DALTON

Multimetallic complexes of molybdenum(II) and tungsten(II) derived from $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}RC_2R)]$ (R = Me or Ph). Crystal structures of $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}MeC_2R)]$ (R = Me or Ph)

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Equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ (R = R' = Me or Ph; R = Me, R' = Ph) and $PhP(CH_2CH_2PPh_2)_2$ (L) reacted in CH_2Cl_2 at room temperature to give the mono(alkyne) complexes $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R')]$ in high yield. The molecular structures of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2R)]$ (R = Me or Ph) have been crystallographically determined. There are two independent molecules in the asymmetric unit which are diastereoisomers. The co-ordination pattern about the metal atom in $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]\cdot 0.75CH_2Cl_2$ **1** is a distorted octahedron with two adjacent phosphorus atoms of the triphosphine, a carbonyl and an iodide ligand in the equatorial plane and an iodide and the but-2-yne ligand occupying axial sites. The complex $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Ph)]$ is also a distorted octahedron, with identical co-ordination to that of **1**, except in that the but-2-yne ligand is substituted by the 1-phenylprop-1-yne ligand. In **1** there is a pendant arm of the triphosphine ligand free to co-ordinate with other species. The reactions of the complexes $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ (R = Me or Ph) as monodentate phosphine ligands with the molybdenum(II) and tungsten(II) complexes $[MI_2(CO)_3(NCMe)_2]$, $[MI_2(CO)_3(NCMe)L']$ (L' = PPh_3, $AsPh_3$ or $SbPh_3$), $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ and $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) were found to give a range of bi- and tri-metallic complexes which have all been characterised.

Halogenoalkyne complexes of molybdenum(II) and tungsten(II) have received considerable attention over the past fifteen years;[1,2] in particular those containing phosphine-donor ligands. Although a wide range of bimetallic complexes containing bridging phosphine ligands such as bis(diphenylphosphino)methane have been reported,[3–16] very few bimetallic phosphine-bridged halogenoalkyne complexes of molybdenum(II) and tungsten(II) have been reported. In view of the stability of the 'four-electron' bis(phosphine) alkyne complexes $[MX_2(CO)L'_2(\eta^2\text{-}RC_2R')]$ (M = Mo or W; X = Cl, Br or I; L' = phosphine; R, R' = alkyl or aryl),[17–23] it was decided to treat the bis(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ (R = R' = Me or Ph; R = Me, R' = Ph)[24] with a potentially linear tridentate phosphine, $PhP(CH_2CH_2PPh_2)_2$ (L) in order to co-ordinate two of the phosphorus atoms to one metal leaving the third free to react with other metal centres.

In this paper we describe the synthesis and molecular structures (for R = R' = Me; R = Me, R' = Ph) of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R')]$. The reactions of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) with $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W), $[MI_2(CO)_3(NCMe)L]$ (M = Mo or W; L = PPh_3, $AsPh_3$ or $SbPh_3$), $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ and $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) to give a number of new bi- and tri-metallic complexes of molybdenum(II) and tungsten(II) are also discussed. A preliminary communication on this work has been reported.[25]

Results and Discussion

The starting materials used, namely $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ (R = R' = Me or Ph; R = Me, R' = Ph) have been prepared by treating the seven-co-ordinate complexes $[WI_2(CO)_3(NCMe)_2]$ with an excess of alkyne.[24] Treatment of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ with 1 equivalent of the triphosphine in CH_2Cl_2 at room temperature affords the bidentate triphosphine complexes $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R')]$ **1**–**3** in high yield. Complexes **1**–**3** have been fully characterised by elemental analysis (C, H and N) (Table 1), IR (Table 1), ^1H (Table 2) and ^{31}P NMR spectroscopy (Table 3) and for **1** by ^{13}C NMR spectroscopy, and also for **1** and **3** by X-ray crystallography. All these complexes are readily soluble in CH_2Cl_2 but less soluble in $CHCl_3$ and only sparingly soluble in diethyl ether. The but-2-yne complex **1** is the most soluble and the diphenylacetylene complex the least. Complexes **1**–**3** are fairly stable in the solid state when stored under nitrogen for several weeks but much more air-sensitive in solution. The infrared spectra all show one carbonyl band at 1957, 1965 and 1969 cm^{-1} respectively, and alkyne stretching bands at 1656, 1601 and 1587 cm^{-1} respectively. The values of the carbonyl stretching bands are in close agreement with those of the appropriate bidentate phosphine complexes $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R')]$ (*n* = 1–6) previously described.[20]

Single crystals of the complexes $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]\cdot 0.75CH_2Cl_2$ **1** and $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Ph)]$ **3** suitable for X-ray work were grown from CH_2Cl_2–Et_2O (4:1) mixtures at −17 °C. The molecular structures are shown in Figs. 1 and 2 respectively. There are two independent molecules in the asymmetric unit which are diastereoisomers. As can be seen from Fig. 1 each molecule has the same ligands co-ordinated in an identical way but they differ in the configuration about the central P atom. Selected bond lengths and angles are presented in Table 4. The co-ordination pattern about the metal atom in complex **1** is a distorted octahedron with two adjacent phosphorus atoms of the triphosphine, a carbonyl and an iodide ligand in the equatorial plane and an iodide and the but-2-yne ligand occupying axial sites. One of the end phosphorus atoms of the triphosphine is unco-

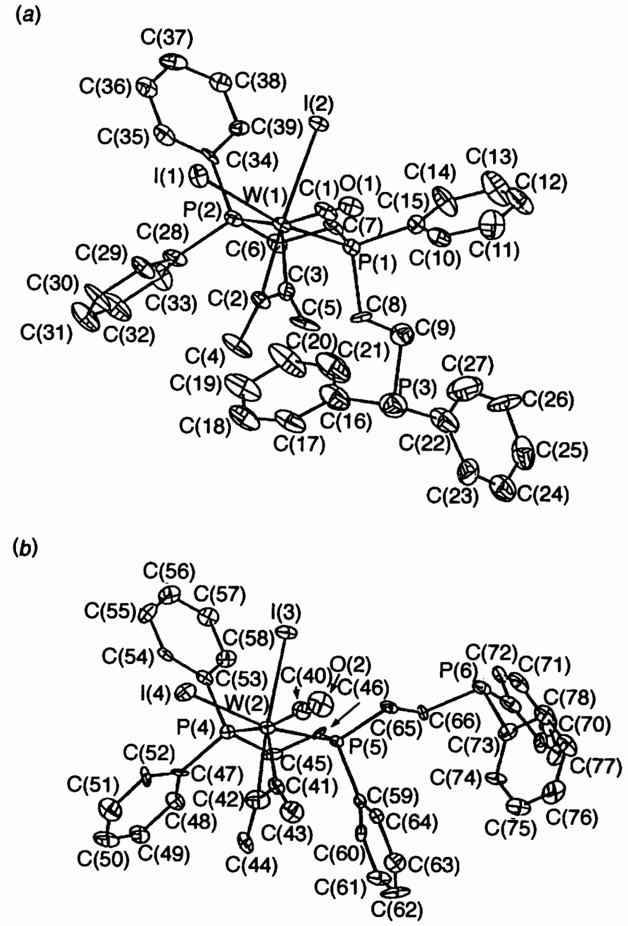


Fig. 1 Crystal structure of the two diastereoisomers present in the asymmetric unit of [$WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)$]·$0.75CH_2Cl_2$ **1**, showing the atom numbering scheme: (*a*) molecule **a**; (*b*) molecule **b** (some labelling removed for clarity)

