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Photosubstitution of carbon monoxide in $W(CO)_6$ by alkyne: NMR detection of thermally unstable alkyne tungsten(0) carbonyl complexes

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Abstract

The NMR method has been used for the identification and characterisation of the unstable terminal alkyne complexes $[W(CO)_5(\eta^2\text{-}HC{\equiv}CR)]$, $[W(CO)_4(\eta^2\text{-}HC{\equiv}CR)_2]$, $[W(CO)(\eta^2\text{-}HC{\equiv}CR)_3]$, and vinylidene derivatives $[W(CO)_5(C{=}CHR)]$ formed in photochemical reactions of $W(CO)_6$ and each of the alkynes $HC{\equiv}CH$, $HC{\equiv}CMe$ and $HC{\equiv}CCMe_3$. The terminal alkyne carbonyl complexes formed after sequential substitution of CO by alkyne were shown to be involved in the cyclotrimerisation of alkynes to arenes, which were detected by NMR spectroscopy and GC-MS analysis in the photochemical reaction of $W(CO)_6$ and each terminal alkyne used. Benzene substitute adducts with $W(CO)_3$ moiety were also observed by NMR in the above reactions.

Keywords: Tungsten; Carbonyl complexes; Alkyne complexes; NMR spectroscopy; Photolysis

1. Introduction

The photochemical and thermal reactions of $W(CO)_6$ with alkynes lead to mixed carbonyl complexes of tungsten with varying number of alkyne ligands (from one to three) [1–11]. These alkyne carbonyl complexes of tungsten(0) can be involved in the catalytic polymerisation and cyclisation of alkynes [9,10]. Compounds which are stable enough to be isolated and characterised in a pure state under normal conditions are of the type $[W(CO)(RC{\equiv}CR')_3]$, $R = R' = Et$ [2], Ph [3–5], SMe [6], *p*-tolyl, *i*-Pr [8]; $R = Ph$, $R' = Me$ [4] and benzo-15-crown-5 [7]. Especially interesting reactivity was observed for $[W(CO)(PhC{\equiv}CPh)_3]$ in which the CO ligand can be replaced by other two-electron donor ligands: MeCN [12], PPh_3 [12] and PMe_3 [13,14]. In the reaction of $[W(CO)(PhC{\equiv}CPh)_3]$ with an excess of $PhC{\equiv}CPh$ the coupling of alkyne molecules and the formation of a cyclobutadiene [15] and a carbene complex [16,17] was observed. However, similar complexes were not obtained with terminal alkynes. In photochemical reaction of $W(CO)_6$ with terminal alkynes, the formation of the unstable $[W(CO)_5(\eta^2\text{-}HC{\equiv}CR)]$ compound and its rearrangement to the vinylidene compound $[W(CO)_5({=}C{=}CHR)]$, initiating the polymerisation of terminal alkynes by $W(CO)_6$ have been postulated [9,10]. The first direct evidence for such a transformation has been obtained by IR and UV–Vis spectroscopy from matrix-isolation studies of alkyne complexes formed in photochemical reaction of $W(CO)_6$ with terminal alkynes at 20 K [11]. There are only a few examples of fully characterised terminal alkyne-substituted tungsten(0) carbonyls. At low temperature (ca. 210 K) it was possible to isolate thermally unstable $[W(CO)_5(\eta^2\text{-}HC{\equiv}CPh]$ and $[W(CO)_5(\eta^2\text{-}HC{\equiv}CCOOMe)]$ after substitution of CH_2Cl_2 by alkyne in $[W(CO)_5(CH_2Cl_2)]$ [18]. The $[W(CO)(HC{\equiv}CPh)_3]$ was isolated in the reaction of $[W(CO)_3(NCEt)_3]$ with $HC{\equiv}CPh$ and was shown to exist as a mixture of isomers in solution [19].

Because of our continuing interest in the catalytic activity of $W(CO)_6$ in the polymerisation and cyclisation of alkynes, it was our aim to investigate whether

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the catalytically important intermediate compounds generated photochemically from $W(CO)_6$ and terminal alkynes and observed recently by IR measurements [11] can be characterised by NMR spectroscopy.

Recently, we demonstrated the first observation and NMR spectral characterisation of thermally unstable alkene-substituted tungsten carbonyls, viz. $[W(CO)_5(\eta^2\text{-}CH_2{=}CHR)]$, *cis*-$[W(CO)_4(\eta^2\text{-}CH_2{=}CHR)_2]$ (R = H, Me and Et), *mer*-$[W(CO)_3(\eta^2\text{-}CH_2{=}CH_2)_3]$ and *fac*-$[W(CO)_3(\eta^2\text{-}CH_2{=}CH_2)_3]$ formed in photochemical reactions of $W(CO)_6$ or *trans*-$[W(CO)_4(\eta^2\text{-}CH_2{=}CHR)_2]$ in alkene-saturated hydrocarbon solutions at temperatures in the range 200–293 K [20,21]. NMR spectroscopy has proven very valuable in identifying and spectroscopically characterising and monitoring the reactive 18-electron species generated photochemically in solution at low temperatures [20,21].

2. Experimental

2.1. Materials and method

Manipulation of chemicals was carried out under nitrogen using standard Schlenk techniques. Solvents and liquid reagents were dried and distilled from CaH_2 under nitrogen prior to use. Acetylene was passed through cooled (ca. 200 K) *n*-hexane to remove the acetone stabiliser. Propyne was used as supplied (Aldrich, 99% grade). IR spectra were measured with Nicolet FT-IR model 400 instrument. ^{1}H- and ^{13}C-NMR (proton coupled and decoupled) spectra were recorded with a Bruker AMX 300 instrument operating at 300 and 75.5 MHz, respectively. All chemical shifts are referenced to residual solvent protons for ^{1}H-NMR and to the chemical shift of the solvent for ^{13}C-NMR. In toluene-d_8 solvent the methyl resonances at δ_H 2.10 in ^{1}H-NMR and δ_C 20.4 in ^{13}C-NMR were used as internal standards. In $CDCl_3$ solvent the proton resonance at δ_H 7.24 in ^{1}H-NMR and δ_C 77.0 in ^{13}C-NMR were used as internal standards. The photolysis source was an HBO 200W high-pressure Hg lamp.

2.2. Photochemical reactions

Photochemical reactions involving $W(CO)_6$ and alkyne ($HC\equiv CH$, $MeC\equiv CH$, $^tBuC\equiv CH$, $EtC\equiv CEt$ and $MeC\equiv CC\equiv CMe$) occuring in *n*-hexane solution at ca. 270 K were investigated by following the IR spectra of the sample at room temperature. The products of these reactions in toluene-d_8 or $CDCl_3$ solution were tracked by ^{1}H- and ^{13}C-NMR measurements at temperatures in the range 200–300 K. In a typical experiment, a solution of $W(CO)_6$ (0.1 g, 0.28 mmol) in freshly distilled *n*-hexane (50 cm^3) was saturated with ethyne or propyne gas for 5 min (*tert*-butylacetylene, 10 equivalents were added using a microlitre syringe) and then irradiated through quartz at ca. 270 K. After different times of photolysis (0.5–4.5 h) the solvent was removed under vacuum at ca. 270 K, the residual solid dissolved in cold toluene-d_8 or $CDCl_3$ (0.7 cm^3), and the resulting solution transferred to the precooled NMR tube.

