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NMR studies of the structure, isomerism and photochemical reactions of *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ complexes

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Abstract

UV broad-band photolysis of $W(CO)_6$ in the presence of propene and 1-butene has been used to synthesise the bis-alkene complexes *trans*-$[W(CO)_4(\eta^2\text{-}CH_2{=}CHCH_3)_2]$ **1** and *trans*-$[W(CO)_4(\eta^2\text{-}CH_2{=}CHCH_2CH_3)_2]$ **2**. The ^{1}H- and ^{13}C-NMR spectra are discussed in detail in relation to the structure and isomerism of these alkene compounds. On the evidence of the spectra measured at different temperatures, the barrier to alkene rotation is ca. 46 and 48 kJ mol^{-1} in **1** and **2**, respectively. The NMR method has been used for the identification and characterisation of the unstable alkene = propene or 1-butene complexes $[W(CO)_5(\eta^2\text{-alkene})]$ and *cis*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ and of hydrido derivatives formed in photochemical reactions of *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ occurring in solution at ca. 200 K. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbonyl complexes; Alkene complexes; NMR spectroscopy; Photolysis; Tungsten; Hydride

1. Introduction

The photolytically induced reactions of $W(CO)_6$ with alkenes lead to mixed carbonyl complexes of tungsten with a varying number of alkene ligands (from 1 to 3), which can be detected by IR and NMR investigations of the reaction mixture [1–11]. The only compounds which are stable enough to be isolated and characterised in a pure state under normal conditions are of the type *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ [2,6–11]. These can be used as model compounds to study alkene reactions catalysed by $W(CO)_6$ [11–16].

Recently, we demonstrated that bis-alkene complexes of the type *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$, where alkene = 1-pentene or cyclopentene, can be converted photochemically to the corresponding *cis* isomers in solid argon matrices at ca. 16 K [10]. The photo-reversible *trans–cis* isomerisation can be also observed in alkane solutions at temperatures ranging from 123 to 263 K [13]. Solution studies have allowed us to detect the 16-electron coordinatively unsaturated species *trans*- and *cis*-$[W(CO)_4(\eta^2\text{-alkene})(s)]$ and *mer*- and *fac*-$[W(CO)_3(\eta^2\text{-alkene})_2(s)]$ (s = solvent molecule occupying the vacant coordination site) on the basis of their IR spectra. In the absence of coordinating ligands, a 16-electron complex transforms into an 18-electron η^3-allyl hydrido complex. Under conditions with an excess of alkene, the 16-electron tetracarbonyl species bind the alkene and form *cis*-$[W(CO)_4(\eta^2\text{-alkene})_2]$, but the 16-electron tricarbonyl species transform to *fac*-$[W(CO)_3(\eta^2\text{-alkene})_3]$ and *mer*-$[W(CO)_3(\eta^2\text{-alkene})_3]$.

In an earlier paper we reported the first observation and ^{1}H-NMR spectral characterisation of thermally unstable ethene complexes, viz. $[W(CO)_5(\eta^2\text{-}C_2H_4)]$, *cis*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$, *mer*-$[W(CO)_3(\eta^2\text{-}C_2H_4)_3]$ and *fac*-$[W(CO)_3(\eta^2\text{-}C_2H_4)_3]$, formed in photochemical reactions of *trans*-$[W(CO)_4(\eta^2\text{-}C_2H_4)_2]$ or $W(CO)_6$ in ethene-saturated hydrocarbon solutions at temperatures in the range 200–293 K [11]. Hence it has been shown that ^{1}H-NMR spectroscopy can be used successfully to identify and monitor reactive 18-electron species generated photochemically in solution at low temperatures [11].

It was our aim, therefore, to investigate whether the catalytically important intermediate compounds generated photochemically from *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$, where alkene = propene (**1**) or 1-butene (**2**), and ob-

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served recently by IR measurements, can be characterised by NMR spectroscopy.

2. Experimental

2.1. Materials and method

Synthesis and manipulation of chemicals were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and distilled from CaH_2 under nitrogen prior to use. Propene and 1-butene was used as supplied (Aldrich, 99% grade). IR spectra were measured with Nicolet FT-IR model 400 instrument. ^1H- and ^{13}C-NMR spectra were recorded with a Bruker AMX 300 instrument operating at 300 and 75.5 MHz, respectively. All chemical shifts are referenced to residual proton or carbon signals in the toluene-d_8 solvent using the methyl resonances at δ_H 2.10 in the ^1H-NMR and δ_C 20.4 ppm in the ^{13}C-NMR spectra as internal standards. ^1H-NMR spectra recorded for methylcyclohexane-d_{14} solutions referenced to $SiMe_4$. The photolysis source was an HBO 200W high-pressure Hg lamp.

2.2. Synthesis

The alkene complexes *trans*-$[W(CO)_4(\eta^2\text{-}CH_2{=}CHCH_3)_2]$ **1**, and *trans*-$[W(CO)_4(\eta^2\text{-}CH_2{=}CHCH_2CH_3)_2]$ **2** were synthesised in the photochemical reactions of $W(CO)_6$ with the appropriate alkene in *n*-hexane solution according to the following procedure. $W(CO)_6$ (0.6 g, 1.7 mmol) was dissolved in 100 cm^3 of *n*-hexane and freezing liquid alkene (3 cm^3, 12 mmol) was added. The solution, at ca. 268 K, was irradiated through quartz with the HBO 200W Hg lamp. The course of the reaction was monitored by IR measurements made on the solution at room temperature. The photolysis was stopped when the IR band of the *trans*-bis(alkene) compound at ca. 1950 cm^{-1} reached its maximum intensity (after about 3 h). The volatile materials were then stripped off the reaction mixture at ca. 268 K and the resulting brown residue was left for 24 h, to allow the monoalkene complex $[W(CO)_5(\eta^2\text{-alkene})]$ to decay. The residue was redissolved in *n*-hexane (3 cm^3) and the solution chromatographed on a silica column using *n*-hexane as the eluent. Collection of the pale-yellow fraction containing the bis(alkene) complex, as monitored by IR spectroscopy, followed by solvent evaporation in vacuo at ca. 268 K, provided 0.2 g, 0.53 mmol of **1** (31% yield based on the amount of $W(CO)_6$ taken) and 0.18 g, 0.43 mmol of **2** (25% yield), each isolated as a pale yellow oil. The compounds **1** and **2** are extremely hydrocarbon soluble and difficult to crystallise. The slight contamination with $W(CO)_6$ was avoided by fractional crystallisation from *n*-hexane. The compound **2** is always contaminated ($<10\%$ by NMR) with *trans*-$[W(CO)_4(\eta^2\text{-}CH_3CH{=}CHCH_3)_2]$ formed through the isomerisation of 1-butene to *cis*- and *trans*-2-butene in the course of the synthesis. The compounds **1** and **2** were characterised by their NMR (Tables 1–3) and IR spectra [13].

1 IR (*n*-hexane): $\nu(CO)$ 2058 vvw, 1990 w, 1954 vs, 1928 w and 1917 w cm^{-1};

2 IR (*n*-hexane): $\nu(CO)$ 2058 vvw, 1990 w, 1952 vs, 1928 w and 1919 w cm^{-1}.

2.3. NMR detection of $[W(CO)_5(\eta^2\text{-alkene})]$

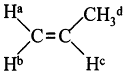
To detect unstable monoalkene pentacarbonyl complexes of tungsten by their NMR spectra, we first converted $W(CO)_6$ (0.1 g, 0.3 mmol) by broad band UV photolysis (<1 h) in the presence of an excess of alkene in *n*-hexane (50 cm^3) at ca. 268 K to a mixture containing the mono- and bis-alkene complexes. After photolysis, the solvent was removed under vacuum and the brown residue dissolved in toluene-d_8 (0.7 cm^3) and transferred to a 5 mm NMR tube for ^1H- and ^{13}C-NMR measurements (Tables 1–3). The relative concentrations of the species present in solution were determined by integrating the ^1H-NMR signals. The signal intensities were calibrated by reference to the integral of the toluene resonance taken to be unity. In the case of the propene reactions, the ^1H-NMR spectrum showed the presence of **1** (96.7%), $[W(CO)_5(\eta^2\text{-}C_3H_6)]$ (3.2%), and hydrido species (0.1%). Similar results were found for the reaction products formed after photolysis of $W(CO)_6$ and 1-butene for the short time: **2** (90%), $[W(CO)_5(\eta^2\text{-1-}C_4H_8)]$ (9%), and hydrido species (1%). However, $[W(CO)_5(\eta^2\text{-1-}C_4H_8)]$ was observed to decay very quickly at ambient temperatures with the formation of the corresponding pentacarbonyl compounds of *cis*- and *trans*-2-butene, recognised by the ^1H signals of the olefinic protons at δ_H 3.72 and 3.97, respectively.

