3-Hexyne Complexes of Molybdenum(II) and Tungsten(II). Crystal Structures of $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ and $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$

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3-Hexyne Complexes, Molybdenum(II), Tungsten(II)

Treatment of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) with two equivalents of EtC_2Et in CH_2Cl_2 at 0°C yields the bis(3-hexyne) complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1** and **2**). Complexes **1** and **2** react with two equivalents of PPh_3 in CH_2Cl_2 to give the complexes $[MI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**3** and **4**). The molecular structure of **4** (M = W) has been crystallographically determined and has a *pseudo*-octahedral geometry with the two PPh_3 ligands *trans* to each other with the two *cis*-iodo-ligands, which together with the carbonyl and 3-hexyne ligand are occupying the equatorial plane. Reaction of **1** and **2** with an equimolar amount of $Ph_2P(CH_2)_nPPh_2$ (for M = Mo, n = 1; for M = W, n = 1 to 6) in CH_2Cl_2 affords the mono(3-hexyne) complexes $[MI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**5** - **11**). The tungsten complex $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**8**) has also been crystallographically characterised and has *cis*-phosphorus atoms in the equatorial plane with the carbonyl and one of the iodo-ligands, with the other iodo-ligand and the 3-hexyne occupying the axial sites.

Introduction

The ability of alkyne ligands to act as four-electron donor ligands to transition-metal centres has been well illustrated in the alkyne complexes of molybdenum(II) and tungsten(II) [1, 2]. Although a number of 2-butyne, methylpropyne, phenylacetylene and related alkyne complexes of molybdenum(II) and tungsten(II) have been prepared [1 - 20], very few 3-hexyne derivatives have been reported; these include the dimeric tungsten complex $[\{W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}EtC_2Et)_2\}_2]$ [21], molybdenum dichloro- and dibromo-phosphine complexes $[MoX_2(CO)L_2(\eta^2\text{-}EtC_2Et)]$ (X = Cl, L = PPh_3; X = Br, L = PEt_3, PPh_3; X = Cl, Br, L_2 = dppe) [22] and the bis(dialkyldithiocarbamate) complexes $[Mo(CO)(S_2CNEt_2)_2(\eta^2\text{-}EtC_2Et)]$ [23] and $[Mo(\eta^2\text{-}PhC_2H)(\eta^2\text{-}EtC_2Et)(S_2CNMe_2)_2]$ [24]. None of the above 3-hexyne complexes have been crystallographically characterised, and until this work no diiodo-3-hexyne complexes of molybdenum(II) and tungsten(II) have been reported.

In 1988 [25], we reported the synthesis and X-ray crystal structures of the tungsten bis(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph). Very recently, [26] we have also described the synthesis and crystal structures of the related molybdenum complexes $[MoI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph). The chemistry of $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (M = Mo, W; R = Me, Ph) with both neutral and anionic ligands has been studied in detail [2, 27]. In this paper we describe the first 3-hexyne diiodo-complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (M = Mo, W) and their reactions with phosphines. The crystal structures of $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ and $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$ are also discussed.

Experimental

Physical measurements and instruments

Elemental analyses (C, H and N) were determined by Glyn Connolly (Department of Chemistry, University of Wales, Bangor) using a Carlo Erba Elemental Analyser MOD 1108 (using helium as a carrier gas). Infrared spectra were obtained as thin $CHCl_3$ films between NaCl plates and recorded on a Perkin-Elmer 1430 ratio recording IR spectrophotometer. ^1H, ^{13}C and ^{31}P NMR spectra

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Table I. Crystal data and structure refinement for **8** and **4**.

