

## 1,4-Diphenylbutadiyne complexes of tungsten(II)

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### Abstract

Equimolar quantities of  $[\text{W}(\text{CO})_3(\text{NCMe})_2]$  and 1,4-diphenylbutadiyne ( $\text{PhC}_2\text{C}_2\text{Ph}$ ) react in  $\text{CH}_2\text{Cl}_2$  at room temperature to eventually give the iodo-bridged dimer  $[\text{W}(\mu\text{-I})(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (1). Reaction of  $[\text{W}(\text{CO})_3(\text{NCMe})_2]$  with two equivalents of  $\text{PhC}_2\text{C}_2\text{Ph}$  eventually afforded  $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (2). The bimetallic 1,4-diphenylbutadiyne complex  $[\text{W}_2\text{I}_4(\text{CO})_2(\text{NCMe})_2(\mu^2, \mu^2', \eta^2, \eta^2'\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (3) was synthesized by reaction of equimolar quantities of 2 and  $[\text{W}_2(\text{CO})_3(\text{NCMe})_2]$ . The reactions of 1 and 2 with mono- and bidentate neutral donor ligands are also described.

**Key words:** Tungsten; Butadiyne; Iodide; Acetonitrile; Carbonyl; Bimetallic

### 1. Introduction

Alkyne complexes of molybdenum and tungsten in oxidation state +2 have received considerable attention during the past 30 years [1–10] and the findings were the subject of an extensive review by Templeton in 1989 [11]. Butadiyne complexes are, however much less well known. Two crystallographically characterized examples are the tungsten(IV) dimeric complex  $[\text{W}_2\text{Cl}_8(\text{py})_2(\mu^2, \mu^2', \eta^2, \eta^2'\text{-PhC}_2\text{C}_2\text{SiMe}_3)]$  [12] and the dimeric cyclopentadienyl complex  $[\text{Mo}(\text{CO})_2\text{Cp}_2(\mu^2, \eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$  which was prepared by the thermolysis of  $[\text{Mo}=\text{CPh}(\text{CO})_3\text{Cp}]$  in octane at 110–115°C [13]. Up to now, as far as we are aware, there have been no reports of simple mononuclear complexes of molybdenum(II) and tungsten(II) with an attached 1,4-diphenylbutadiyne ligand. In this paper we describe the preparation and characterization of a series of new 1,4-diphenylbutadiyne complexes of tungsten(II).

### 2. Results and discussion

The starting material  $[\text{W}(\text{CO})_3(\text{NCMe})_2]$  was prepared by treating *fac*- $[\text{W}(\text{CO})_3(\text{NCMe})_3]$  [14] *in situ* with an equimolar amount of  $\text{I}_2$  at 0°C [15]. Reaction of  $[\text{W}(\text{CO})_3(\text{NCMe})_2]$  with one equivalent of 1,4-di-

phenylbutadiyne ( $\text{PhC}_2\text{C}_2\text{Ph}$ ) in  $\text{CH}_2\text{Cl}_2$  at 0°C with the mixture subsequently allowed to warm to room temperature and stirred for 20 h gave the iodo-bridged dimer  $[\text{W}(\mu\text{-I})(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (1) in high yield. Two equivalents of  $\text{PhC}_2\text{C}_2\text{Ph}$  were found to react with  $[\text{W}(\text{CO})_3(\text{NCMe})_2]$  in  $\text{CH}_2\text{Cl}_2$  at room temperature to give  $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (2), also in high yield. Equimolar quantities of  $[\text{W}(\text{CO})_3(\text{NCMe})_2]$  and 2 reacted in  $\text{CH}_2\text{Cl}_2$  at room temperature to give the novel bimetallic 1,4-diphenylbutadiyne-bridged-complex  $[\text{W}_2\text{I}_4(\text{CO})_2(\text{NCMe})_2(\mu^2, \mu^2', \eta^2, \eta^2'\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (3) in good yield. Reaction of 1 with either four equivalents of L (L =  $\text{PPh}_3$ ,  $\text{PPh}_2\text{Cy}$ ) or two equivalents of  $\text{L}^{\wedge}\text{L}$  ( $\text{L}^{\wedge}\text{L}$  = 2,2'-bipy, 1,10-phen,  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1\text{--}6$ )) in  $\text{CH}_2\text{Cl}_2$  at room temperature afforded the mono ( $\text{PhC}_2\text{C}_2\text{Ph}$ ) complexes  $[\text{W}_2(\text{CO})\text{L}_2(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$  (4 and 5) or  $[\text{W}_2(\text{CO})(\text{L}^{\wedge}\text{L})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$  (6–13), respectively. Equimolar quantities of 2 and 2,2'-bipy reacted in  $\text{CH}_2\text{Cl}_2$  at room temperature to give the cationic bis ( $\text{PhC}_2\text{C}_2\text{Ph}$ ) complex  $[\text{W}(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]\text{I}$  (14). The cationic nature of this complex was confirmed by treating  $[\text{W}(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]\text{I}$  (14) (prepared *in situ*) with  $\text{Na}[\text{BPh}_4]$  in acetonitrile to afford the tetraphenylborate salt  $[\text{W}(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2][\text{BPh}_4]$  (15). All the new complexes described in this paper were characterized by elemental analysis (C, H and N) (Table 1), infrared (Table 2), and  $^1\text{H}$  NMR spectroscopy (Table 3), and in