2.4. Photochemical conversion of **1** and **2**

The solution photochemistries of *trans*-$[W(CO)_4(\eta^2\text{-}CH_2{=}CHCH_3)_2]$ **1** and *trans*-$[W(CO)_4(\eta^2\text{-}CH_2{=}CHCH_2CH_3)_2]$ **2** were investigated by ^1H-NMR measurements at 300 MHz in the temperature range 193–293 K. To confirm the identities of unstable alkene complexes, we also converted $W(CO)_6$ to the same species by broadband UV photolysis (ca. 2 h) of toluene-d_8 solutions in the presence of an excess of the alkene at ca. 200 K. At higher temperatures the unstable *cis*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ compounds decay with dissociation of the alkene ligand.

In a typical NMR experiment, ca. 0.02 M toluene-d_8 solution of a bis-alkene complex was loaded into a 5 mm NMR tube, cooled to the desired temperature and

Table 1
^{1}H-NMR data for free propene and propene carbonyl complexes of tungsten in toluene-d_8 solution

Compound		Temperature (K)	δ, Multiplicity [i]				J (Hz)					
			H^c	H^a	H^b	H^d	$^{3}J_{H^aH^c}$	$^{3}J_{H^bH^c}$	$^{3}J_{H^cH^d}$	$^{2}J_{H^aH^b}$	$^{4}J_{H^aH^d}$	$^{4}J_{H^bH^d}$
		293	5.72, ddq	4.99, ddq	4.94, ddq	1.57, dt	16.9	10.3	6.6	2.2	1.5	1.5
trans-$[W(CO)_4(\eta^2\text{-}C_3H_6)_2]$	**1A**	293	2.94, ddq	2.00, dd	2.33, dd	1.93, d	11.8	9.2	5.9	1.5	– [ii]	– [ii]
		263	2.89, ddq	1.98, dd	2.30, dd	1.93, d						
	1B	293	2.90, ddq	1.96, dd	2.28, dd	1.90, d	11.8	9.2	5.9	1.5	– [ii]	– [ii]
		263	2.85, ddq	1.92, dd	2.25, dd	1.89, d						
$[W(CO)_5(\eta^2\text{-}C_3H_6)]$		293	3.96, ddq	2.82, d	2.94, d	1.62, d	14.7	8.8	5.9	– [ii]	– [ii]	– [ii]
		263	3.79, ddq	2.68, d	2.80, d	1.55, d				– [ii]	– [ii]	– [ii]
cis-$[W(CO)_4(\eta^2\text{-}C_3H_6)_2]$	**I**	293	3.60, ddq	– [iii]	1.69, d	1.72, d	14.7	8.8	5.9	– [ii]	– [ii]	– [ii]
		263	3.47, ddq	2.82, d	1.46, d	1.69, d				– [ii]	– [ii]	– [ii]
	II	293	3.42, ddq	2.83, d	2.16, d	1.75, d	14.7	8.8	5.9	– [ii]	– [ii]	– [ii]
		263	3.25, ddq	2.74, d	2.00, d	1.72, d				– [ii]	– [ii]	– [ii]

[i] d, doublet; q, quartet.

[ii] Not observed.

[iii] Overlap of resonances made it difficult to provide reliable assignments.

photolysed. The sample was then transferred to the precooled sample-holder of the NMR spectrometer and the NMR spectrum of the solution recorded. In subsequent experiments, alkene-saturated toluene-d_8 was used as the solvent for each of the *trans*-bis(alkene) complexes.

2.5. *Calculation of $\Delta G^{\ddagger}$ of conformational change*

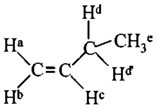
^{1}H- and ^{13}C-NMR spectra of **1** and **2** in toluene-d_8 solution were recorded at ca. 10° intervals from 293 to 193 K, except within a 20° range of the coalescence temperature. In this regime spectra were recorded at 3–5° intervals. The $\Delta G^{\ddagger}$ values were calculated by means of the Eyring equation [17] $\Delta G^{\ddagger} = 19.14T_c(9.97 + \log(T_c/\Delta\nu)$ kJ mol^{-1}, where T_c (K) is the temperature of coalescence of two given signals and $\Delta\nu$ (Hz) their difference in chemical shift. For alkene rotation in **1**, $\Delta G^{\ddagger}$ was found to be: (a) 46.3 kJ mol^{-1} from the coalescence at 224 K of the two doublets assigned to the olefinic hydrogen H^b into a single doublet; and (b) 45.5 kJ mol^{-1} from the coalescence at 223 K of the two singlets assigned to the carbon of the CH_3 groups into a single resonance. For alkene rotation in **2**, $\Delta G^{\ddagger}$ was found to be: (a) 48.6 kJ mol^{-1} from the coalescence at 233 K of the two doublets assigned to the olefinic hydrogen H^b into a single doublet; and (b) 48.0 kJ mol^{-1} from the coalescence at 223 K of the two singlets assigned to the olefinic carbon (=C^2H) of the 1-butene ligand into a single resonance.

3. Results and discussion

3.1. *Synthesis and IR characterisation of the trans-[W(CO)$_4$(η^2-alkene)$_2$] compounds **1** and **2***

The compounds **1** and **2** have each been prepared by the photochemical reaction of $W(CO)_6$ with an excess of alkene in an alkane solution at the temperature of ca. 268 K and are examples of a well-studied group of alkene complexes of the type *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ [1–6,8–11,13–17]. In the course of the photolysis of $W(CO)_6$ in alkene-saturated hexane, the formation of a complex of the type $[W(CO)_5(\text{alkene})]$ was observed initially; this has a skeleton with C_{4v} symmetry and three IR-active ν(CO) vibrations ($2a_1 + e$) (bands observed at 2083 w and 1966 vs cm^{-1}, the third lower frequency ν(CO) band being obscured by the absorption of other species). The photosubstitution of another CO group leads to a mixture of *cis* and *trans* complexes of the type $[W(CO)_4(\eta^2\text{-alkene})_2]$ [3–11], but only the *trans* isomer could be detected by its IR spectrum at room temperature (r.t.). The formation of a *cis* isomer was indicated, however, by ^{1}H-NMR investigations (see below). The IR spectrum of the *trans*

Table 2
^{1}H-NMR data for free 1-butene and 1-butene carbonyl complexes of tungsten in toluene-d_8 solution

