Reaction of the Unsaturated Triosmium Clusters $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ and $[Os_3H(CO)_8\{Ph_2PC(=CH_2)P(Ph)C_6H_4\}]$ with Phosphines and Phosphites; Crystal Structures of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPr^i_3)]$, $[Os_3(CO)_8(Ph_2PCH_2PPh_2)\{P(OMe)_3\}_2]$, and $[Os_3(CO)_8(Ph_2PCH_2PPh_2)(PPh_3)_2]$†

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Treatment of the unsaturated clusters $[Os_3(\mu\text{-}H)(CO)_8\{\mu\text{-}Ph_2PCH_2P(Ph)C_6H_4\}]$ **1a** and $[Os_3(\mu\text{-}H)(CO)_8\{\mu\text{-}Ph_2PC(=CH_2)P(Ph)C_6H_4\}]$ **1b** with two-electron donor ligands gave the saturated clusters $[Os_3(\mu\text{-}H)(CO)_8\{\mu\text{-}Ph_2PCH_2P(Ph)C_6H_4\}L]$ [L = CO **2a** or PR_3 or $P(OR)_3$ **3** (R = Me, Et, Pr^i, Bu or Ph)], $[Os_3(\mu\text{-}H)(CO)_8\{\mu\text{-}Ph_2PC(=CH_2)P(Ph)C_6H_4\}L]$ (L = CO **2b**) and $[Os_3(CO)_8(dppm)L_2]$ **4** [dppm = $Ph_2PCH_2PPh_2$; L = CO, PR_3 or $P(OR)_3$]. Two different isomers of complex **4** are observed depending on the ligand L. All the products have been characterised by IR and NMR spectroscopy. The structures of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPr^i_3)]$ **3a**, $[Os_3(CO)_8(dppm)\{P(OMe)_3\}_2]$ **4a** and $[Os_3(CO)_8(dppm)(PPh_3)_2]$ **4c** have also been established by X-ray crystallography.

Bridging phosphorus ligands have been used a great deal in metal cluster chemistry because of their ability to maintain the metal cluster framework intact during chemical reactions and to act as templates for the synthesis of metal–metal bonds by bridge-assisted reactions. We[1–3] and others[4–6] have shown that these bridging ligands can quite readily undergo C–H and C–P bond-breaking, and M–H, M–C bond-forming, reactions. However, it has also been demonstrated that C–H bond-cleavage reactions can be readily reversed, and that such reactions can provide convenient routes to substituted metal clusters.[7–9]

We have previously reported that the unsaturated cyclometallated cluster $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **1a** undergoes reaction with CO to form the cluster $[Os_3(CO)_{10}(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$),[1] with H_2 to form $[Os_3H_2(CO)_8(dppm)]$,[8] and with diphenylacetylene to form $[Os_3(CO)_7(dppm)(PhC{\equiv}CPh)]$.[10] In this paper we provide full details of the reaction of the triosmium cluster **1a** with CO, and report on the extension of these studies to the reactions of **1a** and $[Os_3H(CO)_8\{Ph_2PC(=CH_2)P(Ph)C_6H_4\}]$ **1b** with phosphines and phosphites. These studies show how two two-electron donor ligands can be added to **1** under very mild reaction conditions.

Results and Discussion

The thermolysis of $[Os_3(CO)_{10}(dppm)]$ in refluxing toluene leads to the formation of the unsaturated cyclometallated cluster $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **1a**.[1] Under the same conditions, the cluster $[Os_3(CO)_{10}(dppen)]$ [dppen = $Ph_2PC(=CH_2)PPh_2$] gives $[Os_3H(CO)_8\{Ph_2PC(=CH_2)P(Ph)C_6H_4\}]$ **1b** which has been characterised as having an analogous structure to **1a** by IR, ^1H and ^{31}P NMR, mass spectroscopy and microanalysis. Both complexes **1a** and **1b** react readily with two-electron donor ligands to give both mono- and bis-addition products. Thus, bubbling CO through a toluene solution of **1a** at room temperature results in complete conversion into the saturated triosmium cluster $[Os_3H(CO)_9\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **2a** after 2 h. This reaction can be reversed by refluxing the toluene solution of **2a** under nitrogen for 4 h. If complex **2a** is allowed to stand under an atmosphere of carbon monoxide at room temperature for 2 d, it is completely converted into $[Os_3(CO)_{10}(dppm)]$. Similar reactions occur with complex **1b**, to give $[Os_3H(CO)_9\{Ph_2PC(=CH_2)P(Ph)C_6H_4\}]$ **2b**, and eventually $[Os_3(CO)_{10}(dppen)]$. The saturated, orthometallated complexes **2a** and **2b** have been characterised spectroscopically and by comparison with $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPr^i_3)]$ **3a** (see below). The spectroscopic data are presented in Tables 1 and 2. Thus, the complexes **2a** and **2b** contain a bridging hydride group and a terminally bound orthometallated phenyl ring. That these complexes undergo further addition of CO at room temperature to form $[Os_3(CO)_{10}(dppm)]$ and $[Os_3(CO)_{10}(dppen)]$, respectively, shows that the transfer of the hydride from the osmium to the orthometallated phenyl ring is facile. This type of behaviour has been observed previously, for example in $[Os_3H_2(CO)_9(HNC_6H_4)]$[11] and $[Os_3H_2(CO)_9\{P(Ph)C_6H_4\}]$.[7]

In order to investigate these addition reactions further, we have studied the reactions of complexes **1a** and **1b** with phosphorus-donor ligands. Typically, a green solution of **1a** was stirred with an excess of ligand at room temperature until the solution became yellow. Reaction times varied from less than 1 min [L = $P(OMe)_3$] to several hours (L = PPh_3). The products usually consisted of mixtures of the monoadduct $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}L]$ **3** and the diadduct $[Os_3(CO)_8(dppm)L_2]$ **4**. In most cases it was not possible to effect a complete separation of these two products by TLC, however they could be readily characterised by IR and ^{31}P and ^1H NMR spectroscopy (Tables 1 and 2). With the tri-isopropylphosphine ligand only the monoadduct **3** was formed. There are numerous structures possible for **3**. However, if it is assumed that the phosphorus ligand is co-ordinated at an equatorial site on one of the unsaturated osmium atoms, and that the hydride ligand remains bridging, then only four need be considered (Fig. 1). The ^1H NMR chemical shift of the hydride ligand in **3** is at high field (ranging from δ −15.9 to −16.9), in agreement with the assumption that the hydride occupies a bridging site. Terminal hydride ligands tend to have ^1H NMR chemical shifts at lower field (for example, at

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Infrared data ν(CO)/cm^{-1} (CH_2Cl_2 solution)

Complex		
1a	$[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$	2066s, 2020s, 1991vs, 1928m
1b	$[Os_3H(CO)_8\{Ph_2PC(CH_2)P(Ph)C_6H_4\}]$	2060s, 2018s, 1990vs, 1930m
2a	$[Os_3H(CO)_9\{Ph_2PCH_2P(Ph)C_6H_4\}]$	2079s, 2047s, 2018vs, 2006(sh), 1976s, 1955(sh), 1935(sh)
2b	$[Os_3H(CO)_9\{Ph_2PC(CH_2)P(Ph)C_6H_4\}]$	2080s, 2040s, 1998vs, 1970s, 1945m
3a	$[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPr^i_3)]$	2057vs, 2018vs, 1987vs, 1965w, 1955w, 1931m
3b	$[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}\{P(OMe)_3\}]$	2026vs, 2020vs, 1997vs, 1979vs, 1965m, 1940m, 1925(sh)
4a	$[Os_3(CO)_8(dppm)\{P(OMe)_3\}_2]$	2043w, 1985s, 1960vs, 1920m
4b	$[Os_3(CO)_8(dppm)\{P(OMe)_3\}_2]$	2052m, 1989s, 1960vs, 1918vs, 1895(sh)
4c	$[Os_3(CO)_8(dppm)(PPh_3)_2]$	2040(sh), 1985s, 1960vs, 1925s, 1880w
4d	$[Os_3(CO)_8(dppm)(PBu_3)_2]$	2035w, 1970s, 1950vs, 1900m, 1875w

Table 2 The NMR data for compounds **1**, **2**, $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}L]$ **3** and $[Os_3(CO)_8(dppm)L_2]$ **4**

