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Synthesis and characterisation of the bidentately attached linear triphos complexes [MXY(CO)(L-P,P')(η^2-RC_2R)] {M = Mo, W; X, Y = Cl, Br, I; L = $PhP(CH_2CH_2PPh_2)_2$; R = Me, Ph}. X-ray crystal structures of [WX_2(CO)(L-P,P')(η^2-PhC_2Ph)] (X = Br and I) and [MoI_2(O){$Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2$-$P$,$P'$,$O$}]

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Abstract

Reaction of equimolar quantities of [MXY(CO)(NCMe)(η^2-RC_2R)$_2$] and L {L = $PhP(CH_2CH_2PPh_2)_2$} in CH_2Cl_2 at room temperature gives the bidentately coordinated triphos complexes [MXY(CO)(L-P,P')(η^2-RC_2R)] (M = Mo, X = Y = I, R = Me or Ph; M = W, X = Y = Br, R = Me or Ph; M = W, X = Br, Cl, Y = I, R = Me or Ph) (**1**–**8**) in high yield. The molecular structures of [WX_2(CO)(L-P,P')(η^2-PhC_2Ph)] (X = Br, I) have been determined crystallographically and are equivalent. The coordination geometry about the tungsten atom in both complexes is distorted octahedral with two adjacent phosphorus atoms in the triphos ligand, a halide and a carbonyl ligand occupying the equatorial plane, with the diphenylacetylene and the other halide atom occupying the axial positions. The ^{13}C-NMR spectrum of WBr_2(CO)(L-P,P')η^2-PhC_2Ph (**4**) shows the diphenylacetylene ligand is donating four electrons to the metal. Refluxing a slightly wet acetonitrile solution of [MoI_2(CO)(L-P,P')(η^2-MeC_2Me)] for 24 h affords the unusual crystallographically characterised molybdenum(IV) oxidised triphos complex [MoI_2(O){$Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2$-$P$,$P'$,$O$}] (**9**). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum; Tungsten; Alkynes; Triphos; Carbonyls; Halide; Crystal structure; Oxide complex

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1. Introduction

Molybdenum(II) and tungsten(II) haloalkyne complexes have been much studied over the years [1,2], including phosphine complexes of the type [MX_2(CO)L_2(η^2-RC_2R')] (M = Mo or W; X = Cl, Br, I; L = monodentate phosphine, L_2 = bidentate phosphine; R,R′ = H, alkyl or aryl) [3–11]. Organotransition-metal complexes containing pendant phosphine groups have been prepared and studied to form bimetallic complexes over the years [12–20]. However, apart from our work very few molybdenum(II) and tungsten(II) complexes containing such groups have been described.

Recently [21], we described the synthesis, molecular structures (R = Me, R′ = Me or Ph) and reactions as monodentate phosphines with molybdenum(II) and tungsten(II) complexes, the bidentately attached linear triphos {linear triphos = $PhP(CH_2CH_2PPh_2)_2$} tungsten complexes [WI_2(CO)(L-P,P')(η^2-RC_2R')] (R = R′ = Me or Ph; R = Me, R′ = Ph). In this paper we extend this work to the preparation of molybdenum complexes and mixed halide complexes of the type [MXY(CO)(L-P,P')(η^2-RC_2R)] {M = Mo, X = Y = I, R = Me or Ph; M = W, X = Y = Br, R = Me or Ph; M = W, X = Br or Cl, Y = I, R = Me or Ph; L = $PhP(CH_2CH_2PPh_2)_2$}. The X-ray crystal structures of [WX_2(CO)(L-P,P')(η^2-

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$\mathrm{PhC_2Ph)]}$ (X = Br, I) are discussed also and the oxidation of $[\mathrm{MoI_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{MeC_2Me})]$ in refluxing acetonitrile to give the crystallographically characterised complex $[\mathrm{MoI_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2\text{-}}P,P',O\}]$.

2. Results and discussion

Equimolar quantities of $[\mathrm{MXY(CO)(NCMe)}(\eta^2\text{-}\mathrm{RC_2R})_2]$ [11,22–24] and L $\{\mathrm{L = PhP(CH_2CH_2PPh_2)_2}\}$ react in $\mathrm{CH_2Cl_2}$ at room temperature to afford eventually the new complexes $[\mathrm{MXY(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{RC_2R})]$ (M = Mo, X = Y = I, R = Me or Ph; M = W, X = Y = Br, R = Me or Ph; M = W, X = Br or Cl, Y = I, R = Me or Ph) (**1**–**8**) via displacement of acetonitrile and an alkyne ligand. Complexes **1**–**8** have been characterised by elemental analysis (C, H and N) (Table 1), IR spectroscopy, ^{1}H-NMR, ^{31}P-NMR spectroscopy (Table 2) and for **4** by ^{13}C-NMR spectroscopy. The complexes $[\mathrm{MoI_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]\cdot 0.5\mathrm{CH_2Cl_2}$ (**2**), $[\mathrm{WBrI(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{MeC_2Me})]\cdot \mathrm{CH_2Cl_2}$ (**5**) and $[\mathrm{WClI(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]\cdot \mathrm{CH_2Cl_2}$ (**8**) were confirmed as solvates by repeated elemental analyses and ^{1}H-NMR spectroscopy. Complexes **1**–**8** are reasonably soluble in chlorinated solvents such as $\mathrm{CH_2Cl_2}$ and $\mathrm{CHCl_3}$; however, they are much less soluble in diethyl ether and hydrocarbon solvents. As expected, the 2-butyne complexes are more soluble than their diphenylacetylene counterparts. All the complexes are air-sensitive in solution, but can be stored in the solid state in the absence of air for several days. It appears that the molybdenum complexes are less stable than their tungsten counterparts, and the mixed halide complexes less stable than their dihalo counterparts.