Compound		Temperature (K)	δ, Multiplicity [i]						J (Hz)						
			H^c	H^a	H^b	H^d	$H^{d'}$	H^e	$^3J_{H^a H^c}$	$^3J_{H^b H^c}$	$^3J_{H^c H^d}$	$^3J_{H^c H^{d'}}$	$^3J_{H^d H^e}$	$^2J_{H^d H^{d'}}$	$^2J_{H^a H^b}$ [iv]
		293	5.77, ddt	4.96, ddt	4.90, ddt	1.94, qddd	– [ii]	0.90, t	17.0	10.2	6.3		7.5	– [ii]	1.9
trans-[W(CO)$_4$(η^2-C$_4$H$_8$)]	**2A**	343	3.03, dddd	2.01, dd	2.34, dd	2.36, qdd	1.35, qdd	1.07, t	12.7	9.5	3.2	6.3	7.1	10.3	1.6
		293	2.98, dddd	1.93, dd	2.28, dd	2.36, qdd	1.25, qdd	1.07, t							
		263	2.94, m	1.87, d	2.24, d	2.36, m	1.18, m	1.06, t							
	2B	343	3.00, dddd	1.97, dd	3.30, dd	2.30, qdd	1.32, qdd	1.06, t	12.7	9.5	3.2	6.3	7.1	10.3	1.6
		293	2.93, dddd	1.89, dd	2.24, dd	2.30, qdd	1.21, qdd	1.06, t							
		263	2.90, m	1.83, d	2.19, d	2.30, m	1.15, m	1.05, t							
[W(CO)$_5$(η^2-C$_4$H$_8$)]		293	4.06, dddd	2.75, d	2.89, d	2.16, dq	1.19, qdd	0.72, t	14.3	8.9	3.8	9.2	7.2	~14	– [ii]
		263	3.90, dddd	– [iii]	2.78, d	– [iii]	– [iii]	0.68, t							
cis-[W(CO)$_4$(η^2-C$_4$H$_8$)$_2$]	**I**	273	3.67, dddd	2.78, d	1.45, d	– [iii]	– [iii]	0.79, t	14.6	8.9	3.8	9.4	7.3	– [ii]	– [ii]
		263	3.63, dddd	2.75, d	1.39, d	– [iii]	– [iii]	0.78, t							
	II	273	3.46, dddd	2.71, d	2.03, d	– [iii]	– [iii]	0.77, t	14.6	8.9					
		263	3.40, dddd	2.69, d	1.97, d	– [iii]	– [iii]	0.76, t			3.8	9.4	7.3	– [ii]	– [ii]

[i] d, doublet, t, triplet, q, quartet m, multiplet.

[ii] Not observed.

[iii] Overlap of resonances made it difficult to provide reliable assignments.

[iv] $^4J_{H^a H^d} = {^4J_{H^b H^d}} = 1.5$ Hz for free 1-butene but for 1-butene ligand not observed.

Table 3
^{13}C-NMR data for free alkene and the *trans*-[W(CO)$_4$(η^2-alkene)$_2$] compounds **1** and **2** in toluene-d_8 solution at 293 K

Compound	^{13}C [b]	δ	$^1J_{CH}$	$^1J_{WC}$	$\Delta\delta$ [c]
H_2C^1=C^2H–CH_3 [a]	C^2	135.7	152		
	C^1	115.4	154, 157		
	CH_3		126		
H_2C^1=C^2H–C^3H_2–CH_3	C^2	140.5	151		
	C^1	113.5	153, 157		
	C^3	27.4	126		
	CH_3	13.4	126		
trans-[W(CO)$_4$(H_2C^1=C^2H–CH_3)$_2$] **1**	CO	199.96		122	
	C^2	50.20	156	10.2	85.5
	C^1	37.35	156, 162	12.7	78.1
	CH_3	24.49, 24.34	131		
trans-[W(CO)$_4$(H_2C^1=C^2H–C^3H_2–CH_3)$_2$] **2**	CO	199.84		122	
	C^2	57.77	154	10.2	82.7
	C^1	35.77, 35.72	158	12.7	77.7, 77.8
	C^3	34.05, 34.18	123		−6.8, −6.7
	CH_3	21.02, 20.99	126		−7.6, −7.7
[W(CO)$_5$(H_2C^1=C^2H–CH_3)]	CO	200.71, 196.37 (1/4)		– [d], 127	–
	C^2	85.31			50.4
	C^1	63.42			52.0
	CH_3	24.31			
[W(CO)$_5$(H_2C^1=C^2H–C^3H_2–CH_3)]	CO	200.94, 196.28 (1/4)		153, 127	
	C^2	91.82	157		48.7
	C^1	61.47	159		51.9
	C^3	32.28			−5.2
	CH_3	18.71	128		−5.5

[a] According to Savitsky et al. [28].
[b] Identification of carbon atoms.
[c] $\Delta\delta = \delta$ (free alkene) $-\,\delta$ (coordinated alkene).
[d] Not observed.

isomer showed an absorption pattern with one strong ν(CO) band at about 1954 cm^{-1} together with a weak one at 1990 cm^{-1} and very weak ones at 2058, 1928 and 1917 cm^{-1}, very similar to those of the *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes studied previously [1–6,8–11,13,18]. Compounds **1** and **2** are stable enough and can be stored in an alkane solution in the dark and at a low temperature (253 K) without noticeable change over periods of months. However, the isomerisation of 1-butene to *cis*- and *trans*-2-butene in the course of synthesis of compound **2** resulted in the formation of *trans*-[W(CO)$_4$(η^2-CH$_3$CH=CHCH$_3$)$_2$] (< 10%) on the evidence of the ^{1}H- and ^{13}C-NMR spectra.

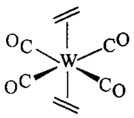
3.2. NMR properties

The ^{1}H-NMR spectrum of **1** and **2** in toluene-d_8 solution at 293 K consists of three groups of signals for the olefinic protons at δ_H about 3.0 (H^c), 2.3 (H^b) and 2.0 (H^a) at 293 K (Figs. 1 and 2, Tables 1 and 2). The shifts of these signals relative to those of the free alkenes are remarkably large, viz. $\Delta\delta = \delta$ (free alkene) $-\,\delta$ (coordinated alkene), ca. 3.0 (H^a), 2.6 (H^b) and 2.8 (H^c). The olefinic protons H^a, H^b and H^c are distinguishable by the value of $^3J_{HH}$. The resonance of the proton H^c is split by two different olefinic protons (H^a and H^b) and the three protons of the methyl group (H^d) and appears in the ^{1}H-NMR spectrum of **1** as a doublet of doublets of quartets with $^3J_{H^aH^c} = 11.8$, $^3J_{H^bH^c} = 9.2$ and $^3J_{H^cH^d} = 5.9$ Hz (Fig. 1). The resonances of the two olefinic protons (H^a and H^b) appear as two doublets of doublets with a coupling constant $^2J_{H^aH^b} = 1.5$ Hz (Table 1, Fig. 1). The olefinic proton–proton coupling constant ($^3J_{H^aH^c}$) at about 12 Hz is much smaller than the value of 17 Hz characterising the uncoordinated alkene (Table 1).

The ^{1}H-NMR characteristics of **2** are very similar to those of **1** but with one exception. Two complex signals of equal intensity at δ_H 2.33 and 1.24 due to two inequivalent protons of the methylene group (CH^{d}H$^{d'}$) of the 1-butene ligand are observed (Fig. 2, Table 2). The chemical shift difference between these two signals (1.1 ppm) is similar to that of analogous complexes of alkenes with longer carbon chain (1.2 ppm) [9]. Because of the inequivalence of the methylene protons (H^d and H$^{d'}$) the signal associated with the olefinic proton H^c appears in the ^{1}H-NMR spectrum of **2** (Fig. 2) as a doublet of doublets of doublets of doublets with $^3J_{H^cH^d} = 3.2$ and $^3J_{H^cH^{d'}} = 6.3$ Hz. The signal for the proton H^d and H$^{d'}$ is very complex but after careful examination at different temperature was resolved as quartet of doublets of doublets with $^{2}J_{\mathrm{H^dH^{d'}}} = 10.3$ Hz (Table 2).

The ^{13}C resonance signals of the olefinic carbon atoms of the free alkene are shifted to much lower frequency ($\Delta\delta$ = ca. 80) on coordination to the tungsten(0) centre in **1** and **2** (Table 3). Similarly, large low-frequency shifts have been observed in the *trans*-[$W(CO)_4(\eta^2$-alkene$)_2$] complexes studied previously [2,6–9,11]. The ^{13}C-NMR spectra of **1** and **2** show satellites due to the coupling between the olefin carbon and ^{183}W nuclei ($I = 1/2$, 14.5% natural abundance); viz. $^{1}J_{\mathrm{WC(1)}} = 12.7$ and $^{1}J_{\mathrm{WC(2)}} = 10.2$ Hz. The coupling constants are consistent with the description of the W(η^2-C=C) unit as belonging to a metallacyclopropane. Hence it appears that alkene ligands in **1** and **2** are strongly bound not only through donation of their (C=C)-π electrons into an empty d orbital of tungsten but mainly through a strong interaction of the (C=C)-π* orbital with the d_π electrons of the metal. The $^{1}J_{\mathrm{CH}}$ values associated with the olefinic carbon atoms increase a little on coordination of the alkene to tungsten (Table 3).

