

Photochemical synthesis, spectroscopic properties and barriers to alkene rotation in the novel bis(alkene) tetracarbonyl complexes of tungsten

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Abstract

Photolysis of $W(CO)_6$ in the presence of twentyfold alkene excess (1-pentene, 1-hexene, 2-hexene, 3-hexene, 1-heptene, 1-octene, 1-decene, cyclopentene, cyclohexene, cycloheptene and cyclooctene) in *n*-hexane leads to the formation of the corresponding bis(alkene)tetracarbonyl complexes of tungsten via the less stable $[(\eta^2\text{-alkene})W(CO)_5]$ complexes; the products have been isolated and characterized by their IR, UV-visible and NMR spectra.

Bis(alkene)tetracarbonyl complexes of tungsten exhibit fluxional behaviour on the NMR time scale due to rotation of the alkene ligands around the axis defined by the metal and the midpoint of the C_2 linkage. The barriers to alkene rotation, which reflects the energy difference between the orthogonal and the parallel arrangement of the two $C=C$ units, of a number of bis(alkene) complexes, have been determined using variable-temperature ^{13}C NMR spectroscopy.

Keywords: Tungsten; Carbonyls; Alkene complexes; Fluxional behaviour

1. Introduction

The rapid development of chemistry of transition metal carbonyls, observed during the past 20 years, was stimulated by the possibility of their application as heterogeneous or homogeneous catalysts or catalyst precursors [1]. Among them, tungsten hexacarbonyl is one of those frequently used as model or real catalyst for many organic reactions, mainly for metathesis [2–5], isomerization [5,6] and polymerization of alkenes and alkynes [7,8]. Coordination of an alkene to the tungsten has often been suggested as an important step in the above mentioned catalytic reactions but has been directly observed only in few cases [5,6a]. Various $[(\eta^2\text{-alkene})_nM(CO)_{6-n}]$ complexes ($n=1,2$) have been generated photochemically from a Group 6 hexacarbonyl, $M(CO)_6$ [5,6a,9–21]. The only previous examples of bis(alkene)tetracarbonyl complexes of tungsten are complexes with methyl acrylate, dimethyl fumarate and ethene [10,15]. In this paper we wish to report the first examples of bis(alkene) compounds with (C_5 – C_{10}) unsubstituted acyclic and cyclic alkenes as ligands.

2. Results and discussion

2.1. Synthesis of $[(\eta^2\text{-alkene})_2W(CO)_4]$

Extended photolysis of hexacarbonyltungsten in the presence of twentyfold alkene excess in *n*-hexane at room temperature results in the formation of $[(\eta^2\text{-alkene})_2W(CO)_4]$ (1–11). The primary photoproduct, as detected by IR spectroscopy, is $[(\eta^2\text{-alkene})W(CO)_5]$, which was shown to be characterized by $\nu(CO)$ bands with wavenumbers and relative intensities plainly suggestive of a C_{4v} $W(CO)_5$ moiety [9]. The $\nu(CO)$ fundamentals of the $W(CO)_5$ unit give rise to three IR absorptions, namely a weak feature at 2073–2083 cm^{-1} (a_1) and two more intense features at 1933–1967 cm^{-1} ($a_1 + e$) (Fig. 1(b)). As expected [10,18], continued irradiation under these conditions results in the loss of a second molecule of CO with the appearance and growth of IR bands due to the complex $[(\eta^2\text{-alkene})_2W(CO)_4]$, where the $W(CO)_4$ fragment has D_{4h} "local symmetry" (one strong band between 1920 and 1950 cm^{-1} (Figs. 1 and 2 and Table 1)). Even after prolonged irradiation, IR spectra show $W(CO)_6$, $[(\eta^2\text{-alkene})W(CO)_5]$ and *trans*- $[(\eta^2\text{-alkene})_2W(CO)_4]$ to be the main carbonyl-containing complexes present in reac-

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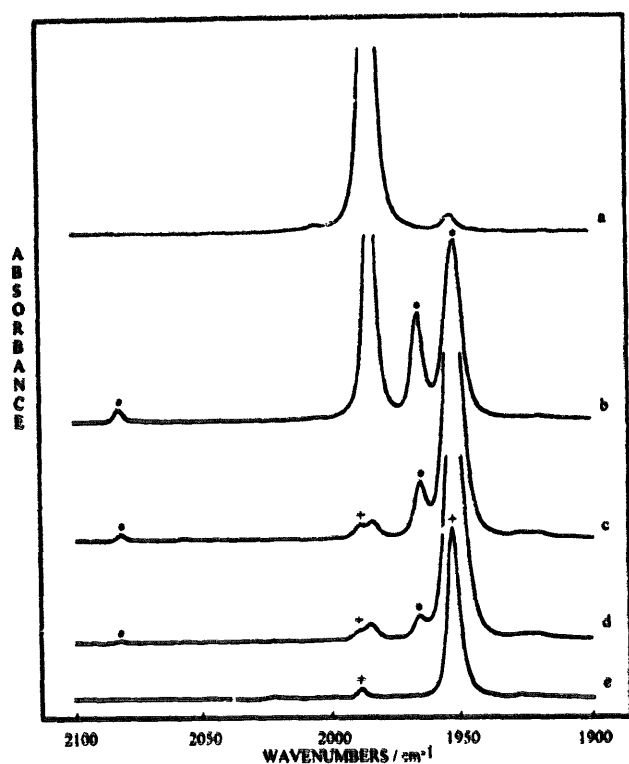


Fig. 1. The CO stretching region of the IR spectrum displayed by solution containing $W(CO)_6$ (3 mmol) and 1-hexene (62 mmol) in *n*-hexane (20 cm³) showing the effect of photolysis: curve a, spectrum before irradiation; curve b, after 2 min photolysis; curve c after 10 min photolysis; curve d, after 30 min photolysis; curve e, spectrum of $trans-[W(CO)_4(\eta^2-1-hexene)_2]$ (2) in *n*-hexane solution after separation from the reaction mixture. Bands are labelled as follows: *, 2082vw, 1965s, 1951vs cm⁻¹ [$W(CO)_3(\eta^2-1-hexene)$]; +, 1988vw, 1952vs $trans-[W(CO)_4(\eta^2-1-hexene)_2]$.

tion mixture (Fig. 1(d)). However, a very careful look at IR spectra monitored at the time of the photosubstitution reaction showed the appearance of two weak bands at about 2050 and about 1920 cm⁻¹ (Fig. 2 and Table 1). Corresponding bands were observed in experiments

