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Cis- and *trans*-bis(diphenylphosphino)ethene seven-coordinate complexes of molybdenum(II) and tungsten(II). Crystal structures of $[MI_2(CO)_3(\textit{cis}\text{-dppen})]$ {M = Mo or W; dppen = bis(diphenylphosphino)ethene}, $[WI(CO)_2(\textit{cis}\text{-dppen})_2]I$, $[MI_2(CO)_2\{P(OR)_3\}(\textit{cis}\text{-dppen})]$ (M = Mo, R = Me; M = W, R = Et or Ph)

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Abstract

Equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and *cis*-dppen {dppen = $Ph_2PCH{=}CHPPh_2$} react in CH_2Cl_2 at room temperature to give good yields of the crystallographically characterised complexes $[MI_2(CO)_3(\textit{cis}\text{-dppen})]$ (**1** and **2**). Treatment of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of *cis*-dppen affords the crystallographically characterised cationic complex $[WI(CO)_2(\textit{cis}\text{-dppen})_2]I$ (**3**). Reaction of $[MI_2(CO)_3(NCMe)_2]$ with one equivalent of *cis*-dppen, followed by addition of an equimolar amount of $P(OR)_3$ affords the mixed ligand complexes $[MI_2(CO)_2\{P(OR)_3\}(\textit{cis}\text{-dppen})]$ (M = Mo or W; R = Me, Et, ^{i}Pr, ^{n}Bu or Ph) (**4**–**13**). The X-ray crystal structures for M = Mo, R = Me; M = W, R = Et or Ph are also determined. Treatment of equimolar quantities of $[MoI_2(CO)_3(NCMe)_2]$ and $P(O^iPr)_3$ gave $[MoI_2(CO)_3(NCMe)\{P(O^iPr)_3\}]$, which reacted in situ with half an equivalent of *trans*-dppen to furnish the bimetallic phosphine-bridged complex $[\{MoI_2(CO)_3\{P(O^iPr)_3\}\}_2(\mu\text{-}\textit{trans}\text{-dppen})]$ (**14**). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: *Cis*- and *trans*-bis(diphenylphosphino)ethene; Seven-coordinate; Molybdenum(II); Tungsten(II); Crystal structures

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1. Introduction

Since the first halocarbonyl donor ligand complex $[MoI_2(CO)_2(diars)]$ was reported by Nigam and Nyholm in 1957 [1], much effort has been put into investigating the synthesis [2–5], structures [6,7] and catalytic activity [8,9] of seven-coordinate complexes of the type $[MX_2(CO)_3L_2]$. Although a large number of seven-coordinate halocarbonyl complexes of molybdenum(II) and tungsten(II) containing mono-, bi- and tridentate phosphine ligands have been reported [2–5,10–23], hitherto, no examples containing the rotationally restricted phosphines *cis*- and *trans*-dppen (dppen = $Ph_2PCH{=}CHPPh_2$) have been described. While there are numerous crystal structures containing the ligands dppe and dppm with a wide range of metals, much less attention has been given to the unsaturated ligands such as dppen. Indeed we found no crystal structures in the Cambridge Crystallographic Database containing this ligand with molybdenum or tungsten apart from the octahedral structures $[Mo(CO)_4(\textit{cis}\text{-dppen})]$ [24], $[Mo(CO)_2(\textit{cis}\text{-dppen})_2]$ [24] and $[Mo(CO)_2(dppe)(\textit{cis}\text{-dppen})]$ [25]. There has, however, been considerable interest in the analogous diarsenic bidentate ligand L_2, {L_2 = *cis*-2,3-bis(dimethylarsino-1,1,1,4,4,4,-hexafluorobut-2-ene} and the structures of $[WI_2(CO)_2\{P(OMe)_3\}$-

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Table 1
Physical and analytical data for *cis*- and *trans*-bis(diphenylphosphino)ethene complexes of molybdenum(II) and tungsten(II)

Complex	Colour	Yield (%)	Analysis (%) {Found (Calc.)}	
			C	H
$[MoI_2(CO)_3(cis\text{-dppen})]$ (**1**)	Reddish orange	59	41.5 (41.8)	2.7 (2.7)
$[WI_2(CO)_3(cis\text{-dppen})]$ (**2**)	Yellow	73	38.2 (37.9)	2.5 (2.4)
$[WI(CO)_2(cis\text{-dppen})_2]I$ (**3**)	Yellow	80	47.5 (48.2)	3.4 (3.4)
$[MoI_2(CO)_2\{P(OMe)_3\}(cis\text{-dppen})]$ (**4**)	Yellow orange	48	39.1 (40.2)	3.4 (3.4)
$[WI_2(CO)_2\{P(OMe)_3\}(cis\text{-dppen})]$ (**5**)	Yellow	53	39.4 (36.9)	2.7 (2.5)
$[MoI_2(CO)_2\{P(OEt)_3\}(cis\text{-dppen})]$ (**6**)	Yellow orange	73	41.8 (42.1)	3.8 (3.8)
$[WI_2(CO)_2\{P(OEt)_3\}(cis\text{-dppen})]$ (**7**)	Yellow	70	38.3 (38.7)	3.5 (3.5)
$[MoI_2(CO)_2\{P(O^iPr)_3\}(cis\text{-dppen})]$ (**8**)	Yellow orange	54	43.8 (44.0)	4.4 (4.3)
$[WI_2(CO)_2\{P(O^iPr)_3\}(cis\text{-dppen})]$ (**9**)	Yellow	68	41.0 (40.5)	3.8 (4.0)
$[MoI_2(CO)_2\{P(O^nBu)_3\}(cis\text{-dppen})]$ (**10**)	Orange	61	45.3 (45.5)	4.4 (4.7)
$[WI_2(CO)_2\{P(O^nBu)_3\}(cis\text{-dppen})]$ (**11**)	Yellow orange	77	42.4 (42.1)	4.4 (4.3)
$[MoI_2(CO)_2\{P(OPh)_3\}(cis\text{-dppen})]$ (**12**)	Orange	49	49.4 (49.6)	3.7 (3.4)
$[WI_2(CO)_2\{P(OPh)_3\}(cis\text{-dppen})]\cdot CH_2Cl_2$ (**13**)	Orange	83	44.0 (43.9)	3.1 (3.1)
$[\{MoI_2(CO)_3\{P(O^iPr)_3\}\}_2(\mu\text{-}trans\text{-dppen})]$ (**14**)	Off-white	66	35.5 (35.6)	4.0 (3.8)

$(L_2)]$ [26], $[WI_2(CO)_3L_2]$ [27] and $[WBr_2(CO)\{P(OMe)_3\}_2L_2]$ [28] are all relevant to the structures reported here. In the first two structures the metal atoms have a distorted capped trigonal prism environment, but in the diphosphite, the metal has a distorted capped octahedral environment.