	8	**4**
Formula	$[WI_2(CO)(dppp)(\eta^2\text{-}EtC_2Et)]$	$[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$
Empirical formula	$C_{35}H_{38}C_{12}I_2OP_2W$	$C_{43}H_{40}I_2OP_2W$
Formula weight	1045.14	1072.34
Temperature(K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/c$	orthorhombic, $P2_12_12_1$
Cell dimensions (Å,°) *a*	18.90(2)	9.823(9)
b	9.632(9)	16.378(17)
c	21.63(2)	25.10(3)
β	107.98(10)	90
Volume (Å^3)	3746(7)	4039(7)
Z, Calculated density (Mgm^{-3})	4, 1.853	4, 1.764
Absorption coefficient (mm^{-1})	4.986	4.500
F(000)	2000	2064
Crystal size (mm)	0.25 × 0.30 × 0.30	0.15 × 0.25 × 0.25
θ Range for data collection (°)	2.40 to 25.93	2.42 to 25.94
Index ranges	$0 \le h \le 23$, $-10 \le k \le 10$, $-26 \le l \le 25$	$0 \le h \le 9$, $-19 \le k \le 19$, $-30 \le l \le 30$
Reflections collected / unique	12362 / 6637	7410 / 5006
R(int)	0.0477	0.0615
Data / restraints / parameters	6637 / 0 / 391	5006 / 36 / 405
Final *R* indices [$I > 2\sigma(I)$] *R*1, *wR*2	0.0504, 0.1227	0.0785, 0.1883
R indices (all data) *R*1, *wR*2	0.0717, 0.1401	0.0911, 0.1959
Extinction coefficient	0.00018(10)	0.00065(10)
Largest diff. peak, hole (eÅ^{-3})	1.950, −1.843	4.124, -1.985
Flack Parameter	—	Z: 0.01(13)

were recorded on a Bruker AC 250 MHz NMR spectrometer. ^{1}H and ^{13}C NMR spectra were referenced to $SiMe_4$, whereas ^{13}P NMR spectra were referenced to 85% H_3PO_4.

Reagents and materials

All reactions and purifications were carried out under an atmosphere of dry nitrogen using standard vacuum/Schlenk line techniques. The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) [28], were prepared by the published method. All solvents and chemicals used were of reagent grade quality and were purchased from commercial sources. The solvents used were dried and distilled before use.

Preparation of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**)

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.50 g, 0.968 mmol) in 20 ml of CH_2Cl_2 at 0 °C was added 3-hexyne (0.218 ml, 0.158 g, 1.926 mmol). The solution was slowly allowed to return to room temperature and stirred at room temperature for 24 h. Filtration, and removal of solvent *in vacuo* gave a brown crystalline powder, which was recrystallized from dichloromethane and diethyl ether, giving pure $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**) (yield = 0.318 g, 56%).

In a similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of 3-hexyne in CH_2Cl_2 at 0°C gave the bis(3-hexyne) complex $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**2**). See Table I for physical and analytical data.

Preparation of $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**4**)

To a stirred solution of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (0.50 g, 0.745 mmol) in CH_2Cl_2 (20 cm^3) was added PPh_3 (0.39 g, 1.48 mmol). After stirring the solution for 48 h, filtration, and removal of solvent *in vacuo* yielded a dark green crystalline powder which was recrystallised from CH_2Cl_2/Et_2O to give pure $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**4**), (yield = 0.76 g, 95%). Single crystals for X-ray crystallography were grown by cooling a CH_2Cl_2/Et_2O mixture at –20 °C for 24 h.

A similar reaction of $[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ with two equivalents of PPh_3 in CH_2Cl_2 at room temperature gave the complex $[MoI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**3**). See Table I for physical and analytical data.

Preparation of $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**8**)

To a stirred solution of $[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (0.50 g, 0.74 mmol) in CH_2Cl_2 (15 cm^3) was

Table II. Dimensions in the metal coordination spheres; distances (Å), angles (°).