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selected cases by  $^{13}\text{C}$  (Table 4) and  $^{31}\text{P}$  NMR spectroscopy. All the new complexes 1–15 are reasonably stable in the solid state when stored under nitrogen, but very much less stable in solution. They are all moderately soluble in chlorinated solvents such as  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , but only slightly soluble in hydrocarbon solvents and diethyl ether. The alkyne derivatives 1–3 are also generally more soluble than the 2,2'-bipy and phosphine complexes 4–15.

The formation of the dimeric complex  $[\text{W}(\mu\text{-I})(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (1) is likely to proceed *via* initial displacement of two CO ligands to give  $[\text{W}_2(\text{CO})(\text{NCMe})_2(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$ , which then dimerizes to give 1, since we have previously observed this behaviour with other alkynes  $\text{RC}_2\text{R}$  reacting with  $[\text{W}_2(\text{CO})_3(\text{NCMe})_2]$  [16]. The most likely structure of 1 which was suggested previously for other alkynes [16], is shown in Fig. 1. Reaction of  $[\text{W}_2(\text{CO})_3(\text{NCMe})_2]$

TABLE 1. Physical and analytical data for the 1,4-diphenylbutadiyne complexes of tungsten(II)

Complex	Colour	Yield (%)	Analytical data (found(calc.)(%))		
1	$[\text{W}(\mu\text{-I})(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$	Brown/black	91	C	32.2 (32.2)
				H	1.9 (1.9)
				N	1.9 (2.0)
2	$[\text{W}_2(\text{CO})(\text{NCMe})_2(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$	Deep Gold	94	C	45.8 (46.0)
				H	2.5 (2.5)
				N	1.8 (1.5)
3	$[\text{W}_2\text{I}_4(\text{CO})_2(\text{NCMe})_2(\mu^2, \mu^{2'}, \mu^2, \mu^{2'}\text{-PhC}_2\text{C}_2\text{Ph})_2]$	Orange/brown	98	C	32.3 (32.1)
				H	2.1 (1.9)
				N	1.9 (2.0)
4	$[\text{W}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$	Brown	79	C	54.0 (53.4)
				H	3.4 (3.4)
				N	–
5	$[\text{W}_2(\text{CO})(\text{PPh}_2\text{Cy})_2(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$	Green/brown	80	C	52.1 (52.9)
				H	4.8 (4.4)
				N	–
6	$[\text{W}_2(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$	Brown/black	81	C	39.6 (39.5)
				H	2.4 (2.3)
				N	3.2 (3.4)
7	$[\text{W}_2(\text{CO})(1,10\text{-phen})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$	Dark brown	71	C	40.1 (41.0)
				H	2.4 (2.1)
				N	3.0 (3.3)
8	$[\text{W}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2)(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$	Bottle green	88	C	47.5 (47.9)
				H	3.3 (3.1)
				N	–
9	$[\text{W}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$	Green/brown	59	C	47.7 (48.4)
				H	3.4 (3.2)
				N	–
10	$[\text{W}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$	Green/brown	77	C	49.3 (48.9)
				H	3.7 (3.4)
				N	–
11	$[\text{W}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$	Green/brown	52	C	48.6 (49.5)
				H	3.8 (3.5)
				N	–
12	$[\text{W}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2)(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$	Dark brown	64	C	49.0 (49.9)
				H	3.8 (3.6)
				N	–
13	$[\text{W}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2)(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$	Black	73	C	49.6 (50.2)
				H	4.0 (3.8)
				N	–
14	$[\text{W}(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]\text{II}$	Brown	89	C	50.5 (50.3)
				H	2.9 (2.8)
				N	3.0 (2.7)
15	$[\text{W}(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]\text{-}[\text{BPh}_4]$	Brown	29	C	65.6 (66.0)
				H	3.9 (4.0)
				N	2.2 (2.3)

