)$_5$] and ' free ' L. The reaction is shown to be photochromic since subsequent irradiation with visible light regenerates [W(CO)$_5$L]. Additional evidence for photodetachment of L is obtained from experiments on [W(CO)$_5$(py)] in carbon monoxide and nitrogen matrices when u.v. photolysis produces [W(CO)$_6$] and [W(CO)$_5$(N$_2$)] respectively. The results are related to solution studies of the photochemical substitution reactions of [W(CO)$_5$L] complexes and to luminescence studies in organic glasses at 77 K. The work considerably extends the scope of the matrix-isolation technique as a means of studying the mechanisms of photochemical processes.

It has been stated[1,2] that the low-temperature matrix-isolation technique is a poor test of photochemical mechanisms involving the displacement of bulky groups because only small ligands have been shown to be detached, *e.g.* photolysis of [Mo(CO)$_5${P(C$_6$H$_{11}$)$_3$}] in an organic glass at 77 K causes loss of CO alone.[3] Similarly it has been reported[4] that the vapour-phase flash photolysis[†] of tricarbonyl(η-cyclobutadiene)iron gives free cyclobutadiene while photolysis in noble-gas matrices at 8—12 K gives dicarbonyl(η-cyclobutadiene)-iron and free CO.[5] In this paper we describe the production of [W(CO)$_5$] and L on photolysis of [W(CO)$_5$L] (L = pyridine, 3-bromopyridine, or hydrogen sulphide) complexes in argon and methane matrices at 10 K and we relate the findings to studies of luminescence spectra and lifetimes[6] and of quantum yields of substitution reactions[7,8] for a range of [W(CO)$_5$L] complexes. Preliminary results have been reported elsewhere.[9]

EXPERIMENTAL

Cryogenic temperatures (*ca.* 10 K) were obtained using a Displex CSA-202 closed-cycle helium refrigeration system (Air Products and Chemicals Inc.). The matrices were deposited onto the cooled CsI or LiF central window by a slow-spray-on arrangement in which the organometallic compounds were introduced *via* a glass sublimation sample container (heated to 52 °C for L = pyridine or 3-bromopyridine and at room temperature for L = hydrogen sulphide) and co-condensed with the matrix gas from a glass bulb through a needle valve (Hoke micro-mite). Gas mixtures of organic ligand and matrix gas (mol ratio 1 : 1 500) were made up by standard manometric techniques and matrices were prepared by the pulsed method of Rochkind.[10]

Infrared spectra were recorded on a Grubb–Parsons Spectromajor grating spectrometer modified to suppress the grating change to 1 850 cm^{-1}. The gas-phase absorptions of CO and DCl were regularly used for calibration. Resolution was 1 cm^{-1} in the region studied and the reproducibility of measurement was $\pm$0.5 cm^{-1}.

Photolysis was effected by a medium-pressure mercury arc (Philips HPK 125 W) which was water-cooled. The wavelength-selective photolysis was achieved using the following filters: $320 < \lambda < 390$ nm, Corning glass filter (catalogue no. 9863); $\lambda > 330$ nm, soda-glass disc (7 mm thickness); $230 \leqslant \lambda < 350$ nm, quartz solution cell (pathlength 10 mm) containing AnalaR Co[SO$_4$] and AnalaR Ni[SO$_4$] in water, with dilution-adjusted cut-on and cut-off points; $\lambda > 380$ nm, quartz gas cell (pathlength 25 mm) containing Cl$_2$ (1.5 atm)[‡] + soda-glass disc (7 mm thickness).

Matrix gases were B.O.C. ' Grade X ' while [W(CO)$_6$], pyridine (py), and 3-bromopyridine (3Br-py) were purchased from B.D.H. Ltd. The complexes [W(CO)$_5$(py)] and [W(CO)$_5$(3Br-py)] were prepared and purified by the literature method[11] (Found: C, 29.35; H, 1.35; N, 3.30. Calc. for C$_{10}$H$_5$NO$_5$W: C, 29.8; H, 1.25; N, 3.45%. Found: C, 25.3; H, 0.80; N, 3.10. Calc. for C$_{10}$H$_4$BrNO$_5$W: C, 24.9; H, 0.85; N, 2.90%). The complex [W(CO)$_5$(SH$_2$)] was kindly donated by Professor M. Herberhold.