The infrared spectra of complexes **1**–**8** all show a single carbonyl band in their spectra in the range 1955–1979 cm^{-1}. Complexes with identical halide groups and alkyne ligands have similar carbonyl stretching bands, which suggests that as expected the metal has little effect on σ-donor/π-acceptor properties of the carbonyl ligand. The complexes **1**–**8** also have alkyne (C≡C) stretching frequencies at considerably lower wavenumber than for the unattached alkyne.

Single crystals of $[\mathrm{WX_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]$ (X = Br and I) suitable for X-ray crystallography were grown from concentrated solutions of $\mathrm{CH_2Cl_2/Et_2O}$ (4:1) mixtures at −17°C for several weeks. It should be noted that the diiodide complex $[\mathrm{WI_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]$ has been prepared previously [21]. The molecular structures of $[\mathrm{WBr_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]$ (**4**) and $[\mathrm{WI_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]$ (**10**), respectively, are shown in Figs. 1 and 2 together with the atomic numbering scheme, and the atomic coordinates and bond lengths and angles are given in Table 3.

The structures of $[\mathrm{WX_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]$ {X = Br (**4**), X = I(**10**)} are shown in Figs. 1 and 2, together with the atomic numbering schemes. The structures are equivalent but not isomorphous. The metal atoms can best be considered as occupying a distorted octahedral environment with the diphenylacetylene ligand occupying one site *trans* to an iodine. Dimensions are given in Table 3. Two of the phosphorus atoms in the triphos ligand are bonded to the metal, with P(1) *trans* to carbonyl giving rise to a longer bond (2.589 (4) Å) in (**4**), (2.563 (3) Å) in $[\mathrm{WI_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]$ (**10**) than P(4) *trans* to iodide (2.489(4), 2.513 (3) Å). This arrangement of atoms in the metal coordination sphere is equivalent to that found for $[\mathrm{WI_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{MeC_2Ph})]$ and $[\mathrm{WI_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{MeC_2Me})]$ [21] where the third phosphorus atom of the triphos is unattached. However, in $[\mathrm{WI_2(CO)(dppm)}(\eta^2\text{-}\mathrm{MeC_2Me})]$, the two phosphorus atoms are *trans* to an iodine and the but-2-yne [6].

In $[\mathrm{WI_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]$, the iodine I(3) *trans* to the diphenylacetylene forms a longer bond {2.840(2) Å} than the iodine I(2) *trans* to phosphorus P(4). This is true also for the W–Br distances in the complex $[\mathrm{WBr_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]$ (**4**), which

Table 1
Physical and analytical data for the complexes $[\mathrm{MXY(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{RC_2R'})]$ (**1**–**8**) and $[\mathrm{MoI_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2\text{-}}P,P',O\}]$ (**9**)[a]

Complex		Colour	Yield (%)	Analysis (%)	
				C	H
1	$[\mathrm{MoI_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{MeC_2Me})]$	Brown	88	48.2 (48.5)	3.8 (4.1)
2	$[\mathrm{MoI_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]0.5\mathrm{CH_2Cl_2}$	Brown	91	52.2 (52.5)	3.4 (3.9)
3	$[\mathrm{WBr_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{MeC_2Me})]$	Purple	85	48.5 (48.8)	4.0 (4.1)
4	$[\mathrm{WBr_2(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]$	Blue	91	54.6 (54.3)	4.2 (4.0)
5	$[\mathrm{WBrI(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{MeC_2Me})].\mathrm{CH_2Cl_2}$	Purple	89	43.4 (44.0)	3.7 (3.8)
6	$[\mathrm{WBrI(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})]$	Green	79	52.3 (52.0)	3.8 (3.8)
7	$[\mathrm{WClI(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{MeC_2Me})]$	Purple	94	48.9 (48.6)	4.6 (4.1)
8	$[\mathrm{WClI(CO)(L\text{-}}P,P')(\eta^2\text{-}\mathrm{PhC_2Ph})].\mathrm{CH_2Cl_2}$	Green	84	51.3 (51.2)	4.3 (3.9)
9	$[\mathrm{MoI_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2\text{-}}P,P',O\}].0.5\mathrm{CH_2Cl_2}$	Dark brown	80	44.9 (44.4)	3.9 (3.9)

[a] Calculated values in parentheses.