Complex	L	^{31}P-$\{^1H\}$[a]	^1H[b]
1a		-18.0 [d, $J(P_AP_B)$ 69.6], -20.2(d)	-13.4 [dd, $J(P_AH)$ 28.9, $J(P_BH)$ 12.1]
1b		8.6 [d, $J(P_AP_B)$ 132], -1.2(d)	-13.3 [dd, $J(P_AH)$ 30.0, $J(P_BH)$ 10.0]
2a		-13.5 [d, $J(P_AP_B)$ 70.9], -22.4(d)	-16.5 [dd, $J(P_AH)$ 9.3, $J(P_BH)$ 1.1]
2b		1.1 [d, $J(P_AP_B)$ 115], -11.5(d)	-16.6 [d, $J(P_AH)$ 10.0]
3a	PPr^i_3	13.4 [dd, $J(P_XP_A)$ 7.5, $J(P_XP_B)$ 23.2], -13.3 [dd, $J(P_AP_X)$ 7.5, $J(P_AP_B)$ 67.7], -28.6 [dd, $J(P_BP_X)$ 23.2, $J(P_AP_B)$ 67.7]	-16.7(m)
3b	$P(OMe)_3$	104.7 [dd, $J(P_XP_A)$ 11.5, $J(P_XP_B)$ 37.9], -14.3 [dd, $J(P_AP_X)$ 11.5, $J(P_AP_B)$ 70.4], -22.9 [dd, $J(P_BP_X)$ 37.9, $J(P_AP_B)$ 70.4]	-16.9 [t, $J(PH)$ 11.2]
3c	PPh_3	-4.7 [dd, $J(P_XP_A)$ 8.9, $J(P_XP_B)$ 21.9], -13.2 [dd, $J(P_AP_X)$ 8.9, $J(P_AP_B)$ 71.0], -23.0 [dd, $J(P_BP_X)$ 21.9, $J(P_AP_B)$ 71.0]	-15.9 [t, $J(PH)$ 9.7]
3d	PBu_3	-26.8 [d, $J(P_XP_A)$ 21.7], -13.6 [dd, $J(P_XP_A)$ 21.7, $J(P_AP_B)$ 71.6], -22.7 [d, $J(P_BP_A)$ 71.6]	
3e	PEt_3	-21.1 [d, $J(P_XP_B)$ 21.8], -13.9 [d, $J(P_AP_B)$ 69.5], -22.7 [dd, $J(P_BP_X)$ 21.8, $J(P_AP_B)$ 69.5]	
3f	$P(OPr^i)_3$	97.6 [dd, $J(P_XP_A)$ 10.5, $J(P_XP_B)$ 37.5], -14.7 [dd, $J(P_AP_X)$ 10.5, $J(P_AP_B)$ 69.7], -22.9 [dd, $J(P_BP_X)$ 37.5, $J(P_BP_A)$ 69.7]	-16.8 [t, $J(PH)$ 10.7]
3g	$P(OBu)_3$	99.2 [dd, $J(P_XP_A)$ 8.0, $J(P_XP_B)$ 36.1], -14.5 [dd, $J(P_AP_X)$ 8.0, $J(P_AP_B)$ 71.4], -22.8 [dd, $J(P_BP_X)$ 36.1, $J(P_AP_B)$ 71.4]	
3h	$P(OPh)_3$	87.5 [dd, $J(P_XP_A)$ 11.7, $J(P_XP_B)$ 39.5], -13.8 [dd, $J(P_AP_X)$ 11.7, $J(P_AP_B)$ 69.4], -21.5 [dd, $J(P_BP_X)$ 39.5, $J(P_BP_A)$ 69.4]	-16.8 [t, $J(PH)$ 11.4]
4a	$P(OMe)_3$	105.7(s), -29.0(s)	
4b	$P(OMe)_3$	108.6 [d, $J(P_XP_B)$ 3.7], 98.9 [d, $J(P_{X'}P_B)$ 5.5], -22.4 [d, $J(P_AP_B)$ 51.4], -27.4 [d of t, $J(P_BP_X)$ 3.7, $J(P_BP_{X'})$ 5.5, $J(P_BP_A)$ 51.4]	
4c	PPh_3	0.4 [d, $J(P_XP_A)$ 7.8], -9.4 (s), -26.9 [dd, $J(P_AP_X)$ 7.8, $J(P_AP_B)$ 53.1], -28.7 [d, $J(P_BP_A)$ 53.1]	
4d	PBu_3	48.7(s), -30.6(s)	
4e	PEt_3	52.5(s), -32.1(s)	
4f	$P(OPr^i)_3$	95.6(s), -30.5(s)	
4g	$P(OBu)_3$	98.4(s), -29.4(s)	
4h	$P(OPh)_3$	75.9 [t, $J(P_XP_A)$ 8.8], -29.0 [t, $J(P_AP_X)$ 8.8]	

[a] Chemical shifts relative to 85% H_3PO_4; coupling constants in Hz. P_X represents phosphine or phosphite adduct, P_A and P_B are the P atoms of dppm (arbitrary assignment). [b] Chemical shifts relative to $SiMe_4$; coupling constants in Hz.

δ −10.1 for $[Os_3H_2(CO)_{10}\{Ph_2PC_6H_4(CH{=}CH_2)\}]$).[12] A comparison of the IR and ^{31}P NMR data for **3** (see Tables 1 and 2) indicates that all these monoadducts adopt the same structure. The ^{31}P NMR spectra essentially consist of three doublets of doublets, with a large coupling constant between the P atoms of the metallated dppm ligand (71.6–67.7 Hz), and smaller coupling constants between these P atoms and the P atom of the added ligand [7.5–11.5 (in some cases this coupling was not resolved well enough to be determined) and 21.7–39.5 Hz (the larger couplings arising for the phosphite ligands, as expected[13])]. The spectroscopic data do not allow a full structural characterisation to be made, although steric factors would suggest that structures **B** and **D** should not be favoured due to the strain forced onto the orthometallated dppm ligand.

A full structural characterisation of the PPr^i_3 derivative **3a** was carried out by X-ray diffraction. This showed that **3a** adopts the structure **C** (L = PPr^i_3) in Fig. 1. The molecular structure is shown in Fig. 2 and selected bond lengths and angles are given in Table 3. Complex **3a** consists of an approximate isosceles triangle of osmium atoms with one long

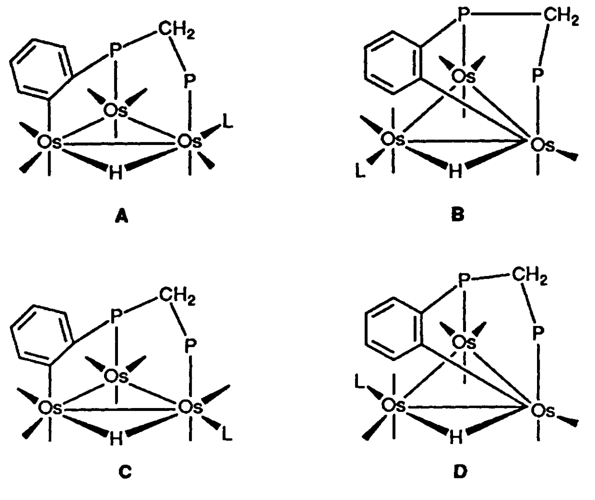


Fig. 1 Possible structures for $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}L]$ **3**