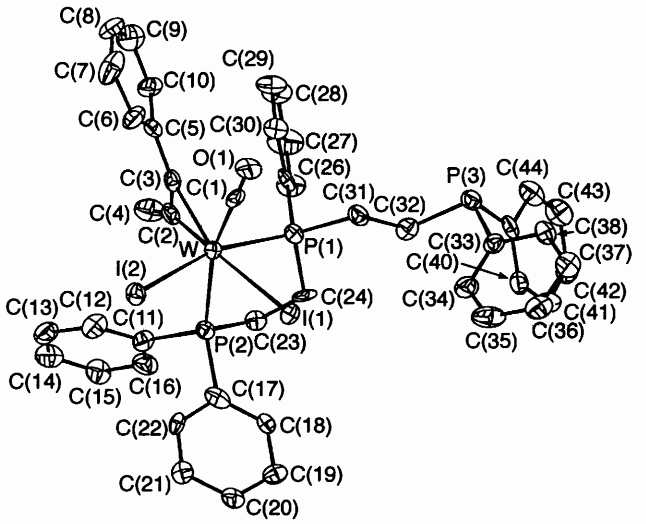
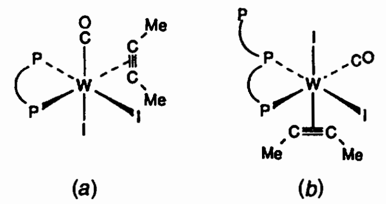


Fig. 2 Crystal structure of [$WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Ph)$] **3**, showing the atom numbering scheme

ordinated and is therefore available to bind to another metal centre.

In 1989 Baker and co-workers[20] reported the synthesis and molecular structure of the bis(diphenylphosphino)methane complex [$WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)$]. It and **1** are both distorted octahedra with the two iodide ligands and the two co-ordinated phosphorus atoms *cis* to each other. However, the complex [$WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)$] has one phosphorus atom *trans* to an iodide ligand and one phosphorus atom *trans* to the but-2-yne ligand in the equatorial plane, whereas in **1** one phosphorus atom is *trans* to an iodide and one *trans* to a carbonyl, as shown in Fig. 3. In the case of [$WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)$] the length of the alkane chain (CH_2) connecting the phosphorus atoms in the dppm ligand is shorter than the triphosphine ligand and the C(2)–W–I(1) bond angle is 107°, thus allowing more space for the but-2-yne ligand to co-ordinate.



(*a*) (*b*)

Fig. 3 Structures of [$WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)$] (*a*) and [$WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)$] (*b*)

The metal–ligand bond lengths in the complexes [$WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)$] and **1** are comparable. The IR spectrum of the former shows a carbonyl stretching band at 1938 cm^{-1}, whereas that of **1** shows a corresponding band at 1957 cm^{-1}. In the latter case there is a phosphine group *trans* to a carbonyl ligand. The π-acceptor phosphine ligand will compete with the CO ligand for electron density from the filled metal d orbitals. This may account for the higher frequency of the carbonyl stretching band of **1** in the IR spectrum. The bend-back angles β (the angle between C≡C and C–R in an alkyne complex, < 90°) of the complexes [$WI_2(CO)(dppm)(\eta^2\text{-}MeC_2Me)$] and **1** are ≈39 and 42.2° respectively.

Complex **1** has the stereochemistry proposed for the thermodynamically favoured blue isomer of the complex [$WI_2(CO)\{Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}MeC_2Me)$].[20] The molecular structure of [$WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Ph)$] **3** is very similar to that of its but-2-yne analogue **1**. From Fig. 2 it can be seen that the co-ordination pattern about the metal atom is a distorted octahedron, identical to that of the two molecules of **1**, with the pendant phosphine group in a similar orientation to molecule **1b**.

The asymmetric unit of compound **1** is comprised of two independent molecules, which are diastereoisomers, whereas **3** contains only one of the two possible diastereoisomers observed in the solution-state ^{31}P NMR spectrum. This is probably due to one isomer being less soluble and hence crystallising first, however another possibility is that both isomers crystallised as different crystal types with data being recorded on only one type. The isomer of **3** that has been structurally characterised is a racemate of compound **1b**. It may therefore be proposed that the crystallographically uncharacterised diastereoisomer of **3** would be a racemate of **1a**. Attempts to separate isomers **1a** and **1b** by column chromatography proved unsuccessful, mainly due to their instability on a variety of packing materials and in different solvents. Also it might be expected that the isomers would have very similar retention times.

In both complexes **1** and **3** the co-ordination pattern about the metal atom is distorted octahedral with identical co-ordination, except that in place of a but-2-yne ligand a 1-phenylprop-1-yne ligand is *trans* to an iodide. A slight lengthening of the W–I bond *trans* to the alkyne, as well as a slightly longer alkyne bond, is observed in **3**, due to the greater electron-withdrawing nature of the phenyl ligand. Table 4 shows that compound **3** exhibits a more distorted geometry than **1** due to the larger cone angle of the 1-phenylprop-1-yne ligand. The conformation of the chelating arm of the triphosphine ligand is maintained in both complexes, as shown by the torsion angles of the P–CH_2–CH_2–P chain [**1a** 54.27(2); **1b** −54.31(2); **3** − 52.15(3)°].

The ^1H NMR spectra of complexes **1**–**3** show broad multiplets at δ 7.3–7.9 which can be assigned to the hydrogens of the phenyl groups of the triphosphine and a broad multiplet

