Crystal structure of *trans*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$ and IR and ^{1}H NMR studies of the reactions of this and related ethene carbonyl complexes of tungsten(0), $[W(CO)_n(\eta^2\text{-}C_2H_4)_{6-n}]$ (n = 3–5)

Teresa Szymańska-Buzar,*[a] Krystyna Kern,[a] Anthony J. Downs,*[b] Timothy M. Greene,[b] Leigh J. Morris[b] and Simon Parsons[c]

[a] *Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50 383 Wrocław, Poland*
[b] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR*
[c] *Department of Chemistry, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, UK EH9 3JJ*

Received (in Cambridge, UK) 4th November 1998, Accepted 4th February 1999

The structure of *trans*-$[W(CO)_4\ (\eta^2\text{-}C_2H_4)_2]$ **1** has been determined by X-ray crystallography at 293 K [orthorhombic, space group *Aba*2, a = 12.458(3), b = 6.370(2), c = 12.557(3) Å, Z = 4, R = 0.022] to confirm that the C=C bonds of the two ethene ligands are mutually staggered while eclipsing the central $W(CO)_4$ unit. Reversible isomerisation of *trans*- to *cis*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$ **2** under the action of selective irradiation has been shown to occur in solid argon matrices at 14–16 K. ^{1}H NMR measurements have also been applied to the identification of not only **1** and **2** but also the labile 18e complexes $[W(CO)_5(\eta^2\text{-}C_2H_4)]$ **3**, *mer*-$[W(CO)_3(\eta^2\text{-}C_2H_4)_3]$ **4**, and *fac*-$[W(CO)_3(\eta^2\text{-}C_2H_4)_3]$ **5** formed by broad-band UV-visible photolysis of ethene-saturated hydrocarbon solutions of **1** or $[W(CO)_6]$ in the temperature range 200–293 K. In these circumstances the mixed ethene carbonyl complexes **2**–**5** decay thermally with dissociation of an ethene ligand and substitution by CO in reactions which have been monitored by reference to the relevant ^{1}H NMR signals. Pseudo-first-order decay constants in the range 0.6–12 × 10^{-4} s^{-1} have thus been estimated with temperature-dependences implying activation energies, E_a, that decrease in the order **3** > **2** > **4** > **5**.

There are significant synthetic, catalytic and theoretical aspects to the interest recently aroused by the alkene complexes derived from photochemical reactions of transition-metal carbonyls.[1–19] We have sought systematically to explore the rôles of these complexes in the reactions of alkenes that are catalysed by Group 6 metal carbonyls by focusing on bis(alkene) complexes of the type *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ and exploiting their photolability with respect to displacement of CO or alkene ligands and isomerisation. One of the principal goals has been to detect, identify and characterise the intermediates by which $[W(CO)_6]$-catalysed alkene reactions evolve.[18–20]

Photolysis of $[W(CO)_6]$ in the presence of an alkene leads to the formation of a thermally more stable *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ complex *via* a less stable $[W(CO)_5(\eta^2\text{-alkene})]$ complex.[1,3,4,7–10,17] The *cis* bis(alkene) complex $[W(CO)_4(\eta^2\text{-alkene})_2]$, inferior in thermodynamic stability to the *trans* isomer, has been shown[7–11] to function as an intermediate, and there is general recognition[2,21] too that this has a key rôle to play in catalytic cycles for metathesis, isomerisation and other reactions of alkenes mediated by $[W(CO)_6]$. Recent studies have demonstrated[19] that, under the action of selective irradiation, reversible photoisomerisation of *trans*- to *cis*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ complexes (alkene = pent-1-ene or cyclopentene) can be induced in solid argon matrices at low temperatures. Several of the more stable *trans* isomers have been isolated as solids or liquids that are long-lived at ambient temperatures;[9,17] crystallographic studies reported to date[3,22] reveal structures in which the C=C bonds of the two alkene ligands are mutually staggered but eclipse the central $W(CO)_4$ fragment.

IR studies of the photolysis of *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ (alkene = prop-1-ene, but-1-ene or cyclopentene) in alkane solutions at temperatures ranging from 123 to 263 K have led to the detection of the 16e coordinatively unsaturated species *trans*- and *cis*-$[W(CO)_4(\eta^2\text{-alkene})(\text{solv})]$ and *mer*- and *fac*-$[W(CO)_3(\eta^2\text{-alkene})_2(\text{solv})]$ wherein a solvent molecule (solv) occupies the vacant coordination site.[20] With an excess of alkene the 16e tetracarbonyl species react to form *cis*-$[W(CO)_4(\eta^2\text{-alkene})_2]$, whereas the 16e tricarbonyl species form both *mer*- and *fac*-$[W(CO)_3(\eta^2\text{-alkene})_3]$. The identities and structures of the relevant complexes have been assigned on the basis of the ν(CO) bands in their IR spectra.[20]

Although the synthesis and spectroscopic properties of the simplest *trans* bis(alkene) complex, *trans*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$ **1**, have been reported,[1,9] neither its structure nor its photochemical behaviour has been established definitively. Here we report (i) the crystal structure of **1** as determined by X-ray crystallography and its ^{1}H and ^{13}C NMR properties in hydrocarbon solution; (ii) the results of matrix-isolation experiments involving IR detection of the effects of selective irradiation of **1** or its photoproducts; (iii) ^{1}H NMR characterisation of the less stable ethene complexes *cis*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$ **2**, $[W(CO)_5(\eta^2\text{-}C_2H_4)]$ **3**, *mer*-$[W(CO)_3(\eta^2\text{-}C_2H_4)_3]$ **4**, and *fac*-$[W(CO)_3(\eta^2\text{-}C_2H_4)_3]$ **5**, formed by broad-band UV-visible photolysis of **1** or $[W(CO)_6]$ in ethene-saturated hydrocarbon solutions at temperatures in the range 200–293 K; and (iv) exploitation of these ^{1}H NMR spectra for kinetic measurements of the decay of complexes **2**–**5** in thermal reactions initiated by dissociation of the ethene ligand.

Table 1 Crystal data and structure refinement for *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **1**

Empirical formula	WC$_8$H$_8$O$_4$
Formula weight	351.99
λ/Å	0.710 73
T/K	200(2)
Crystal system	Orthorhombic
Space group	*Aba*2
a/Å	12.458(3)
b/Å	6.370(2)
c/Å	12.557(3)
V/Å^3	996.5(5)
Number of reflections for cell	72 ($15 < \theta < 16°$)
Z	4
D_c/Mg m^{-3}	2.346
μ/mm^{-1}	11.571
F(000)	648
Reflections collected	3058
Independent reflections	884 ($R_{\text{int}} = 0.0556$)
Goodness-of-fit on F^2	1.107
Conventional R [$F > 4\sigma(F)$]	$R_1 = 0.0221$ (635 data)
Weighted R (F^2 and all data)	$wR_2 = 0.0506$

Experimental

Materials and synthesis of *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] 1

Synthesis and manipulation of chemicals were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried and distilled from CaH$_2$ under nitrogen prior to use. Tungsten hexacarbonyl (Aldrich), ethene (Aldrich, 99% grade), [^{2}H$_4$]ethene (C.D.N. Isotopes) and argon (B.O.C., 'Research' grade) were used as supplied. The photolysis sources were an HBO 200 high-pressure Hg lamp (for synthesis and the solution studies) and a Spectral Energy 1000 W Hg–Xe arc lamp (for the matrix experiments). Selective irradiation of matrix samples was carried out with the aid of a suitable interference filter transmitting light centred at 313 nm (fwhh 16 nm) or 445 nm (fwhh 13 nm).