In 1986 [29], we described the synthesis of the highly versatile seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W). These complexes are prepared by reacting the zero-valent complexes *fac*-$[M(CO)_3(NCMe)_3]$ (prepared in situ) [30] with an equimolar amount of I_2 at 0°C. In this paper, we describe the reactions of $[MI_2(CO)_3(NCMe)_2]$ and their phosphite derivatives with *cis*- and *trans*-dppen. The molecular structures of $[MI_2(CO)_3(cis\text{-dppen})]$ {M = Mo or W; dppen = bis(diphenylphosphino)ethene}, $[WI(CO)_2(cis\text{-dppen})_2]I$, $[MI_2(CO)_2\{P(OR)_3\}(cis\text{-dppen})]$ (M = Mo, R = Me; M = W, R = Et or Ph) are also discussed.

2. Results and discussion

2.1. Synthesis and crystal structures of $[MI_2(CO)_3(cis\text{-dppen})]$ (1 and 2)

Reaction of equimolar quantities of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) and *cis*-dppen in CH_2Cl_2 at room temperature gave the acetonitrile displaced products $[MI_2(CO)_3(cis\text{-dppen})]$ (**1** and **2**) probably via a dissociative mechanism, since the bis(acetonitrile) complexes obey the effective atomic number rule. Complexes **1** and **2** have been characterised by elemental analysis (C, H and N) (Table 1), IR and ^1H-NMR spectroscopy (Tables 2 and 3), in selected cases by ^{31}P-NMR spectroscopy (Table 4), and by X-ray crystallography. They are both moderately soluble in CH_2Cl_2, $CHCl_3$, but insoluble in hydrocarbon solvents and diethyl ether. They are stable in the solid state when stored under dinitrogen, but decompose rapidly when exposed to air in solution. The IR spectra of **1** and **2** show three carbonyl bands, which suggests there is one isomer in solution. This was confirmed by the ^1H-NMR spectra (Table 3), and the ^{31}P-NMR spectrum of **1**, which showed a single resonance at $\delta = 54.8$ ppm which suggests the complex is fluxional at room temperature.

Suitable single crystals of **1** for X-ray crystallography were grown by cooling (−17°C) a concentrated solution of $[MoI_2(CO)_3(cis\text{-dppen})]$ (**1**) in $CDCl_3$ in an NMR tube for 2 weeks. Suitable single crystals of the tungsten complex $[WI_2(CO)_3(cis\text{-dppen})]$ (**2**) were obtained by cooling (−17°C) a concentrated CH_2Cl_2

Table 2
IR data [a] for the *cis*- and *trans*-dppen complexes of molybdenum(II) and tungsten(II)

Complex	ν(CO) (cm^{-1})
1	2066 s; 1979 s; 1928 s
2	2022 s; 1967 s; 1918 s
3	1933 s; 1866 s
4	1955 s; 1872 s
5	1946 s; 1866 m
6	1951 s; 1878 s
7	1944 s; 1864 s
8	1953 s; 1876 s
9	1940 s; 1861 s
10	1951 s; 1880 s
11	1932 s; 1830 s
12	1958 s; 1880 s
13	1948 s; 1866 s
14	2030 m; 1972 s; 1938 s

[a] Recorded as thin $CHCl_3$ films between NaCl plates. m, medium; s, strong.

Table 3
Proton NMR data [a] for the *cis*- and *trans*-dppen complexes of molybdenum(II) and tungsten(II)

Complex	δ (ppm)/J (Hz)
1	7.8–7.3 (m, 20H, $\mathit{Ph}_2PCH{=}CHP\mathit{Ph}_2$); 3.95 (s, 2H, $Ph_2C\mathit{H}{=}C\mathit{H}PPh_2$)
2	7.8–7.2 (m, 20H, $\mathit{Ph}_2PCH{=}CHP\mathit{Ph}_2$); 3.9 (br, s, 2H, $Ph_2PC\mathit{H}{=}C\mathit{H}PPh_2$)
3	7.6–6.9 (m, 40H, Ph); 4.0 (s, 4H, $Ph_2PC\mathit{H}{=}C\mathit{H}PPh_2$)
4	7.9–7.3 (br, m, 20H, Ph); 4.0 (s, 2H, $Ph_2PC\mathit{H}{=}C\mathit{H}PPh_2$); 3.75 {d, 9H, $P(OC\mathit{H}_3)_3$}
5	7.9–7.2 (br, m, 20H, Ph); 4.0 (br, 2H, $Ph_2PC\mathit{H}{=}C\mathit{H}PPh_2$); 3.7 {d, 9H, $P(OC\mathit{H}_3)_3$}
6	7.9–7.3 (br, m, 20H, Ph); 4.2 {qt, 6H, $P(OC\mathit{H}_2CH_3)_3$}; 3.9 (br, 2H, $Ph_2PC\mathit{H}{=}C\mathit{H}PPh_2$); 1.3 {t, 9H, $P(OCH_2C\mathit{H}_3)_3$}
7	7.9–7.2 (br, m, 20H, Ph); 4.15 {qt, 6H, $P(OC\mathit{H}_2CH_3)_3$}; 4.0 (br, 2H, $Ph_2PC\mathit{H}{=}C\mathit{H}PPh_2$); 1.4 {t, 9H, $P(OCH_2C\mathit{H}_3)_3$}
8	7.9–7.0 (br, m, 20H, Ph); 4.35 (br, 3H, $P\{OC\mathit{H}{-}(CH_3)_2\}_3$); 3.6 (s, 2H, $Ph_2PC\mathit{H}{=}C\mathit{H}PPh_2$); 1.28 (d, 18H, $P\{OCH(C\mathit{H}_3)_2\}_3$)
9	8.0–7.0 (br, m, 20H, Ph); 4.86 (br, 3H, $P\{OCH(CH_3)_2\}_3$); 4.2 (br, 2H, $Ph_2PC\mathit{H}{=}C\mathit{H}PPh_2$); 1.3 (d, 18H, $P\{OCH(CH_3)_2\}_3$)
10	8.0–7.1 (br, m, 20H, Ph); 4.12 {br, qt, 6H, $P(OC\mathit{H}_2{-}CH_2CH_2CH_3)_3$, +2H, $Ph_2PC\mathit{H}{=}CHPPh_2$}; 1.65 {m, 6H, $P(OCH_2C\mathit{H}_2CH_2CH_3)_3$}; 1.4 {m, 6H, $P(OCH_2CH_2C\mathit{H}_2CH_3)_3$}; 0.95 {t, 9H, $P(OCH_2CH_2CH_2C\mathit{H}_3)_3$}
11	8.1–6.9 (br, m, 20H, Ph); 4.1 {br, m, 6H, $P(OC\mathit{H}_2CH_2CH_2CH_3)_3 + 2H$, $PhPC\mathit{H}{=}C\mathit{H}PPh_2$}; 1.68 {m, 6H, $P(OCH_2C\mathit{H}_2CH_2CH_3)_3$}; 1.45 {m, 6H, $P(OCH_2CH_2C\mathit{H}_2CH_3)_3$}; 0.95 {t, 9H, $P(OCH_2CH_2CH_2C\mathit{H}_3)_3$}
13	7.6–6.8 (br, m, 35H, Ph); 5.3 (s, 2H, CH_2Cl_2); 3.7 (br, s, $Ph_2PC\mathit{H}{=}C\mathit{H}PPh_2$)
14	7.75–7.3 (br, m, 20H, Ph); 4.8 (br, m, 6H, $P\{OC\mathit{H}(CH_3)_2\}_3$); 3.7 (s, 2H, $Ph_2PC\mathit{H}{=}C\mathit{H}PPh_2$); 1.5 {d, 36H, $P\{OCH(C\mathit{H}_3)_2\}_3$}

[a] Spectra recorded in $CDCl_3$ at 25°C, referenced to $SiMe_4$. s, singlet; m, multiplet; d, doublet; qt, quintet; t, triplet; br, broad.

solution of **2** to which a few drops of diethyl ether had been added.

