

The photochemical behaviour of matrix-isolated $W(CO)_6$ in the presence of alkynes [☆]

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Received 30 November 1994; in revised form 13 February 1995

Abstract

The outcome of UV photolysis of $W(CO)_6$ molecules isolated in a solid CH_4 or Ar matrix in the presence of an alkyne $RC\equiv CR'$ ($R, R' = H, H; Me, H; \text{ or } Me, Me$) at ca. 20 K has been monitored by recording the IR and UV–vis absorption spectra of the deposit. The results indicate that irradiation with light having wavelengths near 313 nm results in the formation of the (η^2 -alkyne)tungsten pentacarbonyl complex, $[(\eta^2-RC\equiv CR')W(CO)_5]$, in addition to $[X \cdots W(CO)_5]$ ($X = CH_4$ or Ar), and free CO. In the case of a terminal alkyne, e.g. $HC\equiv CH$ or $MeC\equiv CH$, however, photolysis under these conditions gives, in addition to the η^2 -alkyne complex and in significantly greater yield, what appears to be the vinylidene derivative $[R(H)C=C=W(CO)_5]$ ($R = H$ or Me). Prolonged irradiation with UV light ($\lambda = \text{ca. } 313 \text{ or } 369 \text{ nm}$) causes the various pentacarbonyl complexes to lose CO with the formation of tetracarbonyl species; prominent among the products issuing from the $W(CO)_6/C_2H_2$ system are $[(\eta^2-HC\equiv CH)(\eta^1-H_2C=C)W(CO)_4]$ (in C_2H_2 -rich matrices) and $[(\eta^2-HC\equiv CH)W(CO)_4]$ in which the alkyne is acting formally as a 4e ligand. The results are significant in relation to the likely intermediate stages in the photocatalytic polymerization of terminal alkynes induced by tungsten hexacarbonyl.

Keywords: Tungsten; Carbonyl; Alkynes; Infrared spectroscopy; Polymerization of alkynes; Vinylidene

1. Introduction

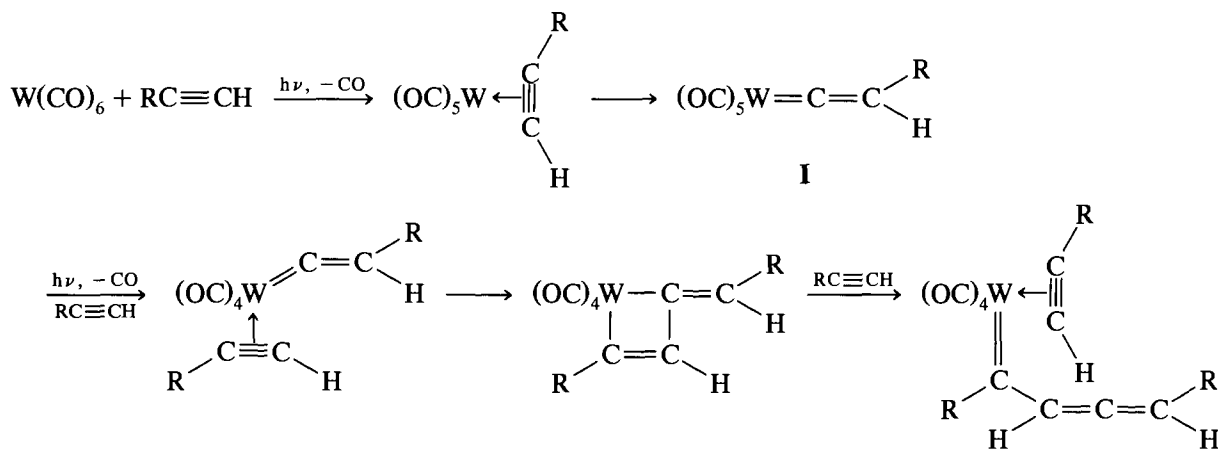
The rôle of transition-metal carbonyls — and particularly those of the Group 6 metals — in homogeneous catalytic and photocatalytic processes is a matter of considerable interest [2]. The photocatalytic polymerization of 1-alkynes in the presence of $[W(CO)_6]$ proceeds, according to one proposal [3], as shown in Scheme 1. Such a catalytic cycle involves the formation of a number of very labile intermediates, including a vinylidene complex **I** which derives from the rearrangement of the initial η^2 -alkyne complex $[(\eta^2\text{-alkyne})W(CO)_5]$, but positive experimental evidence of these intermediates is generally lacking. In an attempt to meet this deficiency, we have appealed to the matrix-isolation technique [4] in order to explore the photochemical

behaviour of molybdenum and tungsten hexacarbonyl in the presence of an alkyne $RC\equiv CR'$, where $RC\equiv CR' = HC\equiv CH, MeC\equiv CH, \text{ or } MeC\equiv CMe$.

In our matrix experiments with molybdenum hexacarbonyl in the presence of $RC\equiv CR'$ molecules [5], we drew on the IR and UV–vis spectra of the matrices to show that UV photolysis results in the formation of a complex of the type $[(\eta^2-RC\equiv CR')Mo(CO)_5]$. In addition, the IR spectra gave notice of what we take to be the vinylidene complex $[R(H)C=C=Mo(CO)_5]$, in the event that the precursor is a 1-alkyne, $RC\equiv CH$ ($R = H$ or Me). Continued irradiation with near-UV light ($\lambda = 300\text{--}400 \text{ nm}$) gives rise to further photodissociation of CO with the formation of $Mo(CO)_4$ derivatives, including $[(\eta^2-RCCR')Mo(CO)_4]$, in which the alkyne group functions formally as a 4e donor. It was a natural extension of these studies to investigate the behaviour of tungsten hexacarbonyl in similar circumstances, with the added incentive coming from the observation that $W(CO)_6$ is superior to $Mo(CO)_6$ as a catalyst for the polymerization of 1-alkynes [6].

[☆] For preliminary accounts of this research see ref. [1].

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Scheme 1.

Table 1

IR spectrum of a solid argon matrix doped with $W(CO)_6$ and C_2H_2 [$W(CO)_6 : C_2H_2 : Ar = ca. 1 : 200 : 2000$] at ca. 20 K; effects of photolysis with light of different wavelengths^a

Wavenumber/ cm^{-1} and intensity ^a	Behaviour on photolysis ^b				Assignment	
	On deposition	$\lambda = 313$ nm	$\lambda = 445$ nm	$\lambda = 369$ nm	Molecule	Mode
2141 ^c w,sh	—	↑	↑	↑	CO	ν_{CO}
2138 ^c w	—	↑	↑	↑		
2121 ^c w	↑	↓	↑	↑	W(CO) ₆	ν_{CO} , ^d a_{1g}
2116 ^c w	↑	↓	↑	↑		
2097 w	—	↑	↓	↑	Ar ··· W(CO) ₅	ν_{CO} , a_1
2093 w	—	↑	↑	↓	A	ν_{CO} , a_1
2083 w,sh	—	—	—	↑	C	ν_{CO} , a_1
2079 w	—	↑	↓	↑↓	B	ν_{CO} , a_1
2064 w	—	—	↑	↓	W(CO) ₄ species ^e	ν_{CO} , a_1
2053 w	—	↑	unchanged	↑	W(CO) ₄ species ^e	ν_{CO} , a_1
2037 w	—	—	↑	↑↓	E	ν_{CO} , a_1
2014 w	↑	↓	—	—	W(CO) ₆	ν_{CO} , ^d e_g
2010 ^c m,br	—	—	—	↑	C	ν_{CO} , b_1
2006 ^c m,br	—	—	↑	↓		
2002 m,sh	—	↑	↓	↑↓	B	ν_{CO} , e
1976–1989 ^c vs	↑	↓	↑	↑	W(CO) ₆	ν_{CO} , t_{1u}
1978 m	—	↑	↑	↓	A	ν_{CO} , e
1963 ^c s	↑	↑	↓	↑	[C ₂ H ₂] ₂ + B + Ar ··· W(CO) ₅	$\nu_{CC} + \nu_{CO}$, e
1959 ^c m,sh	—	↑	↓	↓		
1950 w	—	↑	↑	↓	A	ν_{CO} , a_1
1939 w	—	↑	↓	↑	W(CO) ₄ species ^e	ν_{CO} , b_2
1932 mw	—	↑	↓	↑	Ar ··· W(CO) ₅	ν_{CO} , a_1
1926 w,sh	—	↑	↓	↓	W(CO) ₄ species ^e	ν_{CO} , a_1
1918 ^c m	—	↑	↓	↓	W(CO) ₄ species ^e	ν_{CO} , a_1
1917 ^c m	—	↑	↓	↓		
1915 ^c m	—	↑	↓	↓		
1894 w	—	↑	↓	↓	W(CO) ₄ species ^e	ν_{CO} , b_1
1889 w,br	—	—	↑	↓	W(CO) ₄ species ^e	ν_{CO} , b_1
1875 w	—	↑	↑	↑↓	E	ν_{CO} , b_1
1808 w,br	—	↑	↑	↑↓	E	ν_{CC}
1774 w,br	—	↑	↑	↓	A	ν_{CC}
1641 w	—	—	↑	↑↓	E	ν_{CC}
1615 w	—	—	↑	↑↓		
1574 w	—	↑	↓	—	B	ν_{CC}
1522 w	—	—	↑	↑	C	ν_{CC}