The spectral features are fully consistent with the pseudo-octahedral geometry of the complexes **1** and **2** having the two alkene molecules mutually *trans*, orthogonal and each C=C linkage eclipsing one of the two OC–W–CO vectors of the equatorial $W(CO)_4$ unit. Indeed, the C_2H_4 analogue of **1** and **2** has been shown by X-ray studies to have such a structure [11].



3.3. Isomerism

The structures of *trans*-bis(alkene) complex become much more complicated and interesting once ethene is replaced by an unsymmetrically substituted alkene. There are two possible isomers **A** and **B** for **1** and **2** based on the orthogonal eclipsing of the OC–W–CO vectors by the two alkene ligands [2,8,11]. Because of the rotation of the two alkene ligands in solution, the isomer **B** exists as two rotamers **B**–**I** and **B**–**II** which could be detected at low temperature by the limiting ^{1}H- and ^{13}C-NMR spectra.

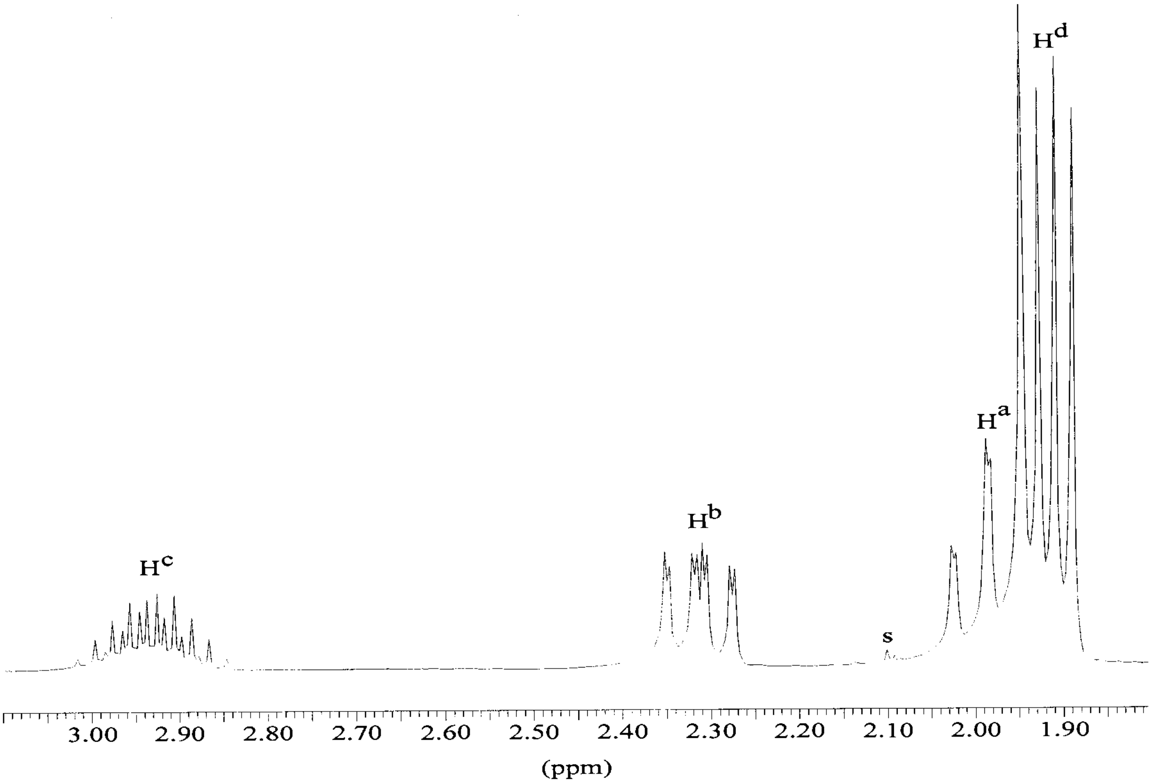
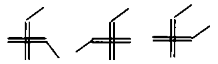


Fig. 1. The ^{1}H-NMR spectrum (300 MHz) of **1** in toluene-d_8 solution at 293 K. S denotes a solvent resonance. Proton signals in the propene ligand are labelled as follows:



A **B-I** **B-II**

The two isomers **A** and **B** have been observed by ^{1}H- and ^{13}C-NMR investigations of **1** and **2** in solution at r.t. and are found to occur in equal abundance. The ^{1}H-NMR spectra of **1** and **2** each show a pair of signals for the protons of the alkene ligand with integral intensities in the ratio 1:1 (Tables 1 and 2, Figs. 1 and 2). The ^{13}C-NMR spectrum of **1** at r.t. consists of a single signal due to olefinic carbons and a pair of signals for the carbon of the methyl groups, with comparable intensity (Table 3, Fig. 4). For compound **2**, a pair of signals was observed at r.t. for C^1, C^3 and CH_3 (Table 3). The isomers **A** and **B** show minimal differences in the ^{1}H (< 0.1 ppm) and ^{13}C (< 0.2 ppm) chemical shifts of the alkene ligands in the temperature range 293–243 K (Tables 1–3).

Both the ^{1}H- and ^{13}C-NMR spectra of compounds **1** and **2** change significantly with decreasing temperature (Figs. 3 and 4), indicating that the complexes are fluxional at ambient temperatures as a result of rotation of the alkene ligands at a rate that is fast on the NMR time-scale. As the temperature decreased from r.t., broadening of the signals due to isomer **B** occurred and a coalescence temperature was reached in the range 223–233 K. Each alkene ligand resonance due to isomer **B** started to split into two resonances as the temperature was decreased further. Below 213 K the structure became static and two resonances for the alkene protons and carbons were observed; these were attributed to **B**–**I** and **B**–**II** and were accompanied by resonances with twice the intensity due to isomer **A** (Figs. 3 and 4). In the ^{13}C-NMR spectrum of **1** at 293 K, there appeared two carbon resonances due to the methyl group at δ_C 24.49 and 24.34 corresponding to isomer **A** and **B** with comparable intensities. The lower frequency resonance coalesced at ca. 223 K but split into two resonances at lower temperature. At 203 K three resonances at δ_C 24.88, 24.71 and 24.27, were observed for the methyl groups of **1B**–**I**, **1A** and **1B**–**II**, respec-

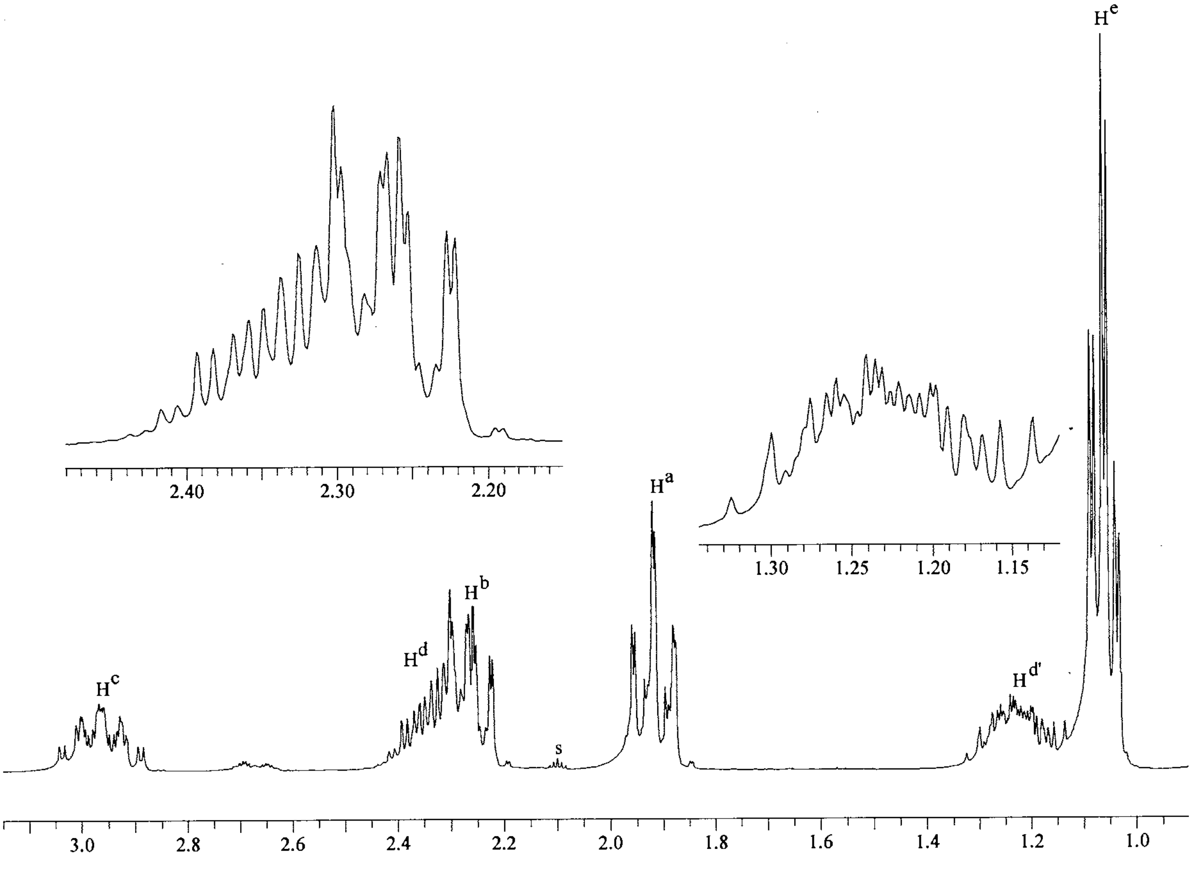
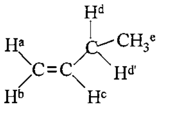