The molecular structures of **1** and **2** are shown in Figs. 1 and 2, together with their common atom numbering schemes. The structures of **1** and **2** are equivalent with the metal atom bonded to three carbonyl atoms, two iodine atoms and the bidentate *cis*-dppen ligand. The geometry of the metal coordination sphere can best be considered as a distorted capped octahedron with C(200) in the capping position, the other two carbonyls in the capped face together with one of the phosphorus atoms P(3) from the bidentate dppen ligand. The other phosphorus atom P(4) from this ligand, together with the two iodine atoms make up the uncapped face. The dimensions in the two structures are as expected and almost equivalent reflecting the similar radii of Mo and W. It is particularly noticeable that the bonds to P(3) are ca. 0.09 Å shorter than bonds to P(6), no doubt because of lengthening in the latter case due to the *trans*-effect of the carbonyl ligand. This geometry is typical of structures of the type $[WI_2(CO)_3(L{-}L)]$ (M = Mo, W; L–L = bidentate ligand) and can be compared, in particular, with structures containing dppe e.g. $[MoBr_2(CO)_3(dppe)]$ [31], $[WI_2(CO)_3(dppe)]$ [32], and $[MoI_2(CO)_3(dppe)]$ [33].

2.2. Synthesis and crystal structure of $[WI(CO)_2(cisdppen)_2]I$ (3)

Reaction of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of *cis*-dppen in CH_2Cl_2 at room temperature gave the cationic complex $[WI(CO)_2(\mathit{cis}\text{-dppen})_2]I$ (**3**) in 80% yield. The complex was fully characterised in the normal manner (see Tables 1–4). Complex **3** is slightly more soluble in chlorinated solvents, and is more stable to oxidation than **1** and **2**. The infrared spectrum shows two carbonyl bands at 1933 and 1866 cm^{-1}, which suggests the carbonyl groups are *cis*- to each other and this is confirmed by the X-ray crystal structure (Fig. 3). The ^{31}P-NMR spectrum ($CDCl_3$, 25°C) shows a single resonance at $\delta = 37.8$, $J_{wp} = 160.5$ Hz, which intimates the four phosphorus atoms are in the same environment and suggests the complex is fluxional at room temperature (Fig. 3).

Suitable single crystals for X-ray analysis were grown by cooling a concentrated CH_2Cl_2 solution of **3** to −17°C, to which had been added a few drops of diethyl ether. The structure for **3** is shown in Fig. 3,

Table 4
$^{31}P\{^1H\}$-NMR data [a] for selected *cis*- and *trans*-dppen complexes of molybdenum(II) and tungsten(II)

Complex	δ (ppm)/J (Hz)
1	54.8 (s, *cis*-dppen)
3	37.8 (s, $J_{W{-}P} = 160.5$ Hz, *cis*-dppen)
4	131.9 {dd, (br-*cis*, 1P, $J_{P{-}P} = 215$ Hz-*trans*)-$\mathit{P}(OMe)_3$}; 73.8 {s, br-*cis*-dppen); 37.5 {dd, (br-*cis*, $J_{P{-}P} = 215$ Hz-*trans*)*cis*-dppen}
5	105.2 {dd, (br-*cis*, $J_{P{-}P} = 210$ Hz-*trans*)-$\mathit{P}(OMe)_3$}; 55.5 {s, br-*cis*-dppen, $J_{W{-}P} = 206$ Hz}; 23.0 {dd, (br-*cis*-, $J_{P{-}P} = 210$ Hz-*trans*)*cis*-dppen}
6	128.5 {dd, ($2J_{P{-}P} = 23$ Hz-*cis*-dppen, $J_{P{-}P} = 203$ Hz-*trans*)$\mathit{P}(OEt)_3$}; 73.9 {s, br-*cis*-dppen, $J_{W{-}P} = 228$ Hz}; 36.2 {dd, ($J_{P{-}P} = 23$ Hz-*cis*-dppen, $J_{P{-}P} = 203$ Hz-*trans*)*cis*-dppen}
7	97.2 {dd, (br-*cis*, $J_{P{-}P} = 185$ Hz-*trans*)-$\mathit{P}(OEt)_3$}; 52.6 {s, br, -*cis*-dppen, $J_{W{-}P} = 180$ Hz}; 20.2 {dd, (br-*cis*, 1P, $J_{P{-}P} = 185$ Hz-*trans*)*cis*-dppen}
13	82.9 {dd, ($2J_{P{-}P} = 27$ Hz-*cis*, $J_{P{-}P} = 231$ Hz-*trans*), $\mathit{P}(OPh)_3$}; 33.9 {t, br, -*cis*-dppen}; 21.5 {dd, ($2J_{P{-}P} = 27$ Hz-*cis*, $J_{P{-}P} = 231$ Hz-*trans*)*cis*-dppen}
14	155.85 {br, s, $\mathit{P}(O^iPr)_3$}; 12.15 (br, s, *trans*-dppen)

[a] Spectra recorded in $CDCl_3$ at 25°C and referenced to 85% H_3PO_4. dd, doublet of doublets; s, singlet; br, broad; t, triplet.

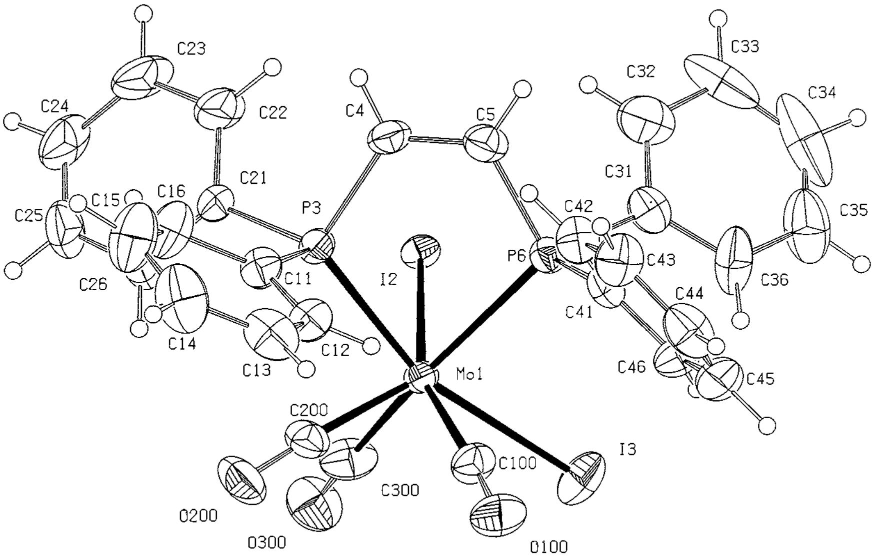

Fig. 1. ORTEP representation of **1**, together with the atom numbering scheme. Ellipsoids shown at 30% probability.

