

Reactions of the Bis(alkyne) Complexes $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ (R = Me or Ph) with Mono- and Bi-dentate Phosphine-donor Ligands and the X-Ray Crystal Structure of $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]^\dagger$

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Reaction of the complexes $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ (R = Me or Ph) either with 2 equivalents of L {L = PMe_3 , PEt_3 , PBu^n_3 , PMe_2Ph , PMePh_2 , PEt_2Ph , PEtPh_2 , $\text{PPh}_2(\text{CH}_2\text{CH}=\text{CH}_2)$ [PPh_3 and $\text{PPh}_2(\text{C}_6\text{H}_{11})$ for R = Me only]} or 1 equivalent of L_2 { $\text{L}_2 = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2, 3, 4$, or 6) or $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ for R = Me only} in CH_2Cl_2 at room temperature affords good yields of the compounds $[\text{Wl}_2(\text{CO})\text{L}_2(\eta^2\text{-RC}_2\text{R})]$ (**1**)—(**24**) by successive substitutions of acetonitrile and an alkyne ligand. X-Ray crystallographic studies were carried out on the complex $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ (**19**). Crystals of (**19**) are monoclinic, space group $P2_1/n$ with $a = 12.208(4)$, $b = 13.395(2)$, $c = 20.820(6)$ Å, and $\beta = 104.31(2)^\circ$. The structure was refined to $R = 0.052$ ($R' = 0.060$) for 2 860 reflections with $F_o > 3\sigma(F_o)$. The tungsten co-ordination may be described in terms of a pseudo-octahedral structure. The bidentate phosphine ligand, but-2-yne, and an iodide ligand occupy the four equatorial sites, and the carbonyl and iodide ligands the two axial sites. The but-2-yne ligand is oriented so that it is approximately coplanar with the axial ligands. Phosphorus-31 n.m.r. and i.r. spectral studies are interpreted to suggest the likely structures for the other $[\text{Wl}_2(\text{CO})\text{L}_2(\eta^2\text{-RC}_2\text{R})]$ complexes. The barrier to but-2-yne rotation of a number of complexes has been determined by variable-temperature ^1H n.m.r. spectroscopy. These results are discussed in terms of the electronic and steric effects of the phosphorus-donor ligands and also the di-iodo complexes are compared with the analogous dibromo and dichloro complexes reported by other workers. The ^{13}C n.m.r. chemical shifts of the alkyne contact carbons suggest that the alkyne ligand is acting as a four-electron donor in these complexes.

The ability of alkynes to act as four-electron donors when bonded to a transition-metal centre by utilising both sets of filled p_π orbitals has become increasingly important in recent years.¹ Although a variety of cationic cyclopentadienyl alkyne complexes of molybdenum(II) and tungsten(II) containing phosphine ligands has been reported,² it is only more recently that halide alkyne complexes of molybdenum(II) and tungsten(II) containing phosphine ligands have received attention. In 1983 Templeton and co-workers³ reported the synthesis of the complexes $[\text{MX}_2(\text{CO})\text{L}_2(\eta^2\text{-RC}_2\text{R})]$ [M = Mo or W; X = Cl or Br; L = PEt_3 or PPh_3 ; $\text{L}_2 = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$], and in the same year Davidson and Vasapollo⁴ described the preparation of $[\text{WBr}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-RC}_2\text{R}')]]$ (R = R' = Me or Ph; R = Me, R' = Ph). More recently Bennett and Boyd⁵ reported the preparation of the cyclo-octyne complexes $[\text{MBr}_2(\text{CO})(\text{PEt}_3)_2(\eta^2\text{-C}_8\text{H}_{12})]$ (M = Mo or W). The only di-iodo phosphine carbonyl complex of this type to be reported is $[\text{Wl}_2(\text{CO})_2(\text{PMe}_3)(\eta^2\text{-PhC}_2\text{H})]$ by Umland and Vahrenkamp⁶ in 1982. The lack of iodide complexes of this type is probably due to the fact that Davidson and Vasapollo⁷ utilised the bromide-bridged dimer $[\{\text{W}(\mu\text{-Br})\text{Br}(\text{CO})_4\}_2]$ as a starting point for their investigations. Although the bromide-bridged dimers $[\{\text{M}(\mu\text{-Br})\text{Br}(\text{CO})_4\}_2]$ (M = Mo or W) have been prepared in high yield⁸ by reaction of $[\text{M}(\text{CO})_6]$ with Br_2 at -78°C , the iodide-bridged dimers $[\{\text{M}(\mu\text{-I})\text{I}(\text{CO})_4\}_2]$ were prepared only in poor yield.⁹ However, Templeton and co-workers¹⁰ pre-

pared the bis(phosphine) halide complexes by treating the zerovalent compounds $[\text{M}(\text{CO})_4\text{L}_2]$ with X_2 (X = Cl, Br, or I) to give $[\text{MX}_2(\text{CO})_3\text{L}_2]$. They reported that reaction of $[\text{Ml}_2(\text{CO})_3\text{L}_2]$ with alkynes was slow and only decomposition products were isolated from these reactions.¹⁰

In recent years we have been investigating the reactions of the highly versatile complexes $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ (R = Me or Ph)¹¹ which are prepared by treating $[\text{Wl}_2(\text{CO})_3(\text{NCMe})_2]$ ¹² with 2 equivalents of alkyne in CH_2Cl_2 at 0°C . In this paper we describe the reactions of these complexes with phosphine donor ligands. The X-ray crystal structure of $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ is also described.

Results and Discussion

The complexes $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ (R = Me or Ph) react in CH_2Cl_2 at room temperature either with 2 equivalents of L {L = PMe_3 , PEt_3 , PBu^n_3 , PMe_2Ph , PMePh_2 , PEt_2Ph , PEtPh_2 , or $\text{PPh}_2(\text{CH}_2\text{CH}=\text{CH}_2)$ [PPh_3 and $\text{PPh}_2(\text{C}_6\text{H}_{11})$ for R = Me only]} or 1 equivalent of the bidentate ligands L_2 { $\text{L}_2 = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1, 2, 3, 4$, or 6) or $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]$ (for R = Me only)} to give good yields of the new di-iodo alkyne complexes $[\text{Wl}_2(\text{CO})\text{L}_2(\eta^2\text{-RC}_2\text{R})]$ (**1**)—(**24**) by successive displacement of acetonitrile and an alkyne ligand. All the new complexes (**1**)—(**24**) have been fully characterised by elemental analysis (C, H, and N) and i.r. spectroscopy (Table 1) and ^1H and ^{13}C n.m.r. spectroscopy (Table 2). The complex $[\text{Wl}_2(\text{CO})\{\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\}(\eta^2\text{-MeC}_2\text{Me})]\cdot\text{Et}_2\text{O}$ (**24**) was confirmed as a diethyl ether solvate by repeated elemental analyses and ^1H and ^{13}C n.m.r. spectroscopy. The structure of the complex $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ is also described.

