Photochemical behaviour of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes in low temperatures

IR characterization of catalytically important intermediates

Teresa Szymańska-Buzar,*,[a] **Krystyna Kern**[a] **and Derk J. Stufkens**[b]

[a] *Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50–383 Wrocław, Poland*
[b] *Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, J.H. van't Hoff Research Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

UV irradiation (313 or 367 nm) of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] [alkene = propene (**1**), 1-butene (**2**), cyclopentene (**3**)] complexes in an alkane solution at temperatures ranging from 123 to 263 K leads to two primary photoprocesses, alkene and CO loss. The loss of the alkene is accompanied by the formation of 16-electron coordinatively unsaturated species: *trans*- and *cis*-[W(CO)$_4$(η^2-alkene)(s)], **A** (s = solvent molecule). The CO loss leads to the formation of *mer*- and *fac*-[W(CO)$_3$(η^2-alkene)$_2$(s)]. In the case of propene and 1-butene, the 16-electron complex **A** transforms into the IR detected *cis*-[WH(π-allyl)(CO)$_4$], **B**. Under conditions of excess alkene, the 16-electron tetracarbonyl species **A** binds alkene and forms *cis*-[W(CO)$_4$(η^2-alkene)$_2$], **C**, but the 16-electron tricarbonyl species transforms to *fac*-[W(CO)$_3$(η^2-alkene)$_3$], **D**, and *mer*-[W(CO)$_3$(η^2-alkene)$_3$], **E**. The relative amounts of the photoproducts **A**–**E** were dependent on the temperature, photolysis time, type of alkene ligand, photolysing radiation wavelength and the presence in solution of free alkene.

There has been considerable interest[1–14] in alkene carbonyl complexes of tungsten and their structural and spectroscopic properties since their first observation in 1963 by Stolz *et al.* Research on this class of complexes, which contain one or more alkene ligands, has tended to focus on their behaviour as intermediates in catalytic reactions.[8,15–22] In particular, this involves intermediates formed from Group 6 metal carbonyls and especially tungsten,[8,13,19–22] whose catalytic activity in reactions involving isomerization,[15] hydrogenation[16,21,22] or metathesis[17,18] of alkenes is very well-known.

Photolysis of [W(CO)$_6$] in the presence of an excess of alkene leads to the formation of a thermally more stable *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complex *via* a less stable [W(CO)$_5$(η^2-alkene)] complex.[1,3,5,6,9,12,14] It was established many years ago that two molecules of alkene coordinate to the M(CO)$_4$ moiety (M = Cr, Mo and W) in positions that are mutually *trans* and orthogonal.[1,3,9,10,12] *cis*-Bis(alkene) complexes were suspected to be involved as intermediate products.[9–12] Recently, we demonstrated that bis(alkene) complexes of the type *trans*-[W(CO)$_4$(η^2-alkene)$_2$] can be formed in the photochemical reactions of W(CO)$_6$ and C$_5$–C$_8$ cyclic and C$_5$–C$_{10}$ acyclic alkenes. The *trans* structure of those complexes has been assigned based on their IR spectra containing only one strong CO stretching vibration band.[14]

Following our demonstration of the photo-reversible isomerization of *trans*- to *cis*-[W(CO)$_4$(η^2-alkene)$_2$] complexes in low-temperature matrices,[19] we now report the photochemical conversion of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] (**1**–**3**, alkene = propene, 1-butene, cyclopentene) in an alkane solution at low temperatures. Of particular interst has been the detection of important intermediates in the catalytic cycle for W(CO)$_6$ photocatalysed reactions of alkenes. Such intermediates can be formed in the rearrangement of coordinatively unsaturated species appearing after CO or alkene loss from a *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complex. As was shown earlier, all these 16-electron complexes exhibit geometries based upon the octahedron with the solvent occupying the vacant coordination site.[20–23] These species were identified through the ν(CO) band in their IR spectra, and their reactivities toward alkenes probed in an alkane solution.

Experimental

Materials and methods

Syntheses and manipulation of chemicals were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use.

The *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes [alkene = propene (**1**), 1-butene (**2**), cyclopentene (**3**)] were synthesized in a photochemical reaction of W(CO)$_6$ and alkene in hexane, according to the procedures described previously.[14]

The low-temperature irradiation was carried out at Amsterdam. The photolysis source was an Oriel Corp. Model 6137 high-pressure mercury lamp, equipped with a 5 cm quartz water filter. Selective irradiation was carried out with the aid of suitable interference filters transmitting light centered at 313 or 367 nm and a cut-off filter transmitting light above 420 nm. The course of the photoreaction was readily monitored by using a BIO-RAD FTS-60A instrument employing a variable-temperature cell that serves as the reaction vessel.

In a typical experiment $\approx 1 \times 10^{-3}$ M solution of a bis(alkene) complex, **1**–**3**, in hexane or pentane was loaded into a home-built 0.1 mm path length IR cell equipped with CaF$_2$ windows. This cell was then cooled to the desired temperature using an Oxford Instruments DN 1704/54 liquid-nitrogen cryostat with CaF$_2$ and quartz windows and photolysed with a high-pressure Hg lamp at the precise temperature. The frozen solution was obtained at 123 K for pentane and 153 K for hexane. The photoproducts were detected by IR. In additional experiments, an appropriate alkene solution was used as the solvent for the bis(alkene) complex.

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* E-mail: tsz@chem.uni.wroc.pl

Results and Discussion

Photogeneration of coordinatively unsaturated species

The alkene complexes, which have been investigated by IR techniques in this work, are examples of a well-studied group of alkene complexes of the type *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$.[14] The IR spectra of compounds of this type in an alkane solution show one intense band at about 1950 cm^{-1}, together with a weak one at 1990 cm^{-1} and very weak ones at about 2050, 1920 and 1910 cm^{-1} (Table 1, Fig. 1). The additional weak band at about 1980 cm^{-1} is associated with the t_{1u} ν(CO) mode of $[W(CO)_6]$, **G** an unwanted impurity remaining from the synthesis of the bis(alkene) complex.