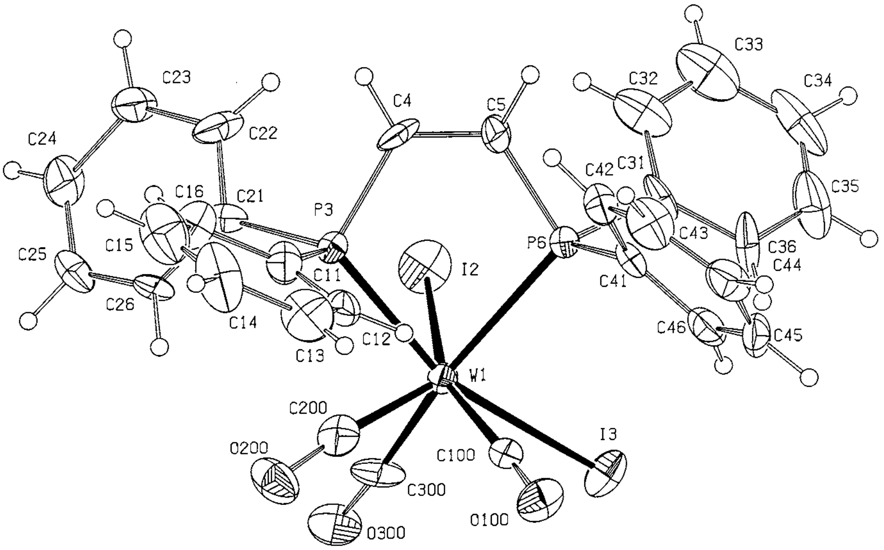

Fig. 2. ORTEP representation of **2**, together with the atom numbering scheme. Ellipsoids shown at 30% probability.

together with the atomic numbering scheme. Although the data for this complex are poor, they are of sufficient quality to show the basic geometry of the complex. In **3** the metal atom is seven-coordinate being bonded to two bidentate *cis*-dppen ligands, named A and B, two carbonyls and an iodine atom. The metal geometry is best considered as a capped octahedron, with C(100) in the capping position, C(200), two phosphorus atoms from different ligands P(3A) and P(3B) in the capped face while P(6A), P(6B) and the iodine atom occupy the uncapped face. The carbonyl in the capped face C(200) is *trans* to the iodine in the uncapped face. The bond lengths to the two phosphorus atoms in the capped face are significantly shorter at 2.513(6), 2.543(7)Å than the bonds to the phosphorus atoms in the uncapped face at 2.605(6), 2.629(7)Å. There have been several structure determinations containing the stoichiometry $[MX(CO)_2(P–P)_2]^+$, (M = Mo, W; X = halogen; L–L = bidentate phosphorus ligand), and the majority of these have the capped trigonal prismatic structure with the halogen in the capping position, four phosphorus atoms in the capped face and two carbonyls in the remaining edge, e.g. for example $[WI(CO)_2(dppe)_2]I$ [34]. It is not clear why **3** has the capped octahedral structure but it could be due to the relative inflexibility of the unsaturated dppen ligand which necessarily forms a closely planar chelate ring.

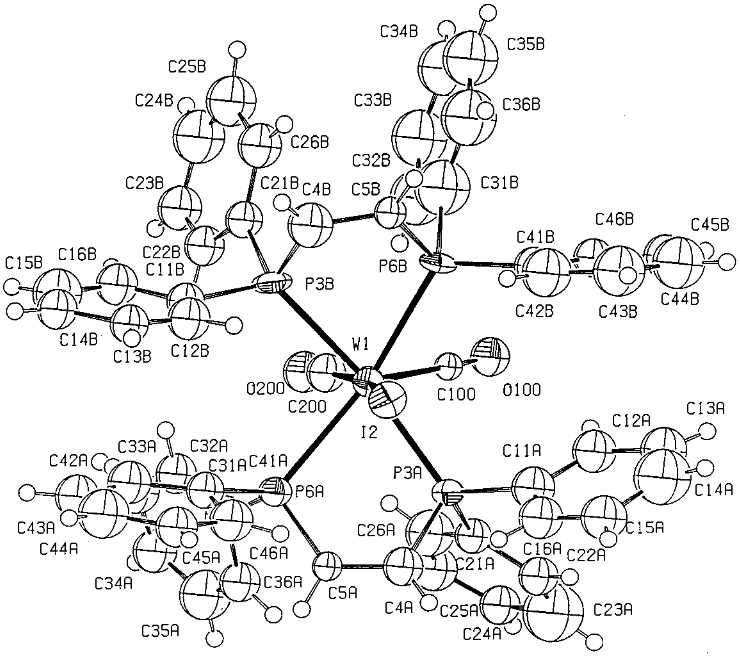

Fig. 3. ORTEP representation of 3, together with the atom numbering scheme. Ellipsoids shown at 30% probability.

2.3. Synthesis and selective crystal structures of $[MI_2(CO)_2\{P(OR)_3\}(cis\text{-}dppen)]$ (4–13)

Treatment of $[MI_2(CO)_3(NCMe)_2]$ with an equimolar amount of *cis*-dppen in CH_2Cl_2 at room temperature gave $[MI_2(CO)_3(cis\text{-dppen})]$, which react in situ with one equivalent of $P(OR)_3$ to eventually give the mixed-ligand seven-coordinate complexes $[MI_2(CO)_2\{P(OR)_3\}(cis\text{-dppen})]$ (M = Mo or W; R = Me, Et, ^{i}Pr, ^{n}Bu or Ph) (**4**–**13**) in good yield. Complexes **4**–**13** have all been fully characterised (see Tables 1–4). The complex $[WI_2(CO)_2\{P(OPh)_3\}(cis\text{-dppen})]\cdot CH_2Cl_2$ (**13**) was confirmed as a CH_2Cl_2 solvate by repeated elemental analysis and ^{1}H-NMR spectroscopy. Complexes **4**–**13** are all considerably more soluble than **1**–**3**, which is almost certainly due to the solubilising properties of the phosphite ligands. Their stability is similar to complexes **1**–**3**.