^a Spectrum covers the range 1500–2200 cm^{-1} . w = weak, m = medium, s = strong, v = very, br = broad, sh = shoulder. ^b Symbols showing the effects of photolysis: ↑ appears and/or grows; ↓ decays; — absent or obscured. ^c Bands split by matrix site effects. ^d Vibrational mode activated in IR absorption through a lowering of molecular symmetry imposed by the matrix cage. ^e W(CO)₄ species of the type LL'W(CO)₄ where L, L' represents any two of the same or different ligands from Ar, C₂H₂, or =C=CH₂ (see Table 3).

2. Experimental details

The experiments were carried out at Oxford with the cryogenic, photolytic, and spectroscopic equipment described previously [5,7]. The matrices were formed by either pulsed [8] or slow, continuous deposition of the vapours, and the operating procedures conformed closely to the practices developed in earlier studies of this kind [5,7].

The matrix gases Ar and CH₄ were used as supplied by B.O.C. ("Research" grade). Samples of W(CO)₆ (99% pure, supplied by Aldrich) were purified before use by sublimation in vacuo. Each of the alkynes from the commercial sources listed was purified before use by fractional condensation in vacuo: ethyne (B.O.C.), propyne (Matheson), but-2-yne (Aldrich), and [¹³C₁]-ethyne, ¹²C¹³CH₂ (98.8 atom% ¹³C; C/D/N Isotopes Inc.). Perdeuteriated ethyne, C₂D₂, was prepared by

Table 2

Spectroscopic and photochemical properties of alkyne or vinylidene tungsten carbonyl products identified on photolysis of Ar or CH₄ matrices containing W(CO)₆ and an alkyne

Product	IR bands		UV-vis bands/ nm	Effects of photolysis			
	$\nu_{\text{CO}}/\text{cm}^{-1}$	$\nu_{\text{CC}}/\text{cm}^{-1}$		$\lambda = 313 \text{ nm}$	$\lambda = 445 \text{ nm}$	$\lambda = 369 \text{ nm}$	
A,	2093 ^a 1978 ^a 1950 ^a	2090 ^b 1972.5 ^b 1944 ^b	1774 ^a (1630 ^{a,c}) (1743 ^{a,d})	ca. 370 ^b	↑ ↓	↑	↓
A,	2089 ^a 1970.5 ^a 1940 ^a	2086 ^b 1965 ^b 1934 ^b	1891 ^a	ca. 370 ^b	↑	↑	↓
A,	2068 ^a 1962 ^a 1940 ^a	2082 ^b 1962 ^b 1931.5 ^b	^c	ca. 370 ^b	↑	↑	↓
B,	2079 ^a 2002 ^a 1959 ^a	2077 ^b 2000 ^b 1952 ^b	1574 ^a (1486 ^{a,c}) (1547 ^{a,d})	364 ^b 460 ^b	↑	↓	↑ ↓
B,	2073 ^a 1996 ^a 1948 ^a	2070 ^b ^{b,e} 1950 ^b	1693 ^a	367 ^b 465 ^b	↑	↓	↑ ↓
C,	2083 ^a 2008 ^a ^c	ca. 2080 ^b 2005 ^b ^c	1522 ^a	^{b,e}	—	↑	↑
E,	2037 ^a ^{a,e} ^{a,e} 1875 ^a		1808 ^a (1643 ^{a,c}) 1641 ^a (1577 ^{a,c}) 1615 ^a (1552 ^{a,c})	^{a,e}	—	↑	↑ ↓
E,	2030 ^a ^{a,e} ^{a,e} ca. 1890 ^a		1757 ^a	^{a,e}	—	↑	↑ ↓

^a Ar matrix.

^b CH₄ matrix.

^c Relates to C₂D₂ derivative.

^d Relates to ¹²C¹³CH₂ derivative.

^e Obscured by absorptions due to other species.

dropwise addition of D₂O (99.9 atom% D; Aldrich) to solid calcium carbide (East Anglia Chemicals) and also purified by fractional condensation in vacuo.

3. Results and discussion

Tungsten hexacarbonyl, W(CO)₆, was isolated in an argon or methane matrix (X) doped with the alkyne, RC≡CR' (R,R' = H,H; Me,H; or Me,Me), typically in the proportions W(CO)₆ : RC≡CR' : X = ca. 1 : 100 : 2000, and at a temperature of ca. 20 K. Exposure of the matrix to UV radiation with wavelengths near 313 nm was observed, on the evidence of its IR spectrum, to result in photodissociation of the W(CO)₆ with the formation of free CO [9] and the unsaturated C_{4v} molecule W(CO)₅ [7,10] which binds a molecule of either the matrix, X, or the alkyne, RC≡CR'. As revealed by the details set out in Tables 1–3 and illustrated, for the W(CO)₆/MeC≡CH and W(CO)₆/HC≡CH systems, in Figs. 1 and 2, the nature of the coordinated ligand influences significantly the spectro-

scopic properties of the W(CO)₅ fragment, with the results to be discussed hereafter. As expected [10,11], and in keeping with the matrix photochemistry of Mo(CO)₆/alkyne mixtures [5], continued irradiation with light having λ = ca. 313 nm results in the loss of a second molecule of CO, with the appearance and growth of IR bands due to complexes of W(CO)₄, e.g. [X₂W(CO)₄] and [(RC≡CR')XW(CO)₄] (X = CH₄ or Ar), where the W(CO)₄ moiety has C_{2v} symmetry.

The ν_{CO} fundamentals of the W(CO)₅ unit give rise to three IR absorptions, namely a weak feature at 2060–2100 cm⁻¹ (a₁) and two more intense features at 1920–2010 cm⁻¹ (a₁ + e). In experiments with but-2-yne, MeC≡CMe, we found the region associated with the high-energy a₁ mode to contain not one but two bands which, on the evidence of their response to selective photolysis (q.v.), originate in two distinct products. The known weak complex [X ··· W(CO)₅] [10,11] is clearly identifiable with the band at higher wavenumber (2095 or 2092 cm⁻¹ for X = Ar or CH₄, respectively), whereas an alkyne-containing product A must be responsible for the band at lower wavenumber

Table 3
Spectroscopic properties of alkyne or vinylidene tungsten carbonyl products formed in low-temperature matrices (ca. 20 K)

Adduct type LW(CO) ₅ , C _{4v} L =	Medium	IR-active ν _{CO} wavenumber/cm ⁻¹			Lowest-energy spin-allowed ligand-field transition/nm ^a	
		a ₁	e	a ₁		
Ar	Ar	2095	1963	1932	437 ^b	
CH ₄	CH ₄	2092	1957.5	1926	410	
HC≡CH	Ar	2093	1978	1950	n.s.	
	CH ₄	2090	1972.5	1944	ca. 370	
	n-hexane ^c	2095	1967	1952	n.s.	
MeC≡CH	Ar	2089	1970.5	1940	n.s.	
	CH ₄	2086	1965	1934	ca. 370	
	n-hexane ^c	2088	1960	1944	n.s.	
MeC≡CMe	Ar	2083.5	1966	1940	n.s.	
	CH ₄	2082	1962	1931.5	ca. 370	
H ₂ C=C=	Ar	2079	2002	1959	n.s.	
	CH ₄	2077	2000	1952	364, 460	
Me(H)C=C=	Ar	2073	1996 ^d	1948	n.s.	
	CH ₄	2070		1950	367, 465	
LL'W(CO) ₄ , C _{2v} L,L' =		a ₁	b ₂	a ₁	b ₁	
Ar, Ar	Ar	2053	1939	1926	1894	n.s.
CH ₄ , CH ₄	CH ₄	2052	1932 ^d	1924	1887	^e
H ₂ C=C=, Ar	Ar	2064		^d	1889	n.s.
H ₂ C=C=, CH ₄	CH ₄	2063		1916	1893	^e
H ₂ C=C=, HC≡CH	Ar	2037	^d	^d	1875	n.s.
H ₂ C=C=, HC≡CH	CH ₄	2034	^d	^d	1868	^e
HC≡CH, Ar	Ar	ca. 2054	^d	^d	ca. 1890	n.s.
HC≡CH, CH ₄	CH ₄	ca. 2054	^d	^d	ca. 1890	^e
Me(H)C=C=, CH ₄	CH ₄	2048	^d	1915	1885	^e
Me(H)C=C=, MeC≡CH	Ar	2030	^d	^d	ca. 1890	^e
Me(H)C=C=, MeC≡CH	CH ₄	2026	^d	^d	^d	^e
MeC≡CMe, CH ₄	CH ₄	ca. 2050	^d	1911	1886	^e

^a n.s. not studied. ^b Ref. [10]. ^c Solution, Ref. [18]. ^d Obscured by absorptions due to [W(CO)₆], [(η²-alkyne)W(CO)₅], [R(H)C=C=W(CO)₅] (R = H or Me), [X ··· W(CO)₅] (X = Ar or CH₄), or other species. ^e Matrices showed a weak band centred near 520 nm which may have been due to one or more W(CO)₄ species.