Trans-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **1** was synthesised as follows. Ethene was bubbled through a solution of [W(CO)$_6$] (0.6 g, 1.7 mmol) in *n*-hexane (100 cm^3) held at *ca.* 263 K while being irradiated with the unfiltered output of the HBO 200 Hg lamp. The course of the reaction was monitored by IR measurements made on the solution at room temperature, and photolysis was stopped when the IR band of **1** at 1966 cm^{-1} reached its maximum intensity (after about 3 h). The volatile materials were then stripped off the reaction mixture at *ca.* 273 K and the brown residue was left for 24 h to allow the monoethene complex [W(CO)$_5$(η^2-C$_2$H$_4$)] **3** to decay. The residue was redissolved in *n*-hexane (3 cm^3) and separation of **1** was achieved by column chromatography on silica using *n*-hexane as the eluent. Crystallisation of the product from concentrated *n*-hexane solution at *ca.* 250 K gave 0.27 g (0.8 mmol) of white crystals of **1** (47% yield based on the amount of [W(CO)$_6$] taken). The product was characterised by its IR and NMR spectra.[9,23] IR (hexane): ν(CO) 2059vvw, 1997w, 1966vs, 1936w cm^{-1}. ^{1}H NMR ([^{2}H$_8$]toluene, 293 K): δ 2.12 (s, 2C$_2$*H*$_4$, $^3J_{\text{HH}(trans)} = 12.2$, $^3J_{\text{HH}(cis)} = 9.9$, $^2J_{\text{HH}} = 1.5$ Hz). ^{13}C-{^{1}H} NMR ([^{2}H$_8$]toluene, 293 K): δ 198.02 (s, 4*C*O, $^1J_{\text{WC}} = 119.5$), 31.20 (s, 2*C*$_2$H$_4$, $^1J_{\text{WC}} = 11.3$ Hz). ^{13}C NMR ([^{2}H$_8$]toluene, 293 K): δ 31.20 (t, 2*C*$_2$H$_4$, $^1J_{\text{CH}} = 161.0$ Hz).

Spectroscopic and matrix-isolation experiments

IR spectra of solutions were recorded on a Nicolet model 400 FT-IR, spectra of matrices on a Mattson 'Galaxy' FT-IR instrument, with a spectral resolution in the second case of 1 cm^{-1}. Matrices were formed by slow, continuous deposition of the vapour of [W(CO)$_6$] or **1** with an excess of argon; the equipment and operating procedures have been described previously.[24]

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 spectrometer operating at 300 and 75.5 MHz, respectively. Spectra of [^{2}H$_8$]toluene solutions were calibrated internally by reference to the methyl resonance of residual [^{2}H$_7$]toluene occurring at δ 2.10 in the ^{1}H and δ 20.4 in the ^{13}C NMR spectra, respectively. ^{1}H NMR spectra of [^{2}H$_{14}$]methylcyclohexane solutions were referenced externally to SiMe$_4$.

Photochemical reactions involving **1** or [W(CO)$_6$] and ethene occurring in alkane solution at room temperature or in argon matrices at 14–16 K were investigated by following the IR spectra of the samples. The products of these reactions in [^{2}H$_8$]toluene or [^{2}H$_{14}$]methylcyclohexane solution were tracked by ^{1}H NMR measurements at temperatures in the range 198–350 K. In a typical experiment a solution of **1** (0.15 g, 0.4 mmol) in freshly distilled *n*-hexane (50 cm^3) was saturated with ethene gas for 15 min and then irradiated through quartz at about 285 K for 2 h under a continuous ethene purge. The IR spectrum of the resulting brown solution exhibited ν(CO) bands attributable to **1** and additional features at 2050 and 2013 cm^{-1} indicating the formation of *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **2** (*q.v.*). After photolysis the solvent was removed under vacuum at 265 K, the residual solid dissolved in [^{2}H$_8$]toluene (0.7 cm^3), and the resulting solution transferred to a 5 mm NMR tube. The ^{1}H NMR spectrum of this sample at 263 K indicated 45% conversion of **1**, mainly (45%) to *mer*-[W(CO)$_3$(η^2-C$_2$H$_4$)$_3$] **4** (*q.v.*).

The photochemical changes were also followed directly by ^{1}H NMR measurements. In a typical experiment a [^{2}H$_8$]toluene solution *ca.* 0.02 M in the bis(ethene) complex **1** or a [^{2}H$_{14}$]methylcyclohexane solution *ca.* 0.1 M in **1** contained in a 5 mm NMR tube was cooled to the desired temperature and subjected to broad-band UV-visible irradiation. The tube was transferred to the precooled sample-holder of the NMR spectrometer, and the ^{1}H NMR spectrum of the solution recorded. In some experiments the solvent was saturated with ethene prior to dissolution of **1** or [W(CO)$_6$]. The relative concentrations of the species present in solution were determined by integrating the ^{1}H NMR signals, the measurements being normalised with respect to the area under the toluene resonance.

Kinetic studies

The samples destined for kinetic measurements were generally prepared by the photochemical reaction of ethene with [W(CO)$_6$] (0.05 M) in [^{2}H$_8$]toluene solution saturated with ethene contained in an NMR tube. The sample temperature was maintained at *ca.* 200 K prior to NMR measurements. The rate of decay of a given ethene complex was then determined by monitoring its ^{1}H NMR signal as a function of time at a minimum of three different temperatures in the following ranges: 343–353 K for [W(CO)$_5$(C$_2$H$_4$)] **3**, 263–273 K for *cis*-[W(CO)$_4$(C$_2$H$_4$)$_2$] **2**, 258–283 K for *mer*-[W(CO)$_3$(C$_2$H$_4$)$_3$] **4**, and 228–238 K for *fac*-[W(CO)$_3$(C$_2$H$_4$)$_3$] **5**.

Crystallography

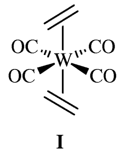
Details of the crystal data, data collection, structure solution and refinement are given in Table 1. All data were collected on a Stoë Stadi-4 four-circle diffractometer with graphite-monochromated Mo-Kα radiation in the ω–2θ mode.

CCDC reference number 440/099. See http://www.rsc.org/nj/1999/407/ for crystallographic files in .cif format.

Results and discussion

Synthesis and spectroscopic characterisation of *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] 1

Broad-band photolysis of an *n*-hexane solution of [W(CO)$_6$] gives in the presence of an excess of ethene at *ca.* 283 K the bis(ethene) complex *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **1** as the major product. The IR spectrum of the solution witnessed initially the formation of [W(CO)$_5$(η^2-C$_2$H$_4$)] **3**, with ν(CO) bands at 2086 (0.15), 1973 (0.95) and 1955 (1) cm^{-1} (relative intensities being given in parentheses), as illustrated in Fig. 1a. That photosubstitution of a second CO group then leads to both *trans*- and *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] (**1** and **2**, respectively) is also signalled by the IR spectrum (Fig. 1b). Thus the formation of the *cis* isomer **2** is indicated by the growth of two ν(CO) bands at 2050 and 1913 cm^{-1} (relative intensities 1 : 1.5); the other two ν(CO) bands are obscured by more intense absorptions associated with **3** and the *trans* isomer **1**. The *cis* isomer of [W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] was first spotted as a thermally labile photoproduct deriving from [W(CO)$_6$] in ethene-doped liquid xenon solution at 195 K, being identified by its IR spectrum with ν(CO) bands at 2050, 1957 and 1910 cm^{-1}.[7] The IR spectrum of *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **1** is dominated by one intense band at 1966 (1) cm^{-1} accompanied by three weaker ones at 2059 (0.003), 1997 (0.11) and 1936 (0.06) cm^{-1} (see Fig. 1c). This tallies with previous reports,[7,9,24] the pattern of ν(CO) bands mirroring closely that of other *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes that have been studied previously.[1,3,17,19,20] The spectrum can be interpreted[19,24] on the basis of the structure **I** conforming to D_{2d} symmetry. Compound **1** is long-lived under ambient conditions; it can be stored as an alkane solution in the dark for months without noticeable change.