2.3. NMR tube reactions

The photochemical reactions were also followed directly by ^{1}H-NMR measurements at low temperature. In a typical experiment a solution of $W(CO)_6$ (0.01 g, 0.03 mmol) in toluene-d_8 or $CDCl_3$ (0.7 cm^3) was saturated with ethyne or propyne gas for 2.5 min, (*tert*-butylacetylene, 10 equivalents were added using a microlitre syringe), and the tube was closed by a glass cap. After cooling to ca. 200 K the tube was subjected to broad-band UV–Vis irradiation. The tube was transferred to the precooled sample holder of the NMR spectrometer and the ^{1}H-NMR spectrum of the solution recorded.

2.4. IR and NMR data for $[W(CO)_3(\eta^6\text{-}C_6H_3Me_3)]$ (7)

The arene complexes $[W(CO)_3(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$ (**7a**) and $[W(CO)_3(\eta^6\text{-}1,2,4\text{-}C_6H_3Me_3)]$ (**7b**) were prepared according to literature procedures [22] and characterised by IR and NMR spectroscopy.

7a. IR (*n*-hexane): ν(CO) 1974 s, 1901 s. ^{1}H-NMR ($C_6D_5CD_3$, 294 K): δ_H 4.17 s (3C*H*), 1.88 s (3C*H*$_3$); ($C_6D_5CD_3$, 243 K): δ_H 3.97 s (3C*H*), 1.82 s (3C*H*$_3$); ($CDCl_3$, 294 K): δ_H 5.10 s (3C*H*), 2.46 s (3C*H*$_3$); ($CDCl_3$, 243 K): δ_H 5.16 s (3C*H*, $^1J_{CH}$ = 174 Hz), 1.82 s (3C*H*$_3$, $^1J_{CH}$ = 129 Hz). ^{13}C{^{1}H}-NMR ($CDCl_3$, 294 K): δ_C 212.03 (3*C*O), 109.79 (3*C*Me$_3$), 89.86 (3*C*H), 20.42 (3*C*H$_3$); ($CDCl_3$, 243 K): δ_C 212.52 (3*C*O), 109.66 (3*C*Me$_3$), 90.28 (3*C*H), 20.46 (3*C*H$_3$).

7b. IR (*n*-hexane): ν(CO) 1973 s, 1899. ^{1}H-NMR ($C_6D_5CD_3$, 294 K): δ_H 4.77 d (1C*H*^{6}, $^3J_{H6H5}$ = 6.4 Hz), 4.49 d (1C*H*^{3}, $^4J_{H5H3}$ = 1.7 Hz), 4.41 dd (1C*H*^{5}, $^3J_{H6H5}$ = 6.4 Hz, $^4J_{H5H3}$ = 1.7 Hz), 1.84 s, 1.81 s, 1.65 s (3C*H*$_3$); ($C_6D_5CD_3$, 243 K): δ_H 4.59 d (1C*H*^{6}), 4.22 d (1C*H*^{3}), 4.21 dd; ($CDCl_3$, 294 K): δ_H 5.34 d (1C*H*^{6}), 5.10 d (1C*H*^{3}), 5.00 dd (1C*H*^{5}), 2.16 s, 2.10 s, 2.01 s (3C*H*$_3$); ($CDCl_3$, 243 K): 5.67 d (1C*H*^{6}, $^3J_{H6H5}$ = 6.1 Hz, $^1J_{CH}$ = 172 Hz), 5.39 d (1C*H*^{3}, $^4J_{H5H3}$ = 1.1 Hz, $^1J_{CH}$ = 173 Hz), 5.27 dd (1C*H*^{5}, $^3J_{H6H5}$ = 6.1 Hz, $^4J_{H5H3}$ = 1.1 Hz, $^1J_{CH}$ = 174 Hz), 2.39 s, 2.33 s, 2.23 s (3C*H*$_3$, $^1J_{CH}$ = 129 Hz). ^{13}C{^{1}H}-NMR ($CDCl_3$, 293 K): δ_C 211.96 (3*C*O), 108.86, 104.31 (3*C*Me$_3$), 94.76, 93.54, 89.72 (3*C*H), 20.20, 18.90, 18.69 (3*C*H$_3$); ($CDCl_3$, 243 K): δ_C 212.57 (3*C*O), 109.96, 109.77, 104.81 (3*C*Me$_3$), 95.77, 94.03, 90.14 (3*C*H), 20.21, 19.03, 18.88 (3*C*H$_3$).

3. Results and discussion

3.1. Characterisation of $[\mathrm{W(CO)_5}(\eta^2\text{-alkyne})]$ (**1**) compounds

Broad-band photolysis of an *n*-hexane solution of $\mathrm{W(CO)_6}$ in the presence of an excess of alkyne ($\mathrm{HC{\equiv}CR}$, R = H, Me, ^{t}Bu; $\mathrm{EtC{\equiv}CEt}$ and $\mathrm{MeC{\equiv}CC{\equiv}CMe}$) gives rise initially to $[\mathrm{W(CO)_5}(\eta^2\text{-alkyne})]$ (**1**), as was judged by IR and ^{1}H-NMR spectroscopic monitoring (Table 1). The IR and NMR spectra of pentacarbonyl alkyne compounds of tungsten are very similar and reveal a similar structure for all complexes. Fig. 1 illustrates representative IR spectral changes accompanying the irradiation of $\mathrm{W(CO)_6}$ in the presence of alkyne. The IR spectrum of the irradiated solution shows three ν(CO) absorption bands characteristic of a molecule $[\mathrm{W(CO)_5L}]$ with C_{4v} symmetry. The π-acidity of alkyne ligands is reflected in the ν(CO) frequency. The ν(CO) vibrations for stronger π-acid ethyne complexes are observed at higher frequency: a weak vibration (a_1) at 2091 cm^{-1}, a very strong one (e) at 1964 cm^{-1}and a strong one (a_1) at 1951 cm^{-1}, than for *tert*-butylacetylene (2086, 1964 and 1946 cm^{-1}) or propyne (2086, 1960 and 1943 cm^{-1}) complexes. Prolonged irradiation causes a decrease in the intensity of these bands as the subsequent photochemical reaction of compound **1** but ν(CO) bands of the secondary products could not be observed in solution due to their low concentration. The precipitate which is formed contains several bands in the ν(CO) region 2150–1800 cm^{-1} (Fig. 1c), indicating the formation of a mixture of compounds unidentifiable here by IR. Investigations of the reaction products by NMR at low temperature allowed us to detect several compounds, the highest concentration always being for the compound **1**. Alkynepentacarbonyltungsten(0) species could be fully characterised by NMR (Table 1). Of the six alkyne adducts observed, the internal alkyne complexes are much more stable than terminal alkyne compounds.