Table 2
Infrared[a], ^{1}H[b]- and ^{31}P[c]-NMR spectroscopic data for the complexes $[\mathrm{MXY(CO)(L}\text{-}P,P')(\eta^2\text{-}\mathrm{RC_2R})]$

Complex	υ(C≡O) cm^{-1}	υ(C≡C) cm^{-1}	^{1}H-NMR data (δ) ppm	^{31}P-NMR data (δ)
1	1976 (s)	1588(w)	7.9–7.4 (m, 25H, Ph); 3.1 (s, 6H, $\mathrm{C_2Me}$); 2.6–2.4 (m, 8H, $\mathrm{CH_2}$)	37.8 (d, 1P, $J_{\mathrm{P-P}} = 26$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph}$); 31.4 (d, 1P, $J_{\mathrm{P-P}} = 30$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph}$); 14.4 (s, 2P, $\mathrm{C_2H_4}P\mathrm{Ph_2}$); -13.7 (m, 2P, $\mathrm{C_2H_4}P\mathrm{Ph_2}$)
2	1979 (s)	1589 (w)	7.9–7.4 (m, 35H, Ph); 5.3 (s, 1H, $\mathrm{CH_2Cl_2}$); 2.5–2.2 (m, 8H, $\mathrm{CH_2}$)	34.4 (d, 1P, $J_{\mathrm{P-P}} = 29$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph_2}$); 32.2 (d, 1P, $J_{\mathrm{P-P}} = 31$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph_2}$); 12.8 (s, 2P, $\mathrm{C_2H_4}P\mathrm{Ph_2}$); -13.5 (m, 2P, $\mathrm{C_2H_4}P\mathrm{Ph_2}$)
3	1958 (s)	1656 (w)	7.9–7.4 (m, 25H, *Ph*); 3.1 (s, 6H, $\mathrm{C_2Me}$); 2.6–2.4 (m, 8H, $\mathrm{CH_2}$)	32.6 (d, 1P, $J_{\mathrm{P-P}} = 34$ Hz, $J_{\mathrm{W-P}} = 282$ Hz; $\mathrm{C_2H_4}P\mathrm{Ph}$); 30.1 (d, 1P, $J_{\mathrm{P-P}} = 34$ Hz, $J_{\mathrm{W-P}} =$ 279 Hz; $\mathrm{C_2H_4}P\mathrm{Ph}$); 11.3 (s, 1P, $J_{\mathrm{W-P}} = 279$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph_2}$); 5.6 (s, 1P, $J_{\mathrm{W-P}} = 280$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph_2}$); -13.5 (m, 2P, $\mathrm{C_2H_4}P\mathrm{Ph_2}$)
4	1963 (s)	1655 (w)	7.9–7.5 (m, 35H, Ph); 2.8–2.6 (m, 8H, $\mathrm{CH_2}$)	34.8 (d, 1P, $J_{\mathrm{P-P}} = 30$ Hz, $J_{\mathrm{W-P}} = 297$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph}$); 29.6 (d, 1P, $J_{\mathrm{P-P}} = 37$ Hz, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{C_2H_4}P\mathrm{Ph}$); 5.1 (d, 1P, $J_{\mathrm{P-P}} = 36$ Hz, $J_{\mathrm{W-P}} = 295$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph_2}$); -13.6 (m, 2P, $\mathrm{C_2H_4}P\mathrm{Ph_2}$)
5	1958 (s)	1586(w)	7.9–7.5 (m, 25H, Ph); 5.3 (s, 2H, $\mathrm{CH_2Cl_2}$); 3.1, 3.0 (s, 6H, $\mathrm{C_2Me}$); 2.4–2.2 (m, 8H, $\mathrm{CH_2}$)	31.2 (d, 1P, $J_{\mathrm{P-P}} = 20$ Hz, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{C_2H_4}P\mathrm{Ph}$); 11.3 (s, 1P, $J_{\mathrm{W-P}} = 265$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph}$); 5.0 (d, 1P, $J_{\mathrm{P-P}} = 30$ Hz, $J_{\mathrm{W-P}} = 282$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph_2}$); -2.5 (s, 1P, $J_{\mathrm{W-P}} = 260$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph_2}$); -13.6 (m, 2P, $\mathrm{C_2H_4}P\mathrm{Ph_2}$)
6	1964 (s)	1588 (w)	7.9–7.6 (m, 35H, Ph); 2.4–2.2 (m, 8H, $\mathrm{C}H_2$)	33.1 (d, 1P, $J_{\mathrm{P-P}} = 20$ Hz, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{C_2H_4}P\mathrm{Ph}$); 26.1 (s, 1P, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{C_2H_4}P\mathrm{Ph}$); 5.3 (d, 1P, $J_{\mathrm{P\text{-}P}} = 21$ Hz, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{C_2H_4}P\mathrm{Ph_2}$); -4.2 (d, 1P, $J_{\mathrm{P\text{-}P}} = 30$ Hz, $\mathrm{C_2H_4}P\mathrm{Ph_2}$); -13.5 (m, 2P, $\mathrm{C_2H_4}P\mathrm{Ph_2}$)
7	1955 (s)	1657 (w)	7.9–7.4 (m, 25H, Ph); 3.05, 3.0, 2.95, 2.9 (s, 6H, $\mathrm{C_2Me}$); 2.4–2.2 (m, 8H, $\mathrm{CH_2}$)	35.2 (d, 1P, $J_{\mathrm{P-P}} = 22$ Hz, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{CH_2}P\mathrm{Ph}$); 33.6 (d, 1P, $J_{\mathrm{P-P}} = 21$ Hz, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{CH_2}P\mathrm{Ph}$); 23.4 (s, 1P, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{C_2H_4}P\mathrm{Ph_2}$); 15.1 (s, 1P, $\mathrm{C_2H_4}P\mathrm{Ph_2}$); -13.7 (m, 2P, $\mathrm{C_2H_4}P\mathrm{Ph_2}$)
8	1963 (s)	1600 (w)	7.9–7.4 (m, 35H, Ph); 5.3 (s, 2H, $\mathrm{CH_2Cl_2}$); 2.6–2.4 (m, 8H, $\mathrm{CH_2}$)	36.8 (d, 1P, $J_{\mathrm{P-P}} = 22$Hz, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{CH_2}P\mathrm{Ph}$); 35.7 (d, 1P, $J_{\mathrm{P-P}} = 23$Hz, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{C_2H_4}P\mathrm{Ph}$); 10.3 (s, 1P, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{C_2H_4}P\mathrm{Ph_2}$); 7.9 (s, 1P, $J_{\mathrm{W-P}} =$ N.O., $\mathrm{C_2H_4}P\mathrm{Ph_2}$); -13.6 (m, 2P, $\mathrm{C_2H_4}P\mathrm{Ph_2}$)