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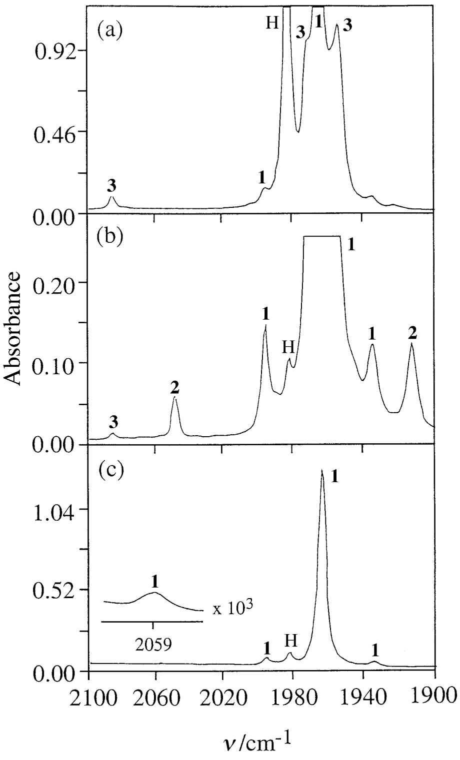


Fig. 1 ν(CO) region of the IR absorption spectrum of [W(CO)$_6$] **H** in ethene-saturated *n*-hexane solution at room temperature: (a) after broad-band UV-visible photolysis for 90 min at 283 K and (b) after broad-band UV-visible photolysis for a further 60 min at 283 K, showing the formation of the ethene carbonyl complexes **1**, **2** and **3**. (c) Spectrum of virtually pure *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **1**.

In the ^{1}H NMR spectrum of a [^{2}H$_8$]toluene solution of **1** at 293 K the four ethene hydrogens give rise to a singlet at δ 2.12. With respect to free ethene this resonance shows a remarkably large shift, $\Delta\delta = \delta$(free ethene) $- \delta$(coordinated ethene) = 3.16. The singlet is accompanied by satellites due to ^{13}C-{^{1}H} coupling ($^1J_{\mathrm{CH}} = 161$ Hz), and each satellite is split by coupling between the ethene protons with $^3J_{\mathrm{HH}(trans)} = 12.2$, $^3J_{\mathrm{HH}(cis)} = 9.9$, and $^2J_{\mathrm{HH}} = 1.5$ Hz. Coordination of free ethene thus results in a slight increase in $^1J_{\mathrm{CH}}$ (from 156.4[25a] to 161.0 Hz) and an appreciable *decrease* in the proton coupling constants ($^3J_{\mathrm{HH}(trans)} = 19.0$, $^3J_{\mathrm{HH}(cis)} = 11.5$, and $^2J_{\mathrm{HH}} = 2.3$ Hz for free ethene[25b]).

The ^{13}C resonance moves from δ 123.3 in free ethene to δ 31.20 in the coordinated ligand in **1**. This is the largest low-frequency shift to be reported to date for a *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complex.[3,9,11,17] The ^{13}C resonance of **1** appears as a triplet with $^1J_{\mathrm{CH}} = 161$ Hz and is accompanied by satellites due to coupling between the ethene carbon and the ^{183}W nucleus ($I = 1/2$, 14.5% natural abundance). The coupling constant $^1J_{\mathrm{WC}} = 11.3$ Hz lends some weight to the description of the W–η^2-C$_2$H$_4$ unit as a metallocyclopropane. The NMR properties indicate overall that each ethene ligand in **1** is strongly bound, partly through donation of its C$_2$-π electrons into a vacant d$_\sigma$ orbital but mainly through a strong interaction of the C$_2$-π^* acceptor orbital with a d$_\pi$ occupied orbital of the tungsten. The results are also consistent with the *trans* staggered bis(ethene) geometry **I** inferred from the IR spectrum.

Crystal structure of *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] 1

Solving the molecular structure of **1** on the basis of X-ray diffraction analysis of a single crystal at 200 K has not proved to be altogether straightforward. The structure of **1** is reported here in the space group *Aba*2. It may also be described, however, in the related centrosymmetric group *Cmca*, and so it is necessary to justify the use of the lower symmetry space group. The pattern of intensities displayed by the reflections, allied to symmetry considerations, implied that the W atom could be placed at (000); the origin was then fixed by selecting a plausible CO unit from a subsequent difference synthesis. The structure was completed by iterative cycles of least-squares refinement and difference Fourier synthesis (SHELXL-97[26]). In *Aba*2 the origin is a special position of ..2 symmetry, and the molecule is ordered with the two ethene units staggered with respect to each other: in *Cmca* the ethene units are disordered by the inversion centre. H atoms were located in a difference synthesis performed in *Aba*2 and the positions refined subject to similarity restraints on the C–H distances and the geminal and vicinal H···H distances; a single isotropic displacement parameter was also refined for these atoms. Since the H atom positions were not obvious from difference maps in *Cmca*, refinement in these circumstances involved placing the H atoms in ideal positions and then allowing them to ride on their parent C atoms. Refinement in *Aba*2 converged to $R[F > 4\sigma(F)] = 0.0221$ for 75 parameters, and in *Cmca* to 0.0267 for 42 parameters. The additional parameters in the non-centrosymmetric model comprise the Flack x [0.56(5)], 19 positional parameters [W(z), 4 H atoms and one CO group] and 13 displacement parameters [12 for the CO groups and one overall U_{iso}(H)].

The position of the W atom means that it contributes to only half the data set [$k + l = 2n$ for *Cmca* and $h + k = 2n$ for *Aba*2]. Although the data exhibit centric intensity statistics overall, the value of $|E^2 - 1|$ for the weak data originating exclusively in the light atoms is 0.697 (*i.e.* strongly acentric). In addition, $R[F > 0]$ calculated for all these data is 0.0335 for the *Aba*2 refinement as against 0.0523 for the *Cmca* refinement. These factors are also reflected in variance analyses of F_c^2 against $|F_o^2|/|F_c^2|$ which show no abnormal systematic trends for the non-centrosymmetric space group, but 'tail' up to 9.2 for the weakest data in the centrosymmetric group. The weak data therefore favour the non-centrosymmetric description.

While such broad statements cannot be applied to high-symmetry cases, it remains true that centred orthorhombic crystal structures are fairly rare and can be mistaken for twinned monoclinic structures. The structure of **1** may also be modelled in the $P2_1/c$ space group with a cell having the dimensions $a = 7.04$, $b = 12.45$, $c = 6.38$ Å and $\beta = 116.94°$. Here we note that the second glide plane confirming the orthorhombic symmetry might easily be missed since it affects a zone of weak reflections. With the W atom again residing at (000), this structure represents a reduction in symmetry from $2/m$ in *Cmca* to -1 (*cf.* the reduction to ..2 in *Aba*2). Refinement can be achieved as above to give results broadly similar to those in the *Cmca* refinement. The apparent disorder in the ethene units may also be modelled with twinning *via* a two-fold rotation about $\mathbf{c}_{\mathrm{monoclinic}}$ (-1 0 -1/0 -1 0/0 0 1). The twin component refines to a rather low 0.42(1) with a final $R[F > 4\sigma(F)] = 0.0301$ and difference map extrema of $+1.03$ and -1.80 e Å^{-3}; weak difference peaks of 0.68 and 0.58 e Å^{-3} are observed in the region of the ethene unit. While these refinement statistics are poorer than those associated with either of the orthorhombic refinements, they are reasonably acceptable for a compound of this type. The monoclinic model is, however, *chemically* different from the orthorhombic ones because it has mutually *eclipsed* ethene units. This quite misleading result can again be rejected on the basis of the weak data for which $R[F > 0] = 0.060$.

Although the crystal structure of **1** is best referred to *Aba*2, the structure of the W(CO)$_4$ unit can be efficiently modelled in *Cmca*. It does not seem unreasonable to apply as restraints in *Aba*2 the constraints on the positional and displacement parameters of this fragment which are generated when it is modelled in *Cmca*. The C–O and W–CO bond lengths and the anisotropic displacement parameters of the centrosymmetrically related C and O atoms were therefore restrained to be similar. Although this procedure barely affected the agreement indices or convergence, it improved the precision of the relevant parameters.

