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Photochemical reaction of $W(CO)_6$ with $SnCl_4$ Part IV: synthesis of new tungsten alkyne complexes: X-ray crystal structure of $[W_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}Cl)_2(O)(\eta^2\text{-}PhC{\equiv}CPh)_5]$

Teresa Szymańska-Buzar *, Tadeusz Głowiak

Institute of Chemistry, University of Wroclaw, 50-383 Wroclaw, Poland

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Abstract

Reaction of $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ (**1**) with alkynes (phenylacetylene, *tert*-butylacetylene, 3-hexyne and diphenylacetylene at room temperature initially affords the mixture of products $[WCl_2(CO)_2(\eta^2\text{-alkyne})_2]$ (**2**–**5**) and $[WCl(SnCl_3)(CO)(\eta^2\text{-alkyne})_2]$ (**2′**–**5′**) in quantitative yields.

Tungsten(II) alkyne complexes are very labile in solution and lose CO ligands. After exposure of a mixture of $[WCl_2(CO)_2(\eta^2\text{-}PhC{\equiv}CPh)_2]$ and $[WCl(SnCl_3)(CO)(\eta^2\text{-}PhC{\equiv}CPh)_2]$ to moist air the complex $[W_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}Cl)_2(O)(\eta^2\text{-}PhC{\equiv}CPh)_5]$ (**6**) was isolated and its structure determined by X-ray crystallography. The molecule consists approximately of an isosceles triangle of W atoms joined by triply-bridging oxygen. The longer edge is bridged by two chlorine atoms. The shorter edges are bridged by hydroxy groups.

Compound **6** is noteworthy since it is among the first of the trinuclear complexes in which a mixed-valence $W_2^{II}W^{IV}$–$(\mu_3\text{-}O)$ core has been established. It is also unique in being the first tungsten compound to be isolated containing two different triply-bridged, μ_3-O and μ_3-Cl, ligands.

Keywords: Tungsten; Tin; Crystal structure; Trinuclear compound; Mixed-valence alkyne complex; Hydroxo bridges

1. Introduction

In continuation of our research into the catalytic activity of Group 6 metal carbonyls in the presence of Lewis acids [1], we have investigated the photochemical reaction of $W(CO)_6$ with $SnCl_4$. Our work has led to the discovery and structural characterization of a new dinuclear, seven-coordinate derivative of tungsten(II), $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ (**1**), which is a unique example of the halo carbonyls of Group 6 metals with an M–Sn bond [2].

Compound **1** provides an excellent starting material for complexes of the type $[WCl_2(CO)_3L_2]$ and $[WCl(SnCl_3)(CO)_3L_2]$ with L = acetonitrile, phosphine, bipyridyne, etc.' [3]. During attempts to prepare $[WCl(SnCl_3)(CO)_3L_2]$ in the photochemical reaction of $W(CO)_6$ with $SnCl_4$ in the presence of $L = PPh_3$, a compound of tungsten(IV), *cis*-$[WCl_4(OPPh_3)_2]$, was discovered and characterized by X-ray crystallography [4].

In this paper we report the reaction of $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ (**1**) with alkynes (phenylacetylene, *tert*-butylacetylene, 3-hexyne and diphenylacetylene).

Our work has led to the synthesis and characterization of a new tungsten chloro carbonyl alkyne compounds. Accidently, we discovered an unusual mixed-valence μ_3-oxo trimeric tungsten diphenylacetylene complex which arose from a mixture of products formed in the reaction of **1** and diphenylacetylene on exposure to moist air. An X-ray analysis shows that it is $[W_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}Cl)_2(O)(PhC{\equiv}CPh)_5]$ (**6**); this is the first structurally characterized alkyne compound with trinuclear geometry and the first containing a mixed valence $W_2^{(II)}W^{(IV)}O$ core.

2. Results and discussion

The reaction of alkynes with tungsten(II) compounds to give six-coordinate alkyne complexes has been stud-

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* Corresponding author.

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ied for more than 20 years [5]. A wide range of alkyne compounds of tungsten(II) have been reported, but far fewer bis(alkyne) compounds have been prepared. Recently, Baker and coworkers [6] reported the reaction of $[WI_2(CO)_3(NCMe)_2]$ with alkynes to give $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me and Ph), in which the labile acetonitrile ligands can be replaced by CO [7], and $[WI_2(CO)_2(\eta^2\text{-}RC_2R)_2]$ are formed. However, the bis(diphenylacetylene) complex $[WI_2(CO)_2(\eta^2\text{-}PhC_2Ph)_2]$ could not be isolated, since it dimerized to give the iodide-bridged dimer $[W(\mu\text{-}I)I(CO)(\eta^2\text{-}PhC_2Ph)_2]_2$ [7]. Single-crystal X-ray diffraction studies of the $[WI_2(CO)_2(\eta^2\text{-}MeC_2Me)_2]$ revealed that the two carbonyl ligands occupy a mutual trans position and the alkynes occupy a mutual cis position about the octahedrally coordinated metal centre [7].

The synthesis method of W^{II} bis(alkyne) complexes described in this paper are only comparable with the reactions of alkynes RC_2R', (R = R' = Me, Et, Ph; R = Ph, R' = Me) with $[W(\mu\text{-}Br)Br(CO)_4]_2$ in which dimeric $[W(\mu\text{-}Br)Br(CO)(\eta^2\text{-alkyne})_2]_2$ as prepared by Davidson and Vasapollo [8]. It is noteworthy that Davidson and coworkers [9,10] reported the preparation of a monomeric five-coordinate complex $[WBr_2(CO)(\eta^2\text{-}CF_3C_2CF_3)_2]$ when $[W(\mu\text{-}Br)Br(CO)_4]_2$ was treated with electron-withdrawing alkynes such as bis(hexafluorobut-2-yne). Starting from the same bromo carbonyl dimer of tungsten(II), Cotton and Meadows obtained new monomeric six-coordinate complex $[WBr_2(CO)_2(\text{cyclooctadiene})]$ [11]. Thus, it may be that monomer–dimer equilibrium depends on the steric and electronic properties of alkyne.

2.1. Reaction of $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ (1) with alkynes

Tungsten(II) halocarbonyl compound **1** gave an orange solution in toluene or dichloromethane, but on addition of an excess (1 : 4) of alkyne (*tert*-butylacetylene, phenylacetylene, 3-hexyne or diphenylacetylene) for 1 h the solution became greenish-yellow. The IR spectrum of the reaction mixture shows the decay of the bands at 2100, 2020 and 1942 cm^{-1}; these are attributable to **1** and the appearance of a strong intensity band of the alkyne complex in the 2100–2050 cm^{-1} region which is alkyne-dependent. The solution was filtered, and after evaporation of solvent in vacuo the content was examined by IR and NMR. We showed that products of the type $[WCl_2(CO)_2(\eta^2\text{-alkyne})_2]$ and $[WCl(SnCl_3)(CO)(\eta^2\text{-alkyne})_2]$ were present according to Eq. (1):

$$[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3] + 4\ \text{alkyne} \rightarrow [WCl_2(CO)_2(\eta^2\text{-alkyne})_2] + [WCl(SnCl_3)(CO)(\eta^2\text{-alkyne})_2] + 4\ CO \qquad (1)$$

In the reaction between **1** and alkynes the coordination of alkyne ligands is accompanied by loss of carbonyl ligands and chlorine-bridge cleavage.

The two compounds which are formed according to Eq. (1) differ considerably in stability and solubility. The compounds of type $[WCl(SnCl_3)(CO)(\eta^2\text{-alkyne})_2]$ are very soluble in hydrocarbons and have never been isolated separately. This coordinatively unsaturated species is in some way too reactive to be isolated and undergoes decomposition by elimination of CO. The $SnCl_3^-$ group is a poor σ donor and excellent π acceptor. CO is a poorer π acceptor than $SnCl_3^-$ and when the CO is trans to it the electron density is preferentially donated to tin, thus labilizing the trans CO ligand [12]. A logical decomposition route to the above compound involves the loss of a carbonyl ligand. The oxidation of W^{II} to a W^{IV} oxo compound can also occur even in the presence of oxygen traces.