In **4**:			
W(1)-C(100)	1.93(2)	W(1)-C(73)	2.03(3)
W(1)-C(74)	2.03(3)	W(1)-P(1)	2.584(5)
W(1)-P(2)	2.599(6)	W(1)-I(2)	2.843(3)
W(1)-I(3)	2.900(3)		
C(100)-W(1)-C(73)	110.2(11)	C(100)-W(1)-C(74)	72.9(11)
C(73)-W(1)-C(74)	37.3(11)	C(100)-W(1)-P(1)	91.9(7)
C(73)-W(1)-P(1)	95.3(6)	C(74)-W(1)-P(1)	98.6(7)
C(100)-W(1)-P(2)	89.2(7)	C(73)-W(1)-P(2)	95.3(6)
C(74)-W(1)-P(2)	92.9(7)	P(1)-W(1)-P(2)	168.2(2)
C(100)-W(1)-I(2)	71.9(8)	C(73)-W(1)-I(2)	177.9(8)
C(74)-W(1)-I(2)	144.8(8)	P(1)-W(1)-I(2)	84.34(15)
P(2)-W(1)-I(2)	84.88(15)	C(100)-W(1)-I(3)	162.9(8)
C(73)-W(1)-I(3)	87.0(8)	C(74)-W(1)-I(3)	124.2(8)
P(1)-W(1)-I(3)	85.91(15)	P(2)-W(1)-I(3)	89.57(16)
I(2)-W(1)-I(3)	90.95(7)		
In **8**:			
W(1)-C(100)	1.967(10)	W(1)-C(54)	2.006(10)
W(1)-C(53)	2.023(9)	W(1)-P(1)	2.545(3)
W(1)-P(5)	2.633(3)	W(1)-I(3)	2.824(2)
W(1)-I(2)	2.862(3)		
C(100)-W(1)-C(54)	109.7(4)	C(100)-W(1)-C(53)	72.1(4)
C(54)-W(1)-C(53)	37.7(4)	C(100)-W(1)-P(1)	96.8(3)
C(54)-W(1)-P(1)	86.4(3)	C(53)-W(1)-P(1)	91.7(3)
C(100)-W(1)-P(5)	160.0(3)	C(54)-W(1)-P(5)	88.6(3)
C(53)-W(1)-P(5)	125.6(3)	P(1)-W(1)-P(5)	92.15(11)
C(100)-W(1)-I(3)	83.9(3)	C(54)-W(1)-I(3)	102.3(3)
C(53)-W(1)-I(3)	97.4(3)	P(1)-W(1)-I(3)	170.54(6)
P(5)-W(1)-I(3)	84.39(10)	C(100)-W(1)-I(2)	82.5(3)
C(54)-W(1)-I(2)	162.3(3)	C(53)-W(1)-I(2)	151.8(3)
P(1)-W(1)-I(2)	79.22(7)	P(5)-W(1)-I(2)	81.74(7)
I(3)-W(1)-I(2)	91.55(6)		

added $Ph_2P(CH_2)_3PPh_2$ (0.307 g, 0.744 mmol). After 24 h, filtration and removal of solvent *in vacuo* gave a green crystalline powder which was dissolved in the minimum quantity of CH_2Cl_2/Et_2O, and cooled to –20 °C for 24 h to afford suitable single crystals for X-ray analysis of $[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**8**). (Yield = 0.635 g, 89%).

Similar reactions of equimolar quantities of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ and $Ph_2P(CH_2)_nPPh_2$ in CH_2Cl_2 at room temperature gave the complexes $[MI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}EtC_2Et)]$ (M = Mo, n = 1; M = W, n = 1, 2, 4, 5, 6) (**5 - 7, 9 - 11**). See Table I for physical and analytical data.

X-ray data collection and processing for **4** *and* **8**

Crystal data are given in Table I, together with refinement details. Data were collected with MoKα radiation using the MAR-research Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analyses were carried out with the XDS program [29]. The structures were solved using direct methods with the SHELX-86 program [30]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Empirical absorption corrections were carried out using the DIFABS program [31]. The structures were then refined on F^2 using the SHELXL-93 program [32]. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

Table III. Physical and analytical data for the 3-hexyne complexes **1 - 11**.

Compound (**No.**): Colour	Yield (%)	Analytical data: Found (Calcd.[a]) % C	H	N
$[MoI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1**):				
brown	56	30.3 (30.9)	3.9 (4.0)	2.5 (2.4)
$[WI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**2**):				
yellow	79	27.0 (26.9)	3.5 (3.4)	2.0 (2.1)
$[MoI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**3**):				
brown	48	52.3 (52.3)	4.1 (4.1)	—
$[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**4**):				
green	95	48.2 (48.2)	3.7 (3.8)	—
$[MoI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**5**):				
brown	81	45.2 (45.4)	3.8 (3.8)	—
$[WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**6**):				
green	88	41.3 (41.2)	3.7 (3.5)	—
$[WI_2(CO)\{Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**7**):				
green	40	41.7 (41.9)	3.6 (3.6)	—
$[WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**8**):				
green	89	42.5 (42.5)	3.9 (3.8)	—
$[WI_2(CO)\{Ph_2P(CH_2)_4PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**9**):				
green	61	43.1 (43.2)	4.0 (3.9)	—
$[WI_2(CO)\{Ph_2P(CH_2)_5PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**10**):				
green	31	43.3 (43.8)	4.3 (4.1)	-
$[WI_2(CO)\{Ph_2P(CH_2)_6PPh_2\}(\eta^2\text{-}EtC_2Et)]$ (**11**):				
green	88	44.7 (44.3)	4.4 (4.2)	—

[a] Calculated values in parenthesis.