The IR spectra of **4**–**13** all show, as expected, two carbonyl bands which suggests *cis*-carbonyls. The room temperature ^{31}P-NMR spectra (Table 4) of **4**, **5**, **6**, **7** and **13** all have three resonances for the three different phosphorus atoms which suggests the complexes are not fluxional at room temperature on the NMR timescale. For example, complex **13** has resonances at $\delta = 82.9$ ppm and is a doublet of doublets due to the $P(OPh)_3$ coupling with both the approximately *cis*- and *trans*-phosphorus atoms of the *cis*-dppen ligand. The resonance at $\delta = 33.9$ ppm is an unresolved triplet due to a coupling of the $P(OPh)_3$ and phosphorus on the dppen ligand which are approximately *trans*- to each other (see Fig. 6). The other phosphorus resonance at $\delta = 21.5$ ppm is as expected a doublet of doublets.

Suitable single crystals for X-ray analysis of $[MI_2(CO)_2\{P(OR)_3\}(cis\text{-dppen})]$ (M = Mo, R = Me; M = W, R = Et or Ph) (**4**, **7** and **13**) were grown by cooling (−17°C) CH_2Cl_2:Et_2O (80:20) concentrated solutions of **4**, **7** and **13**, respectively. The structures of **4**, **7** and **13** are shown in Figs. 4–6, together with their atomic numbering schemes. In **4**, **7** and **13**, the metal atom is also seven-coordinate, but this time the complex is neutral with the metal bonded to two iodide

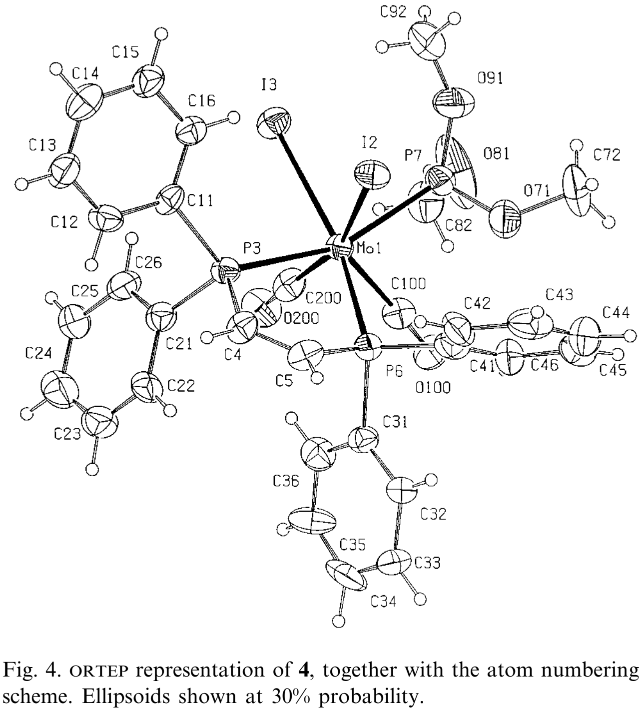

Fig. 4. ORTEP representation of 4, together with the atom numbering scheme. Ellipsoids shown at 30% probability.

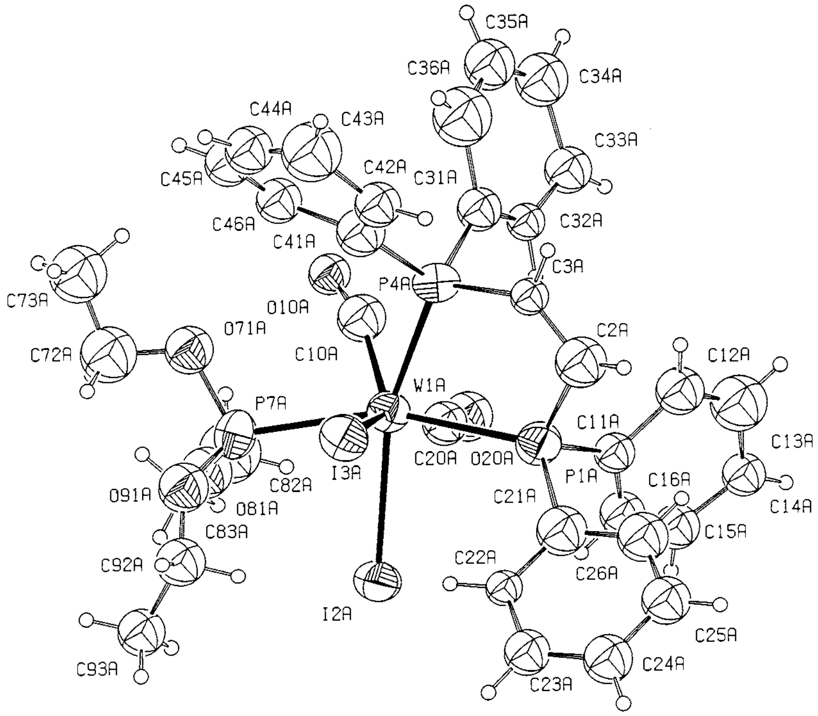

Fig. 5. ORTEP representation of **7**, together with the atom numbering scheme. Ellipsoids shown at 30% probability.

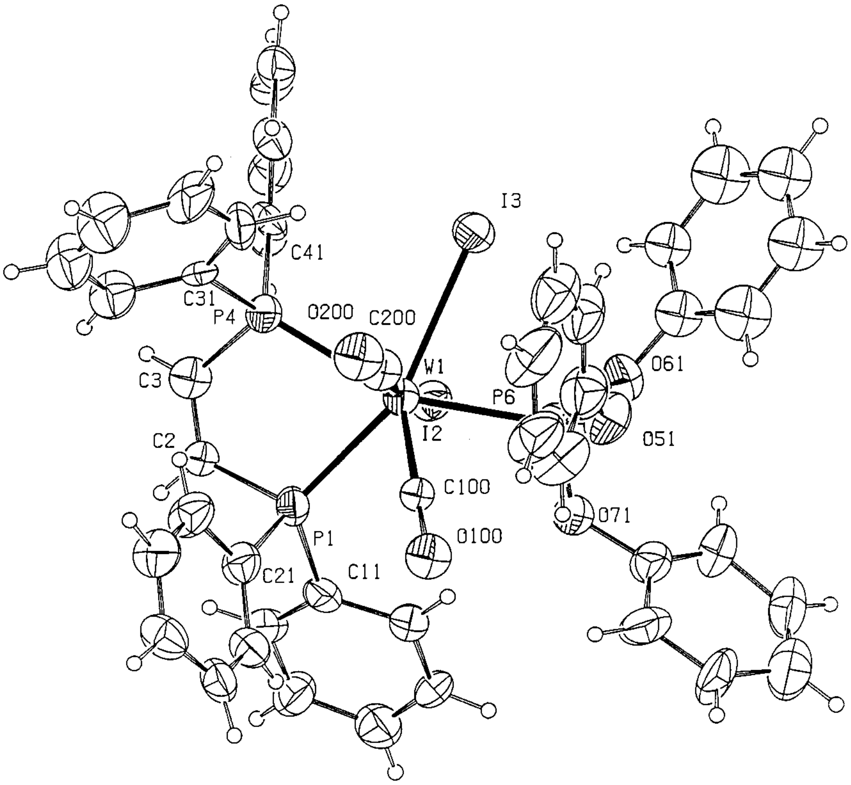

Fig. 6. ORTEP representation of **13**, together with the atom numbering scheme. Ellipsoids shown at 30% probability.

