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Matrix-isolation studies of intermediates in the photochemical reaction of $W(CO)_6$ with CCl_4

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Abstract

The photolysis of $W(CO)_6$ molecules isolated in CCl_4-doped Ar matrices at ca. 20 K or in solid CCl_4 matrices at ca. 70 K has been monitored by recording the IR and UV–Vis absorption spectra of the deposits. The results confirm the formation of the unsaturated carbonyl fragment $W(CO)_5$, which weakly binds a molecule of either argon or CCl_4; the 1:1 stoicheiometry of the CCl_4 complex is consistent with the effects of varying the concentration of the CCl_4 in the Ar matrix. The complex $CCl_4 \cdots W(CO)_5$ is characterised by a near-UV absorption centred at 380 nm and by IR bands due to the ν(C–O) fundamentals near 2088, 1973, and 1943 cm^{-1}. Interconversion between the three species $W(CO)_6$, $Ar \cdots W(CO)_5$, and $CCl_4 \cdots W(CO)_5$ can be achieved by irradiation of an Ar matrix with light of the appropriate wavelength. Ligation of the CCl_4 to the $W(CO)_5$ fragment is assessed on the basis of UV–Vis and IR spectra considered to arise from the complex $CCl_4 \cdots W(CO)_5$.

Introduction

Elucidation of the processes occurring in photochemical reactions is one of the main applications of the matrix-isolation technique [1]. Much attention has been focused on this approach to reactions of transition-metal carbonyls because of the photocatalytic properties of these compounds in various chemical processes [2]. The primary photochemical step is the loss of a molecule of carbon monoxide with the formation of a co-ordinatively unsaturated species, e.g. $Cr(CO)_5$ [3]. This product is typically very short-lived in solution at ambient temperatures; in perfluoromethylcyclohexane solutions flushed with CO at room temperature, for example, $Cr(CO)_5$ has a half-life of only 13 μs [4]. By contrast, trapping in a solid noble-gas matrix at low temperatures gives access to $Cr(CO)_5$ only weakly perturbed and with an unlimited lifetime; under such conditions it may be characterised by IR and UV–Vis spectroscopy [5].

The unusual reactivity of co-ordinatively unsaturated metal carbonyls, whether in solution or in a low-temperature matrix, is illustrated by the formation of loosely bound adducts of the type $X \cdots M(CO)_5$, where M is Cr, Mo, or W and X is a

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solvent or matrix molecule [4–6]. The nature of X influences the energies of the IR and UV–Vis absorption bands associated with the $M(CO)_5$ fragment. For example, studies involving a variety of matrices (Ne, SF_6, Ar, Kr, Xe, CH_4, CO, and N_2) have shown that the lowest-energy ligand-field transition of $Cr(CO)_5$ occurs at relatively high energy for $N_2 \cdots Cr(CO)_5$ ($\lambda = 364$ nm) and low energy for $Ne \cdots Cr(CO)_5$ ($\lambda = 624$ nm) [5]. With the switch from $Cr(CO)_5$ to $W(CO)_5$, this transition shifts to higher energies, cf. $Ar \cdots Cr(CO)_5$ $\lambda = 533$ nm and $Ar \cdots W(CO)_5$ $\lambda = 437$ nm [5]. The findings can be explained overall in terms of formation of a unit $X \cdots M(CO)_5$ in which X has entered the vacant co-ordination site of the square-pyramidal $M(CO)_5$ fragment to bind weakly to the metal centre [5]. With this knowledge it has been possible to investigate matrices containing metal carbonyls as well as reagents like O_2 [7], CO_2 [8], and N_2O [8], and so follow the reactions subsequently induced by photolysis.

Photochemical reactions in solution of tungsten hexacarbonyl with halides of elements A drawn from group 4, 13, or 14, AX_n are known to produce systems which are catalytically active with respect to olefin metathesis [9]. A series of tungsten compounds afforded by the reactions has been identified, but these are mostly the stable products of decomposition of the catalytically active intermediates [10]. Amongst the halides that act as initiators of the photo-induced olefin metathesis brought about by $W(CO)_6$ is carbon tetrachloride; this may function as an electron acceptor in the charge-transfer complexes through which the reactions are believed to proceed [9,11]. It was therefore a logical extension of these earlier studies to investigate the photochemical behaviour of $W(CO)_6$ in the presence of CCl_4 in a low-temperature matrix.

Experimental

The cryogenic equipment used at Oxford has been described elsewhere [8,12]. An Air Products 'Displex' CS 202B closed-cycle helium refrigerator gave CsI window temperatures in the range 20–80 K inside a shroud maintained at a pressure below 10^{-7} Torr. Gas mixtures were prepared in a glass vacuum line by standard manometric techniques and the matrices formed by pulsed deposition [13]. The photolysis source was an Oriel 500-W medium-pressure mercury arc, the radiation from which was filtered with a 4-cm column of distilled water to reduce the potential heating effects. For experiments involving more selective irradiation a suitable Balzers interference filter ($\lambda = 313$, 369, or 425 nm, bandpass ca. 15 nm) was used. IR spectra were recorded on a Perkin–Elmer Model 580A dispersive spectrophotometer or a Mattson 'Galaxy' FT-IR instrument; UV–Vis spectra were recorded on a Perkin–Elmer–Hitachi Model 330 spectrophotometer.

The matrix gases Ar and CO were used as supplied by B.O.C. ('research' grade). Samples of $W(CO)_6$ (99% pure, supplied by Koch–Light) and CCl_4 (99.5% pure, supplied by Aldrich) were purified before use by fractional condensation *in vacuo*.