† [Bis(diphenylphosphino)methane](η -but-2-yne)carbonyldi-iodo-tungsten.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Physical, analytical,^a and i.r.^b data for the complexes [W₁₂(CO)L₂(η²-RC₂R)]

Complex	Colour	Yield (%)	Analysis (%)		I.r. (cm ⁻¹)	
			C	H	v(CO)	v(C≡C)
(1) [W ₁₂ (CO)(PMe ₃) ₂ (η ² -MeC ₂ Me)]	Blue-grey	37	19.4 (19.7)	3.5 (3.6)	1 935s	1 645vw
(2) [W ₁₂ (CO)(PMe ₃) ₂ (η ² -PhC ₂ Ph)]	Dark green	30	31.5 (31.7)	3.5 (3.6)	1 948s	1 650vw
(3) [W ₁₂ (CO)(PEt ₃) ₂ (η ² -MeC ₂ Me)]	Pale purple	78	26.6 (27.0)	4.9 (4.8)	1 932s	1 610vw
(4) [W ₁₂ (CO)(PEt ₃) ₂ (η ² -PhC ₂ Ph)]	Dark green	97	37.2 (36.8)	4.7 (4.6)	1 945s	1 670vw
(5) [W ₁₂ (CO)(PBU ⁿ) ₂ (η ² -MeC ₂ Me)]	Dark green (oil)	76	39.4 (37.7)	6.9 (6.5)	1 923s	1 635vw
(6) [W ₁₂ (CO)(PBU ⁿ) ₂ (η ² -PhC ₂ Ph)]	Dark green (oil)	43	47.8 (44.7)	3.3 (4.2)	1 938s	1 682w
(7) [W ₁₂ (CO)(PMe ₂ Ph) ₂ (η ² -MeC ₂ Me)]	Green	75	32.1 (31.7)	3.7 (3.6)	1 938s	1 660vw
(8) [W ₁₂ (CO)(PMe ₂ Ph) ₂ (η ² -PhC ₂ Ph)]	Green	51	40.7 (40.5)	3.5 (3.5)	1 956s	1 672vw
(9) [W ₁₂ (CO)(PMePh ₂) ₂ (η ² -MeC ₂ Me)]	Green	86	40.4 (40.5)	3.6 (3.5)	1 902s	1 660w
(10) [W ₁₂ (CO)(PMePh ₂) ₂ (η ² -PhC ₂ Ph)]	Green	42	47.4 (47.2)	3.4 (3.2)	1 942s	1 670vw
(11) [W ₁₂ (CO)(PEt ₂ Ph) ₂ (η ² -MeC ₂ Me)]	Green	87	41.2 (41.8)	3.8 (3.8)	1 935s	1 652vw
(12) [W ₁₂ (CO)(PEt ₂ Ph) ₂ (η ² -PhC ₂ Ph)]	Green	44	42.7 (43.1)	4.1 (4.1)	1 946s	1 660vw
(13) [W ₁₂ (CO)(PEtPh ₂) ₂ (η ² -MeC ₂ Me)]	Green	86	36.3 (35.3)	4.3 (4.3)	1 940s	1 661w
(14) [W ₁₂ (CO)(PEtPh ₂) ₂ (η ² -PhC ₂ Ph)]	Green	48	48.6 (48.2)	3.9 (3.3)	1 958s	1 665vw
(15) [W ₁₂ (CO){PPh ₂ (CH ₂ CH=CH ₂) ₂ (η ² -MeC ₂ Me)]	Pale green	76	43.5 (43.2)	3.6 (3.7)	1 940s	1 632w
(16) [W ₁₂ (CO){PPh ₂ (CH ₂ CH=CH ₂) ₂ (η ² -PhC ₂ Ph)]	Green	47	48.0 (47.3)	3.8 (3.7)	1 952s	1 630w
(17) [W ₁₂ (CO)(PPh ₃) ₂ (η ² -MeC ₂ Me)]	Green	97	47.7 (47.2)	3.6 (3.5)	1 940s	1 645vw
(18) [W ₁₂ (CO){PPh ₂ (C ₆ H ₁₁) ₂ (η ² -MeC ₂ Me)]	Green	98	47.1 (46.6)	4.9 (4.6)	1 950s	1 642vw
(19) [W ₁₂ (CO){Ph ₂ P(CH ₂)PPh ₂ }(η ² -MeC ₂ Me)]	Green	92	39.5 (39.9)	3.4 (3.1)	1 938s 1 928s ^c	1 648vw 1 643w
(20) [W ₁₂ (CO){Ph ₂ P(CH ₂) ₂ PPh ₂ }(η ² -MeC ₂ Me)]	Blue-green	40	40.2 (40.6)	3.6 (3.3)	1 943s 1 955s ^c	1 634vw 1 634w
(21) [W ₁₂ (CO){Ph ₂ P(CH ₂) ₃ PPh ₂ }(η ² -MeC ₂ Me)]	Green	73	41.1 (41.2)	3.6 (3.5)	1 940s	1 648vw
(22) [W ₁₂ (CO){Ph ₂ P(CH ₂) ₄ PPh ₂ }(η ² -MeC ₂ Me)]	Green	69	42.1 (41.9)	3.9 (3.6)	1 930s	1 658vw
(23) [W ₁₂ (CO){Ph ₂ P(CH ₂) ₆ PPh ₂ }(η ² -MeC ₂ Me)]	Green	69	43.9 (43.2)	4.1 (3.9)	1 940s	1 660vw
(24) [W ₁₂ (CO){Fe(η ⁵ -C ₅ H ₄ PPh ₂) ₂ }(η ² -MeC ₂ Me)-Et ₂ O	Yellow	23	44.6 (45.0)	3.8 (3.9)	1 932s	1 610vw

^a Calculated values in parentheses. ^b Recorded in CHCl₃ as thin films between NaCl plates. ^c Spectra run as KBr discs.

PPh₂}(η²-MeC₂Me)] has been determined by X-ray crystallography. The complexes are all highly coloured (see Table 1) analogous to other complexes of molybdenum(II) and tungsten(II), which have a four-electron alkyne ligand.^{2b,3,4,7,10} Bis(alkyne) complexes such as [W₁₂(CO)(NCMe)(η²-RC₂-R)₂]¹¹ and [Mo(CO)(η²-RC₂R')₂(η⁵-C₅H₅)] [BF₄]¹³ which have both alkyne ligands donating an average of three electrons each to the metal centre are usually yellow or orange. The compounds are all reasonably air-stable in the solid state, but decompose slowly in solution when exposed to air. The most soluble complexes are with L = PEt₃ and PBUⁿ, which are soluble in Et₂O. All the other complexes are soluble in chlorinated solvents such as CHCl₃ and CH₂Cl₂, but are only slightly soluble in Et₂O and hydrocarbon solvents.

The structure of [W₁₂(CO){Ph₂P(CH₂)PPh₂}(η²-MeC₂-

Me)] (19) is shown in Figure 1. Selected bond lengths and angles are given in Table 5. The structure of (19) can be conveniently described in terms of a distorted octahedron with the but-2-yne ligand occupying one site. However, the strong bending back of the methyl carbons (C-C-Me ≈ 141°) suggests considerable contribution from the metallacyclopentenyl form. The bis-(diphenylphosphino)methane, but-2-yne, and an iodide ligand occupy the four equatorial sites, with the two axial sites being occupied by a carbonyl and an iodide ligand. As expected the but-2-yne ligand is approximately parallel to the axial ligands. The two W-P distances are significantly different with that *trans* to the alkyne ligand some 0.15 Å longer than that *trans* to iodide. The W-I distances also reflect differences in *trans* influences with that *trans* to carbonyl ≈ 0.1 Å longer than that *trans* to phosphorus.