atoms, two carbonyls, a bidentate *cis*-dppen ligand and a monodentate phosphite ligand. In a recent paper [35], we have described nine crystal structures of complexes of the form $[MI_2(CO)_2\{P(OR)_3\}(L–L)]$ (M = Mo, W, R = Me, Et, ^{i}Pr, Ph; L–L = dppm or dppe). The structures of **4**, **7** and **13** are all very similar and, indeed, some are isomorphous (see Section 3) to those with the dppe ligand, with the metal atom in a capped octahedral environment, with a carbonyl in the capping position, one carbonyl, one phosphorus from the phosphite ligand and one from the bidentate ligand in the capped face and the other phosphorus from the bidentate ligand, and two iodide ligands in the uncapped face.

These three structures (**4**, **7** and **13**) show no significant structural changes as a consequence of containing the unsaturated bidentate *cis*-dppen ligand. One feature of these structures, and the nine described previously [35], is that neither the change of metal, nor the identity of the alkyl group R in the phosphite has any systematic difference on the stereochemistry around the metal atom.

*2.4. Synthesis of $[\{MoI_2(CO)_3\{P(O^iPr)_3\}\}_2(\mu\text{-}trans\text{-}dppen)]$ (**14**)*

Reaction of $[MoI_2(CO)_3(NCMe)_2]$ with an equimolar amount of $P(O^iPr)_3$ in CH_2Cl_2 at room temperature gives $[MoI_2(CO)_3(NCMe)\{P(O^iPr)_3\}]$, which reacts in situ with half an equivalent of *trans*-$Ph_2PCH{=}CHPPh_2$ to eventually give the phosphine-bridged bimetallic complex $[\{MoI_2(CO)_3\{P(O^iPr)_3\}\}_2(trans\text{-dppen})]$ (**14**). Complex **14** was characterised in the normal manner (see Tables 1–4), and has similar stability and solubility to complexes **4**–**13**.

The IR spectrum of complex **14**, has three carbonyl bands, which suggests that each metal centre, as expected, has an identical arrangement of ligands. This is confirmed by the ^{31}P-NMR spectrum ($CDCl_3$, 25°C) of **14**, which has two resonances at $\delta = 155.85$ and 12.15 ppm. The low field resonance (155.85) for the equivalent triisopropylphosphite ligands, and a higher field resonance (12.15) for the equivalent *trans*-$Ph_2PCH{=}CHPPh_2$ phosphorus atoms. Several unsuccessful attempts were made to grow suitable single crystals for X-ray analysis of **14**. However, we have recently described the preparation and X-ray crystal structure [36] of the closely related complex $[\{MoI_2(CO)_3\{P(O^iPr)_3\}\}_2(\mu\text{-dppb})]$ $\{dppb = Ph_2P(CH_2)_4PPh_2\}$, which indeed shows that the molybdenum centres are in identical environments to each other. It seems that the most likely structure for the bimetallic complex **14** is the bridged structure shown in Fig. 7.

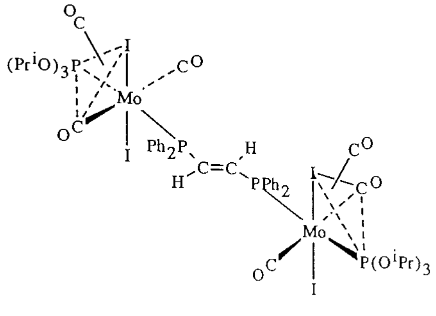

Fig. 7. Proposed structure of $[\{MoI_2(CO)_3\{P(O^iPr)_3\}\}_2(\mu\text{-}trans\text{-dppen})]$ (**14**).

2.5. Conclusions

We have shown that our highly versatile seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) can react with *cis*- and *trans*-dppen to give a wide range of the first examples of *cis*- and *trans*-$Ph_2PCH{=}CHPPh_2$ seven-coordinate complexes, six of which have been structurally characterised. The structures of the seven-coordinate complexes have been compared and show a wide range of types depending on the types of ligand attached to the metal.

The six structures, all of which contain the unsaturated bidentate dppen ligand, are shown in Figs. 1–6, respectively, together with the common numbering schemes. The envelope conformation of the five-membered bidentate ring is found in all structures but there are various degrees of fold. Thus deviations of the two carbon atoms from the M (M = Mo, W), P(3), P(6) plane are in (**1**) 0.40, 0.34, (**2**) 0.33, 0.30, (**3**) 0.58, 0.36; 0.85, 0.80, (**4**) 0.43, 0.50, (**7**) 0.36, 0.33; 0.37, 0.23, (**13**) 0.41, 0.49 Å. This contrasts with the dppe bidentate ligand in which the two carbon atoms are on opposite sides of the M, P, P plane.

3. Experimental

All reactions and work-up procedures described in this paper were carried out under an atmosphere of dry nitrogen using conventional vacuum line and Schlenk tube techniques. The solvents used CH_2Cl_2 and Et_2O were dried and distilled before use. The starting materials used, $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W) were prepared by the published procedure [29]. The phosphines, *cis*- and *trans*-$Ph_2PCH{=}CHPPh_2$ and other chemicals were purchased from commercial sources.

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

3.1. Syntheses

*3.1.1. Syntheses of $[MI_2(CO)_3(cis\text{-dppen})]$ (**1** and **2**)*

To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.969 mmol) in CH_2Cl_2 (50 cm^3) was added *cis*-dppen (0.384 g, 0.969 mmol). The colour changed from dark brown to orange–red. Filtration and removal of

Table 5
Crystal data and structure refinement details for structures **1**–**4**, **7** and **13**

