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Matrix-isolation studies of alkyne complexes in the photochemical reactions of Mo(CO)$_6$ with alkynes [☆]

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Abstract

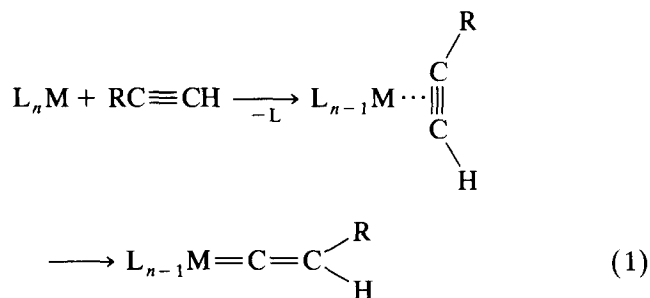Photolysis of a low-temperature matrix X (X = Ar or CH$_4$) doped with molybdenum hexacarbonyl and an alkyne RC≡CR′ (HC≡CH, MeC≡CH, or MeC≡CMe) leads to the formation of the corresponding alkyne complex of molybdenum pentacarbonyl, [(η^2-RC≡CR′)Mo(CO)$_5$], in addition to [X ··· Mo(CO)$_5$] and CO; the products have been detected and characterised by their IR and UV–vis absorption spectra. The species [(η^2-RC≡CR′)Mo(CO)$_5$], unlike [X ··· Mo(CO)$_5$], is stable with respect to irradiation in the green region of the visible spectrum, and a scheme has been devised for the photochemical interconversion of the three species [Mo(CO)$_6$], [(η^2-RC≡CR′)Mo(CO)$_5$] and [X ··· Mo(CO)$_5$] in a mixed matrix composed of RC≡CR′ and X molecules. An η^2-alkyne complex of the type [(RC≡CH)Mo(CO)$_5$] (R = H or Me) undergoes rearrangement to give what is believed to be a vinylidene complex [R(H)C=C=Mo(CO)$_5$]. Continued irradiation at λ = 313 nm causes the various pentacarbonyl complexes to lose CO with the formation of tetracarbonyl species. More significantly, irradiation at λ = 369 nm also results in photoejection of CO; this favours the formation of a product believed, on the evidence of its IR spectrum and of experiments with C$_2$D$_2$ and ^{12}C^{13}CH$_2$, to be [(η^2-RCCR′)Mo(CO)$_4$] (R,R′ = H,H or Me,Me) in which the alkyne is acting formally as a 4e ligand. The IR spectra serve notice of further changes on prolonged photolysis under these conditions. The results are discussed in relation to intermediates in the catalytic polymerization of 1-alkynes.

Keywords: Molybdenum; Carbonyl; Alkynes; Photolysis; Matrix isolation

1. Introduction

Reactions between transition-metal carbonyls and unsaturated organic molecules such as alkynes are of particular interest because of their relevance to organometallic synthesis [2] and to catalysis by transition-metal compounds [3]. By using molybdenum carbonyl compounds as catalysts, for example, alkynes can be metathesized [4], polymerized [5,6] or cyclo-oligomerized [5–7]. The catalytic reactions of alkynes with a Group 6 hexacarbonyl, M(CO)$_6$, as the catalyst precursor are widely believed [3,6,8,9] to involve the initial formation of an [(η^2-alkyne)M(CO)$_5$] complex, but there is little direct experimental evidence that this is the true catalytic intermediate. At the same time, there has been much interest in the rearrangement of a 1-alkyne to a

vinylidene at a d^6 metal centre [10], as in reaction (1) which may well be the initiation step in the polymerization of 1-alkynes.

$$L_nM + RC≡CH \xrightarrow[-L]{} L_{n-1}M \cdots \underset{\underset{H}{\overset{\displaystyle\|}{\underset{\displaystyle C}{\|}}}}{\overset{\displaystyle C-R}{}}$$

$$\longrightarrow L_{n-1}M=C=C{\overset{\displaystyle R}{\underset{\displaystyle H}{}}} \qquad (1)$$

L = 2-electron ligand

The matrix-isolation technique has proved extremely valuable as a means of identifying and characterising unstable species formed in photochemical reactions [11]. For example, it provided the first clearcut evidence for the formation of loosely bound adducts of the type

[X · · · M(CO)$_5$], where M is Cr, Mo or W and X is a molecule such as Ar, CH$_4$, CO$_2$ or CCl$_4$, on UV photolysis of M(CO)$_6$ molecules held in a solid, rigid matrix at low temperatures [12,13]. It was, then, a logical application of this method to investigate the photochemical behaviour of molybdenum hexacarbonyl in the presence of alkynes RC≡CR′, where RC≡CR′ = HC≡CH, MeC≡CH or MeC≡CMe.

2. Experimental details

The cryogenic equipment used at Oxford has been described elsewhere [13]. An Air Products "Displex" CS 202 closed-cycle helium refrigerator gave CsI window temperatures in the range 16–40 K inside a shroud maintained at a pressure below 10^{-7} Torr. Each gas mixture was prepared in a glass vacuum line by standard manometric techniques and the matrices were formed either by quenching pulses of the mixture [14] or by slow, continuous codeposition of the Mo(CO)$_6$ with the alkyne-doped matrix gas. 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. Selective irradiation was carried out with the aid of a suitable interference filter transmitting light at the following wavelengths: λ = 313, 369 or 445 nm, bandpass ca. 15 nm; or λ = 300–400 and 680–900 nm. IR spectra were recorded on a Perkin Elmer 580A dispersive spectrophotometer or a Mattson "Galaxy" FT–IR instrument; the spectral resolution was typically 1–2 cm^{-1}. UV–vis spectra were recorded on a Perkin Elmer–Hitachi Model 330 spectrophotometer.

The matrix gases Ar and CH$_4$ were used as supplied by B.O.C. ("Research" grade). Samples of Mo(CO)$_6$ (99% pure, supplied by Koch-Light) were purified before use by sublimation in vacuo. Each of the following 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 [^{13}C$_1$]ethyne, ^{12}C^{13}CH$_2$ (98.8 atom% ^{13}C; C/D/N Isotopes Inc.). Perdeuteriated ethyne, C$_2$D$_2$, was prepared by dropwise addition of D$_2$O (99.9 atom% D; Aldrich) to solid calcium carbide (East Anglia Chemicals) and also purified by fractional condensation in vacuo.

3. Results and discussion

The hexacarbonyl Mo(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 Mo(CO)$_6$:RC≡CR′:X = ca. 1:100:2000 and at a temperature of ca. 20 K. Exposure of the matrix to ultraviolet radiation (λ = ca. 313 nm) was observed, on

the evidence of its IR and UV–vis spectra, to result in photodissociation of CO and the formation of the unsaturated C_{4v} molecule Mo(CO)$_5$ [12] which weakly binds a molecule of either the matrix X or the alkyne RC≡CR′. As expected [15], continued irradiation under these conditions results in the loss of a second molecule of CO with the appearance and growth of IR bands due to complexes of the type X$_n$(RCCR′)$_{2-n}$Mo(CO)$_4$, where n = 0–2 and the Mo(CO)$_4$ fragment has C_{2v} symmetry.

Moving the wavelength of the photolysing radiation to λ = 445 nm so that it entered the lowest-energy spin-allowed ligand–field transition of the known complex [X · · · Mo(CO)$_5$] centred near 427 nm (Ar) or 404 nm (CH$_4$) [12] caused the growth of the IR and optical bands arising from a new product A, viz. a complex of the type [RC≡CR′ · · · Mo(CO)$_n$], and from the hexacarbonyl, at the expense of those associated with [X · · · Mo(CO)$_5$]. Hence A was shown to be characterised by ν_{CO} bands with wavenumbers (in cm^{-1}) and relative intensities plainly suggestive of a C_{4v} Mo(CO)$_5$ moiety: 2080–2090(w), 1955–1972(s), and 1931–1952(m) (w = weak; s = strong; and m = medium) [12,13]. With an ethyne- or propyne-doped matrix, A was found also to display a broad, weak band centred near 1822 and 1902 cm^{-1}, respectively, and attributable to a fundamental approximating to the ν_{CC} mode of the coordinated alkyne molecule [16,17]. The corresponding band of the complex A formed from but-2-yne may occur near 2060 cm^{-1} but, if so, was obscured by an absorption due to the much more abundant free alkyne [18]. The complex A was found also to give rise typically to two IR absorptions near 600 cm^{-1} attributable to Mo–C–O bending modes. In addition, A was distinguished by a band in the near-UV region of the UV–vis spectrum centred at a wavelength varying from 360 to 385 nm depending upon the identities of the alkyne, RC≡CR′, and the matrix material, X.