Table 1 Physical, analytical[a] and IR[b] data for complexes 1–25

Complex	Colour	Yield (%)	Analysis (%)			IR/cm^{-1}		
			C	H	N	ν(C≡O)	ν(C≡N)	ν(C≡C)
1 $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]\cdot0.75CH_2Cl_2$	Blue-green	93	42.7 (42.7)	3.5 (3.7)	—	1957s	—	1656w
2 $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$	Bright green	94	50.1 (49.9)	3.7 (3.7)	—	1965s	—	1601w
3 $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Ph)]$	Green	94	47.2 (47.2)	3.7 (3.7)	—	1969s	—	1587w
4 $[MoI_2(CO)_3(NCMe)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$	Green	84	34.0 (34.5)	2.7 (2.8)	0.6 (0.9)	1958s, 1851m	2298w	1655w
5 $[WI_2(CO)_3(NCMe)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$	Dark green	92	32.5 (32.6)	2.6 (2.7)	0.6 (0.9)	1967s, 1889m	2328w	1659w
6 $[MoI_2(CO)_3(NCMe)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}]$	Brown-black	90	40.0 (39.1)	2.9 (2.8)	0.6 (0.8)	2024m, 1966s, 1904s	2254w	1711w
7 $[WI_2(CO)_3(NCMe)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}]$	Green	88	36.9 (37.2)	2.6 (2.6)	0.5 (0.8)	2017s, 2007m, 1948s	2289w	1711w
8 $[MoI_2(CO)_3\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}_2]$	Brown-black	83	37.9 (38.2)	3.1 (3.2)	—	2023s, 1959s, 1873m	—	1590w, 1551w
9 $[WI_2(CO)_3\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}_2]$	Green	76	37.3 (37.0)	3.1 (3.0)	—	2018s, 1977s, 1947s, 1892m, 1866m	—	1604w, 1550w
10 $[MoI_2(CO)_3\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2]$	Dark green	56	43.0 (43.3)	3.2 (3.1)	—	2024w, 1966s, 1905s, 1834m	—	1591w, 1550w
11 $[WI_2(CO)_3(PPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$	Green	66	38.5 (39.2)	3.0 (3.0)	—	2016s, 1945s, 1914s	—	1573w, 1550w
12 $[MoI_2(CO)_3(PPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}]$	Black	85	44.2 (44.8)	3.2 (3.1)	—	2025s, 1966s	—	1590w
13 $[WI_2(CO)_3(PPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}]$	Green	81	43.3 (42.8)	3.0 (3.0)	—	2017s, 1945s, 1913m	—	1602w
14 $[MoI_2(CO)_3(AsPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]\cdot0.5CH_2Cl_2$	Brown-black	79	39.1 (39.5)	3.0 (3.0)	—	2024s, 1962s, 1998s	—	1550w
15 $[WI_2(CO)_3(AsPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$	Green	69	38.9 (38.3)	3.0 (2.9)	—	2017s, 1945s, 1914s	—	1578w
16 $[MoI_2(CO)_3(AsPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}]$	Black	87	43.9 (43.8)	3.2 (3.0)	—	2024s, 1964s	—	1578w
17 $[WI_2(CO)_3(AsPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}]$	Green	67	42.0 (41.9)	3.0 (2.9)	—	2018s, 1969s, 1946s, 1915s	—	1575w
18 $[MoI_2(CO)_3(SbPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]\cdot0.5CH_2Cl_2$	Brown-black	84	38.0 (38.5)	3.2 (2.9)	—	2024w, 1961s	—	1549w
19 $[WI_2(CO)_3(SbPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]\cdot0.5CH_2Cl_2$	Green	47	38.5 (37.7)	3.0 (2.8)	—	2017s, 1945s, 1913m	—	1550w
20 $[WI_2(CO)_3(SbPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}]$	Green	56	41.8 (41.0)	3.0 (2.9)	—	2018s, 1968s, 1946s, 1913m	—	1602w
21 $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$	Green	81	41.8 (42.5)	3.3 (3.3)	1.2 (0.8)	1953s, 1879m	2322w	1590w
22 $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}]$	Green	77	46.5 (46.2)	3.3 (3.3)	0.5 (0.7)	1954s, 1882m	2297w	1601w
23 $[MoCl(GeCl_3)(CO)_2(PPh_3)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2]$	Brown-black	69	47.4 (47.4)	3.4 (3.4)	—	1969s, 1881m	—	1601w
24 $[WI_2(CO)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2(\eta^2\text{-}MeC_2Me)]\cdot0.5CH_2Cl_2$	Green	77	43.8 (43.4)	3.2 (3.2)	—	2054s, 1971s	—	1602w, 1550w
25 $[WI_2(CO)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2(\eta^2\text{-}PhC_2Ph)]$	Dark green	88	45.6 (45.2)	3.2 (3.2)	—	2088s, 1968s	—	1601w, 1581w, 1540w

[a] Calculated values in parentheses. [b] Spectra recorded in $CHCl_3$ as thin films between NaCl plates; s = strong, m = medium, w = weak.

at δ 2.4–2.7 which can be assigned to its CH_2 groups. In addition **1** showed four but-2-yne methyl resonances at δ 3.15, 3.1, 2.95 and 2.9 and a resonance at δ 5.3 due to CH_2Cl_2 which conforms with the solid-state structure having 0.75 CH_2Cl_2 in the crystal lattice. Elemental analysis results for complex **1** are also consistent with such a solvate. However, when it is obtained as a dry powder there appears to be no CH_2Cl_2 in the NMR sample, hence stoichiometric reactions of **1** and **2** are calculated in terms of the non-solvated complexes.

Complex **3** showed two resonances at δ 3.0 and 2.9 corresponding to the methyl group of the 1-phenylprop-1-yne ligand. Attempts to measure the barrier to but-2-yne rotation of the two isomers of **1** were unsuccessful since no coalescence of the but-2-yne resonances occurred at 60 °C.

The ^{31}P NMR spectrum of complex **1** showed five resonances at δ −13.7 (m, 2P, $C_2H_4PPh_2$), −2.7 (s, 1P, C_2H_4PPh), 4.3 (s, 1P, C_2H_4PPh), 19.5 (d, 1P, J_{PP} = 30, $C_2H_4PPh_2$) and 23.1 (d, 1P, J_{PP} = 25 Hz, $C_2H_4PPh_2$). The high-field multiplet at δ − 13.7 indicates the presence of two isomers in solution, each with an unco-ordinated phosphorus atom and is two overlapping doublets. It is coupled to the resonances at δ 19.5 and 23.1 which could be due to the co-ordinated central phosphorus atom of the triphosphine ligand. The resonances at δ −2.7 and 4.3 can therefore be assigned to the terminal phosphorus atoms of the triphosphine ligand co-ordinated to the tungsten. These show no coupling and this may be due to the two co-ordinated phosphorus atoms of the triphosphine ligand being bound in an approximate *cis*-coplanar conformation with a resultant zero coupling constant. The ^{31}P NMR spectrum of **2** also showed five resonances (Table 3) which could indicate the presence of two isomers of the complex in solution. The presence of two isomers in solution is consistent with the two isomers shown for the solid-state structure of **1** [Fig. 1(*a*) and 1(*b*)]. The ^{31}P NMR spectrum of **3** also has five resonances which also indicates the presence of two isomers in solution. X-Ray crystallography showed only one isomer in the asymmetric unit (Fig. 2). This is likely to be due to the least soluble isomer crystallising out of solution. All successive crystallisations of **3** gave morphologically identical crystals.

The ^{13}C NMR spectrum of the but-2-yne complex **1** shows six resonances at δ 234, 230, 224, 222, 213 and 212 which may be assigned to four alkyne carbons and two carbonyl carbons respectively, associated with the alkyne ligands donating four electrons to the metal centre[26] and in accord with the ^{31}P NMR data and solid-state structure.

It is likely that the mechanism for the formation of the complexes $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R')]$ **1–3** involves initial displacement of acetonitrile by an end phosphorus atom of the triphosphine ligand (see Scheme 1). Evidence to support this proposal comes from the previously reported[20] reaction of $[MoI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ with an equimolar amount of PPh_3 to give $[MoI_2(CO)(PPh_3)(\eta^2\text{-}PhC_2Ph)_2]$. Several attempts to study the low-temperature (−10 °C) reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with an equimolar amount of triphosphine to give $[WI_2(CO)(L\text{-}P)(\eta^2\text{-}MeC_2Me)_2]$ were largely unsuccessful. Although an initial orange solution which may be due to this complex is formed, it rapidly turned deep green, and low-temperature ^{31}P NMR spectroscopy showed only the two diastereoisomers due to complex **1**. In order to account for the formation of the two diastereoisomers as shown in Figs. 1 and 2, it is statistically likely that after co-ordination of one end of the triphosphine ligand there will be 50% of the unco-ordinated phosphine group pointing up and a 50% chance of it pointing down. After final co-ordination of the central phosphorus atom an equal chance of the formation of each stereoisomer shown in Fig. 1(*a*) and 1(*b*) is observed in both the solution and the solid state.