Results and Discussion

The starting materials used in this research, $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) were prepared by treating the zero-valent complexes *fac*-$[M(CO)_3(NCMe)_3]$ (prepared *in situ*) with one equivalent of I_2 at 0 °C [28]. Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) with two equi-

Table IV. Infrared data[a] for the 3-hexyne complexes **1** - **11**.

Compound No.	$\nu(C\equiv O)$ cm^{-1}	$\nu(C\equiv N)$ cm^{-1}	$\nu(C\equiv C)$ cm^{-1}
1	2059(s)	2290(w)	1604(w)
2	2056(s)	2253(w)	1634(w)
3	1952(s)	—	1664(w)
4	1942(s)	—	1654(w)
5	1943(s)	—	1658(w)
6	1931(s)	—	1603(w)
7	1930(s)	—	1654(w)
8	1942(s)	—	1656(w)
9	1936(s)	—	1639(w)
10	1934(s)	—	1635(w)
11	1935(s)	—	1658(w)

[a] Spectra recorded in $CHCl_3$ as thin films between NaCl plates; s = strong, w = weak.

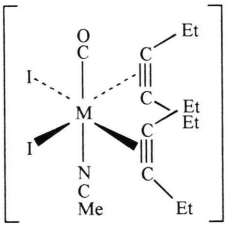

Fig. 1. Proposed structure of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1** and **2**).

Table V. ^1H NMR data[a] for selected 3-hexyne complexes[a].

Complex	^1H NMR (δ) ppm
1	3.15 - 3.4 (br, m, 4H, $C\equiv CCH_2$), 2.9 - 3.1 (br, m, 4H, CH_2), 2.75 (s, 3H, $NCCH_3$), 1.2 - 1.35 (t, 12H, CH_3)
2	3.2 - 3.4 (m, 4H, CH_2), 2.9 - 3.1 (m, 4H, $C\equiv C\text{-}CH_2$), 2.85 (s, 3H, $NCCH_3$), 1.2 (dt, 12H, CH_3)
3	7.1 - 7.65 (br, m, 30H, *Ph*), 2.6 - 3.4 (br, m, 4H, $C\equiv CCH_2$), 0.55 - 1.3 (dt, 6H, CH_3)
4	7.2 - 7.65 (br, m, 30H, *Ph*), 3.15 (dq, 4H, $C\equiv CCH_2$), 0.70 (t, 6H, CH_3)
5	6.8 - 7.35 (br, m, 20H, *Ph*), 4.5 - 4.7 (q, 2H, $C\equiv CCH_2$, J = 10 Hz), 3.35 - 3.6 (q, 2H, CH_2), 2.9 - 3.15 (br, 2H, $C\equiv CCH_2$), 0.9 - 1.25 (t, 6H, CH_3, J = 7.5 Hz)
6	7.0 - 7.8 (br, m, 20H, *Ph*), 4.55 - 4.85 (dt, 2H, J = 8 Hz, PCH_2), 3.6 (q, 2H, $C\equiv CCH_2$, J = 7.5 Hz), 3.1 - 3.3 (q, 2H, $C\equiv CCH_2$, J = 7.3 Hz), 1.05 - 1.25 (t, 6H, CH_3, J = 7.5 Hz)
7	7.5 - 8.1 (m, 20H, *Ph*), 3.7 (br, m, 4H, Ph_2PCH_2), 3.4 (q, 4H, $C\equiv CCH_2$), 1.4 (t, 6H, CH_3)
8	7.4 - 8.0 (m, 20H, *Ph*), 3.5 (q, 4H, $C\equiv CCH_2$), 3.3 (br, m, 4H, Ph_2PCH_2), 1.2 (t, 6H, CH_3), 0.8 (br, m, 2H, $Ph_2PCH_2CH_2$)
9	6.8 - 7.7 (br, m, 20H, Ph), 3.35 - 3.45 (m, 4H, Ph_2PCH_2), 3.3 (q, 4H, $C\equiv CCH_2$), 2.6 - 3.15 (br, m, 4H, $Ph_2PCH_2CH_2$), 1.0 - 1.25 (t, 6H, CH_3)
10	6.9 - 7.6 (br, m, 20H, Ph), 3.2 - 3.4 (br, m, 4H, $Ph_2PCH_2CH_2$), 2.95 - 3.2 (br, m, 4H, $C\equiv CCH_2$, 0.8 - 1.35 (t, 6H, CH_3), 0.8 - 1.35 (br, m, 6H, $Ph_2PCH_2CH_2CH_2CH_2$)
11	7.2 - 7.7 (m, 20H, Ph), 3.4 (q, 4H, $C\equiv CCH_2$), 3.0 (br, m, 4H, Ph_2PCH_2), 2.4 (br, m, 4H, $Ph_2PCH_2CH_2$), 0.8 (t, 6H, CH_3), 0.5 (br, m, 4H, $Ph_2PCH_2CH_2CH_2$)