Irradiation into this band of A with photolysing light having λ = 369 nm resulted in depletion of the matrix in A and regeneration of both [X · · · Mo(CO)$_5$] and [Mo(CO)$_6$]. Although the results of the experiments leave little doubt that the reversible interconversion of A, [X · · · Mo(CO)$_5$], and [Mo(CO)$_6$] is the primary photochemical process, other changes in the IR spectra testify that significant secondary reactions are also taking place. It is noteworthy, for example, that whereas photolysis at λ = 445 nm reduces the concentration of free CO (with the regeneration of [Mo(CO)$_6$]), photolysis at λ = 369 nm augments this concentration. Hence it appears that coordination to an alkyne molecule photosensitises the Mo(CO)$_5$ fragment to further loss of CO, giving rise, presumably, to Mo(CO)$_4$ derivatives. At least one such derivative incorporating an alkyne group in one form or another (C) has been identified. This usually makes its first appearance in the later stages of visible photolysis (λ = 445 nm), but is most conspicu-

ous on near-UV photolysis (λ = 369 nm) which causes its concentration to rise, reach a maximum, and then slowly decrease, with the simultaneous appearance of another new product **D**. Positive characterisation of these products is made difficult by the overlapping of IR bands associated with the numerous ingredients of the matrix (e.g. [Mo(CO)$_6$], [X $\cdots$ Mo(CO)$_5$], **A**, other Mo(CO)$_4$ species, free CO [19], and free alkyne and its oligomers [16a,20]) and by the weakness of distinctive IR absorptions originating in the coordinated alkyne fragment (with extinction coefficients nearly an order of magnitude smaller than for the ν_{CO} fundamentals of the same molecule). In these circumstances it was not feasible to carry out useful experiments with ^{13}CO-enriched Mo(CO)$_6$ in order to pin down the stoicheiometry and likely structure of the metal carbonyl fragment, although some experiments with deuteriated and mono-^{13}C-substituted ethyne were performed, with results to be described subsequently.

When Mo(CO)$_6$ supported in a matrix doped with a 1-alkyne (HC≡CH or MeC≡CH), but not with MeC≡CMe, was irradiated with UV light at wavelengths close to 313 nm, the IR spectrum of the matrix displayed, in addition to the usual signs of free CO, [Mo(CO)$_6$], [X $\cdots$ Mo(CO)$_5$] and **A**, at least one additional ν_{CO} absorption, which we ascribe to yet another distinct product **B**. The versions of **B** derived from ethyne and propyne were both characterised by ν_{CO} bands near 2070 and 2000 cm^{-1}. Unlike **A**, **B** did not build up on irradiation with visible light (λ = 445 nm); matrices containing relatively low concentrations ($\leqslant 2$ mol%) of alkyne showed little effect, whereas with alkyne-rich (5–10 mol%) matrices the concentration of **B** was found to decrease upon such irradiation. The response to 369-nm light was hard to assess because of the masking effects of other bands (associated particularly with product **C**).

Representative IR and UV–vis absorption spectra are illustrated in Fig. 1, while Table 1 lists the IR absorptions for a methane matrix initially containing Mo(CO)$_6$ and C$_2$H$_2$, together with their individual responses to the various conditions of photolysis. Summaries of the spectroscopic results for the different molybdenum carbonyl complexes are given in Tables 2 and 3. The alkyne-containing photoproducts **A**, **B**, **C** and **D** were identified by the distinctive photochemical properties outlined above (and see Table 1, for example), the attribution of IR absorptions to a particular product being based on the recognition of common growth–decay characteristics. Numerous tests were carried out to determine the effects of annealing the matrices at temperatures up to ca. 35 K at different stages of photolysis, but in no case did this result in any significant change in the IR spectrum of the matrix.

Each of the product-types will now be considered in turn.

3.1. A, [(η^2-RC≡CR')Mo(CO)$_5$]

The spectroscopic properties show fairly clearly that **A** is an adduct of the type alkyne $\cdots$ Mo(CO)$_5$. This identification is consistent with the IR spectrum of **A**, with the near-UV band at 360–385 nm attributable to the lowest-energy spin-allowed ligand-field transition of such a molecule, and with the obvious photochemical relationship which the molecule bears to the other six-coordinated species [Mo(CO)$_6$] and [X $\cdots$ Mo(CO)$_5$] (X = Ar or CH$_4$). The position of the ligand-field transition implies that the coordinated alkyne ligand lies between pyridine (λ = 385 nm [21]) and PCl$_3$ (λ = 355 nm [21]) or N$_2$ (λ = 352 nm [22]) in the overall degree to which it perturbs the Mo(CO)$_5$ unit, with this perturbation decreasing in the order HC≡CH > MeC≡CH > MeC≡CMe. The IR band that is most responsive to the nature of the interaction with Mo(CO)$_5$ is the lower-frequency a_1 mode, approximating to ν_{CO} for the unique axial CO group, i.e. the one *trans* to the foreign substituent. This feature undergoes a blue shift of 4–20 cm^{-1} with the switch from [X $\cdots$ Mo(CO)$_5$] to
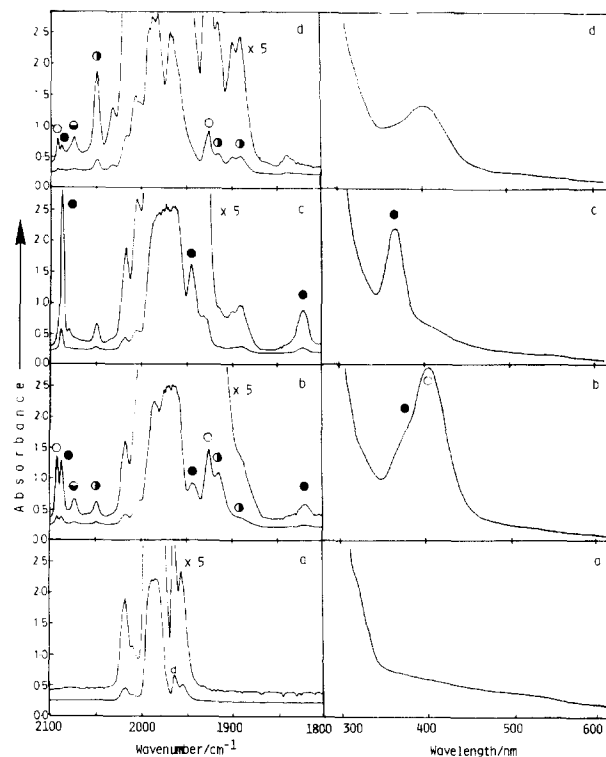

Fig. 1. IR absorption spectrum in the region 1800–2100 cm^{-1} and UV–vis absorption spectrum in the region 300–600 nm displayed by a solid CH$_4$ matrix containing Mo(CO)$_6$ and C$_2$H$_2$ with the composition Mo(CO)$_6$:C$_2$H$_2$:CH$_4$ = ca. 1:100:2000 at 20 K, showing the effects of short-term photolysis at different wavelengths. (a) Spectra of the matrix after deposition. (b) Spectra after photolysis at λ = 313 nm. (c) Spectra after photolysis at λ = 445 nm. (d) Spectra after photolysis at λ = 369 nm. Bands are labelled as follows: ○ [CH$_4$ $\cdots$ Mo(CO)$_5$]; ● **A**, [(η^2-C$_2$H$_2$)Mo(CO)$_5$]; ◖ **B**, [H$_2$C=C=Mo(CO)$_5$]; ◐ Mo(CO)$_4$ species; and "d" [HC≡CH]$_2$.