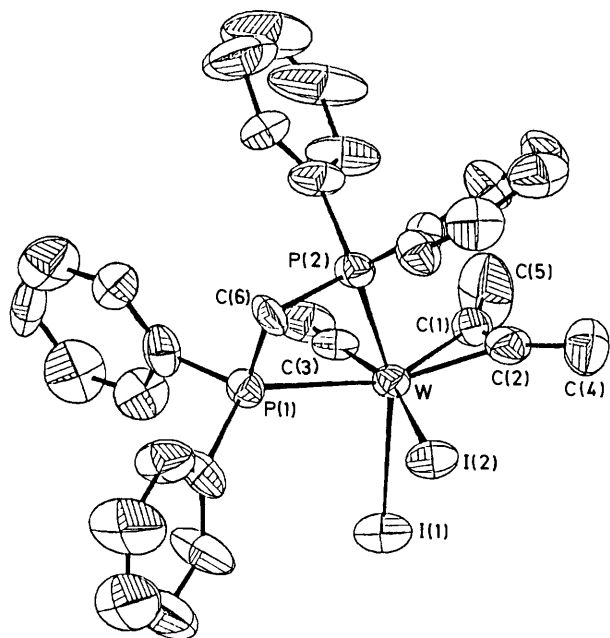


Figure 1. ORTEP diagram showing the structure of $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ (**19**). Ellipsoids shown at 50% probability

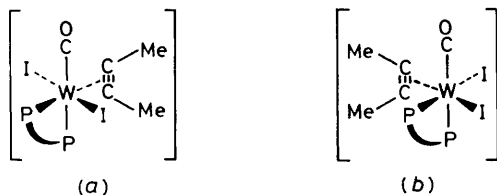


Figure 2. Possible structures of the blue isomer of $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ (**20**)

The ^{31}P n.m.r. spectrum of complex (**19**) in solution (Table 3) is in accord with the *X*-ray crystal structure shown in Figure 1. The complexes $[\text{Wl}_2(\text{CO})\text{L}_2(\eta^2\text{-MeC}_2\text{Me})]$ $\{\text{L}_2 = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 3, 4$, or 6) or $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2]\}$ containing bidentate phosphine donor ligands are all likely to have the same stereochemistry as (**19**) in view of their similar colour and i.r. spectroscopic properties. However, reaction of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ with $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ in CH_2Cl_2 at room temperature gives a blue precipitate with a pale green solution. The i.r. spectrum of the green solution in CHCl_3 shows a carbonyl band at $\nu(\text{CO})$ 1943 cm^{-1} , whereas an i.r. spectrum of the insoluble blue isomer of $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ (**20**) run as a KBr disc shows $\nu(\text{CO})$ 1955 cm^{-1} which is at a higher wavenumber than for (**19**) [$\nu(\text{CO})$ (KBr disc) 1928 cm^{-1}]. It is proposed that the thermodynamically more stable blue isomer of (**20**) has a different stereochemistry with a phosphorus atom *trans* to a carbonyl ligand [Figure 2(a) and (b)] compared to the likely structure of the green isomer of (**20**) in solution (Figure 1). Since phosphines are π -acceptor ligands there will be competition for electron density in the filled metal *d* orbitals from the empty *d* orbitals on the phosphorus and the empty π^* orbitals of the *trans*-carbonyl ligand. This would result in a higher carbonyl stretching band for the isomers shown in Figure 2 compared to that for the *X*-ray structure of (**19**) shown in Figure 1 with the carbonyl ligand *trans* to a halide. It is interesting that Templeton and co-workers¹⁰ prepared the molybdenum com-

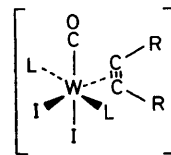


Figure 3. Proposed structure of $[\text{Wl}_2(\text{CO})\text{L}_2(\eta^2\text{-RC}_2\text{R})]$ ($\text{L} =$ monodentate phosphine, $\text{R} = \text{Me}$ or Ph)

plexes $[\text{MoBr}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\eta^2\text{-RC}_2\text{R}')]]$ ($\text{R} = \text{R}' = \text{Et}$ or Ph ; $\text{R} = \text{H}$, $\text{R}' = \text{Bu}^n$ or Ph), and from their detailed spectroscopic studies they ruled out the structure shown in Figure 1 as determined by *X*-ray crystallography for (**19**). However, they were unable to distinguish unambiguously between the isomers in Figure 2(a) and (b) although they tended to favour (a). Unfortunately we were unable to carry out ^{31}P n.m.r. studies of compound (**20**) due to the lack of solubility of the blue isomer in a variety of solvents. The bis(monodentate phosphine) complexes (**1**)–(**18**) are highly likely to have the geometry shown in Figure 3 with *trans*-phosphine ligands. Templeton and co-workers¹⁰ reported the *X*-ray crystal structure of $[\text{MoBr}_2(\text{CO})(\text{PEt}_3)_2(\eta^2\text{-PhC}_2\text{H})]$ which has this geometry and the ^{31}P n.m.r. spectra of several of the complexes (Table 3) show a single resonance. Variable-temperature ^{31}P n.m.r. spectroscopy was carried out on $[\text{Wl}_2(\text{CO})\{\text{PPh}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}_2(\eta^2\text{-MeC}_2\text{Me})]$ (**15**). A single sharp resonance was observed from $+25$ down to -90°C , hence there was no evidence for *trans*-*cis* isomerism in this complex. It should also be noted that Davidson and Vasapollo⁷ reported the preparation of the bis(triphenylphosphine) complexes $[\text{WBr}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-RC}_2\text{R}')]]$ ($\text{R} = \text{R}' = \text{Me}$ and Ph ; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$) and these were also found to show a single ^{31}P resonance and hence the *trans* geometry was proposed.

The reactions of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ with 2 equivalents of *L* in CH_2Cl_2 are likely to proceed *via* successive displacements of acetonitrile and an alkyne ligand respectively. It is likely that these reactions have associative type mechanisms, which have been previously proposed for reaction of phosphines or phosphites with four-electron-alkyne complexes of molybdenum(II) and tungsten(II).^{2b,14} It is also probable that the acetonitrile ligand is replaced first since reaction of $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{Ph})_2]$ with 1 equivalent of PPh_3 in CH_2Cl_2 gave a good yield of the acetonitrile-substituted product $[\text{MoI}_2(\text{CO})(\text{PPh}_3)(\eta^2\text{-PhC}_2\text{Ph})_2]$ which was isolated and fully characterised (see Experimental section). However, reaction of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ with 1 equivalent of *L* ($\text{L} =$ monodentate phosphines) under a variety of different conditions always gave a mixture of $[\text{Wl}_2(\text{CO})\text{L}_2(\eta^2\text{-RC}_2\text{R})]$, $[\text{Wl}_2(\text{CO})\text{L}(\eta^2\text{-RC}_2\text{R})_2]$, and $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$. For example, reaction of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ with 1 equivalent of PPh_3 in CH_2Cl_2 after 4 h gave an i.r. spectrum which showed carbonyl bands at $\nu(\text{CO})$ 1990 cm^{-1} for $[\text{Wl}_2(\text{CO})(\text{PPh}_3)(\eta^2\text{-MeC}_2\text{Me})_2]$, 1940 cm^{-1} for $[\text{Wl}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$, and at 2050 cm^{-1} for $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ with approximately equal intensity. Hence having formed some of $[\text{Wl}_2(\text{CO})\text{L}(\eta^2\text{-RC}_2\text{R})_2]$ there is a competition between $[\text{Wl}_2(\text{CO})\text{L}(\eta^2\text{-RC}_2\text{R})_2]$ and $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ for *L*. Attempts were also made to prepare the 1:1 products $[\text{Wl}_2(\text{CO})\text{L}(\eta^2\text{-RC}_2\text{R})_2]$ with $\text{L} = \text{PPh}(\text{C}_6\text{H}_{11})_2$ and $\text{P}(\text{C}_6\text{H}_{11})_3$, *i.e.* very bulky ligands, in order to slow down the reaction with a second equivalent of *L*. Although it was possible to obtain these products for $\text{R} = \text{Me}$ they were very unstable and difficult to isolate in the pure state.