The molecular structure of **1** is illustrated in Fig. 2; bond distances and angles are listed in Table 2. As expected,[3,9,12,22,27] the C=C bonds of the two η^2-coordinated ethene ligands are staggered with respect to each other but eclipse the W(CO)$_4$ fragment. The preference for this configuration is easily understood in terms of optimum metal → π^*(alkene) back donation.[9,12,27] Because of the single-faced π-acceptor character of an alkene molecule there will be no competition for metal d_π electron density between two such molecules if they are in a *trans* orthogonal orientation. Measuring 1.413(13) Å, the C=C bonds of the coordinated ethene molecules are elongated by 0.074 Å with respect to the free molecule.[28] They are thus roughly halfway between the bonds in free ethene (r_z 1.339 Å)[28] and cyclopropane (r_z 1.513 Å).[29] Comparisons with other ethene complexes[30] show them to be substantially longer than the corresponding bonds

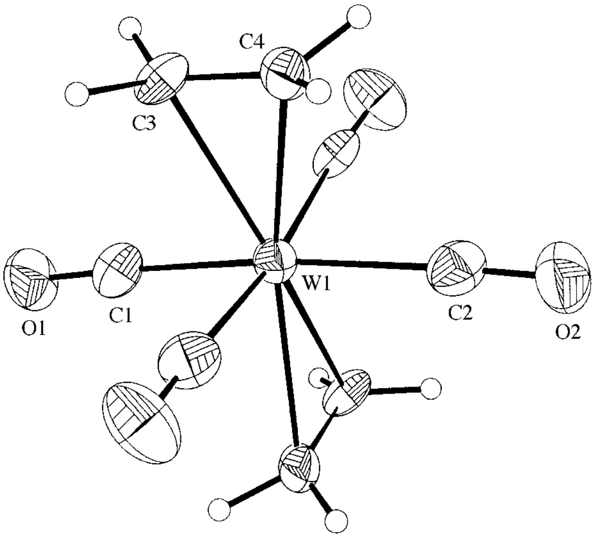


Fig. 2 Structure of *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] as determined by X-ray diffraction of a single crystal at 200 K.

Table 2 Bond lengths (Å) and angles (°) for crystalline *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **1**[a]

W(1)–C(2)	2.033(10)	C(1)–O(1)	1.151(11)
W(1)–C(2^i)	2.033(10)	C(2)–O(2)	1.142(10)
W(1)–C(1)	2.045(9)	C(3)–C(4)	1.413(13)
W(1)–C(1^i)	2.045(9)	C(3)–H(31)	0.98(4)
W(1)–C(4)	2.299(9)	C(3)–H(32)	0.98(4)
W(1)–C(4^i)	2.299(9)	C(4)–H(41)	0.98(4)
W(1)–C(3)	2.315(9)	C(4)–H(42)	0.98(4)
W(1)–C(3^i)	2.315(9)		
C(2)–W(1)–C(2^i)	92.3(9)	C(2)–W(1)–C(3^i)	86.3(4)
C(2)–W(1)–C(1)	171.8(7)	C(2^i)–W(1)–C(3^i)	111.1(4)
C(2^i)–W(1)–C(1)	90.9(3)	C(1)–W(1)–C(3^i)	85.5(5)
C(2)–W(1)–C(1^i)	90.9(3)	C(1^i)–W(1)–C(3^i)	76.7(5)
C(2^i)–W(1)–C(1^i)	171.8(7)	C(4)–W(1)–C(3^i)	154.8(3)
C(1)–W(1)–C(1^i)	87.0(9)	C(4^i)–W(1)–C(3^i)	35.7(3)
C(2)–W(1)–C(4)	75.4(5)	C(3)–W(1)–C(3^i)	155.4(5)
C(2^i)–W(1)–C(4)	87.1(5)	O(1)–C(1)–W(1)	175.1(13)
C(1)–W(1)–C(4)	112.3(5)	O(2)–C(2)–W(1)	176.2(14)
C(1^i)–W(1)–C(4)	86.3(5)	C(4)–C(3)–W(1)	71.5(5)
C(2)–W(1)–C(4^i)	87.1(5)	C(4)–C(3)–H(31)	121(4)
C(2^i)–W(1)–C(4^i)	75.4(5)	W(1)–C(3)–H(31)	115(5)
C(1)–W(1)–C(4^i)	86.3(5)	C(4)–C(3)–H(32)	131(4)
C(1^i)–W(1)–C(4^i)	112.3(5)	W(1)–C(3)–H(32)	117(6)
C(4)–W(1)–C(4^i)	154.9(5)	H(31)–C(3)–H(32)	99(5)
C(2)–W(1)–C(3)	111.1(4)	C(3)–C(4)–W(1)	72.8(5)
C(2^i)–W(1)–C(3)	86.3(4)	C(3)–C(4)–H(41)	134(4)
C(1)–W(1)–C(3)	76.7(5)	W(1)–C(4)–H(41)	110(5)
C(1^i)–W(1)–C(3)	85.5(5)	C(3)–C(4)–H(42)	124(4)
C(4)–W(1)–C(3)	35.7(3)	W(1)–C(4)–H(42)	111(5)
C(4^i)–W(1)–C(3)	154.8(3)	H(41)–C(4)–H(42)	99(5)

[a] Symmetry transformations used to generate equivalent atoms: i 1 $-x$, $-y$, z.

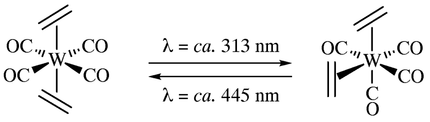
in K[PtCl$_3$(η^2-C$_2$H$_4$)]·H$_2$O [1.375(4) Å][31a] and [Pt(η^2-C$_2$H$_4$)$_2$(η^2-C$_2$F$_4$)] [1.365(8) Å],[31b] comparable with those in [Pt(η^2-C$_2$H$_4$)$_3$] [1.402(7) Å][31b] and the tungsten(IV) compound [W(O)Cl$_2$(η^2-C$_2$H$_4$)(PMePh$_2$)$_2$] [1.404(17) Å],[31c] but shorter than those in *mer*-[W(CO)$_3$(η^2-C$_2$H$_4$)(η^4-nor)] (nor = norbornadiene) [1.48(1) Å][11] and [Ta(η^5-C$_5$Me$_5$)(η^2-C$_2$H$_4$)(CHCMe$_3$)(PMe$_3$)] [1.477(4) Å].[31d] As in other ethene complexes, the hydrogen atoms of the C$_2$H$_4$ ligands are bent away from the metal giving an angle (α) of about 37° between the normals to the two methylene planes. There are various factors (the nature of the metal centre, the overall stereochemistry at this centre, and the effects of other ligands) which inhibit any clearcut correlation between the dimensions of the metal–C$_2$H$_4$ unit and the nature and strength of the bonding. However, the results of the present study are in keeping with the NMR properties of *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] (*q.v.*), while coming perhaps less close to a metallocyclopropane formulation than these properties might suggest.