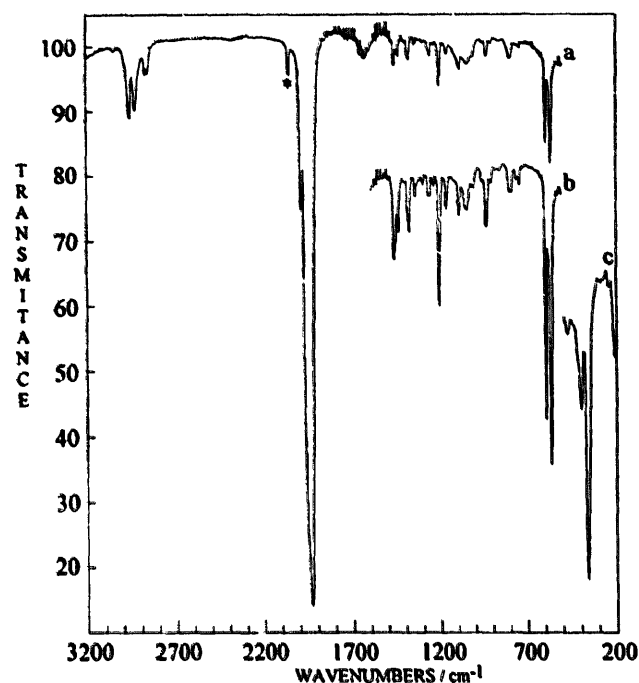


Fig. 2. The IR spectra of $trans-[W(CO)_4(\eta^2-1-pentene)_2]$ (1) in KBr (curve a), the peak denoted by an asterisk corresponding to the a_1 mode of $cis-[W(CO)_4(\eta^2-1-pentene)_2]$ with C_{2v} symmetry (2056 cm⁻¹ in Table 1), of 1 at a higher concentration (curve b) in KBr and of 1 recorded as film between CsI plates (curve c). The spectra of the analogous bis(alkene) complexes are virtually identical.

with a cyclic alkene such as cycloheptene and also an internal alkene such as 3-hexene, whereas with terminal alkenes it was possible to detect only the band at about 2050 cm⁻¹. The circumstances leave little doubt that these are two (a_1 and b_1 respectively) of the four IR-active $\nu(CO)$ fundamentals of a $W(CO)_4$ fragment with C_{2v} symmetry. The other two fundamentals are expected to occur in the region 2000–1900 cm⁻¹ but were obscured presumably by more intense bands due to $W(CO)_6$, $[(\eta^2-alkene)W(CO)_5]$ and $trans-[(\eta^2-alkene)_2W(CO)_4]$.

Table 1
IR data for complexes $trans-[(\eta^2-alkene)_2W(CO)_4]$, where the frequencies are measured in KBr pellets^a

Complex	Alkene	$\nu(CO)$ (D_{2d}, b_2, e) (cm ⁻¹)	$\delta(W-CO)$ (cm ⁻¹)	$\nu(W-C_2)$ (cm ⁻¹)	$\nu(W-CO)$ (cm ⁻¹)	$\nu(C\equiv C)$ (cm ⁻¹)	$\nu(CO)$ ^b ($C_{2v}, a_1, a_1, b_1, b_2$) (cm ⁻¹)
1	1-Pentene	1986 w, 1932 vs (1943)	594 w, 566 w	362 w ^c	398 vw ^c	1208 w	a_1 2056 vw
2	1-Hexene	1987 w, 1936 vs (1947)	594 w, 567 w	^d	^d	1204 w	a_1 2056 vw
3	<i>trans,cis</i> -2-Hexene	1979 w, 1929 vs (1946)	599 w, 567 w	^d	^d	^d	a_1 2049 vw
4	<i>trans</i> -3-Hexene	1978 w, 1928 vs (1935)	600 w, 566 w	^d	^d	1217 w	a_1 2046 vw b_2 1916 s
8	Cyclopentene	1975 w, 1923 vs (1940)	599 w, 567 w	^d	^d	1214 w	a_1 2046 vw
9	Cyclohexene	1967 w, 1926 vs (1934)	603 m, 570 m	^d	^d	1200 w	a_1 2042 vw
10	Cycloheptene	1966 w, 1932 vs (1940)	597 m, 567 m	^d	^d	1201 w	a_1 2042 vw b_2 1919 s

^a Frequencies in parentheses are for measurements in *n*-hexane solution.

^b Frequencies for $cis-[(\eta^2-alkene)_2W(CO)_4]$ complex which can exist in equilibrium with the *trans* complex.

^c Spectra were recorded as films between CsI plates.

^d Frequencies were not recorded for this complex.

kene)₂W(CO)₄]. The intensity patterns and energies of these two bands, which could be observed, are wholly consistent with the formation of a C_{2v} W(CO)₄ moiety; indeed the spectrum resembled quite closely that of *cis*-[W(CO)₄L₂], where L = C₂H₄ (observed by Turner and coworkers [20]) in liquid xenon at -78°C (a₁, 2050 cm⁻¹; a₁ + b₁, 1958 cm⁻¹; b₂, 1914 cm⁻¹) and L₂ = norbornadiene (a₁, 2042 cm⁻¹; a₁ + b₁, 1956 cm⁻¹; b₂, 1909 cm⁻¹ [22]). These results suggest that *cis*-bis(alkene) complexes can be formed and exist in the equilibrium with *trans* isomer; however, the position of the equilibrium lies in favour of the more thermodynamically stable *trans* isomer [23]. This is also in agreement with liquid xenon [20] and flash photolysis [19] studies, which revealed that in the primary photochemical step [(η²-alkene)M(CO)₅] compounds lose a *cis* CO group, but the stabilities of the *cis* isomer of bis(alkene)tetracarbonyl compounds are much lower than those the *trans* isomers [23].

The new compounds 1–11 are very soluble in hydrocarbon solvents. This has led to problems in obtaining crystalline samples suitable for elemental analysis. However, IR and NMR spectroscopy has proved a powerful and reliable means of analysis for these compounds.

Solid bis(alkene) complexes 1–11 and solutions of these complexes in an inert solvent such as *n*-hexane can be handled at room temperature whereas solutions of this complexes in a chlorinated solvent such as CH₂Cl₂ are not so stable. The bis(alkene) complexes are stable in toluene-*d*₈ solutions in closed NMR tube for a long period (more than 1 week). The stability and catalytic activity of bis(alkene)complexes will be the subject of separate publication.

Attempts to prepare *trans*-[W(CO)₄(η²-2-hexene)₂] (3) in a photochemical reaction of W(CO)₆ with a mixture of *trans*- and *cis*-2-hexene led to a mixture of products, including tetracarbonyltungsten coordinated with *trans*- and *cis*-2-hexene in a ratio similar to the ratio of the starting alkene isomers (67.8% *trans*-2-hexene and 32.2% *cis*-2-hexene), as deduced by ¹H NMR spectroscopy.