The tungsten(II) alkyne complexes **2–5** are very labile in solution toward loss of CO ligands. From a

Table 1
IR, ^1H NMR and $^{13}C\{^1H\}$ NMR for reaction products of $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ (1) and alkynes

Compounds		IR (Nujol) (cm^{-1})		^1H NMR δ (ppm)	$^{13}C\{^1H\}$ NMR δ(ppm)	
No	alkyne	ν(CO)	ν(C≡C)		CO	C≡
(2)	HC≡CPh	2108sh, 2096vs	— [a]	HC≡12.41,	— [a]	— [a]
(3)	$HC{\equiv}C^tBu$	2075vs	— [a]	HC≡11.34, 11.09	208.04, 206.51	170.31, 154.96
(4)	EtC≡CEt	2048(br)	1640w		207.70	170.89, 159.22
(4')	EtC≡CEt				207.80	183.96, 179.72
(5)	PhC≡CPh	2094, 2087	1614w		201.75	185.50, 169.88
(6)	PhC≡CPh	—	1624w	*H*O 5.04	—	203.01, 201.43 190.37, 187.11 164.93

[a] Not observed.

mixture of products only the diphenylacetylene complex **5** was obtained in a pure state by repeated recrystallization from CH_2Cl_2–heptane. Although it is very labile and air-sensitive in solution, it can be stored for a month as a solid at 293 K under nitrogen. The analysis corresponds most closely to the formulation $[WCl_2(CO)_2(\eta^2\text{-PhC}{\equiv}\text{CPh})_2]$ (**5**). The complex **5** was fully characterized by IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The complex shows one split (2094 and 2087 cm^{-1}) strong absorption band due to $\nu(CO)$ (Table 1); the ^{13}C NMR spectra show one signal for the CO group at 201.75 ppm and two signals (185.50 and 169.88 ppm) for two equivalent but asymmetrically bonded diphenylacetylenes.

The similarities in the IR and NMR spectra of **2–5** suggest a similar monomeric structure (Table 1). However, the possibility that **2–5** dimerize in solution to form dinuclear species with seven-coordinate metal atoms and then successive elimination of carbon monoxide cannot be ruled out at present. Based on the IR and NMR data, we cannot exclude the possibility of the bis(alkyne) complex structure in which chlorine bridges have been totally or partly preserved. Unfortunately, tungsten(II) alkyne complexes were too unstable for molecular-weight studies in solution. The unsymmetrical dimeric species $[(\text{alkyne})_2(CO)_2W(\mu\text{-Cl})_3W(SnCl_3)(CO)(\text{alkyne})_2]$ is likely to be a component of the reaction mixture in the cases of 3-hexyne, phenylacetylene and *tert*-butylacetylene reactions, and for this reason complexes of the type $[WCl_2(CO)_2(\eta^2\text{-alkyne})_2]$ could not be isolated in a pure state.

Reactions involving terminal alkynes and **1** are more complex and analogues of **5** have not been well-characterized. The terminal alkynes added to **1** in an excess undergo fast polymerization and yield poly(alkynes); the phenylacetylene gives a reddish-orange solution of poly(phenylacetylene), and *tert*-butylacetylene gives white poly(*tert*-butylacetylene). The fact that **1** polymerizes terminal alkynes establishes that addition and elimination of terminal alkynes from the metal center can occur readily. Interestingly, **1** acts as a terminal-alkyne polymerization catalyst in toluene or dichloromethane at room temperature in the absence of cocatalyst. Probably, tin chloride present in the reaction mixture plays the role of cocatalyst. Another possibility is that tungsten(IV) compounds, present as an impurity in **1**, polymerize terminal alkynes. The poly(phenylacetylene) obtained as an orange powder was recrystallized from CH_2Cl_2–CH_3OH and analyzed by gel-permeation chromatography. The molecular weight measured using toluene solutions and monitoring refractive index was high enough (8330 vs. polystyrene standards 0.5×10^3–2880×10^3 MW). The course of the reaction did not appear to depend upon the solvent, as the same mixture of products was obtained when dichloromethane or toluene were used.

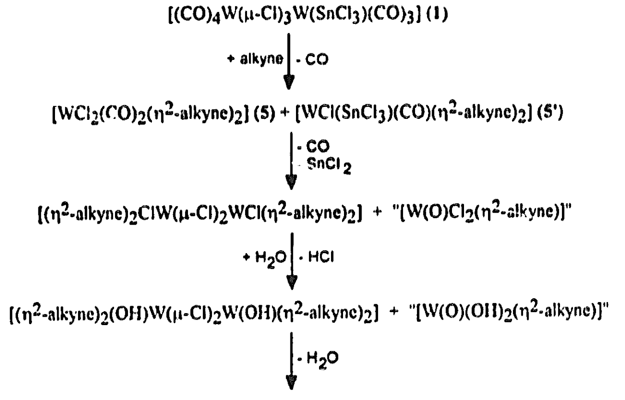
On attempted recrystalization, **2–5** evolved carbon monoxide and dimerized to probably give compounds of the type $[W_2Cl_4(\eta^2\text{-alkyne})_4]$.

Compound **5** in the presence of moist air and on standing yields a pale yellow crystalline solid. From an X-ray crystallographic study the compound was shown to be $[W_3(\mu_3\text{-O})(\mu\text{-OH})_2(\mu\text{-Cl})_2(O)(\eta^2\text{-PhC}{\equiv}\text{CPh})_5]$ (**6**). The yields were small (ca. 10% yield based on the amount of **1** used) but reproducible.

It is not immediately apparent how the compound **6** is formed. Although **5** is very labile and air-sensitive in solution, they can be stored for a month as a solid under nitrogen at 293 K. However, IR spectra of **5** in CH_2Cl_2 solution indicates that the carbon monoxide is lost, and it is thought that the first step in the reaction is the removal of carbon monoxide to form a dimeric complex of the type $[W_2Cl_4(\eta^2\text{-alkyne})_4]$; on exposure to moist air this will rapidly hydrolyze with evolution of hydrogen chloride to give a tungsten-hydroxo compound.

The dimeric $[W_2Cl_4(\eta^2\text{-alkyne})_4]$ can be prepared from $[WCl_2(CO)_2(\eta^2\text{-alkyne})_2]$; loss of CO must yield fragments such as $[WCl_2(\eta^2\text{-alkyne})_2]$. Owing to the bridging propensity of the Cl atom and the desire for W(II) to exhibit six-coordination, it seems reasonable that $[WCl_2(\eta^2\text{-alkyne})_2]$ will tend to dimerize. Doubtless the second step is in reality several steps, and it also involves a change in the number of chlorine atoms per tungsten atom and the appearance of oxygen atoms and hydroxo groups. Presumably the oxygen atoms and hydroxo groups arise from hydrolysis of the W–Cl bond. Hydrolysis is a common mode of decomposition for the organometallic complexes of the electropositive metals, and many organometallic oxo and hydroxo complexes have been prepared by this route [13].

The various conversions and interconversions of the tungsten alkyne complexes have been summarized in Scheme 1. We assume that **1** is first converted into monomeric alkyne complexes $[WCl_2(CO)_2(\eta^2\text{-alkyne})_2]$ and $[WCl(SnCl_3)(CO)(\eta^2\text{-alkyne})_2]$, which by elimina-



$$\begin{array}{c}
[(CO)_4W(\mu\text{-Cl})_3W(SnCl_3)(CO)_3]\ (1)\\
{\scriptstyle +\,\text{alkyne}}\ \big\downarrow\ {\scriptstyle -\,CO}\\
[WCl_2(CO)_2(\eta^2\text{-alkyne})_2]\ (5) + [WCl(SnCl_3)(CO)(\eta^2\text{-alkyne})_2]\ (5')\\
\big\downarrow\ {\scriptstyle -\,CO,\ -\,SnCl_2}\\
[(\eta^2\text{-alkyne})_2ClW(\mu\text{-Cl})_2WCl(\eta^2\text{-alkyne})_2]\ +\ \text{"}[W(O)Cl_2(\eta^2\text{-alkyne})]\text{"}\\
{\scriptstyle +\,H_2O}\ \big\downarrow\ {\scriptstyle -\,HCl}\\
[(\eta^2\text{-alkyne})_2(OH)W(\mu\text{-Cl})_2W(OH)(\eta^2\text{-alkyne})_2]\ +\ \text{"}[W(O)(OH)_2(\eta^2\text{-alkyne})]\text{"}\\
\big\downarrow\ {\scriptstyle -\,H_2O}\\
[W_3(\mu_3\text{-O})(\mu\text{-OH})_2(\mu\text{-Cl})_2(O)(\eta^2\text{-PhC}{\equiv}\text{CPh})_5]\ (6)
\end{array}$$

Scheme 1.

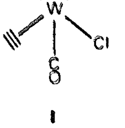
tion of CO and $SnCl_2$ and formation of chloro bridges gives the dimeric compound of tungsten(II). However, we must also presume the presence of the W^{IV} compound, the hypothetical '[$WOCl_2$(alkyne)]' or '[WCl_4(alkyne)]' compounds, which interact with W^{II} dimer leading to formation of trimeric species. The W^{IV} compound may be formed as an oxidation product of the W^{II} compound **5** or **5'**. It is worth mentioning that the W^{IV} compound $[WCl_4(OPPh_3)_2]$ has been formed in similar conditions [3]. The $[WCl_4(alkyne)]_2$ compounds have been isolated as dimers with chloro bridges in the reaction of WCl_6 with $PhC{\equiv}CH$ and $Me_3SiC{\equiv}CH$ [14a], and $HC{\equiv}CH$ [14b] in CCl_4 and CH_2Cl_2 respectively. They were characterized by IR and NMR methods. Partial hydrolysis of $[WCl_4(HC{\equiv}CH)]_2$ in acetonitrile solution yields $[WCl_2(HC{\equiv}CH)(CH_3CN)_3]^+[WOCl_4(CH_3CN)_3]^-$ by redox-disproportionation [14b].