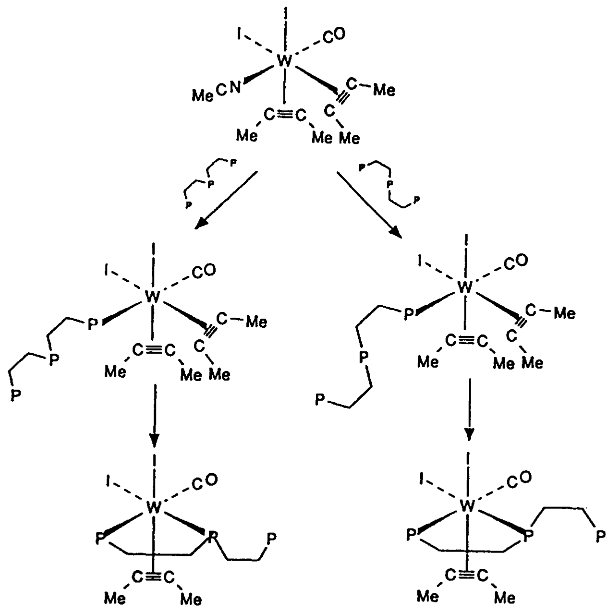
Table 2 Proton NMR data δ* for complexes **1–25**

Complex	δ
1	7.9–7.3 (m, 25 H, Ph), 5.3 (s, 1.5 H, CH_2Cl_2), 3.15, 3.1, 2.95, 2.9 (4s, 6 H, C_2Me), 2.5–2.4 (m, 8 H, $PhPCH_2$)
2	7.9–7.33 (br m, 35 H, Ph), 2.7–2.5 (br m, 8 H, $PhPCH_2$)
3	7.9–7.3 (m, 30 H, Ph), 3.0, 2.9 (2s, 3 H, C_2Me), 2.6–2.4 (m, 8 H, $PhPCH_2$)
4	7.9–7.3 (br m, 25 H, Ph), 3.15, 3.1, 3.0, 2.9 (4s, 6 H, C_2Me), 2.7–2.5 (8 H, $PhPCH_2$), 2.3 (s, 3 H, NCMe)
5	7.9–7.3 (br m, 25 H, Ph), 3.1, 3.0, 2.9, 2.85 (4s, 6 H, C_2Me), 2.6–2.3 (br m, 8 H, $PhPCH_2$), 2.1 (s, 3 H, NCMe)
6	7.7–7.3 (br m, 35 H, Ph), 2.1 (s, 3 H, NCMe), 2.8–2.4 (br m, 8 H, $PhPCH_2$)
7	7.9–7.4 (br m, 35 H, Ph), 2.4 (s, 3 H, NCMe), 2.8–2.4 (br m, 8 H, $PhPCH_2$)
8	7.7–7.3 (br m, 50 H, Ph), 3.0, 2.9 (2s, 12 H, C_2Me), 2.9–2.7 (br m, 16 H, $PhPCH_2$)
9	7.7–7.3 (m, 50 H, Ph), 3.0, 2.95 (2s, 12 H, C_2Me), 2.88–2.5 (m, 16 H, $PhPCH_2$)
10	7.9–7.3 (br m, 70 H, Ph), 2.6–2.5 (br m, 16 H, $PhPCH_2$)
11	7.9–7.3 (m, 40 H, Ph), 3.1, 2.85 (2s, 6 H, C_2Me), 2.6–2.4 (m, 8 H, $PhPCH_2$)
12	7.9–7.3 (m, 50 H, Ph), 2.6–2.4 (m, 8 H, $PhPCH_2$)
13	7.9–7.3 (br m, 50 H, Ph), 2.6–2.4 (br m, 8 H, $PhPCH_2$)
14	7.9–7.3 (m, 40 H, Ph), 5.3 (s, 1 H, CH_2Cl_2), 3.1, 2.85 (2s, 6 H, C_2Me), 2.6–2.4 (m, 8 H, $PhPCH_2$)
15	7.9–7.3 (m, 40 H, Ph), 3.0, 2.9 (2s, 6 H, C_2Me), 2.8–2.5 (m, 8 H, $PhPCH_2$)
16	7.9–7.3 (br m, 50 H, Ph), 2.6–2.4 (br m, 8 H, $PhPCH_2$)
17	7.9–7.3 (br m, 50 H, Ph), 2.6–2.4 (br m, 8 H, $PhPCH_2$)
18	7.7–7.3 (m, 40 H, Ph), 5.3 (s, 1 H, CH_2Cl_2), 3.1, 3.0 (2s, 6 H, C_2Me), 2.6–2.4 (m, 8 H, $PhPCH_2$)
19	7.9–7.3 (m, 40 H, Ph), 5.3 (s, 1 H, CH_2Cl_2), 3.1, 2.9 (2s, 6 H, C_2Me), 2.6–2.4 (m, 8 H, $PhPCH_2$)
20	7.7–7.3 (br m, 50 H, Ph), 2.6–2.4 (br m, 8 H, $PhPCH_2$)
21	7.9–7.3 (br m, 40 H, Ph), 3.1, 2.9 (2s, 6 H, C_2Me), 2.6–2.4 (br m, 8 H, $PhPCH_2$), 2.2 (s, 3 H, NCMe)
22	7.7–7.3 (br m, 50 H, Ph), 2.8–2.7 (br m, 8 H, $PhPCH_2$), 2.3 (s, 3 H, NCMe)
23	7.9–7.3 (br m, 85 H, Ph), 2.8–2.5 (br m, 16 H, $PhPCH_2$)
24	7.9–7.3 (m, 70 H, Ph), 5.3 (s, 1 H, CH_2Cl_2), 3.0–2.8 (br m, s, 6 H, C_2Me), 2.7–2.5 (m, 16 H, $PhPCH_2$)
25	7.9–7.3 (m, 80 H, Ph), 2.6–2.4 (m, 16 H, $PhPCH_2$)

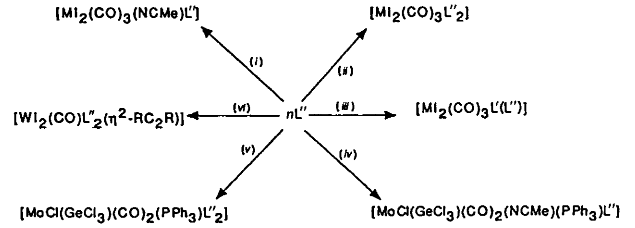
* Spectra recorded in $CDCl_3$ (+25 °C) and referenced to $SiMe_4$: s = singlet, br = broad, d = doublet, m = multiplet.

Two unsuccessful attempts to co-ordinate the unattached phosphorus atom in complex **1** were made. Refluxing a CH_2Cl_2 solution of **1** for 24 h gave only the starting complex after working up the reaction mixture. Also, after reaction of **1** with an equimolar amount of $ONMe_3\cdot2H_2O$ in NCMe for 12 h only starting materials were recovered. Trimethylamine *N*-oxide has been previously shown to react with, for example, $[M(CO)_6]$ in NCMe to give the carbonyl-displaced products $[M(CO)_5(NCMe)]$ and CO_2.[27] It may be that the steric crowding of the triphosphine and but-2-yne ligands hinders attack by the $ONMe_3$ on the carbonyl ligand in complex **1**.

The reactions of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ (R = Me **1** or Ph **2**) with molybdenum(II) and tungsten(II) complexes are extensive and summarised in Scheme 2. Reactions with 1 equivalent of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W)[28] in CH_2Cl_2 at room temperature gave the bimetallic complexes $[MI_2(CO)_3(NCMe)\{(\mu\text{-}L\text{-}P,P')WI_2(CO)(\eta^2\text{-}RC_2R)\}]$ **4–7** in high yield. These and other multimetallic complexes **8–25**



Scheme 1



Scheme 2 L″ = $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ (R = Me or Ph). All reactions were carried out in CH_2Cl_2 at room temperature. (*i*) L″ with an equimolar quantity of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) for 24 h; (*ii*) 2L″ with $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) for 24 h; (*iii*) $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with an equimolar quantity of L′ (L′ = PPh_3, $AsPh_3$ or $SbPh_3$) for 1, 3 or 5 min respectively, followed by an *in situ* reaction with L″ for 10 min; (*iv*) L″ with an equimolar quantity of $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ for 24 h; (*v*) $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ with 2L″ for 24 h; (*vi*) $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) with 2L″ for 24 h

described were characterised by elemental analysis (C, H and N) (Table 1), IR (Table 1), ^{1}H NMR (Table 2) and in selected cases by ^{31}P NMR spectroscopy (Table 3). Complexes **14**, **18**, **19** and **24** were confirmed as $0.5CH_2Cl_2$ solvates by repeated elemental analysis and ^{1}H NMR spectroscopy. In the case of **6** FAB mass spectral data were also obtained. The complexes **4**–**7** are all fairly soluble in dichloromethane and chloroform but only sparingly in diethyl ether. However, **1**–**3** are more soluble than **4**–**7**. These complexes are fairly stable in the solid state under nitrogen for a few days but less stable than **1**–**3**.