	1	**2**	**3**	**4**	**7**	**13**
Formula	$MoI_2(CO)_3$-(dppen)	$WI_2(CO)_3$-(dppen)	$[WI(CO)_2$-$(dppen)_2]ICH_2Cl_2$	$MoI_2(CO)_2$(dppen)-$(P(OMe)_3)\cdot EtOH$	$WI_2(CO)_2$-(dppen)$(P(OEt)_3)$	$WI_2(CO)_2$-(dppen)$(P(OPh)_3)$
Empirical formula	$C_{29}H_{22}I_2MoO_3P_2$	$C_{29}H_{22}I_2WO_3P_2$	$C_{55}H_{46}Cl_2I_2O_2P_4W$	$C_{33}H_{37}I_2MoO_6P_3$	$C_{34}H_{35}I_2MoO_5P_3$	$C_{46}H_{39}I_2O_5P_3W$
Formula weight (g)	799.19	975.01	1371.35	972.27	1054.18	1202.33
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Spacegroup	*Pbca*	*Pbca*	$P2_1/c$	$C2/c$	$P2_1/a$	$P2_1/c$
Unit cell dimensions						
a (Å)	16.91(2)	16.91(2)	10.608(12)	36.73(4)	10.292(8)	16.270(17)
b (Å)	16.454(18)	16.404(18)	12.891(14)	10.729(12)	18.998(14)	14.411(16)
c (Å)	21.26(2)	21.22(2)	43.16(5)	19.99(2)	21.37(3)	21.42(2)
α (°)	90	90	90	90	69.92(1)	90
β (°)	90	90	96.30(1)	113.04(1)	89.63(1)	106.51(1)
γ (°)	90	90	90	90	75.54(1)	90
Volume (Å^3)	5915(12)	5887(12)	5866(11)	7249(14)	3765(6)	4814(9)
Z	8	8	4	8	4	4
D_{calc} (g cm^{-3})	1.795	2.200	1.553	1.782	1.860	1.659
Absorption coefficient (mm^{-1})	2.028	8.895	3.258	2.239	4.872	3.822
$F(000)$	3096	3608	2664	3664	2016	2320
Crystal size (mm)	0.25 × 0.25 × 0.20	0.20 × 0.17 × 0.15	0.25 × 0.25 × 0.15	0.20 × 0.15 × 0.15	0.25 × 0.20 × 0.20	0.25 × 0.25 × 0.25
θ Range for data collection (°)	2.65–25.92	2.92–26.01	2.24–26.13	2.16–26.02	2.61–25.96	2.33–26.05
Index ranges	$-20 \leq h \leq 20$ $0 \leq k \leq 18$ $25 \leq l \leq 25$	$-11 \leq h \leq 14$ $0 \leq k \leq 19$ $-18 \leq l \leq 20$	$0 \leq h \leq 11$ $-14 \leq k \leq 14$ $-53 \leq l \leq 52$	$0 \leq h \leq 45$ $-9 \leq k \leq 9$ $-24 \leq l \leq 22$	$0 \leq h \leq 12$ $-21 \leq k \leq 23$ $-26 \leq l \leq 26$	$-17 \leq h \leq 15$ $0 \leq k \leq 16$ $-24 \leq l \leq 24$
No. reflections collected	19316	9655	13734	6927	12202	10266
No. unique reflections (R_{int})	5409 (0.0386)	3714 (0.0688)	8291 (0.0356)	4553 (0.0373)	12202	5654 (0.1033)
Data/restraints/parameters	5409/0/335	3714/144/335	8291/0/263	4553/0/396	12202/0/817	5654/36/420
Final R indices $[I>2\sigma(I)]$						
R_1	0.0798	0.1009	0.1255	0.0663	0.0903	0.1050
wR_2	0.2324	0.2857	0.3450	0.2072	0.2113	0.2491
R Indices (all data)						
R_1	0.0940	0.1234	0.1383	0.1020	0.1374	0.2125
wR_2	0.2485	0.3131	0.3508	0.2313	0.2378	0.3032
Extinction coefficient	0.0008(3)	0.00000(13)	0.0026(13)	0.00035(3)	0.00015(11)	0.0000(2)
Largest difference peak and hole (e Å^{-3})	4.606, −2.121	4.384, −2.339	3.264, −2.178	1.414, −0.848	2.284, −1.613	3.666, −1.705

most of the solvent in vacuo after 24 h yielded analytically pure orange–red crystals of $[MoI_2(CO)_3($*cis*-dppen$)]$ (**1**) (0.477 g, 59%). Single crystals of $[MoI_2(CO)_3$(dppen)$]$ (**1**), suitable for X-ray crystallography were obtained from the NMR sample (in $CDCl_3$).

The tungsten analogue $[WI_2(CO)_3($*cis*-dppen$)]$ (**2**) was prepared in an exactly analogous manner to complex **1** above. However, suitable single crystals for X-ray analysis were grown by adding a few drops of Et_2O to a concentrated CH_2Cl_2 solution of $[WI_2(CO)_3($*cis*-dppen$)]$ (**2**), and cooling in the fridge (−17°C) for 1 week. See Table 1 for physical and analytical data.

3.1.2. *[WI(CO)$_2$(cis-dppen)$_2$]I (3)*

To a stirred solution of $[WI_2(CO)_3(NCMe)_2]$ (0.800 g, 1.325 mmol) in CH_2Cl_2 (50 cm^3) was added *cis*-dppen (1.05 g, 2.65 mmol) with continuous stirring under a stream of dry N_2 for 24 h. Filtration and removal of most of the solvent in vacuo yielded a yellow solid. The complex was recrystallised by redissolving in CH_2Cl_2, concentrating the solution and adding a few drops of Et_2O to give, after cooling at −17°C for 1 week, suitable single crystals for X-ray analysis of $[WI(CO)_2($*cis*-dppen$)_2]I$ (**3**) (yield of pure product = 0.94 g, 80%).

3.1.3. *[MI$_2$(CO)$_2${P(OR)$_3$}(cis-dppen)] (M = Mo, W; R = Me, Et, ^{i}Pr, ^{n}Bu and Ph)*

A typical example: to a solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.969 mmol) in CH_2Cl_2 (50 cm^3) was added *cis*-dppen (0.384 g, 0.969 mmol) with stirring under a stream of dry N_2. An immediate colour

Table 6
Molecular dimensions (distances (Å) and angles (°)) for structures **1**, **2**, **4**, **7** and **13**