The reaction of carbonyl complexes with oxygen is the conventional way of preparing organometallic oxo complexes. Upon exposure of the reaction mixture to air the $[WCl_2(CO)_2(\eta^2\text{-alkyne})_2]$ complex can take up O_2 from air and lose the carbon monoxide and alkyne ligand to give '[$WOCl_2$(alkyne)]'. There are a few examples for a reaction of this type beginning with the formation of $[W(O)(C_5H_5)(C_6H_5)(PhC{\equiv}CPh)]$ [15]. Tungsten(II) compounds, for example $[WCl_2(PMePh_2)_4]$, can reduce even CO_2 to form an oxo complex, $[W(O)Cl_2(CO)(PMePh_2)_2]$ [16].

An understanding of the mechanism of these reactions will certainly be an objective in future work, but for the present we can more fruitfully turn to a discussion of the structure, properties, and bonding of the new trinuclear complex **6**.

2.2. *Spectroscopic properties of tungsten alkyne complexes*

The spectroscopic properties of tungsten(II) bis(alkyne) complexes **2–5** are somewhat similar to those identified by Baker and coworkers [6,7] who suggested a similar bis(alkyne) structure depicted by **I**, and hence with two mutually *trans*-CO ligands and both of the coordinated alkyne and chlorine ligands cis to each other. Thus, one broad band or two closely spaced ν(CO) bands are observed in the IR spectrum near 2100 cm^{-1} due to coordinated CO. The $\nu(C{\equiv}C)$ bands are observed near 1630 cm^{-1} (Table 1).



I

All our W^{II} complexes of the type $[WCl_2(CO)_2(\eta^2\text{-alkyne})_2]$ **2–5** showed bands due to terminal ν(W–Cl) in the region 300–200 cm^{-1}, but in the IR spectrum of crude products containing W–Sn compounds few other bands were observed in this region. In the IR spectrum of **6**, $\nu(W{-}Cl_2{-}W)$ frequencies were observed as very weak and weak bands at 282 and 239 cm^{-1}.

The IR spectrum of **6** is characterized by a strong band at 972 cm^{-1} assigned to the W=O stretch. That is in good agreement with the short W–O bond (1.697(7) Å) found in **6**. Such a high position for the ν(W=O) band as in **6** was observed only in $[W(O)Cl(neopentyl)_3]$ (977 cm^{-1}) [17]. The ν(OH) frequency in **6** gives one strong, sharp band at 3545 cm^{-1}. This unusually low ν(OH) frequency can only be compared with that observed at 3550 cm^{-1} for $[Re(CO)_3(\mu_3\text{-}OH)]_4$ [18]. The ν(W–OH–W) were observed as middle intensity bands at 631 and 601 cm^{-1}. The protons of both hydroxo bridges, which were located by X-ray diffraction study of **6**, were detected by ^1H NMR spectroscopy as a singlet at δ 5.04 ppm. The protons of the OH groups in **6** show rapid exchange, when D_2O is added to a sample in an NMR tube. The OH signals at δ 5.04 ppm disappear, while the water signals at δ 4.79 ppm are increased.

$^{13}C\{^1H\}$ NMR data for compounds **3–5** are consistent with the solid-state structure of $[WI_2(CO)_2(\eta^2\text{-}MeC{\equiv}CMe)_2]$ described by Baker and coworkers [7]. The carbonyl resonances of **3–5** appear from δ 208.04 to 201.75 ppm (Table 1). In the spectrum of **5**, one signal of two equivalent CO groups was observed at 201.75 ppm and two signals, at 185.5 and 169.88 ppm of the acetylenic carbon of an asymmetricaly bonded but two equivalent diphenylacetylenes were detected. The carbonyl signal at 201.75 ppm shows coupling to tungsten $J^{183}{}_{W-^{13}C} = 121.3$ Hz with a satellite intensity of 14%. The larger more sterically demanding alkynes such as *tert*-butylacetylene lead to a more distorted structure of compound **3**; hence there must be two inequivalent CO groups. Two signals of equal intensity at δ 208.04 and 206.51 ppm are present. Two alkynes are equivalent in **3** but bonded unsymmetrically. The acetylenic carbon signals at 170.31 and 154.96 ppm were observed.

The $^{13}C\{^1H\}$ NMR spectrum of the crude product formed in the reaction of **1** and 3-hexyne showed two singlet peaks of intensity 1 : 2 at 207.80 and 207.70 ppm assignable to CO ligands which indicated the presence of two compounds, $[WCl(SnCl_3)(CO)(\eta^2\text{-}EtC{\equiv}CEt)_2]$ (**4'**) and $[WCl_2(CO)_2(\eta^2\text{-}EtC{\equiv}CEt)_2]$ (**4**). The acetylenic carbon resonances were observed at 183.96 and 179.72 ppm for W–Sn compound **4'** but at 170.89 and 159.22 ppm for **4**. The spectrum changed when the sample was cooled, suggesting the presence in the solution of the two species. This was supported by the IR spectrum (Table 1) which showed a broad carbonyl band and by the ^1H NMR spectrum which consisted of a number of overlapping multiplets, the shape and position of which were temperature-dependent.

The room temperature ^{1}H NMR spectrum of **2** showed the expected acetylenic proton resonances of coordinated phenylacetylene at δ 12.41 ppm; the proton resonances of coordinated *tert*-butylacetylene in **3** were observed at δ 11.34 and 11.04 ppm, in accord with the Templeton and coworkers observation that acetylenic protons in formal 16 electron compounds may be observed in the range 10–14 ppm [19,20].

^{13}C{^{1}H} NMR spectra of **6** are consistent with the solid-state structure. There are five equal intensity acetylenic carbon resonances in the range from δ 203.01 to 164.93 ppm and five C(ipso) resonances between 140.77 and 134.80 ppm, which is in agreement with five inequivalent acetylenic carbons in five alkyne ligands and the same surroundings around two equivalent tungsten atoms. The third tungsten in the molecule of **6** coordinates alkyne symmetrically and shows one signal in the NMR spectrum. No fluxional processes were observed in the ^{13}C{^{1}H} NMR spectra for **6** from −70 to 23°C.

Previously it has been established [21] that the degree to which an alkyne acts as a greater than two-electron donor can be correlated with the ^{13}C chemical shifts of the alkyne carbon atoms. The position of acetylenic carbon resonances in the range 184–155 ppm for **2**–**5** indicates that the alkyne ligands donate an average of three electrons each to the tungsten atoms. Thus compounds **2**–**5** are six-coordinate complexes which formally have a 16-electron configuration and can therefore be described as coordinatively unsaturated. The stability of this type of compound underlines the important role that the second (perpendicular) set of filled π orbitals on the alkyne have in stabilizing formally electron-deficient complexes. By Templeton's criterion it is clear that chemical shifts of the acetylenic carbons at 203–187 ppm in **6** are diagnostic of four-electron donor alkyne ligands ($2\sigma + 2\pi$) [21]; this suggests substantial donation from the second alkyne filled π orbital, $\pi\perp$, into the vacant metal dπ orbital and indicates that this interaction is stronger than acetylene in **6**, whose carbon resonance is at 164 ppm. In contrast, it is known [21] that in complexes containing an alkyne ligand and additional π-donor ligands (e.g. RC_2R, O^{2-}, etc.) the set of π-donor ligands compete with one another for vacant metal dπ orbitals. Thus, for two coparallel cis alkyne ligands, donation from two $\pi\perp$ orbitals is restricted because both alkyne $\pi\perp$ orbitals overlap the same metal dπ orbital and a three-center four-electron interaction results so that the alkyne ligands may be somewhat less than a four-electron donor. For the same reason the acetylene cis to be oxo ligand does not behave as a four-electron donor to the oxotungsten(IV) moiety, but rather as a three-electron donor [19]. We believe that the four acetylenic carbon resonances in the region from 203 to 187 ppm belong to two asymmetrically bonded alkynes at the two equivalent tungsten(II) ions, and the signal at 164.93 ppm belongs to a symmetrically bonded alkyne at the oxotungsten(IV) moiety in **6**. This is consistent with the proposal [19] that π donation from the oxo ligand to the metal should lead to a reduced $\pi\perp$ donation from the alkyne and that the alkyne carbon resonance is shifted to higher field.