Generally, the UV photolysis of bis(alkene)tetracarbonyl complexes of tungsten in a hydrocarbon solution (above 193 K) or glass (pentane 123 K, hexane 153 K) leads to loss of the IR absorption due to the starting complex and growth of new ν(CO) bands associated with the coordinatively unsaturated 16-electron species. For instance, at 193 K in hexane, bands due to *trans*-$[W(CO)_4(\eta^2\text{-}1\text{-}C_4H_8)_2]$, **2**, decrease in intensity, which is accompanied by the growth of a set of four new bands at 2030, 1926, 1913 and 1871 cm^{-1} (Fig. 1). The CO band intensity pattern is in agreement with a C_{2v} symmetry of the $W(CO)_4$ skeleton in *cis*-$[W(CO)_4(\eta^2\text{-}1\text{-}C_4H_8)(s)]$, **2A**; the

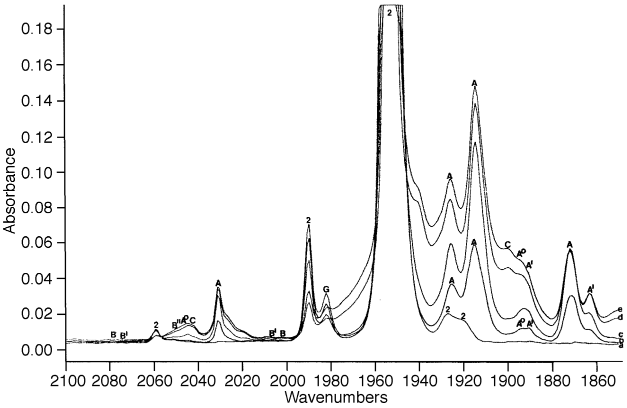


Fig. 1 IR absorption spectral changes resulting from UV ($\lambda = 313$ nm) irradiation of *trans*-$[W(CO)_4(\eta^2\text{-}1\text{-}C_4H_8)_2]$ **2**, in hexane solution at 193 K; curve (*a*) is before irradiation and curves (*b*), (*c*), (*d*) and (*e*) are after 10, 40, 130 and 250 min irradiation, respectively. Bands are labelled as follows: **A^O**, *trans*-$[W(CO)_4(\eta^2\text{-}1\text{-}C_4H_8)(s)]$; **A**, *cis*-$[W(CO)_4(\eta^2\text{-}1\text{-}C_4H_8)(s)]$; **A^I**, *fac*-$[W(CO)_3(\eta^2\text{-}1\text{-}C_4H_8)_2(s)]$; **B**, *cis*-$[WH(\eta^3\text{-}C_4H_7)(CO)_4]$; **B^I**, *mer*-$[WH(\eta^3\text{-}C_4H_7)(CO)_3(\eta^2\text{-}C_4H_8)]$; **B^{II}**, *mer*-$[WH(\eta^3\text{-}C_4H_7)(CO)_3(\eta^2\text{-}C_4H_8)]$; **C**, *cis*-$[W(CO)_4(\eta^2\text{-}1\text{-}C_4H_8)]$; **G**, $W(CO)_6$

Table 1 Infrared spectral data for relevant complexes[a]