(2065–2085 cm^{-1}). By contrast, experiments involving a 1-alkyne, viz. $\text{HC}\equiv\text{CH}$ or $\text{MeC}\equiv\text{CH}$, showed no less than three bands in this region. The response to irradiation at different wavelengths, allied to the experience of earlier studies [5,10,11], implies that there are now three distinct products, viz. (a) $[\text{X} \cdots \text{W}(\text{CO})_5]$, (b) the ethyne or propyne form of **A** (absorbing at ca. 2092 or 2088 cm^{-1} , respectively), and (c) a second tungsten carbonyl derivative of the alkyne **B** (absorbing at ca. 2078 or 2072 cm^{-1} for the ethyne or propyne version, respectively). The difference of behaviour between a 1-alkyne like $\text{HC}\equiv\text{CH}$ or $\text{MeC}\equiv\text{CH}$ (giving two metal carbonyl derivatives **A** and **B**) and an internal alkyne like $\text{MeC}\equiv\text{CMe}$ (giving only one derivative **A**) finds obvious parallels with the matrix photochemistry of $\text{Mo}(\text{CO})_6$ in similar circumstances [5]. Indeed, all the spectroscopic signs suggest that $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ follow similar pathways and give rise to analogous products, and the labels **A**, **B**, **C**, etc., reflect the presumption that tungsten follows molybdenum in the stoichiometry and structure of many, if not all, of its

alkyne-containing photoproducts. However, the relative yields of the products derived from the two hexacarbonyls are by no means comparable. Thus, of the three bands occurring in the region 2060–2100 cm^{-1} that due to **B** is the most intense when $\text{W}(\text{CO})_6$ is the precursor, but the least intense when $\text{Mo}(\text{CO})_6$ is the precursor [5].

In addition to the high-energy $a_1 \nu_{\text{CO}}$ fundamental, it was possible to associate with each of the products **A** and **B** two more IR absorptions in the range 1930–2010 cm^{-1} . Problems of overlap with the absorptions of other metal carbonyls (e.g. $[\text{W}(\text{CO})_6]$, $[\text{X} \cdots \text{W}(\text{CO})_5]$ and various $\text{W}(\text{CO})_4$ derivatives) and of the free alkyne in one form or another [12–14] hampered this identification and precluded useful experiments with ^{13}CO -enriched $\text{W}(\text{CO})_6$ aimed at definitive characterisation of the metal carbonyl fragments in **A** and **B**. However, the ν_{CO} bands, by their number and intensity and wave-number patterns, are plainly suggestive of a C_{4v} $\text{W}(\text{CO})_5$ moiety in both **A** and **B**. Additional IR absorptions near 600 cm^{-1} could be traced to $\text{W}-\text{C}-\text{O}$ bending modes of these complexes.

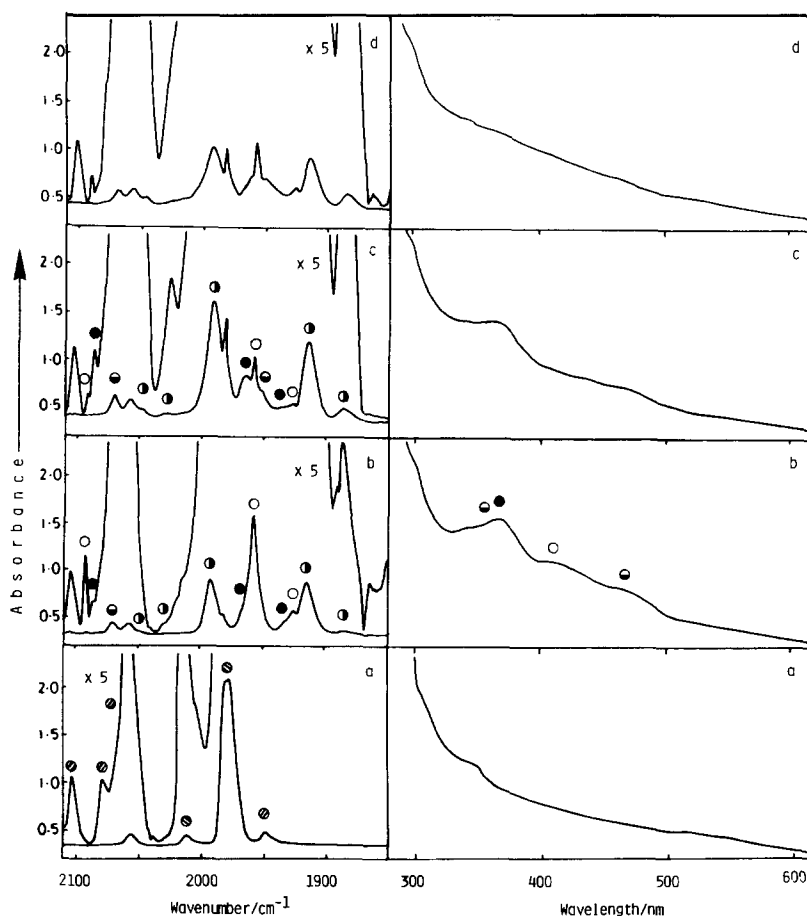


Fig. 1. IR absorption spectrum in the region 1850–2100 cm^{-1} and UV-vis absorption spectrum in the region 300–600 nm displayed by a solid CH_4 matrix containing $\text{W}(\text{CO})_6$ and $\text{MeC}\equiv\text{CH}$ with the composition $\text{W}(\text{CO})_6 : \text{MeC}\equiv\text{CH} : \text{CH}_4 = \text{ca. } 1 : 250 : 5000$ at 20 K, showing the effects of short-term photolysis at different wavelengths. (a) Spectra of the matrix after deposition. (b) Spectra after photolysis at $\lambda = 313$ nm. (c) Spectra after photolysis at $\lambda = 445$ nm. (d) Spectra after photolysis at $\lambda = 369$ nm. Bands are labelled as follows: \circ $[\text{CH}_4 \cdots \text{W}(\text{CO})_5]$; \bullet **A**, $[\eta^2 - \text{MeC}\equiv\text{CH}]\text{W}(\text{CO})_5$; \odot **B**, $[\text{Me}(\text{HC}=\text{C}=\text{W}(\text{CO})_5)]$; \ominus $\text{W}(\text{CO})_4$ species; \otimes free $[\text{MeC}\equiv\text{CH}]$ or $[\text{MeC}=\text{CH}]_n$; and \otimes $[\text{W}(\text{CO})_6]$.