Fig. 2. The ^{1}H-NMR spectrum (300 MHz) of **2** in toluene-d_8 solution at 293 K. The signals of the olefinic protons (H^d) and ($H^{d'}$) are shown with scale expansion. S denotes a solvent resonance. Proton signals in the propene ligand are labelled as follows:



tively. Similar variable-temperature ^{1}H- and ^{13}C-NMR spectra were observed for compound **2**. From these NMR data the free energy barrier to alkene rotation, $\Delta G^{\ddagger}$, was calculated to be 46 kJ mol^{-1} for **1** and 48 kJ mol^{-1} for **2**. These values are close to those reported for other *trans*-[W(CO)$_4$(η^2-alkene)$_2$] complexes. For *trans*-[W(CO)$_4$(η^2-1-C$_5$H$_{10}$)$_2$], for example $\Delta G^{\ddagger}$ was calculated to be 48.5 kJ mol^{-1}[9].

3.4. Photoreactivity of the trans-[W(CO)$_4$(η^2-alkene)$_2$] complexes *1* and *2*

To our knowledge there have been several previous reports on the photoreactivity of tungsten carbonyl complexes containing alkene ligands [3,7,10,11, 13,19,20]. The identities and structures of the relevant complexes have been assigned mainly on the basis of their IR spectra. Recently we have shown that ^{1}H-NMR spectroscopy can be profitably exploited to identify unstable 18-electron species generated photochemically in solution at low temperature [11]. Here we report the first ^{1}H-NMR characterisation of compounds formed by photolysis of **1** and **2**. Photolysis of the compounds in toluene-d_8 or methylcyclohexane-d_{14} solution in an NMR tube for 2 h at ca. 200 K gave new proton resonances assignable to the uncoordinated and coordinated alkene ligand. In the photolysis of **1** in toluene-d_8 solution the olefinic protons of free propene were observed at δ 5.72 (ddq, 1 H^{c}), δ 4.99 (dd, 1 H^{a}) and δ 4.94 (dd, 1 H^{b}) (Table 1). In the photolysis of **2**, in similar conditions, free 1-butene, and *cis*- and *trans*-2-butene were detectable by their ^{1}H-NMR spectra. The proportions of these three isomers of butene changed as a function of reaction time, as demonstrated by integration of the proton (H^{c}) signal at δ 5.77 for 1-butene, δ 5.46 for *cis*-2-butene and δ 5.35 for *trans*-2-butene. Irradiation of **2** for 3.5 h at ca. 200 K produced a mixture containing 42% 1-butene, 3% *cis*-2-butene, and 55% *trans*-2-butene. After warming this mixture to 293 K the proportion of *trans*- to *cis*-2-butene decreased in favour of the *cis* isomer (23% 1-butene, 45% *cis*-2-butene, and 32% *trans*-2-butene). After keeping the mixture for 2 months in a refrigerator at 253 K, the

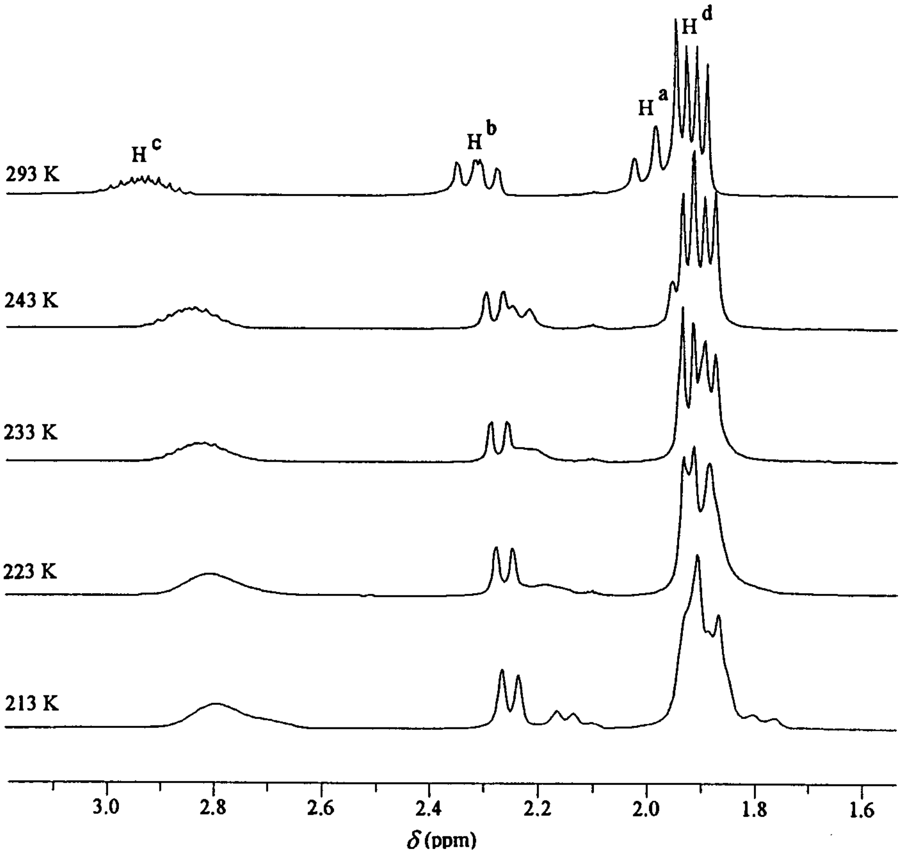
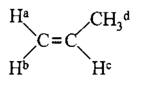


Fig. 3. The variable-temperature ^{1}H-NMR spectrum of **1** in toluene-d_8 solution showing the dynamic behaviour and the restricted rotation of the propene ligand. Proton signals in the propene ligand are labelled as follows:



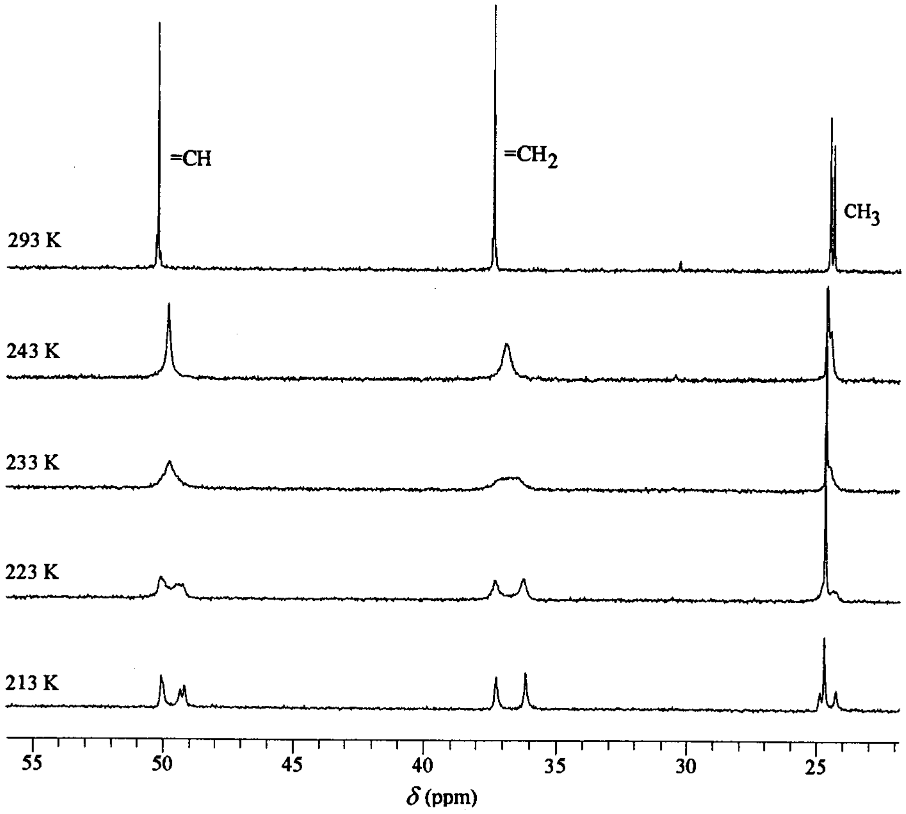
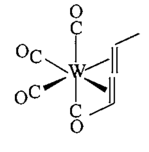
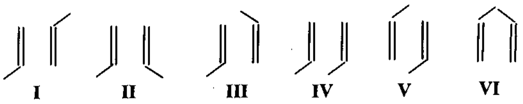


Fig. 4. The alkene region of the variable-temperature $^{13}C\{^1H\}$-NMR spectrum of **1** in toluene-d_8 solution showing the dynamic behaviour and the restricted rotation of the propene ligand.

distribution of the butene isomers (2% 1-butene, 29% *cis*-2-butene, and 69% *trans*-2-butene) is close to that to be expected at thermodynamic equilibrium [21]. This indicates fast exchange in solution between coordinated and free alkene, even at low temperature. For a terminal alkene coordinated to the tungsten centre double bond migration occurs, but for an internal alkene *cis–trans* isomerisation takes place.

Prolonged broad-band UV irradiation of **1** and **2** at ca. 200 K gave three new signals characteristic of H^c of the coordinated alkene all of very low intensity (Fig. 5). In the reaction of **1** at 263 K, these signals were observed at δ 3.79, 3.47 and 3.25, i.e. at lower frequency than the H^c signal of **1**. These three signals each appeared as a doublet of doublets of quartets with identical proton–proton coupling constants $^3J_{H^aH^c} =$ 14.7, $^3J_{H^bH^c} = 8.8$ and $^3J_{H^cH^d} = 5.9$ Hz, indicating similar interactions with the tungsten centre. The observed value of $^3J_{H^aH^c}$ (14.7 Hz) is intermediate between that of 11.8 Hz for coordinated propene in **1** and that of 16.9 Hz for free propene. Warming the photolysed solution to r.t. resulted, however, in decay of the two lower frequency signals, and at 293 K a single product with H^c at δ 3.96 could be observed (Fig. 5). This feature has been assigned to H^c of $[W(CO)_5(\eta^2\text{-}C_3H_6)]$.





Two signals, which decay at r.t., could be tentatively assigned to H^c of very unstable *cis* isomers of the bis-alkene complexes which are formed by photoisomerisation of **1** and **2** (Tables 1 and 2). The reproducible intensity ratio 3:2 of these two signals assigned to H^c of *cis* isomers in all the experiments, with **1** and **2** in the temperature range 193–293 K, indicates the presence of the two thermodynamically more favourable isomers out of the six possible forms (**I**–**VI**) resulting with coordination of two equivalent alkenes having inequivalent ends in the mutually *cis* position and parallel alignment of the C=C linkage. In solution the isomers **I** and **V**, and **II** and **VI** could represent a pair of two rotamers arising from rotatory motion of both alkene molecules by 180°. However, on the basis of the spectral data available (observed below the decomposition temperature of the compounds, viz. 293 K), we are unable to ascertain whether the two mutually *cis* alkene ligands are static or rapidly rotating.

The *cis* isomer of $[W(CO)_4(\eta^2\text{-}C_3H_6)_2]$ was first observed by IR studies as a thermally labile product during the photolysis of $W(CO)_6$ in the presence of C_3H_6 in a rigid alkane glass at 77 K [3]. We were able to show that *cis*-$[W(CO)_4(\eta^2\text{-}C_3H_6)_2]$ can be detected in alkane solution by its IR spectrum, even at 263 K [13]. The present studies show that this isomer can be formed and detected by ^{1}H-NMR spectroscopy at higher temperatures, until 293 K.

Small amounts of the pentacarbonyl compound $[W(CO)_5(\eta^2\text{-alkene})]$ that is produced in the photochemical reactions of **1** and **2** are believed to form by photolytic alkene loss from the bis-alkene complex, followed by reaction with CO present in the reaction mixture. Another possible origin of the pentacarbonyl compound is decomposition of the *cis* isomer formed after the *trans–cis* isomerisation process. The thermal decay of *cis*-bis(alkene) compounds, which can be monitored by ^{1}H-NMR measurements, is always accompanied by an increase in intensity of signals due to the monoalkene pentacarbonyl species (Fig. 5).

With toluene-d_8 as the solvent, the proton chemical shifts of some alkene complexes vary significantly with temperature (shifting to lower field as the temperature increases), although others remain almost unchanged over the entire temperature range 213–293 K, as shown in Figs. 3 and 5. Most noticeable is the high frequency shift of the signal due to the olefinic proton H^c of the monoalkene pentacarbonyl compounds and the *cis* isomers of the bis-alkene species; the effect is smallest for the olefinic proton signals of the two mutually *trans* alkene ligands in **1** or **2** (Tables 1 and 2). By contrast, with methylcyclohexane-d_{14} as the solvent, the chemical shifts vary but little with temperature. Similar behaviour was observed previously for the analogous ethene complexes of tungsten [11].