All the alkyne complexes (**1**)–(**24**) exhibit a single strong carbonyl stretching band in the i.r. spectrum between 1902 and 1958 cm^{-1} (Table 1). The weak ($\text{C}\equiv\text{C}$) stretching bands between

Table 2. Proton and ^{13}C n.m.r. data* for the complexes $[\text{Wl}_2(\text{CO})\text{L}_2(\eta^2\text{-RC}_2\text{R})]$

Complex	^1H	^{13}C
(1)	3.14 (s, 6 H, MeC_2), 1.47 (t, J_{PH} 4.2, 18 H, Me)	222.38 (t, $\text{C}\equiv\text{C}$), 208.37 (s, CO), 22.90 (s, MeC_2), 18.31 (t, Me)
(2)	7.58–7.26 (br m, 10 H, PhC_2), 1.91–1.54 (br m, 18 H, Me)	221.06 (s, $\text{C}\equiv\text{C}$), 208.2 (s, CO), 138.63 (s, PhC), 129.92 (s, <i>o</i> -Ph), 128.57 (s, <i>m</i> -Ph), 128.42 (s, <i>p</i> -Ph), 18.94 (t, J_{PC} 15.4, Me)
(3)	3.17 (s, 6 H, MeC_2), 1.76 (br s, 12 H, CH_2), 0.91 (t, J_{PH} 7.4, 18 H, Me)	225.19 (t, $\text{C}\equiv\text{C}$), 201.6 (s, CO), 20.66, 19.75, 18.84 (t, CH_2 and MeC_2), 7.93 (Me)
(4)	7.62–7.35 (br m, 10 H, PhC_2), 2.63–1.93 (m, J_{PH} 3.5, 12 H, CH_2), 0.93 (qnt, J_{PH} 7.6, 18 H, Me)	225.32 (t, J_{PC} 6.2, $\text{C}\equiv\text{C}$), 214.0 (s, CO), 139.15 (br s, PhC_2), 130.35 (s, <i>o</i> -Ph), 129.57 (s, <i>m</i> -Ph), 128.81 (s, <i>p</i> -Ph), 20.76 (t, J_{PC} 13.2, CH_2), 8.45 (s, Me)
(5)	3.15 (s, 6 H, MeC_2), 1.35 (br s, 36 H, CH_2), 0.92 (s, 18 H, Me)	
(6)	7.48–7.22 (br m, 10 H, PhC_2), 1.38 (br s, 36 H, CH_2), 0.91 (s, 18 H, Me)	
(7)	7.22 (br m, 10 H, Ph), 2.37 (s, 6 H, MeC_2), 2.17–1.91 (m, 12 H, Me)	222.59 (m, $\text{C}\equiv\text{C}$), 221.89 (br s, CO), 137.33 (t, PhC_2), 128.8 (s, <i>o</i> -Ph), 128.18 (s, <i>m</i> -Ph), 127.39 (s, <i>p</i> -Ph), 22.290 (s, MeC_2), 17.15, 16.99 (q, J_{PC} 16, Me)
(8)	7.29–7.12 (m, 10 H, PhC_2 and 10 H, Ph), 2.28–1.91 (dt, J_{PH} 4.2, 12 H, Me)	221.82 (m, $\text{C}\equiv\text{C}$), 220.78 (br s, CO), 138.52, 137.36, 136.06 (m, Ph and PhC_2), 18.97, 18.06 (q, J_{PC} 14, Me)
(9)	7.43–7.17 (br m, 20 H, Ph), 2.55 (t, J_{PH} 4.2, 6 H, Me), 2.21 (6 H, MeC_2)	224.03 (br s, $\text{C}\equiv\text{C}$), 220.47 (br s, CO), 136.32, 135.67 (m, PhP), 132.81, 131.38, 130.34, 129.43, 127.87 (m, Ph), 23.0 (s, MeC_2), 20.53 (t, J_{PC} 18, Me)
(10)	7.34–7.0 (br m, 10 H, PhC_2 and 20 H, Ph), 2.62 (t, J_{PH} 4, 6 H, Me)	222.86 (br m, $\text{C}\equiv\text{C}$), 139.93 (s, PhC_2), 134.24 (s, PhP), 132.81, 129.82, 128.0 (m, Ph), 20.92 (br s, Me)
(11)	7.21 (br s, 10 H, Ph), 2.34 (br s, 6 H, MeC_2 and 12 H, CH_2), 1.26–0.78 (m, J_{PH} 7.2, 18 H, Me)	223.51 (t, $\text{C}\equiv\text{C}$), 219.22 (br s, CO), 136.19 (t, PhP), 129.43, 127.74 (m, Ph), 29.76 (MeC_2), 27.7, 20.79, 19.36, 18.45 (q, J_{PC} 14.3 and 22.5, CH_2), 18.71, 18.06 (d, J_{PC} 10.2, Me)
(12)	7.1 (br m, 20 H, PhC_2), 2.46 (br s, 8 H, CH_2), 1.11, 0.80 (dd, J_{PH} 7.2, 12 H, Me)	223.51 (t, $\text{C}\equiv\text{C}$), 220.29 (br s, CO), 138.39, 136.45, 135.28, 133.98 (m, PhC_2 and PhP), 129.95, 129.17, 127.87 (m, Ph), 21.57, 20.4 (q, J_{PC} 14.3, CH_2), 8.71 (s, Me)
(13)	7.46–7.22 (br m, 20 H, Ph), 3.0 (br d, 4 H, CH_2), 2.11 (s, 6 H, MeC_2), 0.70 (q, J_{PH} 7.2, 6 H, Me)	218.0 (br s, $\text{C}\equiv\text{C}$), 213.89 (m, $\text{C}\equiv\text{O}$), 125.4, 123.58, 121.76, 120.98, 119.29 (m, Ph), 21.18 (s, MeC_2), 8.62 (s, Me)
(14)	7.35–6.92 (br m, 10 H, PhC_2 and 20 H, Ph), 3.53–3.3 (m, 4 H, CH_2), 1.20 (t, J_{PH} 7.2, 3 H, Me), 0.61 (t, J_{PH} = 7.2, 3 H, Me)	222.47 (s, $\text{C}\equiv\text{C}$), 221.17 (s, CO), 133.33, 133.07 (m, PhC_2 and PhP), 130.08, 129.43, 128.0 (m, Ph), 15.33 (s, CH_2), 8.44 (s, Me)
(15)	7.58–7.17 (br m, 20 H, Ph), 5.16 (m, 2 H, CH_2P), 4.70 (m, 2 H, CH_2), 4.10 (m, 2 H, CH_2), 3.32 (m, 2 H, CH), 2.07 (m, 6 H, MeC_2)	222.49 (t, J_{PC} 5.5, $\text{C}\equiv\text{C}$), 221.0 (br s, CO), 134.32 (s, PhC_2), 132.59, 130.96, 129.04, 127.64 (m, Ph), 119.78 (t, J_{PC} 4.5, CH_2), 37.32 (t, J_{PC} 13.7, CH_2), 23.10 (s, MeC_2)
(16)	7.36–6.92 (br m, 10 H, PhC_2 and 20 H, Ph), 5.28 (br s, 2 H, CH_2P), 4.87 (m, 2 H, CH_2), 4.16 (br s, 2 H, CH_2), 3.74 (br s, 2 H, CH)	221.69 (br s, $\text{C}\equiv\text{C}$), 139.56 (br s, Ph), 133.46, 130.21, 127.87 (m, PhC_2 and Ph), 119.68 (m, CH), 37.43 (t, J_{PC} 14.5, CH_2)
(17)	7.59–7.35 (dm, 30 H, Ph), 2.33 (t, J_{PH} 1.4, 6 H, MeC_2)	
(18)	7.67, 7.34 (br m, 20 H, Ph), 2.98 (s, 6 H, MeC_2), 2.00, 1.59 (br m, 22 H, C_6H_{11})	
(19)	7.81–7.43 (br m, 20 H, Ph), 3.0 (s, 6 H, MeC_2), 1.23 (s, 2 H, CH_2)	223.08 (d, J_{PC} 6, $\text{C}\equiv\text{C}$), 208.40 (s, CO), 133.15, 132.79, 132.04, 131.53, 130.26, 128.81, 128.41 (m, Ph), 31.27 (t, J_{PC} 24.8, CH_2), 21.71 (s, MeC_2)
(20)	7.68–7.1 (br m, 20 H, Ph), 2.98 (s, 6 H, MeC_2), 1.56 and 1.23 (s, 4 H, CH_2)	
(21)	7.86–7.28 (br m, 20 H, Ph), 3.29 (s, 6 H, MeC_2), 2.28–2.0 (br m, 6 H, CH_2)	
(22)	7.37–7.16 (br m, 20 H, Ph), 2.83 (br s, 4 H, CH_2P), 2.03 (s, 6 H, MeC_2), 0.88 (br s, 4 H, CH_2)	
(23)	7.55–7.17 (br m, 20 H, Ph), 2.77 (br s, 4 H, CH_2P), 2.05 (s, 6 H, MeC_2), 1.25 (s, 4 H, CH_2), 0.92 (br s, 4 H, CH_2)	
(24)	7.65 (br s, 20 H, Ph), 4.85 (br s, 8 H, CH_2), 2.76 (br s, 6 H, MeC_2)	