In the ^{1}H-NMR spectra of the terminal alkyne $[\mathrm{W(CO)_5}(\eta^2\text{-}\mathrm{HC{\equiv}CR})]$ compounds studied here, the acetylenic proton resonance appears at ca. 4 ppm in toluene-d_8 solution and at ca. 5 ppm in $\mathrm{CDCl_3}$ solution (Table 1). A similar chemical shift has been observed previously by Templeton et al. for the acetylenic pro-

Table 1
^{1}H- and ^{13}C-NMR characteristics of $[\mathrm{W(CO)_5}(\eta^2\text{-alkyne})]$ (**1**) compounds

Compound	Solvent	T (K)	^{1}H-NMR, δ_H (ppm), J (Hz)	^{13}C-NMR δ_C(ppm), J (Hz)
$[\mathrm{W(CO)_5(HC{\equiv}CH)}]$	$\mathrm{C_7D_8}$	293	4.47 s, $^2J_\mathrm{WH}$ 4.4	Not observed
	$\mathrm{C_7D_8}$	243	4.07 s	202.50 (1 CO), $^1J_\mathrm{WC}$ 153; 195.72 (4 CO), $^1J_\mathrm{WC}$ 125; 62.53 dd ($\equiv C$H), $^1J_\mathrm{CH}$ 255, $^2J_\mathrm{CH}$ 41, $^1J_\mathrm{WC}$ 7.3
	$\mathrm{CDCl_3}$	293	5.83 s	Not observed
	$\mathrm{CDCl_3}$	233	5.86 s	203.16 (1 CO); 195.32 (4 CO); 65.37 s ($\equiv C$H)
$[\mathrm{W(CO)_5(HC{\equiv}CCH_3)}]$	$\mathrm{C_7D_8}$	293	3.79 q (CH), $^4J_\mathrm{HH}$ 2.4, $^2J_\mathrm{WH}$ 4.5; 2.05 d (CH_3), $^4J_\mathrm{HH}$ 2.4	Not observed
	$\mathrm{C_7D_8}$	243	3.46 q (CH), 1.86 d (CH_3)	202.03 (1 CO), $^1J_\mathrm{WC}$ 156; 196.28 (4 CO), $^1J_\mathrm{WC}$ 126; 72.94 dq ($\equiv C$), $^2J_\mathrm{CH}$ 44.9, $^2J_\mathrm{C(CH3)}$ 9.0; 52.51 dq ($\equiv C$H), $^1J_\mathrm{CH}$ 255, $^3J_\mathrm{CH}$ 3.6, $^1J_\mathrm{WC}$ 7.2; 9.98 q (CH$_3$), $^1J_\mathrm{CH}$ 133
	$\mathrm{CDCl_3}$	293	4.81 q (CH), 2.82 d (CH_3)	Not observed
	$\mathrm{CDCl_3}$	243	4.83 q (CH), 2.83 d (CH_3)	202.47 (1 CO); 195.93 (4 CO); 74.03 ($\equiv C$); 53.64 ($\equiv C$H); 11.61 (CH$_3$)
$[\mathrm{W(CO)_5(HC{\equiv}CC(CH_3)_3)}]$	$\mathrm{C_7D_8}$	293	4.24 s (CH), $^2J_\mathrm{WH}$ 5.0; 1.19 s (3CH_3)	Not observed
	$\mathrm{C_7D_8}$	243	3.93 s (CH), 1.16 s (3CH_3)	203.30 (1 CO), $^1J_\mathrm{WC}$ 145; 197.14 (4 CO), $^1J_\mathrm{WC}$ 124; 96.26 ($\equiv C$); 54.41 ($\equiv C$H); 34.17 s (C(CH$_3$)$_3$); 31.10 (3 CH$_3$),
	$\mathrm{CDCl_3}$	243	5.19 s (CH), 1.44 s (3CH_3)	203.48 (1 CO), $^1J_\mathrm{WC}$ 146; 196.64 (4 CO), $^1J_\mathrm{WC}$ 125; 97.28 dq ($\equiv C$), $^2J_\mathrm{CH}$ 37.3, $^3J_\mathrm{CH}$ 6.0, $^1J_\mathrm{WC}$ 9.3; 54.60 d ($\equiv C$H), $^1J_\mathrm{CH}$ 250, $^1J_\mathrm{WC}$ 6.6; 34.03 (C(CH$_3$)$_3$); 31.45 dq (3 CH$_3$), $^1J_\mathrm{CH}$ 127, $^3J_\mathrm{CH}$ 9.0
$[\mathrm{W(CO)_5(CH_3CH_2C{\equiv}CCH_2CH_3)}]$	$\mathrm{CDCl_3}$	243	2.80 q (CH_2), $^3J_\mathrm{HH}$ 7.4; 1.31 t (CH_3), $^3J_\mathrm{HH}$ 7.4	202.40 (1 CO), $^1J_\mathrm{WC}$ 154; 196.27 (4 CO), $^1J_\mathrm{WC}$ 126; 71.93 s ($\equiv C$), $^1J_\mathrm{WC}$ 7.2; 21.77 tq (CH$_2$), $^1J_\mathrm{CH}$ 133, $^2J_\mathrm{CH}$ 4.5; 16.58 qt (CH$_3$), $^1J_\mathrm{CH}$ 129, $^2J_\mathrm{CH}$ 4.5
$[\mathrm{W(CO)_5(C^1H_3C^2{\equiv}C^3C^4{\equiv}C^5C^6H_3)}]$	$\mathrm{CDCl_3}$	243	s (C$^1H_3$), 2.19 s (C$^6H_3$)	204.05 (1CO), $^1J_\mathrm{WC}$ 153; 195.78 (4CO), $^1J_\mathrm{WC}$ 126; 91.65 (C^2); 70.24 (C^5); 65.13 (C^4); 55.66 (C^3); 14.73 (C^1); 5.08 (C^6)
$[\{\mathrm{W(CO)_5}\}_2\mathrm{(C^1H_3C^2{\equiv}C^3C^3{\equiv}C^2C^1H_3)}]$	$\mathrm{CDCl_3}$	243	2.99 s (C$^1H_3$)	(1CO), $^1J_\mathrm{WC}$ 148; 195.21 (4CO), $^1J_\mathrm{WC}$ 126; 83.73 (C^2), $^1J_\mathrm{WC}$ 8.3; 60.40 (C^3), $^1J_\mathrm{WC}$ 5.5; 15.20 (C^1)

