

Photo-reversible isomerisation of *trans*- to *cis*-[W(CO)₄(η²-alkene)₂] complexes in low-temperature matrices

T. Szymańska-Buzar ^{a,*}, M. Jaroszewski ^a, A.J. Downs ^{b,*}, T.M. Greene ^b, L.J. Morris ^b

^a Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

^b Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, UK

Received 22 July 1996; revised 15 August 1996

Abstract

Reversible isomerisation of *trans*- to *cis*-[W(CO)₄(η²-alkene)₂] complexes has been induced in argon matrices at low temperatures under the action of selective irradiation. UV photolysis (λ = 313 nm) of *trans*-[W(CO)₄(η²-alkene)₂] (alkene = cyclopentene or 1-pentene) in an argon matrix at 16 K results in formation of the *cis* isomer as the primary photoprocess. The isomerisation is reversed under the action of visible light (λ = 445 nm). Species such as [W(CO)₄(alkene)(Ar)] are also formed in small concentrations. Experiments involving annealing, selective photolysis and the use of CO- or alkene-doped matrices have been performed to investigate the mechanism of the photo-isomerisation process. These studies suggest a dissociative mechanism via expulsion of the alkene ligand.

Keywords: Tungsten; Carbonyl; Alkene; Photochemistry; Matrix isolation; Isomerism

1. Introduction

The reactions between transition-metal carbonyls and unsaturated organic ligands have been the focus of much attention owing to their possible application in heterogeneous [1,2] and homogeneous catalysis [3–5]. Of particular interest are the reactions of the Group 6 carbonyls with alkenes, for the complexes they afford have been proposed as catalysts or catalytic precursors in reactions involving isomerisation [6–9], metathesis [2,10–14], or hydrogenation [15–18] of the unsaturated ligand.

Bis(alkene) tetracarbonyl complexes of the elements Mo and W were first observed in 1963 by Stolz et al. [19], who described how UV photolysis of *n*-hexane solutions of [M(CO)₆] (M = Mo or W) and an excess of alkene produced [M(CO)₄(alkene)] in the first instance and *trans*-[M(CO)₄(alkene)₂] on further irradiation, the latter species being isolated for the propene- and butadiene-substituted complexes. That the *trans* rather than the *cis* isomer is formed in these circumstances is in contrast to most examples of photo-substitution by ligands other than alkenes at monosubstituted d⁶ metal carbonyl centres [20–23]. Experiments performed by Pope and

Wrighton [24] have demonstrated that UV photolysis of [W(CO)₄(alkene)] isolated in a methylcyclohexane matrix at 77 K results in loss of a CO molecule that is *cis* to the alkene ligand. This clearly implies that further replacement of CO by alkene should afford the *cis*-[W(CO)₄(alkene)₂] complex, the product predicted under kinetic control. That such reactions yield the *trans* isomer suggests superior thermodynamic stability for this compared with the *cis* form, a proposal afforded by theoretical calculations [25,26]. Consequently, the *cis* isomers of the [W(CO)₄(alkene)₂] species have been observed only at low temperatures or as transients in the gas phase. Thus, UV photolysis of a liquid xenon solution of [M(CO)₆] (M = Cr, Mo or W) in the presence of C₂H₄ at –78 °C has been shown to result in the formation of *cis*-[M(CO)₄(alkene)₂], along with the *trans* isomer [27]. The decomposition of the *cis* complex was studied but yielded no evidence of isomerisation to the *trans* congener. The molecules *cis*-[M(CO)₄(C₂H₄)₂] (M = Cr or W) have also been detected using time-resolved infrared absorption techniques following pulsed laser photolysis of the parent hexacarbonyl in the presence of C₂H₄ [28,29].

Although it is clear from these earlier accounts that complexes of the type [M(CO)₄(alkene)₂] are more stable when the alkene ligands are located *trans* to each

* Corresponding authors.

other, there is a general recognition that the catalytic cycle for metathesis, isomerisation and hydrogenation reactions of olefins involves $M(\text{CO})_4$ units coordinated to two organic ligands occupying positions that are mutually *cis* [3,7,13]. Furthermore, recent experiments [30] have shown that thermal reactions of complexes of the type *trans*- $[\text{W}(\text{CO})_4(\text{alkene})_2]$ afford (π -allyl)metal hydride compounds, important intermediates in the catalytic cycle for isomerisation and metathesis of alkenes.

It was our aim, therefore, to investigate how the catalytically active *cis*- $[\text{W}(\text{CO})_4(\text{alkene})_2]$ complex can be formed from the thermodynamically more stable *trans*- $[\text{W}(\text{CO})_4(\text{alkene})_2]$ isomer, an initial step which appears vital to the catalytic rôle of these compounds. That the technique of matrix isolation is ideally suited to such a study has been demonstrated previously, both in the investigation of alkyne polymerisation mediated by molybdenum or tungsten hexacarbonyl [31] and in the successful characterisation of catalytic intermediates in the $[\text{Fe}(\text{CO})_5]$ -alkene system [32–34].