Complex	*T*/K	ν(CO)/cm^{-1} (rel abs)[b]
trans-$[W(CO)_4(\eta^2\text{-}C_3H_6)_2]$ **1**	298	2058 (1), 1990 (4), 1954 (70), 1928 (1.6), 1917 (1.5)
	153	2059 (1), 1990 (5), 1952 (78), 1926 (1.5), 1918 (1.5)
trans-$[W(CO)_4(\eta^2\text{-}1\text{-}C_4H_8)_2]$ **2**	263	2058 (1), 1990 (6.7), 1954 (127), 1928 (2), 1919 (1.8)
trans-$[W(CO)_4(\eta^2\text{-}C_5H_8)_2]$ **3**	298[c]	2047 (1), 1980 (3.6), 1936 (24), 1916 (1.9), 1907 (1.7)
	173[d]	2048 (1), 1980 (6.3), 1938 (110), 1915 (4), 1905 (4.8)
	16[e]	2051(vvw), 1943(vs), 1919(vvw), 1909(vvw)
cis-$[W(CO)_4(\eta^2\text{-}C_3H_6)(s)]$ **1A**	193	2030 (1), 1926 (1), 1913 (1.3), 1872 (1)
	77[f]	2044 (1), 1885 (1.1)
cis-$[W(CO)_4(\eta^2\text{-}1\text{-}C_4H_8)(s)]$ **2A**	193	2030 (1), 1926 (1), 1913 (1.2), 1871 (1.1)
cis-$[W(CO)_4(\eta^2\text{-}C_5H_8)(s)]$ **3A**	123[c]	2033(vw), 1926(s), 1912(vs), 1867(vw)
	16[e]	1932.5, 1929.0
$[W(CO)_4]$	20[g]	2052, 1932, 1924, 1886
fac-$[W(CO)_3(\eta^2\text{-}C_3H_6)_2(s)]$ **1A^I**	193	1893 (1), 1863 (1)
fac-$[W(CO)_3(\eta^2\text{-}1\text{-}C_4H_8)_2(s)]$ **2A^I**	193	1893 (1), 1863 (1.2)
fac-$[W(CO)_3(\eta^2\text{-}C_5H_8)_2(s)]$ **3A^I**	123[c]	1973 (1), 1887 (1), 1863 (1)
$[WI(\eta^3\text{-}C_3H_5)(CO)_4]$	293[h]	2075(w), 2008(m), 1960(s)
cis-$[WH(\eta^3\text{-}C_3H_5)(CO)_4]$ **1B**	153	2077 (1), 1999 (1), 1961 (2.7)
cis-$[WH(\eta^3\text{-}C_4H_7)(CO)_4]$ **2B**	153	2077 (1), 2000 (0.9), 1961 (2.5)
mer-$[WH(\eta^3\text{-}C_3H_5)(CO)_3(\eta^2\text{-}C_3H_6)]$ **1B^I**	193	2070 (1), 2006 (1.1), 1918 (1.5)
mer-$[WH(\eta^3\text{-}C_4H_7)(CO)_3(\eta^2\text{-}1\text{-}C_4H_8)]$ **2B^I**	233	2070, 2005
mer-$[WH(\eta^3\text{-}C_3H_5)(CO)_3(\eta^2\text{-}C_3H_6)]$ **1B^{II}**	233	2050(vw), 1934(vs), 1913(s)
mer-$[WH(\eta^3\text{-}C_4H_7)(CO)_3(\eta^2\text{-}1\text{-}C_4H_8)]$ **2B^{II}**	263	2052 (1), 1935 (9.5), 1913 (3.7)
cis-$[W(CO)_4(\eta^2\text{-}C_3H_6)_2]$ **1C**	213	2042 (1), 1900 (2)
	203[i]	2042 (1), 1900 (1.7)
	77[f]	2039 (1), 1890 (1.5)
cis-$[W(CO)_4(\eta^2\text{-}1\text{-}C_4H_8)_2]$ **2C**	263	2041 (1), 1901 (1.5)
cis-$[W(CO)_4(\eta^2\text{-}C_5H_8)_2]$ **3C**	203[d]	2036 (1), 1955(s), 1945(vs), 1891 (1.6)
	16[e]	2052(w), 1954(m), 1949(vs), 1897(m)
$[W(CO)_4(\eta^4\text{-NBD})]$	182[j]	2042, 1956, 1909.2
cis-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$	195[k]	2050, 1957, 1910
fac-$[W(CO)_3(\eta^2\text{-}C_3H_6)_3]$ **1D**	203[i]	1974, (1), 1909 (0.9), 1873 (0.9)
fac-$[W(CO)_3(\eta^2\text{-}C_5H_8)_3]$ **3D**	303[d]	1966 (1), 1909, 1863 (1)
mer-$[W(CO)_3(\eta^2\text{-}C_3H_6)_3]$ **1E**	203[i]	2020 (1), 1938 (5.2), 1928 (3)
mer-$[W(CO)_3(\eta^2\text{-}C_5H_8)_3]$ **3E**	203[d]	2020(vw), 1928(s)
$[W(CO)_5(\eta^2\text{-}C_3H_6)]$ **1F**	213	2083 (1), 1964 (7.1)
	77[f]	2082 (1), 1961 (7.5), 1944 (9)
$[W(CO)_5(\eta^2\text{-}1\text{-}C_4H_8)]$ **2F**	233	2083 (1), 1965 (6.5)
$[W(CO)_5(\eta^2\text{-}C_5H_8)]$ **3F**	203[d]	2080(w), 1961(s)
$[W(CO)_6]$ **G**	263	1983
	153	1981

[a] In hexane solvent unless otherwise noted. [b] Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, vvw = very very weak. [c] In pentane. [d] In pentane containing 4% cyclopentene. [e] In argon; from ref. 19. [f] In methylcyclohexane; from ref. 8. [g] In CH_4; from ref. 23. [h] In cyclohexane; from ref. 28. [i] In hexane saturated with propene. [j] In liquid Xe; from ref. 21. [k] In liquid Xe; from ref. 9.

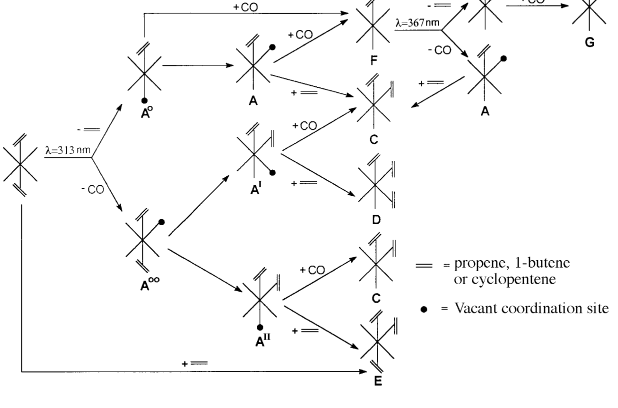
vacant coordination site with a loosely associated hexane molecule (s) occupies a *cis* position to the alkene.[13] For bis-unsaturated $W(CO)_4$ in CH_4 matrix these ν(CO) bands were detected at 2052, 1932, 1924 and 1886 cm^{-1}.[23] For coordinatively unsaturated $[W(CO)_4(\eta^2\text{-}1\text{-}C_5H_8)]$ only two of the four ν(CO) bands, at 1932 and 1929 cm^{-1}, were observed in Ar matrix.[19]

Simultaneously with **2A**, bands due to the tricarbonyl 16-electron species *fac*-$[W(CO)_3(\eta^2\text{-}1\text{-}C_4H_8)_2(s)]$, **2A^I**, formed after CO loss, appear at 1893 and 1863 cm^{-1} (Fig. 1). The third band of **2A^I** was detected at about 1970 cm^{-1} when the wavelength of the photolysing radiation was 367 nm. Under such conditions the $[W(CO)_5(\eta^2\text{-alkene})]$, **F**, absorption in the same region (1965 cm^{-1}) could not be generated (see below). The appearance of analogous bands due to the coordinatively unsaturated **A^I** was observed in the reaction of propene and the cyclopentene complexes **1** and **3** (Table 1). A similar pattern of bands (1981, 1904 and 1890 cm^{-1}) was also observed for coordinatively unsaturated *fac*-$[W(CO)_3(\eta^4\text{-NBD})(s)]$ (NBD = norbornadiene) formed in the photolysis of $[W(CO)_4(\eta^4\text{-NBD})]$ in room temperature *n*-heptane solution.[21]

The intensity of bands belonging to the species **A** (formed after alkene loss), is much higher than that of bands due to **A^I** (formed after CO loss). This gives good grounds for believing that the alkene is more easily photoejected from the bis(alkene)tetracarbonyl complex of tungsten than is a carbon monoxide ligand and that the yield of the photoproduction ($\lambda = 313$ nm) of species **A** is higher than that of **A^I**.