* Spectra run in CDCl_3 (+25 °C) referenced to SiMe_4 ; J in Hz. s = Singlet; br = broad; d = doublet; dd = doublet of doublets; m = multiplet; q = quartet; t = triplet; qnt = quintet; dt = doublet of triplets.

Table 3. ^{31}P N.m.r. data* for selected complexes $[\text{Wl}_2(\text{CO})\text{L}_2(\eta^2\text{-RC}_2\text{R})]$

Complex	$\delta(^{31}\text{P})/\text{p.p.m.}; J$ in Hz
(1)	–30.60 (s, J_{WP} 272)
(2)	–42.49 (s, $J_{\text{WP}} \approx 268$)
(4)	–17.08 (s, J_{WP} 256)
(7)	–31.60 (s, J_{WP} 268)
(15)	–9.20 (s, J_{WP} 267)
(17)	9.87 (s, J_{WP} 268)
(19)	–23.38 (d, $^2J_{\text{PP}}$ 40.56), –47.33 (d, $^2J_{\text{PP}}$ 40.55)

* Spectra recorded in CDCl_3 , referenced to H_3PO_4 .

1 610 and 1 682 cm^{-1} for compounds (1)–(24) are at considerably lower wavenumber than for the unco-ordinated alkyne ligands. This is to be expected since there is considerable back donation of electron density from the filled metal orbitals to the empty π^* type orbitals on the alkyne ligand when it is co-ordinated to the metal, as shown by the bending back of the methyl groups on the but-2-yne ligand in the X-ray crystal structure of (19) (Figure 1).

The room-temperature ^1H n.m.r. spectra (Table 2) for the complexes (1)–(24) showed the expected features for the static structures shown in Figures 1–3. Variable-temperature ^1H n.m.r. spectra were recorded for complexes (1), (3), (5), (7), (9), (11), (13), and (17)–(19) (Table 4). This gave an insight into

Table 4. Rotational barriers for but-2-yne complexes of the type $[\text{MX}_2(\text{CO})\text{L}_2(\eta^2\text{-MeC}_2\text{Me})]$

Complex	T_c/K	$\Delta\nu/\text{Hz}$	$\Delta G^\ddagger(T_c)/\text{kJ mol}^{-1}$	Ref.
$[\text{Wl}_2(\text{CO})(\text{PMe}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$	211	61.87	42.5	This work
$[\text{Wl}_2(\text{CO})(\text{PMe}_2\text{Ph})_2(\eta^2\text{-MeC}_2\text{Me})]$	231	107.55	45.6	This work
$[\text{Wl}_2(\text{CO})(\text{PMePh}_2)_2(\eta^2\text{-MeC}_2\text{Me})]$	243	87.63	48.5	This work
$[\text{Wl}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$	256	119.48	50.4	This work
$[\text{Wl}_2(\text{CO})(\text{PEtPh}_2)_2(\eta^2\text{-MeC}_2\text{Me})]$	265	455.73	49.4	This work
$[\text{Wl}_2(\text{CO})(\text{PEt}_2\text{Ph})_2(\eta^2\text{-MeC}_2\text{Me})]$	288	237.60	55.5	This work
$[\text{Wl}_2(\text{CO})(\text{PEt}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$	285	55.67	58.3	This work
$[\text{Wl}_2(\text{CO})(\text{PBu}^n)_2(\eta^2\text{-MeC}_2\text{Me})]$	285	47.87	58.7	This work
$[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$	251.5	125.51	49.5	This work
$[\text{Wl}_2(\text{CO})\{\text{PPh}_2(\text{C}_6\text{H}_{11})\}_2(\eta^2\text{-MeC}_2\text{Me})]$	296	10.39	64.8	This work
$[\text{MoBr}_2(\text{CO})(\text{PEt}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$	256	29.44	52.3	10
$[\text{MoCl}_2(\text{CO})(\text{PEt}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$	215	8.0	45.9	10
$[\text{MoCl}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$	208	211.2	38.8	10
$[\text{WCl}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$	191	26.24	38.8	10
$[\text{WBr}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$	210.15	120.92	41.1	7

how the electronic and steric effects of different functional groups attached to the phosphorus atoms affect the barriers to but-2-yne rotation. Comparisons are also made with analogous dichloro and dibromo complexes reported by Templeton and co-workers¹⁰ and by Davidson and Vasapollo.⁷ The activation barriers (ΔG^\ddagger) for but-2-yne rotation were calculated using the Gutowsky-Holm equations^{15,16} and standardised to a 400-MHz instrument.