2. Experimental details

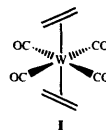
The cryogenic equipment used at Oxford has been described elsewhere [31]. The matrices were formed by slow, continuous deposition of the vapour of the *trans*- $[\text{W}(\text{CO})_4(\text{alkene})_2]$ with an excess of the matrix gas; the operating procedures followed closely the practices developed in earlier studies of this kind [31]. Pure argon or argon doped to 2% with either CO or alkene was employed as the matrix gas. IR spectra were recorded using a Mattson 'Galaxy' FT-IR instrument, with a spectral resolution of 1 cm^{-1} . UV–visible spectra were recorded with a Perkin–Elmer–Hitachi Model 330 spectrophotometer. The photolysis source was a Spectral Energy 1000 W Hg–Xe arc lamp, Model LH152. Selective irradiation was carried out with the aid of a suitable interference filter transmitting light centred at 313 nm (fwhh 16 nm), 363 nm (fwhh 38 nm) or 445 nm (fwhh 13 nm).

The bis(alkene)tungsten tetracarbonyl complexes were synthesised according to the procedures described previously [35], being purified before use by sublimation *in vacuo*. Samples of $[\text{W}(\text{CO})_6]$ (Aldrich), cyclopentene (Aldrich) and 1-pentene (Aldrich) were purified by fractional condensation *in vacuo* prior to use. The matrix gases Ar and CO were used as supplied by B.O.C. ('Research' grade).

3. Observation of photo-induced *trans* \leftrightarrow *cis* isomerisation of $[\text{W}(\text{CO})_4(\text{alkene})_2]$

Fig. 1 illustrates representative IR spectral changes accompanying the irradiation of *trans*- $[\text{W}(\text{CO})_4(\text{cyclo-$

pentene) $_2]$ isolated in an argon matrix at 16 K. In none of the experiments reported here was there any discernible alteration in the absorptions associated with the alkene ligand. This is a result of their weakness when compared with features in the $\nu(\text{CO})$ region of the spectrum. Our analyses are based therefore on the observation of absorptions arising from the $\nu(\text{CO})$ modes. The IR spectrum recorded after deposition (Fig. 1(a)) shows a strong band at 1943.1 cm^{-1} , together with a very weak one at 2051.2 cm^{-1} . Studies of the vibrational spectrum of *trans*- $[\text{W}(\text{CO})_4(\text{ethene})_2]$, **I**, have demonstrated that the molecule conforms to D_{2d} symmetry [36]. We have therefore chosen to describe the $\nu(\text{CO})$ vibrations of *trans*- $[\text{W}(\text{CO})_4(\text{cyclopentene})_2]$ by imposing local D_{2d} symmetry on the $\text{W}(\text{CO})_4$ fragment. In this case, the $\nu(\text{CO})$ modes span the irreducible representations $a_1 + b_2 + e$. Of the two modes allowed in IR absorption ($b_2 + e$), the e mode is surely responsible for the absorption at 1943.1 cm^{-1} , but the b_2 mode, expected near 1990 cm^{-1} , was not in evidence, being obscured perhaps by a weak feature at 1985.9 cm^{-1} (q.v.). The weak high-frequency band at 2051.2 cm^{-1} must then be associated with the a_1 $\nu(\text{CO})$ mode of *trans*- $[\text{W}(\text{CO})_4(\text{cyclopentene})_2]$, which, although formally IR-silent under D_{2d} symmetry, is rendered weakly active by the reduction in symmetry of the molecule imposed by the saturated portion of the alkene ligand. Tungsten hexacarbonyl is identified with the weak band at 1985.9 cm^{-1} [37], being an unavoidable impurity remaining from the synthesis of the bis(alkene) complex. The electronic spectrum of *trans*- $[\text{W}(\text{CO})_4(\text{cyclopentene})_2]$ isolated in an argon matrix (not illustrated) exhibits a maximum at ca. 300 nm on the tail of a band centred at shorter wavelength. We chose, therefore, to irradiate the matrix initially with light falling within this tail and having $\lambda \approx 313\text{ nm}$.



The effect of such photolysis for a period of 15 min is illustrated in Fig. 1(b). A decline in the intensity of bands due to the *trans* isomer is accompanied by the appearance of a set of four new bands centred at 2051.5, 1954.1, 1949.3 and 1897.2 cm^{-1} . The frequencies and relative intensities of the new bands compare well with those of documented *cis*-bis(alkene)tetracarbonyl and (η^4 -diene)tetracarbonyl complexes [19,24,38]. The fea-