2.3. *Structure of* $[W_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}Cl)_2(O)(\eta^2\text{-}PhC{\equiv}CPh)_5]$ *(6)*

The compound **6** is formed of discrete trinuclear molecules having the structure shown in Fig. 1. In Fig. 2 we have further simplified the structure by omitting all atoms other than the tungsten atoms and those bonded to them. Table 2 contains the fractional coordinates and isotropic thermal parameters. The bond distances and the important bond angles are given in Table 3.

The basic structural units of **6** are three tungsten atoms, which are linked by one oxygen atom. The triply bridging oxo atom lies above the plane defined by the three tungsten atoms and the oxygen is displaced 0.699(6) Å out of this plane (Table 4). The W–O–W angles (106.82(26), 106.84(26) and 113.22(27)°) at the central oxygen are close to the tetrahedral angle.

The molecule consists of an approximate isosceles triangle of W atoms. Two of the W–W distances are almost equal at 3.294(1) and 3.304(1) Å; the third is different, at 3.418(1) Å. The three W–(μ_3-O) distances range from 2.041(6) to 2.062(6) Å.

The longer edge of the isosceles triangle of W atoms is bridged by two chlorine atoms. The shorter edges are

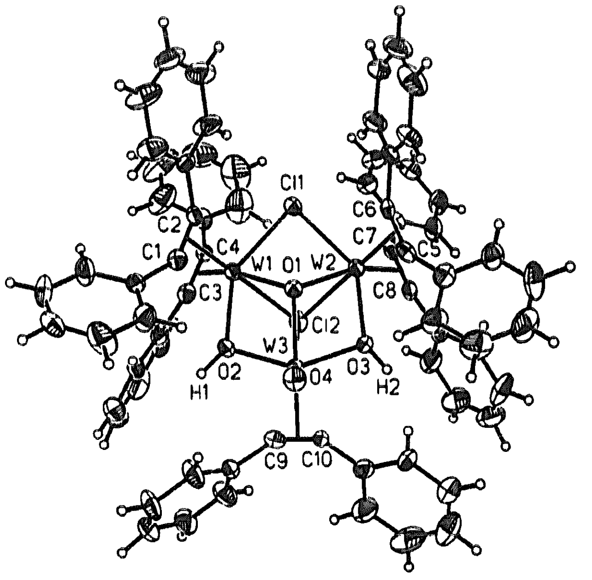


Fig. 1. An ORTEP drawing of the $[W_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}Cl)_2(O)(\eta^2\text{-}PhC{\equiv}CPh)_5]$ (**6**) molecule, giving the atomic labeling scheme.

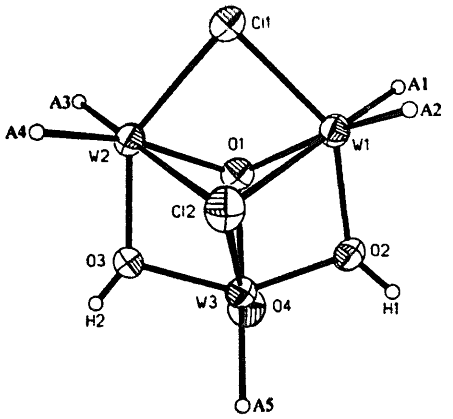


Fig. 2. An ORTEP drawing of only the tungsten atoms and those ligand atoms bonded to them in **6**. A – represents the midpoint of the C≡C linkage.

bridged by hydroxy groups. The contraction of two W–W distances in **6** is undoubtedly a reflection of the smaller size of the μ_2-OH group compared with that of the μ_2-Cl. However, there is another possible cause. One of the bridging Cl atoms lies only 0.184(2) Å above and the other 2.088(2) Å below the plane defined by the three tungsten atoms. Both the W–OH–W bridges are very unsymmetrical, with W(1)–O(2) and W(2)–O(3) the same distance apart (2.132(6) Å) while the W(3)–O(2) and W(3)–O(3) distances average 2.017(6) Å. The W–O–W angles are 104.91(27) and 105.70(27)°. There are no μ_2-OH-bridged tungsten structures for comparison. In complex $[W(CO)_3(\mu_3\text{-}OH)]_4^{4-}$ the average W–O distance is 2.24(1) Å and the average W–O–W angle is 106(3)° [22]. In an unusual tungsten complex containing a bridging hydroxo group between tungsten and boron, the W–O bond (2.194(6) Å) is in a similar range [23]. The positions of the H atoms of both hydroxo groups were located by a difference Fourier map, with O–H distances of 0.956 and 0.892 Å, but not refined.

The coordination spheres of the two tungsten atoms, W(1) and W(2), are identical while the W(3) atom differs in both the type of ligand involved and the oxidation state. W(1) and W(2) are bonded to two terminal phenylacetylene molecules, two bridging chlorine and to μ_3-O and μ-OH bridges. W(3) shares the μ_3-O and μ-OH bridges with W(1) and W(2) and has only one additional phenylacetylene and one terminal oxo ligand in its coordination sphere. Apart from its bonds to the μ_3-O and alkyne ligand, W(3) is strongly bonded to the oxygens of the hydroxy group linking the W(1) and W(2) and is very strongly bonded to a terminal oxygen atom (W(3)–O(4) = 1.679(7) Å).

The imbalance in the distribution of electronegative terminal ligands would, by itself, tend to make W(3) effectively more oxidized than W(1) and W(2). This is apparent in the shortening of both W(3)–(μ-OH) bonds lengths (2.017(6) Å (av)) compared with W(1)–(μ-OH) and W(2)–(μ-OH) bonds (mean 2.132(6) Å).

The coordination spheres of the individual tungsten atoms are not easily described in terms of regular polyhedra. While the six ligands (two mutually cis alkynes, chlorines and oxygens) around W(1) and W(2) have an arrangement that comes close to octahedral, there are some sizeable deviations from that idealized arrangement. The angles subtended at the W(1) and W(2) atoms by the midpoints (A) of both alkyne carbon–carbon triple bonds is 99.60(40)° and 100.24(40)° respectively, whereas the O(1)–W(1)–O(2) angle is only 71.08(23)° and the Cl(1)–W(1)–Cl(2) angle is 77.84(8)°. The *trans*-ClW (alkyne) units are also slighly bent at the metal atom, the Cl(2)–W–A angle (A represents the midpoint of the C≡C linkage) being, 175.62(29)° (av). The coordination sphere of W(3) with five ligands is close to trigonal bipyramidal, but the W(3)–Cl(2) distance of 3.052(3) Å indicates little single bond and complete the coordination sphere of W(3) to octahedral. The arrangement of W(3) is highly distorted from octahedral geometry with O(1)–W(3)–O(4) angle of 101.37(29)°, an O(1)–W(3)–O(3) angle of 72.76(24)°, an O(1)–W(3)–O(2) angle of 72.93(24)°, and an O(2)–W(3)–O(3) angle of 137.23(25)°. Furthermore, the O(4)–W(3)–A(5) angle is 101.49(37)° and the O(4)–W(3)–Cl(2) angle is 164.35(24)°; thus the terminal oxygen O(4) is approximately cis to the alkyne and trans to the Cl(2) (Figs. 1 and 2).

The bond lengths observed here between the W atoms and its immediate neigbors are comparable with values found for other tungsten compounds. In support of this we may compare the W–O bond (1.697(7) Å) found in **6** with the W–O distance of 1.69(2) Å found in $[W(O)(C_5H_5)(C_6H_5)(PhC{\equiv}CPh)]$ [15], the 1.697(15) Å observed in $[W(O)(CHCMe_3)(PMe_3)_2Cl_2]$ [24], the 1.689(13) and 1.726(10) Å found in $[W_2O_3(CH_2CMe_3)_6]$ [25] and the 1.692(8) Å in the anion $[WOCl_4(THF)]$ [26]. However, shorter W=O bond lengths, 1.661(11) Å in $[W(O)(CHCMe_3)(PEt_3)Cl_2]$ [27] and 1.669(18) Å for the $[WOCl_4\{(C_6H_5N)_2O\}]$ [28] complex, have been observed; the length of this bond is somewhat variable, and is probably sensitive to the nature of the other substituents in the coordination sphere but generally indicates significant oxygen-to-metal π bonding as usual for oxotungsten groups.