At 193 K, **A** and **A^I** are stable enough that even prolonged (250 min) UV photolysis gives new photoproducts in very low yields [Fig. 1(*b*–*e*)]. The two new bands centred at 2040 and 1900 cm^{-1}, which appear and grow together in the same way and may thus be assigned together to a common absorber, were identified as two out of the four bands belonging to *cis*-$[W(CO)_4(\eta^2\text{-alkene})_2]$, **C** [Fig. 1(*c*–*e*)]. **C** can be formed in a reaction of the coordinatively unsaturated tetracarbonyl species **A** with an early photoejected alkene, as was proved in experiments with a higher concentration of free alkene (see below). The full identification of ν(CO) bands characteristic for **C** was possible only in experiments carried out in the presence of excess alkene (see below).

As shown in Scheme 1, the coordinatively unsaturated 16-electron species *trans*-$[W(CO)_4(\eta^2\text{-alkene})(s)]$, **A^O**, and *mer*-$[W(CO)_3(\eta^2\text{-alkene})_2(s)]$, **A^{OO}**, the precursors of *cis*-$[W(CO)_4(\eta^2\text{-alkene})(s)]$, **A**, and *fac*-$[W(CO)_3(\eta^2\text{-alkene})_2(s)]$, **A^I**, are formed as the primary photoproducts. However, at temperatures higher than 193 K, only bands due to **A** and **A^I** can be observed. That indicates very fast *trans*–*cis* isomerization after an alkene or CO loss in alkane solution. Similar photochemical processes have been observed in a number of other carbonyl compounds of tungsten, where they have been attributed to excited-state isomerization of coordinatively unsaturated species.[8,13,19–23]



Scheme 1 Alkene complexes formed in UV photolysis of *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ carried out in an alkene solution at temperatures ranging from 123 to 263 K. The relative amounts of the photoproducts **A**–**E** are dependent on the temperature, photolysis time and the presence in solution of free alkene

Upon photolysis ($\lambda = 313$ nm) of compound **1** at lower temperature (153 K) in frozen hexane, one intense band centred at 1897 cm^{-1}, together with very weak one at 2042 cm^{-1}, appear (Fig. 2). This can be due to the primary photoproduct species **A^O**, which has the same D_{4h} symmetry as the starting compound **1** but with a vacant coordination site, occupied by solvent molecule, *trans* to the coordinated alkene. The frequencies of these two bands are very close to the frequencies of bands characteristic for **C**. However, they are different in intensity and in photochemical behaviour. **C** disappears (isomerizes to *trans*) under the influence of visible light, $\lambda > 420$ nm, but the 16-electron species **A^O** does not change under such conditions. The 16-electron species **A^{OO}** formed after CO loss (Scheme 1) can also be observed in frozen alkane after UV irradiation (Fig. 2), with bands at 2019, 1918 and 1904 cm^{-1}, but the proof of this assignment is not very strong because of the very low intensity of the bands, due to formation of **A^I** after CO loss from species **A^{OO}**. The pattern of ν(CO) bands due to the coordinatively unsaturated 16-electron species **A^O**, **A^{OO}**, **A** and **A^I** is similar in intensity to those of the 18-electron compounds **1**, **E**, **C** and **D**, respectively, but generally shifted to lower frequencies (Table 1).

The results presented here have unequivocally confirmed the identities of the 16-electron species and have demonstrated that coordinatively unsaturated intermediates exhibit geometries based upon the octahedron with the solvent specifically occupying the vacant coordination site. This permits a consideration of solvated intermediates as analogues of the coordination complexes from which they are derived.[20–23]

The rearrangement of coordinatively unsaturated 16-electron species

In the absence of coordinating ligands a coordinatively unsaturated alkene metal complex can transform into an 18-electron allyl hydrido complex. This rearrangement is especially well-documented in photochemical reactions of $[Fe(CO)_4(\eta^2\text{-alkene})]$ complexes.[24–26] After photochemical CO loss at low temperature, $[FeH(\eta^3\text{-allyl})(CO)_3]$ was detected by IR[24,25] and ^1H NMR[26] investigations. A similar rearrangement proposed by Pope and Wrighton in the $W(CO)_6$-catalyzed isomerization of alkenes has never been directly evidenced in their studies.[8]