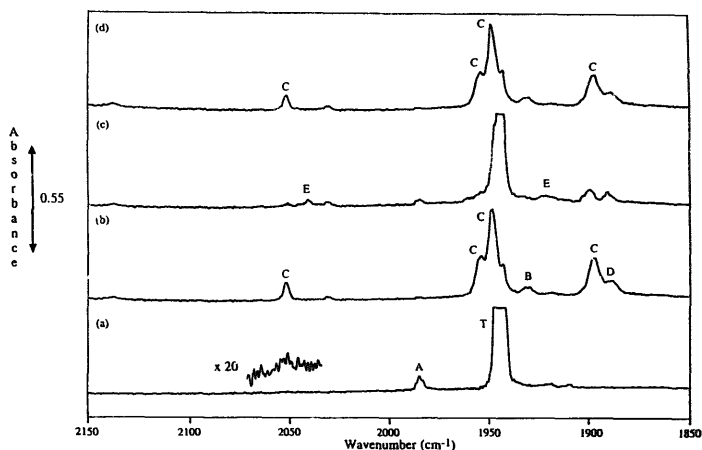


Fig. 1. IR absorption spectrum in the region $2150\text{--}1850\text{ cm}^{-1}$ of $\text{trans-[W(CO)}_4(\text{cyclopentene})_2]$ isolated in a pure argon matrix at 16 K showing the effects of photolysis at different wavelengths. (a) Spectrum of the matrix after deposition. (b) Spectrum after photolysis for 15 min at $\lambda = 313\text{ nm}$. (c) Spectrum after subsequent photolysis for 15 min at $\lambda = 445\text{ nm}$. (d) Spectrum after a further 2 min photolysis at $\lambda = 313\text{ nm}$. Bands are labelled as follows: (A) W(CO)_6 ; (B) $\text{cis-[W(CO)}_4(\text{LXAr})]$; (C) $\text{cis-[W(CO)}_4(\text{L})_2]$; (D) $\text{cis-[W(CO)}_4(\text{Ar})_2]$; (E) $\text{trans-[W(CO)}_4(\text{L})(\text{Ar})]$; (T) $\text{trans-[W(CO)}_4(\text{L})_2]$, where L = cyclopentene.

tures may thus be assigned with confidence to the $\text{cis-[W(CO)}_4(\text{alkene})_2]$ molecule. Photolysis was observed also to give rise to additional bands at 2030.8,

1932.5, 1929.0 and 1890.0 cm^{-1} . Concurrent with these changes in the IR spectrum was the decay of the 300 nm absorption in the UV-visible spectrum, while a new

Table 1

Wavenumbers of IR bands due to $\nu(\text{CO})$ modes observed following deposition and subsequent photolysis of argon matrices containing $\text{trans-[W(CO)}_4(\text{cyclopentene})_2]$ ^a

Wavenumber (cm^{-1})	Dep.	Subsequent photolysis at $\lambda =$			Assignment ^b
		313 nm 15 min	445 nm 15 min	313 nm 2 min	
2138.2	—	vw	=	↑	CO
2051.5	—	w	↓	↑	$\text{cis-[W(CO)}_4(\text{L})_2]$, a ₁
2051.2	vwv	—	c	c	$\text{trans-[W(CO)}_4(\text{L})_2]$, a ₁
2040.4	—	—	vw	↓	$\text{trans-[W(CO)}_4(\text{L})(\text{Ar})]$, a ₁
2030.8	—	vwv	=	=	d
1985.9	w	↓	↑	↓	W(CO)_6 , t _{1g}
1954.1	—	m	↓	↑	$\text{cis-[W(CO)}_4(\text{L})_2]$, b ₁
1949.3	—	s	↓	↑	$\text{cis-[W(CO)}_4(\text{L})_2]$, a ₁
1943.1	vs	↓	↑	↓	$\text{trans-[W(CO)}_4(\text{L})_2]$, e
1932.5	—	w	↓	↑	$\text{cis-[W(CO)}_4(\text{L})(\text{Ar})]$, b ₁
1929.0	—	w	↓	↑	$\text{cis-[W(CO)}_4(\text{L})(\text{Ar})]$, a ₁
1920(br)	—	—	w	↓	$\text{trans-[W(CO)}_4(\text{L})(\text{Ar})]$, e
1919(br)	vwv	c	c	c	$\text{trans-[W(}^{12}\text{CO)}_4(^{13}\text{CO)(L})_2]$, e
1909(br)					
1897.2	—	m	↓	↑	$\text{cis-[W(CO)}_4(\text{L})_2]$, b ₂
1890.0	—	w	↓	↑	$\text{cis-[W(CO)}_4(\text{Ar})_2]$, b ₂

^a s strong; m medium; w weak; v very; br broad; dep. on deposition; — absent; = unchanged; ↑ increases; ↓ decreases. ^b L = cyclopentene. ^c Obscured. ^d See text.

broad band centred near 400 nm was seen to develop. That this band is associated with the *cis* isomer is apparent from IR spectral changes occasioned by a subsequent period of photolysis with light having $\lambda \approx 445$ nm (Fig. 1(c)) and so falling within the envelope of the 400 nm absorption. Bands assigned to the *cis* isomer were seen to decrease while the bands due to the *trans* species regain some of their initial intensity. Additional bands appear at 2040.4 and 1920(br) cm^{-1} . The band at 1985.9 cm^{-1} due to $[\text{W}(\text{CO})_6]$ was observed to grow while the bands at 1932.5 and 1929.0 cm^{-1} decay.

A further period of irradiation using light at $\lambda \approx 313$ nm regenerates the *trans* isomer at the expense of its *cis* counterpart. The features at 2040.4, 1985.9 and 1920 cm^{-1} are diminished, whilst that at 1890.0 cm^{-1} increases in intensity. The response of the various bands to photolysis is summarised in Table 1.

It has thus been clearly demonstrated that selective photolysis can bring about photo-isomerisation of *trans*- to *cis*- $[\text{W}(\text{CO})_4(\text{cyclopentene})_2]$. Although most of the induced changes are concerned with this transformation, there are evidently some side-reactions which give rise to weaker bands in the IR spectrum.

Of these weaker features, the one at 1890.0 cm^{-1} is readily assignable to the species *cis*- $[\text{W}(\text{CO})_4(\text{Ar})_2]$; this has been characterised previously by a band at 1894 cm^{-1} following prolonged broad-band photolysis of $[\text{W}(\text{CO})_6]$ trapped in an argon matrix [39]. It may be that such a species is produced by a number of separate pathways, either through expulsion of the two alkene fragments from the $\text{W}(\text{CO})_4(\text{alkene})_2$ reagent or via a monoalkene-substituted intermediate. A slight prefer-

ence for the latter route is afforded by the observation that returning to a photolysis wavelength of ca. 313 nm, following irradiation at $\lambda = 445$ nm, causes accretion of both the *cis*-bis(alkene)tetracarbonyl isomer and the *cis*-bis(argon)tetracarbonyl complex.