It should be noted that the above synthetic procedure does not allow the isolation of tetramethylethylene complex with a yield higher than 1%. This, we believe, results from steric factors.

2.2. IR spectra

A *trans* structure has been assigned to bis(alkene)tetracarbonyl complexes of tungsten on the basis of the IR spectra [24,25]. In the IR spectrum 1–11, one strong band appears in the carbonyl stretching region between 1920 and 1950 cm⁻¹ (e_g) as is expected for D_{4h} "local symmetry" of the W(CO)₄ moiety [24,25]. The results

are given in Table 1 and typical spectra are shown in Figs. 1 and 2.

Comparison of the IR data 1–11 (Table 1) shows that in nearly all cases the numbers of features assignable to CO mode and (alkene)₂W mode are very similar to each other and to those for *trans*-[W(CO)₄(η²-ethene)₂] analysed by Davidson and Davies [25]. Two features in the part IR spectrum between 600 and 570 cm⁻¹ are assigned to W–C–O deformation. The W–C₂ stretch was found at 362 cm⁻¹ for the 1-pentene complex. The C=C stretching vibration is known to be strongly coupled to the CH₂ deformation mode. A medium intensity IR band at about 1200 cm⁻¹ is the only candidate for the C=C stretch in [(η²-alkene)₂W(CO)₄]. This means that C=C stretching bands have about 440 cm⁻¹ lower wavenumber than that observed for the free alkene (about 1640 cm⁻¹). This suggests weakening of the alkene bond strength due to back donation of electron density from the filled metal dπ orbitals into empty π* orbitals on the alkene and substantial rehybridization of double C=C bond towards the single C–C bond. Bands at about 1460 and 1440 cm⁻¹ can be assigned as the CH₂ scissors deformation modes and at about 1380 cm⁻¹ as the CH₃ deformation mode. In the CH stretching region there are four weak bands: two stronger bands at about 2960 and 2930 cm⁻¹, and weaker bands at about 2870 and 2860 cm⁻¹ (Fig. 2(a)).

It is also desired to check that two weaker bands appear at a higher frequency than the main CO band in the bis(alkene) compounds. The intensities of these bands appear to be reproducible from sample to sample but the highest frequency band is extremely weak and the lower frequency band appears only as an unresolved shoulder on the most intense e_g band. The most reasonable interpretation is that one of these two additional bands, at about 1980 cm⁻¹, results from reducing the true molecular symmetry to D_{2d}. In D_{2d} symmetry the b_{1g} mode become the IR-active b₂ mode [25]. This very weak band at about 2050 cm⁻¹ is presumably one of four IR-active ν(CO) fundamentals of a W(CO)₄ fragment with C_{2v} symmetry, on the supposition that the *cis*-[(η²-alkene)₂W(CO)₄] complex can exist in equilibrium with the *trans* complex. The position of equilibrium lies in favour of the more thermodynamically stable *trans* isomer [23]. Davidson and Davis [25] explained the presence of this very weak band at 2060 cm⁻¹ in the spectrum of *trans*-[W(CO)₄(η²-C₂H₄)₂] as formally inactive under D_{2d} symmetry but very slightly active by the weak interaction in solution a₁ mode. In our studies we observed this additional band also in the solid (KBr pellets or film). In the spectra of cycloheptene and *trans*-3-hexene complexes it was possible to observe also the lower frequency band at about 1920 cm⁻¹ (b₂), presumably the other band from the four IR-active ν(CO) fundamentals of a W(CO)₄ fragment with C_{2v} symmetry (Table 1).

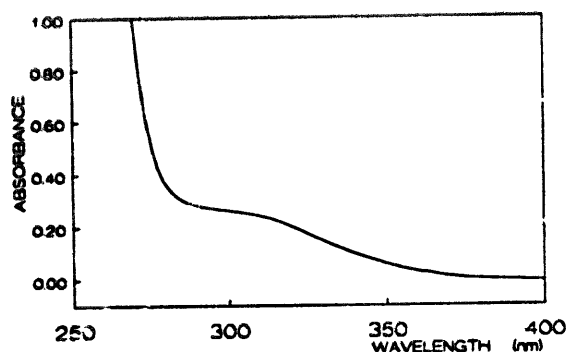


Fig. 3. Electronic absorption spectrum of *trans*-[W(CO)₄(η²-1-hexene)₂] (2) in *n*-hexane (*c* = 1.14 mM; *d* = 1 mm; ε_{λ = 300 nm} = 2271 M⁻¹cm⁻¹). The spectra of the analogous bis(alkene) complexes are virtually identical.

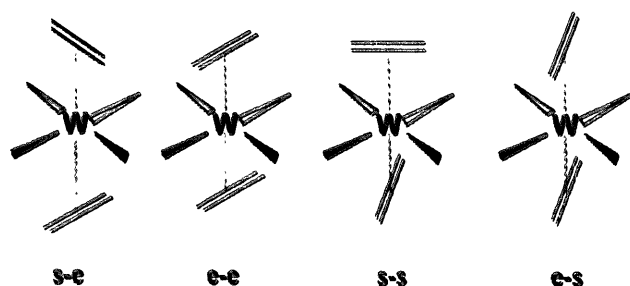
The molecular symmetry of *D*_{2d} assumed by IR for 1–11 is consistent with a mutually staggered conformation for the alkene ligands in *trans*-[W(CO)₄(η²-CH₂=CHCO₂CH₃)₂] revealed by X-ray structure analysis [10].

2.3. Electronic absorption spectra

The electronic absorption spectrum of the *trans*-[(η²-alkene)₂W(CO)₄] exhibits bands in UV region and in the visible–near-UV region. In *n*-hexane solution there is a weak band at about 300 nm (ε = 2271 M⁻¹cm⁻¹) and an intense band below 280 nm for *trans*-[W(CO)₄(η²-1-hexene)₂] (1) (Fig. 3). This spectrum is essentially identical with the spectra of those of the linear alkene and cyclic alkene complexes presented here. Although these spectra have not been assigned, the 300 nm absorption is probably M → π*CO and LF in character.

2.4. NMR studies

A quasi-octahedral *trans*-[(η²-alkene)₂M(CO)₄] complexes may show a variety of structures, with the olefinic ligands either eclipsed or staggered as in the structures in Scheme 1. The model complex *trans*-[Mo(CO)₄(η²-C₂H₄)₂] has been theoretically studied by Veillard and coworkers [26]. They predicted that the



Scheme 1.