[RC≡CR′ ··· Mo(CO)₅], with a wavenumber which follows the order HC≡CH > MeC≡CH > MeC≡CMe, controlled presumably by the increasing donor power of the ligands in this series. It has been suggested that the extent of M → CO back donation (M = metal atom) is

reflected in the variation of the second a_1 and the e ν_{CO} fundamentals of the M(CO)₅ moiety. As the alkyne changes from HC≡CH to MeC≡CH to MeC≡CMe, these modes shift to lower wavenumbers, indicating that the extent of back donation from the metal to the alkyne

Table 1

IR spectrum of a solid methane matrix doped with Mo(CO)₆ and C_2H_2 [Mo(CO)₆ : C_2H_2 : CH₄ = ca. 1 : 100 : 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	λ = 313 nm	λ = 445 nm	λ = 369 nm	Molecule	Mode
2141 [c] w	—	↑	↓	↑	} CO	ν_{CO}
2137 [c] w	—	↑	↓	↑		
2092 w	—	↑	↓	↑	CH₄ · Mo(CO)₅	ν_{CO}, a_1
2088 w	—	↑	↑	↓	A	ν_{CO}, a_1
2083 w	—	—	↑	↑	C	ν_{CO}, a_1
2078 [c] w	—	↑	↓	↑	} B	ν_{CO}, a_1
2074 [c] w	—	↑	↓	↑		
2069 vw	—	—	↑	↑	Mo(CO)₄ species [d]	ν_{CO}
2064 vw	—	—	↑	↓	Mo(CO)₄ species [d]	ν_{CO}
2056 w	—	↑	↑	↑	Mo(CO)₄ species [d]	ν_{CO}, a_1
2049 w	—	↑	unchanged	↑	Mo(CO)₄ species [d]	ν_{CO}, a_1
2032 w	—	—	—	↑	Mo(CO)₄ species [d]	ν_{CO}
2020 [c] w	↑	↓	↑	↓	} Mo(CO)₆	ν_{CO}, e_g [e]
2018 [c] w	↑	↓	↑	↑		
2015 w	—	↑	↓	↓	Mo(CO)₄ species [d]	ν_{CO}
2010 vw	↑	↓	—	—	Mo(^{12}CO)₅(^{13}CO)	ν_{CO}, a_1
2006 w	—	—	↑	↑	C	ν_{CO}, b_1
2000 w	—	↑	↓	↑	B	ν_{CO}, e
1992 [c] m	—	—	↑	↑		
1989 [c] vs	↑	↓	—	—		
1987 [c] vs	↑	↓	↑	↑	} Mo(CO)₆	ν_{CO}, t_{1u}
1985 [c] vs	↑	↓	—	—		
1983 [c] vs	↑	↓	—	—		
1982 [c] vs	↑	↓	—	—		
1974 [c] s	—	—	↑	↓	A	ν_{CO}, e
1971 [c] vs	—	↑	↓	↓	} CH₄ · Mo(CO)₅	ν_{CO}, e
1969 [c] vs	—	↑	↓	↓		
1968 [c] vs	—	↑	↑	↓	A	ν_{CO}, e
1966 [c] vs	—	↑	↓	↑	CH₄ · Mo(CO)₅	ν_{CO}, e
1965 s	↑	↑	↓	↓	[C_2H_2]₂	ν_{CC}
1945 w	—	↑	↑	↓	A	ν_{CO}, a_1
1942 [c] w	—	↑	↓	—	} Mo(CO)₄ species [d]	ν_{CO}, b_2
1941 [c] w	—	↑	↓	—		
1931 vw	↑	↓	↑	↓	[C_2H_2]₂ · Mo(CO)₆	ν_{CC}
1930 [c] m	—	↑	↓	—	} CH₄ · Mo(CO)₅	ν_{CO}, a_1
1927 [c] m	—	↑	↓	↑		
1917 w	—	—	—	↑	Mo(CO)₄ species [d]	ν_{CO}
1915 [c] w	—	↑	↓	—	} Mo(CO)₄ species [d]	ν_{CO}
1913 [c] w	—	↑	↓	↓		
1900 [c] w	—	↑	↓	↑	} Mo(CO)₄ species [d]	ν_{CO}
1898 [c] w	—	↑	↓	↓		
1893 [c] w	—	↑	unchanged	↓	} Mo(CO)₄ species [d]	ν_{CO}
1891 [c] w	—	—	↑	↑		
1889 w	—	↑	↑	↓	Mo(CO)₄ species [d]	ν_{CO}
1843 vw	—	—	↑	↓	Mo(CO)₄ species [d]	ν_{CC}
1822 w,br	—	↑	↑	↓	A	ν_{CC}
1669 w	—	—	↑	↑	C	ν_{CC}

[a] Spectrum covers the range 1500–2200 cm⁻¹; w = weak, m = medium, s = strong, v = very, br = broad. [b] Photolysis conditions do not include the effects of prolonged irradiation. ↑ appears and/or grows; ↓ decays; — absent or obscured. [c] Bands split by matrix site effects. [d] Mo(CO)₄ species of the type LL′Mo(CO)₄ where L,L′ represents any two of the same or different ligands from CH₄, C_2H_2, or =C=CH₂ (see Table 3). [e] Vibrational mode activated in IR absorption through a lowering of molecular symmetry imposed by the matrix cage.

decreases in the order HC≡CH > MeC≡CH > MeC≡CMe. The complexes RC≡CH ··· Mo(CO)₅ (R = H or Me) have been detected previously by their ν_{CO} bands following UV photolysis of Mo(CO)₆ in the presence of the alkyne in n-hexane solution [23], with results similar to those from our matrix experiments.

The observation of a band attributable to what is, at least in part, the ν_{CC} mode of the coordinated alkyne discloses a red shift of 152 and 235 cm⁻¹ relative to the corresponding mode of free HC≡CH [16] and MeC≡CH [17], respectively. It is far from certain, however, that the mode does not derive in part from other motions within the alkyne molecule, that it has the same make-up in different alkyne molecules, or that this make-up is retained on coordination of a given alkyne molecule to a metal centre. It was not possible to assess the effect of replacing C₂H₂ in A by C₂D₂ because of masking by absorptions due to [C₂D₂]ₙ aggregates [16,20]. However, replacement of normal C₂H₂ by ¹²C¹³CH₂ caused the band at ca. 1822 cm⁻¹ to shift to 1789 cm⁻¹, but with no hint of any splitting or broadening. The obvious inference to be drawn from this experiment is that the carbon atoms of the coordinated C₂H₂ molecule are equivalent, and the shift tallies exactly with that predicted for the vibration of a diatomic molecule composed of pseudo-atoms with masses of 13 (¹²CH) or 14 a.m.u. (¹³CH).