Complexes with phosphines which are better σ donors would be expected to have higher barriers to but-2-yne rotation, since increasing the electron density on the metal would result in increased back donation to the π^* orbitals of the alkyne ligand and hence hinder rotation. The ligand cone angle (θ) has been used to describe the steric effects of a wide variety of phosphorus donor ligands,¹⁷ and it would be expected that the larger the cone angle the higher is the barrier to rotation of the alkyne ligand. From Table 4, di-iodo complexes with ligands having similar electronic properties, *i.e.* PMe_3 (**1**) and PEt_3 (**3**), but significantly different cone angles (for PMe_3 , $\theta = 118^\circ$; PEt_3 , $\theta = 132^\circ$), have, as expected, barriers of 42.5 and 58.3 kJ mol^{-1} respectively. Also the ligands PEt_3 (**3**) and PBu^n_3 (**5**) with similar electronic properties and cone angles (for PBu^n_3 , $\theta = 132^\circ$) have very similar barriers to but-2-yne rotation. However, having the poorer σ -donor PPh_3 ligand (cone angle = 145°), complex (**17**) was found to have a lower barrier than either the bis PEt_3 or PBu^n_3 compounds which suggests that electronic effects are dominant in this comparison. An increase in activation energy from steric effects and a decrease from electronic effects would be expected across the series PMe_3 , PMe_2Ph , PMePh_2 , and PPh_3 . The results in Table 4 indicate that it is the steric effects which are predominant and from a plot of cone angle *versus* ΔG^\ddagger for these phosphine ligands a reasonable straight line is obtained (Figure 4). However, for the PEt_3 to PPh_3 series electronic effects appear to be important (Figure 4). It is interesting that the complex $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{-}$

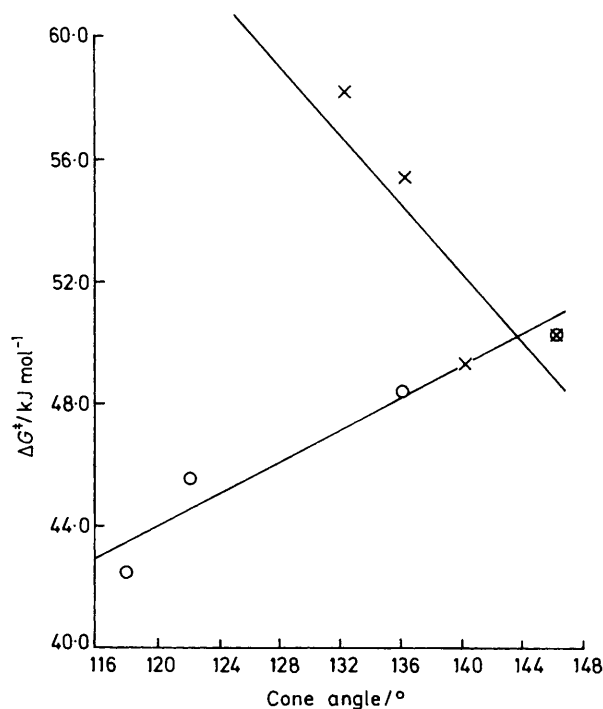


Figure 4. The relationship between the barrier to but-2-yne rotation (ΔG^\ddagger) and the cone angle of the phosphine ligand in the series of complexes $[\text{Wl}_2(\text{CO})\text{L}_2(\eta^2\text{-MeC}_2\text{Me})]$ [$\text{L} = \text{PMe}_3$, PMe_2Ph , PMePh_2 , or PPh_3 (\circ); PEt_3 , PEt_2Ph , PEtPh_2 , or PPh_3 (\times)]

$\text{PPh}_2\}\{\eta^2\text{-MeC}_2\text{Me}\}$ (**19**) has a similar barrier to that of $[\text{Wl}_2(\text{CO})(\text{PMePh}_2)_2(\eta^2\text{-MeC}_2\text{Me})]$ (**9**); $\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$ and 2PMePh_2 have similar electronic properties but different stereochemistries (Figures 1 and 3). The highest barrier to but-2-yne rotation was observed for the complex $[\text{Wl}_2(\text{CO})\{\text{PPh}_2(\text{C}_6\text{H}_{11})\}_2(\eta^2\text{-MeC}_2\text{Me})]$ (**18**) ($\Delta G^\ddagger = 64.8 \text{ kJ mol}^{-1}$) where the $\text{PPh}_2(\text{C}_6\text{H}_{11})$ ligand has a large cone angle, $\theta = 153^\circ$. Several attempts were made to prepare the complexes $[\text{Wl}_2(\text{CO})\{\text{PPh}(\text{C}_6\text{H}_{11})\}_2(\eta^2\text{-MeC}_2\text{Me})]$ and $[\text{Wl}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2(\eta^2\text{-MeC}_2\text{Me})]$ without success, presumably due to the very large cone angles of $\text{PPh}(\text{C}_6\text{H}_{11})_2$ and $\text{P}(\text{C}_6\text{H}_{11})_3$. The complex $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ was treated with 2 equivalents of EPh_3 ($\text{E} = \text{As}$ or Sb) in refluxing CHCl_3 , although some reaction occurred there was considerable decomposition, and we were unfortunately not able to compare the PPh_3 , AsPh_3 , and SbPh_3 series.

As stated in the Introduction, Templeton and co-workers¹⁰ and Davidson and Vasapollo⁷ were unable to prepare any di-iodo alkyne complexes, however they prepared several dichloro and dibromo complexes and measured barriers to but-2-yne rotation of some of their complexes (Table 4). It is useful to compare the series $[\text{MX}_2(\text{CO})\text{L}_2(\eta^2\text{-MeC}_2\text{Me})]$ ($\text{X} = \text{Cl}$, Br , or I ; $\text{L} = \text{PEt}_3$ or PPh_3) in order to see if the electronic and steric effects of the halides can be correlated with the barrier to but-2-yne rotation for these complexes. It should be noted that some of Templeton's complexes are of molybdenum, however the complexes $[\text{MCl}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$ ($\text{M} = \text{Mo}$ or W) both have the same barrier to but-2-yne rotation ($\Delta G^\ddagger = 38.8 \text{ kJ mol}^{-1}$). It can be presumed that the metal has little effect in this system. From a consideration of ΔG^\ddagger *versus* electronegativity¹⁸ for both the PEt_3 and PPh_3 series of complexes, as expected in all cases the complexes with the more electronegative halogen atoms have the lower barriers to alkyne rotation. It was also found that the larger the halide¹⁹ the higher is the barrier to but-2-yne rotation. It is likely that electronic

and steric effects of both different halide and phosphine ligands affect the barrier of but-2-yne rotation in these complexes.