	1 (M = Mo)	**2** (M = W)		**4** (M = Mo)	**7** (M = W)		**13** (M = W)
				a	b		
Bond lengths			*Bond lengths*				
M(1)–C(100)	1.984(10)	2.01(3)	M(1)–C(100)	1.941(13)	1.96(2)	1.952(18)	1.84(2)
M(1)–C(200)	1.966(11)	1.87(3)	M(1)–C(200)	2.004(19)	2.00(2)	2.00(2)	1.89(3)
M(1)–C(300)	2.082(14)	2.00(2)	M(1)–P(7)	2.488(4)	2.510(6)	2.501(6)	2.471(8)
M(1)–P(6)	2.608(3)	2.593(6)	M(1)–P(6)	2.492(4)	2.480(6)	2.475(6)	2.516(6)
M(1)–P(3)	2.509(3)	2.510(5)	M(1)–P(3)	2.599(4)	2.614(5)	2.593(5)	2.603(7)
M(1)–I(2)	2.846(3)	2.848(4)	M(1)–I(2)	2.879(3)	2.868(2)	2.895(3)	2.883(4)
M(1)–I(3)	2.882(2)	2.879(3)	M(1)–I(3)	2.916(3)	2.910(3)	2.905(3)	2.861(4)
Bond angles			*Bond angles*				
C(100)–M(1)–C(200)	72.6(5)	74.0(11)	C(100)–M(1)–C(200)	71.1(5)	71.7(9)	71.4(7)	72.8(11)
C(200)–M(1)–C(300)	72.7(5)	73.8(10)	C(100)–M(1)–P(7)	73.2(5)	75.2(6)	73.9(6)	73.6(6)
C(100)–M(1)–C(300)	109.3(5)	107.4(10)	C(200)–M(1)–P(7)	110.7(4)	108.3(6)	107.5(7)	102.6(9)
C(300)–M(1)–P(6)	158.7(4)	157.7(8)	C(100)–M(1)–P(6)	71.7(4)	71.1(5)	71.5(6)	70.7(3)
C(200)–M(1)–P(6)	128.4(3)	128.3(8)	C(200)–M(1)–P(6)	108.6(4)	108.4(7)	108.7(5)	108.2(8)
C(100)–M(1)–P(6)	83.1(4)	83.7(6)	P(7)–M(1)–P(6)	113.4(1)	117.8(2)	117.2(2)	122.3(2)
C(300)–M(1)–P(3)	113.0(4)	115.2(9)	C(100)–M(1)–P(3)	128.8(5)	128.0(6)	129.4(6)	131.1(6)
C(200)–M(1)–P(3)	72.7(3)	70.9(7)	C(200)–M(1)–P(3)	83.5(4)	82.5(5)	84.1(5)	86.2(9)
C(100)–M(1)–P(3)	112.2(4)	112.3(7)	P(7)–M(1)–P(3)	157.8(1)	156.8(1)	157.0(2)	155.2(2)
P(6)–M(1)–P(3)	75.9(1)	76.0(7)	P(6)–M(1)–P(3)	75.8(1)	75.7(2)	75.9(2)	75.2(2)
C(100)–M(1)–I(2)	159.3(4)	159.5(7)	C(100)–M(1)–I(2)	125.7(4)	125.4(6)	124.7(5)	119.6(7)
C(200)–M(1)–I(2)	127.7(4)	126.2(8)	C(200)–M(1)–I(2)	163.0(3)	162.7(6)	163.7(5)	167.4(8)
C(300)–M(1)–I(2)	77.4(4)	78.4(7)	P(7)–M(1)–I(2)	79.5(1)	81.2(1)	77.9(1)	80.5(2)
P(3)–M(1)–I(2)	81.2(1)	81.2(1)	P(6)–M(1)–I(2)	78.0(1)	78.1(1)	77.6(1)	86.3(2)
P(6)–M(1)–I(2)	85.2(1)	84.9(2)	P(3)–M(1)–I(2)	83.1(1)	83.7(1)	82.9(1)	79.6(2)
C(100)–M(1)–I(3)	75.1(4)	75.7(7)	C(100)–M(1)–I(3)	125.0(3)	126.3(5)	126.3(5)	133.5(3)
C(200)–M(1)–I(3)	124.8(3)	127.4(7)	C(200)–M(1)–I(3)	75.6(4)	74.4(7)	74.9(3)	78.9(8)
C(300)–M(1)–I(3)	77.6(5)	75.8(9)	P(7)–M(1)–I(3)	79.4(1)	77.4(1)	77.9(1)	77.6(2)
P(3)–M(1)–I(3)	162.4(1)	161.6(1)	P(6)–M(1)–I(3)	162.5(1)	161.0(1)	160.9(1)	154.9(2)
P(6)–M(1)–I(3)	89.6(1)	88.9(1)	P(3)–M(1)–I(3)	88.1(1)	86.2(1)	86.1(1)	81.5(3)
I(2)–M(1)–I(3)	87.9(1)	87.1(1)	I(2)–M(1)–I(3)	93.6(1)	94.2(1)	94.3(8)	90.0(1)

change from dark brown to yellowish brown was observed. After stirring for 20 min, $P(OEt)_3$ (0.161 g, 0.969 mmol) was added. Filtration and removal of solvent in vacuo after 1 h yielded a yellow solid, which was recrystallised from CH_2Cl_2:Et_2O (80:20) to afford analytically pure crystals of [$MoI_2(CO)_2\{P(OEt)_3\}$(*cis*-dppen)] (**6**) (yield = 0.686 g, 73%).

The other molybdenum complexes were prepared in an exactly analogous manner. For the W complexes, a similar procedure was followed, but the mixture was stirred for 3 h, after addition of the $P(OR)_3$ ligand, instead of for 1 h as in the Mo complexes. See Table 1 for physical and analytical data for complexes **4**–**13**.

3.1.4. [$\{MoI_2(CO)_3(P(O^iPr)_3)\}_2$(μ-*trans*-dppen)] (**14**)

To a solution of [$MoI_2(CO)_3(NCMe)_2$] (0.500 g, 0.969 mmol) dissolved in CH_2Cl_2 (30 cm^3) at room temperature, under a stream of dry N_2, was added $P(O^iPr)_3$ (0.202 g, 0.969 mmol). The mixture was stirred for 1 min, after which *trans*-dppen (0.192 g, 0.484 mmol) was added and the solution was stirred for a further 3 h. The resulting brown solution was filtered through Celite, the solvent reduced in vacuo to half its volume, and a few drops of Et_2O was added. After cooling the CH_2Cl_2:Et_2O (80:20) mixture to −17°C for 72 h, an analytically pure off-white powder of [$\{MoI_2(CO)_3\{P(O^iPr)_3\}\}_2$(μ-*trans*-dppen)] (**14**) (yield = 0.540 g, 66%) was isolated.

3.1.5. Crystallography — crystal structure determinations

Crystal data for the six compounds are given in Table 5 together with refinement details. Molecular dimensions are given in Table 6. For all compounds, data were collected with Mo–K_α radiation using the MarResearch Image Plate System. The crystals were positioned at 70 mm from the Image Plate. A total of 95 frames were positioned at 2° intervals with a default counting time of 2 min. However, frames for compounds **3** and **4** were measured for 5 and 15 min, respectively. Compounds **1** and **2** were isomorphous. Complex **4** was isomorphous with [$WI_2(CO)_2\{P(OEt)_3\}$(dppe)] [35], but with an ethanol solvent molecule disordered over two overlapping sites, and **7** with $[MoI_2(CO)_2\{P(OEt)_3\}(dppm)]$ [35]. Data analyses were carried out with the XDS program [37]. The structures were solved using direct methods with the SHELXL program [38].

In the majority of structures (**1**, **2**, **4**, **7** and **13**) all non-hydrogen atoms were refined with anisotropic thermal parameters. In **3**, only the W, I and P atoms were refined anisotropically and two of the phenyl rings were constrained at calculated geometry. In **13**, the phenyl rings were refined anisotropically, but with thermal parameters constrained to be compatible with those of atoms in the same rings. All structures were corrected for absorption using empirical methods [39]. The structures were then refined on F^2 using SHELXL [40]. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

4. Supplementary material

For complexes **1**–**4**, **7** and **13**, tables of remaining molecular dimensions not included in the paper, anisotropic and isotropic thermal parameters, and hydrogen coordinates are available. The data have been lodged with the Cambridge Crystallographic Database, CCDC nos. 135506 to 135511 inclusive. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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