It is now well established by Cotton and coworkers [29] that tungsten, in oxidation states of IV or thereabouts, has a marked tendency to form trinuclear, triangular cluster species. One of the well-characterized types of compound is the trinuclear oxo-centered metal carboxylate of general composition $[W_3(\mu_3\text{-}O)_2(O_2CR)_6L_3]^{2+}$ [30] or $[W_3(\mu_3\text{-}O)(O_2CR)_6L_3]^{2+}$ [29]. The coordination about the tungsten centers in the monooxo compound is slightly distorted octahedral, with four

Table 2
Final atomic coordinates and equivalent isotropic thermal parameters (Å^2) with esds in parentheses for $[W_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}Cl)_2(O)(\eta^2\text{-}PhC{\equiv}CPh)_5]$ (**6**)

Atom	x	y	z	U_{eq} [a]
W(1)	0.45519(3)	0.35395(2)	0.20148(2)	0.02910(11)
W(2)	0.62704(3)	0.32625(2)	0.30399(2)	0.02883(11)
W(3)	0.40935(3)	0.37031(2)	0.33952(2)	0.03049(11)
Cl(1)	0.6286(2)	0.33081(14)	0.19588(10)	0.0367(5)
Cl(2)	0.4798(2)	0.23186(14)	0.27491(11)	0.0411(6)
O(1)	0.5112(4)	0.3879(3)	0.2787(3)	0.0288(14)
O(2)	0.3442(4)	0.3668(4)	0.2616(3)	0.036(2)
O(3)	0.5330(4)	0.3364(4)	0.3743(2)	0.034(2)
O(4)	0.3934(5)	0.4591(4)	0.3650(3)	0.047(2)
C(1)	0.3972(7)	0.4464(5)	0.1668(4)	0.035(2)
C(11)	0.3134(7)	0.4948(6)	0.1637(4)	0.037(2)
C(12)	0.2829(9)	0.5360(7)	0.2101(5)	0.061(3)
C(13)	0.2066(10)	0.5856(8)	0.2045(7)	0.082(5)
C(14)	0.1619(8)	0.5936(7)	0.1535(6)	0.059(3)
C(15)	0.1878(9)	0.5513(8)	0.1066(6)	0.070(4)
C(16)	0.2640(9)	0.5032(8)	0.1125(5)	0.062(3)
C(2)	0.4780(6)	0.4381(5)	0.1432(4)	0.034(2)
C(21)	0.5370(7)	0.4772(6)	0.1035(4)	0.035(2)
C(22)	0.5096(10)	0.5469(8)	0.0848(6)	0.071(4)
C(23)	0.5651(13)	0.5909(8)	0.0486(7)	0.090(5)
C(24)	0.6478(12)	0.5622(10)	0.0312(6)	0.079(5)
C(25)	0.6759(10)	0.4942(12)	0.0469(7)	0.099(6)
C(26)	0.6183(10)	0.4500(8)	0.0827(6)	0.078(5)
C(3)	0.3640(7)	0.2833(5)	0.1592(4)	0.036(2)
C(31)	0.2685(7)	0.2529(6)	0.1619(4)	0.044(3)
C(32)	0.1938(7)	0.2962(7)	0.1791(5)	0.049(3)
C(33)	0.1058(10)	0.2652(11)	0.1867(6)	0.083(5)
C(34)	0.0929(11)	0.1914(18)	0.1759(8)	0.125(10)
C(35)	0.1656(14)	0.1461(9)	0.1561(7)	0.096(6)
C(36)	0.2539(9)	0.1770(8)	0.1501(5)	0.065(4)
C(4)	0.4454(6)	0.2724(5)	0.1381(4)	0.032(2)
C(41)	0.4943(8)	0.2314(6)	0.0955(5)	0.046(3)
C(42)	0.4652(13)	0.2327(9)	0.0387(6)	0.096(6)
C(43)	0.5150(20)	0.1946(12)	0.0057(7)	0.131(8)
C(44)	0.5899(16)	0.1537(13)	0.0100(10)	0.117(7)
C(45)	0.6144(14)	0.1465(12)	0.0613(9)	0.122(7)
C(46)	0.5670(13)	0.1840(11)	0.1054(7)	0.109(6)
C(5)	0.7048(7)	0.4026(6)	0.3502(5)	0.039(2)
C(51)	0.7167(8)	0.4340(6)	0.4072(5)	0.047(3)
C(52)	0.6415(9)	0.4630(7)	0.4382(5)	0.062(3)
C(53)	0.6590(12)	0.4878(9)	0.4944(6)	0.086(5)
C(54)	0.7453(14)	0.4834(9)	0.5193(6)	0.088(5)
C(55)	0.8187(12)	0.4542(10)	0.4902(7)	0.088(5)
C(56)	0.8033(9)	0.4313(7)	0.4328(5)	0.062(3)
C(6)	0.7408(6)	0.3977(5)	0.2993(4)	0.033(2)
C(61)	0.8141(7)	0.4310(6)	0.2652(5)	0.042(3)
C(62)	0.8512(7)	0.4990(6)	0.2828(5)	0.051(3)
C(63)	0.9234(10)	0.5308(8)	0.2495(8)	0.082(5)
C(64)	0.9573(10)	0.4954(10)	0.2021(8)	0.084(5)
C(65)	0.9185(9)	0.4303(11)	0.1857(5)	0.080(5)
C(66)	0.8471(8)	0.3976(8)	0.2161(5)	0.061(3)
C(7)	0.7100(6)	0.2289(5)	0.3003(4)	0.035(2)
C(71)	0.7676(6)	0.1757(5)	0.2679(4)	0.032(2)
C(72)	0.8137(8)	0.1188(7)	0.2982(5)	0.051(3)
C(73)	0.8689(9)	0.0687(7)	0.2694(5)	0.060(3)
C(74)	0.8804(7)	0.0722(6)	0.2121(5)	0.050(3)
C(75)	0.8349(9)	0.1272(7)	0.1811(5)	0.055(3)
C(76)	0.7805(7)	0.1803(6)	0.2093(5)	0.046(3)
C(8)	0.6752(6)	0.2364(5)	0.3516(4)	0.033(2)
C(81)	0.6593(7)	0.2033(6)	0.4070(4)	0.040(2)
C(82)	0.6823(9)	0.2378(7)	0.4567(5)	0.062(3)
C(83)	0.6628(12)	0.2064(9)	0.5099(5)	0.079(5)
C(84)	0.6165(11)	0.1417(11)	0.5128(7)	0.086(5)
C(85)	0.5932(12)	0.1022(10)	0.4625(8)	0.097(5)
C(86)	0.6135(10)	0.1342(8)	0.4114(6)	0.074(4)
C(9)	0.2877(7)	0.3167(6)	0.3669(4)	0.040(3)
C(91)	0.1883(7)	0.3082(6)	0.3500(4)	0.043(3)
C(92)	0.1422(8)	0.2387(7)	0.3515(6)	0.064(4)
C(93)	0.0503(9)	0.2335(8)	0.3379(6)	0.071(4)
C(94)	0.0026(8)	0.2946(9)	0.3239(6)	0.071(4)
C(95)	0.0403(8)	0.3624(8)	0.3204(6)	0.072(4)
C(96)	0.1368(8)	0.3706(7)	0.3337(6)	0.066(4)
C(10)	0.3501(6)	0.3081(6)	0.4052(4)	0.033(2)
C(101)	0.3667(8)	0.2783(7)	0.4615(5)	0.047(3)
C(102)	0.4353(8)	0.3110(8)	0.4968(5)	0.063(4)
C(103)	0.4499(10)	0.2907(10)	0.5523(6)	0.081(4)
C(104)	0.3988(14)	0.2357(10)	0.5747(6)	0.089(5)
C(105)	0.3299(14)	0.2019(10)	0.5446(8)	0.101(6)
C(106)	0.3124(10)	0.2234(9)	0.4863(6)	0.081(4)

[a] $U_{eq} = 1/3[\Sigma_{ij} U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j]$.

oxygen atoms from bridging carboxylate groups; the central triply-bridging oxygen, and a terminal ligand atom complete the coordination to each tungsten ion. The truly significant quantitative differences between the structure of $[W_3O(O_2CR)_6L_3]^{n+}$ and **6** is in the W–W distances. In the $[W_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$ ion, two W–W bonds lengths with an average value of 2.685(1) Å and the third W–W bond of 2.495(1) Å were found [29]. In $[W_3(\mu_3\text{-}O)_2(O_2CR)_6L_3]^{2+}$ slightly longer W–W distances were observed [30] (average 2.745(1) Å), but all are consistent with the existence of a W–W single bond. In the present compound, the W–W distances varied from 3.418(1) to 3.294(1) Å. The apparent differences are significant, and maybe in part due to the lower formal oxidation number, $2\frac{2}{3}$ in the present case vs. $3\frac{1}{3}$ in the acetate compound but primarily indicate the absence of a metal–metal bond in **6**.

There are no cases where the dimensions can be compared between two complexes with the same ligands connected to the M_3O core, differing only by the number of electrons. However, in general, the mean M–O distance in a mixed-valence $M_2^{III}M^{II}O$ complex is greater than in the corresponding $M_3^{III}O$ [31].