RESULTS AND DISCUSSION

Photolysis of [W(CO)$_5$(3Br-py)] *and* [W(CO)$_5$(py)] *in Argon and Methane Matrices.*—The i.r. spectrum of [W(CO)$_5$(3Br-py)], isolated at high dilution in an argon matrix, in the terminal CO stretching region (1 850—2 150 cm^{-1}) is shown in Figure 1(*a*). The cluster of bands in the 1 900—1 950 cm^{-1} region comprises the two intense fundamentals ($E + A_1$, C_{4v}) which are considerably complicated by matrix splittings.[12] The i.r. spectrum of [W(CO)$_5$(py)] in a methane matrix shows much less extensive splitting and the three groups of bands corresponding to the $2A_1 + E$ modes expected for C_{4v} point-group symmetry are clearly discernible (Table 1). However, in order to demonstrate the photochromic process most clearly, an experiment involving [W(CO)$_5$(3Br-py)] in an argon matrix was chosen. An i.r. solution spectrum of [W(CO)$_5$(3Br-py)] showed no [W(CO)$_6$] absorption so that the [W(CO)$_6$] found in this (Figure 1) and other matrix experiments appears to have been generated by thermal decomposition since the

---

[†] Vapour-phase flash photolysis is often accompanied by considerable thermolysis.[2]

[‡] Throughout this paper: 1 atm = 101 325 Pa.

amount present was dependent on the spray-on temperature used and the particular complex. However, the presence of the $[W(CO)_6]$ impurity served as a useful marker to ensure that the cryostat was reproducibly placed in the spectrometer beam.

After photolysis for 3 h with a filtered medium-pressure mercury arc ($320 < \lambda < 390$ nm), the bands of $[W(CO)_5(3Br\text{-}py)]$ clearly decreased in intensity [Figure 1(*b*)] with concomitant production of three new absorptions at 2 097.3vvw, 1 962.8s, and 1 930.7m cm^{-1}. The same new absorptions were produced from $[W(CO)_5(py)]$ although the lower-wavenumber band was masked to a greater extent by parent absorptions, a problem difficult to overcome in view of the lower photolysis efficiency of $[W(CO)_5(py)]$. The upper band at 2 097.3 cm^{-1} was not detected at the relatively low concentration of $[W(CO)_5]$ generated. In neither case were any new absorptions observed at 2 138 cm^{-1} where 'free' CO absorbs, as would be expected if photoejection of a CO ligand had taken place. The sharp doublet at 1 990 cm^{-1}, which is due to $[W(CO)_6]$, remained unaffected by the photolysis (Figure 1).

TABLE 1

Infrared band positions (cm^{-1}) for $[W(CO)_5L]$ complexes in the terminal CO stretching region for argon and methane matrices at 10 K

$[W(CO)_5(py)]$				$[W(CO)_5(3Br\text{-}py)]$				$[W(CO)_5(SH_2)]$			
	CH_4		Ar		CH_4		Ar		CH_4		Ar
A_1	2 074.7	A_1	2 076.8	A_1	2 075.1	A_1	2 078.1	A_1	2 082.5	A_1	2 087.0
E	1 938.7	E + A_1	1 947.2	E + A_1	1 945.2	E + A_1	1 949.8	E	1 953.4	E	1 958.8
	1 935.0		1 939.9		1 935.8		1 943.8		1 947.6		1 953.5
	1 926.1		1 933.9		1 930.5		1 940.1				
A_1	1 920.6		1 926.9		1 924.5		1 937.0	A_1	1 938.9	A_1	1 944.5
	1 914.5				1 919.3		1 929.6		1 931.7		1 941.4

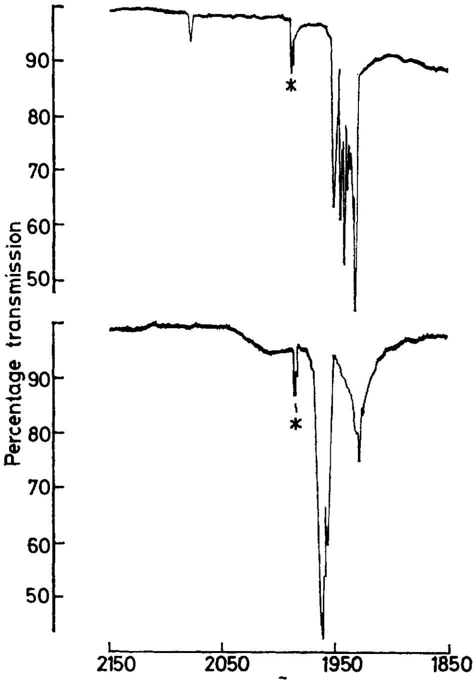


FIGURE 1 Infrared spectra from an experiment with $[W(CO)_5(3Br\text{-}py)]$ isolated at high dilution in an argon matrix at 10 K: (*a*) after deposition and (*b*) after photolysis with $320 < \lambda < 390$ nm for 3 h. The doublet marked with an asterisk is due to $[W(CO)_6]$