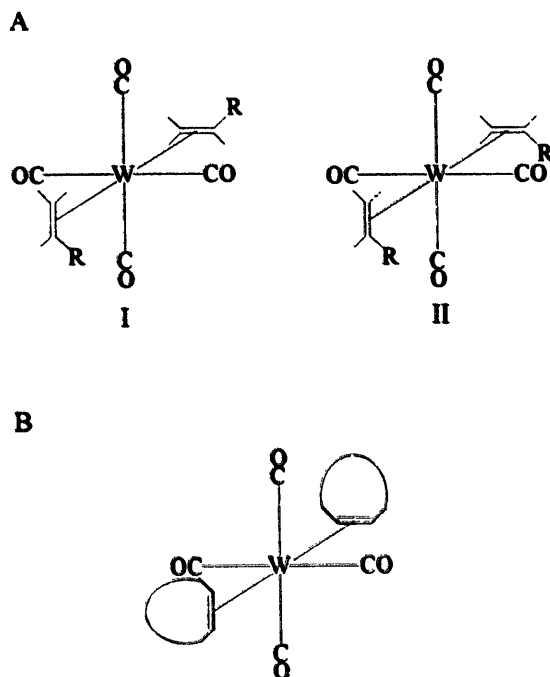


Fig. 4. Proposed solid state structure of the *trans*-[(η²-alkene)₂W(CO)₄] complexes based on X-ray structure [10]: A, two isomeric forms of the acyclic alkene complexes 1–7; B, cyclic alkene complexes 8–11.

most stable conformation is staggered(s)–eclipsed (s-e) with a carbon–carbon double bond of the alkene ligands orthogonal to each other but each eclipsing a CO–Mo–CO vector. This results suggest the following order of energy for the four most symmetrical conformers: s=e < s=s < e=e < e=s (Scheme 1). Furthermore, it was found that the s=e bonding arrangement is only 5 kcal mol⁻¹ more stable than s=s, and 6.3 kcal mol⁻¹ more stable than e=e [26]. The orientational preference s=e bonding arrangement results from the fact that two alkenes, *trans* to each other, will prefer to bond with orthogonal metal orbitals rather than to the same orbital. X-ray structure analysis of [W(CO)₄(η²-methyl acrylate)₂] [10] has revealed the *trans*-staggered arrangement of the olefin ligands. Accordingly we propose such a structure for bis(alkene) complexes 1–11 (Fig. 4), since it is compatible with the ¹H and ¹³C NMR spectra as will now be described.

In the ¹³C NMR spectrum of acyclic alkene complexes at ambient temperature, magnetic inequivalency of both alkenes was observed. There are two resonances at δ = 36.49 and 36.54 ppm for olefin carbon in =CH₂ and two resonances at δ = 40.70 and 40.85 ppm for the –CH₂ group in the complex of 1-hexene (2) (see Table 3 below). Similar very small splittings were observed for other complexes of linear but not for cyclic alkenes (see Table 3 below), indicating that the phenomenon is dependent on the nature of the alkene, whether it is symmetrical or not. This suggests that the acyclic alkene

Table 2

¹H NMR data for selected *trans*-[(η²-alkene)₂W(CO)₄] complexes at 293 K in toluene-*d*₆: δ (ppm); Δδ(ppm) = δ(free olefin) - δ(coordinated olefin)

n	δH ^a	δH ^b	δH ^c	δH ^d	δH ^{d'}	δ(CH ₂)	δ(CH ₃)	Δδ(H ^a)	Δδ(H ^b)	Δδ(H ^c)
n = 1	2.31	1.96	2.99	~ 2.4	1.19	1.42	0.90	2.59	2.90	2.68
n = 2	2.32	1.97	3.00	~ 2.4	1.6–1.2	1.6–1.2	0.90	2.62	2.91	2.68
n = 3	2.33	1.99	3.04	~ 2.4	1.6–1.2	1.6–1.2	0.92	2.56	2.85	3.04

δ H ^a	δ CH ^b H ^{b'}	δ CH ₃	Δδ H ^a
3.08	2.59	1.01	2.29
	2.48	1.00	
	2.37		
	2.27		

C _n H _{2n-2}	δ H ^a	δ CH ^b H ^{b'}	δ CH ^c H ^{c'}	δ CH ^d H ^{d'}	Δδ H ^a
n = 5	3.53	2.75 2.35	1.62 1.40		2.14
n = 6	3.41	2.70 2.42	1.45 1.28		2.20
n = 7	3.10	2.65	1.70	1.24	2.41

complexes exist in two isomeric forms. Isomerism presumably results from different position of substituents R in one alkene with respect to other and to the carbonyl ligands as shown in Fig. 4(a). Unfortunately, since each would be expected to exhibit similar NMR spectroscopy

features, we are unable to identify the observed isomers structurally.

Dramatic upfield shifts of the olefin proton by about 2.2–2.9 ppm (Table 2) and olefin carbon-13 resonances by about 69–84 ppm (Table 3) of the alkene ligands

Table 3

¹³C NMR data for selected *trans*-[(η²-alkene)₂W(CO)₄] complexes, recorded at 273 K in toluene-*d*₆

Complex	Alkene	δ (ppm)					¹ J(W=C) (Hz)	Δδ ^a (=CH ₂) (ppm)	Δδ ^a (=CH-) (ppm)
		=CH	=CH ₂	-CH ₂ -	CH ₃	CO			
1	1-Pentene	55.67	36.51, 36.47	43.16, 43.01, 29.37,	13.87	199.87	122	78.50	83.15
2	1-Hexene	56.06	36.54, 36.49	40.85, 40.70, 38.54,	14.22	199.98	122	77.81	81.35
4	<i>trans</i> -3-Hexene	61.53, 61.42		22.71	20.92	201.79, 201.73	124	—	69.58
5	1-Heptene	36.50, 36.46	56.08	41.15, 41.00, 36.19,	14.31	199.97, 199.86	123	77.97	84.17
				31.88, 23.10					
8	Cyclopentene	62.20		34.20, 19.65	—	201.82	125	—	68.53
9	Cyclohexene	56.21		30.19, 22.89	—	202.60	—	—	70.98
10	Cycloheptene	56.60		34.85, 32.99, 30.85	—	201.74	—	—	74.95

^a Upfield coordination shifts Δδ of C=C units; Δδ = δ (free olefin) - δ (coordinated olefin).