Photochemistry of [W(CO)$_6$] + C$_2$H$_4$ and *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]: matrix-isolation studies

Irradiation of [W(CO)$_6$] isolated in an ethene-doped (2%) argon matrix at 16 K with UV light at $\lambda = ca.$ 313 nm results in the decay of the absorptions associated with the hexacarbonyl and the appearance and growth of new absorptions in the ν(CO) region of the IR spectrum. Comparison with earlier studies[19,32] enables these new features to be identified with the formation of free CO and the tungsten carbonyls [W(CO)$_5$(Ar)], [W(CO)$_5$(η^2-C$_2$H$_4$)], and *cis*- and *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$]. Such experiments are hampered, however, by the appearance of bands at *ca.* 2040 and 1894 cm^{-1} exhibited by the matrix initially and which grew on photolysis, thereby obscuring important regions of the spectrum. These errant bands are associated with loosely bound [C$_2$H$_4$]$_2$ dimers present in the matrix.[33]

To overcome the problems of ethene aggregates, similar experiments have been carried out with [W(CO)$_6$] isolated in a [^{2}H$_4$]ethene-doped argon matrix. Irradiation at $\lambda = ca.$ 313 nm can then be seen initially to give rise to free CO and the pentacarbonyl derivatives [W(CO)$_5$(Ar)] and [W(CO)$_5$(η^2-C$_2$D$_4$)] (see Table 3). Continued irradiation results in the formation of the tetracarbonyl derivatives *cis*-[W(CO)$_4$L$_2$] (L = C$_2$D$_4$ or Ar), *cis*-[W(CO)$_4$(C$_2$D$_4$)(Ar)], *trans*-[W(CO)$_4$(C$_2$D$_4$)$_2$] and *trans*-[W(CO)$_4$(C$_2$D$_4$)(Ar)] at the expense of the pentacarbonyl intermediates. The relevant molecules can be identified by their IR spectra and by drawing on the results of previous photochemical studies of [W(CO)$_6$]–alkene systems.[1,9,19,20] Switching to radiation with $\lambda = ca.$ 445 nm then reverses the substitution process with the regeneration of [W(CO)$_6$] and the pentacarbonyl species (see Table 3). The rigid matrix permits the trapping of 16e and 14e intermediates like [W(CO)$_n$(Ar)$_{6-n}$] (n = 4 or 5) but suffers from the disadvantage of restricting severely the formation of products incorporating two or more ethene ligands.

A clearer picture of the photochemistry of the bis(ethene) complexes [W(CO)$_4$(C$_2$H$_4$)$_2$] is gained from experiments with *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] isolated in an undoped argon matrix. As illustrated in Fig. 3 and detailed in Table 4, irradiation of the matrix with light first at $\lambda = ca.$ 313 nm and then at $\lambda = ca.$ 445 nm follows exactly the pattern of behaviour noted previously in similar studies of the bis(cyclopentene) and bis(pent-1-ene) complexes.[19] Thus, photolysis at $\lambda = ca.$ 313 nm results in isomerisation of *trans*- to *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] as the primary photoprocess, whereas this isomerisation is reversed by visible light centred near $\lambda = 445$ nm [eqn. (1)]. There are also signs of secondary products, notably [W(CO)$_4$(η^2-C$_2$H$_4$)(Ar)] and [W(CO)$_4$(Ar)$_2$],[32] implying that isomerisation is initiated not intramolecularly but by photodissociation of a W–C$_2$H$_4$ bond. Once again, however, the chemical changes open to the molecules are restricted by the rigidity of the matrix support and the inability of a product molecule like C$_2$H$_4$ to escape from the matrix cage wherein it is generated.



1

2

(1)

Solution photochemistry of [W(CO)$_6$] + ethene: ^{1}H NMR studies

The progress of the changes occurring on photolysis of an ethene-saturated [^{2}H$_8$]toluene solution containing [W(CO)$_6$] at about 200 K has also been tracked by ^{1}H NMR measurements. Hence it has been possible to detect 18e ethene carbonyl complexes that are relatively short-lived at ambient temperatures. Fig. 4 illustrates the ^{1}H signals which appear after broad-band UV-visible photolysis of such a solution at 213 K. The only new signal with significant intensity to be observed after brief photolysis occurring at δ 2.40 must be attributed to the mono-ethene complex [W(CO)$_5$(η^2-C$_2$H$_4$)]

Table 3 ν(CO) region of IR spectrum of [W(CO)$_6$] trapped in a C$_2$D$_4$-doped (2%) argon matrix at *ca.* 16 K showing the effects of sequential irradiation with UV and visible light

		Sequential photolysis at λ^a/nm						
$\tilde{\nu}^a$/cm^{-1}	Deposition^a	313 (1560 s)	313 (3360 s)	313 (4260 s)	445 (600 s)	445 (1200 s)	313 (300 s)	Assignment^b
2137.4	–	vvw	↑	↑	=	=	↑	CO
2089.1	–	vvw	=	↓	↑	↑	↓	[W(CO)$_5$(L)], a$_1$
2056.8	–	–	vvw	↑	↓	–	↑	*cis*-[W(CO)$_4$(L)$_2$], a$_1$
2051.5	–	vvw	↑	↓	↑	=	↓	*cis*-[W(CO)$_4$(L)(Ar)], a$_1$
2034.2	–	–	vvw	↑	↑	=	↑	*mer*-[W(CO)$_3$(L)$_3$]
1991.7	m	↓	↓	↓	↑	↑	↓	[W(CO)$_6$], t$_{1u}$
1986.4	vs	↓	↓	↓	↑	↑	↓	
1976.3	–	–	sh	↓	↑	↑	↓	[W(CO)$_5$(L)], e
1962.8	–	s	↑	↓	^{c}	^{c}	↑	[W(CO)$_5$(Ar)], e
1961.3	–	–	–	–	m	↑	↓	*trans*-[W(CO)$_4$(L)$_2$], e
1955.6	–	mw	sh	↓	↑	↑	↓	[W(CO)$_5$(L)], a$_1$
1932(br)	–	w	↑	↓	↓	–	↑	[W(CO)$_5$(Ar)], a$_1$
1909.8	–	–	w	↑	↓	=	↑	*cis*-[W(CO)$_4$(L)$_2$], b$_2$
1893.9	–	–	w	↑	↓	–	↑	*cis*-[W(CO)$_4$(Ar)$_2$], b$_2$

[a] ↑ increases; ↓ decreases; = unchanged; – absent; s strong; m medium; w weak; v very; sh shoulder; br broad. [b] L = C$_2$D$_4$. [c] Obscured.

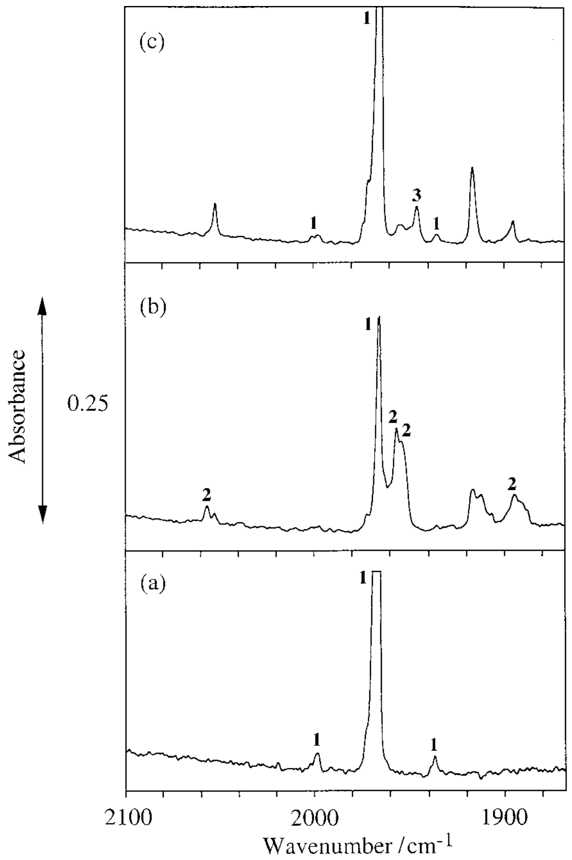


Fig. 3 ν(CO) region of the IR absorption spectrum of *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **1**, isolated in an argon matrix at *ca.* 14 K showing the effects of sequential UV and visible photolysis: (a) prior to photolysis; (b) after photolysis at $\lambda = ca.$ 313 nm for 60 min, showing isomerisation to *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **2**; and (c) after photolysis at λ = *ca.* 445 nm for 60 min, showing regeneration of **1**.