In a separate experiment with approximately twice as much $[W(CO)_5(3Br\text{-}py)]$ on the window, the regions where potential free ligands might absorb were carefully monitored. After photolysis ($320 < \lambda < 390$ nm), for 30 min, weak new absorptions were observed at 1 006.6 and 700.2 cm^{-1} but no absorption at 2 138 cm^{-1} (free CO) was detected under any signal-expansion conditions (up to ×5). On re-running the spectrum, after leaving the sample exposed to the radiation from the Nernst glowbar of the i.r. spectrometer overnight (17 h), the bands at 1 006.6 and 700.2 cm^{-1} had decreased considerably in intensity. Reverse photolysis caused by the visible component of radiation from Nernst glowbars is a common hazard in this type of work.[13] Similarly, on examining the free-ligand regions for $[W(CO)_5(py)]$ a single weak new band was observed at 702.0 cm^{-1} on photolysis ($320 < \lambda < 390$ nm) of a matrix containing a large amount of sample. The ejection of the bulky ligand rather than CO was confirmed by separate matrix-isolation experiments on pyridine and 3-bromopyridine in argon matrices (Table 2). Absorptions due to co-ordinated py and 3Br-py were very weak and could thus not be conveniently used to monitor photolyses.

TABLE 2

Band positions (cm^{-1}) of the most intense i.r. absorptions of pyridine and 3-bromopyridine as pure liquids and isolated in argon matrices (mol ratio 1 : 1 500) at 10 K

	Pure liquid *	Argon matrix
py	703	702.0
3Br-py	1 000 700	1 006.6 700.2

* Data from L. Corrsin, B. J. Fox, and R. C. Lord, *J. Chem. Phys.*, 1953, **21**, 1170.

The photochromic nature of matrices containing $[W(CO)_5(py)]$ and $[W(CO)_5(3Br\text{-}py)]$ was more conveniently demonstrated by effecting forward photolysis with $\lambda > 330$ nm for 2.5 min and subsequently irradiating with $\lambda > 380$ nm for 15 min (Figure 2), whereupon the broad product band at 1 962.8 cm^{-1} decreased in intensity with corresponding increases in the intensities of the parent bands. The observation of a common species with terminal carbonyl-stretching bands at 1 962.8 and 1 930.7 cm^{-1} on photolysis of two distinct $[W(CO)_5L]$ complexes in argon suggests that the ligand L is ejected [equation (1)]. Comparison of the bands of the product with the bands of $[W(CO)_5]$ [2 097.3vvw, 1 963.0 (sharp), and 1 932.1br cm^{-1}] formed on photolysis of $[W(CO)_6]$ in argon [14] confirmed the identity of the metal fragment in these experiments as $[W(CO)_5]$. The broadness of the product band at 1 962.8 cm^{-1} and the disparity between the position of the lower-wavenumber band of the product fragment and $[W(CO)_5]$ generated from $[W(CO)_6]$ can be rationalised in terms of the $[W(CO)_5]$ fragment

$$[W(CO)_5L] \underset{h\nu'}{\overset{h\nu,\ \text{Argon, 10 K}}{\rightleftharpoons}} [W(CO)_5] + L \qquad (1)$$

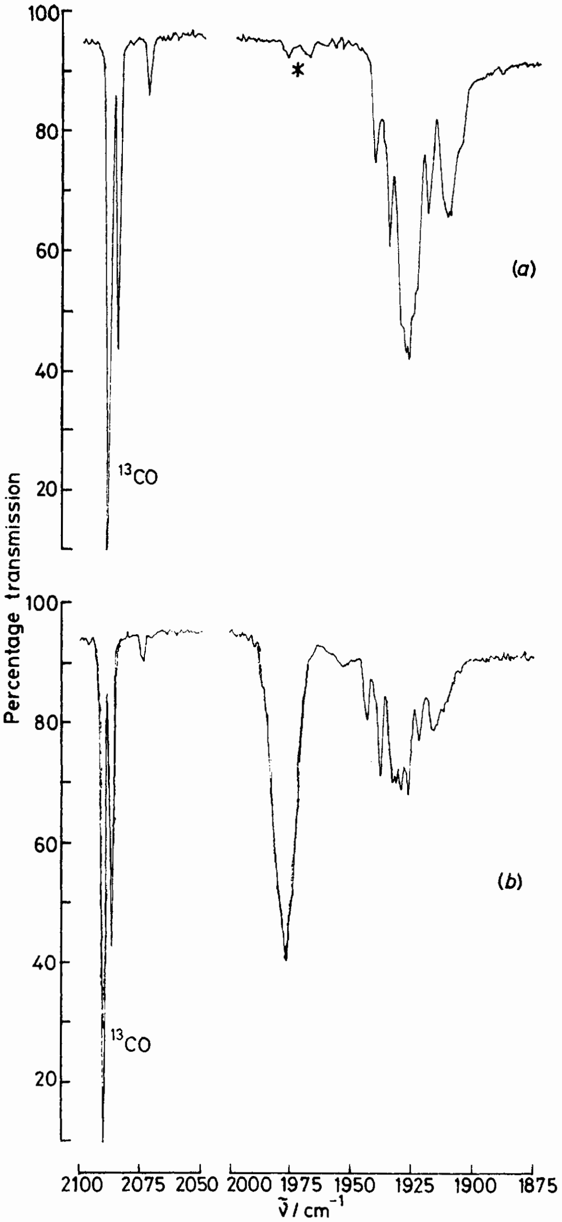


FIGURE 3 Infrared spectra from an experiment with $[W(CO)_5(py)]$ isolated in a CO matrix at 10 K: (*a*) after deposition and (*b*) after photolysis with $320 < \lambda < 390$ nm for 20 min plus annealing. Doublet as in Figure 1