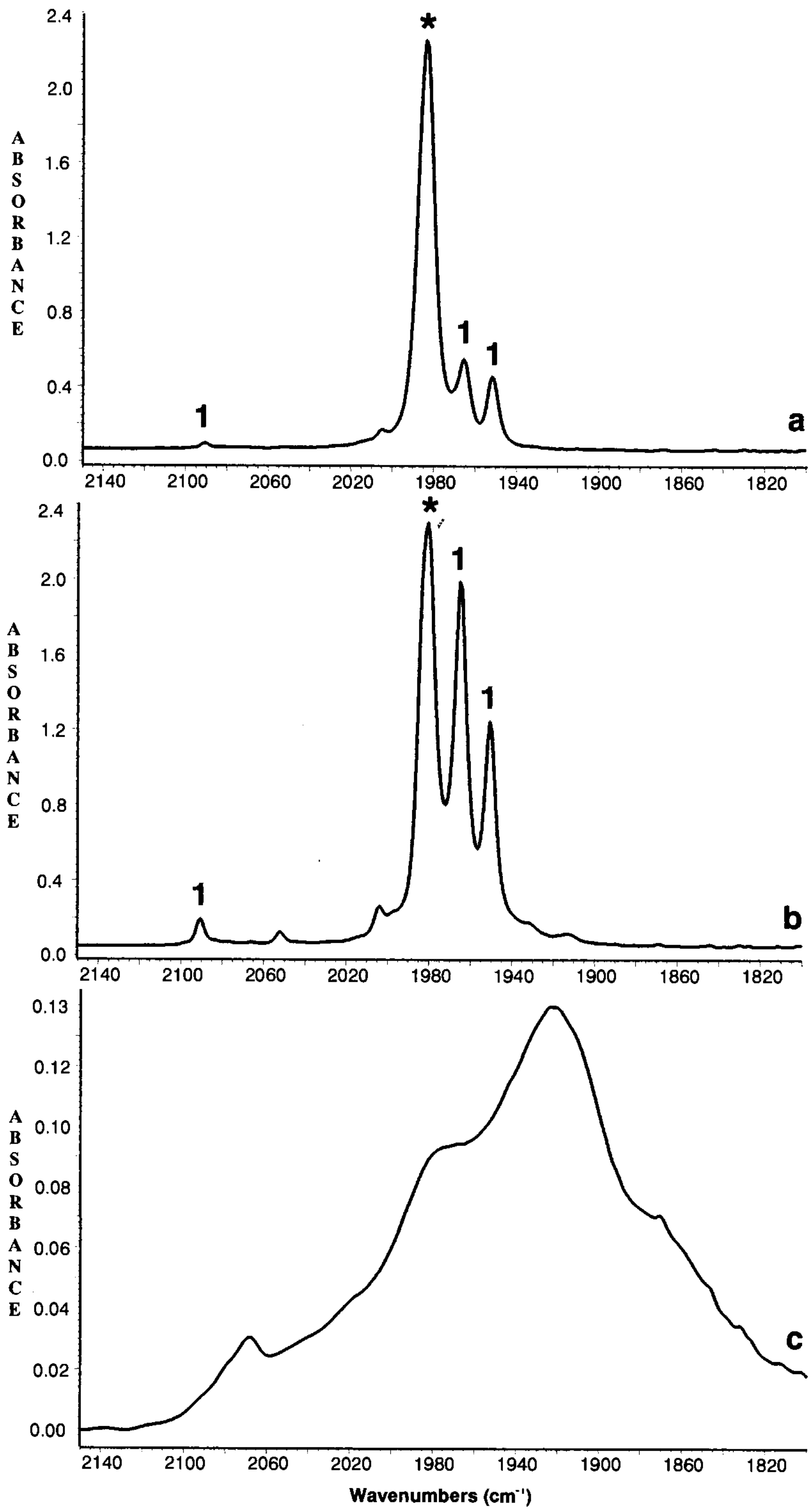


Fig. 1. ν(CO) region of the IR absorption spectrum of $W(CO)_6$ and ethyne reaction products formed after broad-band UV–Vis photolysis in *n*-hexane solution at ca. 273 K: (a) after 10 min and (b) after irradiation for a further 10 min, showing the formation of $[W(CO)_5(\eta^2\text{-}HC{\equiv}CH)]$ (bands denoted by **1**); (c) IR spectrum (KBr disc) of the precipitate formed in the above photochemical reaction. Band denoted by an asterisk (*) is due to $W(CO)_6$.

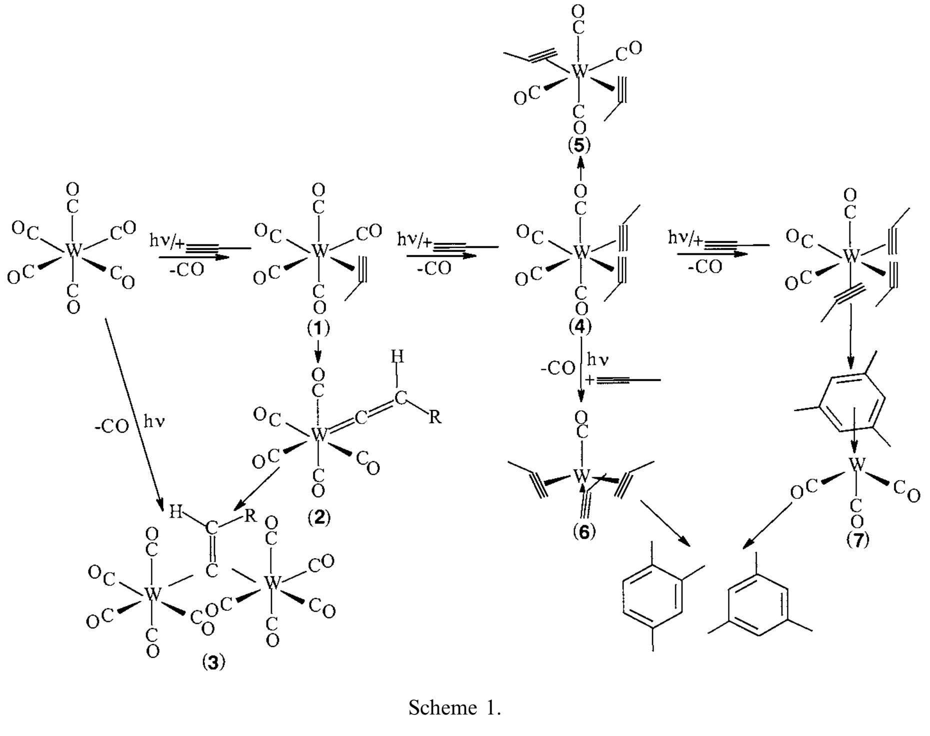
tons of *fac*-$[W(CO)_3(dppe)(HC{\equiv}CR)]$, R = H, *n*-Bu and Ph, $\delta_H = 5.78$ (CD_2Cl_2), 4.49 (CD_2Cl_2) and 6.21 (benzene-d_6), respectively [23]. Such a small coordination shift $\Delta\delta_H$ from 2 to 4 ppm, is indicative of alkyne behaving as a formal two-electron donor to tungsten [24,25]. In good agreement with this description of bonding is the small value of ca. 5 Hz of $^2J_{WH}$ (Table 1).

The ^{13}C-NMR spectra are the most informative in showing resonances for the alkyne carbons. The chemical shifts δ_C of the acetylenic carbon atoms (≡*C*H) are in the range 52–65 ppm and the acetylenic carbon atoms (≡*C*R) are in the range 72–97 ppm (Table 1). That means the ^{13}C resonance signals of the acetylenic carbon atoms (≡*C*H) of the free alkyne are shifted to higher field ($\Delta\delta_C \approx 10$) on coordination to the tungsten(0) centre in [W(CO)$_5$(η^2-HC≡CR)]. Similar acetylenic carbon resonances have been reported for other tungsten(0) alkyne complexes ($\delta_C = 79.8$ and 65.2 for [W(CO)$_5$(η^2-HC≡CPh)] [18] and $\delta_C = 82.4$ and 76.5 for [W(CO)$_3$(dppe)(HC≡CPh)] [23]). The $^1J_{CH} = 255$ Hz and $^2J_{CH} = 41$ Hz are unprecedently large for [W(CO)$_5$(η^2-HC≡CH)] relative to $^1J_{CH} = 249$ Hz and $^2J_{CH} = 49.3$ Hz for free ethyne [26]. Similar coupling constants are observed here for other alkyne pentacarbonyl compounds of tungsten(0) (Table 1). The coupling constant of acetylenic carbon to tungsten $^1J_{WC} \approx 7$ Hz also reflects very weak tungsten–alkyne bonding. All these NMR data are consistent with weak coordination of alkyne ligands and the alkyne ligands acting formally as two-electron donors [24,25].

Moreover, what we take to be a significant feature of these alkyne pentacarbonyl complexes of tungsten(0) is the value of carbonyl carbon resonances δ_C and tungsten–carbon coupling $^1J_{WC}$ (Table 1). The value of $\delta_C \approx 203$ and $^1J_{WC} \approx 150$ for a carbonyl ligand *trans* to an alkyne ligand is higher than for a carbonyl ligand *cis* to an alkyne ligand ($\delta_C \approx 196$ and $^1J_{WC} = 126$). A similar relation has been observed for the analogous alkene pentacarbonyl complexes of tungsten [20,21]. This indicates shorter and stronger tungsten–carbonyl bonds *trans* to alkyne or alkene ligands than *trans* to carbonyl ligands. By contrast, competition for a d$_\pi$ orbital of tungsten causes an alkyne ligand *trans* to CO to interact weakly with the tungsten atom. This was proved by X-ray crystal structure analysis of [W(CO)$_5$(η^2-HC≡CPh)], where the W–C bond distance of the carbonyl ligand *trans* to phenylacetylene of 1.969(10) Å is shorter than the W–C bond distance *cis* to the alkyne ligand (2.05 Å average) [18].