3. Prolonged photolysis then gives rise to additional ^{1}H resonances originating in bis(ethene) and tris(ethene) derivatives. Those at δ 2.02 and 2.01 can be associated with *cis*- and *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$], *i.e.* **2** and **1** respectively, whereas two resonances having a common origin at δ 2.54 and 1.52 and with relative intensities of 1:2 clearly belong to *mer*-[W(CO)$_3$(η^2-C$_2$H$_4$)$_3$] **4**. The only sign of *fac*-[W(CO)$_3$(η^2-C$_2$H$_4$)$_3$] **5**, is a resonance of very low intensity at δ 2.45 (see Fig. 4). Various criteria have been applied to identify positively the carriers of the different signals: (*i*) the known NMR properties of the stable complex **1**; (*ii*) the distinctive spectrum of **4**; (*iii*) the effects of photolysis time allied to the conclusions drawn from IR studies regarding the evolution and distribution of a given product; (*iv*) analogies with the NMR properties of related complexes; and (*v*) the thermal decay properties of the product. In connection with (*iv*) we note that the signal due to the two mutually *trans* ethene ligands in *mer*-[W(CO)$_3$(η^2-C$_2$H$_4$)$_3$] **4** occurs in almost the same position as the ethene resonance of *mer*-[W(CO)$_3$(η^2-C$_2$H$_4$)(η^4-nor)] (δ 1.55),[11] and that the ethene resonance in [W(CO)$_5$(η^2-C$_2$H$_4$)] **3** is close to that in [Cr(CO)$_5$(η^2-C$_2$H$_4$)] (δ 2.67 in [^{2}H$_6$]benzene solution).[15]

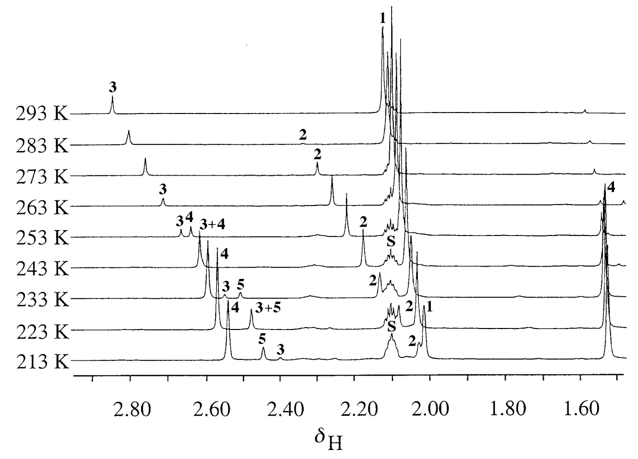


Fig. 4 ^{1}H NMR spectra illustrating the thermal decay of the tungsten ethene carbonyl complexes **2**, **3**, **4** and **5** in [^{2}H$_8$]toluene solution as the temperature is increased from 213 to 293 K in 10 K intervals. The compounds were generated by broad-band UV-visible photolysis of [W(CO)$_6$] in an ethene-saturated solution at *ca.* 200 K. **S** denotes a solvent resonance.

Raising the temperature of the photolysed solution causes several of the ^{1}H signals to decay, and at room temperature the spectrum consists only of the features at δ 2.12 and 2.84 originating in the complexes **1** and **3**, respectively (Fig. 4). With [^{2}H$_8$]toluene as the solvent the chemical shifts of most of the ^{1}H signals due to the ethene complexes move to significantly higher frequency as the temperature increases in the range 198–293 K. Only the signal due to **1** and the low-frequency signal of **4** suffer little change of chemical shift (Fig. 4); most conspicuous are the high-frequency shifts displayed by the protons of the compounds **2** and **3**. With [^{2}H$_{14}$]methylcyclohexane as the solvent, however, the ^{1}H shifts vary but little with temperature. Table 5 lists the ^{1}H chemical shifts as functions of both solvent and temperature.

Table 4 ν(CO) region of IR spectrum of *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **1** trapped in an argon matrix at *ca.* 14 K showing the effects of sequential irradiation with UV and visible light

		Sequential photolysis at λ^a/nm			
$\tilde{\nu}$/cm^{-1}	Deposition[a]	313 (900 s)	313 (3900 s)	445 (1800 s)	Assignment[b]
2057.3	–	w	↑	↓	*cis*-[W(CO)$_4$(L)$_2$], a$_1$
2053.9	–	vw	↑	↑	*trans*-[W(CO)$_4$(L)(Ar)], a$_1$
1999.0	w	↓	↓	↑	*trans*-[W(CO)$_4$(L)$_2$], a$_1^c$
1972.9	–	m	↓	↑	[W(CO)$_5$(L)], e
1967.6	vs	↓	↓	↑	*trans*-[W(CO)$_4$(L)$_2$], e
1957.5	–	s	↑	↓	*cis*-[W(CO)$_4$(L)$_2$], b$_1$
1954.1	–	s	↑	↓	*cis*-[W(CO)$_4$(L)$_2$], a$_1$
1948.4	–	[d]	[d]	m	[W(CO)$_5$(L)], a$_1$
1936.8	w	=	↓	↑	*trans*-[W(CO)$_4$(L)$_2$], e[c]
1918.0	–	w	↑	↑	*trans*-[W(CO)$_4$(L)(Ar)], e
1897.2	–	m	↑	↓	*cis*-[W(CO)$_4$(L)$_2$], b$_2$
1894.4	–	m	↑	↓	*cis*-[W(CO)$_4$(Ar)$_2$], b$_2$

[a] ↑ increases; ↓ decreases; = unchanged; – absent; s strong; m medium; w weak; v very. [b] L = C$_2$H$_4$. [c] *trans*-[W(^{12}CO)$_3$(^{13}CO)(C$_2$H$_4$)$_2$]. [d] Obscured.

Table 5 ^1H chemical shifts for different tungsten ethene carbonyl complexes **1**–**5** as a function of solvent and temperature

Complex	C_7D_{14}, δ		C_7D_8, δ			
					$\delta = xT + y^a$	
	293 K	213 K	293 K	213 K	10^4x	y
$[W(CO)_5(\eta^2\text{-}C_2H_4)]$ **3**	3.50	3.49	2.84	2.40	47^b	1.47^b
					81^c	0.66^c
mer-$[W(CO)_3(\eta^2\text{-}C_2H_4)_3]$ **4**	3.13	3.11	2.73	2.54	25	2.01
	1.70	1.67	1.56	1.52	4	1.43
fac-$[W(CO)_3(\eta^2\text{-}C_2H_4)_3]$ **5**	3.09^d	3.05	2.68^e	2.45	29	1.83
cis-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$ **2**	2.91	2.83	2.39	2.02	46	1.04
trans-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$ **1**	2.35	2.33	2.12	2.01	14^f	1.71^f

[a] Equation of the linear plot of δ *vs.* T in the temperature range $T = 198$–293 K unless stated otherwise. [b] Applies to the temperature range $T = 238$–293 K. [c] Applies to the temperature range $T = 198$–233 K. [d] Value calculated from the equation $\delta = 0.0005T + 2.95$. [e] Value calculated from the equation $\delta = 0.0029T + 1.83$. [f] Applies to the temperature range $T = 203$–353 K.

[$^2H_8$]Toluene solutions give shifts which vary linearly with temperature in the range 198–293 K, except in the case of **3** which is characterised by two distinct temperature regimes of linear dependence (198–233 and 238–293 K, see Table 5). These results point to solvent interactions which are more specific for the unsaturated toluene than for the saturated methylcyclohexane molecules; possibly ethene–toluene exchange is a significant factor for the more labile W–C_2H_4 moieties.

For the unstable ethene complexes **2**–**5**, the change in ^1H chemical shift with respect to free ethene, $\Delta\delta$, for the ethene ligand *trans* to a CO group increases from 2.4 to 2.9 in the order **3** < **4** < **5** < **2**. For the mutually *trans* ethene ligands of **1** and **4**, by contrast, $\Delta\delta$ is substantially larger, *viz*, 3.16 and 3.72, respectively. This difference reflects on the one hand the competition that exists with CO, a better π-acceptor than ethene, for the d_π orbitals of tungsten, thereby weakening the *trans*-W–C_2H_4 interaction, and on the other the lack of such competition between two *trans*, mutually staggered ethene ligands.