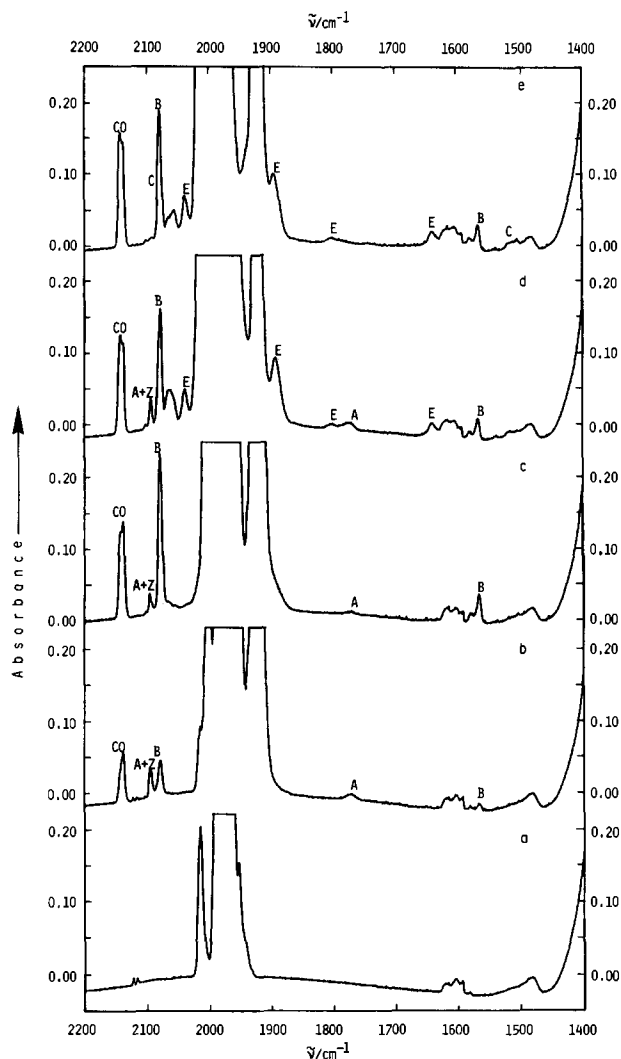


Fig. 2. IR absorption spectra showing the weaker bands in the region $1400\text{--}2200\text{ cm}^{-1}$ displayed by a solid Ar matrix containing $\text{W}(\text{CO})_6$ and C_2H_2 with the composition $\text{W}(\text{CO})_6 : \text{C}_2\text{H}_2 : \text{Ar} = \text{ca. } 1:150:1500$ at 20 K. (a) After deposition. (b) After 10 min with $\lambda = 313\text{ nm}$. (c) After 40 min with $\lambda = 313\text{ nm}$. (d) After 30 min with $\lambda = 445\text{ nm}$. (e) After 30 min with $\lambda = 369\text{ nm}$. For identities of species **A**, **B**, **C** and **E** see text; **Z** = $[\text{Ar} \cdots \text{W}(\text{CO})_5]$.

Absorptions due to the coordinated alkyne were less easy to detect. With extinction coefficients typically nearly an order of magnitude smaller than for the ν_{CO} modes and wavenumbers close to those of the free alkyne, these were at risk of being obscured by other, more intense absorptions. With suitably thick matrix samples, however, the $\text{W}(\text{CO})_6/\text{C}_2\text{H}_2$ system did show a weak, broad band at 1774 cm^{-1} which appeared to track the ν_{CO} features of **A**. Replacement of normal $^{12}\text{C}_2\text{H}_2$ by $^{12}\text{C}^{13}\text{CH}_2$ or $^{12}\text{C}_2\text{D}_2$ caused the wavenumber to decrease to 1743 or 1630 cm^{-1} , respectively, with no suggestion of significant splitting or broadening in either case. The obvious conclusion to be drawn is that the band corresponds to what is essentially the ν_{CC} mode of the coordinated C_2H_2 molecule. In addition, it

was possible to detect a second weak absorption at 1574 cm^{-1} which paralleled in its growth and decay the ν_{CO} features associated with the product **B**. The equivalent transition came at 1547 and 1486 cm^{-1} for $^{12}\text{C}^{13}\text{CH}_2$ and $^{12}\text{C}_2\text{D}_2$ versions of **B**, respectively, again with no hint of any splitting or broadening. Hence it is reasonable to infer that this transition too corresponds more or less closely to a ν_{CC} fundamental of the coordinated C_2H_2 moiety.

The UV-vis spectra of methane matrices supporting $\text{W}(\text{CO})_6$ and $\text{RC}\equiv\text{CR}'$ also witnessed the formation of the photoproducts **A** and **B** (see, for example, Fig. 1). An adduct of $\text{W}(\text{CO})_5$ formed by photolysis at $\lambda = \text{ca. } 313\text{ nm}$ is characterised by a near-UV or visible band attributable to the $b_2^2 e^4 a_1^0 b_1^0 \rightarrow b_2^2 e^3 a_1^1 b_1^0$ ligand-field transition [10]. For the adduct $[\text{CH}_4 \cdots \text{W}(\text{CO})_5]$ this band was observed to be centred at $\lambda = 410\text{ nm}$, in keeping with earlier reports [10]. As expected, then, irradiation of the matrix with visible light having $\lambda = \text{ca. } 445\text{ nm}$ caused this band to decay (see Fig. 1), with a concomitant decrease in the intensities of the IR absorptions due to $[\text{CH}_4 \cdots \text{W}(\text{CO})_5]$. Such visible photolysis favoured the growth of the IR bands due to **A**; this was matched by the growth of a near-UV absorption centred at $\lambda = \text{ca. } 370\text{ nm}$. Matrices containing ethyne or propyne displayed, besides these features, two other absorptions, one in the visible region at $460\text{--}465\text{ nm}$ and the other in the near-UV region at $364\text{--}367\text{ nm}$ (see Fig. 1). Most prominent after exposure of the matrix to UV light ($\lambda = \text{ca. } 313\text{ nm}$), these bands appeared to correlate with the IR bands ascribed to the product **B**. The overlapping of the near-UV bands of **A** and **B** was presumed to be one of the factors leading to a response to photolysis at selected wavelengths which was decidedly less clearcut for the tungsten than for the analogous molybdenum systems [5]. However, while promoting the formation of **A**, irradiation with visible light ($\lambda = \text{ca. } 445\text{ nm}$) had little effect on **B** except in alkyne-rich (5–10 mol%) matrices which fostered the decay of this product together with the simultaneous accretion of free CO. Irradiation with near-UV light ($\lambda = \text{ca. } 369\text{ nm}$) effected the extinction of both **A** and **B**.

Photolysis at wavelengths shorter than 400 nm invariably led to a build-up of free CO. With tungsten carbonyls, as with molybdenum carbonyls [5], it appears that coordination to an alkyne moiety photosensitises the $\text{M}(\text{CO})_5$ unit ($\text{M} = \text{Mo}$ or W) to further fragmentation into free CO and lower carbonyls like $\text{M}(\text{CO})_4$. The ν_{CO} region of the IR spectrum witnessed the appearance and growth of bands attributable to species of the type $[\text{LL}'\text{W}(\text{CO})_4]$ [10], where **L** and **L'**, which may be the same or different, represent matrix or alkyne molecules. In the circumstances, it was not feasible to identify positively all the possible permutations of products of this type. Nevertheless, by dint (i) of systematic variations of matrix composition, (ii) of examining the

response of the various bands to irradiation with light of different wavelengths, and (iii) of comparisons with the spectroscopic properties already established for such molecules [11,15], we have arrived at the assignments included in Table 3.

Two products in particular came to light under these conditions, and especially on photolysis with light having $\lambda = 369$ nm. One was favoured by prolonged photolysis at wavelengths in the range 300–400 nm. The ethyne version of this was characterised by ν_{CO} bands near 2083 and 2008 cm^{-1} , as well as a weak feature at 1522 cm^{-1} at the low-energy end of the region characteristic of ν_{CC} modes. Unfortunately, though, the C_2D_2 and $^{12}\text{C}^{13}\text{CH}_2$ counterparts of the last band could not be located because of the masking effects of absorptions due to the free alkyne [12,13]. In its spectroscopic and photochemical properties, the carrier of these features finds a close parallel with an analogous product generated from $\text{Mo}(\text{CO})_6$ supported in an ethyne-doped matrix [5], and in keeping with which we label the tungsten product **C**. The second product, which we label **E**, did not have an obvious counterpart in the $\text{Mo}(\text{CO})_6/\text{C}_2\text{H}_2$ system. Its formation was favoured by relatively high concentrations of ethyne (5–10 mol%) and appeared to be linked with the decay of **B**, making its first appearance on visible photolysis ($\lambda = 445$ nm), building up and then decaying on prolonged near-UV photolysis ($\lambda = 369$ nm). **E** was distinguished in the observable portions of its IR spectrum by ν_{CO} bands near 2035 and 1870 cm^{-1} (see Table 3). In addition, it showed no less than three weak bands at wavenumbers suggestive of ν_{CC} modes; these occurred at 1808, 1641 and 1615 cm^{-1} for the C_2H_2 version and at 1643, 1577 and 1552 cm^{-1} for the C_2D_2 version (but with a significant change in the relative intensities of the two absorptions at lowest wavenumber, in that $I_{1641} > I_{1615}$ whereas $I_{1577} < I_{1552}$).