Results

Irradiation of an Ar matrix containing only $W(CO)_6$ ($Ar : W(CO)_6$ = ca. 5000 : 1) with light having λ = ca. 313 nm resulted, as reported previously [5,14], in the formation of the adduct $Ar \cdots W(CO)_5$, characterised by the growth of a visible

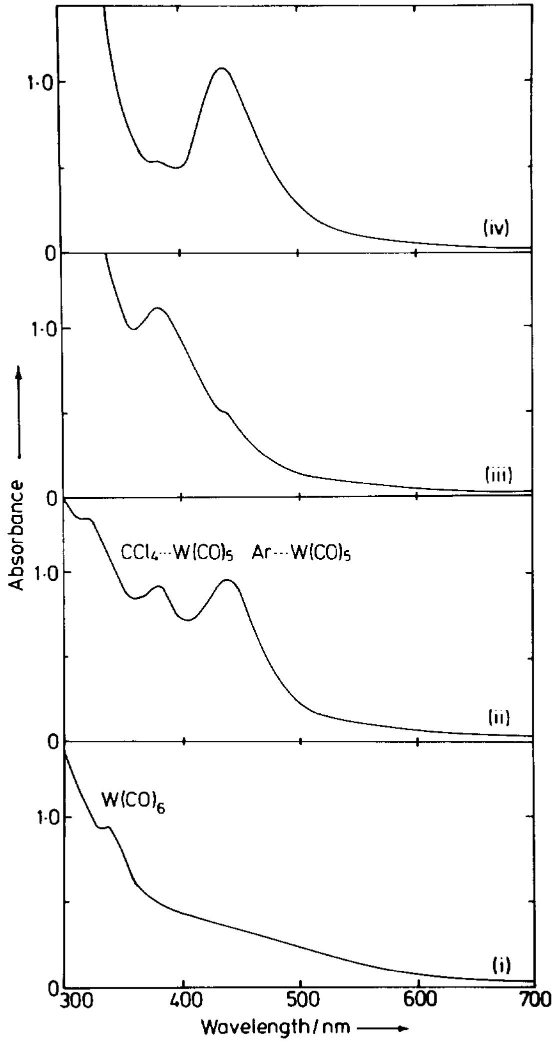


Fig. 1. UV–Vis spectrum of a CCl_4-doped Ar matrix containing $W(CO)_6$ (Ar: $W(CO)_6$: CCl_4 = ca. 2000 : 1 : 100) at 20 K: (i) after deposition; (ii) after 60-min photolysis at λ = ca. 313 nm, showing the appearance of bands due to Ar ··· $W(CO)_5$ and CCl_4 ··· $W(CO)_5$; (iii) after 30-min photolysis at λ = ca. 435 nm, showing the conversion of Ar ··· $W(CO)_5$ to CCl_4 ··· $W(CO)_5$; and (iv) after 30-min photolysis at λ = ca. 369 nm, showing the conversion of CCl_4 ··· $W(CO)_5$ to Ar ··· $W(CO)_5$.

band centred at λ = 437 nm attributable to the $b_2^2e^4a_1^0b_1^0 \rightarrow b_2^2e^3a_1^1b_1^0$ ligand-field transition. By contrast, irradiation of an Ar matrix containing both $W(CO)_6$ and CCl_4 (typically with Ar : $W(CO)_6$: CCl_4 = 2000 : 1 : 100) with light having λ = ca. 313 nm gave rise to the appearance and growth of not just one UV–Vis absorption band, but two such bands, one at 437 nm relatively more intense than the other at 380 nm (see Fig. 1). There can be little doubt in the circumstances that the more intense band is again associated with the adduct Ar ··· $W(CO)_5$ and that a new species **A** is formed in the presence of CCl_4. These same circumstances, combined with the accumulated experience gained from similar studies involving matrix-isolated metal carbonyls [7,8,15,16], suggest that **A** is an adduct of the type

Table 1

(a) Wavenumbers of C–O stretching bands in the IR spectrum of an argon matrix containing $W(CO)_6$ and CCl_4 after photolysis at λ = ca. 313 nm

IR wavenumbers (cm^{-1})[a]	Effect of photolysis at λ = 435 nm[b]	Effect of photolysis at λ = 369 nm[b]	Assignment
2142	↓	↓	CO
2137	↓	↓	
2096	↓	↑	$Ar\cdots W(CO)_5$, ν(C–O) (a_1)
2088	↑	↓	$CCl_4\cdots W(CO)_5$, ν(C–O) (a_1)
1986[c]	↑	↑	$W(CO)_6$, ν(C–O) (t_{1u})
1973	↑	↓	$CCl_4\cdots W(CO)_5$, ν(C–O) (e)
1963	↓	↑	$Ar\cdots W(CO)_5$, ν(C–O) (e)
1943	↑	↓	$CCl_4\cdots W(CO)_5$, ν(C–O) (a_1)
1932	↓	↑	$Ar\cdots W(CO)_5$, ν(C–O) (a_1)

(b) Wavelengths of absorptions in the UV–Vis spectrum of an argon matrix containing $W(CO)_6$ and CCl_4 after photolysis at λ = ca. 313 nm

Wavelengths of UV–Vis absorption maxima (nm)[d]	Effect of photolysis at λ = 435 nm[b]	Effect of photolysis at λ = 369 nm[b]	Assignment
225	–[e]	–[e]	$W(CO)_6$
239	–[e]	–[e]	$Ar\cdots W(CO)_5$
285	–[e]	–[e]	$W(CO)_6$
330	↑	↑	$W(CO)_6$
380	↑	↓	$CCl_4\cdots W(CO)_5$
437	↓	↑	$Ar\cdots W(CO)_5$

[a] Error limits ±2 cm^{-1}. [b] ↓ Band decays; ↑ band grows. [c] Band shows multiplet structure due to matrix splitting. [d] Error limits ±2 nm. [e] Not studied.