All the available evidence points therefore to the

Table 2
Spectroscopic and photochemical properties of alkyne or vinylidene molybdenum carbonyl products identified on photolysis of Ar or CH₄ matrices containing Mo(CO)₆ and an alkyne

Product	IR bands				UV–vis bands/nm		Effects of photolysis		
	ν_{CO}/cm^{-1}		ν_{CC}/cm^{-1}				$\lambda = 313$ nm	$\lambda = 445$ nm	$\lambda = 369$ nm
A, HC≡CH ··· Mo(CO)₅	2090 [a] 1972 [a] 1952 [a]	2088 [b] 1969 [b] 1946 [b]	ca. 1820 [a] (1789 [a,c])	1822 [b]	360 [a]	368 [b]	↑	↑	↓
A, MeC≡CH ··· Mo(CO)₅	2086 [a] 1963 [a] 1943 [a]	2084 [b] 1959 [b] 1933 [b]	1902 [b]		372 [a]	379 [b]	↑	↑	↓
A, MeC≡CMe ··· Mo(CO)₅	2082 [a] 1957 [a] 1937 [a]	2081 [b] 1956 [b] 1931 [b]	–		380 [a]	385 [b]	↑	↑	↓
B, H₂C=C=Mo(CO)₅	2075 [a] 2001 [a]	2074 [b] 2000 [b]	–		–		↑	↓	↑?
B, MeHC=C=Mo(CO)₅	2070 [a]	2069 [b] 2001 [b]	–		–		↑	↓	↑?
C, HC≡CH ··· Mo(CO)₄	2082 [a] 2006 [a] 1963 [a,d]	2083 [b] 2006 [b]	1670 [a] (1565 [a,d]) (1641 [a,c])	1669 [b]	–		–	↑	↑
C, MeC≡CMe ··· Mo(CO)₄	2088 [a] 2007 [a]		1736 [a]		–		–	↑	↑
C₂H₂ version of **D**	1954 [a] 1946 [a]		? (1469 [a,d])		–		–	–	↑

[a] Ar matrix.
[b] CH₄ matrix.
[c] Relates to ¹²C¹³CH₂ derivative.
[d] Relates to C₂D₂ derivative.

conclusion that **A** is to be formulated as $[(\eta^2\text{-}RC{\equiv}CR')Mo(CO)_5]$ with the structure **I**. The signs are

I
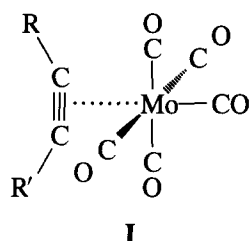
that the mutual perturbation of the two components, $RC{\equiv}CR'$ and $Mo(CO)_5$, is only modest, the alkyne acting as quite a weak 2e-donor, not unlike an alkene molecule in similar circumstances [24], and presumably with but a small elongation of the $C{\equiv}C$ bond. Comparatively few η^2-alkyne derivatives of molybdenum have been described previously, although similar derivatives of tungsten are more familiar. Hence it is evident that stable, isolable η^2-alkyne complexes are usually characterised by a stronger $M \cdots$ alkyne interaction than that

suggested by the spectroscopic properties of **A**. For example, representative η^2-ethyne complexes in which the ethyne functions formally as a 2e donor have ν_{CC} modes typically in the range 1610–1800 cm^{-1} [25], as exemplified by the following (wavenumbers in cm^{-1}): $[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}C_2H_2)]$ 1613 [25]; *trans*-$[Ir(PPr^i_3)_2(Cl)(\eta^2\text{-}C_2H_2)]$ 1700 [25]; *trans*-$[Rh(PPr^i_3)_2(Cl)(\eta^2\text{-}C_2H_2)]$ 1712 [25]; $[(\eta^5\text{-}C_5H_5)Cr(NO)(CO)(\eta^2\text{-}C_2H_2)]$ 1720 [25]; $[Ir(SnCl_3)(CO)(PPh_3)_2(\eta^2\text{-}C_2H_2)]$ 1678 [25]; $[(\eta^5\text{-}C_5H_5)RuL_2\,(\eta^2\text{-}C_2H_2)]^+$, L = PMe$_2$Ph 1750 [26a] and L = PMe$_3$ 1748 [26b]; $[Ni(PPh_3)_2(\eta^2\text{-}C_2H_2)]$ 1630 [26c]; and $[Cu\{HN(2\text{-}C_5H_4N)_2\}(\eta^2\text{-}C_2H_2)]^+$ 1795 [26d]. Likewise, the crystal structures of the complexes $[(\eta^5\text{-}C_5H_5)Ru(PMe_2Ph)_2(\eta^2\text{-}C_2H_2)]^+[BF_4]^-$ [26a], $[Ni(PPh_3)_2(\eta^2\text{-}C_2H_2)]$ [26c] and $[Cu\{HN(2\text{-}C_5H_4N)_2\}(\eta^2\text{-}C_2H_2)]^+[BF_4]^-$ [26d] show that coordination elongates the $C{\equiv}C$ bond of the alkyne molecule by up to 4 pm. The copper compound comes closest to **A** in its behaviour with ν_{CC} = 1795 cm^{-1} and a $C{\equiv}C$ distance not perceptibly different from that in free ethyne.
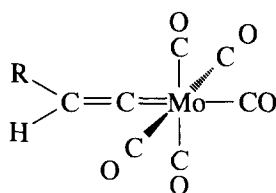
Table 3

Spectroscopic properties of alkyne or vinylidene molybdenum carbonyl products formed in low-temperature matrices (ca. 20 K) [a]

Adduct type $LMo(CO)_5$, C_{4v} L =	Medium	IR-active ν_{CO} wavenumber/cm^{-1}			Lowest-energy spin-allowed ligand–field transition/nm
		a_1	e	a_1	
Ar	Ar	2095	1972.5	1931.5	427
CH$_4$	CH$_4$	2092.5	1966	1926	404
HC≡CH	Ar	2090	1972	1952	360
	CH$_4$	2088	1969	1945.5	368
	n-hexane [b]	2092	1974	1950	—
MeC≡CH	Ar	2086	1963	1943	372
	CH$_4$	2084	1959	1933	379
	n-hexane [b]	2085	1963	1940	—
MeC≡CMe	Ar	2082	1957	1937	380
	CH$_4$	2080.5	1955.5	1931	385
H$_2$C=C=	Ar	2075	2001	[c]	[d]
	CH$_4$	2074	2000	[c]	[d]
Me(H)C=C=	Ar	2070	[c]	[c]	[d]
	CH$_4$	2069	2001	[c]	[d]

$LL'Mo(CO)_4$, C_{2v} L,L' =	Medium	a_1	b_2	a_1	b_1	Lowest-energy
Ar,Ar	Ar	2062	1948	—	1891	—
CH$_4$,CH$_4$	CH$_4$	2056	1945	1927	1887	520
C$_2$H$_2$,Ar	Ar	2051.5	[c]	1919	1893	—
C$_2$H$_2$,CH$_4$	CH$_4$	2050	[c]	1918	1891	—
[e]	Ar	2035	[c]	1918	—	—
[e]	CH$_4$	2032	[c]	1916	1899	—
MeC≡CH,Ar	Ar	2048	[c]	1918	1888	—
MeC≡CH,CH$_4$	CH$_4$	2043	[c]	1917.5	1887	—
MeC≡CMe,Ar	Ar	2032	[c]	1913	1886	—
MeC≡CMe,CH$_4$	CH$_4$	2032	[c]	1913	1882	—

[a] These results are based, where possible, on optimum conditions, with dilute matrices and relatively short photolysis times; accordingly, the wavenumbers for a given species do not necessarily tally exactly with the results given in Table 1. [b] Solution, Ref. [22]. [c] Obscured by absorptions due to $[Mo(CO)_6]$, $[(\eta^2\text{-alkyne})Mo(CO)_5]$, and $[X \cdots Mo(CO)_5]$ (X = Ar or CH$_4$). [d] Obscured by absorptions due to $[X \cdots Mo(CO)_5]$. [e] $Mo(CO)_4$ species generated by photolysis at λ = ca. 369 nm may have L,L' = C$_2$H$_2$,C$_2$H$_2$; C$_2$H$_2$,=C=CH$_2$; or X,=C=CH$_2$ (X = Ar or CH$_4$).