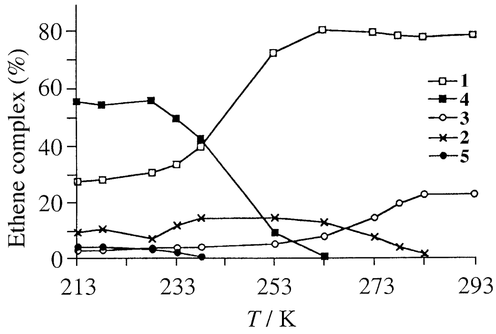
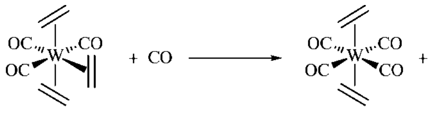
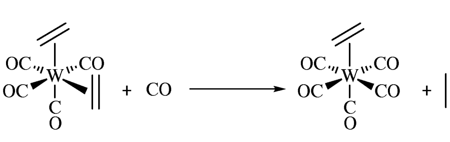


Fig. 5 Thermal reactions of ethene carbonyl complexes of tungsten in [$^2H_8$]toluene solution as the temperature is raised from 213 to 293 K.



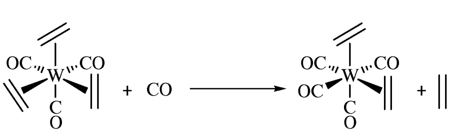
4 **1** (2)

Least stable of the ethene complexes is *fac*-$[W(CO)_3(\eta^2\text{-}C_2H_4)_3]$ **5**, which can be detected only at low temperatures, so that the chemical shift of δ 2.68 at 293 K given in Table 5 has to be extrapolated from the temperature-dependence of the measured shift at temperatures < 273 K. IR studies of alkane solutions have demonstrated that *cis*-$[W(CO)_4(\eta^2\text{-}C_3H_6)_2]$ survives at temperatures as high as 263 K;[20] on the evidence of the present studies the corresponding bis(ethene) complex, **2**, survives long enough in toluene or methylcyclohexane solution to be detected even at 293 K. Over time the resonances of **2**, **4** and **5** decrease in intensity while those of **1** and **3** are observed to grow (Fig. 4 and 5). If the temperature of the solution is raised above 228 K, the decay of **4** can be witnessed. No additional intermediate being detectable, the consumption of **4** must be supposed to give rise only to compound **1** *via* the substitution reaction (2) (see Fig. 5). Similarly we find that the decay of **2** at temperatures above 253 K correlates with the accretion of **3** [as in eqn. (3)]. These conclusions are supported by the rate constants (*q.v.*) for the disappearance of **4** and **2** which match those for the recovery of **1**



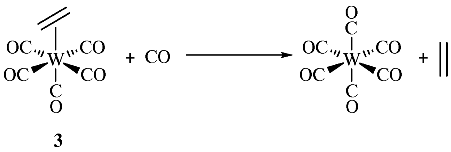
2 **3** (3)

and **3**, respectively, implying simple interconversion reactions linking these two pairs of species. The decay of **5** at temperatures below 253 K appears to profit **2**, indicating the interconversion (4). Hence the complexes **2**, **4** and **5** all decay



5 **2** (4)

thermally *via* reactions in which the CO present in the photolysed reaction mixture displaces a coordinated ethene ligand. The ^1H signal due to the monoethene complex **3** is observed to decay at a measurable rate only at temperatures in the range 343–353 K, again with the release of free ethene and, presumably, the formation of $[W(CO)_6]$:

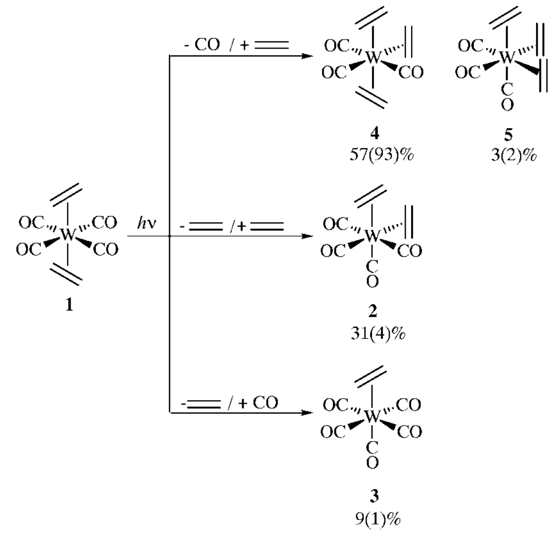


3 (5)

Hence the results presented here leave little room for doubting the identities of the labile ethene carbonyl derivatives responsible for the different ^1H resonances.

Solution photochemistry of *trans*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$ 1: ^1H NMR studies

IR measurements made at room temperature indicate that broad-band UV photolysis of **1** in ethene-saturated hexane solution at *ca.* 265 K yields initially the *cis* isomer **2** as the



Scheme 1 The yields of ethene carbonyl complexes formed after broad-band UV-visible photolysis of *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **1** at *ca.* 200 K for 2 h. The proportions determined by ^{1}H NMR measurements are reported with respect to the total yield of products at 213 K; figures in parentheses relate to the effects of photolysis in the presence of an excess of ethene.

sole detectable product, but that prolonged photolysis causes both the bis(ethene) complexes to give place to the tris(ethene) isomers **4** and **5**. These products could be detected by their ^{1}H NMR spectra by evaporating the hexane at 265 K and dissolving the residue in [^{2}H$_8$]toluene. On the evidence of the NMR spectrum of the resulting solution, the reaction mixture contained typically **1** (55%), **4** (40%), **5** (<1%), and also **3** (2%). The high concentration of **4** thus produced was made possible by the removal of CO from the reaction mixture during photolysis, thereby inhibiting the regeneration of the more stable bis(ethene) complex **1**. These findings tend to confirm the results of earlier studies to the effect that UV photolysis of **1** favours cleavage of W–CO rather than W–C$_2$H$_4$ bonds, yielding mainly *mer*-[W(CO)$_3$(η^2-C$_2$H$_4$)$_3$] **4**.

Broad-band UV-visible photolysis of **1** in [^{2}H$_8$]toluene solution contained in an NMR tube at about 200 K enabled us to observe the formation of all the products **2**–**5** in the proportions shown in Scheme 1. The major product is now the tris(ethene) complex **4** (57%), a result consistent with a pathway involving initial CO loss to form coordinatively unsaturated [W(CO)$_3$(η^2-C$_2$H$_4$)$_2$] followed by trapping of free C$_2$H$_4$. Such a mechanism will obviously be inhibited by the presence in excess of the leaving ligand. Hence it is noteworthy that the yields of the CO-rich complexes **2** and **3** are higher when photolysis is carried out in the absence of additional ethene. By contrast, the yields of **4** increase dramatically (up to 93% in a typical experiment) when photolysis is carried out in the presence of an excess of ethene (see Scheme 1). Thus, an excess of ethene suppresses the isomerisation of **1** to **2**, tending instead to favour the regeneration of **1**. At the same time the photochemical conversion of **1** to other products decreases (typically from 40 to 26%) when the solution contains an excess of ethene. These results therefore endorse the inference drawn from earlier IR measurements[19,20] that *trans*-to-*cis* isomerisation occurs through photolytic alkene loss, formation and pseudo-rotation of the coordinatively unsaturated species [W(CO)$_4$(η^2-alkene)], and subsequent re-coordination of the alkene molecule to give the relatively stable *cis*-[W(CO)$_4$(η^2-alkene)$_2$]. Of *thermal* interconversion of the two isomers, however, we find no evidence.

Broad-band photolysis of **1** also produces small amounts of the monoethene complex **3** (Scheme 1). Hence ethene-loss from [W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] competes with CO-loss and whether the unsaturated species [W(CO)$_4$(η^2-C$_2$H$_4$)] takes up CO or C$_2$H$_4$ depends upon the conditions of the experiment and the composition of the solvation shell enclosing the reaction intermediate.