$[CCl_4]_n\cdots W(CO)_5$ (where $n = 1, 2, \ldots$). Subsequent photolysis of the matrix with radiation having λ = ca. 435 nm for 30 min caused the near-UV absorption at 380 nm, as well as the mid-UV shoulder at 330 nm due to $W(CO)_6$ [5,14], to grow at the expense of the visible band at 437 nm [Fig. 1, trace (iii)]. By contrast, subsequent irradiation of the matrix with light having λ = ca. 369 nm for 30 min caused the band at 380 nm to decay, with a concomitant growth of the shoulder at 330 and the band at 437 nm [Fig. 1, trace (iv)]. This behaviour is wholly consistent with the response to photolysis shown by $Cr(CO)_6$, $Mo(CO)_6$, or $W(CO)_6$ when isolated in a 'mixed' matrix; such experiments give rise to two adducts of the type $X\cdots M(CO)_5$ (where M = Cr, Mo, or W, and X = Ar, Xe [5], N_2 [15], or CO_2 [8]), the relative proportions of which reflect their photochemical properties and the composition of the matrix.

Figure 2 illustrates the IR spectra of photolysed Ar matrices containing $W(CO)_6$ alone [trace (ii)] and $W(CO)_6$ in the presence of CCl_4 [traces (iii)–(v)]. After photolysis of an Ar matrix containing only $W(CO)_6$ ($Ar : W(CO)_6 = 2000 : 1$) with radiation having λ = ca. 313 nm, the IR spectrum witnessed a decay of the absorptions due to $W(CO)_6$ to the accompaniment of the appearance and growth of new absorptions at 2142 and 2137 cm^{-1} (due to photo-ejected CO) and 2096, 1963, and 1932 cm^{-1} (due to the ν(C–O) modes of the complex $Ar\cdots W(CO)_5$); changes were also observed in the region near 600 cm^{-1} corresponding to W–C–O deformation modes of $W(CO)_6$ and $Ar\cdots W(CO)_5$. These results are identical in

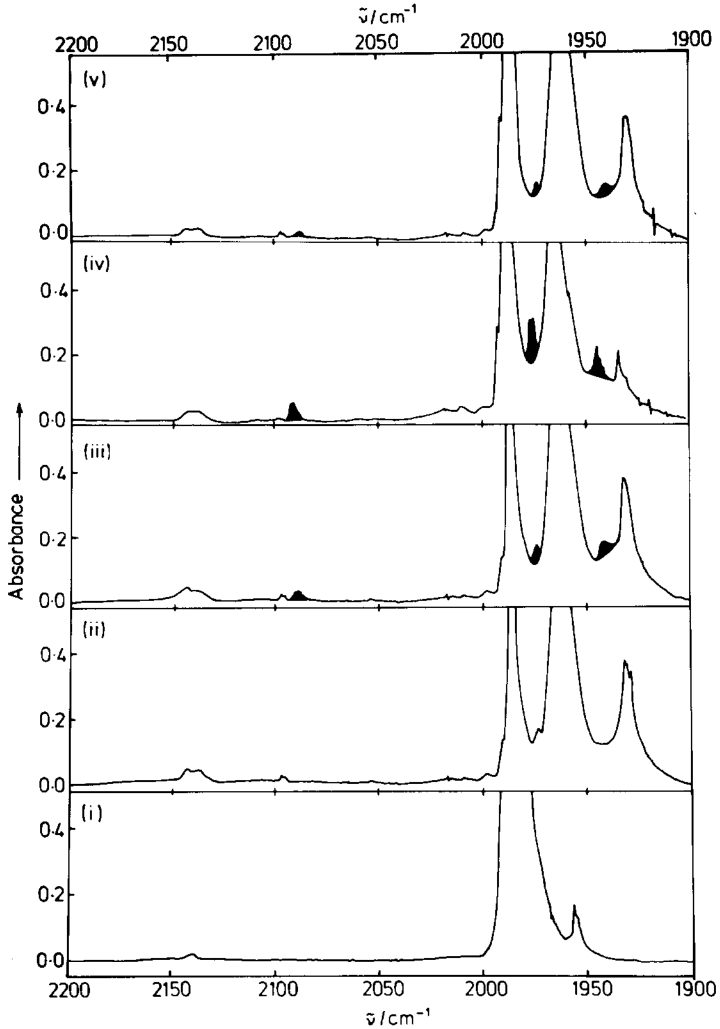


Fig. 2. C–O Stretching region of the IR spectrum displayed by an Ar matrix containing $W(CO)_6$ (Ar:$W(CO)_6$ = ca. 2000:1) at 20 K showing the effects of photolysis: (i) spectrum of the matrix after deposition; (ii) spectrum after 60-min photolysis at λ = ca. 313 nm. (iii) Spectrum of a CCl_4-doped Ar matrix containing $W(CO)_6$ (Ar:$W(CO)_6$:CCl_4 = ca. 2000:1:50) after 60-min photolysis at λ = ca. 313 nm. (iv) Spectrum of the same matrix as in (iii) after 60-min photolysis at λ = ca. 435 nm. (v) Spectrum of the same matrix as in (iii) and (iv) after 60-min photolysis at λ = ca. 369 nm.

all essential details with those described previously by Perutz and Turner [5,14]. Irradiation of an Ar matrix containing $W(CO)_6$ as well as CCl_4 in the proportions 2000:1:50 at wavelengths near 313 nm resulted in the growth of new bands at 2142 and 2137 cm^{-1} associated with free CO, accompanied by features due to ν(C–O) modes of co-ordinated CO groups at 2096, 2088, 1973, 1963, 1943, and 1932 cm^{-1} [Fig. 2(iii) and Table 1]. The introduction of CCl_4 into the matrix produced noticeably broader IR absorptions reflecting presumably the greater range of matrix sites to which the guest molecules now had access. The presence of more than one metal-containing photoproduct in the CCl_4-doped matrix was demonstrated by *further* photolysis for 1 h at wavelengths near 435 nm [Fig. 2(iv)]; this caused a reduction in the intensity of the bands at 2096, 1963, and 1932 cm^{-1} (due to Ar $\cdots$ $W(CO)_5$) and a simultaneous growth of the bands at 2088, 1973, and 1943 cm^{-1} (presumably due to **A**), as well as that at 1986 cm^{-1} (due to $W(CO)_6$). Subsequent photolysis for 1 h at wavelengths near 369 nm resulted in growth of the bands at 2096, 1986, 1963, and 1932 cm^{-1} at the expense of those at 2088, 1973, and 1943 cm^{-1} [Fig. 2(v)]. Table 1 lists the relevant IR bands, together with their suggested assignments.