[a] Spectra recorded in $CDCl_3$ (+25 °C) and referenced to $SiMe_4$; s = singlet, br = broad, d = doublet, m = multiplet, t = triplet, q = quartet.

valents of EtC_2Et in CH_2Cl_2 at room temperature gave good yields of the bis(3-hexyne) complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (**1** and **2**). Both complexes **1** and **2** were characterised by elemental analysis (C, H and N) (Table III), IR (Table IV) and ^1H NMR spectroscopy (Table V). Both complexes are air-sensitive in solution, but can be stored under nitrogen or argon in the solid state for an indefinite period. The complexes are very soluble in polar organic solvents such as CH_2Cl_2 and $CHCl_3$, but only slightly soluble in diethyl ether. The IR spectra for **1** and **2** show carbonyl stretching bands at $\nu(C\equiv O)$ = 2059 and 2056 cm^{-1} respectively. These are in very similar positions to their related 2-butyne derivatives $[MI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ $\{\nu(C\equiv O) = 2061\ cm^{-1}$ (M = Mo) [26], 2050 cm^{-1} (M = W) [25]$\}$. The nitrile bands $\nu(N\equiv C)$ at 2290 and 2253 cm^{-1} are typical of complexes where the acetonitrile is acting purely as a σ-donor ligand [33]. The weak alkyne stretching bands at 1604 and 1634 cm^{-1} for **1** and **2** are considerably lower than for the uncoordinated alkyne, which is expected since there is back-donation of electron density from filled metal d-type orbitals to empty π^*-orbitals on the 3-hexyne ligands. The X-ray crystal structures of a number of bis(alkyne) complexes, $[MI_2(CO)(NCR)(\eta^2\text{-}R'C_2R')_2]$ (M = W, R = Me, R' = Me, Ph [25]; M = Mo, R = Me, R' = Me, Ph [26]; M = W, R' = Me, R = Bu^t [34], Ph [35], $CH_2(3\text{-}C_4H_3S)$ [36]) have been reported and all have the structure shown in Fig. 1. It is very likely the structure of the bis(3-hexyne) complexes **1** and **2** is very similar as shown in Fig. 1, since the spectroscopic properties are closely related to the previously reported bis(alkyne) complexes of molybdenum(II) and tungsten(II) [1, 2, 25 - 27, 34 - 36]. The ^1H NMR spectra of **1** and **2** show two different sets