The relative concentration of photochemically generated compound **1** depends first of all on the time of irradiation and temperature. Prolonged irradiation leads to dissociation of the next molecules of CO and the formation of a compound containing two or three alkyne ligands (Scheme 1).

Thermally unstable compound **1** can decompose to release the weakly bonded alkyne or isomerise to give vinylidene species [W(CO)$_5$(C=CHR)] (**2**) detected here by ^{1}H-NMR (see Section 3.2). It is known that the vinylidene complex can be formed only by photochemical reaction of coordinated terminal alkynes such as HC≡CH, MeC≡CH and ^{t}BuC≡CH but the pentacarbonyl alkyne adducts formed by reaction of internal alkynes such as EtC≡CEt or MeC≡CC≡CMe are much more stable. In photochemical reaction of W(CO)$_6$ and 2,4-hexadiyne two adducts, with one and two pentacarbonyl moieties, were characterised by NMR (Table 1).



Scheme 1.

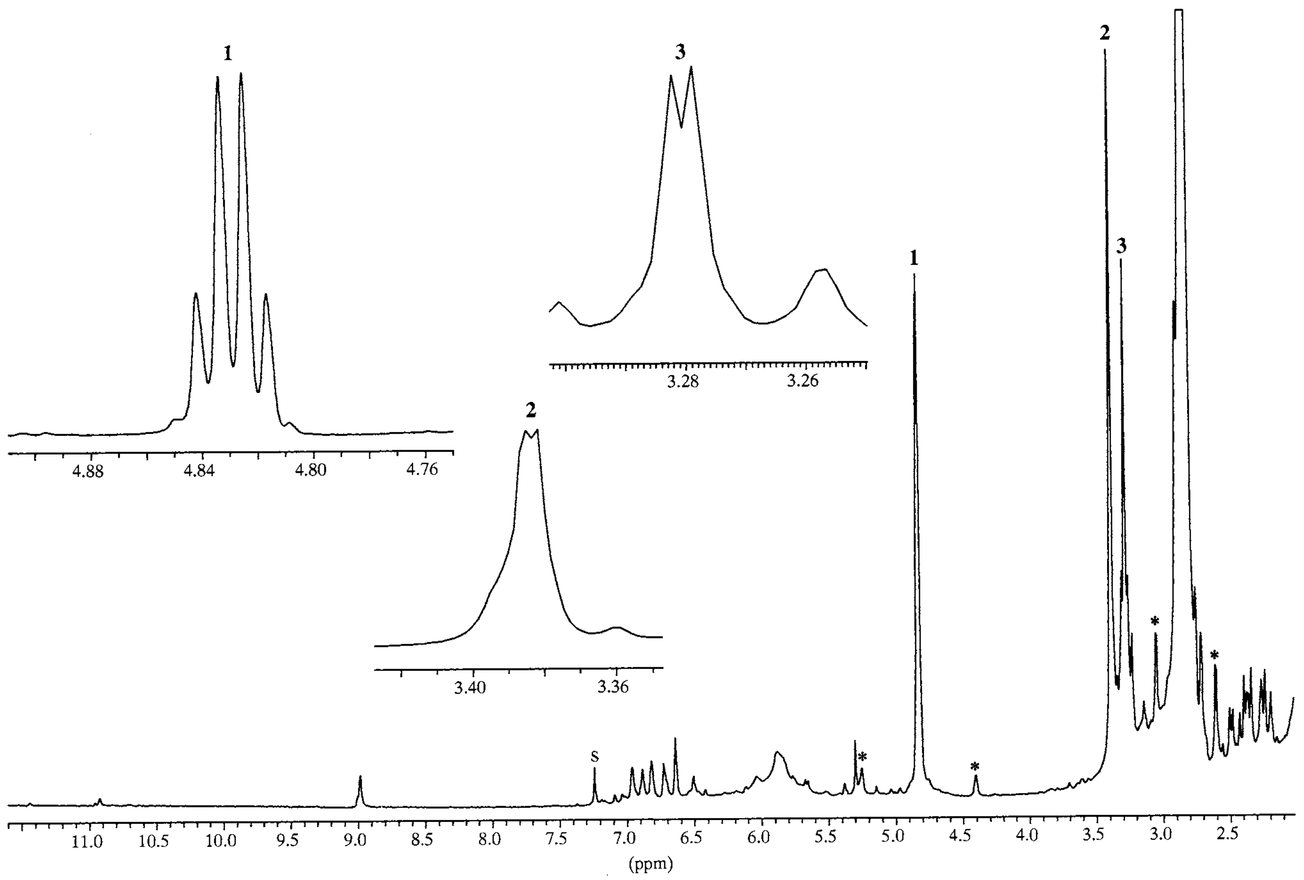


Fig. 2. The part of the ^{1}H-NMR spectrum (300 MHz) in $CDCl_3$ solution at 243 K of $W(CO)_6$ and propyne reaction products formed after 2 h broad-band UV–Vis photolysis in *n*-hexane solution at ca. 273 K. The proton signals are labelled as follows: (**1**) $\delta_H = 4.83$, [$W(CO)_5(\eta^2$-*H*C≡CMe)]; (**2**) $\delta_H = 3.38$, [$W(CO)_5$(C=C*H*Me)]; (**3**) $\delta_H = 3.28$, {$W(CO)_5\}_2(\mu$-C=C*H*Me)]. The signals due to compounds **1**, **2** and **3** are shown at scale expansion in the inset. The signals denoted by an asterisk (*) are due to ^{13}C satellites.

3.2. NMR characteristic of the vinylidene species

The isomerisation of an η^2-coordinated to a transition metal terminal alkyne into a vinylidene ligand is a well known process [27–31]. In d^6 octahedral complexes this rearrangement is promoted by a repulsion between filled d_π of the metal and $\pi_\perp$ orbitals of the alkyne ligand (4e-2-centre d_π–$\pi_\perp$ conflict) [30,31].