The most obvious interpretation of these results is that irradiation at λ = ca. 313 nm causes $W(CO)_6$ to photodissociate in the mixed matrix with the formation of free CO and the two weakly bound adducts Ar $\cdots$ $W(CO)_5$ and CCl_4 $\cdots$ $W(CO)_5$. The CCl_4 adduct is characterised by IR bands due to ν(C–O) fundamentals at 2088, 1973, and 1943 cm^{-1}, with relative intensities paralleling those of Ar $\cdots$ $W(CO)_5$ [5,14].

Further experiments were carried out to determine the effect of varying the CCl_4 concentration of the matrix, but otherwise maintaining the same conditions as before. With a matrix containing not 2.5% but 5% CCl_4 ($Ar:W(CO)_6:CCl_4$ = 2000:1:100), the IR bands of both the precursors and photoproducts were broader still. Thus, the features at 1963 and 1973 cm^{-1} could no longer be even partially resolved and those at 1943 and 1932 cm^{-1} were correspondingly less clearly defined. In other respects, however, the course of photolysis was marked by the same changes as before. Doubling the CCl_4 concentration resulted roughly in a doubling of the yield of the CCl_4 complex relative to Ar $\cdots$ $W(CO)_5$ consistent with the assignment of the stoichiometry $W(CO)_5:CCl_4$ = 1:1 for that complex. Annealing the matrix at temperatures up to 35 K at different stages in this and other experiments caused no significant change in the pattern or relative intensities of the IR bands.

In a logical extension of these studies, experiments were also carried out with $W(CO)_6$ isolated in a neat CCl_4 matrix ($CCl_4:W(CO)_6$ = ca. 500:1, deposition temperature ca. 70 K). As the matrix concentration of CCl_4 increased, so the energy of the t_{1u} ν(C–O) fundamental of the parent $W(CO)_6$ decreased (from 1987 cm^{-1} for a pure Ar matrix to 1977 cm^{-1} for a pure CCl_4 matrix). Figure 3 illustrates the effects of photolysis on the ν(C–O) region of the IR spectrum of the CCl_4 matrix. Exposure to radiation with λ = ca. 313 nm caused bands to appear and grow at 2138, 2088, 1962, and 1930 cm^{-1}; subsequent exposure to radiation with λ = ca. 369 nm caused the intensities of all these bands to decrease, with a simultaneous growth of the features due to $W(CO)_6$. The most obvious explanation is that the band at 2138 cm^{-1} arises from free CO whereas the other three new bands arise from CCl_4 $\cdots$ $W(CO)_5$. The red shifts of 11–13 cm^{-1} experienced by the two lower-energy ν(C–O) modes of the complex when CCl_4 replaces Ar as the matrix material are in keeping with the behaviour of the parent molecule $W(CO)_6$.

As noted previously, photolysis of a matrix containing both $W(CO)_6$ and CCl_4 resulted typically in changes in the IR spectrum near 600 cm^{-1}, corresponding to W–C–O bending modes of the species $W(CO)_6$, Ar $\cdots$ $W(CO)_5$, and CCl_4 $\cdots$ $W(CO)_5$. Under none of the conditions tried so far, however, has it proved possible to detect any change in the IR absorptions associated with CCl_4. This is not surprising in view of the large excess of CCl_4 molecules perturbed only by the matrix environment or by the presence of neighbouring CCl_4 molecules and whose