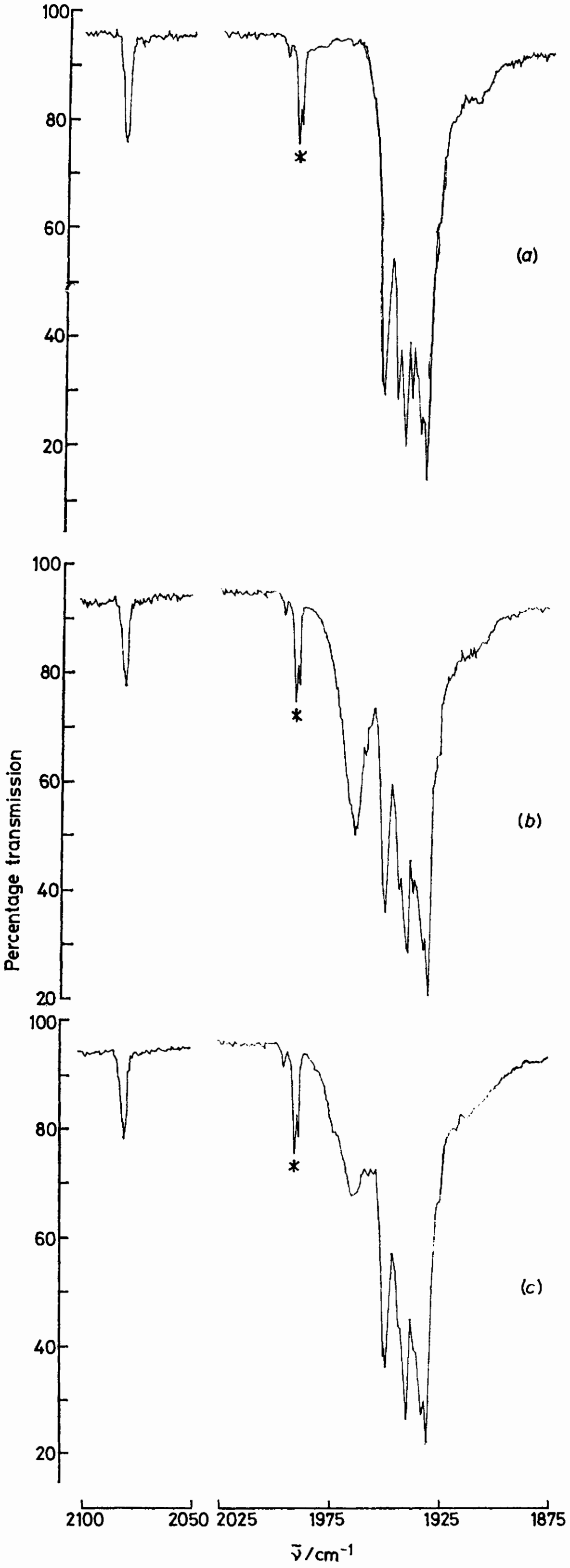


FIGURE 2 Infrared spectra from a separate experiment with $[W(CO)_5(3Br\text{-}py)]$ isolated in an argon matrix at 10 K: (*a*) after deposition, (*b*) after photolysis with $\lambda > 330$ nm for 2.5 min, and (*c*) after further photolysis with $\lambda > 380$ nm for 15 min. Doublet as in Figure 1

interacting very weakly with the ejected ligand (pyridine, 3-bromopyridine, or H_2S) which will also cause distortion of the matrix cage, *i.e.* $[W(CO)_5] \cdots py$ as for $[Cr(CO)_5] \cdots CO$.[15]