During the course of the photochemical reaction of $W(CO)_6$ and terminal alkyne, two signals characteristic of two different vinylidene ligands coordinated to the tungsten centre have been observed in ^{1}H-NMR spectra, at a position at least 1 ppm lower than the acetylenic proton signals of the η^2-alkyne compound **1** (C=CH_2: toluene-d_8, 294 K, $\delta_H = 2.84$ and 2.81; 243 K $\delta_H = 2.61$ and 2.59; $CDCl_3$, 243 K, $\delta_H = 3.67$ and 3.39; C=C*H*CH_3: toluene-d_8, 243 K, $\delta_H = 2.70$ and 2.51; $CDCl_3$, 243 K, $\delta_H = 3.38$ q, $^3J_{HH} = 1$ Hz, and 3.28 q, $^3J_{HH} = 1$ Hz, $^3J_{WH} = 13$ Hz, $I = 1/2$, 27%; C=CH^tBu: $CDCl_3$, 243 K, $\delta_H = 3.44$ and 3.41). Both signals shift similarly with changes in the temperature and solvent. These ^{1}H-NMR data are comparable with those obtained for the tungsten vinylidene complex [$W(CO)_3$(dppe)(C=CHPh)], where the vinylidene proton was observed at $\delta_H = 4.42$ in $CDCl_3$ [31], i.e. much lower than the acetylenic proton in its alkyne complex counterparts ($\delta_H = 6.76$ in CD_2Cl_2 [23]). The highest concentration of vinylidene species was achieved in the reaction of propyne with $W(CO)_6$. In this reaction the intensity of the signal due to the vinylidene proton ($\delta_H = 3.38$ in $CDCl_3$) exceeded the intensity of the acetylenic proton signal at $\delta_H = 4.83$ of [$W(CO)_5(\eta^2$-HC≡CCH_3)] (Fig. 2). The lowest concentration of the vinylidene species was observed in the reaction of *tert*-butylacetylene. The intensity ratio between both vinylidene signals changes with reaction time, but at the begining the lower field signal is always more intense. Only in propyne reaction, after prolonged irradiation (3–4 h), did these two signals achieve almost equal intensity (Fig. 2). The latter vinylidene proton signal has been correlated with three carbon signals in the ^{13}C-NMR spectrum: at δ_C 209.41, 205.13 and 197.07 (toluene-d_8, 243 K) of ethyne reaction products and at δ_C 210.61, 205.39 and 197.84 ($CDCl_3$, 243 K) of propyne reaction products (Fig. 3). However, in the *tert*-butylacetylene reaction this kind of compound was formed only in trace amounts. The signal at δ ca. 198 is accompanied by ^{183}W satellites ($^1J_{WC} = 64$ Hz, $I = 1/2$, $14.5\% \times 2 = 29\%$), indicating bridging carbon between two equivalent tungsten centres. The latter signal appears as a singlet in the proton-coupled ^{13}C-NMR spectrum, meaning that this carbon is not carrying the proton and excludes the origin of this signal being the bridging alkyne ligand. The carbon signal of the bridging carbonyl ligands in the tungsten carbonyl clusters have always been observed about 40 ppm higher than that for terminal carbonyls [32]. On the basis of this observation, the formation of two vinylidene complexes, the mononuclear $[W(CO)_5(C{=}CHR)]$(**2**) and the dinuclear $[\{W(CO)_5\}_2(\mu\text{-}C{=}CHR)]$ (**3**) has been postulated (Scheme 1). Compound **3** is formed under photochemical conditions, as the result of the interaction of the coordinatively unsaturated pentacarbonyltungsten moiety with the vinylidene ligand. There are many example of compounds with bridging vinylidene ligands reported in the literature [29,33–35], however there are only a few reports of complexes containing the tungsten pentacarbonyl moiety. One of them is $[W_2(CO)_9(\mu\text{-}C(OMe)CH{=}CH_2)]$, formed in the interaction of the α,β-unsaturated carbene pentacarbonyltungsten complex with the $W(CO)_5$ moiety, generated in a photochemical reaction. In the NMR spectrum of this compound the signal of α-carbon for the bridging carbene ligand appears at δ_C 232.56, that is 77 ppm lower than in its terminal carbene counterparts [36,37]. The chemical shift values of α-carbon observed for other dimetallic bridging carbene complexes are in the range 200–100 ppm which is at a much higher field than for mononuclear compounds [38]. The concentration of the mononuclear vinylidene species **2** is too low to detect the low-field resonance of the α-vinylidene carbon but the signal of the β-carbon was observed at δ_C 112.53 ($C{=}CH_2$). The carbonyl carbon resonances for the latter compound **2** were detected at δ_C 202.03 (1CO) and 195.76 (4CO), very close to the signals of the ethyne compound **1** (Table 1).

In this way we were able to detect the rearrangement products of $[W(CO)_5(\eta^2\text{-}HC{\equiv}CR)]$ complexes not only by IR spectra of low-temperature matrix [11] but also by NMR investigations.

3.3. Complexes of tungsten(0) with two or three alkyne ligands

The photosubstution of two CO groups by alkyne molecules in $W(CO)_6$ can lead to *cis*-$[W(CO)_4(\eta^2$-

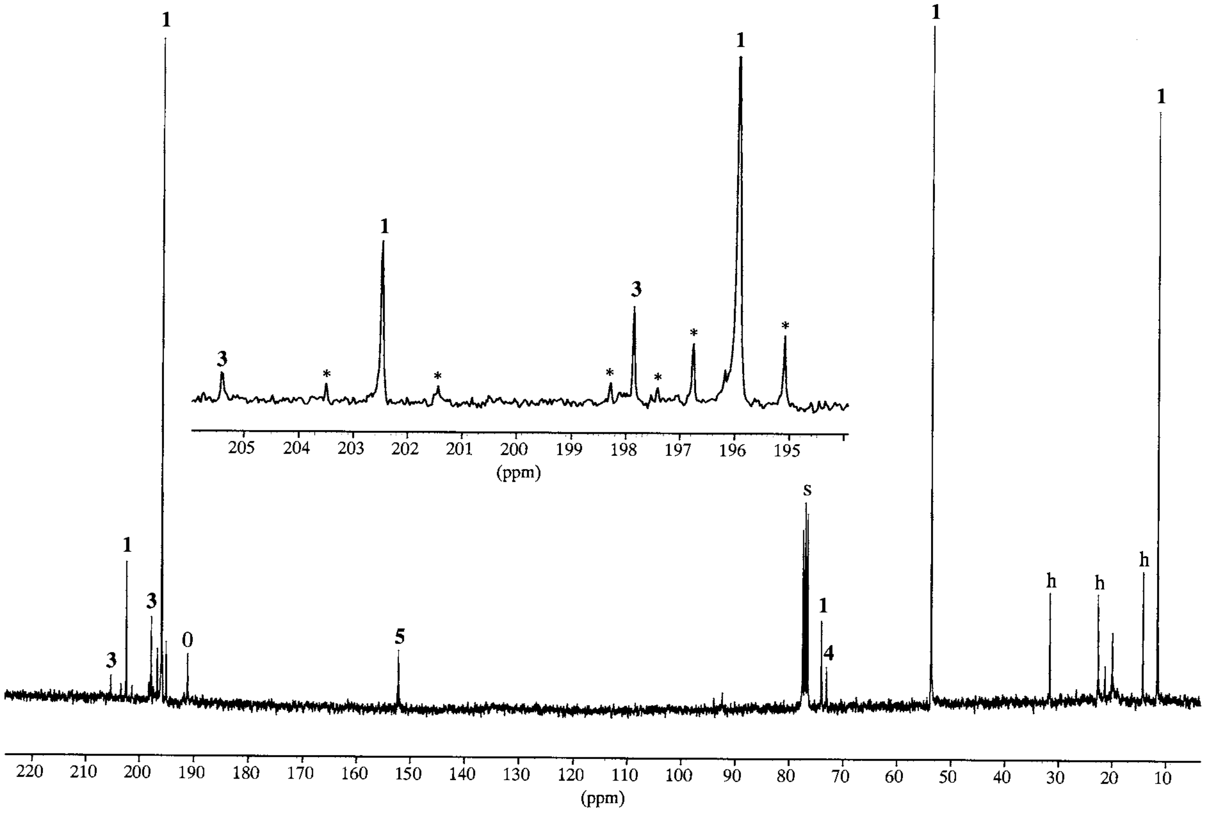
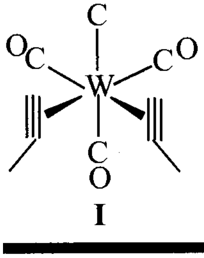