The two bands centred at 1929.0 and 1932.5 cm^{-1} appear to respond in the same way to photolysis and may thus be assigned together to a common absorber. Later experiments using CO-doped matrices (vide infra) gave good grounds for believing that the alkene is more easily photo-ejected from the bis(alkene)tetracarbonyl complex than is a carbon monoxide ligand; this is as might be expected from simple bonding considerations which render the alkene less strongly bound in the ground state than is CO [24]. It is to be anticipated, therefore, that side-reactions produce species of the form $[\text{W}(\text{CO})_5(\text{alkene})(\text{Ar})]$ with either a *cis* or a *trans* configuration. The photochemistry of $[\text{W}(\text{CO})_5(\text{alkene})]$ (alkene = C_2H_4 , C_3H_6 or $1\text{-C}_5\text{H}_{10}$) isolated in organic glasses has been investigated previously [24]. Although preferential loss of the alkene was observed, the authors did manage to characterise the species $[\text{W}(\text{CO})_5(\text{alkene})]$, noting that the main absorption was likely to be obscured by the presence of $\nu(\text{CO})$ bands due to $[\text{W}(\text{CO})_5]$ at 1951 and 1921 cm^{-1} . In the studies reported here, the matrix contained only trace quantities of $[\text{W}(\text{CO})_6]$ and so was almost free from $[\text{W}(\text{CO})_5(\text{Ar})]$, a condition demonstrated by the absence of a band at 1962.3 cm^{-1} arising from the *e* $\nu(\text{CO})$ mode of this molecule [37]. It seems plausible, therefore, to assign the pair of bands at 1929.0 and 1932.5 cm^{-1} to the main $\nu(\text{CO})$ absorptions of $[\text{W}(\text{CO})_5(\text{alkene})(\text{Ar})]$. That

Table 2

Wavenumbers of IR bands due to $\nu(\text{CO})$ modes observed following deposition and subsequent photolysis of argon matrices containing *trans*- $[\text{W}(\text{CO})_4(1\text{-pentene})_2]$ ^a

Wavenumber (cm^{-1})	Dep.	Subsequent photolysis at $\lambda =$			Assignment ^b
		313 nm 14 min	445 nm 18 min	313 nm 16 min	
2136.9	—	vw	=	↑	CO
2062.6	vww	↓	—	—	<i>trans</i> - $[\text{W}(\text{CO})_4(\text{L})_2]$, a ₁
2052.5	—	w	↓	↑	<i>cis</i> - $[\text{W}(\text{CO})_4(\text{L})_2]$, a ₁
2044.8	—	—	w	↓	<i>trans</i> - $[\text{W}(\text{CO})_4(\text{L})(\text{Ar})]$, a ₁
2028.4	—	vww	=	↑	^c
1994.2	m	↓	↑	↓	<i>trans</i> - $[\text{W}(\text{CO})_4(\text{L})_2]$, b ₂
1986.4	w	↓	↑	↓	$\text{W}(\text{CO})_6$, t _{1u}
1973.4	—	vww	↑	↓	^c
1958.5	vs	↓	↑	↓	<i>trans</i> - $[\text{W}(\text{CO})_4(\text{L})_2]$, e
1949.3	—	m	↓	↑	<i>cis</i> - $[\text{W}(\text{CO})_4(\text{L})_2]$, b ₁
1942.1	—	m	↓	↑	<i>cis</i> - $[\text{W}(\text{CO})_4(\text{L})_2]$, a ₁
1932.0	vw	d	d	d	<i>trans</i> - $[\text{W}(^{12}\text{CO})_3(^{13}\text{CO})(\text{L})_2]$, e
1924.2					
1922.8	—	—	w	↓	<i>trans</i> - $[\text{W}(\text{CO})_4(\text{L})(\text{Ar})]$, e
1897.7	—	in	↓	↑	<i>cis</i> - $[\text{W}(\text{CO})_4(\text{L})_2]$, b ₂
1890(sh)	—	w	d	↑	<i>cis</i> - $[\text{W}(\text{CO})_4(\text{Ar})_2]$, b ₂

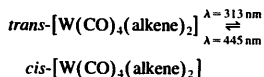
^a s strong; m medium; w weak; v very; sh shoulder; dep. on deposition; — absent; = unchanged; ↑ increases; ↓ decreases. ^b L = 1-pentene. ^c See text. ^d Obscured.

the features are discerned after photolysis at $\lambda \approx 313$ nm and decay on further irradiation at $\lambda \approx 445$ nm lends some weight to their assignment to the *cis* isomer, by comparison with the behaviour of the disubstituted parent. The broad band at 1920 cm^{-1} and the feature at 2040.4 cm^{-1} can then be attributed to *trans*-[W(CO)₂(alkene)(Ar)]. Their appearance following irradiation at $\lambda \approx 445$ nm and subsequent decay following irradiation at $\lambda \approx 313$ nm are consistent with this tentative association.