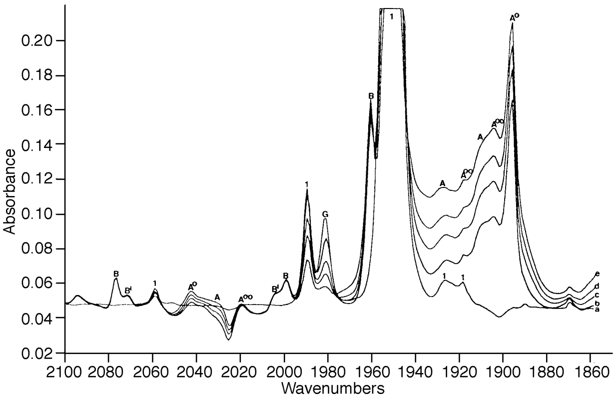


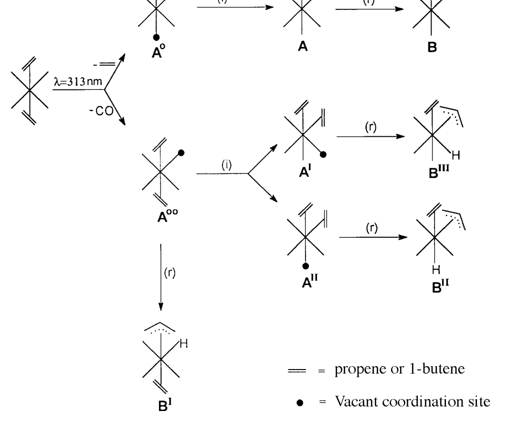
Fig. 2 IR absorption spectral changes accompanying UV ($\lambda = 313$ nm) irradiation of *trans*-$[W(CO)_4(\eta^2\text{-}C_3H_6)_2]$, **1**, in frozen hexane at 153 K; curve (*a*) is before irradiation and curves (*b*), (*c*), (*d*) and (*e*) are after 15, 45, 75 and 135 min irradiation, respectively. Bands are labelled as follows: **A^O**, *trans*-$[W(CO)_4(\eta^2\text{-}1\text{-}C_3H_6)(s)]$; **A^{OO}**, *mer*-$[W(CO)_3(\eta^2\text{-}1\text{-}C_3H_6)_2(s)]$; **A**, *cis*-$[W(CO)_4(\eta^2\text{-}1\text{-}C_3H_6)(s)]$; **B**, *cis*-$[WH(\eta^3\text{-}C_3H_5)(CO)_4]$; **B^I**, *mer*-$[WH(\eta^3\text{-}C_3H_6)]$; **G**, $W(CO)_6$

The first evidence for the transformation of bis(alkene)tetracarbonyl compounds of tungsten to allyl hydrido compounds were obtained from our earlier ^{1}H NMR studies.[18] On heating of alkene complexes in an NMR tube we observed the appearance of two signals due to hydrido ligands at about -3 ppm with the characteristic tungsten–hydrido coupling constant of *ca.* 17 Hz. More recently, similar results were obtained from UV photolysis of toluene-d_8 solutions of **1** and **2** at 203 K. The signals at about -3 ppm of the hydrido ligands generated photochemically at a lower temperature can be observed even at room temperature.[27]

In these studies, the photochemically generated and coordinatively unsaturated alkene metal complexes **A**, in the absence of coordinating ligands can transform to the 18-electron tetracarbonyl allyl hydrido complexes **B** (Scheme 2). The ν(CO) bands of a hydrido complex **B** would be expected to occur at a higher wavenumber than the bands of the corresponding bis(alkene)tetracarbonyl complex **C**, because of the higher oxidation state of the metal centre. The appearance of a weak band at a high wavenumber, 2077 cm^{-1}, was observed in the UV photolysis of **1** and **2** at different temperatures. Over the time of photolysis this band does not change in intensity.

The identification of **B** was possible after photolysis of a frozen solution of compounds **1** and **2**. The three new bands centred at 2077 and 1999 cm^{-1} were assigned to **B** (Fig. 2). The frequencies and relative intensities of these new bands compare well with those of the documented complex [WI(allyl)(CO)$_4$] [2075(w), 2008(m) and 1960(s) cm^{-1}].[28] Together with **B**, two new bands appear. The positions of the bands at 2070, 2006 and 1918 cm^{-1} are very close to the bands of species **B** but they are lower in intensity. These bands can be assigned to an isomer of **B** (*exo*/*endo*) or rather to [WH(allyl)(η^2-alkene)(CO)$_3$], **B$^{\mathrm{I}}$**, formed after rearrangement of the coordinatively unsaturated tricarbonyl species **A$^{\mathrm{OO}}$** (Scheme 2). Other allyl hydrido species such as **B$^{\mathrm{II}}$** and **B$^{\mathrm{III}}$**, isomers of **B$^{\mathrm{I}}$**, can also be formed as a result of the isomerization and rearrangement of **A$^{\mathrm{OO}}$** (Scheme 2).

When photolysis was performed at a higher temperature, the new ν(CO) bands, probably belonging to the rearrangement products, can be especially well observed (Fig. 3) because of the absence of bands due to coordinatively unsaturated species. The three new ν(CO) bands at 2050(vw), 1935(vs) and 1913(s) cm^{-1} may be of the tricarbonyl hydridoallyl complex and suggest a *mer* configuration of the CO groups as in **B$^{\mathrm{II}}$** rather than the *fac* configuration of **B$^{\mathrm{III}}$**. The characteristic feature of this species is its sensitivity to visible light radiation. It decays after irradiation with light having $\lambda > 420$ nm, whilst **B** does not change and **B$^{\mathrm{I}}$** increases in abundance. One possible explanation of this behaviour under the influence of visible light is the isomerization of **B$^{\mathrm{II}}$** to **B$^{\mathrm{I}}$**. The species **B$^{\mathrm{III}}$** has never been detected. The concentration of forms that were described as allyl hydrido species was very low in all experiments performed.



Scheme 2 The isomerization (i) and rearrangement (r) of coordinatively unsaturated species observed after UV photolysis of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] in an alkane solution in the absence of coordinating ligands, at temperatures ranging from 123 to 263 K