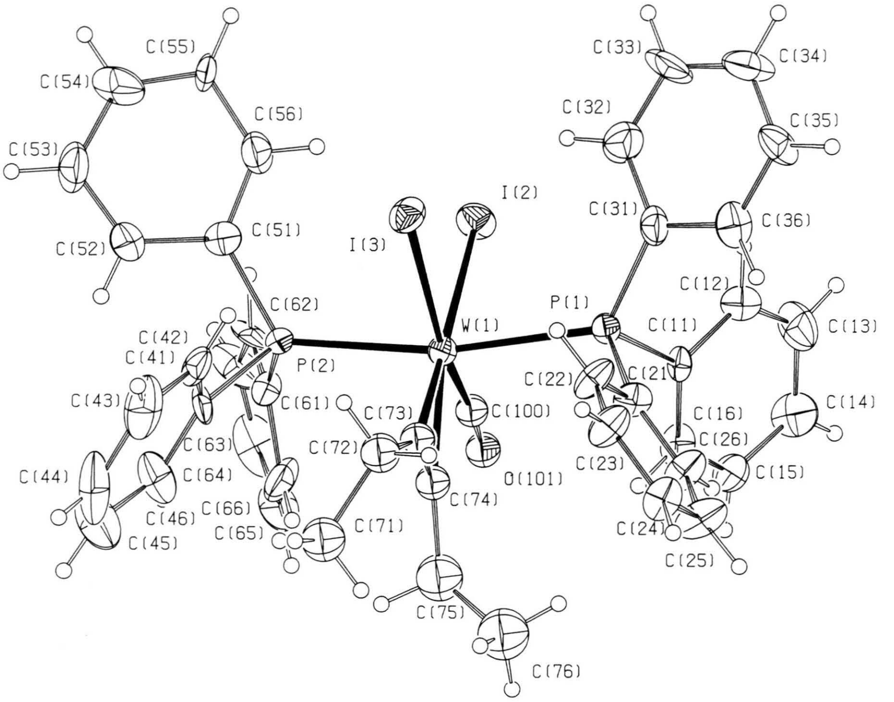

Fig. 2. The structure of $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**4**) with the atom numbering scheme. Ellipsoids are shown at 30% probability.

Table VI. ^{13}C NMR data (δ) for selected 3-hexyne complexes[a].

Complex	^{13}C NMR (δ) ppm
1	6.85 (s, CH_3.CN); 12.37, 13.86, 14.109, 14.37 (s, CH_2CH_3); 25.92, 29.19 (s, CH_2); 129.55 (s, C≡N); 172.18, 163.48 (s, C≡C); 217.06 (s, C≡O)
2	5.04 (s, CH_3.CN); 13.63, 13.75 (s, CH_2CH_3); 25.73, 29.35 (s, CH_2CH_3); 128.63 (s, C≡N); 160.82, 171.45 (s, C≡C); 206.54 (s, C≡O)
5	12.49, 13.41, 13.77, 14.50 (s, CH_3), 28.13, 29.64, 31.68 (s, CH_2); 54.59 (s, PCH_2); 128.25, 128.40, 128.63, 128.92, 129.08, 130.46, 131.63, 131.85, 132.04, 132.29, 133.32, 133.67, 133.82 (s, Ph); 210.1, 212 (C≡C) 228.90 (C≡O)
9	12.27, 13.48, 14.35, 15.28 (s, CH_2CH_3); 22.66, 24.91, 25.39 (s, PCH_2CH_2, CH_2CH_3); 28.87, 29.67, 30.97, 31.75, 34.21, 53.51, 65.84 (s, PCH_2); 127.55, 127.87, 128.61, 129.51, 130.27, 130.55, 130.94, 132.16, 133.69 (s, Ph); 203.10, 205.02 (s, C≡C), 222.75 (s, C≡O)

[a] Spectra recorded in $CDCl_3$ (+25 °C) and referenced to $SiMe_4$; s = singlet.

Table VII. ^{31}P NMR data (δ) for selected 3-hexyne complexes[a].

Complex	^{31}P NMR (δ) ppm
3	δ(P) = –2.69
4	δ(P) = –15.93, J(W-P) = 272.54 Hz
8	$\delta(P_A)$ = –23.733, $\delta(P_B)$ = –36.21
9	$\delta(P_A)$ = 3.66, $\delta(P_B)$ = –9.50, $J(W\text{-}P_B)$ = 270.78 Hz
11	$\delta(P_A)$ = –9.47, $\delta(P_B)$ = –15.79

[a] Spectra recorded in $CDCl_3$ (+25°C) and referenced to H_3PO_4.

of CH_2 groups, which conform with the structure shown in Fig. 1. The room temperature ^{13}C NMR spectra of **1** and **2** have alkyne carbon contact resonances at δ = 172.18 and 163.48 (for **1**) and 160.82 and 171.45 (for **2**). Templeton and Ward [37] have correlated ^{13}C NMR alkyne contact carbon chemical shifts with the number of electrons donated by the alkyne to the metal. The resonances observed for complexes **1** and **2** are in accord with the two alkynes donating a total of six electrons to the metal centre, which also enables the complexes to obey the effective atomic number rule.