There remains in the spectrum a weak absorption at 2030.8 cm^{-1} still to be explained. That the band arises from the high-frequency $\nu(\text{CO})$ mode of some carbonyl formed via a side-reaction is almost certain, but the congestion of the lower frequency region of the spectrum, likely to include any stronger bands of the same absorber, hampers a definitive analysis. Possible contenders are species such as [W(CO)₂(cyclopentene)₂(Ar)] and [W(CO)₂(cyclopentene)(Ar)₂]. Complexes of the type *mer*-[(η^2 -alkene)(η^1 -norbornadiene)W(CO)₂] (alkene = (*Z*)-cyclooctene or ethene) have been prepared [40]. The IR spectrum of the complex dissolved in *n*-hexane gives $\nu(\text{CO})$ bands at the following frequencies (in wavenumbers): 2019.5(w), 1942.5(s) and $1932.5(\text{m})\text{ cm}^{-1}$ for alkene = (*Z*)-cyclooctene; and 2028(w) and 1951.5(vs, slightly broadened) for alkene = ethene. It follows that a W(CO)₂ fragment coordinated to one or two cyclopentene ligands may well give rise to the band at 2030.8 cm^{-1} , the lower frequency features being obscured by prominent bands of the *cis*- and *trans*-[W(CO)₂(cyclopentene)₂] species.

Experiments similar to those detailed above were carried out with the *trans*-[W(CO)₂(1-pentene)₂] complex. The results obtained were broadly in line with those yielded by the cyclopentene complex. The details of the observed spectral changes, along with assignment of the infrared features, are given in Table 2. As in the previous experiments, the band at 2028.4 cm^{-1} may have its origin in a species of the type [W(CO)₂(1-pentene)₂(Ar)] or [W(CO)₂(1-pentene)(Ar)₂]. It is also to be noted that there was no sign of *cis*-[W(CO)₂(1-pentene)(Ar)]. Another weak feature was observed at 1973.4 cm^{-1} , but with a response to photolysis that gave no clues to its assignment; this has no counterpart in the cyclopentene experiments.

Hence, it has been clearly established that the following isomerisation may be induced with light of the appropriate wavelengths:



The demonstration of this reversible reaction represents a significant step forward in understanding how *trans*-[W(CO)₂(alkene)₂] complexes act as catalysts for a

range of alkene reactions, as discussed earlier. What remained unclear, however, at this stage in our study was the mechanism by which such an isomerisation takes place. The elucidation of this mechanism formed the next part of our investigation.

4. Investigation of the mechanism of isomerisation

There are, in theory, two possible pathways by which *trans* ↔ *cis* isomerisation of a W(CO)₂(alkene)₂ complex may occur: (i) an intramolecular rearrangement or (ii) a dissociative mechanism, whereby a ligand is lost from the disubstituted complex, only to rebind at a different site and thereby generate the alternative isomer. In an attempt to differentiate between these two possibilities, three separate approaches were adopted. The first involved annealing studies to investigate if judicious warming of the matrix could induce *cis* → *trans* conversion. The second expedient was to undertake the initial photolysis at different wavelengths with a view to discovering whether exclusive *trans* → *cis* isomerisation could be engineered. The final device was to explore the use of doped matrices to trap any unsaturated intermediate produced via a dissociative route.

4.1. Annealing studies

Matrices containing *trans*-[W(CO)₂(cyclopentene)₂] or *trans*-[W(CO)₂(1-pentene)₂] complexes were initially photolysed at $\lambda \approx 313$ nm to generate the *cis* isomer and then annealed to temperatures between 30 and 37 K. The deposit was then re-cooled to 16 K and any changes were assessed by reference to the IR spectrum. In both cases the *cis* isomer appeared to survive this modest rise in temperature; bands due to the *cis* species underwent only very slight changes probably reflecting variations of the matrix environment experienced by the molecule during the annealing cycle. The only significant change that could be discerned with both complexes was the appearance on annealing of *trans*-[W(CO)₂(alkene)(Ar)]. That the *cis* isomer is stable at matrix temperatures up to 37 K is in line with the observation that *cis*-[W(CO)₂(C₂H₄)₂] is long-lived in liquid xenon at $-78\text{ }^\circ\text{C}$ [27].

4.2. Selective photolysis studies

Initial irradiation of an argon matrix containing *trans*-[W(CO)₂(cyclopentene)₂] with light having $\lambda \approx 445$ nm had no effect on the IR spectrum of the deposit, as expected on the basis of the earlier UV-visible studies. However, encroaching into the envelope of the electronic transition centred near 300 nm, by using light with $\lambda \approx 363$ nm, was observed to bring about the

decay of the trans isomer, with the appearance of its cis counterpart, as shown by the IR spectrum illustrated in Fig. 2(b). Although most of the other side-products which had been observed previously were missing, the growth of a weak band at 1890.0 cm^{-1} clearly signalled the formation of *cis*- $[\text{W}(\text{CO})_2(\text{Ar})_2]$ [39]. Subsequent photolysis at $\lambda \approx 445\text{ nm}$ produced, predictably, conversion of the cis to the trans isomer, as well as the appearance of the other species noted in the earlier photolysis studies.

Similar experiments were performed using *trans*- $[\text{W}(\text{CO})_2(1\text{-pentene})_2]$. The complex appeared less photosensitive to irradiation at ca. 363 nm , but prolonged irradiation lasting approximately 3 h resulted in the clean generation of the cis isomer. Further photolysis at $\lambda \approx 445\text{ nm}$ regenerated the trans species but gave rise also to the other species brought to light in the earlier experiments.