Kinetics of the disappearance of the ethene carbonyl complexes 2, 3, 4 and 5

To observe the labile ethene carbonyl complexes, we first exposed a [^{2}H$_8$]toluene solution of [W(CO)$_6$] with an excess of ethene in an NMR tube at *ca.* 200 K to broad-band UV-visible radiation for *ca.* 2 h. As noted previously, all four ethene complexes **2**, **3**, **4** and **5** decay with the dissociation of free ethene at temperatures >200 K. The rate of disappearance of each of the complexes has been monitored by reference to the integrated intensities of the relevant ^{1}H signals; this has been carried out in the presence of 1 to 5 equivalents of ethene over times spanning at least three half-lives under pseudo-first-order conditions. The measurements have been made for the decay of each of the four complexes **2**–**5** at a minimum of three different temperatures. The rate constants k estimated in this way give linear ln k *vs.* $1/T$ plots, tending to confirm the first-order dependence of the rate on the concentration of the ethene complex. Various experiments were carried out in an effort to ascertain the effects of adding CO to the photolysed reaction mixture (*e.g.* by bubbling the gas through the sample in the NMR tube). There was some acceleration of the decay of the photo-products, amounting in the case of the complex **3** to a roughly two-fold increase in the rate, but it proved impossible to secure more quantitative results. In the circumstances, the pseudo-first-order rate constants reported here relate to conditions which were standardised as far as possible giving reproducible results, with the CO deriving *exclusively* from the initial photolysis stages; they

Table 6 Activation energies, E_a, and pseudo-first-order rate constants, k, for the thermal decay of the tungsten ethene carbonyl complexes **2**–**5** by reaction with CO in [^{2}H$_8$]toluene solution

Complex	E_a/kJ mol^{-1}	T/K	$10^{-3}\tau$/s	10^4k/s^{-1}
[W(CO)$_5$(η^2-C$_2$H$_4$)] **3**	198	343	11.2	0.6
		348	3.5	1.9
		353	1.6	4.3
cis-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **2**	121	263	11.2	0.6
		268	2.2	3.0
		273	1.5	4.5
mer-[W(CO)$_3$(η^2-C$_2$H$_4$)$_3$] **4**	65	258	7.5	0.9
		268	6.1	1.1
		270	1.6	4.1
		283	0.6	11.6
fac-[W(CO)$_3$(η^2-C$_2$H$_4$)$_3$] **5**	40	228	2.5	2.7
		233	1.4	4.9
		238	1.0	6.5

must therefore be viewed as order-of-magnitude rather than definitive estimates, but giving significant *comparative* measures, as well as rough guides to the relevant activation barriers. Table 6 gives a summary of the kinetic results, including the rate constants measured at different temperatures and activation energies E_a deduced from the appropriate Arrhenius plots. Hence it emerges that the exchange reactions are opposed by E_a values which decrease in the order **3** [reaction (5)] > **2** [reaction (3)] > **4** [reaction (2)] > **5** [reaction (4)].

All the signs are that the substitution reactions are activated by dissociation of a tungsten–ethene bond,[19,20] so that the E_a values represent lower limits for the dissociation energy of this bond. It is significant then that the unimolecular decay constant we have extracted from the NMR measurements for *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **2** is comparable with the corresponding value reported for *cis*-[Cr(CO)$_4$(η^2-C$_2$H$_4$)$_2$] in the gas phase.[10] At 198 kJ mol^{-1}, the activation energy for reaction (5) is substantially larger than the values variously estimated for the corresponding reaction of [Cr(CO)$_5$(η^2-C$_2$H$_4$)] in liquid xenon solution ($\Delta H^{\ddagger} = 60$ kJ mol^{-1})[7] or in the gas phase ($E_a = 105$ kJ mol^{-1}).[34] It is also larger than the value of 97 kJ mol^{-1} opposing ethene loss from [(η^5-C$_5$H$_5$)Nb(CO)$_3$(η^2-C$_2$H$_4$)] in supercritical ethene solution.[35] The pattern is entirely consistent with the importance of metal–ethene bond-breaking in the rate-determining step[7,19,20,34,35] since third-row transition metals form appreciably stronger bonds to ethene than do first- or second-row transition metals. However, meaningful estimates of $\Delta S^{\ddagger}$ associated with the present CO-for-C$_2$H$_4$ substitution reactions must await further experiments in which the concentration of CO is a known and controllable quantity.

Conclusions

The relatively stable bis(ethene) complex *trans*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **1** has been characterised not only by its spectroscopic properties but also by its crystal and molecular structure, as determined by X-ray crystallography. The results confirm that the C=C bonds of the two ethene ligands are mutually staggered while eclipsing the central W(CO)$_4$ framework, and that the W–C$_2$H$_4$ interaction is a comparatively strong one, while still falling short of the metallocyclopropane limit. Reversible isomerisation of *trans*- to *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **2** has been shown by IR measurements to be the primary change occurring on selective UV or visible photolysis of solid argon matrices at 14–16 K. In addition, ^{1}H NMR measurements have been applied for the first time to the identification of the labile ethene complexes *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] **2**, [W(CO)$_5$(η^2-C$_2$H$_4$)] **3**, *mer*-[W(CO)$_3$(η^2-C$_2$H$_4$)$_3$] **4**, and *fac*-[W(CO)$_3$(η^2-C$_2$H$_4$)$_3$] **5**, formed by broad-band photolysis of ethene-saturated hydrocarbon solutions of **1** or [W(CO)$_6$] in the temperature range 198–293 K. Only by photolysis at low temperatures has it been possible to generate these species at concentrations high enough to permit their detection by ^{1}H NMR measurements. The results of these experiments confirm that tungsten–ethene photodissociation is the principal reaction pathway in the photolysis of **1**, initiating the photoisomerisation of the *trans* to the *cis* isomer **2** or, in the presence of free CO, giving access to the monoethene complex [W(CO)$_5$(η^2-C$_2$H$_4$)].

Of particular interest are the first kinetic studies of the thermal decay of the ethene complexes **2**–**5** made possible by ^{1}H NMR measurements on hydrocarbon solutions at temperatures ranging from 198 to 353 K. The decay proceeds in each case by the substitution of CO (formed during photolysis) for ethene, complex **4** transforming to **1**, **2** to **3**, **5** to **2**, and **3** to [W(CO)$_6$] [eqn. (2), (3), (4) and (5), respectively]. By reference to the integrated intensities of the relevant ^{1}H signals we have estimated pseudo-first-order rate constants at various temperatures to secure linear Arrhenius plots from which activation energies E_a have been deduced for the decay reactions. Hence E_a has been found to decrease in the order **3** > **2** > **4** > **5**. *fac*-[W(CO)$_3$(η^2-C$_2$H$_4$)$_3$] is the least stable of the ethene complexes, giving place to *cis*-[W(CO)$_4$(η^2-C$_2$H$_4$)$_2$] in a reaction with E_a = *ca.* 40 kJ mol^{-1}. By contrast, the conversion of [W(CO)$_5$(η^2-C$_2$H$_4$)] to [W(CO)$_6$] is opposed by E_a = *ca.* 198 kJ mol^{-1}. These values compare sensibly with analogous parameters reported for other metal–ethene complexes and may be expected to represent lower limits to the dissociation energies of the appropriate W–C$_2$H$_4$ bonds. Our experiments afford no evidence to suggest that the interconversion of the *trans* and *cis* bis(ethene) complexes **1** and **2** can be realised by thermal means.

Acknowledgements

We acknowledge with gratitude the award of a research grant (to T.S.-B. and A.J.D.) by the British Council, and support from the E.P.S.R.C. for the purchase of equipment at both Oxford and Edinburgh and the funding of an Advanced Fellowship (to T.M.G.) and a research studentship (to L.J.M.). S.P. would like to thank Dr. R. O. Gould for helpful discussions. We thank also Mr. E. J. J. Riddle for his assistance with the matrix-isolation experiments.

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Paper 8/08621D