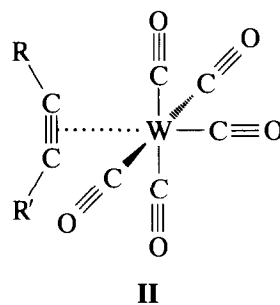
Broad-band UV photolysis was observed to give rise not only to the changes brought about by irradiation at $\lambda = 313$ and 369 nm, but also to additional changes presumably involving the expulsion of more than 2 CO molecules from the $\text{W}(\text{CO})_6$ precursor. However, these conditions gave spectra too complicated to admit of any systematic analysis of the relevant photochemical events. Numerous studies were also carried out to see whether annealing the matrices at temperatures up to ca. 35 K had any effect at different stages in a typical cycle of selective photolysis, viz. $\lambda = 313$, 445, and 369 nm; in the event, the IR spectra showed little change.

Each of the product-types **A**, **B**, **C** and **E** will now be considered in turn.

3.1. **A**, $[(\eta^2\text{-RC}\equiv\text{CR}')\text{W}(\text{CO})_5]$

The spectroscopic and photochemical properties leave little doubt that **A** is an alkyne complex of the type

$[(\eta^2\text{-RC}\equiv\text{CR}')\text{W}(\text{CO})_5]$ ($\text{R}, \text{R}' = \text{H}, \text{H}; \text{Me}, \text{H};$ or Me, Me) with the structure **II**. As noted previously, the near-UV



band at ca. 370 nm can be ascribed to the lowest-energy spin-allowed ligand-field transition of such a molecule. The corresponding transition of other $\text{X} \cdots \text{W}(\text{CO})_5$ systems varies in wavelength from 410 ($\text{X} = \text{CH}_4$), through 388/404 ($\text{X} = \text{pyridine}$) [16], 380 ($\text{X} = \text{CCl}_4$) [7b], 350 ($\text{X} = \text{PCl}_3$) [17], to 346 nm ($\text{X} = \text{CO}_2$) [7a]. Thus, the alkyne ligand lies between CCl_4 and PCl_3 in the overall degree to which it perturbs the $\text{W}(\text{CO})_5$ unit. As with the analogous molybdenum complexes [5], the ν_{CO} fundamentals point to an alkyne molecule functioning as a 2e ligand, to a donor capacity varying in the order $\text{HC}\equiv\text{CH} < \text{MeC}\equiv\text{CH} < \text{MeC}\equiv\text{CMe}$ (in keeping with the decreasing ionization energies of the molecules in this sequence [18]), and to a π -acceptor capacity for the alkyne molecules varying in the reverse order. The complexes $[\text{RC}\equiv\text{CH} \cdots \text{W}(\text{CO})_5]$ ($\text{R} = \text{H}$ or Me) have been detected previously by their ν_{CO} bands following UV photolysis of $\text{W}(\text{CO})_6$ in the presence of the alkyne in n-hexane solution [19], with results close to those of our matrix experiments.

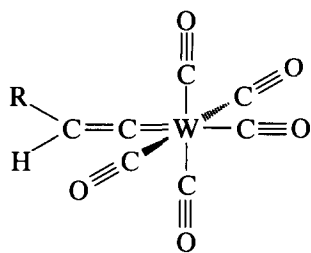
The observation of a weak IR band attributable to what is, in large part, the ν_{CC} mode of the coordinated alkyne discloses a red shift, $\Delta\nu$, of 200 and 246 cm^{-1} relative to the corresponding mode of free ethyne and propyne, respectively [12,13]. The weakening and elongation of the $\text{C}\equiv\text{C}$ bond under the action of coordination are, on this evidence, somewhat greater for $\text{W}(\text{CO})_5$ than for $\text{Mo}(\text{CO})_5$ ($\Delta\nu = 152$ and 235 cm^{-1} [5]), although neither complex involves more than quite weak interaction between the alkyne and d^6 metal carbonyl components (cf. $\Delta\nu = 175\text{--}365$ cm^{-1} for other η^2 -ethyne and -propyne complexes in which the alkyne functions formally as a 2e donor [5,20,21]). The corresponding vibration of the but-2-yne version of **A** could not be identified in our experiments, presumably because of masking by the more intense ν_{CO} bands of this and other species.

3.2. **B**, $[\text{R}(\text{H})\text{C}=\text{C}=\text{W}(\text{CO})_5]$ ($\text{R} = \text{H}$ or Me)

A notable difference between the photochemistries of $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ in alkyne-doped matrices emerges in the case of the 1-alkynes $\text{HC}\equiv\text{CH}$ and $\text{MeC}\equiv\text{CH}$. On photolysis at wavelengths near 313 nm,

these give access to a second reaction channel leading to a photoproduct **B** quite distinct in its photochemistry and spectroscopic properties from **A**. Whereas **B** is only a minor issue when $\text{Mo}(\text{CO})_6$ is the precursor [5], it becomes the main alkyne-containing product delivered by $\text{W}(\text{CO})_6$ under otherwise similar conditions. The tungsten version of **B** is characterised by an IR spectrum including three ν_{CO} bands at the following wavenumbers (in cm^{-1}): 2070–2079(w), 1996–2002(s), and 1948–1959(m) (s = strong; m = medium; w = weak). The number, wavenumbers and relative intensities of these features, allied to the conditions of formation, give every reason for believing that **B** contains a $\text{W}(\text{CO})_5$ fragment [7,10]. The wavenumber of the band identified with the ν_{CC} mode of the coordinated ligand in the ethyne version of **B** is perhaps more in keeping with an $\eta^2\text{-HC}\equiv\text{CH}$ [5] than with an $\eta^1\text{-H}_2\text{C}=\text{C}$ unit, for which ν_{CC} normally falls in the range 1620–1680 cm^{-1} [20–23]. In addition, the wavenumber is significantly more responsive to perdeuteration than is that of the corresponding mode associated with each of the molecules $[\text{H}_2\text{C}=\text{C}=\text{Ni}]$ [22], $[\text{H}_2\text{C}=\text{C}=\text{S}]$ [24], and $[\text{H}_2\text{C}=\text{C}=\text{Se}]$ [25], and there is no hint of discrimination between the two linkage isomers $[\text{H}_2^{13}\text{C}=\text{C}=\text{W}(\text{CO})_5]$ and $[\text{H}_2^{12}\text{C}=\text{C}=\text{W}(\text{CO})_5]$. However, simplified normal coordinate analysis calculations show that the observed spectroscopic properties can be reconciled with an $\text{H}_2\text{C}=\text{C}=\text{W}$ fragment no less than with an $(\eta^2\text{-HC}\equiv\text{CH})\text{W}$ fragment [26]. Furthermore, the UV-vis spectra of the matrices denote that **B** is the carrier of two optical transitions centred at 364–367 and 460–465 nm (q.v.).

The wavenumbers of the ν_{CO} absorptions of **B** carry the clear suggestion that the $\text{W}(\text{CO})_5$ unit is coordinated to a ligand related to the 1-alkyne but which is at once a poorer donor (on the evidence of the lower energy a_1 ν_{CO} mode) and a better π -acceptor (on the evidence of the other two ν_{CO} modes) than the alkyne coordinated in the η^2 -mode featured by **A**. The ligand answering most obviously to this description is $\eta^1\text{-R}(\text{H})\text{C}=\text{C}$ (R = H or Me) [27], and we propose that **B** is the vinylidene derivative $[\text{R}(\text{H})\text{C}=\text{C}=\text{W}(\text{CO})_5]$ with the structure **III**. This identification is supported by the resemblance



III

which **B** bears in the ν_{CO} region of its IR spectrum to the known vinylidene complexes $[\text{Bu}^t(\text{R})\text{C}=\text{C}=\text{W}(\text{CO})_5]$ {R = Me, $\nu_{\text{CO}} = 2088(\text{w}), 1986(\text{w,sh}), 1977(\text{vs}),$ and $1969(\text{s}) \text{ cm}^{-1}$; R = Et, $\nu_{\text{CO}} = 2088(\text{w}), 1986(\text{w,sh}), 1978(\text{vs}),$ and $1970(\text{s,sh}) \text{ cm}^{-1}$ [28]; sh = shoulder}.