The spectroscopic results indicate that, when less energy is supplied to the trans species, it is possible to promote isomerisation with a great reduction, or even to the exclusion, of side-reactions. Although this may appear to favour an intramolecular process, it should also be borne in mind that a dissociative pathway, in which the expelled ligand is imparted with less energy and so may not escape the immediate environment of the precursor to generate side-products, would be no less consistent with the observations recorded. Certainly the identification of small quantities of *cis*- $[\text{W}(\text{CO})_2(\text{Ar})_2]$

in the cyclopentene experiments is suggestive of a dissociative route.

4.3. Studies involving doped matrices

The next experiments to be carried out entailed the isolation of the bis(alkene)tungsten tetracarbonyl complexes in argon matrices containing 2% carbon monoxide. Were a dissociative route to isomerisation to occur, the photo-ejected ligand would most probably be the more weakly bound alkene. The inclusion of CO in the matrix was therefore effected in the hope that any unsaturated metal carbonyl formed on photolysis would bind a molecule of CO and so generate recognisable species such as $[\text{W}(\text{CO})_3(\text{alkene})]$ and subsequently $[\text{W}(\text{CO})_6]$.

The response to photolysis of the *trans*- $[\text{W}(\text{CO})_2(1\text{-pentene})_2]$ complex isolated in a CO-doped argon matrix is displayed in Fig. 3. The changes in intensity of the various IR bands in reply to selective irradiation and the likely origins of the bands are listed in Table 3. Photolysis at $\lambda \approx 363\text{ nm}$ was performed initially, as this had been observed to bring about clean conversion of the trans to the cis isomer in an undoped argon matrix (*vide supra*). Nevertheless, the spectrum shown in Fig. 3(b) shows clearly an increase in the concentration of $[\text{W}(\text{CO})_6]$, with no sign of bands arising from the cis isomer. Further photolysis at $\lambda \approx 313\text{ nm}$ led to the expected appearance of the cis isomer, but with a

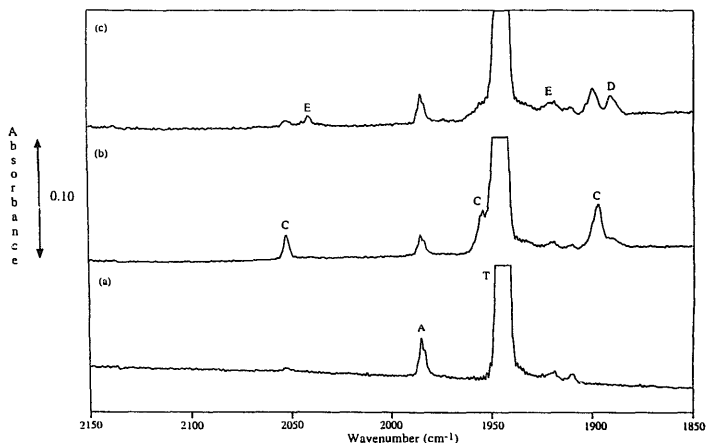


Fig. 2. IR absorption spectrum in the region $2150\text{--}1850\text{ cm}^{-1}$ of *trans*- $[\text{W}(\text{CO})_2(\text{cyclopentene})_2]$ isolated in a pure argon matrix at 16 K showing the effects of photolysis at different wavelengths. (a) Spectrum of the matrix after deposition. (b) Spectrum after photolysis for 31 min at $\lambda \approx 363\text{ nm}$. (c) Spectrum after subsequent photolysis for 6 min at $\lambda \approx 445\text{ nm}$. Bands are labelled as follows: (A) $\text{W}(\text{CO})_6$; (C) *cis*- $[\text{W}(\text{CO})_2(\text{L})_2]$; (D) *cis*- $[\text{W}(\text{CO})_2(\text{Ar})_2]$; (E) *trans*- $[\text{W}(\text{CO})_2(\text{LAr})]$; (T) *trans*- $[\text{W}(\text{CO})_2(\text{L})_2]$, where L = cyclopentene.

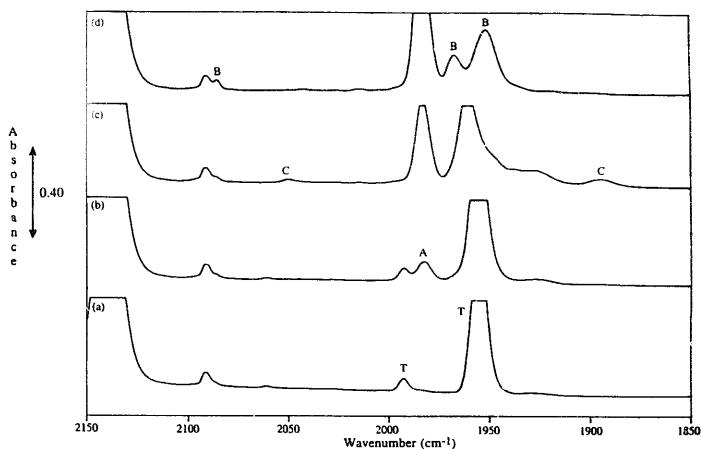


Fig. 3. IR absorption spectrum in the region 2150–1850 cm^{-1} of $\text{trans-}[\text{W}(\text{CO})_5(1\text{-pentene})_2]$ isolated in a CO-doped argon matrix at 16 K showing the effects of photolysis at different wavelengths. (a) Spectrum of the matrix after deposition. (b) Spectrum after photolysis for 120 min at $\lambda \approx 363$ nm. (c) Spectrum after subsequent photolysis for 24 min at $\lambda \approx 313$ nm. (d) Spectrum after subsequent photolysis for 20 min at $\lambda \approx 445$ nm. Bands are labelled as follows: (A) $\text{W}(\text{CO})_6$; (B) $\text{W}(\text{CO})_5(\text{L})$; (C) $\text{cis-}[\text{W}(\text{CO})_5(\text{L})_2]$; (T) $\text{trans-}[\text{W}(\text{CO})_5(\text{L})_2]$, where L = 1-pentene.