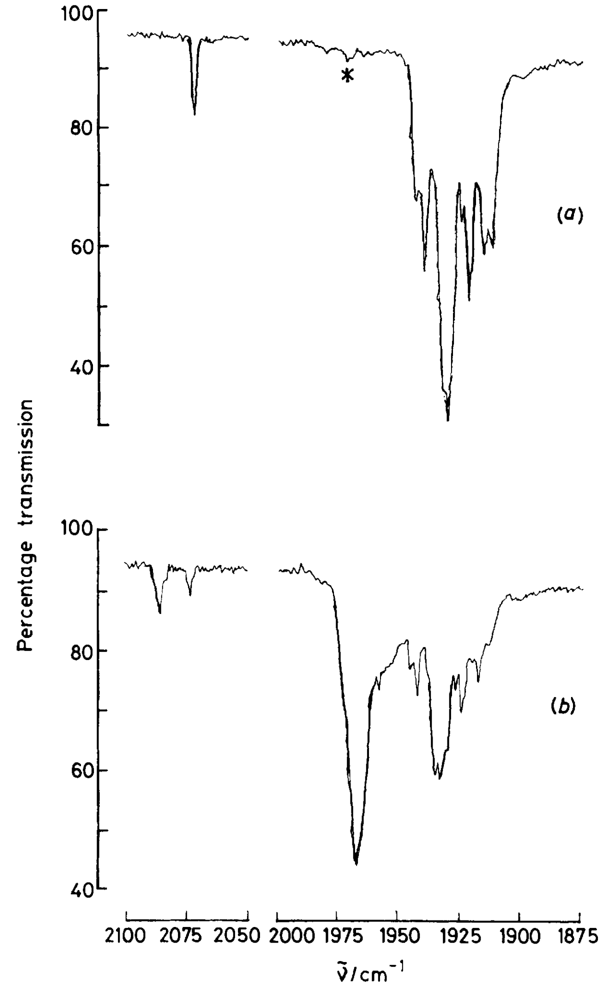


FIGURE 4 Infrared spectra from an experiment with $[W(CO)_5(py)]$ isolated in an N_2 matrix at 10 K: (*a*) after deposition and (*b*) after photolysis with $320 < \lambda < 390$ nm for 45 min. Doublet as in Figure 1

Photolysis of $[W(CO)_5(py)]$ *in Carbon Monoxide and Nitrogen Matrices.*—(*a*) CO *Matrix.* The i.r. spectrum of $[W(CO)_5(py)]$ isolated at high dilution in a pure CO matrix at 10 K is shown in Figure 3(*a*). Three groups of bands are discernible in accordance with C_{4v} symmetry, with the small doublet (marked with an asterisk) arising from a trace amount of $[W(CO)_6]$.

After photolysis with $320 < \lambda < 390$ nm radiation for 20 min the parent bands decreased in intensity with the production of only one new broad intense band at 1 979.7 cm^{-1} [Figure 3(*b*)]. Annealing the matrix sharpened this band to some extent. Its identity was confirmed as the T_{1u} carbonyl-stretching mode of $[W(CO)_6]$ by taking an average of the position of the small doublet attributable to $[W(CO)_6]$ (1 979.6 cm^{-1}). A matrix shift of the bands of $[W(CO)_5]$ can be rejected on the grounds that only one new band is observed and that the typical shift of 2 cm^{-1} for parent absorptions, on changing from methane to carbon monoxide matrices, cannot account for the disparity between the position of the *E* mode of $[W(CO)_5]$ (1 957.2 cm^{-1} in methane) and the new absorption at 1 979.7 cm^{-1}. The broadness of the absorption at 1 979.7 cm^{-1} can be rationalised in terms of a residual interaction with the photoejected pyridine ligand.

(*b*) N_2 *Matrix.* The i.r. spectrum of $[W(CO)_5(py)]$ isolated at high dilution in a pure N_2 matrix at 10 K is shown in Figure 4(*a*).

After photolysis with $320 < \lambda < 390$ nm radiation for 45 min four new bands were observed with a decrease in intensity of all the parent bands [Figure 4(*b*)]. These new absorptions can be attributed to $[W(CO)_5(N_2)]$. The broad weak band at 2 229.2 cm^{-1} is typical of the fundamental stretching vibration of co-ordinated nitrogen,[13] whereas the other three bands at 2 089.8w, 1 970.8s, and 1 962.3 m (sh) cm^{-1} can be attributed to the