Turning now to the W–Cl–W-type linkages. The two W(1)–Cl–W(2) bridges are very different: the W(1)–Cl(1) and W(2)–Cl(1) average distance is 2.506(2) Å, while W(1)–Cl(2) and W(2)–Cl(2) distances average 2.763(3) Å. The W(3)–Cl(2) distance is unprecedentedly long, being 3.052(3) Å. The W–Cl(2)–W angles differ slightly, running from 68.67(6) to 76.40(7)°. We believe that the W–Cl distances can be satisfactorily understood in terms of the W_3–(μ_3-Cl) picture of the bonding with a very unsymmetrical μ_3-Cl bridge.

The first μ_3-Cl bridge was detected by Cotton et al. [32] in a trinuclear tungsten cluster $[W_3O_3Cl_5(CH_3$-

Table 3
Selected bond lengths (Å) and angles (deg) with esds in parentheses for $[W_3(\mu_3\text{-}O)((\mu\text{-}OH)_2((\mu\text{-}Cl)_2(O)(\eta^2Ph_2C_2)_5]$

Bond lengths			
W(1)–W(2)	3.418(1)	W(2)–O(3)	2.132(6)
W(1)–W(3)	3.294(1)	W(2)–Cl(1)	2.513(2)
W(2)–W(3)	3.304(1)	W(2)–Cl(2)	2.753(2)
W(1)–C(1)	1.998(9)	W(3)–C(9)	2.079(10)
W(1)–C(2)	2.042(10)	W(3)–C(10)	2.070(9)
W(1)–C(3)	2.042(9)	W(3)–O(1)	2.062(6)
W(1)–C(4)	2.066(9)	W(3)–O(2)	2.021(6)
W(1)–O(1)	2.041(6)	W(3)–O(3)	2.013(6)
W(1)–O(2)	2.132(6)	W(3)–O(4)	1.697(7)
W(1)–Cl(1)	2.500(2)	O(2)–H(1)	0.956
W(1)–Cl(2)	2.773(3)	O(3)–H(2)	0.892
W(2)–C(5)	2.041(10)	C(1)–C(2)	1.286(13)
W(2)–C(8)	2.049(9)	C(3)–C(4)	1.276(13)
W(2)–C(6)	2.056(10)	C(5)–C(6)	1.296(14)
W(2)–C(7)	2.092(10)	C(7)–C(8)	1.304(13)
W(2)–O(1)	2.053(6)	C(9)–C(10)	1.255(13)
Angles			
W(2)–W(1)–W(3)	58.95(1)	C(6)–W(2)–Cl(1)	84.8(3)
W(2)–W(3)–W(1)	62.40(1)	C(7)–W(2)–Cl(1)	88.4(3)
W(1)–W(2)–W(3)	58.65(1)	O(3)–W(2)–Cl(1)	141.0(2)
C(1)–W(1)–O(1)	105.4(3)	C(5)–W(2)–Cl(2)	159.1(3)
C(1)–W(1)–C(3)	93.1(4)	C(8)–W(2)–Cl(2)	84.6(3)
O(1)–W(1)–C(3)	147.1(3)	O(1)–W(2)–Cl(2)	69.6(2)
C(1)–W(1)–C(2)	37.1(4)	C(6)–W(2)–Cl(2)	162.8(3)
O(1)–W(1)–C(2)	107.6(3)	C(7)–W(2)–Cl(2)	85.1(3)
C(3)–W(1)–C(2)	103.6(4)	O(3)–W(2)–Cl(2)	75.9(2)
C(1)–W(1)–C(4)	105.3(4)	Cl(1)–W(2)–Cl(2)	78.03(8)
O(1)–W(1)–C(4)	148.6(3)	O(4)–W(3)–O(3)	104.9(3)
C(3)–W(1)–C(4)	36.2(4)	O(4)–W(3)–O(2)	106.2(3)
C(2)–W(1)–C(4)	92.8(4)	O(3)–W(3)–O(2)	137.2(2)
C(1)–W(1)–O(2)	82.7(3)	O(4)–W(3)–O(1)	101.4(3)
O(1)–W(1)–O(2)	71.1(2)	O(3)–W(3)–O(1)	72.8(2)
C(3)–W(1)–O(2)	84.9(3)	O(2)–W(3)–O(1)	72.9(2)
C(2)–W(1)–O(2)	118.8(3)	O(4)–W(3)–C(10)	100.3(4)
C(4)–W(1)–O(2)	119.9(3)	O(3)–W(3)–C(10)	84.7(3)
C(1)–W(1)–Cl(1)	120.9(3)	O(2)–W(3)–C(10)	117.3(3)
O(1)–W(1)–Cl(1)	73.9(2)	O(1)–W(3)–C(10)	152.0(3)
C(3)–W(1)–Cl(1)	119.4(3)	O(4)–W(3)–C(9)	101.6(4)
C(2)–W(1)–Cl(1)	85.4(3)	O(3)–W(3)–C(9)	117.7(3)
C(4)–W(1)–Cl(1)	84.5(3)	O(2)–W(3)–C(9)	83.6(3)
O(2)–W(1)–Cl(1)	142.1(2)	O(1)–W(3)–C(9)	150.9(3)
C(1)–W(1)–Cl(2)	159.2(3)	C(10)–W(3)–C(9)	35.2(4)
O(1)–W(1)–Cl(2)	69.3(2)	W(1)–Cl(1)–W(2)	85.97(8)
C(3)–W(1)–Cl(2)	83.7(3)	W(2)–Cl(2)–W(1)	76.40(7)
C(2)–W(1)–Cl(2)	163.1(3)	W(1)–O(1)–W(2)	113.2(3)
C(4)–W(1)–Cl(2)	84.2(3)	W(1)–O(1)–W(3)	106.8(3)
O(2)–W(1)–Cl(2)	76.6(2)	W(2)–O(1)–W(3)	106.8(3)
Cl(1)–W(1)–Cl(2)	77.84(8)	W(3)–O(2)–W(1)	104.9(3)
C(5)–W(2)–C(8)	93.3(4)	W(3)–O(2)–H(1)	119.4
C(5)–W(2)–O(1)	102.8(3)	W(1)–O(2)–H(1)	135.0
C(8)–W(2)–C(6)	104.6(4)	W(3)–O(3)–W(2)	105.7(3)
O(1)–W(2)–C(6)	106.4(3)	W(3)–O(3)–H(2)	112.9
C(5)–W(2)–C(7)	105.6(4)	W(2)–O(3)–H(2)	140.1
C(8)–W(2)–C(7)	36.7(4)	C(2)–C(1)–W(1)	73.3(6)
O(1)–W(2)–O(3)	83.2(3)	C(1)–C(2)–W(1)	69.6(6)
C(8)–W(2)–O(3)	82.0(3)	C(4)–C(3)–W(1)	72.9(6)
O(1)–W(2)–O(3)	70.5(2)	C(3)–C(4)–W(1)	70.9(6)
C(6)–W(2)–O(3)	119.3(3)	C(6)–C(5)–W(2)	72.2(6)
C(7)–W(2)–O(3)	117.4(3)	C(5)–C(6)–W(2)	70.9(6)
C(5)–W(2)–Cl(1)	119.4(3)	C(8)–C(7)–W(2)	69.9(6)
C(8)–W(2)–Cl(1)	123.8(3)	C(7)–C(8)–W(2)	73.4(6)
O(1)–W(2)–Cl(1)	73.5(2)	C(9)–C(10)–W(3)	72.8(6)

Table 4
Least squares plane calculations for $[W_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}Cl)_2(O)(\eta^2\text{-}PhC{\equiv}CPh)_5]$

Plane [a]	Atoms defining plane	Deviation (Å) with esds	Other atom deviation (Å) with esds	
1	W(1)		Cl(1)	0.185(3)
	W(2)		Cl(2)	2.088(3)
	W(3)		O(1)	0.699(6)
			O(2)	0.205(7)
2	W(3)	0.000(1)	W(1)	1.701(1)
	Cl(1)	0.001(2)	W(2)	−1.716(1)
	Cl(2)	−0.001(3)	W(1, 2) [b]	−0.008(1)
	O(1)	−0.009(6)	O(2)	1.885(6)
			O(3)	−1.871(7)
			O(4)	−0.038(7)
3	W(3)	0.000(1)	W(1)	1.708(1)
	W(1, 2) [b]	−0.001(1)	W(2)	−1.710(1)
	Cl(1)	0.013(2)	O(2)	1.887(6)
	Cl(2)	0.000(3)	O(3)	−1.869(6)
	O(1)	−0.003(6)	O(4)	−0.036(7)
	A(5) [c]	0.023(9)		

[a] The angles between the normals to the planes are as follows: plane 1–plane 2, 90.6°; plane 1–plane 3, 90.5°; plane 2–plane 3, 0.1°.
[b] W(1, 2) is the midpoint between W(1) and W(2).
[c] A(5) is the midpoint between C(9) and C(10).