substantial gain in the concentration of $[\text{W}(\text{CO})_6]$. Subsequent irradiation with light centred at ca. 445 nm caused the cis isomer to decay, though with a concomitant increase in intensity of features due not to the trans species, but rather to $[\text{W}(\text{CO})_6]$. A new set of bands attributable to $[\text{W}(\text{CO})_5(1\text{-pentene})]$ was also seen to develop. The assignment of features in the $\nu(\text{CO})$ region to this molecule is confirmed both by comparison with the data available (i) from solution studies carried out during the preparation of the trans complex (2082,

1965 and 1952 cm^{-1} in *n*-hexane) and (ii) from experiments we have carried out to investigate the photolysis of $[\text{W}(\text{CO})_6]$ isolated in argon matrices doped to 2% with 1-pentene. The matrix studies with $[\text{W}(\text{CO})_6]$ revealed that photolysis at ca. 313 nm gives rise to $[\text{W}(\text{CO})_5(\text{Ar})]$ [36]; a further period of photolysis at ca. 445 nm generates the species $[\text{W}(\text{CO})_5(1\text{-pentene})]$, which could be identified with features in the $\nu(\text{CO})$ region of the IR spectrum at 2085.7, 1970.0 and 1953.1 cm^{-1} . The frequency and intensity patterns are

Table 3

Wavenumbers of IR bands due to $\nu(\text{CO})$ modes observed following deposition and subsequent photolysis of argon matrices containing $\text{trans-}[\text{W}(\text{CO})_5(1\text{-pentene})_2]$ and CO^a

Wavenumber (cm^{-1})	Dep.	Subsequent photolysis at $\lambda =$			Assignment ^b
		363 nm 120 min	313 nm 24 min	445 nm 20 min	
2085.7	—	vvw	↑	↑	$\text{W}(\text{CO})_6(\text{L}), a_1$
2061.2	vw	↓	↓	—	$\text{trans-}[\text{W}(\text{CO})_5(\text{L})_2], a_1$
2050.5	—	—	vw	↓	$\text{cis-}[\text{W}(\text{CO})_5(\text{L})_2], a_1$
1992.7	w	↓	↓	—	$\text{trans-}[\text{W}(\text{CO})_5(\text{L})_2], b_2$
1982.6	—	w	↑	↑	$\text{W}(\text{CO})_6, t_{1u}$
1967.6	—	c	↑	m	$\text{W}(\text{CO})_5(\text{L}), e$
1955.6	vs	=	↓	c	$\text{trans-}[\text{W}(\text{CO})_5(\text{L})_2], e$
1951.7	—	c	c	s	$\text{W}(\text{CO})_5(\text{L}), a_1$
1927.6	—	—	w	↓	$\text{trans-}[\text{W}(\text{CO})_5(\text{L})(\text{Ar})], e$
1893.8	—	—	w	↓	$\text{cis-}[\text{W}(\text{CO})_5(\text{L})_2], b_2$

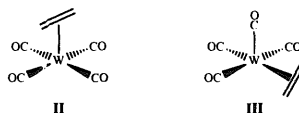
^a s strong; m medium; w weak; v very; dep. on deposition; — absent; = unchanged; ↑ increases; ↓ decreases. ^b L = 1-pentene. ^c Obscured.

in accord with those of closely related molecules of the type $X \cdots W(CO)_5$, where $X = CS$ [41,42], CCl_3 [43], N_2 [44] or CO_2 [45]. The slight shift of frequencies recorded for $[W(CO)_5(1\text{-pentene})]$, as formed in the CO-doped argon matrices, is unremarkable, given the different matrix composition. Our studies of $[W(CO)_5(1\text{-pentene})]$ isolated in matrices of pure argon also showed that photolysis at ca. 363 nm caused a decrease in the intensity of bands associated with this complex, accompanied by a sympathetic increase in features arising from $[W(CO)_5(Ar)]$. This observation explains why we do not observe $[W(CO)_5(1\text{-pentene})]$ after initial photolysis at ca. 363 nm of *trans*- $[W(CO)_5(1\text{-pentene})_2]$ in CO-doped argon matrices.

Analogous experiments were performed using the bis(cyclopentene) complex with the results summarised in Table 4. Again the formation of $[W(CO)_6]$ and $[W(CO)_5(\text{alkene})]$ is the most noteworthy feature. The bands arising from the latter species occur at frequencies close to those (i) of *n*-hexane solutions of the compound (2080, 1961 and 1948 cm^{-1}) and (ii) of a photolysed argon matrix doped with 2% cyclopentene and supporting initially $[W(CO)_6]$ (2082.5, 1973.4 and 1952.7 cm^{-1}).