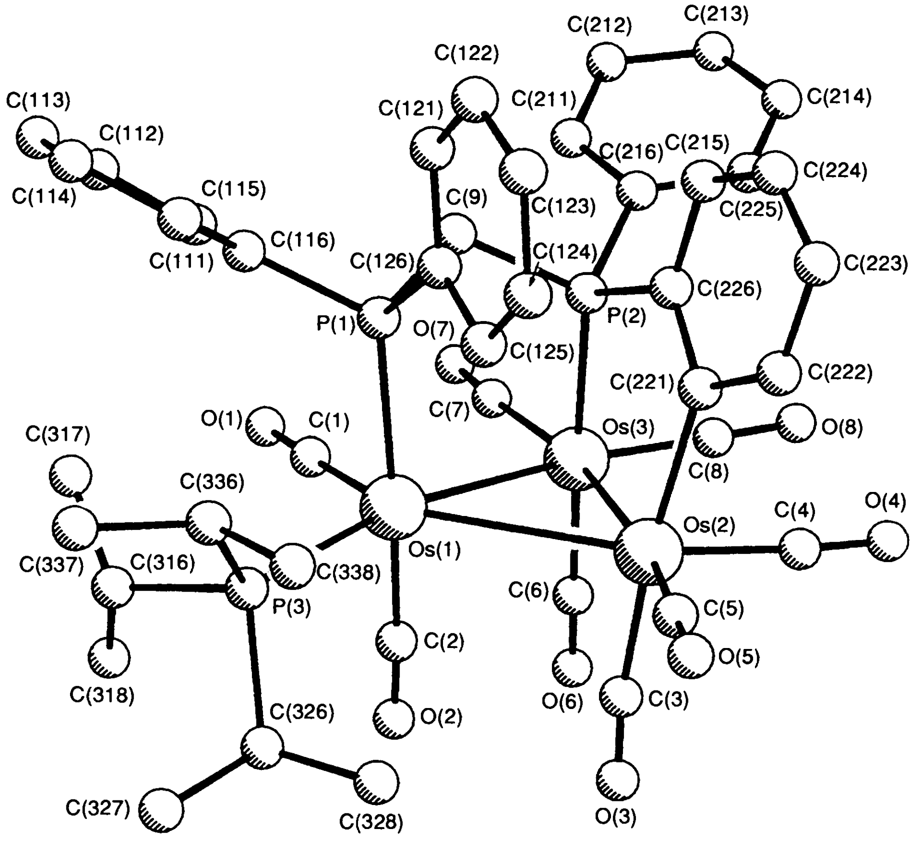


Fig. 2 The molecular structure of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPr^i_3)]$ **3a** with H atoms omitted

Table 3 Selected bond lengths (Å) and angles (°) for $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPr^i_3)]$ **3a**

Os(1)–Os(2)	3.137(2)	Os(2)–C(5)	1.87(4)
Os(1)–Os(3)	2.957(3)	Os(2)–C(221)	2.15(3)
Os(1)–P(1)	2.442(7)	Os(3)–P(2)	2.334(8)
Os(1)–P(3)	2.411(8)	Os(3)–C(6)	1.95(3)
Os(1)–C(1)	1.82(4)	Os(3)–C(7)	1.96(4)
Os(1)–C(2)	1.92(3)	Os(3)–C(8)	1.87(4)
Os(2)–Os(3)	2.848(2)	P(1)–C(9)	1.84(3)
Os(2)–C(3)	1.94(3)	P(2)–C(9)	1.79(3)
Os(2)–C(4)	1.86(4)		
Os(2)–Os(1)–Os(3)	55.64(6)	Os(3)–Os(2)–C(4)	94(1)
Os(2)–Os(1)–P(1)	97.9(2)	Os(3)–Os(2)–C(221)	90.4(7)
Os(2)–Os(1)–P(3)	118.9(2)	Os(1)–Os(3)–Os(2)	65.39(4)
Os(2)–Os(1)–C(2)	87.2(8)	Os(1)–Os(3)–P(2)	85.3(2)
Os(3)–Os(1)–C(1)	86(1)	Os(1)–Os(3)–C(6)	94(1)
Os(3)–Os(1)–C(2)	82.8(9)	Os(1)–Os(3)–C(7)	98(1)
Os(1)–Os(2)–Os(3)	58.97(5)	Os(2)–Os(3)–P(2)	85.6(2)
Os(1)–Os(2)–C(3)	85.8(8)	Os(2)–Os(3)–C(6)	90.8(8)
Os(1)–Os(2)–C(4)	152(1)	Os(2)–Os(3)–C(8)	96(1)
Os(1)–Os(2)–C(5)	112(1)	P(1)–C(9)–P(2)	110(2)
Os(3)–Os(2)–C(3)	90.1(8)		

[Os(1)–Os(2) 3.137(2) Å] and two shorter bonds. The PPr^i_3 ligand is co-ordinated to Os(1) in the equatorial plane, and the result of this addition to the starting cluster **1a** is that the bridging orthometallated phenyl group now adopts a terminal axial co-ordination site, on Os(2). The bridging hydride ligand was not located directly, but from the lengthening of the Os(1)–Os(2) bond, and from the carbonyl ligand distribution [in particular, Os(1)–Os(2)–C(5) 112(1)°], it is considered to bridge the Os(1)–Os(2) edge. The phosphorus atoms of the orthometallated dppm ligand occupy axial co-ordination sites, as required by the co-ordination of one of the phenyl groups of this ligand to Os(2). It is noteworthy that the phosphorus atom P(1) bonded to Os(1) has a significantly longer bond [2.442(7) Å] than the P(2)–Os(3) bond distance [2.334(8) Å]. This is presumably a consequence of the extra electron density on Os(1) due to the presence of the PPr^i_3 ligand, which also shows a relatively long Os(1)–P(3) bond length [2.411(8) Å].

The addition of two phosphorus-donor ligands to the unsaturated clusters **1** leads to reversal of the cyclometallation and gives the tetra(phosphorus donor)-substituted clusters **4**. Again assuming that the phosphorus donors occupy equatorial co-ordination sites, there are four possible structures (Fig. 3). Structure **H** is considered to be most unlikely due to the electron-density imbalance created by having no phosphorus donor co-ordinated to Os(2). Structure **F** may be readily distinguished from **E** and **G** by ^{31}P NMR spectroscopy due to the equivalence of the two monodentate phosphorus-donor ligands, and the equivalence of the two P atoms of the bidentate phosphine ligand. The ^{31}P NMR spectra of the diadducts **4** (Table 2) show that, except for L = PPh_3 (**4c**) and for the minor product obtained when L = $P(OMe)_3$ (**4b**) (see below), the two added ligands, L, are equivalent as are the two phosphorus atoms of the dppm ligand. This indicates that these diadducts have structure **F**. Phosphorus–phosphorus coupling between the ligands L and the dppm ligand was only resolved for L = $P(OPh)_3$; the other spectra showed only slight broadening of the resonances ($J_{PP} < 5$ Hz) and may be regarded as singlets. To confirm the structure of these symmetrical diadducts, a crystal structure determination was carried out on the bis(trimethyl phosphite) derivative **4a**. The molecular structure is shown in Fig. 4 and selected bond lengths and angles are given in Table 4. All the phosphorus atoms are co-ordinated in equatorial sites, with the two phosphite ligands bonded to the same osmium atom, Os(2). This confirms that the diadducts (**4a** and **4d**–**h**) have structure **F** (Fig. 3). The structure of the dppen analogue of **4a**, namely $[Os_3(CO)_8(dppen)\{P(OMe)_3\}_2]$, has also been determined and is essentially identical to that of **4a**.[14]

A minor product of the reaction of the cyclometallated complex **1a** with $P(OMe)_3$ was also isolated. The ^{31}P NMR spectrum of this product **4b** (see Table 2) shows that two phosphite ligands have been added to **1a**, and that these phosphite ligands are not equivalent. Complex **4b** is thus assumed to be a structural isomer of **4a**, and to have structure **E** or **G** (Fig. 3); **E** is preferred since this is the structure adopted by $[Os_3(CO)_8(dppm)(PPh_3)_2]$ **4c** (see below).

The diadduct formed by the reaction of complex **1a** with PPh_3, complex **4c**, has inequivalent PPh_3 ligands, as shown by ^{31}P NMR spectroscopy (Table 2). Only one of the PPh_3 ligands shows coupling to one of the phosphorus atoms of the dppm ligand. The resonance for the other PPh_3 ligands appears as a singlet, and is thus suggested to be co-ordinated to Os(2) as in structure **E** or **G** in Fig. 3, since the diphosphine adducts having structure **F** show no coupling between the phosphine ligands and the dppm ligand. In order to confirm the structure of the bis(triphenylphosphine) complex **4c** a crystal structure determination was carried out. The molecular structure is shown in Fig. 5 and selected bond lengths and angles are given in Table 5. The molecule consists of a triangle of osmium atoms with all the four phosphorus-donor atoms in the equatorial plane. The two triphenylphosphine groups are co-ordinated to different osmium atoms, in a mutually *trans* configuration on Os(1) and Os(2), presumably to minimise steric interactions. Thus, complex **4c** adopts the structure **E** shown in Fig. 3.