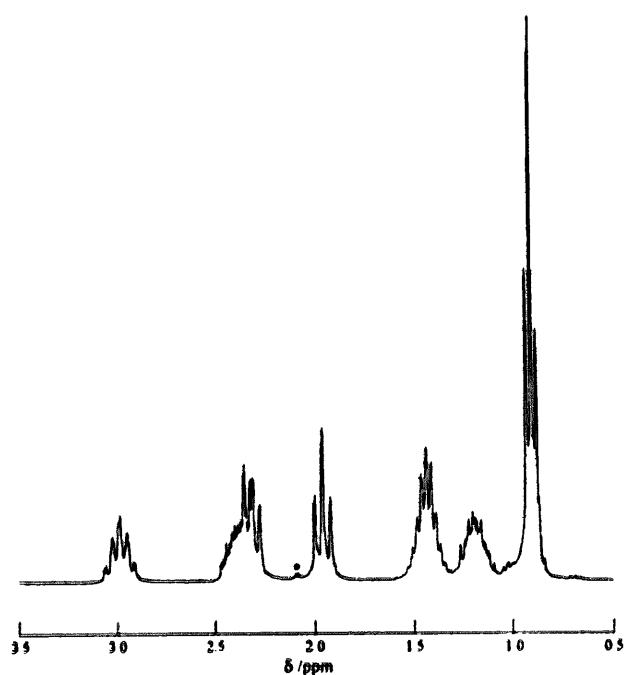


Fig. 5. ^1H NMR spectrum of $\text{trans-}[\text{W}(\text{CO})_4(\eta^2\text{-1-pentene})_2]$ (4) in toluene- d_8 at 300 MHz and $T = 293$ K. The signals denoted by the asterisk arise from protio impurities in toluene- d_8 .

were observed upon coordination to the tungsten(0) centre. In addition, the NMR signals of terminal alkene complexes span a range greater than 1.0 ppm for the olefin protons and 19.5 ppm for the ^{13}C nuclei (Tables 2 and 3).

The proton-coupled ^{13}C spectrum of the 1-hexene complex (2) reveals that $^1J_{\text{CH}} = 157$ and 154 Hz for olefin carbons $=\text{CH}_2$ and $=\text{CH}$ respectively.

The ^1H NMR spectrum at room temperature of terminal alkene complexes 1–3 consists of three complex signals at $\delta \approx 3.0$, 2.3 and 2.0 ppm due to the three olefin protons as well as complex signals at $\delta = 1.4$ ppm due to the methylene protons coupled to the methyl and at $\delta = 0.9$ ppm due to the methyl group. Two complex signals of equal intensity at $\delta = 2.4$ and 1.2 ppm are most probably due to two inequivalent (nearest to olefin bond) methylene protons (Table 2 and Fig. 5).

The inequivalency of methylene protons was also observed in cyclic olefin complexes. The simplest ^1H NMR spectrum is exhibited by $\text{trans-}[\text{W}(\text{CO})_4(\eta^2\text{-cyclopentene})_2]$ (8). As Fig. 6 shows, the multiplet at $\delta = 3.53$ ppm due to the olefin protons and two pairs of complex almost symmetrical signals of intensity 2:1 at $\delta = 2.74\text{--}2.35$ and 1.62–1.40 ppm due to methylene protons are observed in the spectrum of 8 at room temperature.

Since the complex coupling between the CH , CH_2 and CH_3 groups complicates the quantitative analysis of ^1H NMR spectra, ^{13}C NMR was used for subsequent dynamic studies.

The ^{13}C NMR spectrum of $\text{trans-}[\text{W}(\text{CO})_4(\eta^2\text{-1-pentene})_2]$ (1) shown in Fig. 7 is typical for the acyclic alkene complexes 1–7 presented here. At a low temperature (223 K) there are two single resonances for olefin carbons of $=\text{CH}_2$ at $\delta = 34.98$ and 36.14 ppm and two $=\text{CH}$ signals at $\delta = 54.94$ and 55.60 ppm. As the temperature is raised, these signals broaden and coalesce at 236.6 K to give a single sharp resonances at room temperature for $=\text{CH}_2$ at $\delta = 36.49$ ppm and for $=\text{CH}$ at $\delta = 56.06$ ppm, indicating that the species are fluxional on the NMR scale. Even at 183 K the CH_2 and CO signals are broad, indicating that the dynamic process is not completely frozen out. (Spectra obtained at 183 K were also broad but probably because of other factors such as increased solvent viscosity.)

The ^{13}C NMR spectrum of $\text{trans-}[\text{W}(\text{CO})_4(\eta^2\text{-cyclohexene})_2]$ (9) shown in Fig. 8 is typical for cyclic alkene complexes 8–11. At a temperature of 293 K, there is a single resonance for olefin carbon $=\text{CH}$ at $\delta = 56.21$ ppm and at $\delta = 30.19$ and 22.89 ppm for two CH_2 groups of the alkene ring. As the temperature decreased, broadening of the signals occurs and at 205 K approached coalescence. Single olefin carbon resonances observed at 293 K start to split into two resonances as the temperature was decreased further. At 179 K the structure became static and two signals at $\delta = 54.49$ and 56.77 ppm for $=\text{CH}$ and two pairs of signals at $\delta = 22.16\text{--}22.55$ and 29.35–30.18 ppm for two- CH_2 groups were observed. For carbon of the CO group also

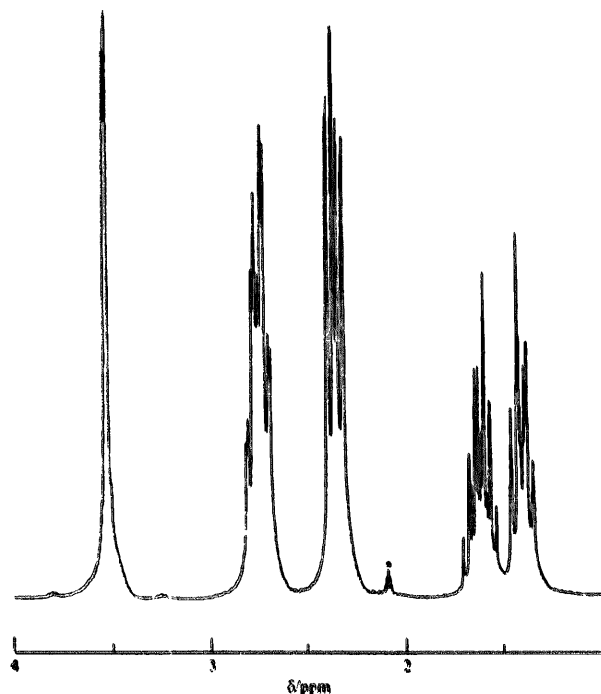


Fig. 6. ^1H NMR spectrum of $\text{trans-}[\text{W}(\text{CO})_4(\eta^2\text{-cyclopentene})_2]$ (8) in toluene- d_8 at 300 MHz and $T = 293$ K. The signals denoted by the asterisk arise from protio impurities in the solvent.