3.2. B, [R(H)C = C = Mo(CO)₅]

As noted previously, the photoproduct **B** was formed only in the presence of a 1-alkyne, viz. HC≡CH or MeC≡CH, being generated on irradiation of the $Mo(CO)_6$ with light at wavelengths near 313 nm and unaffected by exposure to visible light ($\lambda = 445$ nm), except in alkyne-rich matrices. Repeated attempts at detecting one or more IR bands associated with the coordinated alkyne group were, unfortunately, to no avail, being frustrated in all probability by the relatively low yields of the product even under the most favourable conditions. **B** cannot therefore be identified with certainty, but is most likely to be the vinylidene derivative $[R(H)C=C=Mo(CO)_5]$ (R = H or Me) with the structure **II**. This conclusion draws on the circumstances of

$$R,\ H \underset{H}{\overset{R}{>}}C=C=\underset{\underset{O}{\overset{|}{C}}\ \underset{O}{\overset{|}{C}}}{\overset{\overset{O}{\overset{\|}{C}}\ \overset{O}{\overset{/}{C}}}{Mo}}-CO$$

II

the experiments, the intensity and wavenumber pattern of what can be seen of the ν_{CO} modes of **B**, and the implication that the $Mo(CO)_5$ group is coordinated to a ligand which is a better π-acceptor than the η^2-alkyne [27]. It gains weight too from the spectroscopic similarity of the new species (a) to the corresponding tungsten compounds which, being formed in much better yields, can be characterised in more detail [28], and (b) to the known vinylidene tungsten carbonyls [Bu^t(R)C=C= W(CO)₅] [R = Me, ν_{CO} 2088(w), 1986(w,sh), 1977(vs), and 1969(s) cm^{-1}; R = Et, ν_{CO} 2088(w), 1986(w,sh), 1978(vs), and 1970(s,sh) cm^{-1} [29]; sh = shoulder].

In its reactions with many transition-metal centres, M, a 1-alkyne, RC≡CH, is typically susceptible to isomerisation, thereby yielding vinylidene complexes containing one or more M=C=C(R)H units [27]. This is widely believed to entail a 1, 2 hydrogen shift [30,31], although the possibility of a 1,3 hydrogen shift implicating an alkynylmetal hydride intermediate cannot be discounted [32]. The rearrangement is known to be common for octahedral derivatives of d^6 transition metals [33–35]. In view of the importance of alkyne $\pi_\perp$ donation (see Fig. 4) in octahedral d^4 complexes, it has been suggested that the alkyne → vinylidene rearrangement is promoted by the unfavourable 4-electron 2-centre d_π–$\pi_\perp$ conflict in a d^6 complex like [(η^2-RC≡CH)Mo(CO)₅] which has no vacant d_π orbitals.

3.3. C, [(η²-RCCR')Mo(CO)₄]

The product **C** has been characterised reasonably fully only for the systems including ethyne and but-2-yne, but there are no grounds for believing that an analogous product is not formed from $Mo(CO)_6$ and
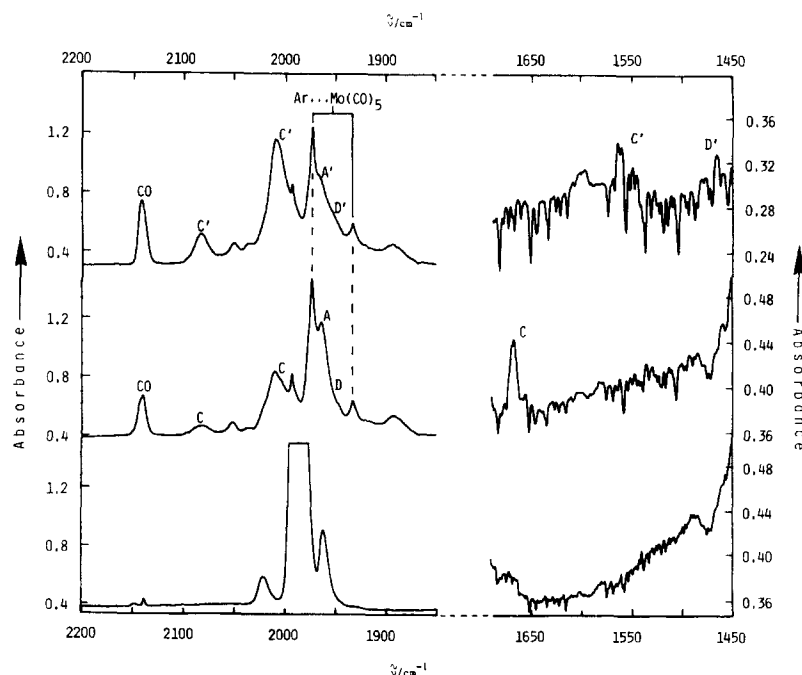

Fig. 2. IR absorption spectra in the regions 1900–2200 and 1450–1650 cm^{-1} displayed by Ar matrices containing $Mo(CO)_6$ and ethyne after irradiation first with light at wavelengths near 313 nm (1 h) and then at wavelengths in the range 300–400 nm (2 h). (a) Sample containing $Mo(CO)_6 + C_2H_2$ after deposition. (b) Same sample after photolysis showing bands due to the photoproduct **C**. (c) Sample containing $Mo(CO)_6 + C_2D_2$ after photolysis showing bands due to the deuteriated photoproducts **C'** and **D'**.

propyne. **C** typically makes its first appearance during the second stage of photolysis, i.e. with light at wavelengths near 445 nm, but gains prominence in the final stage of photolysis, i.e. at $\lambda = 369$ nm, before decaying slowly to give place to the product **D**. These processes can be accelerated somewhat by irradiation at $\lambda = 300$–400 nm after the opening round of photolysis at $\lambda = 313$ nm. No distinct UV–Vis absorption could be ascribed to **C**, and in order to build up the concentration of **C** to a level allowing the detection of its characteristic IR absorptions it was necessary to work with relatively thick matrices typically having the composition $Mo(CO)_6 : RC{\equiv}CR' : X = 1 : 50–400 : 1000–2000$. A second precondition for the detection of **C** appeared to be the presence in the matrix of appreciable concentrations of $Mo(CO)_4$ species (q.v.) and/or the release of free CO from existing metal carbonyls. It is likely, therefore, that **C** is formed from $Mo(CO)_4$ by the attachment of one or more alkyne moieties in some form.

The IR characteristics of **C**, as recorded in Table 2, include ν_{CO} bands at 2083(w), 2006(s), and 1963(m) cm^{-1} and, most distinctively in addition, a weak absorption at 1670 cm^{-1} (for HC≡CH, see Fig. 2) or 1736 cm^{-1} (for MeC≡CMe). Problems of masking by the absorptions of other species made it far from easy to identify the ν_{CO} modes; indeed, the feature at 1963 cm^{-1} could be discerned for the ethyne version of **C** only when C_2H_2 gave place to C_2D_2 (thereby shifting

the strong absorption at ca. 1965 cm^{-1} due to $[C_2H_2]_n$ aggregates [16]). We cannot therefore be certain that all the ν_{CO} bands of **C** have been observed, but the wavenumber and intensity pattern is consistent with the presence of an $Mo(CO)_4$ fragment with local C_{2v} geometry. The same geometry prevails for $Mo(CO)_4$ trapped in an "inert" matrix [15], and for the complex cis-$[(\eta^2\text{-}C_2H_4)_2Mo(CO)_4]$ [24], but the average ν_{CO} frequency of the unit comes out substantially higher in **C**, albeit falling some way short of the corresponding frequency in the peroxo complex $[(\eta^2\text{-}O_2)Mo(CO)_4]$ [36]. Hence we are bound to conclude that the metal atom in **C** is under the influence of a strongly electron-withdrawing group.