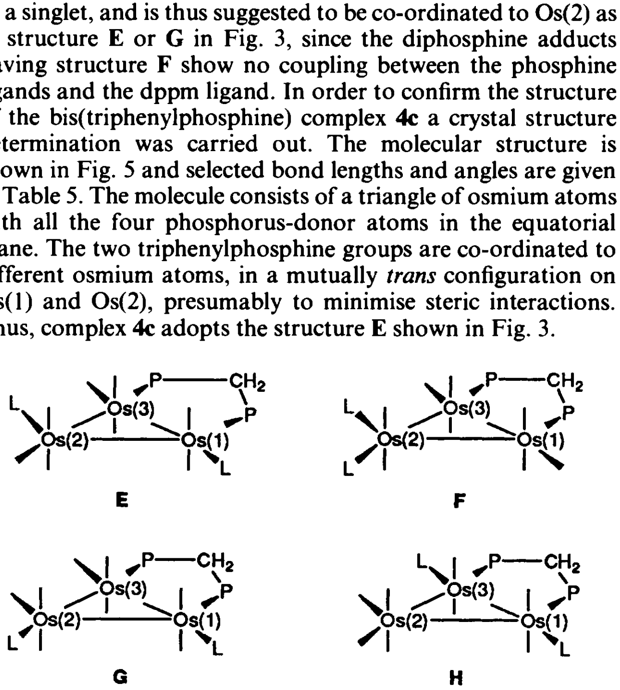


Fig. 3 Possible structures for $[Os_3(CO)_8(dppm)L_2]$ **4**

A number of studies were carried out in order to investigate these reactions further. The minor isomer $[Os_3(CO)_8(dppm)\{P(OMe)_3\}_2]$ **4b** was heated to 50 °C for 12 h. No evidence for the formation of **4a** was obtained. It is thus unlikely that the symmetrical diadducts are formed by rearrangement of any initially formed unsymmetrical diadducts. The reactions of $P(OMe)_3$ and PPh_3 with $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **1a** were followed by ^{31}P NMR spectroscopy. In both cases it was observed that the first products formed were the monoadducts **3b** and **3c**. As the reaction proceeded, peaks due to the diadducts **4a** and **4b** (minor amount) for the reaction with $P(OMe)_3$, and **4c** for the reaction with PPh_3, appeared and increased. However, the resonances due to the monoadducts did not decrease in intensity but remained constant even though the phosphine or phosphite was present in excess. Also, no reaction occurred when the monoadduct $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}\{P(OPr^i)_3\}]$ **3f** was treated with $P(OPr^i)_3$ at room temperature. These observations suggest that the diadduct is *not* formed by further addition to the monoadduct. This is not surprising in view of the fact that such a

Table 4 Selected bond lengths (Å) and angles (°) for $[Os_3(CO)_8(dppm)\{P(OMe)_3\}_2]$ **4a**

Os(1)–Os(2)	2.883(1)	Os(2)–C(4)	1.93(2)
Os(1)–Os(3)	2.894(1)	Os(2)–C(5)	1.92(2)
Os(1)–P(2)	2.320(4)	Os(3)–P(1)	2.319(4)
Os(1)–C(1)	1.87(2)	Os(3)–C(6)	1.98(2)
Os(1)–C(2)	1.91(2)	Os(3)–C(7)	1.88(2)
Os(1)–C(3)	1.87(2)	Os(3)–C(8)	1.95(2)
Os(2)–Os(3)	2.881(1)	P(1)–C(9)	1.84(2)
Os(2)–P(3)	2.258(4)	P(2)–C(9)	1.81(2)
Os(2)–P(4)	2.236(5)		
Os(2)–Os(1)–Os(3)	59.80(4)	Os(1)–Os(2)–C(4)	90.2(5)
Os(3)–Os(1)–P(2)	92.6(1)	Os(1)–Os(2)–C(5)	91.8(5)
Os(2)–Os(1)–C(1)	104.5(6)	Os(1)–Os(3)–Os(2)	59.93(4)
Os(2)–Os(1)–C(2)	86.1(5)	Os(1)–Os(3)–P(1)	91.5(1)
Os(2)–Os(1)–C(3)	87.7(6)	Os(2)–Os(3)–C(6)	91.9(5)
Os(3)–Os(2)–Os(1)	60.30(4)	Os(2)–Os(3)–C(7)	106.4(6)
Os(3)–Os(2)–P(3)	100.1(1)	Os(2)–Os(3)–C(8)	81.7(5)
Os(1)–Os(2)–P(4)	97.5(1)	P(1)–C(9)–P(2)	114.2(9)
P(3)–Os(2)–P(4)	102.3(2)		