TABLE 2. Infrared data<sup>a</sup> for the 1,4-diphenylbutadiyne complexes of tungsten(II)

Complex	$\nu(\text{C}=\text{O})(\text{cm}^{-1})$	$\nu(\text{N}=\text{C})(\text{cm}^{-1})$	$\nu(\text{C}\equiv\text{C})(\text{cm}^{-1})$ (coord.)	$\nu(\text{C}\equiv\text{C})(\text{cm}^{-1})$ (uncoord.)
1	2057s 2003s	2338w 2463w	1606w	2102w
2	2101s	2225w 2299w	1732w	2180w
3	2055s 1995s	2227w 2310w	1710w	—
4	1960s	—	1634w	2165w
5	1956s	—	1588w	1999w
6	1947s	—	1638w	2020w
7	1952s	—	1606w	2021w
8	1956s	—	1588w	2076w
9	1966s	—	1587w	2076w
10	1967s	—	1588w	2076w
11	1959s	—	1588w	2077w
12	1959s	—	1587w	2076w
13	1957s	—	1588w	2077w
14	2078s	—	1604w	2076w
15	2078s	—	1606w	2076w

<sup>a</sup> Spectra were recorded in  $\text{CHCl}_3$  as thin films between NaCl plates. s, strong; w, weak.

TABLE 3. <sup>1</sup>H NMR data<sup>a</sup> for the 1,4-diphenylbutadiyne complexes of tungsten(II)

Complex	<sup>1</sup> H ( $\delta$ )(ppm)
1	2.1 (s, 6H, NCMe); 7.14–7.22 (brm, 20H, Ph)
2	2.52 (s, 3H, NCMe); 7.14–7.96 (brm, 20H, Ph)
3	2.0 (s, 6H, NCMe); 7.27–7.71 (brm, 20H, Ph)
4	7.25–7.80 (brm, Ph)
5	0.82–1.94 (brm, 22H, Cy); 6.84–8.11 (brm, 30H, Ph)
6	7.18–7.52 (brm, 10H, Ph); 7.84 (t, 2H, H's <sub>5,8</sub> 2,2'-bipy); 8.32 (t, 2H, H's <sub>3,10</sub> 2,2'-bipy); 8.80, 8.83 (d, 2H, H's <sub>4,9</sub> 2,2'-bipy); 9.12, 9.14 (d, 2H, H's <sub>3,10</sub> 2,2'-bipy)
7	7.15–7.71 (brm, 10H, Ph); 7.80, 7.84 (d, 4H, H's <sub>3,6,7,10</sub> 1,10-phen); 8.02 (m, 2H, H's <sub>4,9</sub> 1,10-phen); 8.51 (brm, 2H, H's <sub>2,11</sub> 1,10-phen)
8	4.56 (brm, 2H, PCH <sub>2</sub> ); 7.09–7.32 (brm, 30H, Ph)
9	3.8, 4.4 (2×brm, 4H, PCH <sub>2</sub> ); 6.91–8.06 (brm, 30H, Ph)
10	1.72 (brm, 2H, CH <sub>2</sub> ); 2.5, 2.9 (2×brm, 4H, PCH <sub>2</sub> ); 7.14–8.06 (brm, 30H, Ph)
11	1.8 (brm, 4H, CH <sub>2</sub> ); 2.3, 3.1 (2×brm, 4H, PCH <sub>2</sub> ); 7.0–8.3 (brm, 30H, Ph)
12	0.9 (brm, 2H, PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ); 2.3 (brm, 4H, PCH <sub>2</sub> CH <sub>2</sub> ); 3.1 (brm, 4H, PCH <sub>2</sub> ); 7.1–8.2 (brm, 30H, Ph)
13	0.85 (brm 4H, PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ); 2.3 (brm, 4H, PCH <sub>2</sub> CH <sub>2</sub> ); 3.0 (brm, 4H, PCH <sub>2</sub> ); 7.0–7.7 (brm, 30H, Ph)
14	7.1–7.8 (brm, 20H, Ph); 7.8 (t, 2H, H's <sub>5,8</sub> 2,2'-bipy); 8.4 (t, 2H, H's <sub>3,10</sub> 2,2'-bipy); 8.8, 8.88 (d, 2H, H's <sub>4,9</sub> 2,2'-bipy); 9.2, 9.27 (d, 2H, H's <sub>2,11</sub> 2,2'-bipy)
15	6.8–8.1 (brm, 42H, Ph and H's <sub>5,8</sub> 2,2'-bipy); 8.5 (t, 2H, H's <sub>3,10</sub> 2,2'-bipy); 8.9, 8.94 (d, 2H, H's <sub>4,9</sub> 2,2'-bipy); 9.2, 9.24 (d, 2H, H's <sub>2,11</sub> 2,2'-bipy)