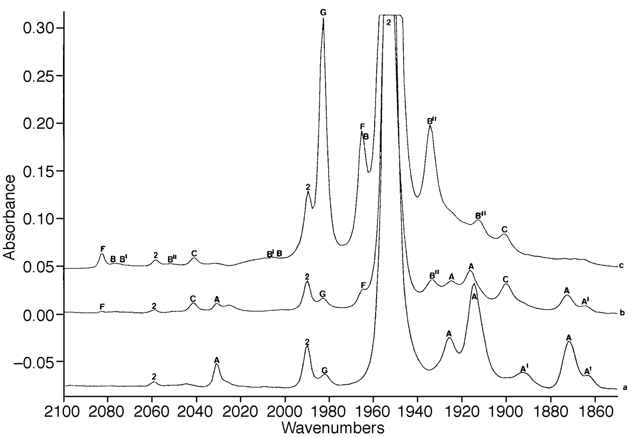


Fig. 3 IR absorption spectral changes accompanying UV ($\lambda = 313$ nm) irradiation of *trans*-[W(CO)$_4$(η^2-1-C$_4$H$_8$)$_2$], **2**, in hexane at different temperatures: (*a*) after 40 min at 193 K; (*b*) after 60 min at 233 K; (*c*) after 30 min at 263 K. Bands are labelled as follows: **A**, *cis*-[W(CO)$_4$(η^2-1-C$_4$H$_8$)(s)]; **A$^{\mathrm{I}}$**, *fac*-[W(CO)$_3$(η^2-1-C$_4$H$_8$)$_2$(s)]; **B**, *cis*-[WH(η^3-C$_4$H$_7$)(CO)$_4$]; **B$^{\mathrm{I}}$**, *mer*-[WH(η^3-C$_4$H$_7$)(CO)$_3$(η^2-C$_4$H$_8$)]; **B$^{\mathrm{II}}$**, *mer*-[WH(η^3-C$_4$H$_7$)(CO)$_3$(η^2-C$_4$H$_8$)]; **C**, *cis*-[W(CO)$_4$(η^2-1-C$_4$H$_8$)$_2$]; **F**, [W(CO)$_5$(η^2-1-C$_4$H$_8$)$_2$]; **G**, W(CO)$_6$

Photoreactivity of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] toward alkenes

When the photoreaction of **1** with excess propene in hexane is monitored at 203 K by IR, no coordinatively unsaturated species **A** or hydride-containing intermediate **B** is observed. The IR reveals the production of *cis*-[W(CO)$_4$(η^2-propene)$_2$], **1C**, together with the *fac*- and *mer*-[W(CO)$_3$(η^2-propene)$_3$] complexes, **1D** and **1E** [Fig. 4(*b*–*d*)]. The formation of the *cis* isomer **1C** is indicated by the CO stretching bands at 2042 and 1900 cm^{-1} with an intensity ratio of 1 : 1.7. Two of the four bands belonging to **1C** are obscured by the much more intense band of starting compound **1** centred at 1953 cm^{-1}. The assignments of the bands for **C** are based on the similarity of the bands to those of model *cis* species [W(CO)$_4$(η^4-NBD)] (2042.0, 1956.0, 1909.2 cm^{-1} in liquid Xe at 182 K)[21] and *cis*-[W(CO)$_4$(η^2-ethene)$_2$] (2050, 1957, 1910 cm^{-1} in liquid Xe at 195 K).[9]

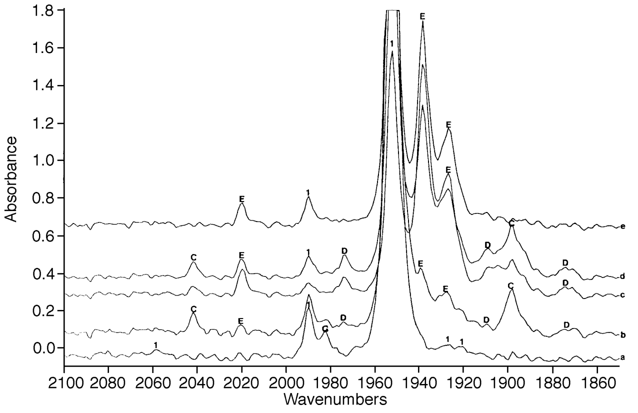


Fig. 4 IR absorption spectral changes resulting from irradiation of *trans*-[W(CO)$_4$(η^2-C$_3$H$_6$)$_2$], **1**, in hexane saturated with propene at 203 K; curve (*a*) is before irradiation; (*b*) after 20 min photolysis at $\lambda = 367$ nm; (*c*) after an additional 80 min photolysis at $\lambda = 367$ nm; (*d*) after 20 + 80 min photolysis at $\lambda = 367$ nm followed by 140 min photolysis at $\lambda = 313$ nm; (e) after a further 50 min photolysis at $\lambda > 420$ nm. Bands are labelled as follows: **C**, *cis*-[W(CO)$_4$(η^2-1-C$_4$H$_8$)$_2$]; **D**, *fac*-[W(CO)$_3$(η^2-1-C$_4$H$_8$)$_3$]; **E**, *fac*-[W(CO)$_3$(η^2-1-C$_4$H$_8$)$_3$]; **G**, W(CO)$_6$

The three weak bands of nearly equal intensities characteristic for *fac*-[W(CO)$_3$(η^2-propene)$_3$], **1D**, are observed at 1974, 1909 and 1873 cm^{-1}. Such a pattern of bands was detected for *fac*-[W(CO)$_3$(η^4-NBD)(η^2-NBD)] (1993.6, 1926.5 and 1900.2 cm^{-1})[22] and for *fac*-[W(CO)$_3$(η^4-NBD)(η^2-C$_2$H$_4$)] (1992, 1929 and 1887 cm^{-1}).[22] Over the time of UV photolysis, the bands for **1D** do not change intensity but the three bands for the *mer* isomer **1E**, at 2020(vw), 1938(vs) and 1928(s) cm^{-1}, increase very much [Fig. 4(*c*,*d*)]. The pattern of IR bands due to **1E** is similar in intensity and position to those of *mer*-[W(CO)$_3$(η^2-(*Z*)-cyclooctene)(η^4-NBD)] observed by Grevels *et al.*[12] at 2019.5(w), 1942.5(s) and 1932.5(m) cm^{-1}. The analogous compounds *mer*-[W(CO)$_3$(η^4-NBD)(η^2-NBD)] and *mer*-[W(CO)$_3$(η^4-NBD)(η^2-C$_2$H$_4$)] have bands at 2017.5, 1943.7, 1933.4 cm^{-1} and 2031, 1940 cm^{-1},[22] respectively.

Subsequent irradiation of the solution with visible light ($\lambda > 420$ nm) destroyed **1C** and regenerated the *trans* isomer **1** [Fig. 4(*e*)]. The bands due to **1D** also decay, whilst those for **1E** increase in intensity. It has thus been clearly demonstrated that selective UV photolysis can isomerize *trans*- to *cis*-bis(alkene) complexes, but visible photolysis has the reverse effect. Also the *fac* (**1D**) isomer transforms into the *mer* (**1E**) isomer under the influence of visible light [Fig. 4(*e*)].