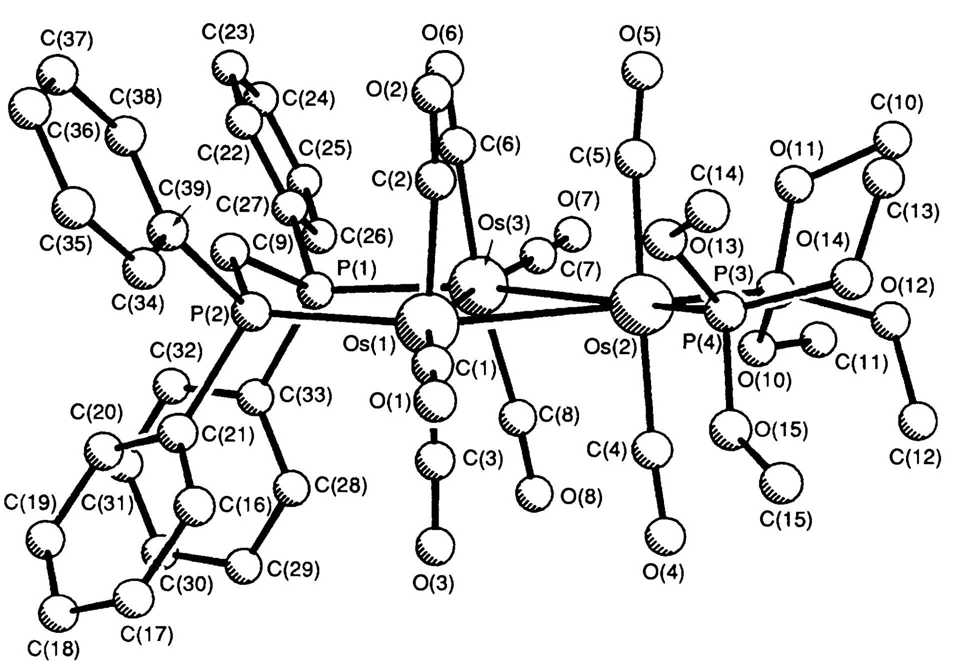


Fig. 4 The molecular structure of $[Os_3(CO)_8(dppm)\{P(OMe)_3\}_2]$ **4a**

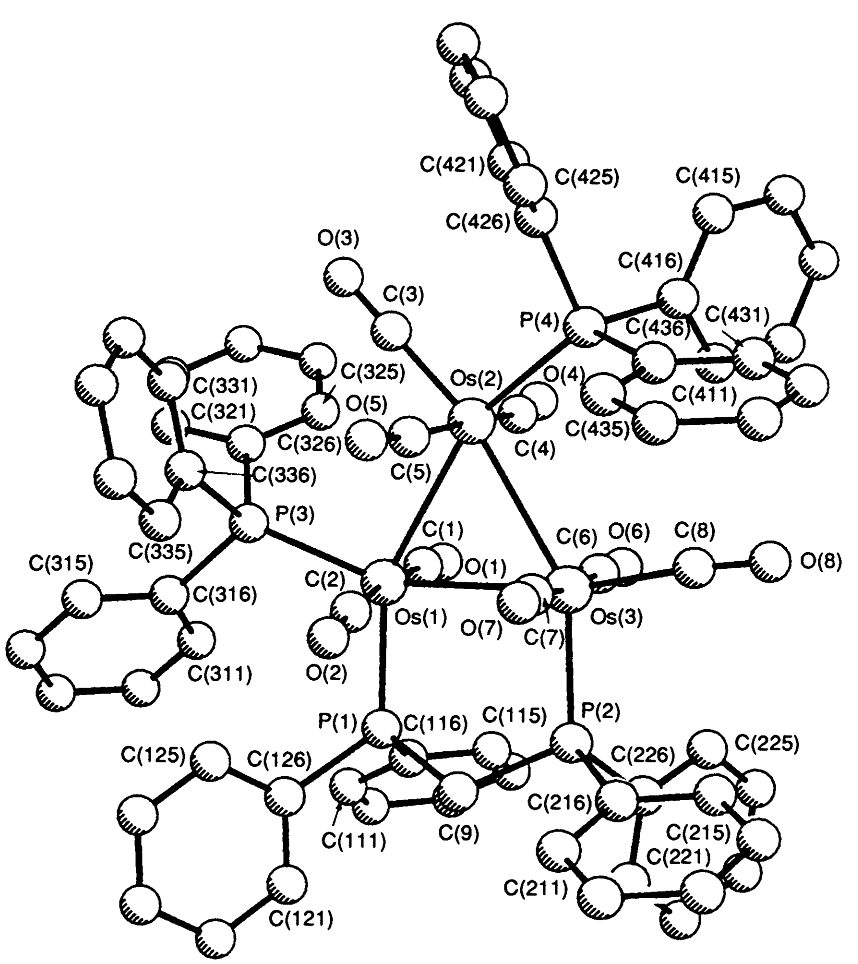
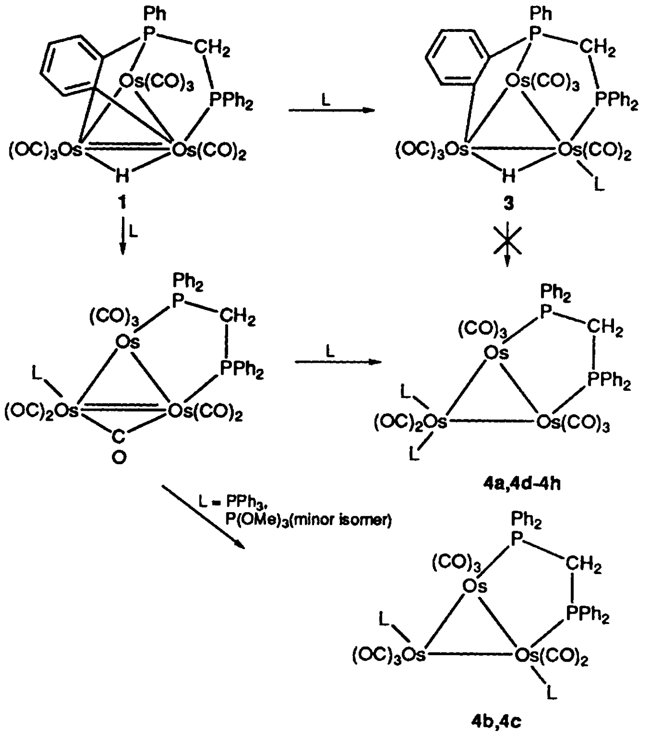


Fig. 5 The molecular structure of $[Os_3(CO)_8(dppm)(PPh_3)_2]$ **4c**

Table 5 Selected bond lengths (Å) and angles (°) for $[Os_3(CO)_8(dppm)(PPh_3)_2]$ **4c**

Os(1)–Os(2)	2.929(2)	Os(2)–C(4)	1.91(2)
Os(1)–Os(3)	2.910(2)	Os(2)–C(5)	1.92(2)
Os(1)–P(1)	2.322(4)	Os(3)–P(2)	2.330(4)
Os(1)–P(3)	2.360(5)	Os(3)–C(6)	1.95(2)
Os(1)–C(1)	1.94(2)	Os(3)–C(7)	1.91(2)
Os(1)–C(2)	1.92(2)	Os(3)–C(8)	1.91(2)
Os(2)–Os(3)	2.922(2)	P(1)–C(9)	1.86(1)
Os(2)–P(4)	2.358(4)	P(2)–C(9)	1.86(1)
Os(2)–C(3)	1.88(2)		
Os(2)–Os(1)–Os(3)	60.06(2)	Os(3)–Os(2)–P(4)	99.4(1)
Os(2)–Os(1)–P(3)	98.3(1)	P(4)–Os(2)–C(3)	94.7(5)
Os(3)–Os(1)–P(1)	92.4(1)	Os(1)–Os(3)–Os(2)	60.30(2)
P(1)–Os(1)–P(3)	109.2(1)	Os(1)–Os(3)–P(2)	93.3(1)
Os(1)–Os(2)–Os(3)	59.65(2)	Os(2)–Os(3)–C(8)	108.2(5)
Os(1)–Os(2)–C(3)	106.4(5)	P(2)–Os(3)–C(8)	98.6(5)
P(1)–C(9)–P(2)	116.0(7)		

reaction would require a phosphine or phosphite ligand moving from one osmium atom to an adjacent Os atom, at room temperature. Although such rearrangements are known, they only occur at high temperature.[7] It seems likely therefore that the diadducts are formed *via* a different route to that of the monoadducts. It is clear from the structure **3a** that the monoadducts are formed by the addition of the donor ligand to **1a** with loss of the unsaturation of the cluster but the retention of the orthometallation of the phenyl ring. We suggest that the diadducts are formed by first addition leading to the



Scheme 1 Proposed routes to the formation of compounds 3 and 4

Table 6 Crystal data, details of data collection and refinement

Complex	3a	4a	4c
Formula	$C_{42}H_{43}O_8Os_3P_3$	$C_{39}H_{40}O_{14}Os_3P_4$	$C_{69}H_{52}O_8Os_3P_4$
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$I2_1/a$	*Pbca*
a/Å	16.414(6)	22.793(1)	26.514(18)
b/Å	12.90(1)	10.273(4)	22.94(2)
c/Å	20.431(8)	38.898(1)	22.346(10)
β/°	94.08(3)	91.58(3)	90
U/Å^3	4315	9105	13 610
Z	4	8	8
D_c/g cm^{-3}	2.06	2.08	1.66
$F(000)$	2528	5392	6544
μ/cm^{-1}	89.79	90.76	60.80
Diffractometer	Rigaku AFC6S	CAD-4	Stoë Stadi-2
Scan mode	ω–2θ	ω–2θ	ω
Total number of reflections	8286	8351	10 545
θ range/°	$6 \leqslant 2\theta \leqslant 50$	$0 \leqslant 2\theta \leqslant 50$	$6 \leqslant 2\theta \leqslant 45$
Number of unique reflections	7989	7744	9455
Number of observed reflections	2885 [$F_o > 4\sigma(F_o)$]	4597 [$F_o > 6\sigma(F_o)$]	6430 [$F_o > 4\sigma(F_o)$]
Absorption correction	DIFABS[17]	Empirical (based on azimuthal scans)	Empirical (based on ω)
Number of refined parameters	295	299	357
Weighting scheme, w	$1/\sigma^2(F)$	$0.1198/[\sigma^2(F) + 0.0518F^2]$	$1/[\sigma^2(F) - 0.000\,316F^2]$
Final R	0.052	0.058	0.057
Final R'	0.060	0.062	0.051

demetallated, but therefore still unsaturated, monoadduct, which is not observed, but immediately reacts with the excess of ligand to give the symmetrical diadduct (Scheme 1).

The observation of a different isomer for the bis(triphenylphosphine) cluster **4c** is probably due to steric reasons, since PPh_3 has the largest cone angle[15] of the phosphines or phosphites producing diadducts in this study. Thus, when the reactive, unsaturated intermediate is formed, the excess of PPh_3, co-ordinates to the unsaturated Os atom having the substituent with the smaller cone angle ($Ph_2PCH_2PPh_2$, cone angle 121°; PPh_3, cone angle 145°),[15] leading to the formation of the unsymmetrical diadduct **4c**.

Experimental

All reactions were carried out under nitrogen unless otherwise stated, using dry, degassed solvents and standard Schlenk-line techniques. Infrared spectra were recorded as dichloromethane solutions in 0.5 mm NaCl cells on a Perkin Elmer 681 spectrometer, NMR spectra on JEOL FX-60 or Bruker WM250 instruments. Chemical shifts are relative to $SiMe_4$ for ^1H and 85% H_3PO_4 for ^{31}P. Microanalyses were carried out in the Department of Chemistry, University of Liverpool. The compounds dppen[16] and $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$[1] were prepared according to published procedures.