The band at 1670 or 1736 cm^{-1} is most plausibly identified with a ligand vibration approximating more or less closely to a ν_{CC} mode. That this occurs for the ethyne derivative at a considerably lower energy than does the corresponding mode of **A** argues for a much stronger metal–alkyne interaction in **C**, with a corresponding enhancement in the degree of charge transfer. For the ethyne version of **C**, the energy of the mode is compatible either with an η^2-C_2H_2 group acting as a 4e ligand, which typically displays a "ν_{CC} mode" in the range 1550–1720 cm^{-1} (e.g. $[(\eta^5\text{-}C_5H_5)W(CO)(Me)\text{-}(\eta^2\text{-}C_2H_2)]$ 1710 cm^{-1} [37a], $[(\eta^5\text{-}C_5H_5)W(O)(Me)\text{-}(\eta^2\text{-}C_2H_2)]$ 1585 cm^{-1} [37b], and $[WCl_4(\eta^2\text{-}C_2H_2)_2]_2$ 1628 cm^{-1} [37c]), or with a vinylidene ligand =C=CH$_2$, the corresponding mode of which normally
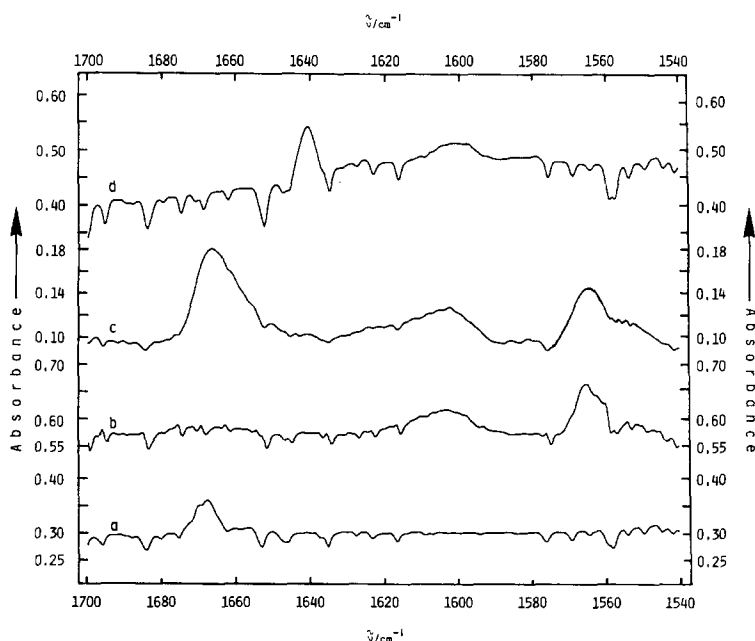

Fig. 3. IR absorption spectra in the region 1540–1700 cm^{-1} showing the ν_{CC} band associated with the photoproduct **C** as displayed by Ar matrices containing $Mo(CO)_6$ and ethyne after irradiation first with light at wavelengths near 313 nm (1 h) and then at wavelengths in the range 300–400 nm (1 h). (a) Sample containing $Mo(CO)_6 + C_2H_2$; (b) sample containing $Mo(CO)_6 + C_2D_2$; (c) sample containing $Mo(CO)_6$ + roughly equimolar proportions of C_2H_2 and C_2D_2; and (d) sample containing $Mo(CO)_6 + {}^{12}C{}^{13}CH_2$.

falls in the range 1620–1680 cm^{-1} [25]. As shown in Fig. 3 and recorded in Table 2, the analogous IR feature displayed by the C_2D_2 version of **C** was found to occur at 1565 cm^{-1}. Experiments with an equimolar mixture of C_2H_2 and C_2D_2 gave an IR spectrum of **C** including only two bands in the region 1500–1700 cm^{-1}, one at 1670 and the other at 1565 cm^{-1}. It is also apparent from Fig. 3 that replacement of normal C_2H_2 by $^{12}C^{13}CH_2$ gave only a single band at 1641 cm^{-1} no broader than that of the parent compound at 1670 cm^{-1}. There are, it is true, circumstances in which specific isotopic labelling of this sort fails to discriminate between the two isotopomers of what is essentially a diatomic ligand coordinated "end-on" to a metal atom. Such is the case, for example, with the *bis*(superoxide) molecules $[(\eta^1\text{-}O_2)_2M]$ (M = Cr or Cu) [38] and with $[(\eta^1\text{-}N_2)Mo(CO)_5]$ [22], and simplified normal coordinate analysis calculations confirm that the same could be true of the unit $H_2C=C=Mo$ if the Mo=C stretching force constant is much smaller than that for C=C stretching. On the other hand, the precedents set by the simple vinylidene nickel complex $[H_2C=C=Ni]$ {formed by photolysis of $[(\eta^2\text{-}C_2H_2)Ni]$ in an argon matrix [16b]} lead us to expect a detectable difference between ν_{CC} for the species $H_2{}^{12}C={}^{13}C=Mo$ and $H_2{}^{13}C={}^{12}C=Mo$. If vibrational spectroscopy is to provide a positive diagnostic test of η^2-alkyne vs. η^1-vinylidene coordination under conditions like these, however, there is a strong case for undertaking a detailed vibrational study of a well authenticated vinylidene derivative like $[(\eta^5\text{-}C_5H_5)Ru(C=CH_2)(PMe_2Ph)_2]^+[BF_4]^-$ [26a] or *trans*-$[(Ph_2PCH_2PPh_2)_2(Cl)Ru=C=CH_2]^+[PF_6]^-$ [39]; this would need to take into account the properties of different isotopomers and also afford a satisfactory normal coordinate analysis treatment.

Table 4 compares **C** with $[Ni=C=CH_2]$ [16b], $[S=C=CH_2]$ [40], $[Se=C=CH_2]$ [41], and $[(\eta^2\text{-}C_2H_2)Ni]$ [16b] in terms of the frequencies of what are ajudged to be the ν_{CC} modes of different isotopomers. In its response to the replacement of the $^{12}C_2H_2$ moiety by either $^{12}C^{13}CH_2$ or $^{12}C_2D_2$, **C** is thus seen to imitate not the vinylidene or ketene derivatives, but the η^2-ethyne complex $[(\eta^2\text{-}C_2H_2)Ni]$.

In summary, the spectroscopic evidence points to the presence of an $Mo(CO)_4$ unit with C_{2v} symmetry and of at least one strongly perturbed η^2-alkyne ligand, with substantial withdrawal of electron density away from the metal. **C** appears to be a relatively stable product and is likely therefore to conform to the 18-electron rule. Possible formulations are, then, (a) $[(\eta^2\text{-}RCCR')Mo(CO)_4]$, **III** {cf. $[(\eta^2\text{-}O_2)Mo(CO)_4]$ [36]}, (b) *cis*-$[(\eta^2\text{-}RCCR')\{R(R')C=C=\}Mo(CO)_4]$, **IV**, and (c) *cis*-$[(\eta^2\text{-}RCCR')_2Mo(CO)_4]$, **V**. The present results afford no definitive test of which of these is correct, but the consensus of the spectroscopic evidence, with its

implications of an alkyne group functioning not as a 2e-donor (as in **IV** and **V**) but as a 4e-donor (as in **III**), favours structure **III**. As noted already, it is impossible

III   **IV**

V
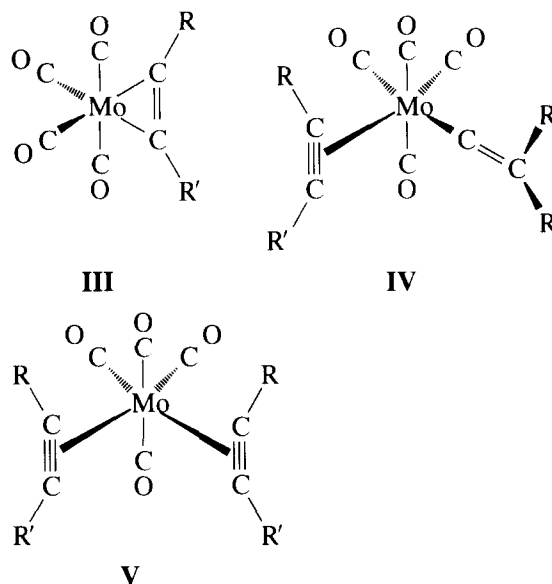
to exclude completely the presence of a vinylidene ligand, as in **IV**, particularly if, for reasons of low intensity and/or masking by other absorptions, one of the ligands did not act as a reporter group in the measured IR spectra. On the other hand, the likelihood of this, or of a related product, is greatly reduced by the finding that the internal alkyne MeC≡CMe, which is not normally converted to its vinylidene isomer C=CMe$_2$ even by coordination to a favourable metal centre, gives rise to a product with all the same photochemical and spectroscopic properties as the ethyne version of **C**.