It has to be said that the wavenumbers of what we take to be the ν_{CC} modes of the coordinated vinylidene ligands $\text{C}=\text{CH}_2$ (1574 cm^{-1}) and $\text{C}=\text{C}(\text{H})\text{Me}$ (1693 cm^{-1}) are out of line with the precedents set by earlier studies, as is the response of the $\text{C}=\text{CH}_2$ mode to deuteration. Thus, ν_{CC} for the $\text{C}=\text{CH}_2$ complex falls below the normal range (1620–1680 cm^{-1} [20–23]) and shifts to much lower wavenumber on deuteration than do the corresponding modes of other vinylidene complexes ($\Delta\nu = 88 \text{ cm}^{-1}$, cf. $[\text{NiCCH}_2]$ 6–9 cm^{-1} [22] and $[(\eta^5\text{-C}_5\text{H}_5)\text{IrH}_2(\text{CCH}_2)]$ 23 cm^{-1} [20]). By contrast, the $\text{C}=\text{C}(\text{H})\text{Me}$ version of **B** has ν_{CC} near the upper end of the normal range (1630–1700 cm^{-1} [21b,23a,27a,29]). While this may cast some doubt on our assignments, there are two major caveats to be entered regarding the characterisation of vinylidene ligands by their ν_{CC} modes.

(a) With but one exception ($[\text{NiCCH}_2]$ [22]), precedents for the ν_{CC} modes of CCH_2 and $\text{CC}(\text{H})\text{Me}$ are based on complexes of metal atoms bearing formal positive charges in the range +1 to +3. In view of the way in which ligands like CO, RNC and N_2 respond through their ν_{CO} , ν_{NC} and ν_{NN} modes, respectively, to the effects of coordination [30], it would be a matter of real surprise were the formally isoelectronic ligands CCH_2 and $\text{CC}(\text{H})\text{Me}$ to be confined in their ν_{CC} modes to ranges as narrow as those prescribed by previous experience. Two items of evidence support this view. Firstly, ν_{CC} for the ligand $\text{CC}(\text{H})\text{Ph}$ is reported to occur at 1568 cm^{-1} in the osmium(0) complex $[(\eta^6\text{-C}_6\text{H}_6)\text{Os}(\text{PPr}_3)_3(\text{CC}(\text{H})\text{Ph})]$ [31], but at wavenumbers ranging from 1590 to 1680 cm^{-1} in complexes of metals in oxidation states > 0 [27a]. Secondly, ν_{CC} moves to significantly lower wavenumber when CCH_2 or a related species changes its mode of ligation from terminal to bridging (e.g. $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu_2\text{-CO})(\mu_2\text{-CCH}_2)]$ 1567 cm^{-1} [32]; $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_2(\mu_2\text{-CO})(\mu_2\text{-CCH}_2)]$ ca. 1580 cm^{-1} [33a]; $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})_4(\mu_2\text{-CCH}_2)]$ 1542 cm^{-1} [33b]; $[\text{Os}_3(\text{CO})_9(\mu_2\text{-H})_2(\mu_3\text{-}\eta^2\text{-CCH}_2)]$ 1331 cm^{-1} [33a,c]; CCH_2 on $\text{Ru}(001)$ 1435 cm^{-1} [33d,e]). These results go so far as to suggest that the coordinated CCH_2 unit in **B** may have some bridging rôle, perhaps involving a second $\text{W}(\text{CO})_n$ fragment. However, the product **B** could be detected from the earliest stages of UV photolysis more-or-less irrespective of the matrix concentration of $\text{W}(\text{CO})_6$, and is unlikely therefore to implicate more than one metal atom.

(b) Characterisation of ν_{CC} of the coordinated CCH_2 ligand is complicated by the potential for coupling between the $\text{C}=\text{C}$ stretching and CH_2 in-plane bending motions [24,32,33]. Any factor tending to depress the

C=C stretching force constant (e.g. by increased π back-donation from the metal) enhances this coupling, ultimately to the point where no one fundamental can be designated, even approximately, as ν_{CC} . In these circumstances, the admixture of ν_{CC} with $\delta(\text{CH}_2)$ in varying degrees gives rise to two fundamentals in the region 1300–1800 cm^{-1} , both showing a substantial response to deuteration. As noted subsequently, the properties of supposed “ ν_{CC} modes” may also be subject to Fermi resonance. Hence it is plain that coordinated vinylidene groups are much less easy to pin down on the basis of their vibrational than of their ^{13}C NMR properties [27].

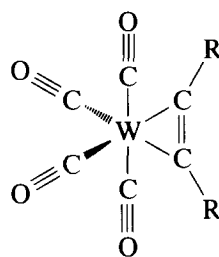
The vinylidene ligand may be expected to emulate a carbene in the spectroscopic properties it confers on the $\text{W}(\text{CO})_5$ substrate, and we note that the ν_{CO} features of **B** are indeed akin to those of the carbene complex $[\text{Ph}_2\text{CW}(\text{CO})_5]$ {2070(m), 1971(s), and 1963(s) cm^{-1} [34]}. In the light of this vinylidene–carbene parallel, it is noteworthy too that the carbene derivative $[\text{Ph}_2\text{CW}(\text{CO})_5]$, like **B**, shows two bands of comparable intensity at the low-energy end of its UV–vis spectrum [15]; these occur at 375 and 485 nm (cf. 364–367 and 460–465 nm for **B**). The same pattern is displayed by other carbene derivatives of the type $[\text{R}(\text{R}'\text{O})\text{CW}(\text{CO})_5]$ [15,35]. The two bands are assigned, in order of decreasing energy, (a) to a spin-allowed ligand-field transition (analogous to that responsible for the near-UV absorption of **A**), and (b) to a spin-allowed $\text{W} \rightarrow$ carbene(π^*) MLCT transition. According to Geoffroy et al. [15], the low-lying $\text{W} \rightarrow$ carbene charge-transfer state is inactive with respect to CO loss, a process associated rather with ligand-field excited states. It seems reasonable therefore to make analogous assignments of the near-UV and visible bands associated with **B**. Light with wavelengths near 369 nm may be expected to destroy **B**, as was observed to be the case, with a simultaneous build-up of $[\text{W}(\text{CO})_6]$, $[\text{X} \cdots \text{W}(\text{CO})_5]$ ($\text{X} = \text{CH}_4$ or Ar), free CO, and other products. In keeping with the notion that the electronic transition at 460–465 nm populates a $\text{W} \rightarrow$ vinylidene charge-transfer state which is inactive to CO loss, **B** was found to be largely unaffected by light with wavelengths near 445 nm as long as the matrix contained no more than ca. 2 mol% of the alkyne. Surprisingly, though, **B** was made photolabile at these wavelengths by the presence of relatively high concentrations of the alkyne (e.g. 5–10 mol%). Irradiation at $\lambda = 445$ nm then resulted in the photoejection of CO with the simultaneous appearance of **E** at the expense of **B**. This behaviour suggests that **B** and the alkyne may form a loosely bound adduct $[\text{R}(\text{H})\text{C}=\text{C}=\text{W}(\text{CO})_5 \cdots \text{alkyne}]$ with access to a relatively low-lying charge-transfer state (provided by visible radiation) in which a $\text{W}-\text{CO}$ bond is effectively ruptured. Such photoactivation of a substrate through weak complexation is by no means

uncommon [36], as demonstrated by the matrix photochemistry of molecules like O_2 [37], O_3 [38], CO_2 [7a] and NO [39].

3.3. **C**, $[(\eta^2\text{-RCCR}')\text{W}(\text{CO})_4]$

All of the tungsten pentacarbonyl complexes $[\text{X} \cdots \text{W}(\text{CO})_5]$, $[(\eta^2\text{-RCCR}')\text{W}(\text{CO})_5]$ and $[\text{R}(\text{H})\text{C}=\text{C}=\text{W}(\text{CO})_5]$ appear to be susceptible to CO loss on prolonged irradiation with light at wavelengths near 313 nm, and, as noted above, the alkyne-derived species are susceptible to such loss under the action of light at considerably longer wavelengths (e.g. $\lambda = 369$ nm). The IR spectra then bore witness to the formation of several products containing the $\text{W}(\text{CO})_4$ fragment with C_{2v} symmetry, each with a characteristic four-band pattern [11]. Some of these can be identified as being of the type $[\text{LL}'\text{W}(\text{CO})_4]$ (see Table 3), where L and L' may be the same or different ligands drawn from the following selection: $\text{X} (= \text{CH}_4$ or Ar); $\eta^2\text{-RC}\equiv\text{CR}'$; or $=\text{C}=\text{C}(\text{H})\text{R}$ ($\text{R} = \text{H}$ or Me). As in the experiments with $\text{Mo}(\text{CO})_6$ [5], however, the present experiments bring to light one particular product, **C**, the ethyne version of which has been characterised by IR absorptions at 2083 and 2008 cm^{-1} (due to ν_{CO} modes) and at 1522 cm^{-1} (in the region associated with ν_{CC} modes). This typically built up during photolysis at wavelengths in the range 300–400 nm.