$[Os_3H(CO)_8\{Ph_2PC(CH_2)P(Ph)C_6H_4\}]$ **1b**.—The compound $[Os_3(CO)_{10}(dppen)]$ (0.250 g, 0.20 mmol) in toluene (50 cm^3) was heated under reflux for 5 h. The resulting brown solution was evaporated to dryness and the brown residue separated by TLC [SiO_2; eluent CH_2Cl_2–heptane (1 : 1 v/v)] to give **1b** as green crystals after recrystallisation from cold acetone–ethanol (0.105 g, 45%) (Found: C, 34.5; H, 2.1%; M + H$^+$, m/z 1192. $C_{34}H_{22}O_8Os_3P_2$ requires C, 34.3; H, 1.9%; M^+, m/z 1191).

Reactions of Compound **1a**.—*With* CO. Carbon monoxide was bubbled through a stirred solution of compound **1a** (0.18 g, 0.153 mmol) in toluene (20 cm^3) at room temperature until the solution became yellow (2 h). The ^{31}P NMR spectrum showed complete conversion into the saturated cluster **2a**. Attempts to recrystallise **2a** under a carbon monoxide atmosphere led to its conversion into $[Os_3(CO)_{10}(dppm)]$ over a period of 2 d. The toluene solution of **2a** was refluxed under nitrogen for 4 h to give a quantitative conversion into **1a**.

Complex **1b** reacts with CO in a similar manner to **1a** giving **2b** and eventually $[Os_3(CO)_{10}(dppen)]$.

With PPr^i_3. A large excess of triisopropylphosphine (0.0525 g, 0.33 mmol) was added to a chloroform solution (5 cm^3) of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (0.0549 g, 0.046 mmol). The solution was stirred at room temperature for 3 h. The resulting yellow solution was evaporated to dryness, and the residue was separated by TLC. Only one band was obtained which yielded the complex $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPr^i_3)]$ **3a** as yellow crystals after recrystallisation from CH_2Cl_2–heptane (0.0497 g, 79%) (Found: C, 36.9; H, 3.0%; M^+, m/z 1339. $C_{42}H_{43}O_8Os_3P_3$ requires C, 37.7; H, 3.2%; M, m/z 1339).

With PPh_3. An excess of PPh_3 (0.043 g, 0.164 mmol) was added to a toluene solution (35 cm^3) of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **1a** (0.1745 g, 0.148 mmol) and the mixture was stirred at room temperature for 7 h. The yellow solution was evaporated to dryness and the residue subjected to TLC which gave four bands. A yellow product was characterised as $[Os_3(CO)_{10}(dppm)]$ (0.0295 g, 18%) on the basis of ^{31}P NMR and IR spectroscopy. A second yellow band was characterised as $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPh_3)]$ **3c** (0.0815 g), although it could not be obtained in a pure form due to contamination by minor product bands, even after a second TLC separation. An orange band was characterised as $[Os_3(CO)_8(dppm)(PPh_3)_2]$ **4c** (0.069 g, 27%) (Found: C, 49.0; H, 3.4%; M^+, m/z 1703. $C_{69}H_{52}O_8Os_3P_4$ requires C, 48.7; H, 3.2%; M, m/z 1703). A fourth yellow band was isolated in a trace amount and was not characterised.

With PBu_3. To a solution of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (0.096 g, 0.08 mmol) in toluene (10 cm^3) was added an excess of PBu_3 (0.063 g, 0.31 mmol). The solution was stirred at room temperature for 1 h and then evaporated to dryness. On TLC of the residue two products were obtained. An orange band was characterised as $[Os_3(CO)_8(dppm)(PBu_3)_2]$ **4d** (0.059 g, 46%) (Found: C, 42.9; H, 4.9%; M^+, m/z 1584. $C_{57}H_{76}O_8Os_3P_4$ requires C, 43.2; H, 4.8%; M, m/z 1584). A yellow band was characterised as $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PBu_3)]$ **3d** (0.052 g) by IR and NMR spectroscopic data, but an analytically pure sample could not be obtained as it was always contaminated by a small amount of **4d**.

Table 7 Fractional atomic coordinates for $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PPr^i_3)]$ **3a**

Atom	*x*	*y*	*z*
Os(1)	0.200 86(7)	0.151 1(1)	0.050 36(5)
Os(2)	0.294 76(8)	0.337 6(1)	−0.007 88(6)
Os(3)	0.141 45(8)	0.367 6(1)	0.046 47(6)
P(1)	0.260 3(4)	0.162 4(6)	0.163 2(3)
P(2)	0.217 6(5)	0.386 2(6)	0.146 6(4)
P(3)	0.246 2(5)	−0.022 9(6)	0.030 0(4)
O(1)	0.045(2)	0.106(2)	0.112(1)
O(2)	0.105(1)	0.133(2)	−0.081 4(9)
O(3)	0.216(2)	0.285(2)	−0.142(1)
O(4)	0.304(2)	0.566(2)	−0.040(1)
O(5)	0.458(2)	0.268(3)	−0.055(1)
O(6)	0.046(1)	0.348(2)	−0.088(1)
O(7)	−0.016(2)	0.342(3)	0.118(1)
O(8)	0.138(2)	0.602(2)	0.033(1)
C(1)	0.107(2)	0.121(3)	0.089(2)
C(2)	0.139(2)	0.143(2)	−0.033(1)
C(3)	0.239(2)	0.300(2)	−0.091(1)
C(4)	0.305(2)	0.477(3)	−0.029(2)
C(5)	0.395(3)	0.296(3)	−0.038(2)
C(6)	0.084(2)	0.352(3)	−0.040(1)
C(7)	0.042(2)	0.346(3)	0.093(2)
C(8)	0.140(2)	0.511(3)	0.038(2)
C(9)	0.215(2)	0.277(2)	0.201(1)
C(111)	0.154(2)	0.054(2)	0.244(1)
C(112)	0.135(2)	−0.017(3)	0.291(2)
C(113)	0.193(2)	−0.083(3)	0.316(2)
C(114)	0.271(2)	−0.083(3)	0.294(2)
C(115)	0.290(2)	−0.006(2)	0.247(1)
C(116)	0.235(2)	0.063(2)	0.221(1)
C(121)	0.398(2)	0.195(3)	0.250(2)
C(122)	0.480(2)	0.207(3)	0.269(2)
C(123)	0.534(2)	0.205(3)	0.224(2)
C(124)	0.512(2)	0.189(3)	0.159(2)
C(125)	0.428(2)	0.179(3)	0.137(2)
C(126)	0.370(2)	0.184(2)	0.184(1)
C(211)	0.121(2)	0.463(3)	0.244(2)
C(212)	0.089(3)	0.539(3)	0.287(2)
C(213)	0.116(3)	0.639(4)	0.277(2)
C(214)	0.175(3)	0.660(4)	0.236(2)
C(215)	0.208(2)	0.586(3)	0.196(2)
C(216)	0.175(2)	0.486(2)	0.201(1)
C(221)	0.357(2)	0.396(2)	0.080(1)
C(222)	0.441(2)	0.427(3)	0.081(2)
C(223)	0.490(2)	0.462(3)	0.137(2)
C(224)	0.454(3)	0.468(3)	0.191(2)
C(225)	0.372(2)	0.446(3)	0.197(2)
C(226)	0.324(2)	0.414(3)	0.140(2)
C(316)	0.171(2)	−0.120(2)	0.046(1)
C(317)	0.145(2)	−0.124(3)	0.116(2)
C(318)	0.092(2)	−0.119(3)	0.001(2)
C(326)	0.256(2)	−0.051(3)	−0.060(2)
C(327)	0.279(2)	−0.162(3)	−0.076(2)
C(328)	0.312(3)	0.024(4)	−0.091(2)
C(336)	0.338(2)	−0.071(2)	0.077(1)
C(337)	0.345(3)	−0.188(3)	0.093(2)
C(338)	0.415(2)	−0.035(3)	0.046(2)

Table 8 Fractional atomic coordinates for $[Os_3(CO)_8(dppm)\{P(OMe)_3\}_2]$ **4a**