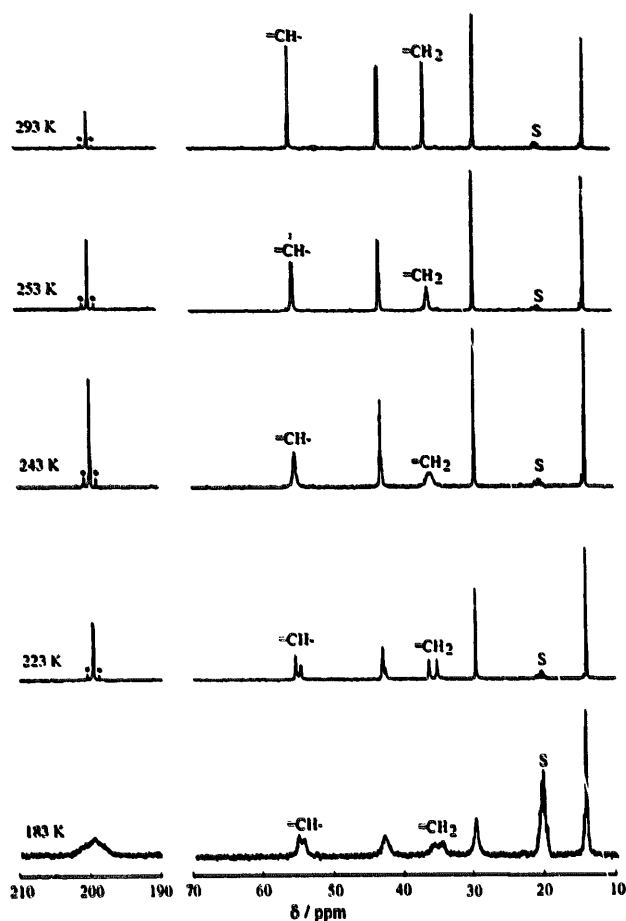


Fig. 7. Variable-temperature ^{13}C NMR spectrum at 75 MHz of *trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-1-pentene})_2]$ (**2**) in toluene- d_8 . The resonances denoted by the asterisk arise from coupling to ^{183}W ($I = \frac{1}{2}$; 14.4% abundance). The signals denoted by S arise from toluene- d_8 .

two signals at 200.57 and 204.74 ppm were observed at 179 K what corresponds to the structure in Fig. 4(b) with two inequivalent CO groups.

This suggests that the alkene adopts a fixed orientation at low temperatures similar to that found in the solid state for $[\text{W}(\text{CO})_4(\eta^2\text{-methyl acrylate})_2]$ [10] and proposed in Fig. 4(a) for acyclic alkene complexes and in Fig. 4(b) for cyclic alkene complexes but, at higher

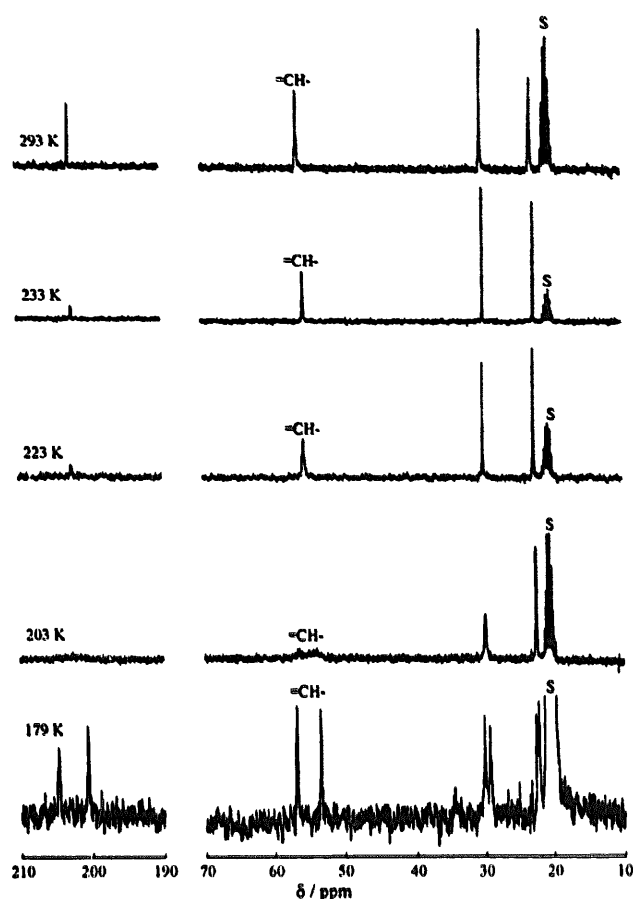


Fig. 8. ^{13}C NMR spectra recorded at various temperatures in toluene- d_8 at 75 MHz showing the temperature-dependent behaviour of the $=\text{CH}$, CH_2 and CO signals for the *trans*- $[\text{W}(\text{CO})_4(\eta^2\text{-cyclohexene})_2]$ (**9**) molecule. The resonances denoted by S arise from toluene- d_8 .

temperatures, alkene propeller rotation averages the two alkene positions, a process for which a barrier to rotation (ΔG^\ddagger) was calculated.

The barrier to alkene rotation, which reflects the energy difference between the orthogonal and the parallel arrangement of the two $\text{C}=\text{C}$ units, of the bis(alkene) complexes **1**, **2** and **8–10** have been determined by variable-temperature ^{13}C NMR spectroscopy. From a

Table 4
Barriers of alkene rotation for complexes *trans*- $(\eta^2\text{-alkene})_2\text{W}(\text{CO})_4$

Complex	Alkene	E_a (kJ mol^{-1})	ΔG^\ddagger ^a (kJ mol^{-1})	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)	T_c (K)	$\Delta\nu$ (Hz)	k ^b
1	1-Pentene	45.7	48.5	-19.8	243.3	86.0	191.09
2	1-Hexene	35.2	47.1	-58.5	236.6	86.3	191.82
5	1-Heptene	—	—	—	≈ 241	86.8	192.82
8	Cyclopentene	46.6	39.9	23.4	210.9	250.8	556.83
9	Cyclohexene	37.2	38.8	-69.6	205.2	255.0	566.38
10	Cycloheptene	55.0	45.8	31.0	234.7	139.8	310.51

^a Values for the energy of activation were obtained from exchange rate constants by application of Arrhenius equation. ΔG^\ddagger were calculated by means of the approximate relationship [27] $\Delta G^\ddagger = 19.14T_c(9.97 + \log(T_c/\Delta\nu))$, where T_c is the coalescence temperature, $\Delta\nu$ the separation of the two olefin carbons $=\text{CH}_2$ in the case of the terminal olefins and $=\text{CH}-$ in the other case.