Treatment of $[MI_2(CO)(NCMe)(\eta^2\text{-}EtC_2Et)_2]$ (M = Mo, W) with two equivalents of PPh_3 in CH_2Cl_2 at room temperature gives the complexes $[MI_2(CO)(PPh_3)_2(\eta^2\text{-}EtC_2Et)]$ (**3** and **4**). Complexes **3** and **4** have also been characterised by

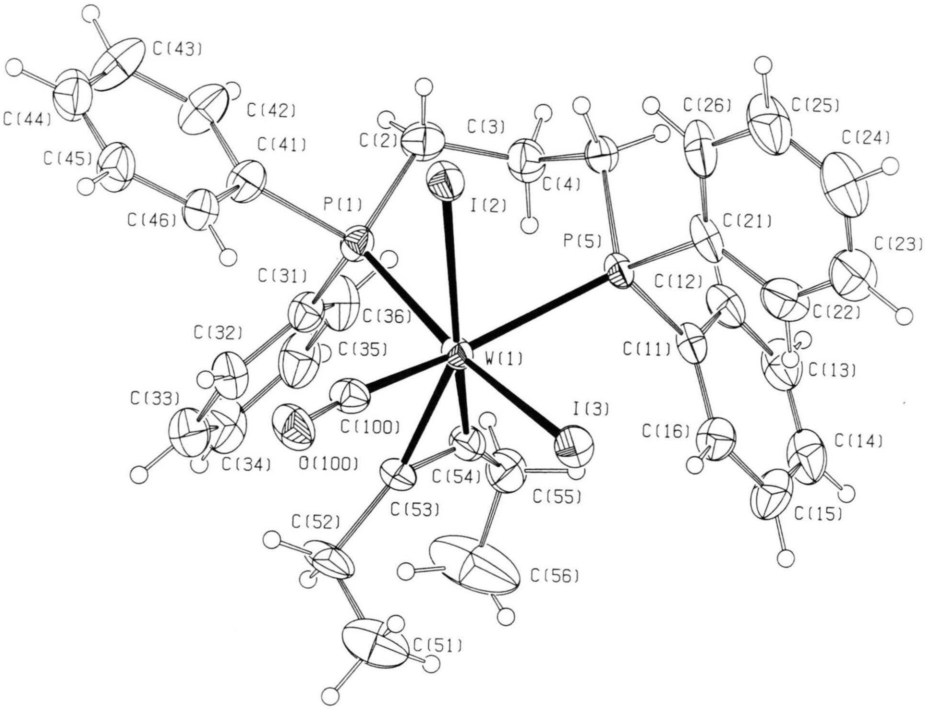

Fig. 3. The structure of [$WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2$-$EtC_2Et)$] (**8**), with the atom numbering scheme. Ellipsoids are shown at 30% probability.

elemental analysis (Table III), IR (Table IV), ^1H NMR (Table V) and ^{31}P NMR spectroscopy (Table VII). Complexes **3** and **4** are more stable in solution, but very much less soluble than their bis-(3-hexyne) precursors **1** and **2**. They are both reasonably soluble in CH_2Cl_2 and $CHCl_3$, however it was difficult to obtain good ^{13}C NMR spectra due to their moderate solubility in polar NMR solvents. The IR and ^1H NMR spectral properties of **3** and **4** are similar to their 2-butyne tungsten analogue, [$WI_2(CO)(PPh_3)_2(\eta^2$-$MeC_2Me)$] [38], which has a carbonyl stretching band at 1940 cm^{-1}, similar to **4** $\{\nu(CO) = 1942\ cm^{-1}\}$ in the same solvent. The ^{31}P NMR spectra for **3** and **4** have single resonances at $\delta = -2.69$ and -15.93, respectively. This suggests a *trans* arrangement of the PPh_3 ligands which is confirmed by the X-ray crystal structure of the tungsten complex **4**, discussed along with the complex [$WI_2(CO)\{Ph_2P(CH_2)_3PPh_2\}$-$(\eta^2$-$MeC_2Me)$] (**8**) below.

Suitable single crystals of [$WI_2(CO)(PPh_3)_2(\eta^2$-$EtC_2Et)$] (**4**) were grown by cooling a CH_2Cl_2/Et_2O solution of **4** to –20°C for 24h. The structure of **4** is shown in Fig. 2 together with the atom numbering scheme. It is discussed and compared with the structure of **8** below.