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

[b] Spectra recorded in $\mathrm{CDCl_3}$ (+25) and referenced to $\mathrm{SiMe_4}$, m = multiplet, s = singlet

[c] Spectra recorded in $\mathrm{CD_2Cl_2}$ (+25) and referenced to $\mathrm{H_3PO_4}$; s = singlet, d = doublet, m = multiplet. N.O. = not observed.

has W–Br (2) 2.618(2) and W–Br(3) 2.629(3). The two W–C(diphenylacetylene) distances are equivalent in both structures within experimental error.

The ^{1}H-NMR spectra of complexes **1**–**8** (Table 2) confirm the structure of **4** shown in Fig. 1. However, all the spectra show a complex series of resonances due to the likely existence of two diastereoisomers in solution as has been observed previously for $[\mathrm{WI_2(CO)(L}\text{-}P,P')(\eta^2\text{-}\mathrm{MeC_2R})]$ (R = Me or Ph) [21].

The ^{31}P-NMR spectra (Table 2) of complexes **1**–**8** all show a high field resonance due to the uncoordinated phosphine of the triphos ligand, $\mathrm{PhP(CH_2CH_2PPh_2)_2}$ at ca. -13.5 ppm. The complexes also all show at least three other resonances due to the probable existence of diastereoisomers in solution, as observed previously for related complexes [21].

In order to elucidate a possible mechanism of the reaction between quantities of $[\mathrm{WI_2(CO)(NCMe)}(\eta^2\text{-}\mathrm{PhC_2Ph})_2]$ and L, the reaction was followed by $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectroscopy at low temperature. At 0°C the $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectrum ($\mathrm{CDCl_3}$) shows only resonances due to the uncoordinated linear triphos at $\delta = -13$ ppm (doublet) and -17 ppm (triplet). On warming the NMR solution to 10°C, the intensity of both resonances at -13 and -17 ppm decreases and two new resonances at -35.6 ppm (triplet, $J_{\mathrm{P-P}} = 30$ Hz) and -4 ppm (brd) appear. It is likely that the resonances at $\delta = -35.6$ ppm and -4 ppm are due to the uncoordinated central phosphorus and the monodentate coordinated phosphorus in the initially formed intermediate, $[\mathrm{WI_2(CO)(L}\text{-}P)(\eta^2\text{-}\mathrm{PhC_2Ph})_2]$, together with the resonance at -13 ppm which can be ascribed to the uncoordinated end phosphorus atom.

After 30 min the resonance at -35.6 has disappeared completely and the resonances for the finally isolated bidentately attached linear triphos complex $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (see Fig. 2) are observed. The resonance at -13 ppm is still observed [21], and is due to the uncoordinated end phosphorus atom in this complex. Similar results are obtained when equimolar quantities of the bis(2-butyne) complex $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ and L in $CDCl_3$ at 10°C, again after 10 min a resonance at $\delta = -33.6$ ppm (triplet, $J_{P-P} = 30$ Hz) due to the uncoordinated central phosphorus atom was observed.