If this identification is correct, we have in $[(\eta^2\text{-}RCCR')Mo(CO)_4]$ (R,R' = H,H or Me,Me) the first example known to us of a d^6 metal centre acting as host to a single alkyne molecule which is functioning effectively as a 4e ligand. Perhaps the nearest analogue to **C** is then the d^4 complex $[W(CO)(S_2CNEt_3)_2(\eta^2\text{-}C_2H_2)]$ where the C≡C bond of the coordinated ethyne unit is ca. 9 pm longer than that in the free alkyne, although the ν_{CC} mode could not be located [42]. Two 4e alkyne ligands are known also to feature in the chromium(0) compounds *cis*-$[(\eta^2\text{-}PhCCPh)_2Cr(CO)_2]$ [43] and *cis*-$[(\eta^2\text{-}PhCCPh)_2Cr(dmpe)]$ (dmpe = Me$_2$PCH$_2$CH$_2$-PMe$_2$) [44], whereas the stable existence of the *tris*(alkyne) complexes $[(\eta^2\text{-}PhCCPh)_3M(CO)]$ (M = Mo [45] or W [46]) implies the donation of a total of 10e by the three alkyne ligands [43,47]. On the other hand, the frontier orbitals of the alkyne molecule [43] and the C_{2v} Mo(CO)$_4$ fragment [48] are such as to suggest not only that a molecule with the structure **III** is feasible, but also that, with an appropriate configuration, it offers the means of 4e donation from the alkyne to the metal centre. With regard to the alkyne, the important orbitals
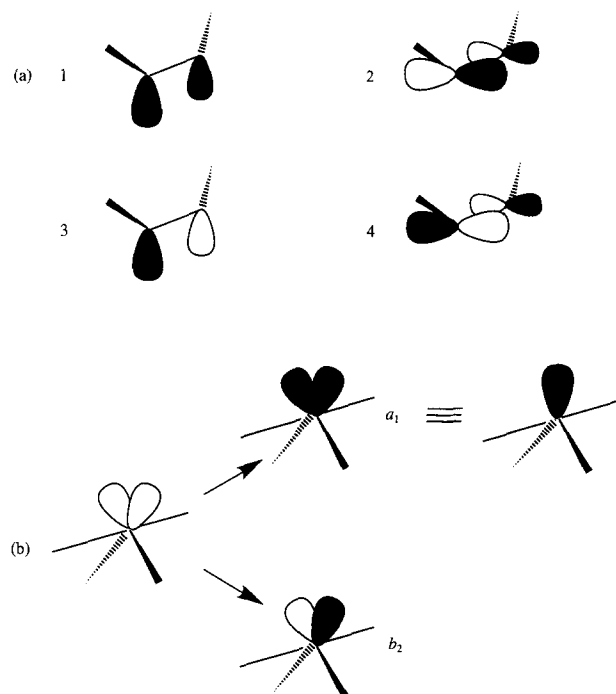
Fig. 4. (a) Frontier orbitals for an alkyne ligand [43]; (b) lowest lying acceptor orbitals for an Mo(CO)$_4$ fragment under C_{2v} symmetry [48].

for metal–alkyne bonding are illustrated in Fig. 4. One π orbital, 1, commonly denoted $\pi_{\parallel}$ and lying in the plane of the alkyne carbon atoms and their immediate substituents, is always involved in metal–alkyne bonding, along the lines of the π system in the Dewar–Chatt–Duncanson model of metal–alkene coordination. The other π donor orbital, $\pi_{\perp}$ 2, is perpendicular to the first and, if this orbital can overlap with a vacant metal orbital, then the alkyne donates more than 2 electrons to the metal. For its part, the Mo(CO)$_4$ fragment possesses two low-lying acceptor orbitals pointing

towards the vacant ligand sites and which are equivalent to a symmetry-adapted set $a_1 + b_2$ (see Fig. 4) [48]. Hence it is evident that significant overlap of 1 with the a_1 acceptor orbital and of 2 with the b_2 acceptor orbital is possible provided that the C≡C axis of the alkyne molecule is aligned parallel to the more or less linear OC–Mo–CO unit in the Mo(CO)$_4$ substrate.

3.4. Product D

The ethyne version of **D** was the last photoproduct to be observed in the photolysis sequence $\lambda = 313$, 445 and 369 nm, its appearance and growth in the final stages of 369 or 300–400 nm photolysis seeming to correlate with the slow, simultaneous decay of **C**. It was best characterised for the Mo(CO)$_6$/C$_2$D$_2$ system by two closely spaced ν_{CO} bands at 1946 and 1954 cm^{-1} and by a band suggesting a ν_{CC} mode at 1469 cm^{-1} (see Fig. 2), but at no stage did the intensities develop sufficiently to admit detailed and convincing studies of the effects of isotopic enrichment. Indeed, despite the performance of several experiments, no clear sign of a C$_2$H$_2$ counterpart to the band at 1469 cm^{-1} could be discerned. The low yield of **D** implicit in the weakness of its IR absorptions must be attributed partly to a less than ideal match of the experimental conditions of photolysis with the (unknown) UV–vis absorption properties of its precursor (probably **C**), partly to competition for the available light from other photochemical changes, and partly to deterioration in the optical transparency of the matrix under the action of prolonged photolysis (typically > 2 h in total).

In these circumstances we can only speculate about the identity of **D**. One possibility involves attachment and rearrangement of a second ethyne molecule to give a vinylidene ligand with an accompanying change of the

Table 4

Comparison of the vibrational properties of the photoproduct C with those of (η^2-C$_2$H$_2$)Ni, H$_2$C=C=Ni, H$_2$C=C=S and H$_2$C=C=Se

Molecule [a]	ν_{CO}/cm^{-1}	ν_{CC}/cm^{-1}				Reference
		^{12}C$_2$H$_2$	^{12}C$_2$D$_2$	^{12}C^{13}CH$_2$		
C	2082, 2006, 1963	1670	1565	1641		This work
H | C |||···Ni C | H	–	1647 ⎫ 1638 ⎬ b 1635 ⎭	1541 ⎫ 1532 ⎬ b 1529 ⎭	1692 ⎫ b 1591 ⎭		[15b]
H_\C=C=Ni H[/]	–	1635 ⎫ b 1624 ⎭	1626 ⎫ b 1618 ⎭	1616 ⎫ b 1605 ⎭	1609 ⎫ b 1598 ⎭	[15b]
H_\C=C=S H[/]	–	1755	1738	1737	1713	[36]
H_\C=C=Se H[/]	–	1695	1681	–		[37]

[a] All molecules isolated in an Ar matrix.
[b] Band split presumably as a result of matrix site effects.

pre-existing η^2-ethyne ligand from a 4e to a 2e donor, giving a product such as cis-$[(\eta^2\text{-}C_2H_2)(H_2C=C=)\text{-}Mo(CO)_4]$. A second choice recognises that activation of a C–H bond of an ethyne molecule may occur to give a product featuring the unit HC≡C–Mo–H. In this case the absorption at 1469 cm^{-1} could well correspond to ν_{MoD} and the apparent absence of a C_2H_2 counterpart then finds a ready explanation in that ν_{MoH} would be expected to occur near 2000 cm^{-1} where it is liable to be obscured by the more intense ν_{CO} absorptions of the various molybdenum carbonyls present in the matrix. Thirdly, the photodissociation of CO brought about at wavelengths near 369 nm suggests yet another interpretation, namely that **D** is simply derived from **C** by the loss of one or more CO groups {cf. the oxometal carbonyls derived under similar conditions from O_2 and $M(CO)_6$ (M = Cr, Mo or W) [36,49] or $Fe(CO)_5$ [50]}. However, further studies extending beyond the scope of the present matrix experiments will be needed before the identity of this product can be settled.