Effect of temperature

Experiments at different temperatures allowed us to detect the various coordinatively unsaturated species. The intermediate species *trans*-[W(CO)$_4$(η^2-alkene)(s)], **A$^{\mathbf{O}}$** and *mer*-[W(CO)$_3$(η^2-alkene)$_2$(s)], **A$^{\mathbf{OO}}$**, can be observed only in frozen alkanes at 123 K for pentane and 153 K for hexane (Fig. 2). At higher temperatures (193 and 203 K) these species isomerize very fast to the IR-detected species *cis*-[W(CO)$_4$(η^2-alkene)(s)], **A**, and *fac*-[W(CO)$_3$(η^2-alkene)$_2$(s)], **A$^{\mathbf{I}}$** (Scheme 1), which are the main products of short-time UV photolysis [Figs. 1(*a*) and 3].

At 233 K and higher, coordinatively unsaturated species are too unstable to be detected. The main products observable by IR at 263 K are W(CO)$_6$, **G**, [W(CO)$_5$(η^2-alkene)], **F**, and the allyl hydride **B$^{\mathbf{II}}$** [Fig. 3(*c*)]. The formation of **G** and **F** at higher temperatures indicates that alkene loss and the formation of thermally unstable [W(CO)$_4$(η^2-alkene)(s)], **A$^{\mathbf{O}}$**, (Scheme 1) is the main photochemical process after irradiation at $\lambda = 313$ nm. **A$^{\mathbf{O}}$** traps early photoejected CO to form **F**. There are two bands at 2083(vw) and 1964(s) cm^{-1} characteristic for **F**. The third strong band predicted for **F** (C_{4v}) is obscured by an intense band of **2** [Fig. 3(*c*)]. Three bands at 2082, 1961 and 1944 cm^{-1} were observed for [W(CO)$_5$(η^2-C$_3$H$_6$)] in methylcyclohexane at 77 K.[8] The UV photolysis of **F** leads to alkene loss and, after CO trapping, the appearance of **G** [Fig. 3(*c*) and Scheme 1].

Another interesting observation is the unexpected stability of the photochemically formed *cis* isomer **C**, which can be observed even at 263 K [Fig. 3(*c*)]. The *cis* isomer of a bis(alkene)tetracarbonyltungsten complex was first observed as a thermally labile product during the photolysis of [W(CO)$_6$] and C$_3$H$_6$ or 1-C$_5$H$_{10}$ in rigid alkane at 77 K.[8] Subsequently, *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] was observed in a liquid Xe solution.[9] More recently, our studies revealed that *cis*-[W(CO)$_4$(η^2-alkene)$_2$] (alkene = 1-pentene and cyclopentene) can be formed in the photochemical isomerization of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] in an argon matrix at 16 K.[19] Here we show that a *cis* isomer can be observed at much higher temperature, even at 263 K.

Effect of photolysing radiation wavelength

The electronic spectrum of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes in an alkane solution exhibit a maximum at about 300 nm.[18] However, the electronic spectrum of the photolysis product of **1** measured in the IR cell applied in these studies is not well-resolved. After UV photolysis of **1** new bands appear in the visible region (>400 nm) but they are very broad.

The photochemical behaviour of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes in low-temperature hydrocarbon glasses or solutions is consistent with previously observed photochemistry in Ar at 16 K.[19] The facile loss of the coordinated alkene after UV ($\lambda = 313$ or 367 nm) photolysis produces the unsaturated alkene transient **A$^{\mathbf{O}}$**, which after *trans–cis* isomerization to **A** and recombination with the alkene gives a *cis* isomer of the original compound (Scheme 1). Subsequent photolysis of **C** at $\lambda > 420$ nm regenerates the *trans* isomer [Fig. 4(*e*)]. Similar *trans–cis* isomerization was also observed for coordinatively unsaturated species, but in contrast to **A$^{\mathbf{O}}$**, the 16-electron species **A$^{\mathbf{OO}}$** formed after CO loss in alkane glass decayed with a simultaneous increase of **A$^{\mathbf{II}}$** after visible light radiation. With visible light photolysis **A$^{\mathbf{I}}$** also decayed, probably by isomerization to **A$^{\mathbf{II}}$** (Scheme 1). **D** isomerizes to **E** under the influence of visible light [Fig. 4(*d*)]. This observation explains why **C** and **D** could not be detected after broad-band photolysis of [W(CO)$_6$] and alkene.

Among the allyl hydrido compounds, only the species detected as **B$^{\mathbf{II}}$** decays under irradiation with light having $\lambda > 420$ nm, whilst **B** does not change and **B$^{\mathbf{I}}$** increases in abundance.

At higher temperatures photolysis with light having $\lambda = 313$ nm leads to the formation of [W(CO)$_5$(η^2-alkene)], **F** [Fig. 3(*b*,*c*)]. However, when subsequent photolysis occurs at $\lambda = 367$ nm, the intensity of bands due to **F** decreases but those of W(CO)$_6$, **G**, increases. The result of the irradiation of compounds **1**–**3** at $\lambda = 367$ nm, irrespective of the temperature, is that **F** does not appear. It is known from the literature that the electronic spectrum of **1F** exhibits a maximum at $\lambda = 355$ nm.[8] Irradiation into this band causes alkene loss and the formation of W(CO)$_5$, very short-lived at higher temperatures, which traps early photoejected CO to form **G**. Thus the photolysis of **1**–**3** with light having $\lambda = 367$ nm prevents the appearance of **F**.

Only selective photolysis allowed us to generate intermediates with a high enough yield for detection by IR. Unfiltered photolysis gave spectra too complicated to allow any systematic analysis of the relevant photochemical events.