The ^{13}C-NMR spectrum (CD_2Cl_2, $+25$°C) for the crystallographically characterised complex **4** shows, apart from all the expected resonances (see Section 3), an alkyne contact carbon resonance at $\delta = 219.7$ ppm, which suggests [25] the diphenylacetylene is donating four electrons to the tungsten, which also enables it to obey the effective atomic number rule.

Refluxing a slightly wet acetonitrile solution of $[MoI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ (**1**) for 24 h gives the oxidised molybdenum(IV) complex $[MoI_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2\text{-}P,P',O\}]\cdot 0.5CH_2Cl_2$ (**9**) in 80% yield. Complex **9** has been characterised by elemental analysis (C, H and N) (Table 1) and by X-ray crystallography. The complex was much less soluble in $CDCl_3$, CD_2Cl_2 and $(CD_3)_2CO$, hence it was very difficult to obtain satisfactory ^1H- and ^{31}P-NMR spectra for complex **9**. It may be that the oxidation of the molybdenum centre in $[MoI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ in a slightly wet refluxing acetonitrile solution proceeds via initial oxidation of the molybdenum(II) centre to the molybdenum(VI) species, $[MoI_2(O)_2(L\text{-}P,P')]$, whereby the pendant phosphorus atom is oxidised intramolecularly by one of the *cis*-Mo=O groups to give the finally isolated molybdenum(IV) complex $[MoI_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2\text{-}P,P',O\}]$ (**9**), which has been characterised crystallographically. This is only a postulate and further studies are required in order to elucidate the mechanism of this unusual reaction. Single crystals for X-ray crystallography of **9** were grown by cooling (-17°C) a concentrated CH_2Cl_2/Et_2O solution (95:5) of **9** for 24 h. The molecular structure of **9** is shown in Fig. 3, together with the atom numbering scheme. The atomic coordinates and bond lengths and angles are given in Table 3.

In the structure of **9**, shown in Fig. 3, the oxidised ligand is tridentate. As in $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$, two phosphorus atoms P(1) and P(4) are chelating to the metal, but in addition O(8), which is bonded to the third phosphorus atom P(7), is also bonded to the metal making up a *fac* arrangement of the tridentate ligand. The two phosphorus atoms are both *trans* to iodine and the two Mo(1)–P distances are equivalent at 2.500(3), 2.505(3) Å, while the coordination sphere is completed by a terminal oxygen atom O(9) at 1.682(6) Å from the metal which is *trans* to the ligand O(8) (Mo(1)–O(8) 2.225(5) Å).

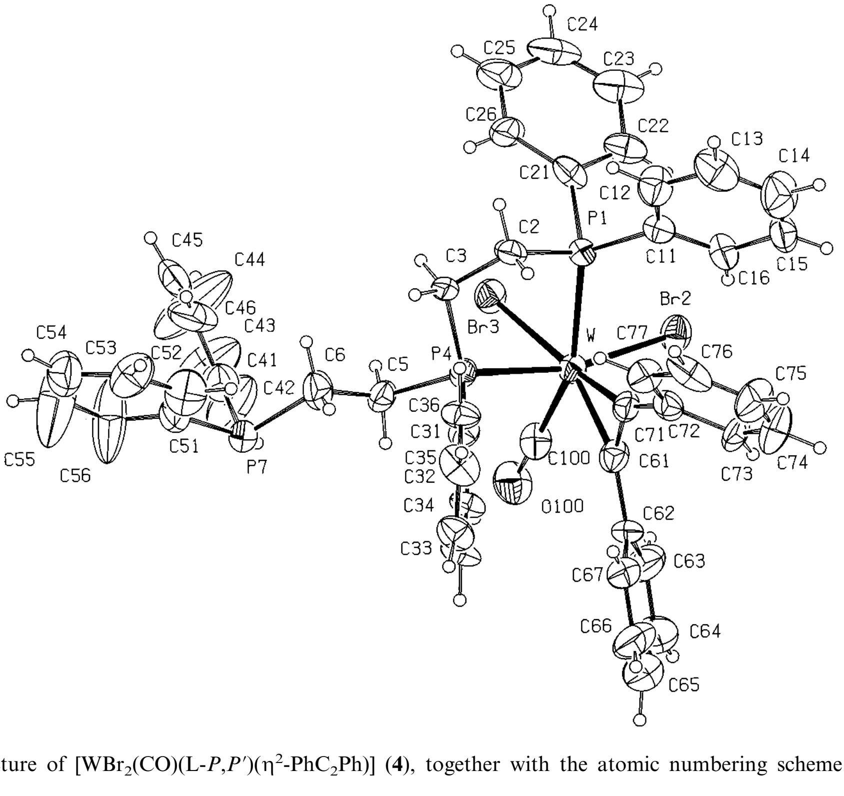

Fig. 1. X-ray crystal structure of $[WBr_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (**4**), together with the atomic numbering scheme. Ellipsoids shown at 30% probability.