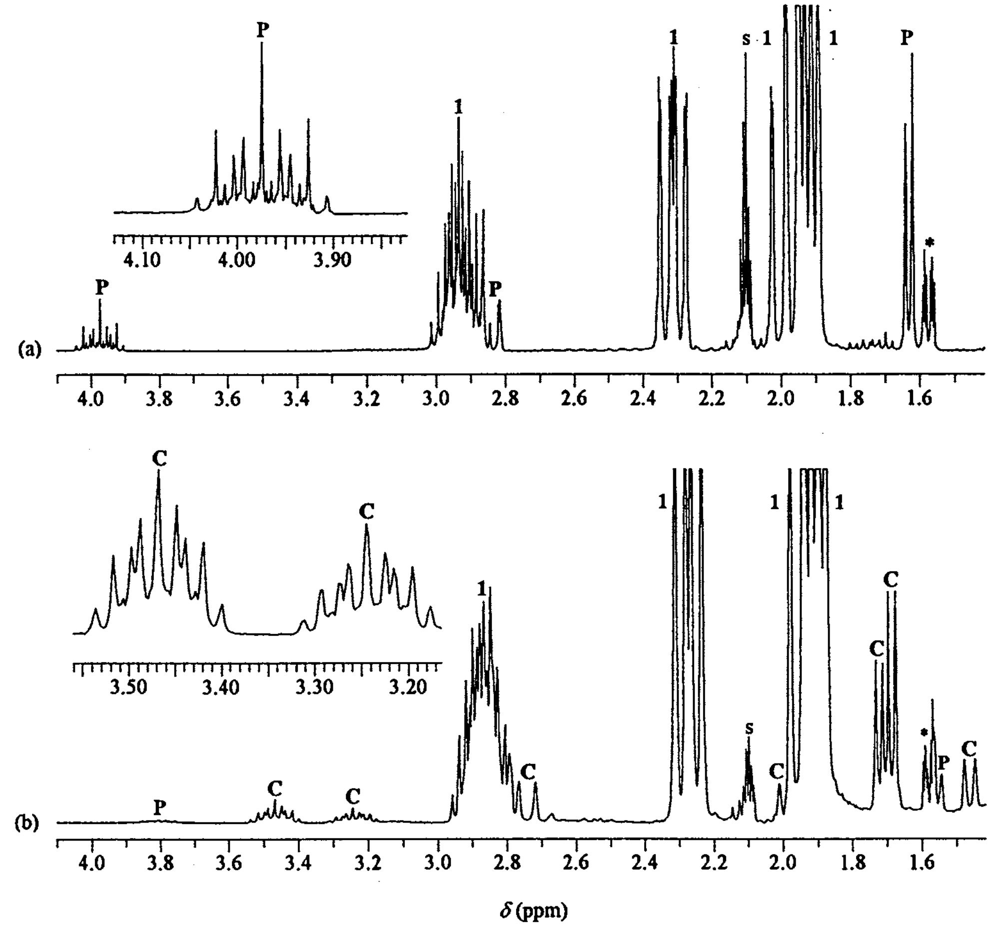


Fig. 5. ^{1}H-NMR spectra of propene carbonyl complexes of tungsten in toluene-d_8 solution. (a) At 293 K signals due to the protons in *trans*-$[W(CO)_4(\eta^2\text{-}C_3H_6)_2]$ (**1**) and $[W(CO)_5(\eta^2\text{-}C_3H_6)]$ (**P**) are observed only. (b) At 263 K signals due to the protons in *cis*-$[W(CO)_4(\eta^2\text{-}C_3H_6)_2]$ (**C**) (two isomers) can be detect after irradiation of **1** at ca. 200 K. The asterisk indicates the proton signal due to the methyl group of free propene; s denotes a solvent resonance. The signals of the olefinic protons (H^c) are shown with appropriate scale expansion above the traces (a) and (b).

3.5. Photochemical reactions of $W(CO)_6$ in the presence of alkene as monitored by ^1H-NMR

When the photochemical reactions of $W(CO)_6$ with an excess of C_3H_6 at ca. 200 K were monitored by ^{1}H-NMR measurements, labile propene complexes could be observed. The only signals to be observed with significant intensity after brief UV photolysis were those due to $[W(CO)_5(\eta^2\text{-}C_3H_6)]$. On prolonged irradiation ^{1}H signals due to the secondary photolysis products, *cis*- and *trans*-$[W(CO)_4(\eta^2\text{-}C_3H_6)_2]$, could be detected (Table 1). However, raising the temperature led to a decrease in the intensity of several signals, and at 293 K the only signals to be observed were those of $[W(CO)_5(\eta^2\text{-}C_3H_6)]$ and **1** at δ 3.96 and 2.90 (H^c), respectively (Table 1). The analogous experiment with irradiation of $W(CO)_6$ in toluene-d_8 saturated with 1-butene was found to take essentially the same course. Under these photochemical conditions, however, 1-butene isomerises to *cis*- and *trans*-2-butene, as indicated by the appearance and growth of the olefinic proton (H^c) resonances at δ 5.35, and 5.46, respectively. The pentacarbonyl complex $[W(CO)_5(\eta^2\text{-}1\text{-}C_4H_8)]$ decays rapidly at ambient temperatures, and the formation of the pentacarbonyl derivative of tungsten with the *cis*- and *trans*-2-butene ligand was detected by their ^{1}H-NMR spectra which featured resonances due to olefinic protons at δ 3.72 and 3.97, respectively.

3.6. NMR data as a criterion in recognising the relative positions of alkene and CO ligands in mixed alkene carbonyl complexes

In the alkene carbonyl compounds that have been characterised by X-ray crystallography, the olefinic carbon of two mutually *trans* staggered alkene ligands is slightly closer to the metal centre (by ca. 0.1Å) than the olefinic carbon of an alkene ligand *trans* to a carbonyl group [2,7,8,11,22–25].

For all known alkene complexes, the changes in ^{1}H and ^{13}C chemical shift with respect to the free alkene, $\Delta\delta$, for the alkene ligand *trans* to a CO group are smaller than for two mutually *trans* alkene ligands [2,7,8,11,22–25]. This phenomenon can be seen to result from the competition created between the vacant π-orbitals of the CO group and those of the alkene ligand for the same d_π orbitals of the tungsten atom. As CO is acknowledged to be a better π-acceptor than is an alkene molecule, the CO competes effectively with a *trans* alkene group for the d_π electrons on the tungsten centre, thereby weakening the back-donation from the d_π orbital of tungsten to the π^* orbital associated with the C=C linkage. Conversely, there is no antagonism between two mutually *trans* staggered alkene ligands, as each interacts with the tungsten via a different d_π orbital. It is this lack of competition for the d_π orbitals of tungsten, that makes the coordination shifts $\Delta\delta$ larger for compounds with mutually *trans* alkene ligands [7,8]. For compounds **1** and **2** $\Delta\delta$ of the olefinic protons is in the range 2.6–3.1 ppm and $\Delta\delta$ of the olefinic carbons is in the range 78–86 ppm. These values are close to those observed for other compounds with mutually *trans* alkene ligands ($\Delta\delta = 2$–5 for olefinic protons and $\Delta\delta = 67$–112 for olefinic carbons) [2,7,8,11,22–25]. For compounds with the alkene ligand *trans* to a CO group, the $\Delta\delta$ values of olefinic protons and carbons are typically found to be substantially smaller, occurring in the range 1–3 and 42–76, respectively [2,7,8,11,22–25]. The complexes $[W(CO)_5(\eta^2\text{-alkene})]$ and *cis*-$[W(CO)_4(\eta^2\text{-alkene})_2]$, where alkene = propene or 1-butene, display olefinic protons with $\Delta\delta$ is in the range 1.8–2.3 ppm; $\Delta\delta$ of the olefinic carbons in $[W(CO)_5(\eta^2\text{-}C_3H_6)]$ and $[W(CO)_5(\eta^2\text{-}C_4H_8)]$ is in the range 50–52 ppm.

Moreover, what we take to be significant feature of these alkene carbonyl complexes of tungsten is the value of $^1J_{WC}$ (Table 3). With mutually *trans* carbonyl ligands coupling between the carbon atom and the tungsten is smaller ($^1J_{WC} = 122$–127 Hz) than for a carbonyl ligand *trans* to an alkene ligand ($^1J_{WC} = 153$ Hz). The increased value of $^1J_{WC}$ is characteristic of a shorter tungsten–carbon bond with enhanced π character. By contrast, competition for a d_π orbital of tungsten, causes an alkene ligand *trans* to CO to interact more weakly with tungsten.

Hence it appears that NMR data provide a useful criterion for identifying the relative positions of alkene and CO ligands in alkene carbonyl complexes of tungsten.