Equimolar quantities of [$MI_2(CO)(NCMe)(\eta^2$-$EtC_2Et)_2$] (M = Mo, W) and $Ph_2P(CH_2)_nPPh_2$ (M = Mo, $n = 1$; M = W, $n = 1$ to 6) react in CH_2Cl_2 at room temperature to yield the mono(3-hexyne) complexes [$MI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}$-$(\eta^2$-$EtC_2Et)$] (**5 - 11**). Complexes **5-11** were fully characterised (see Tables III to VII). They are intermediate in solubility between **1**, **2** and **3**, **4** and similar in air-sensitivity to the bis(PPh_3) complexes **3** and **4**. The colours and spectroscopic properties resemble that of their 2-butyne analogues, [$WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}$-$(\eta^2$-$MeC_2Me)$] reported previously [38]. The room temperature ^{13}C NMR spectra ($CDCl_3$) for **5** and **9** have alkyne contact carbon resonances at $\delta = 210.1$, 212 (for **5**) and 203.10, 205.02 ppm (for **9**) which indicate from Templeton and Ward's [37] correlation that the 3-hexyne is donating four electrons to the metal in these complexes. This enables complexes **5** and **9** to obey the effective atomic number rule. The

^{31}P NMR spectra of [WI$_2$(CO){Ph$_2$P(CH$_2$)$_n$PPh$_2$}(η^2-EtC$_2$Et)] (n = 3, 4 and 6) have two resonances (Table VII), which is expected for a single isomer of **8**, **9** and **11**. In order to obtain information about the solid state structure, suitable crystals of [WI$_2$(CO){Ph$_2$P(CH$_2$)$_3$PPh$_2$}(η^2-EtC$_2$Et)] (**8**) were grown by cooling a CH$_2$Cl$_2$/Et$_2$O solution of **8** to –20 °C for 24 h.

The molecular structure of **8** is shown in Fig. 3 together with the atomic numbering scheme. The structures of **4** and **8** are shown in Figures 2 and 3 together with the atomic numbering schemes. The dimensions in the metal coordination spheres are listed in Table II. In both structures, if the ethyne is considered as occupying one position in the coordination sphere, then the geometry around the metal can be considered to be octahedral. In **4**, the two monodentate phosphorus atoms are mutually *trans* with W(1)-P(1) 2.584 (5), W(1)-P(2) 2.599(6) Å. One iodine is *trans* to the ethyne and the bond to the metal is significantly shorter at 2.843(3) Å than the bond from the iodine *trans* to the carbonyl at 2.900(3) Å. The tungsten to ethyne bond lengths are W(1)-C(73) 2.03(3), W(1)-C(74) 2.03(3) Å, and to the carbonyl 1.93(2) Å. This arrangement of donor atoms around the metal is equivalent to that found in [MoBr$_2$(CO)(PMePh$_2$)$_2$(η^2-MeC$_2$Me)] [39] and [WCl$_2$(CO)(PMe$_2$)$_2$(η^2-PhC$_2$Ph)] [40].

In **8**, the two phosphorus atoms from the dppp ligand are perforce mutually *cis* with a P(1)-W(1)-P(5) angle of 92.1(1)°. The two bond lengths are significantly different in that W-P(1) with P(1) *trans* to iodine is shorter at 2.545(3) Å than W-P(5) with P(5) *trans* to carbonyl. The alkyne is *trans* to iodide with W-C distances 2.01(1), 2.02(1) and W-I(2) at 2.862(3) Å. The remaining distances are W(1)-C(100) 1.97(1) and W(1)-I(3) 2.824(2) Å. Thus I(2) *trans* to ethyne forms a longer bond than I(3) *trans* to phosphorus.

This arrangement of donor atoms around the metal is very different from that found in [WI$_2$(CO)(dppm)(η^2-MeC$_2$Me)] [38] and [WI$_2$(CO)(dppm)(η^2-MeC$_2$Ph)] [41], where the two *cis*-phosphorus atoms are trans to iodine and ethyne rather than iodine and carbonyl as in **8**. It is not clear why this difference is found though the size of the dppp ligand bite compared to that of dppm might be a significant factor.

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