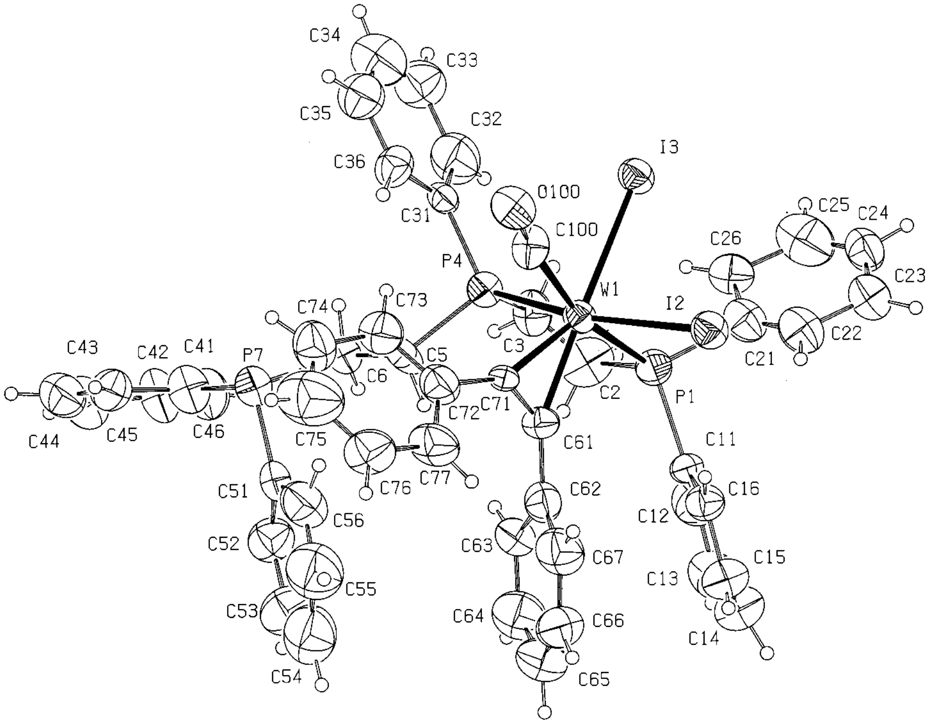

Fig. 2. X-ray crystal structure of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (**10**), together with the atomic numbering scheme. Ellipsoids shown at 30% probability.

This ligand has been found once only before in a transition metal complex, also with molybdenum again with a terminal oxygen in a *trans* position to the oxygen of the ligand, viz bis(2,4,6-trimethylphenylseleno)ato-oxo-*fac*-(2(diphenylphosphino)ethyl)phenylphosphino)-ethyl)diphenylphosphineoxide molybdenum [26].

In conclusion, we have extended the series of $[MXY(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ type complexes, and found the structures of $[WX_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (X = Br, I) crystallise as single diastereoisomers, with the same basic coordination geometry to the structures, $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2R)]$ (R = Me or Ph). The interesting oxidation of both end phosphorus and the molybdenum in $[MoI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ in refluxing acetonitrile to give the crystallographically characterised molybdenum(IV) complex $[MoI_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2\text{-}P,P',O\}]$. We are currently exploring the catalytic activity of complexes **1–9** as alkene metathesis catalysts.

3. Experimental

All reactions and purifications described in this paper were carried out under an atmosphere of dry nitrogen using standard vacuum/Schlenk line techniques. The bis(alkyne) starting materials used in this research, namely $[MXY(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (M = Mo, X = Y = I, R = Me [22] or Ph [23]; M = Mo, X = Y = Br, R = Me or Ph [22]; M = W, X = Y = Br, R = Me or Ph [11]; M = Mo or W, X = Cl (M = Mo only) or Br, Y = I, R = Me or Ph [24]) were prepared by published methods. The solvents used were all dried and purged with dry nitrogen before use. All the chemicals used were purchased from commercial sources and were used without further purification.

Elemental analyses (C, H and N) were recorded on a Carlo Erba Elemental Analyser MOD 1108 (using helium as the carrier gas). Infrared spectra were recorded as $CHCl_3$ films between NaCl plates on a Perkin–Elmer 1600 series FTIR spectrophotometer. ^1H-, ^{13}C- (referenced to $SiMe_4$) and ^{31}P-NMR (85% H_3PO_4) spectra were recorded on a Bruker AC 250 NMR spectrometer.

3.1. Preparation of $[WBr_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (4)

To a solution of $[WBr_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ (0.2 g, 0.26 mmol) in CH_2Cl_2 (20 cm^3) L (0.14 g, 0.26 mmol) was added, and the solution stirred for 17 h. The resulting blue solution was filtered through celite and the solvent removed in vacuo to yield a blue crystalline powder of $[WBr_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (**4**). It was recrystallised from a solution of CH_2Cl_2/diethyl ether 80:20 cooled to −17°C, which afforded crystals suitable for X-ray crystallography. Yield = 0.26 g, 91%. The ^{13}C-NMR ($CDCl_3$, 25°C) has resonances at $\delta =$

219.7 (s, $\underline{C}\equiv\underline{C}$), 213.2 (s, $\underline{C}\equiv O$), 141.3–123.1 (m, Ph), 30.7 (m, $PhP\underline{C}H_2$), 25.0 (m, $PhP\underline{C}H_2$), 22.8 (m, $Ph_2P\underline{C}H_2$ and $\underline{Me}C_2$), 21.7 (m, $Ph_2P\underline{C}H_2$) ppm.