<sup>a</sup> Spectra recorded in  $\text{CDCl}_3$  (+25°C) referenced to  $\text{SiMe}_4$ . brm, broad multiplet; d, doublet; s, singlet; t, triplet.

TABLE 4. <sup>13</sup>C NMR data<sup>a</sup> for selected 1,4-diphenylbutadiyne complexes of tungsten(II)

Complex	<sup>13</sup> C ( $\delta$ ) ppm
3	196.22 (s, CO); 178.41, 172.70, 168.28, 166.46 (s, C≡C); 134.24–123.45 (brm, Ph); 116.95 (s, C≡N); 7.41 (s, CH <sub>3</sub> )
15	211.5 (s, CO); 176.0, 168.2 (2s, C≡C); 136.1 → 121.70 (m, 2,2'-bipy; C's + Ph); 81.60, 77.50 (2s, uncoordinated C≡C).

<sup>a</sup> Spectra recorded in  $\text{CD}_2\text{Cl}_2$  (+25°C) referenced to  $\text{SiMe}_4$ . brm, broad multiplet; m, multiplet; s, singlet.

with two equivalents of  $\text{PhC}_2\text{C}_2\text{Ph}$ , which eventually gives the bis(alkyne) complex  $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (**2**) proceeds *via* the dimeric complex **1**. It should be noted that reaction of **1** with two equivalents of  $\text{PhC}_2\text{C}_2\text{Ph}$  in  $\text{CH}_2\text{Cl}_2$  at room temperature gave **2** by symmetric cleavage of the iodo-bridges. The most likely structure of **2** has the two  $\text{PhC}_2\text{C}_2\text{Ph}$  ligands *cis* and parallel to each other and *trans* to the two iodo-ligands, with CO and NCMe occupying the two axial positions, as shown in Fig. 2. This arrangement of ligands around the tungsten centre was previously observed for the closely related complexes  $[\text{W}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$  (R = Me or Ph) [17],  $[\text{W}_2(\text{CO})_2(\eta^2\text{-MeC}_2\text{Me})_2]$  [18], and  $[\text{W}_2(\text{CO})\{\text{NCCH}_2(3\text{-C}_4\text{H}_3\text{S})\}(\eta^2\text{-MeC}_2\text{Me})_2]$   $\{\text{NCCH}_2(3\text{-C}_4\text{H}_3\text{S}) = \text{thiophene-3-acetonitrile}\}$  [19], which were all crystallographically characterized. The infrared spectrum of (**2**) shows a broad single carbonyl band at 2101  $\text{cm}^{-1}$ , *i.e.* in a similar position to that for the bis(diphenylacetylene) complex, which has  $\nu(\text{C}=\text{O})$  at 2090  $\text{cm}^{-1}$  [17]. There is also a medium band due to the uncoordinated C≡C part of the 1,4-diphenylbutadiyne ligand at 2180  $\text{cm}^{-1}$ . The C≡C band for the coordinated diynes is at 1732  $\text{cm}^{-1}$  a very low wavenumber compared with that for the “free”  $\text{PhC}_2\text{C}_2\text{Ph}$  (2223

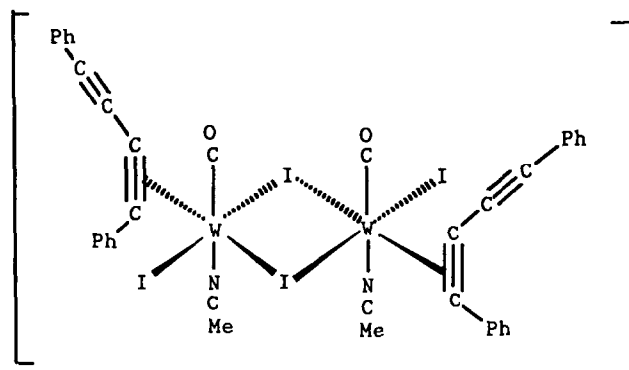


Fig. 1. Proposed structure for  $[\text{W}(\mu\text{-I})\text{I}(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]_2$  (**1**).