The IR properties of **C**, allied to its conditions of formation, suggest that it is $[(\eta^2\text{-RCCR}')\text{W}(\text{CO})_4]$ with the structure **IV**. As with the corresponding molybde-



IV

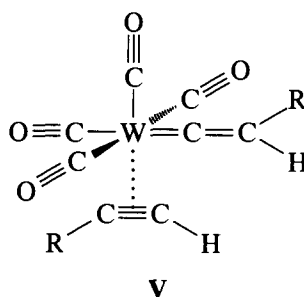
num species [5], the wavenumber of the ν_{CC} mode fails to distinguish between an η^2 -alkyne moiety acting as a 4e ligand, as in **IV**, and an η^1 -vinylidene moiety, $\text{R}(\text{H})\text{C}=\text{C}=\text{C}$, acting as a 2e ligand [20–23]. We favour the first of these options for **C** mainly on the grounds of its spectroscopic and photochemical kinship to the species believed to be $[(\eta^2\text{-RCCR}')\text{Mo}(\text{CO})_4]$ [5]. An important element in the identification of the molybdenum species was the finding that it appears to be formed even by the internal alkyne $\text{MeC}\equiv\text{CMe}$, which is not normally prone to isomerize to its vinylidene isomer. However, **C** plays a much less prominent part in the matrix photochemistry of $\text{W}(\text{CO})_6$ /alkyne mixtures, and experiments with argon matrices incorporating $\text{W}(\text{CO})_6$ / $\text{MeC}\equiv\text{CMe}$ mixtures failed to produce any

positive sign of alkyne-derived products other than $[(\eta^2\text{-MeC}\equiv\text{CMe})\text{W}(\text{CO})_5]$. If our identification of the tungsten version of **C** is correct, the ν_{CC} mode occurs at significantly lower wavenumber in $[(\eta^2\text{-HCCH})\text{W}(\text{CO})_4]$ than in the corresponding molybdenum compound {cf. $\nu_{\text{CC}} = 1522$ (W) and 1670 cm^{-1} (Mo) [15]}. As with complexes of the type $[(\eta^2\text{-RCCR}')\text{M}(\text{CO})_5]$ (M = Mo or W), this finding suggests that the alkyne binds more strongly to tungsten than to molybdenum, at the expense of its C≡C bond. **C** can thus be seen as a forerunner to carbonyl-deficient photoproducts such as $[(\eta^2\text{-RCCR}')_3\text{W}(\text{CO})]$, of which $[(\eta^2\text{-PhCCPh})_3\text{W}(\text{CO})]$ is a relatively stable, well authenticated example [40].

3.4. **E**, $\text{cis}[(\eta^2\text{-RC}_2\text{H})\{\eta^1\text{-R(H)CC}\}\text{W}(\text{CO})_4]$ (R = H or Me)

This product was closely linked to the fate of the product **B**, from which it was generated, together with free CO, initially under the action of visible light ($\lambda = 445$ nm); its concentration was observed to build up and then decline on exposure to near-UV light ($\lambda = 369$ nm). All the indications are that the propyne version of **B** behaves in a similar manner to the ethyne version, although it was formed more slowly and it was possible to identify clearly only one feature associated with a ν_{CC} mode (at 1757 cm^{-1}), other bands presumably being overlaid by more intense absorptions from other sources. An essential precondition to a substantial yield of **E** was an alkyne-rich environment, and so it seems likely that the molecule includes not one but two alkyne moieties in one form or another [i.e. $\text{RC}\equiv\text{CH}$ or $\text{C}=\text{C}(\text{H})\text{R}$]. The two IR absorptions attributable to ν_{CO} modes of **E** (at $2030\text{--}2040$ and $1870\text{--}1900$ cm^{-1}) are consistent with the presence of a $\text{W}(\text{CO})_4$ fragment possessing C_{2v} symmetry; these would then correspond to the high-energy a_1 and low-energy b_1 fundamentals of such a unit, with the intermediate a_1 and b_2 modes being hidden by the strong absorptions of other tungsten carbonyls in the region $1900\text{--}2000$ cm^{-1} . The presence of a band at 1808 cm^{-1} , which shifts to 1643 cm^{-1} for the C_2D_2 version, argues for the presence of an $\eta^2\text{-HC}\equiv\text{CH}$ ligand in the ethyne version of **E**. Somewhat more problematic are the other two bands at 1641 and 1615 cm^{-1} which shift to 1577 and 1552 cm^{-1} when C_2H_2 gives way to C_2D_2 . The change in the relative intensities brought about by perdeuteration of the ligand tends to suggest that these features are the components of a Fermi doublet derived (a) from the ν_{CC} fundamental of a second coordinated C_2H_2 (or C_2D_2) unit and (b) from an overtone or combination involving one or more lower-energy fundamentals of the $\text{W-C}_2\text{H}_2$ ($\text{W-C}_2\text{D}_2$) unit. In fact, a vinylidene–tungsten unit, $\text{H}_2\text{C}=\text{C}=\text{W}$ ($\text{D}_2\text{C}=\text{C}=\text{W}$) is expected to have a CH_2 wagging mode in the neighbourhood of 800 (750) cm^{-1} [22,24,32] and the overtone of this may well be in

resonance with the ν_{CC} fundamental. A similar interpretation would also account for the doublet at $1635/1624$ cm^{-1} displayed by the nickel vinylidene molecule $[\text{H}_2\text{C}=\text{C}=\text{Ni}]$ as formed on visible photolysis of an argon matrix containing the “ π -complex” $[(\eta^2\text{-C}_2\text{H}_2)\text{Ni}]$ [22]. Although we lack positive proof that the second coordinated C_2H_2 unit takes the form of the vinylidene isomer, $\text{H}_2\text{C}=\text{C}$, the circumstances leading to the formation of **E** suggest that we are dealing with $\text{cis}[(\eta^2\text{-RC}_2\text{H})\{\eta^1\text{-R(H)CC}\}\text{W}(\text{CO})_4]$ (R = H or Me) having the structure **V**. Support for this formulation



comes from the wavenumbers of the ν_{CC} modes of the ethyne version of **E** which imply the presence of one C–C unit with a bond order approaching 2 and one C–C unit with a bond order between 2 and 3; **V** represents the only way in which these requirements can be met with a C_{2v} $\text{W}(\text{CO})_4$ substrate so as to comply with the 18e rule. Between the wavenumbers of the observed ν_{CO} modes in **E** and those of the corresponding modes in carbene complexes of the type $\text{cis}[(\eta^2\text{-RC}\equiv\text{CR}')\{\text{Ph}(\text{MeO})\text{C}\}\text{W}(\text{CO})_4]$ [15] we note too a distinct similarity, giving us to believe that the $\text{W}(\text{CO})_4$ unit experiences much the same sort of ligand field in **E** as it does in the mixed carbene alkyne complexes.

With the recognition of **E** as a significant intermediate, $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ again part company in their photochemical behaviours. In an alkyne-rich matrix, the molybdenum version of **B** was found also to decay under the action of visible radiation with the simultaneous loss of CO, but it was not possible to identify any specific metal-containing product [5]. Although there is every likelihood that molybdenum forms an analogue of **E**, the low concentrations in which the precursor **B** is formed militated against fuller characterisation of the photochemical channels disposing of **B**.

4. Conclusions

UV photolysis ($\lambda = 313$ nm) of methane or argon matrices doped with $\text{W}(\text{CO})_6$ and an alkyne, $\text{RC}\equiv\text{CR}'$ (where $\text{R}, \text{R}' = \text{H}, \text{H}; \text{Me}, \text{H};$ or Me, Me), causes the $\text{W}(\text{CO})_6$ to suffer photodissociation of CO with the formation of $[\text{X} \cdots \text{W}(\text{CO})_5]$ ($\text{X} = \text{CH}_4$ or Ar) and the alkyne complex $[(\eta^2\text{-RC}\equiv\text{CR}')\text{W}(\text{CO})_5]$, **A**, wherein the dearth of vacant orbitals on the $\text{W}(\text{CO})_5$ substrate