Effect of a coordinated alkene

Several possible photogenerated intermediates could arise from either W—CO or W—alkene bond breaking or from isomerization. Such intermediates are not readily identifiable, but the identification of particular intermediates is greatly simplified by studying the photolysis of a series of related precursor compounds that yield the same intermediates. The features for propene and 1-butene complexes are very similar. Also the photochemical products of **1** and **2** have almost identical IR characteristics (Table 1). Different behaviour was observed in the case of the photochemical reaction of the cyclopentene complex **3**. Irradiation of compound **3** produced coordinatively unsaturated species but IR spectroscopy showed that neither of these are transformed into allyl hydride. Thus, in the case of this cyclic alkene the activation of the C—H bond has not been observed.

Conclusions

The results presented here go some way towards bridging the gap between low-temperature matrices and the room-temperature solutions in which most preparative and catalytic reactions take place. The solution photochemistry of *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes is similar to their matrix photochemistry.[19] The *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes isomerize to *cis* complexes upon UV irradiation either in matrices or in solution. However, in an alkane solution we can observe also the formation of coordinatively unsaturated

16-electron species, solvated by alkanes, and their *trans–cis* isomerization products. Subsequent irradiation of the solution with visible light ($\lambda > 420$ nm) destroyed nearly all of the products with the *cis* configuration and regenerated the parent compounds. Only selective photolysis allowed us to observe all intermediates.

In an alkane solution it was possible to establish the rearrangement of 16-electron alkene complexes to allyl hydrido complexes that have not been detected in argon matrices.[19] In the case of the photochemical reaction of a cyclopentene complex only *trans–cis* isomerization was observed.

The photochemistry of *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ in alkane solutions and glasses show that *trans* to *cis* isomerization occurs through alkene loss, formation of coordinatively unsaturated species and subsequent coordination of the early photoejected alkene to give the relatively stable *cis*-$[W(CO)_4(\eta^2\text{-alkene})_2]$, **C**. Photolysis in the presence of excess alkene leads to the efficient substitution of CO by the alkene and the formation of the *fac* and *mer* tris(alkene) compounds **D** and **E**.

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References

1 I. W. Stolz, G. R. Dobson and R. K. Sheline, *Inorg. Chem.*, 1963, **2**, 1264.
2 U. Koemm, C. G. Kreiter and H. Strack. *J. Organomet. Chem.*, 1978, **148**, 179.
3 F.-W. Grevels, M. Lindemann, R. Benn, R. Goddard and C. Krüger, *Z. Naturforsch., Teil B: Anorg. Chem. Org. Chem.*, 1980, **35**, 1298.
4 J. A. Banister, S. M. Howdle and M. Poliakoff, *J. Chem. Soc., Chem. Commun.*, 1993, 1814.
5 S. A. Jackson, R. K. Upmacis, M. Poliakoff, J. J. Turner, J. K. Burdett and F.-W. Grevels, *J. Chem. Soc., Chem. Commun.*, 1987, 678.
6 F.-W. Grevels and V. Skibbe, *J. Chem. Soc., Chem. Commun.*, 1984, 681.
7 K. Angermund, F.-W. Grevels, C. Krüger and V. Skibbe, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 904.
8 K. R. Pope and M. S. Wrighton, *Inorg. Chem.*, 1985, **24**, 2792.
9 M. F. Gregory, S. A. Jackson, M. Poliakoff and J. J. Turner, *J. Chem. Soc., Chem. Commun.*, 1986, 1175.
10 F.-W. Grevels, J. Jacke and S. Özkar, *J. Am. Chem. Soc.*, 1987, **109**, 7536.
11 B. H. Weiller and E. R. Grant, *J. Am. Chem. Soc.*, 1987, **109**, 1252.
12 F.-W. Grevels, J. Jacke, P. Betz, C. Krüger and Y.-H. Tsay, *Organometallics*, 1989, **8**, 293.
13 H. Takeda, M. Jyo-o, Y. Ishikawa and S. Arai, *J. Phys. Chem.*, 1995, **99**, 4558.
14 M. Jaroszewski, T. Szymańska-Buzar, M. Wilgocki and J. J. Ziółkowski, *J. Organomet. Chem.*, 1996, **509**, 19.
15 M. Wrighton, G. S. Hammond and H. B. Gray, *J. Organomet. Chem.*, 1974, **70**, 283.
16 R. G. Salomon, *Tetrahedron*, 1983, **39**, 485.
17 T. Szymańska-Buzar, *J. Mol. Catal.*, 1988, **48**, 43.
18 T. Szymańska-Buzar, M. Jaroszewski, M. Wilgocki and J. J. Ziółkowski, *J. Mol. Catal.*, 1996, **112**, 203.
19 T. Szymańska-Buzar, M. Jaroszewski, A. J. Downs, T. M. Greene and L. J. Morris, *J. Organomet. Chem.*, 1997, **531**, 207.
20 G. R. Dobson, P. M. Hodges, M. A. Healy, M. Poliakoff, J. J. Turner, S. Firth and K. J. Asali, *J. Am. Chem. Soc.*, 1987, **109**, 4218.
21 S. A. Jackson, P. M. Hodges, M. Poliakoff, J. J. Turner and F.-W. Grevels, *J. Am. Chem. Soc.*, 1990, **112**, 1221.
22 P. M. Hodges, S. A. Jackson, J. Jacke, M. Poliakoff, J. J. Turner and F.-W. Grevels, *J. Am. Chem. Soc.*, 1990, **112**, 1234.
23 R. N. Perutz and J. J. Turner, *J. Am. Chem. Soc.*, 1975, **97**, 4800.
24 J. C. Mitchener and M. S. Wrighton, *J. Am. Chem. Soc.*, 1983, **105**, 1065.
25 T. M. Barnhart and R. J. McMahon, *J. Am. Chem. Soc.*, 1992, **114**, 5434.
26 T. M. Barnhart, J. De Felippis and R. J. McMahon, *Angew. Chem., Int. Ed. Engl.*, 1993, **7**, 1073.
27 T. Szymańska-Buzar and K. Kern, in preparation.
28 C. E. Holloway, J. D. Kelly and M. H. B. Stiddard, *J. Chem. Soc. A*, 1969, 931

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