Table 3 Phosphorus-31 NMR data for selected complexes *

Complex	δ(*J*/Hz)
1	−13.7 (m, 2 P, $C_2H_4PPh_2$), −2.7 (s, 1 P, C_2H_4PPh), 4.3 (s, 1 P, C_2H_4PPh), 19.5 (d, 1 P, J_{PP} = 30, $C_2H_4PPh_2$), 23.1 (d, 1 P, J_{PP} = 25, $C_2H_4PPh_2$)
2	−13.3 (m, 2 P, $C_2H_4PPh_2$), −4.0 (s, 1 P, C_2H_4PPh), −3.5 (s, 1 P, C_2H_4PPh), 19.8 (d, 1 P, J_{PP} = 30, $C_2H_4PPh_2$), 26.1 (s, br, 1 P, $C_2H_4PPh_2$)
3	−13.5 (m, 2 P, $C_2H_4PPh_2$), −1.2 (s, 1 P, C_2H_4PPh), 7.2 (s, 1 P, C_2H_4PPh), 19.6 (d, 1 P, J_{PP} = 35, $C_2H_4PPh_2$), 22.7 (d, 1 P, J_{PP} = 24, $C_2H_4PPh_2$)
4	2.16 (d), 4.37 (s), 21.27 (m), 39.7 (s)
5	−2.1 (d), 4.1 (d), 22.0 (m), 39.0 (s)
6	−3.7 (m), 19.4 (s), 24.3 (m), 26 (d), 39 (s)
7	−4.2 (m), −2.2 (d), 22.8 (m), 27.0 (m)
8	−2.6 (d), 4.0 (d), 22.0 (m)
9	−3.5 (m), 4.24 (d), 21.9 (m)
10	−4.0 (d), 21.0 (d), 24.7
14	−3.4 (m), 21.5 (m), 23.6 (d)
15	−7.3 (s), −3.95 (m), 21.0 (m)
16	−3.6 (m), 11.3 (s), 24.9 (d)
17	−3.0 (m), 21.0 (d), 22.1 (d)
18	−2.0 (m), 3.9 (m), 22.5 (m)
19	−3.7 (d), 4.24 (d), 20.9 (m)
20	−3.9 (d), 21.3 (d), 26.9 (m)
24	−4.0 (d), −3.4 (m), 20.4 (m)
25	−3.5 (s, br), 21.2 (m), 25.2 (d, br)

* Spectra recorded in $CDCl_3$ referenced to H_3PO_4.

The infrared spectra of the complexes $[MI_2(CO)_3(NCMe)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$ (M = Mo **4** or W **5**) show alkyne stretching bands at 1655 cm^{-1} and 1659 cm^{-1}, respectively, *i.e.* at much lower wavenumbers compared to those of unco-ordinated but-2-yne. These complexes also show three carbonyl stretching bands as opposed to the four predicted, indicating that some of the bands may be masked. The IR spectra for **4** and **5** show broad carbonyl stretching bands at 1958 and 1967 cm^{-1} respectively, which can be assigned to the carbonyl group co-ordinated to $[WI_2(CO)(\text{L-}P,P')(\eta^2\text{-}MeC_2Me)]$ **1** which would not be expected to shift very much when its unco-ordinated phosphorus atom coordinates to another metal centre. Complexes **4**–**7** all show an acetonitrile stretching band in the region of 2300 cm^{-1}. The FAB mass spectrum of $[MoI_2(CO)_3(NCMe)\{\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}]$ **6** shows a peak at *m*/*z* 1147 which could be assigned to a mass peak of $M - I_4$.

The ^{1}H NMR spectra of complexes **4**–**7** conform with the stoichiometry proposed. The ^{31}P NMR data (Table 3) show no resonance at δ −13 indicating that the unco-ordinated phosphorus atom of the complexes $[WI_2(CO)(\text{L-}P,P')(\eta^2\text{-}RC_2R)]$ had attached to another metal centre. Several unsuccessful attempts were made to grow single crystals for X-ray crystallography. Several unsuccessful attempts were also made to obtain ^{13}C NMR spectra for these and other multimetallic complexes described later. This is almost certainly due to poor solubility and instability in solution over the long period of time required to obtain ^{13}C NMR spectra.

Reaction of 2 equivalents of $[WI_2(CO)(\text{L-}P,P')(\eta^2\text{-}RC_2R)]$ (R = Me **1** or Ph **2**) with 1 equivalent of $[MI_2(CO)_3(NCMe)_2]$

Table 4 Selected bond lengths (Å) and angles (°) for the two diastereoisomers of compound **1** and for **3**

Compound **1** Molecule **a**		Molecule **b**		Compound **3**	
W(1)–C(1)	1.970(11)	W(2)–C(40)	2.014(10)	W–C(1)	2.012(10)
W(1)–C(2)	2.025(8)	W(2)–C(42)	2.086(10)	W–C(2)	2.024(10)
W(1)–C(3)	1.997(8)	W(2)–C(41)	2.005(8)	W–C(3)	2.044(9)
W(1)–P(1)	2.470(2)	W(2)–P(5)	2.492(2)	W–P(1)	2.491(2)
W(1)–P(2)	2.556(2)	W(2)–P(4)	2.569(2)	W–P(2)	2.557(2)
W(1)–I(1)	2.815(2)	W(2)–I(4)	2.808(2)	W–I(2)	2.8037(7)
W(1)–I(2)	2.851(4)	W(2)–I(3)	2.849(2)	W–I(1)	2.8615(7)
C(2)–C(3)	1.302(11)	C(42)–C(41)	1.307(12)	C(2)–C(3)	1.324(13)
C(2)–C(4)	1.502(11)	C(42)–C(44)	1.434(12)	C(2)–C(4)	1.489(13)
C(3)–C(5)	1.535(12)	C(41)–C(43)	1.507(12)	C(3)–C(5)	1.444(12)
C(1)–W(1)–C(2)	111.4(4)	C(40)–W(2)–C(42)	109.1(3)	C(1)–W(1)–C(2)	113.0(3)
C(1)–W(1)–C(3)	73.8(4)	C(40)–W(2)–C(41)	72.1(3)	C(1)–W(1)–C(3)	76.1(3)
C(2)–W(1)–C(3)	37.8(3)	C(41)–W(2)–C(42)	37.2(3)	C(2)–W(1)–C(3)	38.0(4)
C(1)–W(1)–P(1)	96.1(3)	C(40)–W(2)–P(5)	96.4(2)	C(1)–W(1)–P(1)	93.9(3)
C(2)–W(1)–P(1)	87.5(2)	C(42)–W(2)–P(5)	87.8(2)	C(2)–W(1)–P(1)	86.4(3)
C(3)–W(1)–P(1)	94.5(2)	C(41)–W(2)–P(5)	95.0(2)	C(3)–W(1)–P(1)	97.6(3)
C(1)–W(1)–P(2)	164.7(3)	C(40)–W(2)–P(4)	168.0(3)	C(1)–W(1)–P(2)	164.5(2)
C(2)–W(1)–P(2)	83.4(2)	C(42)–W(2)–P(4)	82.4(3)	C(2)–W(1)–P(2)	81.4(3)
C(3)–W(1)–P(2)	121.2(2)	C(41)–W(2)–P(4)	119.6(2)	C(3)–W(1)–P(2)	118.9(3)
P(1)–W(1)–P(2)	80.25(7)	P(4)–W(2)–P(5)	80.58(7)	P(1)–W(1)–P(2)	80.97(7)
C(1)–W(1)–I(1)	89.6(3)	C(40)–W(2)–I(4)	88.0(2)	C(1)–W(1)–I(1)	79.0(2)
C(2)–W(1)–I(1)	103.5(2)	C(42)–W(2)–I(4)	102.9(2)	C(2)–W(1)–I(1)	162.3(3)
C(3)–W(1)–I(1)	100.4(2)	C(41)–W(2)–I(4)	98.5(2)	C(3)–W(1)–I(1)	154.7(3)
P(1)–W(1)–I(1)	164.99(5)	P(5)–W(2)–I(4)	166.45(5)	P(1)–W(1)–I(1)	79.61(6)
P(2)–W(1)–I(1)	90.68(6)	P(4)–W(2)–I(4)	92.47(6)	P(2)–W(1)–I(1)	85.66(6)
C(1)–W(1)–I(2)	79.6(3)	C(40)–W(2)–I(3)	82.7(3)	C(1)–W(1)–I(2)	90.2(3)
C(2)–W(1)–I(2)	163.9(2)	C(42)–W(2)–I(3)	164.5(3)	C(2)–W(1)–I(2)	105.5(3)
C(3)–W(1)–I(2)	151.9(2)	C(41)–W(2)–I(3)	153.9(2)	C(3)–W(1)–I(2)	97.7(3)
P(1)–W(1)–I(2)	79.50(6)	P(5)–W(2)–I(3)	80.74(5)	P(1)–W(1)–I(2)	164.73(6)
P(2)–W(1)–I(2)	85.12(6)	P(4)–W(2)–I(3)	85.34(5)	P(2)–W(1)–I(2)	91.30(6)
I(1)–W(1)–I(2)	87.89(4)	I(3)–W(2)–I(4)	87.15(3)	I(1)–W(1)–I(2)	86.73(2)
C(4)–C(2)–C(3)	137.8(8)	C(44)–C(42)–C(41)	140.5(9)	C(4)–C(2)–C(3)	134.0(9)
C(2)–C(3)–C(5)	136.3(7)	C(42)–C(41)–C(43)	133.5(8)	C(2)–C(3)–C(5)	139.1(9)