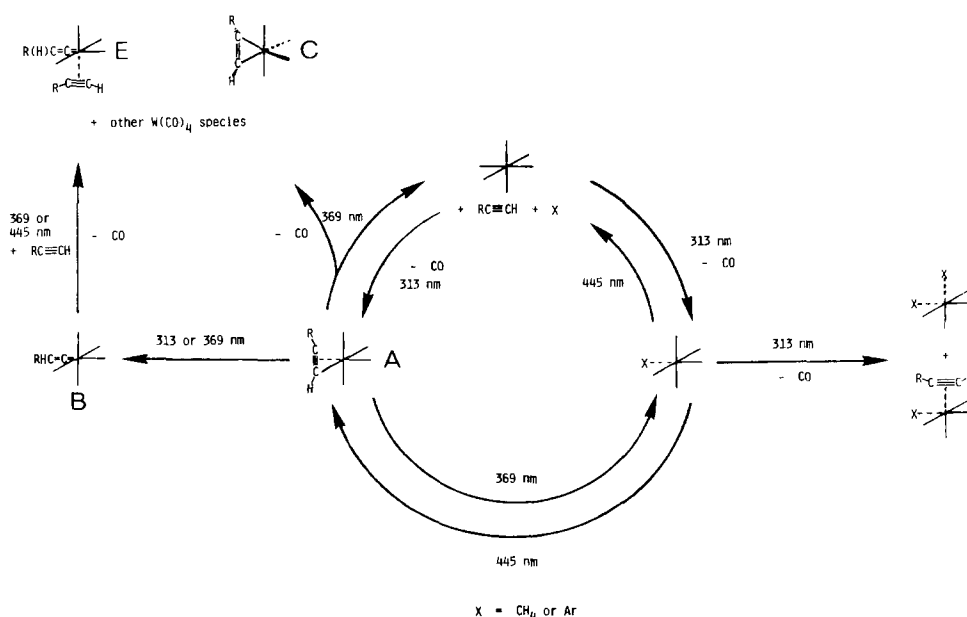
prevents the alkyne from functioning as more than a 2e donor of modest capacity. The alkyne complex has been characterised not only by the IR absorptions due to the ν_{CO} and, in two cases, to the ν_{CC} modes, but also by a near-UV absorption close to 370 nm for which the spin-allowed, ligand-field transition $b_2^2 e^4 a_1^0 b_1^0 \rightarrow b_2^2 e^3 a_1^1 b_1^0$ is probably responsible [10]. Interconversion of the species $[\text{W}(\text{CO})_6]$, $[\text{X} \cdots \text{W}(\text{CO})_5]$, and $[(\eta^2\text{-RC}\equiv\text{CR}')\text{W}(\text{CO})_5]$ proceeds in accordance with the photochemical conditions stipulated in Scheme 2.

As indicated in this Scheme, irradiation of $\text{W}(\text{CO})_6$ at wavelengths near 313 nm in the presence of a 1-alkyne, viz. $\text{HC}\equiv\text{CH}$ or $\text{MeC}\equiv\text{CH}$, results in the formation of the vinylidene complex $[\text{R}(\text{H})\text{C}=\text{C}=\text{W}(\text{CO})_5]$ ($\text{R} = \text{H}$ or Me), **B**, which outstrips the corresponding “ π -complex” $[(\eta^2\text{-RC}\equiv\text{CH})\text{W}(\text{CO})_5]$ as the main alkyne–metal product under these conditions. By contrast, the analogous molybdenum complex $[\text{R}(\text{H})\text{C}=\text{C}=\text{Mo}(\text{CO})_5]$ has been identified as a comparatively rare branch product in similar circumstances.

The vinylidene complex is labile to the loss of CO under the action of near-UV radiation ($\lambda < 400$ nm), and even visible radiation ($\lambda = 445$ nm) promotes such loss when the molecule has access to a comparative abundance of alkyne (5–10 mol%), presumably through the agency of a loosely bound charge-transfer complex $[\text{R}(\text{H})\text{C}=\text{C}=\text{W}(\text{CO})_5 \cdots \text{RC}\equiv\text{CH}]$. Conditions favouring the uptake of a second alkyne molecule lead to the formation of a product **E**, which is believed, on the evidence of the IR spectrum of the ethyne version, to be the mixed η^2 -alkyne vinylidene complex $\text{cis}[(\eta^2\text{-RC}\equiv\text{CH})(\eta^1\text{-R}(\text{H})\text{C}=\text{C})\text{W}(\text{CO})_4]$ ($\text{R} = \text{H}$ or Me). Irradiation with near-UV light causes the photoproduct **E** initially to build up, but in time to decay. However, the

multiplicity of matrix components present at this stage made it impossible to chart subsequent photochemical events with any degree of conviction. Irradiation at wavelengths in the range 300–400 nm undoubtedly gives rise to other complexes of the type $[\text{LL}'\text{W}(\text{CO})_4]$, where L and L' may be the same or different and may be matrix molecules (CH_4 or Ar), η^2 -alkyne, or vinylidene units. Table 3 includes a tentative identification of some of these species on the basis of the measured IR spectra. One product featuring in the later stages of such photolysis is probably $[(\eta^2\text{-RCCR}')\text{W}(\text{CO})_4]$ (e.g. $\text{R}, \text{R}' = \text{H}, \text{H}$), C, in which the alkyne functions formally as a 4e donor. In this regard tungsten appears to emulate molybdenum in its behaviour, but, as with the matrix photochemistry of $\text{Mo}(\text{CO})_6$ /alkyne systems, it was not feasible to determine the subsequent course of events.

The identification of the intermediates $[(\eta^2\text{-RC}\equiv\text{CH})\text{W}(\text{CO})_5]$, $[\text{R}(\text{H})\text{C}=\text{C}=\text{W}(\text{CO})_5]$, and $\text{cis}[(\eta^2\text{-RC}\equiv\text{CH})(\eta^1\text{-R}(\text{H})\text{C}=\text{C})\text{W}(\text{CO})_4]$ is noteworthy in that these represent the first three stages in the mechanism proposed to account for the photochemical polymerization of a terminal alkyne as mediated by a Group 6 metal carbonyl (see Scheme 1). Derived from the isomerization of the η^2 -alkyne complex, $[(\eta^2\text{-RC}\equiv\text{CH})\text{W}(\text{CO})_5]$, the vinylidene derivative $[\text{R}(\text{H})\text{C}=\text{C}=\text{W}(\text{CO})_5]$ is evidently the photoproduct better favoured by photolysis at wavelengths near 313 nm. Such a rearrangement may proceed by way of an η^2 - to η^1 -alkyne slippage, although there is at least one other pathway by which the change may occur [11,41–43], and, for a d^6 transition-metal centre like tungsten(0) in a pseudo-octahedral environment, the change is promoted by the relief of a repulsive 4e interaction between the filled π_{\perp} orbital of the alkyne and a filled d_{π} (t_{2g})



Scheme 2. Matrix photochemistry of $\text{W}(\text{CO})_6$ in the presence of a 1-alkyne.

orbital of the metal [12]. That access to additional alkyne molecules photosensitises the vinylidene complex to loss of CO then accounts for the comparatively facile formation of the mixed η^2 -alkyne vinylidene complex $[(\eta^2\text{-RC}\equiv\text{CH})(\eta^1\text{-R(H)C=C})\text{W(CO)}_4]$, **E**, which is itself photolabile under the influence of UV radiation ($\lambda < 400$ nm), and which is credited with being the key precursor to C–C bond-formation in the W(CO)_6 -catalysed photopolymerization of a 1-alkyne (see Scheme 1). By contrast, although there is circumstantial evidence that the much less abundant molybdenum complex $[\text{R(H)C=C=Mo(CO)}_5]$ behaves in a similar fashion in an alkyne-rich environment, we were unable to secure any direct sign of a molybdenum analogue of **E** [5], most probably for the simple reason of its being in too short supply to admit of spectroscopic detection.

The difference in behaviour between the alkyne derivatives of Mo(CO)_5 and W(CO)_5 may reflect a more favourable free energy balance for the vinylidene isomer in the case of the W(CO)_5 substrate. There is, for example, reason to believe that tungsten is more effective than molybdenum in the degree of π -delocalisation it achieves with the vinylidene ligand $\text{C}=\text{CH}_2$ [44]. It is no less possible, however, that the difference arises merely from subtle changes in the UV–vis absorption characteristics of the $[(\eta^2\text{-RC}\equiv\text{CH})\text{M(CO)}_5]$ and $[\text{R(H)C=C=M(CO)}_5]$ species, according to whether $\text{M} = \text{Mo}$ or $\text{M} = \text{W}$. Whatever the explanation may be, our results clearly suggest an explanation for the superior activity of W(CO)_6 , compared with Mo(CO)_6 , as a catalyst for the polymerization of terminal alkynes [6].

Acknowledgements

We acknowledge with gratitude support (i) from the S.E.R.C. for the purchase of equipment and the funding of a research assistantship (T.M.G.), (ii) from Jesus College, Oxford for the award of a research grant in 1992, and (iii) from the British Council for the award of a travel grant (to T.S.-B.) in 1993.

References and notes

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