Similar reactions of equimolar quantities of $[MXY(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ and L $\{L = PhP(CH_2CH_2PPh_2)_2\}$ in CH_2Cl_2 at room temperature gave the bidentately attached triphos complexes $[MXY(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ (M = Mo, X = Y = I, R = Me or Ph; M = W, X = Y = Br, R = Me; M = W, X = Br, Cl, Y = I, R = Me, Ph) (**1–3**, **5–8**). For physical and analytical data see Table 1.

Table 3
Selected molecular dimensions[a]

(a) Dimensions in the metal coordination sphere for **4** and **10**	**4** X = Br	**10** X = I
W(1)–C(100)	1.981 (18)	2.024 (10)
W(1)–C(61)	2.019 (13)	2.018 (10)
W(1)–C(71)	2.005 (15)	2.040 (7)
W(1)–P(4)	2.489 (4)	2.513 (3)
W(1)–P(1)	2.589 (4)	2.563 (3)
W(1)–X(2)	2.618 (2)	2.816 (2)
W(1)–X(3)	2.629 (3)	2.840 (2)
C(100)–W(1)–C(61)	113.1 (6)	110.0 (4)
C(100)–W(1)–C(71)	75.6 (6)	71.9 (4)
C(61)–W(1)–C(71)	38.1 (5)	38.1 (3)
C(100)–W(1)–P(4)	89.9 (4)	94.4 (3)
C(61)–W(1)–P(4)	90.3 (4)	92.8 (3)
C(71)–W(1)-P(4)	96.9 (4)	93.4 (2)
C(100)–W(1)-P(1)	160.1 (4)	162.9 (3)
C(61)–W(1)-P(1)	84.4 (5)	86.7 (3)
C(71)–W(1)–P(1)	122.5 (4)	124.5 (2)
P(4)–W(1)–P(1)	80.28 (13)	80.92 (9)
C(100)–W(1)–I(2)	95.2 (4)	91.0 (3)
C(61)–W(1)–I(2)	99.7 (4)	96.9 (3)
C(71)–W(1)–I(2)	97.1 (4)	99.91 (19)
P(4)–W(1)–I(2)	165.90 (10)	166.58 (6)
P(1)–W(1)–I(2)	90.72 (12)	90.34 (8)
C(100)–W(1)–I(3)	78.9 (4)	80.1 (3)
C(61)–W(1)–I(3)	164.8 (3)	168.3 (3)
C(71)–W(1)–I(3)	154.4 (4)	150.8 (2)
P(4)–W(1)–I(3)	80.09 (11)	80.33 (7)
P(1)–W(1)–I(3)	82.36 (9)	82.92 (8)
I(2)–W(1)–I(3)	88.00 (9)	88.54 (4)
(b) Dimensions in the metal coordination sphere for **9**		
Mo(1)–O(9)	1.682 (6)	
Mo(1)–O(8)	2.225 (5)	
Mo(1)–P(4)	2.500 (3)	
Mo(1)–P(1)	2.505 (3)	
Mo(1)–I(11)	2.827 (2)	
Mo(1)–I(12)	2.859 (3)	
O(9)–Mo(1)–O(8)	166.6 (2)	
O(9)–Mo(1)–P(4)	90.1 (2)	
O(8)–Mo(1)–P(4)	79.44 (16)	
O(9)–Mo(1)–P(1)	91.1 (2)	
O(8)–Mo(1)–P(1)	79.13 (15)	
P(4)–Mo(1)–P(1)	81.30 (9)	
O(9)–Mo(1)–I(11)	100.2 (2)	
O(8)–Mo(1)–I(11)	89.67 (15)	
P(4)–Mo(1)–I(11)	168.73 (5)	
P(1)–Mo(1)–I(11)	93.89 (7)	
O(9)–Mo(1)–I(12)	98.8 (2)	
O(8)–Mo(1)–I(12)	90.49 (15)	
P(4)–Mo(1)–I(12)	95.25 (7)	
P(1)–Mo(1)–I(12)	169.49 (5)	
I(11)–Mo(1)–I(12)	87.68 (5)	

[a] Distances given in Å; angles given in degrees.

3.2. Preparation of $[MoI_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2\text{-}P,P',O\}]\cdot 0.5CH_2Cl_2$ (**9**)

A suspension of $[MoI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ (0.5 g, 0.54 mmol) in NCMe (40 cm^3) was refluxed for 24 h. The resultant dark brown solution was filtered through celite and the solvent removed in vacuo to afford the dark brown crystalline powder $[MoI_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2\text{-}P,P',O\}]\cdot 0.5CH_2Cl_2$ (**9**), yield = 0.44 g, 80%. Crystals suitable for X-ray crystallography of **9** were grown from a cooled solution (−17°C) of CH_2Cl_2/diethyl ether (95:5).