(M = Mo, R = Me or Ph; M = W, R = Me) in CH_2Cl_2 at room temperature gave the trimetallic complexes $[MI_2(CO)_3\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}RC_2R)\}_2]$ **8–10** in high yield. These complexes are all fairly soluble in dichloromethane and chloroform, but only sparingly in diethyl ether. However, they are less soluble than the monosubstituted complexes **4–7**. They are fairly stable in the solid state when stored under nitrogen for a few days, but much less stable in solution, and less stable than complexes **1–3**.

The infrared spectra of complexes **8–10** all show alkyne stretches in the region of 1600 cm^{-1}. They show a broad carbonyl stretching band in the region of 1950 cm^{-1} which can be assigned to the ligand present in the complexes $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ (R = Me **1** or Ph **2**). The ^1H NMR spectra conform with the stoichiometry of the complexes. The ^{31}P NMR spectra of complexes **8–10** all show three resonances, which indicates the organometallic phosphines $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ are equivalent, and it has often been observed that seven-co-ordinate complexes are fluxional at room temperature.[2] It appears that the diastereoisomers observed in **1** are not seen when the complex acts as a monodentate phosphine and co-ordinates to another metal centre.

Reaction of 1 equivalent of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with an equimolar quantity of L′ (PPh_3, $AsPh_3$ or $SbPh_3$) for 1, 3 and 5 min respectively followed by *in situ* reaction with an equimolar amount of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ (R = Me **1** or Ph **2**) afforded the complexes $[MI_2(CO)_3L'\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}RC_2R)\}]$ **11–20** (L′ = PPh_3, M = W, R = Me; M = Mo or W, R = Ph; L′ = $AsPh_3$, M = Mo or W, R = Me or Ph; L′ = $SbPh_3$, M = Mo or W, R = Me; M = W, R = Ph). They are all fairly soluble in dichloromethane and chloroform but only sparingly in diethyl ether. These complexes are fairly stable in the solid state under nitrogen for a few days, but much more air-sensitive in solution.

The infrared spectra of complexes **11–20** showed carbonyl stretching bands in the region of 1950 cm^{-1}, which could be assigned to the carbonyl group of the monodentate phosphine ligand $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ (R = Me **1** or Ph **2**). All showed an alkyne stretching band in the region of 1590 cm^{-1}, and three or four carbonyl stretching bands indicating that some of these may be masked. The ^1H NMR spectra (see Table 2) are consistent with their conformation as bimetallic complexes. The ^{31}P NMR spectra for selected $AsPh_3$ and $SbPh_3$ complexes show three phosphorus resonances which again indicates the complexes are likely to be fluxional.[2]

Treatment of complexes **1** and **2** with an equimolar amount of $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ in CH_2Cl_2 at room temperature gave $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}RC_2R)\}]$ **21** and **22**. Reaction of 2 equivalents of **2** with 1 equivalent of $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ in CH_2Cl_2 at room temperature yielded $[MoCl(GeCl_3)(CO)_2(PPh_3)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2]$ **23**. As expected these complexes are soluble in dichloromethane and chloroform but only sparingly in diethyl ether. All are far less soluble and less stable than complexes **1–20**, **24** and **25**. These complexes are stable in the solid state under nitrogen for a few days but much less stable in solution.

The infrared spectra of complexes **21** and **22** show broad carbonyl stretching bands at 1953 and 1879 and 1954 and 1882 cm^{-1} respectively. The higher-frequency bands at 1953 and 1954 cm^{-1} are as expected, in a similar position to those of the phosphine ligands **1** and **2**. The IR spectrum of complex **23** shows two carbonyl stretching bands at 1969 and 1881 cm^{-1}. The band at 1969 cm^{-1} is broad and may mask the carbonyl band of complex **2** which is at 1965 cm^{-1}. No acetonitrile bands were observed indicating that both ligands have been displaced. The ^1H NMR spectra of **21–23** are consistent with the formulation of the complexes proposed. Since complex **1** contains a 'four-electron' alkyne[26] it is unlikely the alkyne stretching bands will differ significantly, since the complexes are all of the type $[WI_2(CO)L_2(\eta^2\text{-alkyne})]$.

Reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) with 2 equivalents of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ **2** in CH_2Cl_2 at room temperature gave the complexes $[WI_2(CO)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2(\eta^2\text{-}RC_2R)]$ **24** and **25** in good yield. Both are soluble in dichloromethane and chloroform but only sparingly in diethyl ether. These complexes are fairly stable in the solid state under nitrogen but less stable in solution. The infrared spectra showed weak alkyne stretching bands at 1602, 1550 cm^{-1} for **24** and 1601, 1581 and 1540 cm^{-1} for **25**. Since the structures of four bis(phosphine) complexes $[MoBr_2(CO)(PEt_3)_2(\eta^2\text{-}PhC_2H)]$,[19] $[MoBr_2(CO)(PMePh_2)_2(\eta^2\text{-}MeC_2Me)]$[22] and $[WCl_2(CO)L'_2(\eta^2\text{-}PhC_2Ph)]$ (L′ = PPh_3 or PMe_2Ph)[23] have been crystallographically determined and have *trans*-phosphine ligands, it is very likely that complexes **24** and **25** have this structure as shown in Fig. 4. Several unsuccessful attempts to grow suitable single crystals of **24** and **25** for X-ray crystallography were made. The ^{31}P NMR spectra both show three phosphorus resonances which indicates that the attached organotungsten phosphorus ligands **1** and **2** are equivalent and conforms with the structure shown in Fig. 4. Again it appears that the diastereoisomers of complex **1** are lost after co-ordination to the tungsten centre of the 'free' phosphorus atom in **1**.