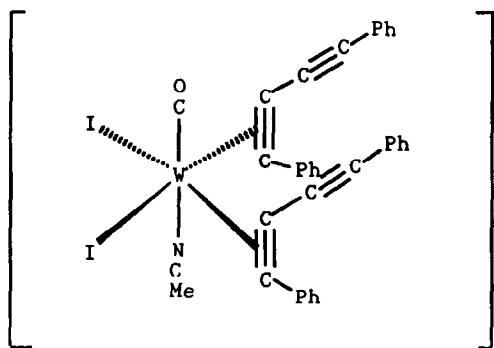


Fig. 2. Proposed structure for  $[WI_2(CO)(NCMe)(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (2).

$\text{cm}^{-1}$  in the Raman spectrum). Several attempts to obtain a satisfactory  $^{13}\text{C}$  NMR spectrum for **2**, were unsuccessful, probably because of the instability in solution even under a nitrogen atmosphere during the prolonged period required for  $^{13}\text{C}$  NMR spectroscopy.

In order to confirm that the uncoordinated alkyne moieties in **2** are *cis* to each other (Fig. 2) and not *trans* to each other, the reaction of equimolar quantities of **2** and  $[WI_2(CO)_3(NCMe)_2]$  was carried out. The product was the highly novel bimetallic 1,4-diphenylbutadiyne-bridged complex  $[W_2I_4(CO)_2(NCMe)_2(\mu^2, \mu^{2'}\text{-}\eta^2, \eta^{2'}\text{-1,4-PhC}_2\text{C}_2\text{Ph})_2]$  (**3**), which must have been formed starting from the geometry shown in Fig. 2. Since it is well known that the substituents attached to an alkyne bend back when coordinated to the metal the probable structure of **3** is shown in Fig. 3. Since the infrared spectrum shows two carbonyl bands, at 2055 and 1995  $\text{cm}^{-1}$ , the most likely structure is that shown in Fig. 3, with *cis*-carbonyl ligands. There are, as expected, four alkyne contact-carbon resonances at  $\delta = 178.41, 172.70, 168.28$  and 166.46 ppm, which is in accord with both halves of the dimer obeying the effective atomic number rule if both diynes donate a

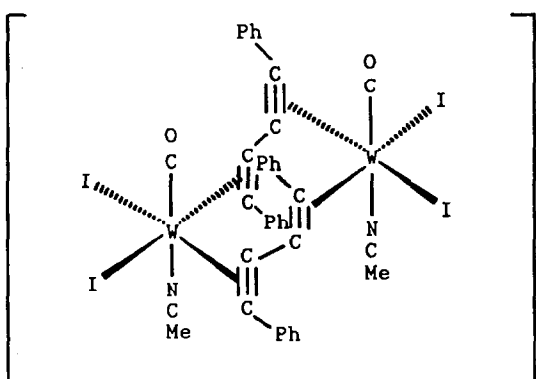


Fig. 3. Proposed structure for the 1,4-diphenylbutadiyne-bridged complex  $[W_2I_4(CO)_2(NCMe)_2(\mu^2, \mu^{2'}, \eta^2, \eta^{2'}\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (**3**).

total of six-electrons to each tungsten centre. These values are in agreement with Templeton and Ward's [20] correlation of the number of electrons donated by an alkyne ligand to a transition-metal centre and the alkyne contact carbon chemical shifts. Several attempts were made to grow suitable single crystals for X-ray crystallography of complexes **1–3** without success. It should be noted that several unsuccessful attempts were also made to prepare the molybdenum analogues of complexes **1** and **2**. These complexes are considerably less stable compared to their tungsten analogues. These observations are in agreement with our previous work on alkyne complexes of molybdenum(II) and tungsten(II) [16,17].