3.3. X-ray crystallography

Crystals of **4**, **9** and $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (**10**) suitable for X-ray crystallography were prepared as described above. Crystal data are given in Table 4, together with refinement details. Data for the compounds were collected with Mo–K_α radiation using the MARresearch Image Plate System. The crystals were positioned at 75 mm $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (**10**) and 70 mm (**4**, **9**) 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 [27]. The structures were solved using direct methods with the SHELX86 program [28]. 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. All three structures were corrected for absorption using empirical methods [29]. The structures were then refined on F^2 using SHELXL [30]. The complexes $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (**10** and **4**) contained no solvent, whereas **9** contained a dichloromethane molecule which was refined with 50% occupancy. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

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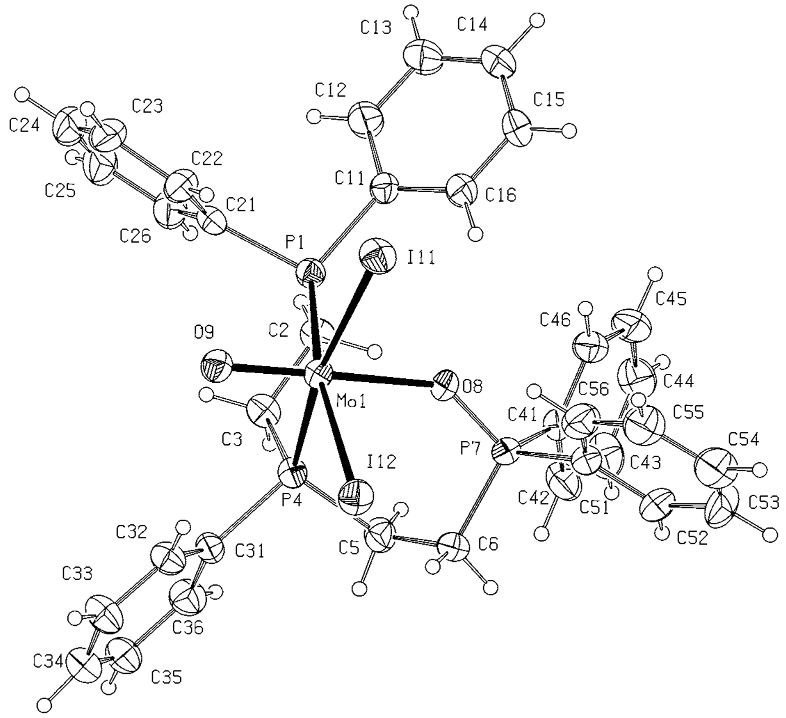

Fig. 3. X-ray crystal structure of [$MoI_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2$-$P,P',O\}$] (**9**), together with the atomic numbering scheme. Ellipsoids shown at 30% probability.

Table 4
Crystal data and structure refinement details for the structures

Compound	**4**	**10**	**9**
Empirical formula	$C_{49}H_{43}Br_2OP_3W$	$C_{49}H_{43}I_2OP_3W$	$C_{34.5}H_{34}ClI_2MoO_2P_3$
Formula weight	1084.41	1178.39	958.72
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$	$P2_1/n$
Unit cell dimensions			
a (Å)	11.526(14)	14.927(14)	12.341(13)
b (Å)	16.577(17)	17.488(14)	13.798(14)
c (Å)	23.82(3)	17.819(14)	22.97(2)
α (°)	(90)	(90)	(90)
β (°)	92.57(1)	98.97(1)	104.20(1)
γ (°)	(90)	(90)	(90)
Volume (Å^3)	4546(9)	4595(7)	3792(7)
Z, calculated density (Mg m^{-3})	4, 1.584	4, 1.704	4, 1.679
Absorption coefficient (mm^{-1})	4.439	3.997	2.200
$F(000)$	2136	2280	1868
Crystal size (mm)	0.35 × 0.25 × 0.15	0.30 × 0.25 × 0.20	0.25 × 0.20 × 0.20
θ range for data collection (°)	2.70–25.99	2.82–24.97	2.58–25.98
Index ranges	$-12 \leq h \leq 0$	$0 \leq h \leq 15$	$0 \leq h \leq 15$
	$-20 \leq k \leq 20$	$-20 \leq k \leq 20$,	$-16 \leq k \leq 16$
	$-28 \leq l \leq 29$	$-21 \leq l \leq 20$	$-28 \leq l \leq 27$
Reflections			
Collected/unique[R_{int}]	12575/7325/(0.0603)	13634/7184[0.0326}	12284/7215 [0.0372]
Data/restraints/parameters	7325/0/505	7184/0/505	7215/0/406
Final R indices [$I > 2\sigma(I)$] R_1	0.0769	0.0400	0.0605
wR_2	0.2080	0.0990	0.1762
R indices (all data) R_1	0.1306	0.0855	0.0853
wR_2	0.2428	0.1582	0.2010
Largest differential peak and hole (e A^{-3})	3.130, −2.403	1.147, −0.774	1.772, −1.001

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