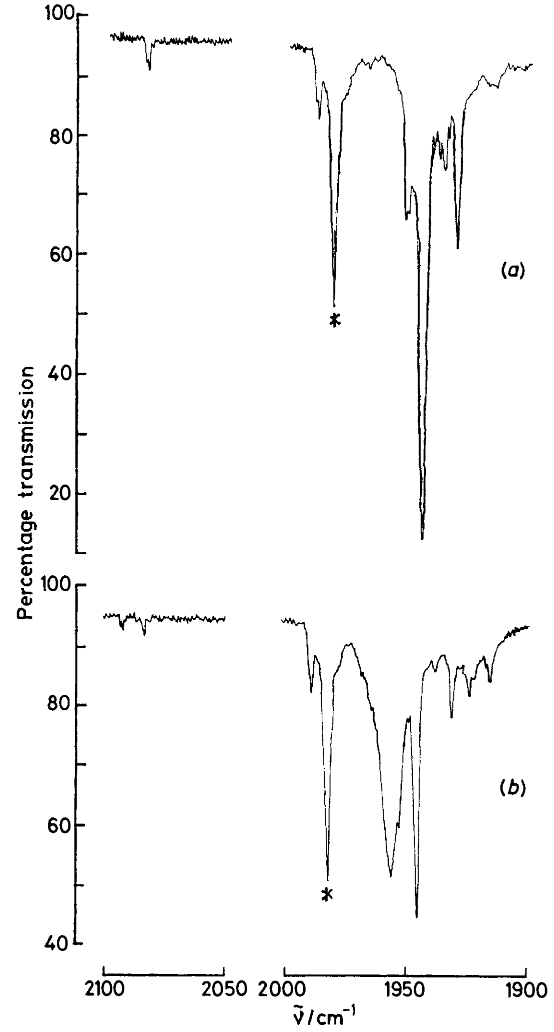


FIGURE 5 Infrared spectra from an experiment with $[W(CO)_5(SH_2)]$ isolated in a CH_4 matrix at 10 K: (*a*) after deposition and (*b*) after photolysis with $\lambda > 330$ nm for 11 min. Doublet as in Figure 1

A_1, E, and lower A_1 carbonyl-stretching modes of a C_{4v} point-group species respectively. This assignment was confirmed by a separate experiment in nitrogen where $[W(CO)_6]$ was irradiated with $230 \leqslant \lambda < 350$ nm. Four new bands were again produced at 2 228.7w,br, 2.091.0w, 1 971.4s, and 1 962.6m cm^{-1}, confirming that the same species was produced from $[W(CO)_5(py)]$ and $[W(CO)_6]$ and that the likely identity of the product was $[W(CO)_5(N_2)]$ with C_{4v} molecular symmetry.

Summarising, both CO and N_2 matrix experiments support the premise that loss of pyridine from $[W(CO)_5(py)]$ is the primary photoprocess on u.v. irradiation and that this step is followed by reaction of $[W(CO)_5]$ with the matrix to produce $[W(CO)_6]$ and $[W(CO)_5(N_2)]$ respectively.

Photolysis of $[W(CO)_5(SH_2)]$ *in Argon and Methane Matrices.*—The i.r. spectrum of $[W(CO)_5(SH_2)]$, isolated at high dilution in a CH_4 matrix, in the terminal CO stretching region, is shown in Figure 5(*a*). Three groups of bands are discernible in accordance with C_{4v} symmetry ($2A_1 + E$), Table 1, with an additional doublet at 1 980 cm^{-1} attributable to $[W(CO)_6]$. The complex $[W(CO)_5(SH_2)]$ is fairly thermally * unstable and even more so *in vacuo*.[16] Consequently more $[W(CO)_6]$ was unavoidably generated by the matrix spray-on process (*ca.* 50% of the intensity of the strongest parent absorption from optical-density plots). Although inconvenient, its presence does not invalidate the results since the photolysis conditions employed were such that $[W(CO)_6]$ was unaffected, *i.e.* its intensity was constant throughout.

After photolysis with $\lambda > 330$ nm for 11 min four new bands were observed at 2 091.8vw, 1 957.3s,br, 1 923.8m,br, and 1 914.7m cm^{-1} with no absorption corresponding to free CO. A separate experiment in methane, where $[W(CO)_5]$ was generated by u.v. photolysis of $[W(CO)_6]$, produced new absorptions at 2 091.8vw, 1 957.2s, and 1 924.3m,br cm^{-1}, confirming that $[W(CO)_5]$ was produced on u.v. photolysis of $[W(CO)_5(SH_2)]$.

The absorption at 1 914.7 cm^{-1} is difficult to assign conclusively but belongs to a different species from that producing the other new bands in that its relative rate of growth and disappearance on forward and reverse photolysis differed from those bands associated with $[W(CO)_5]$. Using $[W(CO)_5(CS)]$ and $[W(CO)_4(CS)]$ as model C_{4v} compounds,[17] approximate force-constant calculations indicated that the E mode of $[W(CO)_4(SH_2)]$ with C_{4v} symmetry could be expected in the 1 910—1 930 cm^{-1} region. We therefore tentatively assign the band at 1 914.7 cm^{-1} as the E mode of $[W(CO)_4(SH_2)]$, with the upper A_1 mode being too weak to detect. This is in accordance with the relatively high intensity of E modes in C_{4v} $[M(CO)_4(CS)]$ complexes (M = Cr, Mo, or W).[17]