^b Exchange rates k were calculated at coalescence temperature by means of the approximate relationship $k = \pi \Delta\nu/2^{1/2}$.

knowledge of the coalescence temperature T_c and the separation $\Delta\nu$ of the two olefin carbon resonances =CH₂ in the case of terminal alkenes and =CH in the other cases, calculations using the equation $\Delta G^\ddagger = 19.14T_c(9.97 + \log(T_c/\Delta\nu))$ [27] allows the barrier to alkene rotation to be calculated. The data in Table 4 show that from the highest barrier to 1-pentene rotation ($\Delta G^\ddagger = 45.8 \text{ kJ mol}^{-1}$), to the lowest barrier, i.e. for cyclohexene ($\Delta G^\ddagger = 38.8 \text{ kJ mol}^{-1}$) there is only a difference of 7 kJ mol^{-1} . Since the accuracy of this method for calculating the barriers to alkene rotation is $\pm 4 \text{ kJ mol}^{-1}$ at best, it appears that the different steric effects of the alkenes in these complexes have little effect on the barrier to alkene rotation. These values of barrier to rotation are smaller than obtained for ethene complexes. Osborn and coworkers [28] reported an estimated barrier of 64.1 kJ mol^{-1} for the rotation about the metal-olefin bond in *trans*-[Mo(η^2 -C₂H₄)₂(dppe)] (dppe = Ph₂PCH₂CH₂PPh₂) on the basis of the ¹H and ³¹P NMR spectra. Mayer and coworkers [29] have shown that ethylene rotation in W(O)Cl₂(η^2 -C₂H₄)(PMePh₂)₂ is slow on the NMR time scale with an activation barrier greater than 71.2 kJ mol^{-1} [29]. A similar value of ΔG^\ddagger was obtained by Grevels et al. [10] for methyl acrylate rotation in [W(CO)₄(η^2 -methyl acrylate)₂] (75.4 kJ mol^{-1}). Strack and coworkers [11] investigating complexes of the type [W(CO)₃(PR'₃)₂(η^2 -RCH=CHR)] observed the dependence of the barrier to alkene rotation on substituents R in the alkene in the range 33.5 – 80.0 kJ mol^{-1} .

Since the tungsten isotope ¹⁸³W (14.4% abundance) is magnetically active ($I = \frac{1}{2}$), coupling between the metal and some of the carbon nuclei, particularly those directly bonded to the metal, is to be expected in alkene complexes. In most cases this was not observed owing to the poor signal-to-noise ratio, but in the cases of 1, 2, 4, 5 and 8 (Fig. 6 and Table 3) quite distinct coupling was observed ($^1J(^{183}\text{W}-^{13}\text{C}) = 122$ – 125 Hz). These values compare closely with that observed for W(CO)₆ ($^1J(^{183}\text{W}-^{13}\text{C}) = 126 \text{ Hz}$).

3. Experimental details

All experiments were performed under nitrogen by standard Schlenk tube techniques. All solvents applied were dried, distilled and deoxygenated. W(CO)₆ (Merck) was used as received.

The photochemical reaction were carried out in glass reactor with a quartz window. An HBO 200 mercury lamp was used as the light source.

¹H and ¹³C NMR spectra were recorded on a Bruker AMX 300 instrument operating at 300 and 75.5 MHz respectively. All spectra were measured in toluene-*d*₆ and calibrated using the methyl resonance of the toluene

at 2.09 ppm in ¹H NMR and at 20.4 ppm in ¹³C NMR spectra as an internal standard. All ¹³C NMR spectra presented here are ¹H decoupled. Only for 2 was the proton-coupled ¹³C spectrum measured in addition. IR spectra obtained from *n*-hexane solution in KBr cell, KBr pellets or as film between CsI plates using a Nicolet FT-IR model 400 and Specord M 80 spectrometers. The UV-visible absorption spectra were recorded on a Hewlett-Packard 8452A spectrophotometer.

3.1. Preparation of *trans*-[(η^2 -alkene)₂W(CO)₄] (1–11)

Preparation of *trans*-[(η^2 -alkene)₂W(CO)₄] was first described in our previous paper [30]. W(CO)₆ (0.2 g, 0.57 mmol) was dissolved in *n*-hexane (20 cm³), and alkene (11.4 mmol) was added with continuous stirring under a stream of a nitrogen. Solution was irradiated for 3–4 h in the case of acyclic alkene and 6–10 h in the case of cyclic alkene at room temperature. Irradiation was continued until hexacarbonyltungsten and intermediately formed (alkene)pentacarbonyltungsten had largely disappeared. After evaporation of the solvent and unreacted alkene at room temperature in vacuo, the brown residue was left overnight at room temperature for decomposition of [(η^2 -alkene)W(CO)₅]. After removing W(CO)₆ via sublimation at 0°C the residue suspended with *n*-hexane (2 cm³) was chromatographed on silica (70–200 mesh) using *n*-hexane as eluent. Collection of the pale-yellow fraction of the bis(alkene) complex, as monitored by IR spectroscopy, followed by solvent evaporation in vacuo at room temperature, yielded a small amount of pale-yellow solid of cyclic olefins or *trans*-3-hexene complex with about 8–10% yield, and a yellow oil of acyclic olefins complexes with about 30–40% yield.

The products were identified as *trans*-[(η^2 -alkene)₂W(CO)₄] by IR, ¹H and ¹³C NMR spectroscopy.

3.1.1. *trans*-[W(CO)₄(η^2 -1-pentene)₂] (1). The yield of 1 was 38%.

IR (hexane): $\nu(\text{CO})$ 1943vs, $\delta(\text{W-CO})$ 593m, 567m cm⁻¹. IR (KBr): $\nu(\text{CO})$ 1986w, 1932vs, $\nu(\text{C}=\text{C})$ 1208, $\delta(\text{W-CO})$ 594m, 566m cm⁻¹. IR (film between CsI plates): $\nu(\text{CO})$ 1928vs, $\delta(\text{W-CO})$ 594m, 566m, $\nu(\text{W-C}_2)$ 362w cm⁻¹.

UV-visible (hexane): $\lambda_{\text{max}} = 300 \text{ nm}$ ($\epsilon = 2271 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

¹H NMR (toluene-*d*₆, 293 K): δ 2.99 (=CH), \approx 2.4 (CHH), 2.31 (=CHH), 1.96 (=CHH), 1.42 (CH₂), 1.19 (CHH), 0.90 (CH₃) ppm.

¹³C(¹H) NMR (toluene-*d*₆, 293 K): δ 199.87 (CO), 55.67 (=CH), 43.16, 43.01 (CH₂); 36.51, 36.47 (=CH₂), 29.37 (CH₂), 13.87 (CH₃) ppm.

3.1.2. *trans*-[W(CO)₄(η²-1-hexene)₂] (2). The yield of 2 was 41%.