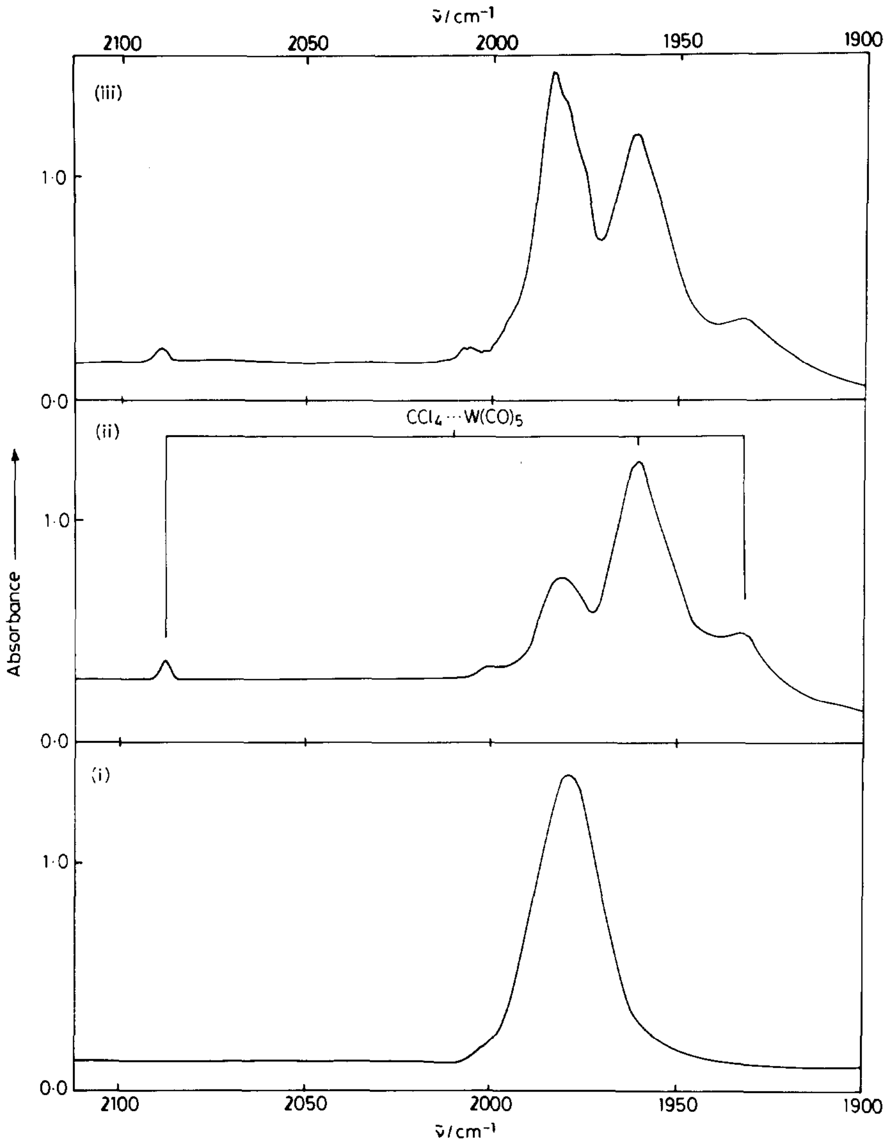


Fig. 3. C–O Stretching region of the IR spectrum displayed by a solid CCl_4 matrix containing $W(CO)_6$ ($CCl_4 : W(CO)_6$ = ca. 500:1) at 70 K: (i) after deposition; (ii) after 60-min photolysis at λ = ca. 313 nm; and (iii) after 60-min photolysis at λ = ca. 369 nm.

relatively broad absorptions tended to swamp the spectrum in the region near 770 cm^{-1} associated with the t_2 ν(C–Cl) mode. The most obvious inference is that co-ordination to $W(CO)_5$ causes only minimal perturbation of CCl_4, as measured by its vibrational properties, making it impossible to distinguish between co-ordinated and free CCl_4 molecules. On the other hand, our searches may have been defeated by the low concentration in which the complex is formed (< 1 : 5000), combined with extinction coefficients for the CCl_4 vibrations which are appreciably smaller than those for the ν(C–O) modes of the $W(CO)_5$ fragment.

Table 2

Spectroscopic data for adducts of the type $X \cdots W(CO)_5$

Adduct	Medium	IR-active ν(C–O) wavenumbers (cm^{-1})			Lowest-energy spin-allowed ligand-field transition (nm)
		High-energy a_1	e	Low-energy a_1	
$CCl_4 \cdots W(CO)_5$	Ar matrix (20 K)	2088 [a]	1973 [a]	1943 [a]	380 [a]
	CCl_4 matrix (70 K)	2088 [a]	1962 [a]	1930 [a]	–
	CO matrix (20 K)	– [b]	1957 [a]	1926 [a]	–
$Ar \cdots W(CO)_5$	Ar matrix (20 K)	2096.8 [a]	1963.0 [a]	1932.7 [a]	437 [c]
methylcyclohexane $\cdots W(CO)_5$	methylcyclohexane solution	2079 [d]	1949 [d]	1922 [d]	425 [e]
$Xe \cdots W(CO)_5$	Xe matrix	–	–	–	417 [c]
$CH_4 \cdots W(CO)_5$	CH_4 matrix	2091.8 [f]	1957.2 [f]	1926.0 [f]	413 [c]
$C_2H_4 \cdots W(CO)_5$	hexane solution	2088 [g]	1973 [g]	1953 [g]	–
$C_2H_2 \cdots W(CO)_5$	hexane solution	2095 [g]	1967 [g]	1952 [g]	–
$C_6H_6 \cdots W(CO)_5$	methylcyclohexane solution	2072 [d]	1930 [d]	1906 [d]	–
$CH_2Cl_2 \cdots W(CO)_5$	methylcyclohexane solution	2085 [d]	1946 [d]	1903 [d]	–
$Et_2O \cdots W(CO)_5$	hexane solution	2074 [g]	1931 [g]	1908 [g]	–
$MeCN \cdots W(CO)_5$	hexane solution	2085 [g]	1948 [g]	1931 [g]	–
$N_2 \cdots W(CO)_5$	CH_4 matrix	2089 [h]	ca. 1972 [h]	1961 [h]	–
pyridine $\cdots W(CO)_5$	CH_4 matrix	2074.7 [i]	ca. 1933 [i]	1917 [i]	388/404 [j]
piperidine $\cdots W(CO)_5$	Ar matrix	2075.6 [k]	1926.8/1932.8 [k]	1917.0/1924.8 [k]	388/410 [j]
$PCl_3 \cdots W(CO)_5$	Ar matrix	2098.5 [l]	1986.1 [l]	2000.0 [l]	350 [l]
$CO_2 \cdots W(CO)_5$	CH_4 matrix	–	1956 [m]	1926 [m]	346 [m]
$CF_2Cl_2 \cdots W(CO)_5$	vapour	–	1976 [n]	1958 [n]	–
$W(CO)_5$	vapour	–	1980 [o]	1942 [o]	–

[a] This work. [b] Obscured by matrix absorption. [c] Ref. 5. [d] D.R. Tyler and D.R. Petrylak, *J. Organomet. Chem.*, 212 (1981) 389. [e] A.J. Lees and A.W. Adamson, *Inorg. Chem.*, 20 (1981) 4381. [f] Ref. 14. [g] Ref. 24. [h] Ref. 15. [i] T.M. McHugh, A.J. Rest and J.R. Sodeau, *J. Chem. Soc., Dalton Trans.*, (1979) 184. [j] Isooctane solution, ref. 22. [k] G. Boxhoorn, G.C. Shoemaker, D.J. Stufkens, A. Oskam, A.J. Rest and D.J. Darensbourg, *Inorg. Chem.*, 19 (1980) 3455. [l] Ref. 23. [m] Ref. 8. [n] Ref. 29. [o] Y. Ishikawa, P.A. Hackett and D.M. Rayner, *J. Phys. Chem.*, 92 (1988) 3863.