Four equivalents of the monodentate phosphine ligands *L* (*L* =  $\text{PPh}_3$  or  $\text{PPH}_2\text{Cy}$ ) react with **1** to give the bis(phosphine) complexes  $[WI_2(CO)L_2(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$  (**4**, **5**). The  $^{31}\text{P}$  ( $^1\text{H}$ ) NMR spectrum ( $\text{CDCl}_3$ , +25°C) of **4** (*L* =  $\text{PPh}_3$ ) shows a single resonance at  $\delta +33.9$  ppm (relative to 85%  $\text{H}_3\text{PO}_4$ ), which suggests that both phosphines are in the same environment *i.e.* *trans* to each other as would be expected from steric considerations. The molecular structure of the closely related complex  $[\text{MoBr}_2(\text{CO})(\text{PET}_3)_2(\eta^2\text{-PhC}_2\text{H})]$  has been crystallographically determined [21] and it is very likely that the structure of complexes **4** and **5** is similar, as shown in Fig. 4.

Reaction of the dimer **1** with two equivalents of the potentially bidentate donor ligands  $L^{\wedge}L$  ( $L^{\wedge}L = 2,2'$ -bipy, 1,10-phen,  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1\text{--}6$ )) in  $\text{CH}_2\text{Cl}_2$  at room temperature gave the symmetrically bridge-cleaved products  $[WI_2(\text{CO})(L^{\wedge}L)(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$  (**6–13**). Attempts to grow suitable single crystals of **6–13** for X-ray crystallography were unsuccessful but the molecular structure of the related but-2-yne complex  $[WI_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2)(\eta^2\text{-MeC}_2\text{Me})]$  was determined previously [22] and it is probable that the structure of **6–13** is similar (Fig. 5). It is noteworthy

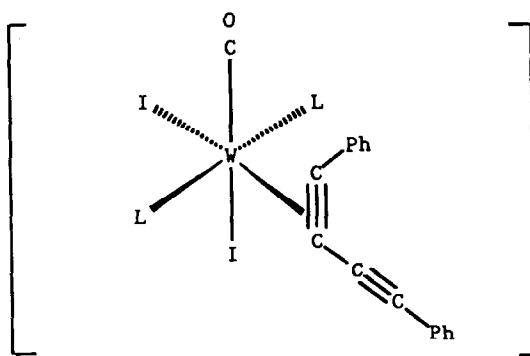


Fig. 4. Proposed structure for  $[WI_2(CO)L_2(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$  [*L* =  $\text{PPh}_3$  (**4**) or  $\text{PPH}_2\text{Cy}$  (**5**)].

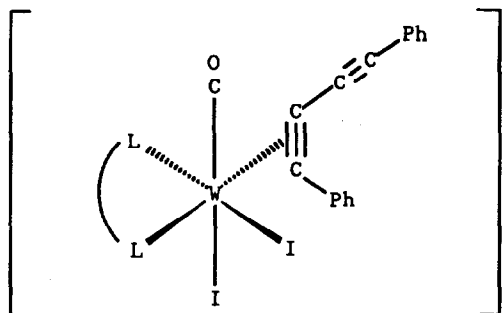


Fig. 5. Proposed structure for  $[W_{12}(CO)(L^2L)(\eta^2-PhC_2C_2Ph)]$  (6–13).

that we have previously reported only bis(alkyne) complexes which contain more electron-rich bidentate nitrogen donor ligands  $[W(CO)(N^{\wedge}N)(\eta^2-RC_2R)_2]I$  ( $R = Me$  or  $Ph$ ;  $N^{\wedge}N = 2,2'$ -bipy, 1,10-phen, *o*-phenylenediamine) from reaction of  $[W_2(CO)(NCMe)(\eta^2RC_2R)_2]$  and  $N^{\wedge}N$  [23]. However, since the dimer **1** has only one alkyne attached to each tungsten, the final product from reaction with  $N^{\wedge}N$  ( $N^{\wedge}N = 2,2'$ -bipy, 1,10-phen) must be the mono(alkyne) complexes **6** and **7**. Attempts to obtain high quality  $^{13}C$  NMR spectra of **6–13** were unsuccessful owing to a combination of relatively poor solubility in a range of deuterated solvents and instability in solution.