The clear implication of these findings is that photolysis of either the *trans* or the *cis* isomer of $[W(CO)_5(\text{alkene})]$ results in disengagement of the alkene ligand. In a pure argon matrix, free from the more strongly coordinating CO ligand in the vicinity of the parent molecule, the uncoupled alkene may reunite with the unsaturated $[W(CO)_5(\text{alkene})]$ fragment and so open the way to generating the alternative isomer. The way in which this occurs may well entail a rearrangement of the unsaturated $[W(CO)_5(\text{alkene})]$ molecule. Such photo-induced rearrangements have been noted, for example, for $[M(CO)_5(CS)]$ ($M = Cr$ or W) [41,42]. Thus, the unsaturated $[W(CO)_5(\text{alkene})]$, like $[W(CO)_5(CS)]$, can be thought of as relaxing from the photo-excited state via a trigonal bipyramidal configuration to the square-pyramidal ground state with a configuration which is the same as (II), or different from (III), that of

the parent *trans* molecule. The 'rotation' of the $W(CO)_5(\text{alkene})$ group thus envisaged allows the sixth coordination site to scan the matrix environment and to 'collect' an alkene molecule, Ar or CO, according to the conditions of the experiment. The apparent direction of the photochemical change is then simply a consequence of the wavelength match or mismatch of the photolysing radiation to the absorption properties of the species being considered.



It is significant, too, that photolysis at ca. 363 nm causes *trans*- $[W(CO)_5(1\text{-pentene})]$ cleanly to be converted to the *cis* isomer in a pure argon matrix, but to yield only $[W(CO)_6]$ when CO is incorporated in the argon matrix. This argues cogently against an intramolecular rearrangement as the primary basis of isomerisation. It may also suggest that the rearrangement involves not the unsaturated intermediate $[W(CO)_5(\text{alkene})]$ but $[W(CO)_5]$ with both alkene molecules temporarily disengaged from the metal and forming part of the matrix environment. The signs are that mono-alkene derivatives of the type $[W(CO)_5(\text{alkene})(Ar)]$ have photochemical properties very similar to those of $[W(CO)_5(\text{alkene})_2]$, making it difficult, if not impossible, to judge whether $[W(CO)_5(\text{alkene})]$ or $[W(CO)_5]$ is the principal active intermediate.

Investigations of the effects of doping the matrix with free alkene were implemented using each of the *trans*- $[W(CO)_5(\text{alkene})]$ complexes isolated in an argon matrix containing 2% of the relevant alkene. The IR spectra of the resulting matrices, though reduced in

Table 4

Wavenumbers of IR bands due to $\nu(CO)$ modes observed following deposition and subsequent photolysis of argon matrices containing *trans*- $[W(CO)_5(\text{cyclopentene})_2]$ and CO^a

Wavenumber (cm^{-1})	Dep.	Subsequent photolysis at $\lambda =$			Assignment ^b
		363 nm 37 min	313 nm 1.5 min	445 nm 6.5 min	
2082.4	—	w	↓	↑	$W(CO)_5(L)$, a_1
2049.6	—	w	↑	↓	<i>cis</i> - $[W(CO)_5(L)_2]$, a_1
2039.5	—	—	—	v↓	<i>trans</i> - $[W(CO)_5(L)(Ar)]$, e
1981.6	w	↑	↑	↑	$W(CO)_6$, t_{1u}
1962.3	—	m	↓	↑	$W(CO)_5(L)$, e
1940.6	s	↓	↓	↑	<i>trans</i> - $[W(CO)_5(L)_2]$, e
1893.4	—	w	↑	↓	<i>cis</i> - $[W(CO)_5(L)_2]$, b_2

^a s strong; m medium; w weak; v very; dep. on deposition; — absent; = unchanged; ↑ increases; ↓ decreases. ^b L = cyclopentene.

quality by the presence of the matrix dopant, exhibited changes in accord with those seen earlier in experiments with pure argon matrices. This is to be expected, and the findings merely support the assumption, based on the work of Pope and Wrighton [24], that alkene-loss dominates the photochemical behaviour of mixed alkene carbonyl complexes of the Group 6 metals.

5. Conclusions

The results reported here make clear that matrix-isolated *trans*-[W(CO)₄(alkene)₂] (alkene = cyclopentene or 1-pentene) undergoes photo-isomerisation when irradiated with UV light at wavelengths near 313 nm to form the thermodynamically less stable *cis* bis(alkene) complex. The isomerisation is reversed when the *cis* isomer is exposed to visible light at wavelengths near 445 nm. Side-reactions that take place during photolysis have led to the partial characterisation in the ν (CO) region of the IR spectrum of the hitherto unknown complexes *trans*-[W(CO)₄(cyclopentene)(Ar)], *cis*-[W(CO)₄(cyclopentene)(Ar)] and *trans*-[W(CO)₄(1-pentene)(Ar)].

Investigations have been carried out to elucidate the mechanism by which photo-isomerisation occurs. Clear evidence was obtained from experiments employing CO-doped argon matrices that the transformation involves dissociation of the alkene ligand as the initial step. There was no clear evidence to support an intramolecular pathway, although we cannot rule out the possibility that such a mechanism plays a minor rôle in the isomerisation process. In the course of these investigations ν (CO) absorptions were also identified for the mono-alkene pentacarbonyl complexes [W(CO)₅(alkene)] (alkene = cyclopentene or 1-pentene) formed by UV photolysis of W(CO)₆ in alkene-doped argon matrices.

We plan to expand the scope of these investigations to take in a wide range of alkene ligands and conditions extending to the solution as well as the matrix-isolated state, with particular reference to isomerisation and other potential reactions involving the coordinated alkene moieties.

Acknowledgements

We acknowledge with gratitude the award of a research grant (to T.S.-B.) by the British Council, and support from E.P.S.R.C. for the purchase of equipment and the funding of a research assistantship (to T.M.G.).

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