Atom	*x*	*y*	*z*
Os(1)	0.345 35(2)	0.304 60(6)	0.384 46(1)
Os(2)	0.370 40(3)	0.448 70(6)	0.322 97(1)
Os(3)	0.461 29(3)	0.294 82(6)	0.356 04(2)
P(1)	0.495 2(2)	0.160 9(4)	0.400 3(1)
P(2)	0.369 6(2)	0.152 5(4)	0.426 6(1)
P(3)	0.421 4(2)	0.537 3(4)	0.279 8(1)
P(4)	0.279 1(2)	0.518 4(5)	0.311 1(1)
C(1)	0.269 1(8)	0.355 6(18)	0.395 4(5)
C(2)	0.314 5(8)	0.173 0(17)	0.354 3(5)
C(3)	0.376 8(9)	0.444 7(19)	0.409 7(5)
C(4)	0.385 8(7)	0.603 1(18)	0.350 2(4)
C(5)	0.357 3(7)	0.298 1(16)	0.294 6(4)
C(6)	0.432 9(7)	0.134 2(16)	0.333 0(4)
C(7)	0.526 9(9)	0.305 8(19)	0.328 0(5)
C(8)	0.485 8(8)	0.465 0(18)	0.373 1(5)
C(9)	0.435 6(7)	0.061 6(16)	0.417 6(5)
O(1)	0.223 5(7)	0.394 0(20)	0.403 8(4)
O(2)	0.293 3(7)	0.089 8(15)	0.338 7(4)
O(3)	0.396 3(8)	0.530 8(14)	0.427 2(3)
O(4)	0.395 4(7)	0.701 0(13)	0.364 8(4)
O(5)	0.346 2(7)	0.216 5(13)	0.275 0(4)
O(6)	0.420 7(7)	0.046 7(13)	0.320 4(4)
O(7)	0.567 1(6)	0.307 9(16)	0.310 2(5)
O(8)	0.505 2(8)	0.559 3(14)	0.384 6(4)
O(10)	0.483 4(7)	0.586 0(18)	0.292 0(4)
O(11)	0.433 9(9)	0.443 3(13)	0.249 9(4)
O(12)	0.398 7(7)	0.659 3(15)	0.258 1(4)
O(13)	0.231 9(6)	0.408 2(16)	0.315 7(4)
O(14)	0.259 5(7)	0.580 0(16)	0.275 1(5)
O(15)	0.260 8(12)	0.634 2(28)	0.335 5(9)
C(10)	0.436 5(17)	0.476 1(39)	0.212 6(11)
C(11)	0.528 7(12)	0.629 4(29)	0.268 5(7)
C(12)	0.381 8(12)	0.781 0(28)	0.274 6(8)
C(13)	0.265 1(17)	0.507 7(37)	0.245 6(11)
C(14)	0.171 5(16)	0.414 2(33)	0.305 8(9)
C(15)	0.221 8(31)	0.716 8(65)	0.337 0(19)
C(16)	0.335 0(5)	0.307 6(12)	0.481 6(3)
C(17)	0.337 1(5)	0.352 3(12)	0.515 5(3)
C(18)	0.380 5(5)	0.306 6(12)	0.538 5(3)
C(19)	0.421 7(5)	0.216 2(12)	0.527 6(3)
C(20)	0.419 5(5)	0.171 5(12)	0.493 7(3)
C(21)	0.376 2(5)	0.217 2(12)	0.470 7(3)
C(22)	0.535 5(4)	−0.091 7(10)	0.380 6(3)
C(23)	0.579 2(4)	−0.176 7(10)	0.370 1(3)
C(24)	0.636 1(4)	−0.130 8(10)	0.365 5(3)
C(25)	0.649 2(4)	0.000 0(10)	0.371 5(3)
C(26)	0.605 5(4)	0.085 0(10)	0.382 1(3)
C(27)	0.548 6(4)	0.039 1(10)	0.386 6(3)
C(28)	0.525 7(5)	0.350 0(9)	0.450 5(3)
C(29)	0.552 0(5)	0.392 0(9)	0.481 3(3)
C(30)	0.584 2(5)	0.304 8(9)	0.501 8(3)
C(31)	0.590 1(5)	0.175 5(9)	0.491 5(3)
C(32)	0.563 7(5)	0.133 4(9)	0.460 7(3)
C(33)	0.531 5(5)	0.220 6(9)	0.440 2(3)
C(34)	0.261 9(6)	0.052 9(11)	0.447 5(4)
C(35)	0.220 4(6)	−0.043 8(11)	0.453 3(4)
C(36)	0.232 1(6)	−0.172 6(11)	0.444 5(4)
C(37)	0.285 3(6)	−0.204 8(11)	0.429 8(4)
C(38)	0.326 8(6)	−0.108 1(11)	0.423 9(4)
C(39)	0.315 2(6)	0.020 7(11)	0.432 8(4)

With PEt_3. This reaction was carried out in the same way as for PBu_3 above to give $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}(PEt_3)]$ **3e** (30%) and $[Os_3(CO)_8(dppm)(PEt_3)_2]$ **4e** (33%).

With $P(OMe)_3$. An excess of $P(OMe)_3$ (0.0605 g, 0.49 mmol) was added to a toluene solution (20 cm^3) of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (0.043 g, 0.037 mmol) at room temperature. An instantaneous colour change from green to yellow occurred. The solution was evaporated to dryness and TLC gave four bands. A yellow band was characterised as $[Os_3(CO)_{10}(dppm)]$ (0.008 g, 17%). A second yellow band was characterised as $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}$-