4. Conclusions

UV photolysis of methane or argon matrices containing $Mo(CO)_6$ and an alkyne, RC≡CR′ (where R,R′ = H,H; Me,H; or Me,Me), results in photodissociation of CO and the formation of the unsaturated C_{4v} molecule $Mo(CO)_5$ which weakly binds a molecule of either the matrix or the alkyne. The alkyne complex, **A**, exhibits a UV absorption band at 360–385 nm which can be identified with the low-energy ligand-field transition $b_2^2e^4a_1^0b_1^0 \rightarrow b_2^2e^3a_1^1b_1^0$ [12]. The IR spectrum, including the effects of mono-^{13}C enrichment in C_2H_2, implies that the alkyne complex is to be formulated as $[(\eta^2\text{-}RC\equiv CR')Mo(CO)_5]$, with the alkyne molecule acting as a relatively modest 2e donor. Interconversion of the

species $[Mo(CO)_6]$, $[X \cdots Mo(CO)_5]$ (X = Ar or CH_4), and $[(\eta^2\text{-}RC\equiv CR')Mo(CO)_5]$ proceeds in accordance with the photochemical conditions specified in Scheme 1. As indicated in this Scheme, irradiation of $[Mo(CO)_6]$ at wavelengths near 313 nm in the presence of a 1-alkyne, viz. HC≡CH or MeC≡CH, results in the formation of an additional complex, **B**, which is believed to be a vinylidene derivative $[R(H)C=C=Mo(CO)_5]$ (R = H or Me); this too is photolabile, and is destroyed by the action of visible light ($\lambda = 445$ nm). Over and beyond these changes, exposure to light first at $\lambda = 313$ and later at 369 or 300–400 nm causes further photodissociation of CO to occur, with the formation of various $Mo(CO)_4$ derivatives. A major product of photolysis in these later stages is a product **C** which, on the evidence of its IR spectrum and of the effects of deuteration or ^{13}C-enrichment, is probably $[(\eta^2\text{-}RC\equiv CR')Mo(CO)_4]$ (R,R′ = H,H or Me,Me) in which the alkyne functions formally as a 4e donor. Continued photolysis with light at wavelengths in the range 300–400 nm results in the slow decay of **C** and the appearance of **D**, another molybdenum carbonyl derivative incorporating RC_2R' units of one sort or another, but the exact identity of which could not be determined.

The characterisation of η^2-alkyne complexes of the type $(\eta^2\text{-}RC\equiv CR')Mo(CO)_5$ is noteworthy because the formation of such compounds must surely be the first step in the photochemical polymerization of terminal alkynes as mediated by Group 6 carbonyl compounds. According to one proposal [51], polymerization then proceeds as shown in Scheme 2, with the second step involving rearrangement of the η^2-1-alkyne to the corresponding vinylidene complex. Our experiments afford evidence of such a rearrangement although, under the photolysis conditions we used, this pathway was favoured less by $[(\eta^2\text{-}1\text{-alkyne})Mo(CO)_5]$ than by $[(\eta^2\text{-}$
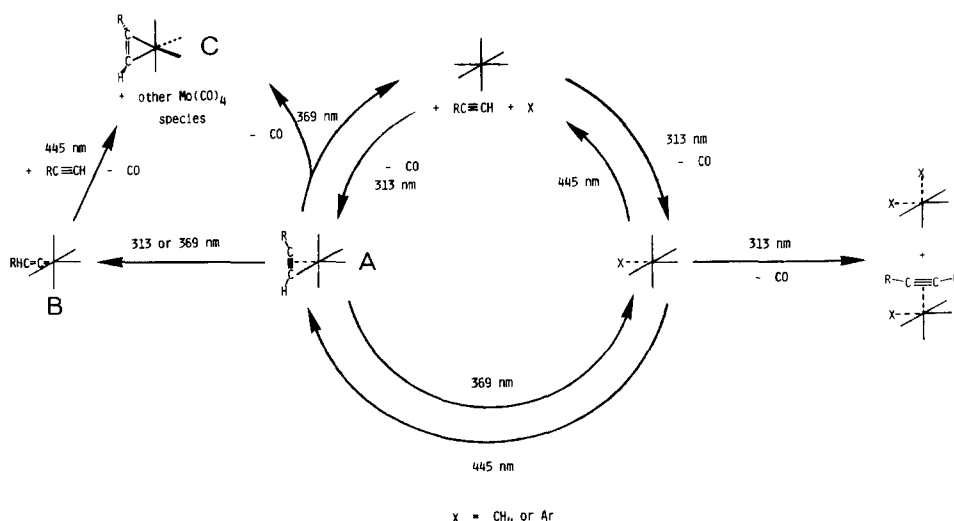
Scheme 1.

Scheme 2.
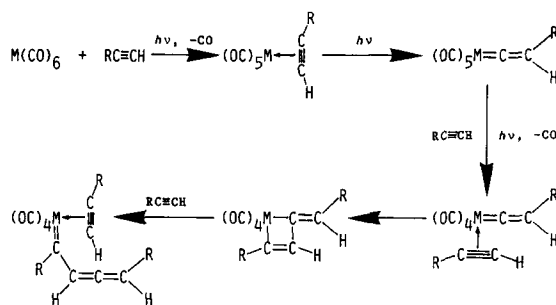
1-alkyne)W(CO)$_5$] [28]. Addition of a second molecule of the 1-alkyne is postulated then to give [(η^2-RC$_2$H)(η^1-R(H)C$_2$)M(CO)$_4$] (M = Mo or W), along the lines of **IV**. Although this may conceivably be the product **D**, no positive sighting of such a product has been made in our experiments. Instead we find in the photoproduct **C** spectroscopic evidence for the formation of an η^2-alkyne complex [(η^2-alkyne)Mo(CO)$_4$] involving strong mutual perturbation of the alkyne and Mo(CO)$_4$ units. This product is also photolabile, however, and could well take up a second 1-alkyne molecule with rearrangement to **IV** under appropriate conditions of photolysis. It is all the more frustrating therefore that our experiments are unable to probe much beyond this point and to identify the product **D** to which **C** ultimately gives way on prolonged irradiation at wavelengths in the range 300–400 nm.

It is doubtful whether conventional matrix experiments using hosts like solid argon or methane can advance this investigation much further. As revealed by the preceding account, there are various factors limiting the present approach to the photochemistry of Mo(CO)$_6$ in the presence of an alkyne. Firstly, there is the weakness of IR absorptions associated with internal vibrations of the alkyne or vinylidene moiety, a problem which has also inhibited matrix studies of dihydrogen [52] and alkene [53] complexes. In an effort to increase the number of molecules intercepted by the analysing beam of the IR spectrometer, it is not possible to increase the concentration of the matrices beyond a certain point without running the risk of forming bi- or poly-metallic products. A very recent development suggests that a polymer film support may provide a means of overcoming some of these problems of near-silent ligands [54]; it would certainly give access to a much wider temperature range than does solid argon or methane, and so help to bridge the gap between cryogenic and room-temperature experiments. A second problem is one inherent in all conventional matrix experiments, namely the low mobility of potential reagents or product molecules; "cage" effects may, for example, inhibit the progress of what would otherwise be efficient photochemical changes. Thirdly, the efficiency of

photolysis depends also on the optical transparency of the supporting medium which, in the case of solid matrices, is prone to deteriorate on prolonged irradiation. To counter these handicaps, future studies might profitably focus on solutions in a very weakly coordinating solvent like liquid xenon [55] or perfluoromethyl-cyclohexane [56] at low temperatures, and interrogate these through their IR and NMR spectra. The methods of time-resolved IR spectroscopy [57] may also lend themselves to an exploration of the kinetic properties of intermediates formed on photolysis of Mo(CO)$_6$/alkyne mixtures either in such solutions or in the gas phase at normal temperatures. With the isolation and characterisation of the compound [(η^2-PhCCPh)$_3$Mo(CO)] [45], it has been demonstrated that replacement of CO by alkyne ligands can lead to relatively stable products. Moreover, we note how photolysis of [Cr(CO)$_6$] in supercritical ethene has been devised [58] to isolate the ethene complex [(η^2-C$_2$H$_4$)Cr(CO)$_5$], which turns out to be relatively long-lived at ambient temperatures, and suggest that this may point the way to isolation of other alkyne– or vinylidene–metal carbonyl complexes, at least from alkynes less susceptible than ethyne to polymerisation under pressure.

Acknowledgements

References and notes

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