Fig. 3. The $^{13}C\{^1H\}$-NMR spectrum (75.5 MHz) in $CDCl_3$ solution at 243 K of the reaction products formed after 2 h broad-band UV–Vis photolysis in *n*-hexane solution at ca. 273 K of $W(CO)_6$ and propyne. The carbonyl region of the spectrum is shown at scale expansion in the inset. The signals are labelled as follows: (**1**) $[W(CO)_5(\eta^2\text{-}HC{\equiv}CMe)]$; (**3**) δ_C 198.28 (α-carbon of the bridging vinylidene ligand in $\{W(CO)_5\}_2(\mu\text{-}C{=}CHMe)]$); (**4**) *cis*-$[W(CO)_4(\eta^2\text{-}HC{\equiv}CMe)_2]$; (**5**) *trans*-$[W(CO)_4(\eta^2\text{-}HC{\equiv}CMe)_2]$; (h) hexane; (0) $W(CO)_6$. The signals denoted by an asterisk (*) are due to ^{183}W satellites.

alkyne)$_2$] (**4**) or *trans*-[W(CO)$_4$(η^2-alkyne)$_2$] (**5**), but IR spectra measured at room temperature did not signal the appearance of the latter compounds (four bands or one band in the carbonyl region, respectively [39]). The reason is that such compounds are too labile. For the same reason, compounds with three alkyne and three carbonyl ligand are unknown. However, in the photochemical reaction of terminal alkyne and W(CO)$_6$ at low temperature studied here by NMR, the acetylenic proton and carbon signals, which could be assigned to two-electron donor alkyne ligands in *trans* and *cis*-bis(alkyne) compounds, have been detected. For ethyne reaction products such signals appear at $\delta_H = 6.96$ and 5.20 in toluene-d_8. For the latter signal tentatively assigned to the *cis* isomer the coupling constants $^1J_{CH} = 229$ Hz and $^2J_{WH} = 3.4$ Hz were observed. The acetylenic carbon signal was identified only for one compound, most probably the *cis* isomer, at δ_C 73.62 as a doublet, with $^1J_{CH} = 229$ Hz, $^1J_{WC} = 14.5$ Hz in toluene-d_8. The acetylenic carbon signal ($\equiv$*C*H) of the *cis*-bis(propyne) compound was observed at δ_C 73.15 d, $^1J_{CH} = 226$ Hz and the *trans*-bis(propyne) signal was detected at δ_C 152.17 d ($^1J_{CH} = 196$ Hz, $^1J_{WC} = 34$ Hz) in CDCl$_3$ at 243 K. In the same sample, signals due to the bis(propyne) compounds in ^{1}H-NMR spectra were observed at δ_H 6.64 and 5.76, the latter tentatively assigned to the *cis* isomer. For the bis(*tert*-butylacetylene) compound **4** two signals of the acetylenic protons were observed in toluene-d_8 at very close positions, δ_H 6.05 and 6.03, and the intensity ratio ca. 1:3, respectively. However, in CDCl$_3$ solution these signals are unresolved and only one resonance at δ_H 6.90 ($^2J_{WH} = 7.5$ Hz) was detected. For these compounds two acetylenic carbon signals ($\equiv$*C*H) were observed at δ_C 102.18 ($^1J_{CH} = 214$ Hz, $^1J_{WC} = 28.7$ Hz) and 95.23 ($^1J_{CH} = 200$ Hz, $^1J_{WC} = 12.6$ Hz, toluene-d_8). These two acetylenic proton and carbon signals could be assigned to two rotational isomers **I** and **II**, produced when two identical unsymmetrical alkyne ligands are bound to a W(CO)$_4$ fragment in the mutually *cis* position and parallel alignment of the C$\equiv$C linkage.

For the *trans* isomer of bis(*tert*-butylacetylene) compound **5** the acetylenic proton signal at δ_H 6.97 and the acetylenic carbon signal at δ_C 148.10 ($\equiv$*C*H) were detected in toluene-d_8 at 243 K. However, we could not detect the signals due to alkyne carbons carrying the *tert*-butyl group. It must be noted that bis(alkyne) compounds **4** and **5** can be observed only at low temperature and just after preparing the sample. Slow decomposition of these compounds was observed even at 243 K.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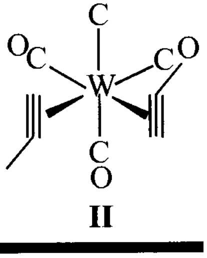
II

Although numerous bis(alkyne) complexes are known, nearly all of these compounds contain the metal in the d^4 configuration and the two alkyne ligands in mutually *cis* position [25]. The first tungsten(0) d^6 complex [W(CO)$_2$(dppe)(DMAC)$_2$] (DMAC = dimethylacetylenecarboxylate) was prepared by Templeton et al. [23]. Recently Wang et al. [40–42] reported a series of tungsten(0) and molybdenum(0) bis(alkyne) complexes of the type [M(CO)$_2$(NN)(alkyne)$_2$], where NN is a bidentate nitrogen ligand. In these compounds two alkyne ligands are mutually *trans* and perpendicular and in ^{13}C-NMR spectra display the acetylenic carbon signals in the region 152–134 ppm [40–42].

The very well known thermodynamically stable alkyne compounds contain three alkyne and one carbonyl ligand [2–7]. In these types of compounds each alkyne is regarded as a 3.3 electron-donor ligand [24]. The characteristic feature of their ^{13}C-NMR spectra is the position of the acetylenic carbon resonances in the region 200–160 ppm and the signal at δ_H ca. 10 ppm for the acetylenic proton ($\equiv$C*H*) [8,12–17,19]. In terminal alkyne–W(CO)$_6$ reaction products investigated here, such signals were detected. Two almost equal intense signals at δ_H 10.56 ($^2J_{WH} = 7$ Hz) and 9.77 ($^2J_{WH} = 9$ Hz), with very close value of tungsten–hydrogen coupling were observed at 243 K in toluene-d_8 solution of ethyne reaction products. When the temperature is increased, the resonances broaden and at ca. 283 K merge into the baseline. The appearance of two proton signals for [W(CO)(HC$\equiv$CH)$_3$] can be explained by the structure of this type of compound [5], in which a weaker interaction between the tungsten centre and three equivalent acetylenic carbon atoms close to the CO ligand was observed, than with other three acetylenic carbon atoms.