Table 9 Fractional atomic coordinates for $[Os_3(CO)_8(dppm)(PPh_3)_2]$ **4c**

Atom	*x*	*y*	*z*
Os(1)	0.233 78(2)	0.080 76(3)	0.176 82(3)
Os(2)	0.185 46(2)	0.175 46(2)	0.110 22(3)
Os(3)	0.140 23(2)	0.059 31(3)	0.112 44(3)
P(1)	0.238 3(2)	−0.015 0(2)	0.210 0(2)
P(2)	0.144 2(2)	−0.041 1(2)	0.127 5(2)
P(3)	0.305 1(2)	0.132 3(2)	0.211 4(2)
P(4)	0.129 2(2)	0.222 0(2)	0.044 0(2)
C(1)	0.197 7(6)	0.099 7(7)	0.249 5(8)
C(2)	0.265 9(6)	0.053 7(6)	0.105 3(8)
C(3)	0.223 8(6)	0.243 0(7)	0.125 4(7)
C(4)	0.144 7(6)	0.190 8(7)	0.178 8(8)
C(5)	0.232 8(6)	0.156 6(6)	0.048 3(7)
C(6)	0.105 8(6)	0.078 4(7)	0.187 0(9)
C(7)	0.175 2(6)	0.048 1(7)	0.038 8(8)
C(8)	0.077 5(7)	0.062 7(7)	0.070 6(8)
O(1)	0.177 8(4)	0.107 8(5)	0.293 5(5)
O(2)	0.285 9(4)	0.033 0(5)	0.064 9(5)
O(3)	0.247 2(4)	0.283 9(5)	0.134 7(5)
O(4)	0.123 5(4)	0.206 8(5)	0.220 3(5)
O(5)	0.262 8(4)	0.149 6(5)	0.010 5(5)
O(6)	0.082 9(5)	0.087 0(6)	0.226 9(6)
O(7)	0.191 9(5)	0.038 0(5)	−0.007 5(6)
O(8)	0.039 8(5)	0.060 5(5)	0.047 1(7)
C(9)	0.206 4(5)	−0.065 6(6)	0.157 1(7)
C(111)	0.243 2(3)	−0.043 5(5)	0.332 2(5)
C(112)	0.222 0(3)	−0.055 1(5)	0.388 0(5)
C(113)	0.169 7(3)	−0.053 8(5)	0.395 2(5)
C(114)	0.138 7(3)	−0.040 9(5)	0.346 6(5)
C(115)	0.160 0(3)	−0.029 3(5)	0.290 8(5)
C(116)	0.212 2(3)	−0.030 6(5)	0.283 6(5)
C(121)	0.299 6(3)	−0.114 0(4)	0.228 7(5)
C(122)	0.344 0(3)	−0.146 2(4)	0.224 5(5)
C(123)	0.387 7(3)	−0.120 3(4)	0.201 9(5)
C(124)	0.386 8(3)	−0.062 2(4)	0.183 5(5)
C(125)	0.342 3(3)	−0.030 0(4)	0.187 7(5)
C(126)	0.298 7(3)	−0.055 9(4)	0.210 3(5)
C(211)	0.176 2(3)	−0.116 3(5)	0.033 7(5)
C(212)	0.167 5(3)	−0.149 4(5)	−0.017 7(5)
C(213)	0.119 2(3)	−0.152 0(5)	−0.042 2(5)
C(214)	0.079 6(3)	−0.121 7(5)	−0.015 5(5)
C(215)	0.088 3(3)	−0.088 6(5)	0.035 8(5)
C(216)	0.136 6(3)	−0.085 9(5)	0.060 4(5)
C(221)	0.105 7(4)	−0.132 9(4)	0.196 7(5)
C(222)	0.070 4(4)	−0.159 9(4)	0.233 7(5)
C(223)	0.026 3(4)	−0.130 6(4)	0.249 6(5)
C(224)	0.017 5(4)	−0.074 3(4)	0.228 5(5)
C(225)	0.052 9(4)	−0.047 3(4)	0.191 5(5)
C(226)	0.096 9(4)	−0.076 6(4)	0.175 6(5)
C(311)	0.330 6(3)	0.066 7(5)	0.310 1(5)
C(312)	0.362 8(3)	0.039 9(5)	0.351 0(5)
C(313)	0.414 7(3)	0.039 7(5)	0.341 0(5)
C(314)	0.434 4(3)	0.066 2(5)	0.290 0(5)
C(315)	0.402 3(3)	0.093 1(5)	0.249 1(5)
C(316)	0.350 3(3)	0.093 3(5)	0.259 1(5)
C(321)	0.337 0(3)	0.218 2(5)	0.294 0(6)
C(322)	0.329 6(3)	0.262 7(5)	0.335 6(6)
C(323)	0.281 3(3)	0.284 9(5)	0.345 4(6)
C(324)	0.240 4(3)	0.262 6(5)	0.313 6(6)
C(325)	0.247 8(3)	0.218 1(5)	0.271 9(6)
C(326)	0.296 1(3)	0.195 9(5)	0.262 2(6)
C(331)	0.352 7(4)	0.221 5(5)	0.145 4(5)
C(332)	0.380 3(4)	0.242 6(5)	0.097 0(5)
C(333)	0.401 5(4)	0.203 8(5)	0.056 0(5)
C(334)	0.395 0(4)	0.143 9(5)	0.063 5(5)
C(335)	0.367 4(4)	0.122.8(5)	0.111 9(5)
C(336)	0.346 3(4)	0.161 6(5)	0.152 9(5)
C(411)	0.041 7(4)	0.206 7(4)	0.113 2(5)
C(412)	−0.006 4(4)	0.221 6(4)	0.133 4(5)
C(413)	−0.028 1(4)	0.274 4(4)	0.116 2(5)
C(414)	−0.001 6(4)	0.312 3(4)	0.078 8(5)
C(415)	0.046 4(4)	0.297 3(4)	0.058 6(5)
C(416)	0.068 1(4)	0.244 5(4)	0.075 8(5)
C(421)	0.159 6(4)	0.337 4(5)	0.054 8(4)
C(422)	0.180 0(4)	0.390 2(5)	0.035 5(4)
C(423)	0.196 3(4)	0.396 2(5)	−0.023 5(4)
C(424)	0.192 2(4)	0.349 5(5)	−0.063 1(4)
C(425)	0.171 9(4)	0.296 7(5)	−0.043 7(4)
C(426)	0.155 6(4)	0.290 6(5)	0.015 2(4)
C(431)	0.058 4(4)	0.178 8(5)	−0.040 1(5)
C(432)	0.045 0(4)	0.149 6(5)	−0.092 4(5)
C(433)	0.082 1(4)	0.124 4(5)	−0.128 2(5)
C(434)	0.132 7(4)	0.128 4(5)	−0.111 7(5)
C(435)	0.146 2(4)	0.157 6(5)	−0.059 4(5)
C(436)	0.109 1(4)	0.182 8(5)	−0.023 6(5)

$\{P(OMe)_3\}]$ **3b** (0.012 g, 24%) (Found: C, 33.9; H, 2.4%; M^+, *m/z* 1303. $C_{36}H_{31}O_{11}Os_3P_3$ requires C, 33.2; H, 2.4%; M^+, *m/z* 1303). An orange band was characterised as $[Os_3(CO)_8(dppm)\{P(OMe)_3\}_2]$ **4a** (0.0105 g, 22%) (Found: C, 33.2; H, 3.2%; M^+, *m/z* 1427. $C_{39}H_{40}O_{14}Os_3P_4$ requires C, 32.8; H, 2.8%; M^+, *m/z* 1427). A third yellow band was characterised by ^{31}P NMR spectroscopy as $[Os_3(CO)_8(dppm)\{P(OMe)_3\}_2]$ **4b** (0.0075 g, 16%) (Found: C, 33.9; H, 3.2%).

With $P(OPr^i)_3$. This reaction was carried out as for that with $P(OMe)_3$ above to give a mixture of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}\{P(OPr^i)_3\}]$ **3f** and $[Os_3(CO)_8(dppm)\{P(OPr^i)_3\}_2]$ **4f** which could not be completely separated by TLC.

With $P(OBu)_3$. This reaction was carried out in the same way as for $P(OMe)_3$ above to give a mixture of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}\{P(OBu)_3\}]$ **3g** and $[Os_3(CO)_8(dppm)\{P(OBu)_3\}_2]$ **4g** which could not be separated by TLC.

With $P(OPh)_3$. This reaction was carried out in the same way as for $P(OMe)_3$ above to give $[Os(CO)_{10}(dppm)]$, and a mixture of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}\{P(OPh)_3\}]$ **3h** and $[Os_3(CO)_8(dppm)\{P(OPh)_3\}_2]$ **4h** which could not be separated by TLC.

Attempted Isomerisation of Compound **4b**.—The complex **4b** (0.050 g, 3.5×10^{-5} mol) in toluene (15 cm^3) was heated to 50 °C for a total of 12 h. Phosphorus-31 NMR spectroscopy showed that no reaction had occurred.

Treatment of Compound **3f** *with* $P(OPr^i)_3$.—An excess of $P(OPr^i)_3$ (0.422 g, 2 mmol) was added to a toluene solution (20 cm^3) of $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}\{P(OPr^i)_3\}]$ **3f** (0.0215 g, 1.5×10^{-5} mol). The solution was stirred for 18 h at room temperature. Phosphorus-31 NMR spectroscopy showed that no reaction had occurred.

X-Ray Crystallography.—Crystals of compounds **3a**, **4a** and **4c** were mounted on glass fibres. Cell dimensions for **3a** and **4c** were obtained by least-squares refinement of 19 reflections using Mo-Kα radiation, λ = 0.710 69 Å, those for **4a** were obtained by least-squares refinement of 25 reflections. Crystal data and experimental details are given in Table 6.

Structure analysis and refinement. Compound **3a**. The Os and P atoms were located by direct methods and the remaining non-hydrogen atoms by Fourier methods. The TEXSAN[18] structure analysis package was used. The Os, P and O atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and allowed to ride on their respective C atoms. The bridging hydride was not located. The final electron-density map showed residual peaks of 1.1 (maximum) and −1.25 (minimum) e $Å^{-3}$. Atom scattering factors were taken from ref. 19. Diagrams were produced using PLUTO.[20] A list of fractional atomic coordinates is given in Table 7.

Compound **4a**. The Os atoms were located by heavy-atom methods and the remaining non-hydrogen atoms by Fourier techniques (SHELX 76[21]). Blocked least-squares refinement with Os, P and O atoms anisotropic. The phenyl groups were refined as regular hexagons with individual isotropic vibration parameters assigned to each C atom, and with H atoms in calculated positions. The final electron-density map showed a residual peak of 3 e $Å^{-3}$, unconnected to the molecule, probably due to disordered solvent. A list of fractional atomic coordinates is given in Table 8.

Compound **4c**. The Os atoms were located by the Patterson method (SHELX 86[22]). The Os, P, O and the non-phenyl C atoms were treated anisotropically. The phenyl rings were constrained to regular hexagons with H atoms in calculated positions. The final electron-density map showed several peaks of approximately 1 e $Å^{-3}$ which are thought to be due to the presence of disordered dichloromethane with a low site-occupancy factor. A list of fractional atomic coordinates is given in Table 9.

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

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