The ^{13}C n.m.r. spectra of these $[\text{Wl}_2(\text{CO})\text{L}_2(\eta^2\text{-RC}_2\text{R})]$ complexes all have alkyne contact carbon shifts above 200 p.p.m. (see Table 2). This indicates that the alkyne ligands are utilising both their filled p_π orbitals to donate electron density to the tungsten. Templeton and Ward²⁰ have correlated ^{13}C alkyne contact carbon shifts with the number of electrons donated to the metal; values above 200 p.p.m. are in accord with the alkyne ligand donating four electrons to the metal. It is often difficult to distinguish between alkyne contact carbon resonances and carbonyl resonances in these four-electron alkyne complexes. However, in view of the X-ray crystal structure of $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ (**19**) described herein, the but-2-yne contact carbons show a resonance at δ 223.08 p.p.m. (d, $J_{\text{P-C}} = 6$ Hz) *i.e.* with phosphorus coupling to the *trans*-but-2-yne ligand. The carbonyl resonance at δ 208.40 p.p.m. shows no phosphorus coupling. Other workers^{2b} have also found that for four-electron alkyne complexes the alkyne contact carbon shifts are at lower field than for the co-ordinated carbonyl ligand.

Experimental

The preparation and purification of the complexes described were carried out under an atmosphere of dry nitrogen using vacuum/Schlenk-line techniques. Dichloromethane was dried over P_2O_5 and distilled before use. The complexes $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ (R = Me or Ph) and $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{Ph})_2]$ were prepared according to the literature method,¹¹ and all chemicals were purchased from commercial sources except $\text{PPh}_2(\text{C}_6\text{H}_{11})$ and $\text{PPh}(\text{C}_6\text{H}_{11})_2$ which were prepared by Open University S304 Summer School Students at Nottingham University. Elemental analyses (C, H, and N) were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas) by Mr. E. Lewis of the Department of Chemistry, University College of North Wales, Bangor. Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer, ^1H , ^{13}C , and ^{31}P n.m.r. spectra either on a JEOL FX 60 or a Bruker WH 400 n.m.r. spectrometer.

$[\text{Wl}_2(\text{CO})(\text{PMe}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$ (**1**).—A solution of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ (0.501 g, 0.813 mmol) in CH_2Cl_2 (10 cm^3) contained in a Schlenk tube was cooled to -196°C and evacuated. An excess of trimethylphosphine (2.44 mmol) was distilled into the Schlenk tube by direct pyrolysis of $[\{\text{AgI}(\text{PMe}_3)_4\}]$ (0.759 g, 0.610 mmol) at 200°C . When the pyrolysis was complete the Schlenk tube was allowed to warm to 20°C and opened to nitrogen. Stirring of the reaction mixture started as soon as the CH_2Cl_2 had melted. The solvent was removed *in vacuo* after stirring the solution for 12 h at room temperature, giving a grey-green oil. The latter was eluted on a silica column and the product collected as a blue-grey band (eluant: diethyl ether). Removal of the solvent *in vacuo* afforded pure $[\text{Wl}_2(\text{CO})(\text{PMe}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$ as a blue-grey crystalline solid (yield 0.20 g, 37%). The complex $[\text{Wl}_2(\text{CO})(\text{PMe}_3)_2(\eta^2\text{-PhC}_2\text{Ph})]$ (**2**) was prepared in an analogous manner (see Table 1 for the physical and analytical data).

$[\text{Wl}_2(\text{CO})(\text{PEt}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$ (**3**).—To a solution of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ (0.500 g, 0.813 mmol) in CH_2Cl_2 (15 cm^3) was added triethylphosphine (0.24 cm^3 , 1.626 mmol). The solution was stirred under N_2 for 13 h. Filtration and removal of solvent *in vacuo* gave a purple crystalline solid, $[\text{Wl}_2(\text{CO})(\text{PEt}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$, which was recrystallised from CH_2Cl_2 . Yield 0.48 g, 78%. Compounds (**5**), (**7**), (**9**), (**11**), (**13**), and (**15**) were prepared in a similar manner.

$[\text{Wl}_2(\text{CO})(\text{PEt}_3)_2(\eta^2\text{-PhC}_2\text{Ph})]$ (**4**).—To a solution of

Table 5. Selected bond lengths (Å) and angles ($^\circ$) for $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ (**19**)

I(1)–W	2.775(4)	I(2)–W	2.862(4)
P(1)–W	2.644(7)	P(2)–W	2.497(6)
C(1)–W	2.040(20)	C(2)–W	2.025(20)
C(3)–W	1.943(19)	C(11)–P(1)	1.827(17)
C(12)–P(1)	1.806(14)	C(6)–P(1)	1.837(18)
C(21)–P(2)	1.822(14)	C(22)–P(2)	1.803(18)
C(6)–P(2)	1.813(19)	C(2)–C(1)	1.283(24)
C(5)–C(1)	1.514(35)	C(4)–C(2)	1.462(31)
O–C(3)	1.161(19)		
I(2)–W–I(1)	87.5(1)	P(1)–W–I(1)	94.9(2)
P(1)–W–I(2)	80.7(2)	P(2)–W–I(1)	158.8(1)
P(2)–W–I(2)	83.9(2)	P(2)–W–P(1)	64.6(2)
C(1)–W–I(1)	101.7(6)	C(1)–W–I(2)	124.5(6)
C(1)–W–P(1)	150.0(5)	C(1)–W–P(2)	99.2(6)
C(2)–W–I(1)	107.7(6)	C(2)–W–I(2)	88.0(7)
C(2)–W–P(1)	154.3(5)	C(2)–W–P(2)	91.4(6)
C(2)–W–C(1)	36.8(7)	C(3)–W–I(1)	86.2(5)
C(3)–W–I(2)	163.7(5)	C(3)–W–P(1)	84.8(6)
C(3)–W–P(2)	96.7(6)	C(3)–W–C(1)	71.6(8)
C(3)–W–C(2)	108.3(9)	C(11)–P(1)–W	126.2(6)
C(12)–P(1)–W	116.8(6)	C(12)–P(1)–C(11)	104.5(8)
C(6)–P(1)–W	92.7(6)	C(6)–P(1)–C(11)	106.5(8)
C(6)–P(1)–C(12)	107.8(8)	C(21)–P(2)–W	121.4(6)
C(22)–P(2)–W	120.0(6)	C(22)–P(2)–C(21)	102.1(7)
C(6)–P(2)–W	98.2(6)	C(6)–P(2)–C(21)	107.0(8)
C(6)–P(2)–C(22)	106.7(9)		
C(111)–C(11)–P(1)	119.5(5)	C(115)–C(11)–P(1)	120.4(5)
C(121)–C(12)–P(1)	115.9(4)	C(125)–C(12)–P(1)	124.0(4)
C(211)–C(21)–P(2)	116.5(5)	C(215)–C(21)–P(2)	123.5(5)
C(221)–C(22)–P(2)	119.1(6)	C(225)–C(22)–P(2)	120.8(6)
C(2)–C(1)–W	71.0(13)	C(5)–C(1)–W	148.1(16)
C(1)–C(2)–W	72.2(12)	C(4)–C(2)–W	146.4(22)
C(4)–C(2)–C(1)	141.3(25)	O–C(3)–W	176.2(16)
C(5)–C(1)–C(2)	141.0(20)	P(2)–C(6)–P(1)	97.8(9)

$[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{Ph})_2]$ (0.500 g, 0.579 mmol) in CH_2Cl_2 (15 cm^3) was added triethylphosphine (0.17 cm^3 , 1.158 mmol). After stirring for 17 h, filtration, and removal of solvent *in vacuo* yielded dark green $[\text{Wl}_2(\text{CO})(\text{PEt}_3)_2(\eta^2\text{-PhC}_2\text{Ph})]$ which was redissolved in CH_2Cl_2 (1 cm^3) and chromatographed on a silica column. The latter was eluted with diethyl ether after light petroleum (b.p. $60\text{--}80^\circ\text{C}$, 100 cm^3) had first been passed through the column (to remove excess of PhC_2Ph). Removal of solvent *in vacuo* gave dark green crystals of (**4**). Yield 0.49 g, 97%. Compounds (**6**), (**8**), (**10**), (**12**), (**14**), and (**16**) were prepared in a similar manner.