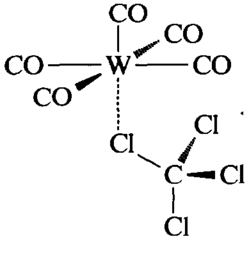
Prolonged exposure of a matrix containing $W(CO)_6$ and CCl_4 to broad-band or filtered UV or visible radiation failed to produce any clear signs of change beyond those already noted. However, matrices relatively rich in CCl_4 and $W(CO)_6$ (e.g. $Ar:W(CO)_6:CCl_4 =$ ca. 500:1:50) did not show quantitative regeneration of $W(CO)_6$ and $Ar \cdots W(CO)_5$ at 30 K on prolonged photolysis with radiation having wavelengths near 369 nm. Instead, weak bands appeared to develop at 2105, 2020, and ca. 1940 cm^{-1} after 60 minutes' photolysis. The intensity pattern and energies of these bands suggest the formation of a $W(CO)_4$ moiety; indeed, the spectrum resembles quite closely that of $[W(CO)_4Cl_2]_2$ [17], but it was not possible to verify the formation of this product. The IR spectrum of the photolysed matrix failed also to reveal any features of appreciable intensity identifiable with products like $\cdot W(CO)_5Cl$, $\cdot W(CO)_5CCl_3$, $:CCl_2$ [18], C_2Cl_4 [19], $\cdot CCl_3$ [20], C_2Cl_6 [20], $\cdot OCCl$ [21], $OCCl_2$ [19], etc. Similar experiments carried out with $W(CO)_6$ and CCl_4 supported in a solid carbon monoxide matrix at 20–30 K led to the growth of bands at 1957 and 1926 cm^{-1} attributable to the complex $CCl_4 \cdots W(CO)_5$ (the region near 2100 cm^{-1} being obscured by strong absorption due to the matrix). However, prolonged photolysis under various conditions failed to give any hint of the absorptions characteristic of $\cdot OCCl$ [21] and $OCCl_2$ [19]. Hence our matrix experiments have failed as yet to provide any clearcut evidence that co-ordination leads to photosensitisation of the CCl_4 in the way that CO_2 and N_2O are activated to photodissociation at relatively long wavelengths [8].

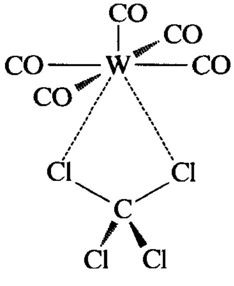
Discussion

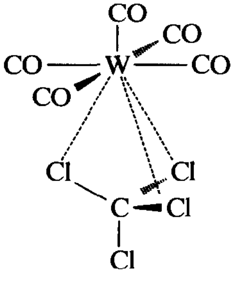
The spectroscopic properties of the species $CCl_4 \cdots W(CO)_5$ give some clues to the nature of the interaction between the CCl_4 and $W(CO)_5$ fragment (see Table 2). The position of the lowest-energy spin-allowed ligand-field transition $b_2^2e^4a_1^0b_1^0 \rightarrow b_2^2e^3a_1^1b_1^0$ of $X \cdots Cr(CO)_5$ systems is highly sensitive to the nature of X, the wavelength varying from 624 nm ($X = Ne$) [5], through 533 ($X = Ar$) [5], 489 ($X = CH_4$) [5], to 364 nm ($X = N_2$) [15]. The corresponding transition of $X \cdots W(CO)_5$ systems is less well documented but appears to follow a similar pattern, albeit over a noticeably narrower energy range. Thus, the wavelength varies from 461 nm ($X = SF_6$) [5], through 437 ($X = Ar$) [5], 417 ($X = Xe$) [5], 413 ($X = CH_4$) [5], 388/404 ($X =$ pyridine) [22], 350 ($X = PCl_3$) [23], to 346 nm ($X = CO_2$) [8]. The corresponding wavelength for $CCl_4 \cdots W(CO)_5$ is 380 nm, implying that perturbation of the $W(CO)_5$ fragment, mainly through σ-bonding one supposes, follows the order $SF_6 < Ar < CH_4 <$ pyridine $\sim CCl_4 < PCl_3 \sim CO_2$. We note too that, when X is a Lewis base like diethyl ether, there is a low-frequency shift of ν(C–O) for the co-ordinated $M(CO)_5$ molecule (M = Cr, Mo, or W) amounting to 30–40 cm^{-1} [24], whereas, when X is a weak π-acceptor like N_2, there is an increase amounting to 10–20 cm^{-1} [15]. The IR band which is most responsive to the nature of X is the low-frequency a_1 mode near 1940 cm^{-1} which approximates to ν(C–O) for the unique axial CO group. That this band undergoes a blue shift of 10 cm^{-1} with the switch from $Ar \cdots W(CO)_5$ to $CCl_4 \cdots W(CO)_5$ might be taken to suggest that CCl_4 is a marginally better π-acceptor than Ar, but the effect is within the range normally associated with 'solvent shifts' and closer scrutiny reveals that other factors are also at work (q.v.).