In conclusion, the novel monodentate phosphines $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ (R = Me **1** or Ph **2**) are excellent precursors to prepare a number of new bi- and trimetallic complexes of molybdenum(II) and tungsten(II).

Experimental

All reactions were carried out at room temperature under a stream of dry nitrogen using standard vacuum Schlenk-line techniques. The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W),[28] $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph)[24] and $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$[29] were prepared by published methods. Dichloromethane and diethyl ether were dried and distilled before use. All chemicals were obtained from commercial sources.

Elemental analyses (carbon, hydrogen and nitrogen) were determined using a Carlo Erba Elemental Analyser MOD 1106 (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, ^{31}C (referenced to $SiMe_4$) and ^{31}P NMR (85% H_3PO_4) spectra on a Bruker AC 250 NMR spectrometer. Fast atom bombardment mass spectrometry was carried out by the EPSRC service at University College Swansea, on a VG-Autospec instrument, using Cs^+ ions at 25 kV as bombarding ions and samples dissolved in a 3-nitrobenzyl alcohol matrix target. For low-resolution measurements the resolution was set at about 3000 and the result was the average of about 20 scans using an external calibration.

Preparations

$[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ 1. To a solution of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (2.01 g, 3.27 mmol) dissolved in CH_2Cl_2 (30 cm^3) at room temperature was added the triphosphine (1.75 g, 3.27 mmol) and the reaction mixture was stirred for 24 h. The resulting green solution was filtered, and the solvent removed *in vacuo* giving a blue-green crystalline powder of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ **1** which was recrystallised by cooling a CH_2Cl_2–diethyl ether (4:1) solution of the complex at −17 °C to yield single crystals of **1**, suitable for X-ray crystallography. Yield 3.40 g, 93%.

Similar reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ (R = R′ = Ph; R = Me, R′ = Ph) with 1 equivalent of triphosphine in CH_2Cl_2 gave the bright green crystalline products

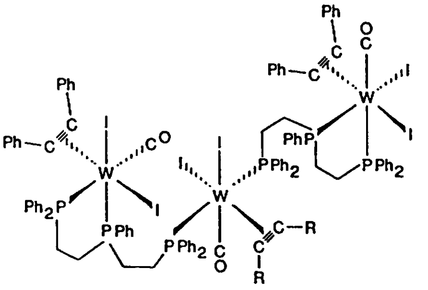


Fig. 4 The likely structure of $[WI_2(CO)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2(\eta^2\text{-}RC_2R)]$ (R = Me **24** or Ph **25**)

$[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R')]$ **2** and **3**. Suitable single crystals of **3** for X-ray crystallography were obtained by cooling a CH_2Cl_2–diethyl ether (4 : 1) solution of the complex at −17 °C. See Table 1 for physical and analytical data.

Reactions of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ (R = Me 1 or Ph 2)

$[MoI_2(CO)_3(NCMe)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$ 4. To a solution of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ (0.21 g, 0.19 mmol) dissolved in CH_2Cl_2 (30 cm^3) at room temperature was added $[MoI_2(CO)_3(NCMe)_2]$ (0.1 g, 0.19 mmol) and the reaction mixture was stirred for 24 h. The resulting green solution was filtered, and the solvent removed *in vacuo* giving a green crystalline powder of $[MoI_2(CO)_3(NCMe)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$ **4** which was recrystallised by cooling a CH_2Cl_2–diethyl ether (4 : 1) solution of the complex at −17 °C. Yield = 0.25 g, 84%.

Similar reactions of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ (R = Me or Ph) with 1 equivalent of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) in CH_2Cl_2 at room temperature gave the complexes $[MI_2(CO)_3(NCMe)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}RC_2R)\}]$ **5**–**7**.

$[MoI_2(CO)_3\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}_2]$ 8. To a solution of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ (0.3 g, 0.28 mmol) dissolved in CH_2Cl_2 (30 cm^3) at room temperature was added $[MoI_2(CO)_3(NCMe)_2]$ (0.07 g, 0.14 mmol) and the reaction mixture was stirred for 24 h. The resulting green solution was filtered, and the solvent removed *in vacuo* giving a brown-black crystalline powder of $[MoI_2(CO)_3\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}_2]$ **8** which was recrystallised by cooling a CH_2Cl_2–diethyl ether solution of the complex at −17 °C. Yield = 0.29 g, 83%.

Similar reactions of 2 equivalents of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ with 1 equivalent of $[MI_2(CO)_3(NCMe)_2]$ (M = W, R = Me; M = Mo, R = Ph) in CH_2Cl_2 at room temperature gave the complexes $[MI_2(CO)_3\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}RC_2R)\}_2]$ **9** and **10**.

$[WI_2(CO)_3(PPh_3)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$ 11. To a solution of $[WI_2(CO)_3(NCMe)_2]$ (0.12 g, 0.20 mmol) dissolved in CH_2Cl_2 (30 cm^3) at room temperature was added PPh_3 (0.05 g, 0.20 mmol) and the reaction mixture was stirred for 1 min, after which time $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ (0.22 g, 0.20 mmol) was added *in situ* and the reaction stirred for 10 min. The solvent was removed *in vacuo* giving a green crystalline powder of $[WI_2(CO)_3(PPh_3)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$ **11** which was recrystallised by cooling a CH_2Cl_2–diethyl ether solution of the complex to −17 °C. Yield = 0.25 g, 66%.

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with an equimolar amount of L′ (L′ = PPh_3, $AsPh_3$ and $SbPh_3$) for 1, 3 or 5 min respectively followed by an *in situ* reaction with 1 equivalent of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}RC_2R)]$ (R = Me or Ph) in CH_2Cl_2 at room temperature gave complexes **12**–**20**.

$[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$ 21. To a solution of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ (0.15 g, 0.14 mmol) dissolved in CH_2Cl_2 (30 cm^3) at room temperature was added $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ (0.10 g, 0.14 mmol) and the reaction mixture was stirred for 24 h. The solvent was removed *in vacuo* giving a green crystalline powder of $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}MeC_2Me)\}]$ **21** which was recrystallised by cooling a CH_2Cl_2–diethyl ether solution of the complex at −17 °C. Yield = 0.19 g, 81%.

A similar reaction of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ with 1 equivalent of $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ in CH_2Cl_2 at room temperature gave the complex $[MoCl(GeCl_3)(CO)_2(NCMe)(PPh_3)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}]$ **22**.

$[MoCl(GeCl_3)(CO)_2(PPh_3)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2]$ 23. To a solution of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (0.19 g, 0.16 mmol) dissolved in CH_2Cl_2 (30 cm^3) at room temperature was added $[MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)]$ (0.06 g, 0.08 mmol) and the reaction mixture was stirred for 24 h. The solvent was removed *in vacuo* giving a brown-black crystalline powder of $[MoCl(GeCl_3)(CO)_2(PPh_3)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2]$ **23** which was recrystallised by cooling a CH_2Cl_2–diethyl ether solution of the complex at −17 °C. Yield = 0.17 g, 69%.