$[\text{Wl}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$ (**17**).—To a stirred solution of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ (0.500 g, 0.813 mmol) in CH_2Cl_2 (15 cm^3) was added triphenylphosphine (0.426 g, 1.624 mmol). Filtration and removal of solvent *in vacuo* after 48 h yielded a dark green crystalline powder which was recrystallised from CH_2Cl_2 to give pure $[\text{Wl}_2(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$. Yield 0.82 g, 97%. The preparation of complexes (**18**) and (**24**) differed only in the reaction times, 3 and 5 d respectively.

$[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ (**19**).—To a stirred solution of $[\text{Wl}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ (1.00 g, 1.626 mmol) in CH_2Cl_2 (20 cm^3) was added bis(diphenylphosphino)methane (0.625 g, 1.626 mmol). After 13 h, filtration and removal of solvent *in vacuo* gave a green crystalline powder which was dissolved in the minimum quantity of CH_2Cl_2 and cooled to -30°C for 17 h. This afforded analytically pure crystals of $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ suitable for X-ray crystallography. Yield 1.35 g, 92%. Compounds (**20**)–(**23**) were prepared in an analogous manner.

Table 6. Fractional atomic co-ordinates ($\times 10^4$) for $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$

Atom	x	y	z
W	4 064(1)	1 848(1)	1 643
I(1)	2 763(1)	185(1)	1 164(1)
I(2)	3 524(1)	1 503(1)	2 886(1)
P(1)	2 321(4)	3 071(3)	1 506(2)
P(2)	4 529(4)	3 569(3)	2 089(2)
C(111)	580(12)	3 511(8)	2 113(7)
C(112)	-453(12)	3 343(8)	2 268(7)
C(113)	-1 061(12)	2 474(8)	2 052(7)
C(114)	-637(12)	1 772(8)	1 681(7)
C(115)	396(12)	1 940(8)	1 526(7)
C(11)	1 005(12)	2 810(8)	1 742(7)
C(121)	1 399(12)	3 147(7)	175(6)
C(122)	982(12)	3 597(7)	-441(6)
C(123)	1 051(12)	4 631(7)	-505(6)
C(124)	1 536(12)	5 213(7)	47(6)
C(125)	1 953(12)	4 763(7)	663(6)
C(12)	1 884(12)	3 730(7)	727(6)
C(211)	6 612(9)	3 681(10)	2 967(6)
C(212)	7 376(9)	3 819(10)	3 580(6)
C(213)	6 982(9)	4 052(10)	4 137(6)
C(214)	5 824(9)	4 148(10)	4 080(6)
C(215)	5 060(9)	4 011(10)	3 466(6)
C(21)	5 454(9)	3 777(10)	2 910(6)
C(221)	5 658(13)	4 185(11)	1 160(7)
C(222)	6 102(13)	4 892(11)	801(7)
C(223)	5 915(13)	5 906(11)	882(7)
C(224)	5 283(13)	6 214(11)	1 321(7)
C(225)	4 840(13)	5 506(11)	1 679(7)
C(22)	5 027(13)	4 492(11)	1 598(7)
C(1)	5 570(15)	1 489(12)	1 444(9)
C(2)	5 651(16)	1 370(13)	2 066(9)
C(3)	3 973(15)	2 167(12)	721(8)
O	3 974(12)	2 325(11)	172(6)
C(4)	6 440(31)	1 019(24)	2 671(14)
C(5)	6 260(28)	1 390(24)	935(15)
C(6)	3 121(13)	3 948(13)	2 125(9)

$[\text{MoI}_2(\text{CO})(\text{PPh}_3)(\eta^2\text{-PhC}_2\text{Ph})_2]$.—To a stirred solution of $[\text{MoI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-PhC}_2\text{Ph})_2]$ (0.470 g, 0.606 mmol) in CH_2Cl_2 (10 cm^3) was added triphenylphosphine (0.160 g, 0.606 mmol). After 4 h. filtration and removal of solvent gave a gold crystalline powder which was recrystallised from CH_2Cl_2 to give pure $[\text{MoI}_2(\text{CO})(\text{PPh}_3)(\eta^2\text{-PhC}_2\text{Ph})_2]$. Yield 0.48 g, 80% (Found: C, 56.2; H, 3.8. Calc. for $\text{C}_{47}\text{H}_{35}\text{I}_2\text{MoOP}$: C, 56.6; H, 3.5%). I.r.: $\nu(\text{CO})$ 1 980s, $\nu(\text{C}\equiv\text{C})$ 1 760w cm^{-1} . ^1H N.m.r. (CDCl_3 , 25 °C): δ 7.38 (m, PhC_2 and Ph).

Crystal Structure Analysis of $[\text{Wl}_2(\text{CO})\{\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})]$ (19).—The single crystal used for the X-ray examination was sealed under nitrogen in a capillary. Following preliminary photographic examination, crystallographic data were obtained using a CAD4 diffractometer, operating in the ω -2 θ scan mode and using graphite-monochromatised Mo- K_2 radiation as previously described.²¹ Relevant details are as follows.

Crystal data. $\text{C}_{30}\text{H}_{20}\text{I}_2\text{OP}_2\text{W}$, $M = 904.16$, monoclinic, $a = 12.208(4)$, $b = 13.395(2)$, $c = 20.820(6)$ Å, $\beta = 104.31(2)^\circ$, $U = 3 299.4(7)$ Å³, space group $P2_1/n$, $Z = 4$, $D_c = 1.82$ g cm^{-3} , $\mu(\text{Mo-}K_2) = 55.4$ cm^{-1} , $F(000) = 1 704$.

Total unique data measured, 4 581 ($1.5 \leq \theta \leq 23^\circ$), 2 860 observed [$I > 1.5\sigma(I)$]. An analytical absorption correction was applied. The structure was solved *via* the heavy-atom

method and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were inserted in calculated positions, allowed to ride on the parent carbons and assigned group U_{iso} values. Computer programs used as given in ref. 22; scattering factor data as in SHELX 80²² (C, H, O, P) or from ref. 23 (W, I). The final R , R' values were 0.052, 0.060 respectively, with weights of $w = 1/[\sigma^2(F) + 0.0012F_0^2]$ giving flat agreement analyses. The final atomic positional parameters are given in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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