The similarity in the pattern and energies of the ν(C–O) IR bands in the complexes Ar $\cdots$ $W(CO)_5$ and CCl_4 $\cdots$ $W(CO)_5$ implies retention of the overall C_{4v} geometry by the $W(CO)_5$ fragment. Oxidative addition to form the 7-co-ordinate $W(CO)_5(Cl)(CCl_3)$ is ruled out by the small shifts of the ν(C–O) bands when CCl_4 replaces Ar; oxidation of the metal centre would surely result in a shift to significantly higher wavenumbers. Overlapping of bands due to the precursor and different photoproducts makes it difficult to estimate reliably the intensities of the three IR-active ν(C–O) mode of CCl_4 $\cdots$ $W(CO)_5$, which span the representation $2a_1 + e$. However, pure CCl_4 matrices show that the ratio $I(e)/[I_1(a_1) + I_2(a_1)]$ is in the order of 4:1, as simple calculations would lead one to expect for a $W(CO)_5$ moiety approximating to a square-based pyramid with the metal atom close to the plane formed by the 4 basal CO ligands [25]. There is some evidence though that the geometry of the $W(CO)_5$ unit changes slightly but significantly when CCl_4 replaces Ar as the sixth ligand. Interconversion of the species Ar $\cdots$ $W(CO)_5$ and CCl_4 $\cdots$ $W(CO)_5$ reveals that the absorption associated with the a_1 ν(C–O) mode at higher frequency grows or decays more sharply for the CCl_4- than for the Ar-complex. Hence it appears that, although this absorption remains the weakest of the three, its extinction coefficient in the CCl_4-complex is appreciably greater than that in the Ar-complex. Similar behaviour has been noted when Xe replaces Ar in chromium pentacarbonyl complexes of the type X $\cdots$ $Cr(CO)_5$ [14], and can be interpreted in terms of a small decrease in the apical-basal OC–Cr–CO angle (from 93° for X = Ar to 91° for X = Xe). A comparable flattening of the basal $W(CO)_4$ unit seems therefore to occur in complexes of the type X $\cdots$ $W(CO)_5$ when Ar gives place to CCl_4; as a result the IR band intensities and energies are modified, and the energy gap between the e and a_1 MO's can be expected to increase appreciably [5].

In the absence of any information about how the vibrational properties of the CCl_4 molecule are modified by co-ordination, it is not possible to define its mode of ligation. In principle, this could involve one, two, or three bridging chlorine atoms, as represented by the structures **I**, **II**, or **III**, respectively. Like $Cr(CO)_5$ [26], C_{4v} $W(CO)_5$ has an unoccupied a_1 MO lying above a fully occupied set of $b_2 + e$ MO's (corresponding to the t_{2g} set of the parent molecule $W(CO)_6$). Molecular orbital calculations on CH_4 $\cdots$ $Cr(CO)_5$ find an attractive potential for a CH_4 molecule approaching the vacant sixth site of $Cr(CO)_5$ to establish a linear Cr $\cdots$ H–C bond [26]. However, the highest occupied molecular orbitals (HOMO's) of CH_4 are the bonding t_2 orbitals (ionisation energy 13.6 eV [27]), whereas the HOMO's of CCl_4 comprise the t_1 set of non-bonding orbitals localised on, and derived from the $3p$ orbitals of, chlorine (ionisation energy 11.69 eV [27]). On this basis, any W $\cdots$ Cl–C unit in CCl_4 $\cdots$ $W(CO)_5$ is expected to be non-linear, but


(I)

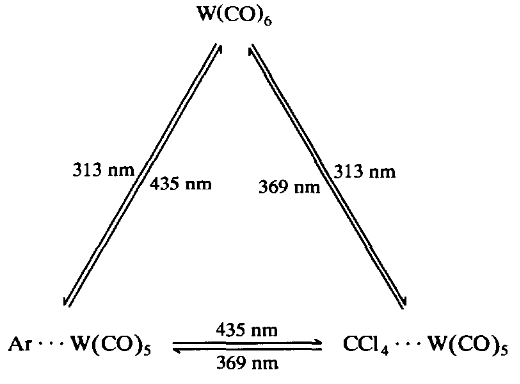

(II)


(III)

detailed MO calculations are needed to assess the roles of σ-donation from, and π-back-donation to, the CCl_4 molecule, as well as repulsive interactions, in determining whether **I**, **II**, or **III** represent a minimum in the $CCl_4 \cdots W(CO)_5$ potential energy surface. Independent studies involving time-resolved IR measurements on gaseous mixtures have revealed reversible complex-formation between $W(CO)_5$ and an alkane [28], fluoroalkane [28], or CF_2Cl_2 [29]. For example, the equilibrium constant $K_p = [W(CO)_5X]/([W(CO)_5]p(X))$ is estimated to be 610 ± 100 atm^{-1} and 3501 ± 1100 atm^{-1} at 300 K for $X = C_2H_6$ and CH_3F, respectively [28], and a bond dissociation energy of 82 ± 3 kJ mol^{-1} has been determined for loss of CF_2Cl_2 from $CF_2Cl_2 \cdots W(CO)_5$ [29]. On the other hand, no such complex has been detected for $X = CH_4$, CF_4, or CHF_3 [28], possibly because the relevant HOMO lies too deep in energy to afford more than a weakly attractive $X \cdots W(CO)_5$ interaction.