$CO_2)(P^nBu_3)_3]$. Comparison of the present structure with that of Cotton et al. cannot be carried very far because of the many differences in detail between the two molecules. The mean W–(μ_3-Cl) distances are equal for the Cotton et al. molecule [32] but different for the present case. For comparison we may cite the W–Cl distances found in $[W_3Cl_7(N^tBu)_3(\mu\text{-}NPh)_3]$, where there are terminal W–Cl bonds with an average W–Cl = 2.387(4) Å, and a W–(μ_3-Cl) triple bridge with W–Cl = 2.642(5) Å [33]; also, there are the W–Cl distances found in the hexanuclear tungsten cluster [34], where the W–Cl terminal bond is 2.413 Å (av), and the W–(μ_3-Cl) bond is 2.496 Å (av). Using these as benchmarks for the different sorts of bond, we think the $W_3(\mu_3\text{-}Cl)$ picture is quite plausible.

The geometry of the coordinated diphenylacetylene molecules is normal for alkyne complexes: the C≡C bond length is increased to 1.291(13) Å (av) in diphenylacetylene molecules coordinated to W(1) and W(2) and only to 1.255(13) Å (av) in diphenylacetylene bonded to W(3); this compares with the value of 1.205 Å for that in diphenylacetylene itself. The bond angles at the alkyne carbon atoms are decreased to 143.8(8)° (av). The W–C distances to the alkyne carbons (average 2.053(10) Å) are quite short, so the overlap of metal d orbitals with the ligand π-system is likely to be substantial. Furthermore, W–C distances in *trans*-ClW(alkyne) units are much shorter (2.034(10) Å (av)) than the others (2.064(10) Å (av)). The W–C distance is sensitive to the extent of donation from $\pi\perp$ to the metal and varies in response to the donor role of the alkyne [20]. The W–C distances in the range 1.998(9)–2.092(10) Å found in **6** illustrate this phenomenon very well. The longest W–C distance (2.074(10) Å (av)) and the shortest C≡C bond (1.255(13) Å (av)) is found when the alkyne competes with a cis oxide π donor ligand. The shortest W–C distance (2.034(10) Å (av)) is found when the alkyne is trans to the chlorine ligand.

It is of interest that both alkyne groups at W(1) and W(2) are asymmetrically bonded, with one W–C bond longer than the other. The structures of bis(alkyne) compounds $[WI_2(CO)_2(\eta^2\text{-}MeC_2Me)_2]$ [7], $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ [6] and $[WI(CO)(C_4H_3N_2S)(\eta^2\text{-}MeC_2Me)_2]$ [35] described by Baker and coworkers also show this asymmetry. The fifth diphenylacetylene molecule is bonded symmetrically to W(3) with the W–C distance (2.070(9) and 2.079(10) Å) and the 'acetylenic' linkage substantially shorter (1.255(13) Å) than that in acetylene coordinated to W(1) and W(2) (1.290(13) Å (av)).

The orientation of the two diphenylacetylene ligands at the same tungsten atom is almost 'perpendicular'. The two cis alkyne ligands are parallel to each other with the A–W–A angles equal at 99.92(40)° (av). One of the PhC≡CPh ligands at W(1) and W(2) occupies a position almost directly trans to the chlorine ligand, with Cl(2)–W–A = 175.62(40)° (av). Consequently, W–Cl(2) distances are abnormally long (2.774(3) and 2.753(3) Å) and significantly longer than the W–Cl(1) distances (2.500(2) and 2.513(2) Å) of Cl(1) in the cis position to the acetylene ligands. A similar influence of the oxo ligand trans to the Cl(2) leads to an unprecedentedly long W(3)–Cl(2) distance (3.052(3) Å) and a decrease in the O(4)–W(3)–Cl(2) angle to 164.35(24)°. This distortion is frequently observed in other complexes containing strongly π-donating ligands trans to Cl [33].

In spite of the pronounced asymmetry induced by the ligands, the tungsten atoms and those bonded to them, as a whole, still retain a mirror plane which bisects the isosceles triangle of metal atoms through the midpoint of the W(1)–W(2) linkage, through the atom W(3) and midpoint of the C(9)–C(10) bond (Table 4).

Having considered all of these individual stereoelectronic components of the molecule, we can now turn to the central question, which is, what is oxidation state of individual metal atoms? Three tungsten atoms possess initially a total of 18 valence electrons. Eight metal electrons are required to form all the metal–ligand bonds. This leaves ten electrons for three tungsten atoms, which indicates a $2\frac{2}{3}$ formal oxidation state for each tungsten atom. However, the imbalance in the distribution of electronegative terminal ligands would, by itself, tend to make W(3) effectively more oxidized than W(1) and W(2). We think, the mixed valence $W_2^{II}W^{IV}O$ core is quite plausible. This raises the question as to whether that compound contains metal–metal bonds. The observed W–W distances 3.418(1), 3.304(1) and 3.294(1) Å in **6** indicate the absence of metal–metal bonds, since they are much longer than the W–W single bonds reported elsewhere, i.e. 3.222(1) Å in $[C_5H_5W(CO)_3]_2$ [36], 2.987(1) Å in $[(C_5H_5)_2W_2(CO)_4(C_2H_2)]$ [37], 3.155 Å in $[WI(CO)_2]_2$ [38] and 3.0256(4) Å in $[W(CO)_4(\mu\text{-}PPh_2)]_2$ [39]. Compound **6** may be considered to have W–W single bonds only on the base of its diamagnetism (Evans method [40]). However, W–W separation is a poor criterion for assessing metal–metal bonding, since it is certainly influenced by the bridging hydroxo groups. Whenever bridging groups are present it is not possible to distinguish unequivocally between the direct coupling of electron spin (M–M) bonding and indirect coupling through the bridges [41]. A better criterion for assessing metal–metal bonding in multibridged systems (than the M-M separation) is the W–OH–W bridging angle, which is normally obtuse in complexes with a non-bonding metal–metal system. In **6** the W–OH–W bridging angle is 105.30(27)° (av). The mean Cl–W–Cl (77.93(8)° (av)) and W–Cl–W (75.05(6)° (av)) angles, which are very sensitive to the nature of W–W bonding are within the range found in $[W_2Br_2(CO)_8]$ [42] and in **1** [2]; this ensures that there is no W–W bonding. A direct W–W bond leads to much larger Cl–W–Cl angles (ca. 90°) and much more acute W–Cl–W angles (ca. 60°) [33,43,44].

3. Experimental details

Physical measurements and analysis were carried out as described previously [3–4] All reactions were carried out under nitrogen by standard Schlenk line techniques. The solvents and reagents applied were dried, distilled and deoxygenated.

IR spectra were recorded with Nicolet FT-IR Model-400 instrument. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on an AMX 300 Brucker spectrometer. The UV–visible absorption spectra were recorded with a Hewlett Packard 8452A spectrophotometer.

3.1. $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ (1)

$[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ (**1**) was prepared by photochemical reaction of $W(CO)_6$ and $SnCl_4$ according to the literature method [1].

3.2. Reaction of 1 with alkynes

1 was prepared from $W(CO)_6$ (1 g, 2.8 mmol) and dissolved in toluene (20 cm^3). The solution was stirred and alkyne (5.6 mmol) was added by syringe (diphenylacetylene as a solution in toluene). The alkynes react immediately and vigorously with the tungsten complex. The solution was set aside at room temperature for ca. 1 h. Solvent was removed in vacuo, leaving a greenish-yellow (orange in the case of phenylacetylene) residue, which was then washed with heptane and pumped dry.

3.2.1. Reaction of 1 with HC≡CPh; $[WCl_2(CO)_2(\eta^2\text{-}HC{\equiv}CPh)_2]$ (2)

Reaction of **1** with HC≡CPh in toluene gives a reddish-orange solution of products. The IR spectrum of the reaction mixture showed a decay of the ν(CO) absorption due to **1** with the accompanying appearance of new absorption at 2096 cm^{-1}. The mixture was left stirring for 1 h. The addition of heptane gave the amorphous orange solid. This was filtered off, washed with heptane and dried in vacuo. Satisfactory analysis could not be obtained for compound **2** owing to its instability and difficulty in separation from the W–Sn alkyne complex and poly(phenylacetylene).

IR (cm^{-1}) (Nujol): ν(C≡O) 2108sh, 2096vs, ν(W–Cl) 340, 320, 288, 276, 236, 214. NMR (ppm) ($CDCl_3$, 293 K): ^1H, δ 12.41, (*H*C≡).