3.7. Photorearrangement of alkene complexes to allyl hydrido derivative

On the evidence if IR studies photolysis of **1** and **2** in solution at low temperature yields the *cis* isomers of the bis-alkene compounds, monoalkene derivatives, the free alkene, and additional products, most probably allyl hydrido complexes of the type $[W(\eta^3\text{-allyl})H(CO)_4]$ (allyl = C_3H_5 or C_4H_7) [13]. When the photochemical reactions of **1** and **2** at ca. 200 K were monitored by ^{1}H-NMR measurements in addition to the new proton signals due to free and coordinated alkene, weak hydride resonances are observed at δ ca. -3 ppm. In the case of the propene complex **1** at 203 K, three such signals were detected at δ -3.08, -3.52 and -4.13 with intensities in the ratio 10:3:5, respectively. The most intense signal was flanked by tungsten satellites with a tungsten–hydride coupling constant $^1J_{WH} = 16.3$ Hz indicating the presence of a W–H bond. After warming the reaction mixture, however, the two signals at lower frequency decreased in intensity (ratio 10:2:3 at 283 K) and at r.t. only one hydride signal could be observed, viz. that at -3.10

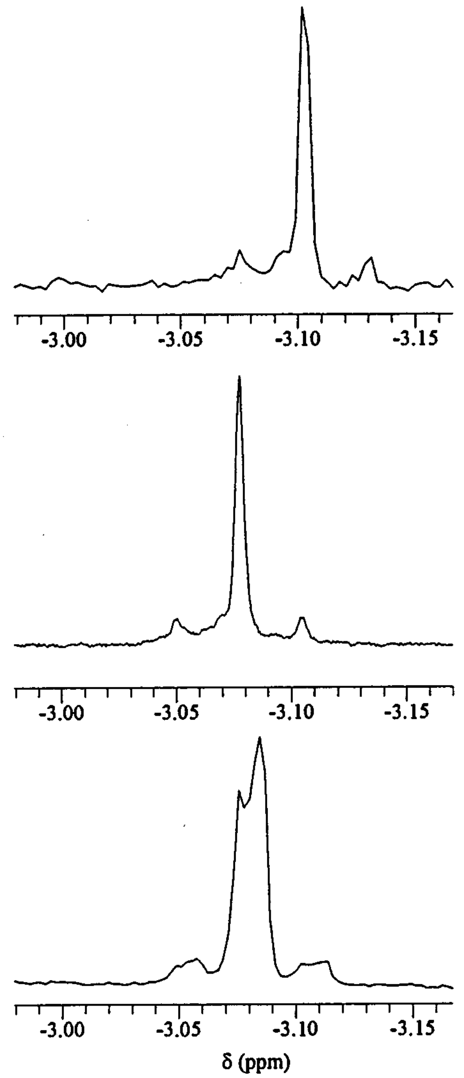
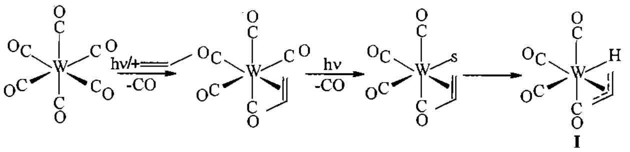


Fig. 6. ^{1}H-NMR spectra in toluene-d_8 solution at 293 K showing the region of the hydride resonance for the derivatives formed after short photolysis times (< 1 h): (a) $W(CO)_6$ and propene in *n*-hexane; (b) $W(CO)_6$ and 1-butene in *n*-hexane; and (c) the same sample as in (b) but after standing for 15 h at ambient temperatures.

ppm. The W–H bond is formed probably only in a thermal process occurring after photolytic alkene or CO loss to give coordinatively unsaturated species. This was indicated by the systematic increase in intensity of the hydride signals as the temperature of the reaction mixture was raised from 203 to 283 K. Only one hydride-containing species was stable enough to be detected at r.t. or higher temperatures. A similar signal was observed previously in studies of the thermal reactions (348 K) of *trans*-$[W(CO)_4(\eta^2\text{-1-}C_5H_{10})_2]$ [12]. The hydride-containing species was also observed by ^{1}H-NMR measurements in experiments involving brief photolysis of $W(CO)_6$ in the presence of an alkene in *n*-hexane at 268 K and giving as the principal products a mixture of $[W(CO)_5(\eta^2\text{-alkene})]$ and *trans*- and *cis*-$[W(CO)_4(\eta^2\text{-alkene})_2]$. In the case of the reactions with propene and 1-butene the hydride signal was detected at δ −3.10 and −3.07, respectively (Fig. 6). When the sample was left to stand at ambient temperature, however, the signal at δ − 3.07 decayed and a new signal at δ −3.08 was observed to appear and grow (Fig. 6c). This may be the result of *exo–endo* isomerisation of the hydrido derivative. Full characterisation of an η^3-allyl moiety has been hampered by the very low concentration of the hydride species in a mixture of products. Because of the relative orientation of the allyl ligand with respect to the W–H bond, the pseudo-octahedral tetracarbonyl complex $[W(\eta^3\text{-allyl})H(CO)_4]$ could exist as two geometric (*exo* and *endo*) isomers which could be distinguished in principle by their ^{1}H-NMR spectra. However, we were unable to identify the resonance of the allyl ligands, and in these circumstances can offer only a tentative assignment of the very weak hydride resonance at δ ca. −3 ppm to the *endo* or *exo* isomer of the complex $[W(\eta^3\text{-allyl})H(CO)_4]$. The two other hydride signals observed at low temperature must be due to more labile hydrido species formed after CO loss from the starting compound [13].

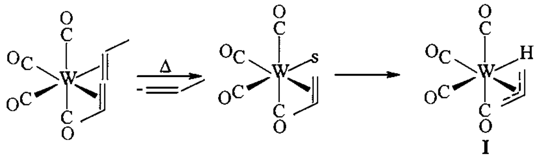
Although it is not possible to identify with certainty the mechanism by which the complex **1** or **2** transforms on photolysis to an allyl hydrido complex, we suggest that the first photochemical step results in alkene loss giving the coordinatively unsaturated 16-electron alkene species $[W(CO)_4(\eta^2\text{-alkene})(s)]$ (s = solvent molecule). The same species can be formed in the photochemical reaction of $W(CO)_6$ with an alkene (Eq. (1)). Evidence that such a process can occur was also



(1)

afforded by our earlier IR studies of bis-alkene complexes contained in low-temperature matrices or hydrocarbon solutions [11,13]. The allyl hydrido compound **I** can result from intramolecular C–H activation of a C–H bond in the coordinatively unsaturated 16-electron alkene complex [13]. However, this process is susceptible to retardation if the coordinatively unsaturated species captures the CO formed parallel in photolysis reaction of **1** and **2** to give the corresponding $[W(CO)_5(\eta^2\text{-alkene})]$ complex. This would then explain why irradiation of $W(CO)_6$ with alkene in a closed system (viz. an NMR tube) leads to the formation of hydrido derivatives only in very low concentrations. By contrast, irradiation of these compounds in an open system with removal of the volatile materials in vacuum gives higher concentrations of the hydrido species (Fig. 6). In reaction mixtures containing the unstable *cis*-

$[W(CO)_4(\eta^2\text{-alkene})_2]$ complex, the hy-drido species must be formed by the thermal rearrangement of that complex after alkene release (Eq. (2)).



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(2)

A similar photolytically initiated rearrangement of coordinated propene to an allyl hydrido compound has been observed for $[Fe(CO)_4(\eta^2\text{-}C_3H_6)]$ and $[(\eta^5\text{-}C_5Me_5)\text{-}Re(CO)_2(\eta^2\text{-}C_3H_6)]$ [26,27]. However, the conversion of the these compounds is more selective and efficient so that different isomers (*exo* and *endo*) of the allyl hydrido product could be identified unambiguously by ^{1}H-NMR studies.

4. Conclusions

The results presented here provide the first ^{1}H- and ^{13}C-NMR spectral characterisation of the compounds *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$, where alkene = propene and 1-butene. These complexes have been shown to exist in several isomeric forms on the basis of their NMR spectra. The spectra of **1** and **2** in solution at low-temperature show that they each exist as a mixture of two rotamers that undergo fast exchange at ambient temperatures. The solution dynamics of these bis(alkene) complexes were investigated by variable-temperature studies, enabling the barrier to alkene rotation to be determined.

^{1}H-NMR measurements have also been applied to the identification of the thermally unstable alkene complexes $[W(CO)_5(\eta^2\text{-alkene})]$ and *cis*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ and an allyl hydrido derivative formed by broad-band UV photolysis of alkene-saturated hydrocarbon solutions of $W(CO)_6$ or *trans*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ at temperatures near 200 K. The compounds *cis*-$[W(CO)_4(\eta^2\text{-alkene})_2]$ are comparatively stable up to about r.t. Only by photolysis at low temperature has it been possible to generate intermediates in yield sufficient for detection by their ^{1}H-NMR spectra.

Of particular interest is the first observation by ^{1}H-NMR spectroscopy of hydride intermediates formed by the photolytically initiated transformations of the propene and 1-butene complexes. This result confirms that alkene complexes of tungsten are capable of entering into C–H activation reactions.

The studies serve also to demonstrate the utility of NMR spectroscopy, the identification of unstable species formed in photochemical reactions in solution at low temperatures.

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