Similar results were obtained for $[W(CO)_5(SH_2)]$ isolated in argon matrices (see Table 1 for the position of the parent CO stretching bands). Thus it appears that on u.v. photolysis of $[W(CO)_5(SH_2)]$ the major process is photodetachment of H_2S, with detachment of CO in preference to H_2S occurring only to a very small extent. The reaction is photochromic since subsequent irradiation with visible light, $\lambda > 380$ nm, produces a decrease in intensity of all the product bands with a simultaneous increase in those of the parent. Monitoring the photochromic process in the region where free H_2S absorbed was unsuccessful since large amounts of H_2S were present as a decomposition product associated with the spray-on process. The reaction appears to be only partially reversible, which can be rationalised in terms of the proximity of the ejected H_2S ligand to the remaining $[W(CO)_5]$ fragment. As u.v. photolysis proceeds some of the photodetached H_2S diffuses away from the $[W(CO)_5]$ fragment to a position where it is no longer able to recombine on electronic excitation. A similar effect has been observed for photodetached CO.[18]

Mechanism.—Photochemical studies of the substitution reactions of $[W(CO)_5L]$ (L = N donor) in solution at room temperature have shown that the quantum yields (Φ) of reactions (2) and (3) are sensitive to wavelength but

$$[W(CO)_5L] \xrightarrow{h\nu} [W(CO)_4L] + CO \qquad (2)$$

$$[W(CO)_5L] \xrightarrow{h\nu} [W(CO)_5] + L \qquad (3)$$

in all cases loss of ligand, L, is much more efficient than that of CO [7] [Φ_L 0.63 at 436, 0.50 at 366, and 0.34 at 254 nm. Φ_{CO} 0.002 at 436, 0.013 at 366, and 0.04 at 254 nm for L = py in iso-octane–pent-1-ene (2 : 1 v/v)].

The reaction is also a function of whether the lowest-energy absorption is ligand field or metal-to-ligand charge transfer: the charge-transfer state is virtually unreactive while the ligand-field state has a high quantum efficiency for L substitution when it is the lowest-energy excited state.[6c] Recent work on photochemical ligand substitution in a series of $[W(CO)_5L]$ complexes (L = N or P donor) has shown that nitrogen-donor complexes undergo unique ligand substitution while phosphorus-donor complexes undergo both efficient carbon monoxide and unique-ligand substitution.[8] This is rationalised in terms of the ability of the ligand L to induce charge on the metal centre and can conveniently be expressed in terms of Graham σ and π parameters.[19] The ligand H_2S is intermediate in its donor/acceptor behaviour between NH_3 and PH_3 and thus can be expected to show a small amount of the character associated with phosphorus-donor complexes, *i.e.* loss of CO as well as loss of L. Experimentally this is found to occur to a very small extent as inferred from the low intensity of the absorption at 1 914.7 cm^{-1} due to $[W(CO)_4(SH_2)]$.

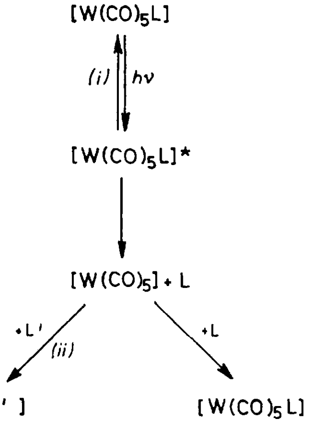
Conclusions.—The photoreactions of $[W(CO)_5(py)]$, $[W(CO)_5(3Br\text{-}py)]$, and $[W(CO)_5(SH_2)]$ show that the ejection of L can take place and moreover this process is reversible. Alternatively the intermediate $[W(CO)_5]$ may react with another ligand L′ as shown in the Scheme. This is the *first time* that ejection of relatively bulky ligands has been demonstrated in matrix-isolation experiments.

This work considerably extends and enhances the scope

---

* Infrared solution spectra also indicated the presence of $[W(CO)_6]$ as an impurity.

of the matrix-isolation technique as a means of studying the mechanisms and primary processes of photochemical reactions and also goes some way towards answering the criticism,[1,2] based on work in organic glasses, which was stated in the opening sentence of the paper. Recent work by Burdett *et al.*[20] on $[M(CO)_5]$ (M = Cr, Mo, or W), generated from $[M(CO)_6]$ in mixed matrices, suggests that the cage effect may be circumvented by an excited-state rearrangement of $[M(CO)_5]$ to leave it in an orientation unfavourable for spontaneous recombination with photo-ejected CO. Similarly, the same mechanism can be applied to $[W(CO)_5]$ generated from $[W(CO)_5L]$ although it is likely that the process operates in organic glasses as well as frozen-gas matrices. The failure [1,3] to observe ejection of bulky ligands in experiments with glasses at 77 K is probably a thermal effect, *i.e.* at 77 K the fragments have more than sufficient thermal energy to undergo a back reaction spontaneously.



SCHEME (*i*) Relaxation process; (*ii*) L′ = CO or N_2

Photodetachment of pyridine also occurs in matrix-isolated $[Cr(CO)_5(py)]$ and $[Mo(CO)_5(py)]$ [21] while PCl_3 has been photochemically generated from matrix-isolated $[M(CO)_5(PCl_3)]$ (M = Cr or W) [22] indicating that the process is not limited to bulky ligands based on pyridine alone.