Equimolar quantities of **2** and 2,2'-bipy give the expected bis(alkyne) complex  $[W(CO)(2,2'-bipy)(\eta^2-PhC_2C_2Ph)_2]I$  (**14**). The previously crystallographically characterized bis(but-2-yne) complex  $[W(CO)(2,2'-bipy)(\eta^2-MeC_2Me)_2][BPh_4]$  [23], and the structures of **14** and its tetraphenylborate analogue **15** are likely to be similar, as shown in Fig. 6. The  $^{13}C$  NMR spectrum of **15** which was considerably more soluble than **14** as its tetraphenylborate salt shows alkyne contact resonances at 168.2 and 176.0 ppm, which indicates [20] both alkynes donate a total of six-electrons to the

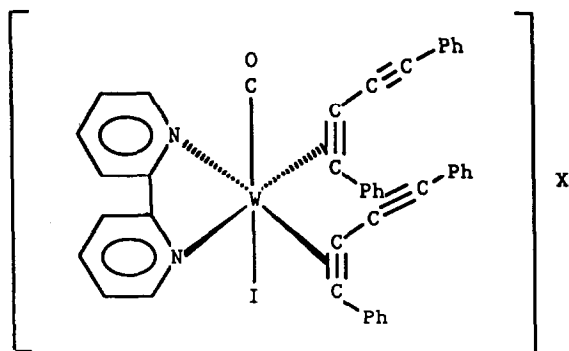


Fig. 6. Proposed structure for  $[W(CO)(2,2'-bipy)(\eta^2-PhC_2C_2Ph)_2]X$  ( $X = I$  (**14**),  $X = [BPh_4]$  (**15**)).

metal. Resonances for the uncoordinated alkyne moieties at  $\delta$  81.60 and 77.50 were also observed.

We are currently studying the reactions of the uncoordinated alkyne moiety of selected complexes reported in this paper with other transition-metal centres with the aim of forming mixed-metal complexes and cyclizing the alkynes to give cyclobutadiene transition-metal complexes.

### 3. Experimental details

All reactions described in this paper were carried out under dry nitrogen by use of standard Schlenk line techniques. The complex  $[W_2(CO)_3(NCMe)_2]$  was prepared by the published method [15]. All other chemicals used were obtained commercially without further purification, except for solvents, which were dried and distilled before use.

Elemental analyses (C, H and N) were determined with a Carlo Erba Elemental Analyser MOD 1106 (with helium as a carrier gas). Infrared spectra were recorded on a Perkin Elmer 1430 ratio recording infrared spectrophotometer.  $^1H$  and  $^{13}C$  NMR spectra were recorded on either a Jeol FX 60 MHz or a Bruker AC 250 MHz or a Bruker WH 400 MHz NMR spectrometer. The  $^1H$  and  $^{13}C$  NMR chemical shifts were determined relative to  $SiMe_4$  and the  $^{31}P$  NMR shift of **4** relative to 85%  $H_3PO_4$ .

#### 3.1. $[W(\mu-I)(CO)(NCMe)(\eta^2-PhC_2C_2Ph)]_2$ (**1**)

To a stirred solution of  $[W_2(CO)_3(NCMe)_2]$  (2.0 g, 3.312 mmol) in  $CH_2Cl_2$  (30  $cm^3$ ) at  $0^\circ C$ , under a stream of dry nitrogen, was added  $PhC_2C_2Ph$  (0.67 g, 3.312 mmol). Effervescence of CO was observed. The mixture was allowed to warm to room temperature and stirred for 20 h. Filtration, followed by removal of the solvent *in vacuo*, gave brown/black crystals of  $[W(\mu-I)(CO)(NCMe)(\eta^2-PhC_2C_2Ph)]_2$  (**1**), which were recrystallized from  $CH_2Cl_2$ . Yield of pure product 2.13 g, 91%.

Similar reaction of  $[W_2(CO)_3(NCMe)_2]$  with two equivalents of  $PhC_2C_2Ph$  in  $CH_2Cl_2$  at  $0^\circ C$  followed by warming to room temperature and stirring to react for 20 h gave the deep gold bis( $PhC_2C_2Ph$ ) complex  $[W_2(CO)_3(NCMe)(\eta^2-PhC_2C_2Ph)_2]$  (**2**). (For physical analytical data see Table 1.)