3.2.2. Reaction of 1 with HC≡C^{t}Bu; $[WCl_2(CO)_2(\eta^2\text{-}HC{\equiv}C^tBu)_2]$ (3)

Reaction of **1** with HC≡C^{t}Bu gives a greenish-yellow solution and a white solid of poly(*tert*-butylacetylene). Filtration followed by removal of the solvent in vacuo gave a greenish-yellow oil. Trituration of the greenish-yellow oily residue with hexane gave a greenish-yellow solid, which was filtered off and pumped dry.

IR (cm^{-1}) (Nujol): ν(C≡O) 2075, ν(C≡C) ca. 1600w (broad), ν(W–Cl) 288, 276, 248, 230, 212. NMR (ppm) ($CDCl_3$, 293 K): ^1H, δ 11.34, 11.09 (*H*C≡), 1.45, 1.33, (s, CH_3). $^{13}C\{^1H\}$, δ 208.04, 206.51 (*C*O), 170.31, 154.96 (s, *C*≡*C*), 41.77, 40.15 (C_1^tBu), 31.74, 29.54 (*C*H_3).

3.2.3. Reaction of 1 with EtC≡CEt; $[WCl_2(CO)_2(\eta^2\text{-}EtC{\equiv}CEt)_2]$(4) and $[WCl(SnCl_3)(CO)(\eta^2\text{-}EtC{\equiv}CEt)_2]$(4′)

The **1** prepared from $W(CO)_6$ (1 g, 2.8 mmol) was dissolved in 20 cm^3 of toluene. 3-hexyne (5.6 mmol) was added to the solution via syringe. The reaction mixture was stirred at room temperature for 1 h. The solvent was removed, and the residue was extracted with 2 × 10 cm^3 of toluene. The extracts were concentrated to ca. 5.0 cm^3 and 10 cm^3 heptane was then added. Green oil was isolated after a few days of cooling at −20°C but could not be crystallized; it was therefore characterized only in solution by spectroscopic methods.

IR (cm^{-1}) (Nujol): ν(C≡O) 2048(broad), (heptane) 2060, ν(C≡C) 1640w (broad), ν(W–Cl) 300, 276, 256, 232, 222. NMR (ppm) ($CDCl_3$, 293 K): ^1H, δ 3.91, 3.49, 3.27, 3.11 (m, CH_2), 1.36, 1.32, 1.29, 1.22 (t,

CH_3). $^{13}C\{^1H\}$, δ 207.80, 207.70 (*C*O), 183.96, 179.72, 170.89, 159.22 ($C \equiv C$), 27.57 (CH_2), 14.91 (CH_3).

3.2.4. Reaction of 1 with $PhC \equiv CPh$; $[WCl_2(CO)_2(\eta^2\text{-}PhC \equiv CPh)_2]$ (5)

The solution of PhC≡CPh in toluene was added to an orange solution of **1**, prepared as describe above, in toluene (20 cm^3) with continuous stirring under a stream of nitrogen. The solution immediately became greenish-yellow and a precipitate formed. After 1 h stirring the addition of heptane gave the amorphous greenish-yellow solid of **5**, which was recrystallised from CH_2Cl_2–heptane.

Anal. Found: C, 53.5; H, 2.8; Cl, 12.3. $C_{30}H_{20}Cl_2W$. Calc: C, 54.0; H, 3.0; Cl, 10.6%. IR (cm^{-1}) (Nujol): $\nu(C \equiv O)$ 2094vs, 2087vs, $\nu(C \equiv C)$ 1614w (broad), $\nu(W–C_2) + \delta(W–C)$ 598vw, 588vw, 574w, 509m, 382w, ν(W–Cl) 288vw, 264vw, 236vw. NMR (ppm) ($CDCl_3$, 293 K): ^1H, δ 7.8–6.8 (m, *Ph*). $^{13}C\{^1H\}$, δ 201.75 ($J_{^{183}W-^{13}C} = 121.3$ Hz) (*C*O), 185.50, 169.88 ($C \equiv C$), 138.22, 135.01 (Ph_{ipso}), 130.52, 128.82, 128.31, 127.34 ($Ph_{o,m}$), 129.01, 127.86 (Ph_p).

3.2.5. Preparation of $[W_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}Cl)_2(O)(\eta^2\text{-}PhC \equiv CPh)_5]$ (6)

During the prolonged crystallization of **5** compound **6** was formed instead (ca. 10% yield based on the amount of **1** used). The complex **5** was crystallized by slow evaporation from a mixture of dichloromethane–toluene–heptane (1 : 10 : 5) yielding pale yellow crystals of **6**. This was washed with heptane, dried and used in the X-ray determination. It is moderately air-stable in the solid state but less so in solution, soluble in CH_2Cl_2 and very slightly soluble in $CHCl_3$ but insoluble in toluene and aliphatic hydrocarbons.

Anal. Found: C, 53.8; H, 3.9; Cl, 4.9. $C_{70}H_{52}Cl_2O_4W$. Calc: C, 53.2; H, 3.2; Cl, 4.5%. IR (cm^{-1}) (Nujol): ν(OH) 3545s, $\nu(C \equiv C)$ 1624w (broad), $\nu(W=O)$ 972s, ν(W–OH–W) 631m, 601m, $\nu(W–C_2)$ 556w, 589w, 596w, $\nu(W–Cl_2–W)$ 282vw, 239w. NMR (ppm) ($CDCl_3$, 293 K): ^1H, δ 5.04 (s, O*H*), 7.8–6.8 (m, *Ph*). $^{13}C\{^1H\}$, δ 203.01, 201.43, 190.37, 187.11, 164.93 ($C \equiv C$), 140.77, 139.51, 138.91, 137.17, 134.80 (Ph_{ipso}), 129.85, 129.66, 129.35, 129.18, 129.11, 128.76, 128.47, 128.21, 127.99, 127.87 ($Ph_{o,m}$), 129.25, 126.92, 128.41, 128.38, 127.74 (Ph_p). UV–vis($CHCl_3$) λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 254(80 000), 292(48 700), 302(18 700), 318(18 500).

3.3. Crystal structure analysis of $[W_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}Cl)_2(O)(\eta^2\text{-}PhC \equiv CPh)_5]$ (6)

Numerous attempts to grow single crystals of $[WCl_2(CO)_2(\eta^2\text{-}PhC \equiv CPh)_2]$ (**5**) complex were made. We obtained crystals which turned out to be extremly poor scatterers of X-rays. Finally, crystals of **6** suitable for X-ray diffraction studies were formed by very slow evaporation of a CH_2Cl_2–toluene–heptane solution of **5**. The single crystals used for X-ray examination were removed from the flask and coated with a light hydrocarbon oil to protect them from the atmosphere.

Table 5
Crystal data and details of refinement for $[W_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}Cl)_2(O)(\eta^2\text{-}PhC \equiv CPh)_5]$ (6)

Chemical formula	$C_{70}H_{52}Cl_2O_4W_3$
Molecular weight	1579.57
Crystal system	monoclinic
Space group	$P2_1/n$
Cell constants	
a (Å)	14.195(3)
b (Å)	17.720(4)
c (Å)	23.225(5)
β(deg)	90.88(3)
U ($Å^3$)	5841(2)
Z	4
T (K)	293(2)
Crystal size (mm^3)	0.15 × 0.15 × 0.25
D_c (g cm^{-3})	1.798
λ(Mo Kα) (Å)	0.71069
μ(Mo Kα) (cm^{-1})	60.35
F(000)	3040
Method of collection	ω–2Θ scan
Reflections determining lattice	40
2Θ range (deg)	22.5 < 2Θ < 26.8
2Θ limit (deg)	2.0–24.0
No. of unique data	8689
No. of data with $I \geq 3\sigma(I)$	5579
Residuals R_1, wR_2	0.0305, 0.0770
Quality of fit	1.097
Final (Δρ) (e $Å^{-3}$)	−0.916/1.255

Crystallographic data were obtained using a KM4 κ-axis computer-controlled [45] four-circle diffractometer, operating in the ω–2θ scan mode and using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). No absorption or extinction corrections were applied. A total of 8689 unique reflections were measured, of which 5579 with $I \geq 3\sigma(I)$ were used to solve and refine the structure in the monoclinic space group $P2_1/n$. Cell dimensions were obtained by a least squares refinement on setting angles of 40 well-spaced reflections in the range 22.5 < θ < 36.8°. The details of the crystal data intensity measurement are given in Table 5.

The structure was solved by heavy-atom methods with the SHELXS-86 program [46] and refined by a full-matrix least squares method, using the SHELXL program [47]. All hydrogens were located. The final atomic positions are given in Table 2. For non-hydrogen atoms, refinement with anisotropic temperature factors converged to $R_1 = 0.0305$ and $wR_2 = 0.0770$. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and the remaining bond lengths and angles. Neutral atomic scattering factors were taken from the SHELXL 93 program [47].

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