$[WI_2(CO)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2(\eta^2\text{-}MeC_2Me)]\cdot 0.5CH_2Cl_2$ 24. To a solution of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (0.09 g, 0.14 mmol) dissolved in CH_2Cl_2 (30 cm^3) at room temperature was added $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ (0.33 g, 0.28 mmol), and the reaction mixture was stirred for 24 h. The resulting green solution was filtered and the solvent removed *in vacuo* giving a green crystalline powder of $[WI_2(CO)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2(\eta^2\text{-}MeC_2Me)]\cdot 0.5CH_2Cl_2$ **24** which was recrystallised from a CH_2Cl_2–diethyl ether solution of the complex at −17 °C. Yield = 0.33 g, 77%.

A similar reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ with 2 equivalents of $[WI_2(CO)(L\text{-}P,P')(\eta^2\text{-}PhC_2Ph)]$ in CH_2Cl_2 at room temperature gave the dark green product $[WI_2(CO)\{(\mu\text{-L-}P,P')WI_2(CO)(\eta^2\text{-}PhC_2Ph)\}_2(\eta^2\text{-}PhC_2Ph)]$ **25**.

X-Ray crystallography

Crystals of complexes **1** and **3** were grown as described in the Experimental section. Information concerning the crystal data and structure refinement is given in Table 5.

Data were recorded on a FAST TV area detector diffractometer, with a molybdenum target [λ(Mo-Kα) = 0.710 69 Å], equipped with an Oxford Cryosystems cryostat and driven by MADNES software operating on a MicroVAX 3200 computer, following previously described procedures.[30] The structures were solved *via* heavy-atom methods (SHELXS),[31] and then subjected to full-matrix least-squares refinement on F_o^2 (SHELXL 93).[32] There are two independent molecules in the asymmetric unit for compound **1**. Non-hydrogen atoms were made anisotropic, with hydrogens in calculated positions (C–H 0.96 Å, with U_{iso} tied to U_{eq} of the parent atoms). The solvent molecules in **1** were freely refined with partial occupancy (75%). Absorption corrections were applied using DIFABS.[33] The *R* indices are defined as $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{\frac{1}{2}}$ $\{w = 1/[\sigma^2(F_o^2) + (0.0715P)^2]$ where $P = [\max.(F_o^2) + 2(F_c^2)]/3\}$ and $R1 = \Sigma(F_o - F_c)/\Sigma(F_o)$. Sources of scattering factor data are given in ref. 32. Diagrams were drawn with SNOOPI,[34] and the coordinates of **1b** inverted so as to show the similarities in stereochemistry between the two molecules.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors,

Table 5 Crystal data and structure refinement for compounds **1** and **3**

	1	**3**
Empirical formula	$C_{39}H_{39}I_2OP_3W\cdot C_{0.75}H_{1.5}Cl_{1.5}$	$C_{44}H_{41}I_2OP_3W$
Formula weight	1116.05	1116.33
T/K	120(2)	150(2)K
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pna2_1$
a/Å	10.056(5)	11.062(2)
b/Å	17.884(8)	22.240(2)
c/Å	24.915(9)	16.927(3)
α/°	105.77(3)	
β/°	94.83(3)	
γ/°	102.41(2)	
U/Å^3	4163(3)	4164.4(10)
Z	4	4
D_c/Mg m^{-3}	1.781	1.781
μ/mm^{-1}	4.496	4.404
F(000)	2146	2152
Crystal size/mm	0.2 × 0.14 × 0.14	0.28 × 0.32 × 0.32
θ range for data collection/°	1.79–25.04	1.83–25.10°
hkl Ranges	−10 to 10, −20 to 13, −28 to 27	−13 to 13, −24 to 20, −19 to 19
Reflections collected	10 095	17 186
Independent reflections	9906	6271
R_{int}	0.0293	0.0641
Absorption correction factors	0.823, 1.175	0.908, 1.193
Data parameters	9901, 889	6271, 461
Goodness of fit on F^2	0.930	1.005
Final R indices	$R1 = 0.0392$	$R1 = 0.0388$
[$I > 2\sigma(I)$]	$wR2 = 0.1031$ (8194 reflections)	$wR2 = 0.0859$ (5442 reflections)
(all data)	$R1 = 0.0509$	$R1 = 0.0479$
	$wR2 = 0.1124$	$wR2 = 0.0873$
Largest difference peak and hole/e Å^3	2.807 and −0.762	3.233 and −0.917

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References

1 J. L. Templeton, *Adv. Organomet. Chem.*, 1989, **29**, 1.
2 P. K. Baker, *Adv. Organomet. Chem.*, 1996, **40**, 45.
3 A. Blagg, A. T. Hutton, P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 1815.
4 J. A. Iggo and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1985, 1009.
5 A. Blagg, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 769.
6 T. G. Schenck, J. M. Downes, C. R. C. Milne, P. B. Mackenzie, H. Boucher, J. Whelan and B. Bosnich, *Inorg. Chem.*, 1985, **24**, 2334.
7 G. B. Jacobsen, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 1489.
8 A. Blagg, P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1987, 1495.
9 G. B. Jacobson, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 1509.
10 S. Onaka, A. Mizuno and S. Takagi, *Chem. Lett.*, 1989, 2037.
11 T. S. A. Hor and L.-T. Phang, *J. Organomet. Chem.*, 1989, **373**, 319.
12 T. S. A. Hor and L.-T. Phang, *J. Organomet. Chem.*, 1990, **381**, 121.
13 T. S. A. Hor and L.-T. Phang, *J. Organomet. Chem.*, 1990, **393**, 345.
14 M. Olmstead, C. H. Lindsay, L. S. Benner and A. L. Balch, *J. Organomet. Chem.*, 1979, **179**, 289.
15 P. K. Baker and K. R. Flower, *Polyhedron*, 1990, **9**, 2507.
16 P. K. Baker, M. van Kampen and D. ap Kendrick, *J. Organomet. Chem.*, 1991, **421**, 241.
17 J. L. Davidson and G. Vasapollo, *J. Chem. Soc., Dalton Trans.*, 1985, 2239.
18 M. A. Bennett and I. W. Boyd, *J. Organomet. Chem.*, 1985, **290**, 165.
19 P. B. Winston, S. J. N. Burgmayer, T. L. Tonker and J. L. Templeton, *Organometallics*, 1986, **5**, 1707.
20 E. M. Armstrong, P. K. Baker, M. E. Harman and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1989, 295.
21 P. K. Baker and P. D. Jackson, *Inorg. Chim. Acta*, 1994, **219**, 99.
22 B. J. Brisdon, A. G. W. Hodson, M. F. Mahon, K. C. Molloy and R. A. Walton, *Inorg. Chem.*, 1990, **29**, 2701.
23 G. R. Clark, A. J. Nielson, A. D. Rae and C. E. F. Rickard, *J. Chem. Soc., Dalton Trans.*, 1994, 1783.
24 E. M. Armstrong, P. K. Baker and M. G. B. Drew, *Organometallics*, 1988, **7**, 319.
25 P. K. Baker, S. J. Coles, M. B. Hursthouse, M. M. Meehan and S. D. Ridyard, *J. Organomet. Chem.*, 1995, **503**, C8.
26 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1980, **102**, 3288.
27 K.-S. Gan, H. K. Lee and T. S. A. Hor, *J. Organomet. Chem.*, 1993, **460**, 197.
28 P. K. Baker, S. G. Fraser and E. M. Keys, *J. Organomet. Chem.*, 1986, **309**, 319.
29 P. K. Baker and D. ap Kendrick, *J. Organomet. Chem.*, 1994, **466**, 139.
30 S. R. Drake, M. B. Hursthouse, K. M. A. Malik and S. A. S. Miller, *Inorg. Chem.*, 1993, **32**, 4653.
31 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
32 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.
33 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158; adapted for FAST geometry by A. Karaulov, University of Wales, Cardiff, 1991.
34 K. Davies and K. C. Prout, University of Oxford, 1993, unpublished work.

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