#### 3.2. $[W_2I_4(CO)_2(NCMe)_2(\mu^2, \mu^2', \eta^2, \eta^2'-PhC_2C_2Ph)_2]$ (**3**)

To a stirred solution of  $[W_2(CO)(NCMe)(\eta^2-PhC_2C_2Ph)_2]$  (0.5 g, 0.549 mmol) in  $CH_2Cl_2$  (15  $cm^3$ ) under a stream of dry nitrogen was added  $[W_2(CO)_3(NCMe)_2]$  (0.3313 g, 0.549 mmol). The solution was stirred for 17 h then filtered. Removal of the

solvent *in vacuo* gave orange/brown crystals of  $[\text{W}_2\text{I}_4(\text{CO})_2(\text{NCMe})_2(\mu^2, \mu^2, \eta^2, \eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (**3**), which were recrystallized from  $\text{CH}_2\text{Cl}_2$ . Yield of pure product 0.38 g, 98%.

### 3.3. $[\text{WI}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$ (**4**)

To a stirred solution of  $[\text{W}(\mu\text{-I})(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (0.5 g, 0.3526 mmol) in  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ) under a stream of dry nitrogen was added  $\text{PPh}_3$  (0.37 g, 1.41 mmol). The solution was stirred for 20 h then filtered and the solvent removed *in vacuo* to give brown crystals of  $[\text{WI}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$  (**4**), which were recrystallized from  $\text{CH}_2\text{Cl}_2$ . Yield of pure product 0.66 g, 79%.

A similar reaction of  $[\text{W}(\mu\text{-I})(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  with four equivalents of  $\text{PPh}_2\text{Cy}$  in  $\text{CH}_2\text{Cl}_2$  at room temperature gave the green/brown complex  $[\text{WI}_2(\text{CO})(\text{PPh}_2\text{Cy})_2(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$  (**5**). (See Table 1 for physical and analytical data.)

### 3.4. $[\text{WI}_2(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$ (**6**)

To a stirred solution of  $[\text{W}(\mu\text{-I})(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (0.5 g, 0.3526 mmol) in  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ) under a stream of dry nitrogen were added two equivalents of 2,2'-bipyridyl (0.11 g, 0.7052 mmol). The solution was stirred for 20 h, filtered and the solvent removed *in vacuo* to give brown/black crystals of  $[\text{WI}_2(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$  (**6**), which were recrystallized from  $\text{CH}_2\text{Cl}_2$ . Yield of pure product 0.469 g, 81%.

Similar reactions of  $[\text{W}(\mu\text{-I})(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  with two equivalents of  $\text{L}^{\wedge}\text{L}$  ( $\text{L}^{\wedge}\text{L} = 1,10\text{-phen}, \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1\text{-}6$ )) in  $\text{CH}_2\text{Cl}_2$  at room temperature afforded the analogous complexes  $[\text{WI}_2(\text{CO})(\text{L}^{\wedge}\text{L})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$  (**7-13**). (See Table 1 for physical and analytical data.)

### 3.5. $[\text{WI}(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]\text{I}$ (**14**)

The procedure described in Section 3.3 but starting from  $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (0.6 g, 0.658 mmol) and 2,2'-bipyridyl (0.106 g, 0.679 mmol), for 20 hrs; filtration followed by removal of the solvent *in vacuo* gave brown crystals of  $[\text{WI}(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]\text{I}$  (**14**), which were recrystallized from  $\text{CH}_2\text{Cl}_2$ . Yield of pure product 0.62 g, 89%.

### 3.6. $[\text{WI}(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2][\text{BPh}_4]$ (**15**)

To a stirred solution of  $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2]$  (0.6 g, 0.679 mmol) in  $\text{NCMe}$  (15  $\text{cm}^3$ ) at room temperature under a stream of dry nitrogen was added 2,2'-bipyridyl (0.106 g, 0.679 mmol) followed by  $\text{Na}[\text{BPh}_4]$  (0.233 g, 0.679 mmol). The solution was stirred for 20 h and the solvent then removed *in vacuo*. The residue was redissolved in  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ) and the solution filtered twice to remove  $\text{NaI}$ . The solvent

volume was reduced to 2  $\text{cm}^3$  and diethyl ether was added dropwise to precipitate the brown product,  $[\text{WI}(\text{CO})(2,2'\text{-bipy})(\eta^2\text{-PhC}_2\text{C}_2\text{Ph})_2][\text{BPh}_4]$  (**15**), which was recrystallized from  $\text{CH}_2\text{Cl}_2$ /diethyl ether. Yield of pure product 0.243 g, 29%.

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