Conclusions

Photolysis of argon matrices containing $W(CO)_6$ and CCl_4 results in photodissociation of CO and the formation of the unsaturated C_{4v} molecule $W(CO)_5$ which weakly binds a molecule of either argon or CCl_4. The two complexes exhibit UV–Vis absorption bands at 437 (Ar) and 380 nm (CCl_4) which can be identified with the low-energy ligand-field transition $b_2{}^2e^4a_1{}^0b_1{}^0 \rightarrow b_2{}^2e^3a_1{}^1b_1{}^0$. The blue shift of the band with the switch from $Ar \cdots W(CO)_5$ to $CCl_4 \cdots W(CO)_5$ implies a significant increase in the energy of the a_1 LUMO of the $W(CO)_5$ fragment, in keeping with the superior power of CCl_4 as a σ-donor. The pattern and energies of the IR-active ν(C–O) fundamentals of the two complexes are similar, although there are grounds for believing that some compression of the apical-basal OC–W–CO bond angle takes place when Ar is replaced by CCl_4. Interconversion of the species $W(CO)_6$, $Ar \cdots W(CO)_5$, and $CCl_4 \cdots W(CO)_5$ proceeds in accordance with the photochemical conditions specified in Scheme 1. Attempts to chart the course of subsequent photochemical changes stemming from the primary product $CCl_4 \cdots W(CO)_5$, and linking with the results of solution studies at ambient temperatures [10], have failed so far to produce any clear evidence of other products. It is possible that bimolecular reactions of photoproducts take place and that a solid matrix is too restrictive of such reactions. Hence, future studies might profitably focus on solutions in a very weakly co-ordinating solvent like xenon



Scheme 1

[25,30] or perfluoromethylcyclohexane [4] at low temperatures, or exploit the methods of time-resolved spectroscopy [28,29,31,32] to probe $W(CO)_6/CCl_4$ mixtures either in such solutions or in the gas phase at normal temperatures.

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References

1 M.J. Almond and A.J. Downs, Spectroscopy of Matrix Isolated Species, Advances in Spectroscopy, Vol. 17, Wiley, Chichester, 1989.
2 T. Szymańska-Buzar, J. Mol. Catal., 48 (1988) 43.
3 M. Wrighton, Chem. Rev., 74 (1974) 401.
4 R. Bonneau and J.M. Kelly, J. Am. Chem. Soc., 102 (1980) 1220.
5 R.N. Perutz and J.J. Turner, J. Am. Chem. Soc., 97 (1975) 4791.
6 G.R. Dobson, P.M. Hodges, M.A. Healy, M. Poliakoff, J.J. Turner, S. Firth and K.J. Asali, J. Am. Chem. Soc., 109 (1987) 4218.
7 M.J. Almond, J.A. Crayston, A.J. Downs, M. Poliakoff and J.J. Turner, Inorg. Chem., 25 (1986) 19.
8 M.J. Almond, A.J. Downs and R.N. Perutz, Inorg. Chem., 24 (1985) 275.
9 T. Szymańska-Buzar and J.J. Ziółkowski, J. Mol. Catal., 43 (1987) 161.
10 T. Szymańska-Buzar, Inorg. Chim. Acta, 145 (1988) 231.
11 D. Borowczak, T. Szymańska-Buzar and J.J. Ziółkowski, J. Mol. Catal., 27 (1984) 355.
12 See, for example, M. Hawkins and A.J. Downs, J. Phys. Chem., 88 (1984) 1527, 3042; M.J. Almond and A.J. Downs, J. Chem. Soc., Dalton Trans., (1988) 809.
13 R.N. Perutz and J.J. Turner, J. Chem. Soc., Faraday Trans. II, 69 (1973) 452.
14 R.N. Perutz and J.J. Turner, Inorg. Chem., 14 (1975) 262; R.N. Perutz, Ph.D. Thesis, University of Cambridge, 1974; M.A. Graham, M. Poliakoff and J.J. Turner, J. Chem. Soc. A, (1971) 2939.
15 J.K. Burdett, A.J. Downs, G.P. Gaskill, M.A. Graham, J.J. Turner and R.F. Turner, Inorg. Chem., 17 (1978) 523.
16 J.J. Turner, J.K. Burdett, R.N. Perutz and M. Poliakoff, Pure Appl. Chem., 49 (1977) 271.
17 J.A. Bowden and R. Colton, Aust. J. Chem., 21 (1968) 2657.
18 L. Andrews, J. Chem. Phys., 48 (1968) 979.
19 H.G. Schnöckel and H.J. Becher, J. Mol. Struct., 25 (1975) 369.
20 L. Andrews, J. Chem. Phys., 48 (1968) 972; L. Andrews, J.M. Grzybowski and R.O. Allen, J. Phys. Chem., 79 (1975) 904.
21 M.E. Jacox and D.E. Milligan, J. Chem. Phys., 43 (1965) 866.
22 C. Moralejo and C.H. Langford, Inorg. Chem., 30 (1991) 567.
23 G. Boxhoorn and A. Oskam, Inorg. Chim. Acta, 29 (1978) 243.
24 P.S. Braterman, Metal Carbonyl Spectra, Academic Press, London, 1975.
25 J.J. Turner, M.B. Simpson, M. Poliakoff, W.B. Maier II and M.A. Graham, Inorg. Chem., 22 (1983) 911.
26 J.-Y. Saillard and R. Hoffmann, J. Am. Chem. Soc., 106 (1984) 2006.
27 K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules, Halsted Press, New York, 1981.
28 C.E. Brown, Y. Ishikawa, P.A. Hackett and D.M. Rayner, J. Am. Chem. Soc., 112 (1990) 2530.
29 P.L. Bogdan, J.R. Wells and E. Weitz, J. Am. Chem. Soc., 113 (1991) 1294.
30 See, for example, J.J. Turner, M.B. Simpson, M. Poliakoff and W.B. Maier II, J. Am. Chem. Soc., 105 (1983) 3898.
31 E. O'Driscoll and J.D. Simon, J. Am. Chem. Soc., 112 (1990) 6580.
32 M. Poliakoff and E. Weitz, Adv. Organomet. Chem., 25 (1986) 277.