Due to the inequivalent ends of the terminal alkynes in [W(CO)(HC$\equiv$CR)$_3$] (**6**) and different orientations of alkyne ligands relative to the CO group, complexes of this type can exist as a mixture of four isomers [19]. This leads to the observation of several acetylenic hydrogen signals in their ^{1}H-NMR spectra. The ^{1}H-NMR spectrum of propyne reaction products at 243 K in toluene-d_8 solution displays four quartets ($^4J_{HH} = 1.4$ Hz) at δ_H 11.08, 10.90, 9.08 and 9.04 in the integral intensity ratio 1:3:3:14, respectively. The most intense signal at δ_H 9.04 is accompanied by satellites due to ^{13}C ($^1J_{CH} = 196$ Hz). Similar signals were observed in the ^{1}H-NMR spectrum at 243 K in toluene-d_8 solution of *tert*-butylacetylene reaction products: δ_H 11.12 ($^1J_{CH} =$ 196 Hz), 10.44 ($^2J_{WH} = 5$ Hz, $^1J_{CH} = 201$ Hz), 9.79 ($^2J_{WH} = 7$ Hz) and 9.00 ($^2J_{WH} = 6$ Hz, $^1J_{CH} = 200$ Hz) in the intensity ratio 13:8:1:4, respectively. In the ^{13}C-NMR spectrum, the acetylenic carbon signal was detected at δ_C 172.71 as a doublet, with $^1J_{CH} \approx 200$ Hz ($\equiv C$H), and a singlet at δ_C 188.00 ($\equiv C^t$Bu). Four resonances at δ_C 226.58, 224.44, 218.16 and 217.92 with the intensity ratio ca. 2:1:12:1, respectively, can be assigned to the CO group in four isomers of [W(CO)(HC≡C^{t}Bu)$_3$]. The intensity ratio of the proton and carbon signals changed as the sample grew older, but the most intense was always the acetylenic proton signal at δ_H 11.12 and the carbonyl carbon signal at δ_C 218.16. These signals could be assigned to the most stable isomer of [W(CO)(HC≡C^{t}Bu)$_3$] compound, containing three chemically equivalent *tert*-butylacetylene ligands, with the same orientation of the alkyne ligands towards CO [43]. Simultaneously, with the disappearance of [W(CO)(HC≡C^{t}Bu)$_3$] signals, the increase of the signals characteristic of 1,3,5-tri-*t*-butylbenzene [44], at δ_H 7.29 (*H*C) and 1.33 (^{t}Bu), δ_C 149.87 (C^tBu) and 119.44 (*C*H) was observed in NMR spectra in CDCl$_3$ solution. This indicates that the decomposition of the labile [W(CO)(HC≡C^{t}Bu)$_3$] complex is the direct way in which the substituted arenes are formed (Scheme 1).

3.4. Identification of [W(CO)$_3$(η^6-arene)] and free arene

The alkyne carbonyl complexes formed in a sequential photosubstitution of carbon monoxide in W(CO)$_6$ by alkyne were shown to be involved in the cyclotrimerisation of alkynes to arenes: benzene, trimethylbenzene and tri-*t*-butylbenzene, which were detected by NMR spectroscopy in photochemical reactions of W(CO)$_6$ and each of the alkynes HC≡CH, HC≡CMe and HC≡CCMe$_3$, respectively. In the case of propyne reaction two different positional isomers of trimethylbenzene (mesitylene and pseudocumene) were detected in the ratio ca. 1:1.5 by GC-MS investigations of the reaction products. The ^{1}H-NMR spectrum (CDCl$_3$) displayed four aromatic protons resonances: δ_H 7.01 d, $^3J_{HH} = 7.9$ Hz, δ_H 6.95 d, $^4J_{HH} = 0.8$ Hz, δ_H 6.90 dd, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 0.8$ Hz and δ_H 6.80 s. The first three signals are due to 1,2,4-trimethylbenzene and the fourth (singlet) due to 1,3,5-trimethylbenzene. In addition to signals assigned to the free arenes, in the ^{1}H- and ^{13}C-NMR spectra of the reaction mixture, resonances due to the η^6-arene ligand derived from an alkyne cyclotrimerisation product (benzene, trimethylbenzene and tri-*t*-butylbenzene) coordinated to the tricarbonyltungsten moiety are readily developed. The resonances of the η^6-arene ligands are solvent dependent. In CDCl$_3$ solution the η^6-arene ligand protons are observed at δ_H ca. 1 ppm higher than in toluene-d_8 solution (see Section 2.4). The six protons of the η^6-benzene ligand are observed at δ_H 5.36 in CDCl$_3$ solution and at δ_H 4.25 in toluene-d_8 solution (293 K). A similar chemical shift was observed for the three protons of η^6-tri-*t*-butylbenzene ligand (δ_H 5.31 and 4.10, respectively). In the ^{13}C-NMR spectrum the signals due to [W(CO)$_3$(η^6-C$_6$H$_6$)] were detected at δ_C 208.27 (3*C*O) and 89.64, $^1J_{CH} = 180$ Hz (C_6H$_6$). Careful examination of specially synthesised compounds with mesitylene and pseudocumene ligands (see Section 2.4) allowed us to detect their formation in every photochemical reaction of propyne and W(CO)$_6$. The photochemical reaction products analysed by NMR at 243 K, just after reaction, contain the mesitylene and pseudocumene complexes in the ratio ca. 1:5. This ratio changes to ca. 1:3 as the sample is warmed and grows older. This could suggest the higher stability of such alkyne compounds, which after decomposition lead to the formation of the η^6-1,3,5-C$_6$H$_3$Me$_3$ ligand then compounds giving the η^6-1,2,4-C$_6$H$_3$Me$_3$ ligand.

According to a generally accepted cyclotrimerisation mechanism [45–48], the reaction proceeds with the photosubstitution of the CO ligands in W(CO)$_6$ by the molecules of alkyne and the formation of metallacycles. Tungstenacyclopentadiene can be formed via oxidative coupling of the two alkyne ligands in the *cis*-bis(alkyne) complex and tungstenacycloheptatriene, as the result of C–C bond formation between the three alkyne ligands in the *fac*-tris(alkyne) complex. The reductive elimination reaction leads to the formation of η^4-butadiene or η^6-arene ligands, respectively. In the photochemical reaction investigated here of W(CO)$_6$ and alkyne, complexes of the type [W(CO)$_3$(η^6-arene)] (**7**) are observed, indicating the formation of *fac*-[W(CO)$_3$(η^2-alkyne)$_3$] compounds as very labile intermediate species (Scheme 1).

Although cyclotrimerisation of alkynes to arenes is not uncommon in homogeneous catalysis by transition metal compounds [45–48], to the best of our knowledge, this is the first direct evidence for transformation of η^2-alkyne ligands coordinated to tungsten to η^6-arene ligands.

4. Conclusions

Studies of alkyne reactions in the presence of tungsten carbonyls have attracted our interest, due in part to the desire to find the intermediate compounds in tungsten-based catalytic processes.

During the course of the photochemical reaction of W(CO)$_6$ and terminal alkyne, besides the ^{1}H-NMR signals due to the alkyne compound [W(CO)$_5$(η^2-HC≡CR)] (**1**), the signals characteristic of the vinylidene ligand coordinated to the pentacarbonyl tungsten moiety have been observed. This kind of compound is responsible for initiating the polymerisation reaction of terminal alkynes [9,10].

Photolysis of W(CO)$_6$ in the presence of alkyne leads to the generation of alkyne carbonyl complexes of tungsten in which C–C coupling of the alkyne ligands has occurred. In addition to signals attributable to the η^2-alkyne ligand in alkyne carbonyl complexes of tungsten, resonances in the aromatic region of the ^{1}H- and ^{13}C-NMR spectra of reaction mixture are readily attributable to the η^6-arene ligand, derived from an alkyne cyclotrimerisation product (benzene, trimethylbenzene and tri-*t*-butylbenzene) coordinated to the $W(CO)_3$ moiety.

Of interest is the formation of free arene observed by ^{1}H- and ^{13}C-NMR spectroscopy in the photochemical reaction of $W(CO)_6$ and HC≡CH, HC≡CMe and HC≡C^{t}Bu. That means that $W(CO)_6$ shows acetylene cyclotrimerisation activity under photochemical conditions.

To the best of our knowledge this paper represents the first study that has simultaneously detected the thermally unstable η^2-alkyne complexes and their rearrangement products, the η^6-arene compounds of tungsten.

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