While the matrix-isolation technique has been able to provide evidence for $[W(CO)_5]$ as an intermediate in the photosubstitution reaction to produce $[W(CO)_5L']$ (Scheme), there still remain questions about (*i*) the nature of $[W(CO)_5L]^*$, *i.e.* the excited state, and (*ii*) whether there are any other energy transfer processes, *e.g.* non-radiative decay processes (relaxation processes) or radiative processes (emission), in addition to the ejection of L. Complexes of the type $[W(CO)_5L]$ are one of the few classes of organometallic compounds which have been observed to luminesce in organic glasses at 77 K.[6] It was hoped to see luminescence from $[W(CO)_5(py)]$ and $[W(CO)_5(3Br\text{-}py)]$ in frozen gas matrices at 10—20 K but so far attempts to record the emission have been unsuccessful.[23,*]

We thank Professor M. Herberhold for the gift of $[W(CO)_5(SH_2)]$, and the S.R.C. for support (to A. J. R.) and for Research Studentships (to T. M. M. and J. R. S.).

[8/650 *Received*, 10*th April*, 1978]

---

[*] *Note added in proof.* Vastly improved instrumentation has now enabled emission spectra to be obtained for $[W(CO)_5(py)]$, $[W(CO)_5(3Br\text{-}py)]$, and $[Mo(CO)_5(py)]$; details will be presented elsewhere.[24]

REFERENCES

[1] J. D. Black, M. J. Boylan, P. S. Braterman, and W. J. Wallace, *J. Organometallic Chem.*, 1973, **63**, C21.

[2] J. P. Simons, ' Photochemistry and Spectroscopy,' Wiley, London, 1971.

[3] J. D. Black and P. S. Braterman, *J. Organometallic Chem.*, 1973, **63**, C19.

[4] W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Comm.*, 1967, 497.

[5] O. L. Chapman, J. Pacansky, and P. W. Wojtowski, *J.C.S. Chem. Comm.*, 1973, 681; A. J. Rest, J. R. Sodeau, and D. J. Taylor, *J.C.S. Dalton*, 1978, 651.

[6] (*a*) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 4336; (*b*) *Inorg. Chem.*, 1972, **11**, 3122; (*c*) M. Wrighton, H. B. Abrahamson, and D. L. Morse, *J. Amer. Chem. Soc.*, 1976, **98**, 4105.

[7] M. Wrighton, G. S. Hammond, and H. B. Gray, *Mol. Photochem.*, 1973, **5**, 179; M. Wrighton, *Inorg. Chem.*, 1974, **13**, 905.

[8] R. M. Dahlgren and J. I. Zink, *Inorg. Chem.*, 1977, **16**, 3154.

[9] A. J. Rest and J. R. Sodeau, *J.C.S. Chem. Comm.*, 1975, 696.

[10] M. M. Rochkind, *Science*, 1968, **160**, 196; see also R. N. Perutz and J. J. Turner, *J.C.S. Faraday II*, 1973, **69**, 452.

[11] R. J. Angelici and M. D. Malone, *Inorg. Chem.*, 1967, **6**, 1731.

[12] A. J. Downs and S. C. Peake in ' Molecular Spectroscopy,' *Specialist Periodical Report*, The Chemical Society, London, 1973, vol. 1.1, p. 523; H. E. Hallam (ed.), ' Vibrational Spectroscopy of Trapped Species,' Wiley, London, 1973.

[13] See, for example, O. Crichton and A. J. Rest, *J.C.S. Dalton*, 1977, 536.

[14] M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 2939.

[15] J. K. Burdett, M. A. Graham, R. N. Perutz, M. Poliakoff, A. J. Rest, J. J. Turner, and R. F. Turner, *J. Amer. Chem. Soc.*, 1975, **97**, 4805.

[16] M. Herberhold and G. Süss, *Angew. Chem. Internat. Edn.*, 1976, **15**, 366.

[17] M. Poliakoff, *Inorg. Chem.*, 1976, **15**, 2022.

[18] M. Poliakoff, *Inorg. Chem.*, 1976, **15**, 2892.

[19] W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 315.

[20] J. K. Burdett, J. M. Grzybowski, R. N. Perutz, M. Poliakoff, J. J. Turner, and R. F. Turner, *Inorg. Chem.*, 1978, **17**, 147.

[21] T. M. McHugh and A. J. Rest, unpublished work.

[22] G. Boxhoorn and A. Oskam, *Inorg. Chim. Acta*, 1978, **29**, L207,243.

[23] J. R. Sodeau, Ph.D. Thesis, University of Southampton, 1977.

[24] T. M. McHugh, R. Narayanaswamy, A. J. Rest, and K. Salisbury, *J.C.S. Chem. Comm.*, to be submitted.