IR (hexane): ν(CO)1947 cm⁻¹. IR (KBr): ν(CO)1987w, 1936vs, ν(C=C)1204w, δ(W-CO) 594m, 567m cm⁻¹.

UV-visible (hexane): λ_{max} = 300 nm (ε = 2271 dm³ mol⁻¹ cm⁻¹).

¹H NMR (toluene-d₈, 293 K): δ 3.00 (=CH), ≈ 2.4 (CHH), 2.32 (=CHH), 1.97 (=CHH), 1.6–1.2 (CHH), 1.6–1.2 (CH₂), 0.92 (CH₃) ppm.

¹³C{¹H} NMR (toluene-d₈, 293 K): δ 199.98 (CO), 56.06 (=CH), 40.85, 40.70, (CH₂), 38.54 (CH₂), 36.54, 36.49 (=CH₂), 22.71 (CH₂), 14.22 (CH₃) ppm.

¹³C NMR (toluene-d₈, 293 K): δ 199.97 (CO), 56.00 (d, ¹J_{CH} = 157 Hz, =CH), 40.77 (t, ¹J_{CH} = 126 Hz, CH₂), 38.58 (t, ¹J_{CH} = 125 Hz, CH₂), 36.48 (t, ¹J_{CH} = 154 Hz, =CH₂), 22.72 (t, ¹J_{CH} = 121 Hz, CH₂), 14.22, (q, ¹J_{CH} = 124 Hz, CH₃) ppm.

3.1.3. *trans*-[W(CO)₄(η²-2-hexene)₂] (3). The yield of 3 was 25%.

IR (hexane): ν(CO)1946 cm⁻¹. IR (KBr): ν(CO)1979w, 1929vs, δ(W-CO) 599m, 567m cm⁻¹.

3.1.4. *trans*-[W(CO)₄(η²-*trans*-3-hexene)₂] (4). The yield of 4 was 24%.

IR (hexane): ν(CO)1945 cm⁻¹. IR (KBr): ν(CO)1978w, 1928vs, ν(C=C)1217w, δ(W-CO) 600m, 566m cm⁻¹.

¹H NMR (toluene-d₈, 293 K): δ 3.08 (=CH), 2.59, 2.48, 2.37, 2.27 (CH₂), 1.01, 1.00 (CH₃) ppm.

¹³C{¹H} NMR (toluene-d₈, 293 K): δ 201.79, 201.73 (CO), 61.42, 61.53 (=CH), 34.07, 34.38 (CH₂), 20.92 (CH₃) ppm.

3.1.5. *trans*-[W(CO)₄(η²-1-heptene)₂] (5). The yield of 5 was 36%.

IR (hexane): ν(CO)1944 cm⁻¹.

¹H NMR (toluene-d₈, 293 K): δ 3.04 (=CH), ≈ 2.4 (CHH), 2.33 (=CHH), 1.99 (=CHH), 1.6–1.2 (CH₂), 0.92 (CH₃) ppm.

¹³C{¹H} NMR (toluene-d₈, 293 K): δ 199.86, 199.97 (CO), 56.08 (=CH), 41.15, 41.00 (CH₂), 36.50, 36.46 (=CH₂), 36.19, 31.88, 23.10 (CH₂), 14.31 (CH₃) ppm.

3.1.6. *trans*-[W(CO)₄(η²-1-octene)₂] (6). The yield of 6 was 32%.

IR (hexane): ν(CO)1950 cm⁻¹.

3.1.7. *trans*-[W(CO)₄(η²-1-decene)₂] (7). The yield of 7 was 30%.

IR (hexane): ν(CO)1951 cm⁻¹.

3.1.8. *trans*-[W(CO)₄(η²-cyclopentene)₂] (8). The yield of 8 was 8%.

IR (hexane): ν(CO)1940 cm⁻¹. IR (KBr):

ν(CO)1975w, ν(CO)1923vs, ν(C=C)1214w, δ(W-CO) 599m, 567m cm⁻¹.

¹H NMR (toluene-d₈, 293 K): δ 3.53 (=CH), 2.78, 2.35, 1.62, 1.40 (CH₂) ppm.

¹³C{¹H} NMR (toluene-d₈, 293 K): δ 201.82 (CO), 62.20 (=CH), 34.20, 19.64 (CH₂) ppm.

3.1.9. *trans*-[W(CO)₄(η²-cyclohexene)₂] (9). The yield of 9 was 8%.

IR (hexane): ν(CO)1934 cm⁻¹. IR (KBr): ν(CO)1967w, 1926vs, ν(C=C)1200w, δ(W-CO) 603m, 570m cm⁻¹.

¹H NMR (toluene-d₈, 293 K): δ 3.41 (=CH); 2.70, 2.42, 1.45, 1.28 (CH₂) ppm.

¹³C{¹H} NMR (toluene-d₈, 293 K): δ 202.63 (CO), 56.21 (=CH), 30.19, 22.89 (CH₂) ppm.

3.1.10. *trans*-[W(CO)₄(η²-cycloheptene)₂] (10). The yield of 10 was 8%.

IR (hexane): ν(CO)1940 cm⁻¹. IR (KBr): ν(CO)1966w, 1932vs, ν(C=C)1201w, δ(W-CO) 597m, 567m cm⁻¹.

UV-visible (hexane): λ_{max} = 300 nm (ε = 2670 dm³ mol⁻¹ cm⁻¹).

¹H NMR (toluene-d₈, 293 K): δ 3.10 (=CH), 2.65, 1.70, 1.24 (CH₂) ppm.

¹³C{¹H} NMR (toluene-d₈, 293 K): δ 201.74 (CO), 57.60 (=CH), 34.85, 32.99, 30.85 (CH₂) ppm.

3.1.11. *trans*-[W(CO)₄(η²-cyclooctene)₂] (11). The yield of 11 was 10%.

IR (hexane): ν(CO)1940 cm⁻¹.

4. Conclusion

It has been shown that the *trans*-[(η²-alkene)W(CO)₄] complexes where alkene = acyclic unsubstituted alkene or cyclic alkene can be prepared by the photolysis of W(CO)₆ in alkene-*n*-hexane solution, and they are enough stable species.

The geometries of bis(alkene) complexes appear to be *trans* staggered on the basis of IR, ¹H and ¹³C NMR spectra.

Bis(alkene)tetracarbonyl complexes of tungsten exhibit fluxional behaviour on the NMR time scale owing to rotation of the alkene ligands. The barriers to alkene rotation, which reflects the energy difference between the orthogonal and the parallel arrangement of the two C=C units, of bis(alkene) complexes, have been determined using variable-temperature ¹³C NMR spectroscopy.

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