Cluster Activation *via* Cyclometallation. Formation of the Cyclometallated Triosmium Carbonyl Cluster $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ and its Reactions with Phosphorus Donor Ligands. The *X*-Ray Crystal Structures of $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ and $[Os_3H(CO)_9\{P(OMe)_3\}(PPh_2)]$†

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Cyclometallation of $[Os_3H(CO)_{10}(PPh_2)]$ (**1**) proceeds smoothly in n-octane, under reflux, to give $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ (**2**) in good yield. An *X*-ray analysis of this product reveals that the phosphorus atom of the μ-$P(C_6H_4)Ph$ group bridges an edge of the osmium triangle, while the α-carbon of the orthometallated ring occupies an axial co-ordination site on the third Os atom. Although not located directly, one hydride bridges the same Os–Os [2.936(2) Å] as the bridgehead P atom while the second bridges the longest Os–Os edge [3.028(3) Å]. Addition of phosphorus donor ligands to (**2**) results in the reversal of cyclometallation to give substituted clusters $[Os_3H(CO)_9L(PPh_2)]$ [L = $P(C_6H_4Me$-*p*$)_3$ (**3**), $P(OMe)_3$ (**4**), or PPh_2H (**5**)]. For each of these substituted clusters only a single structural isomer is obtained, but ^1H and ^{31}P n.m.r. spectroscopy reveals that it is a different isomer for (**3**) compared to those for (**4**) and (**5**). The structure of $[Os_3H(CO)_9\{P(OMe)_3\}(PPh_2)]$ (**4**) has been established by an *X*-ray analysis, which shows that the phosphite ligand occupies an equatorial site on the Os atom of the triosmium triangle which is not involved in the co-ordination to the bridging phosphido- and hydrido-ligands. N.m.r. data are consistent with a similar structure for the phosphine derivative (**5**), while the magnitudes of the phosphorus–phosphorus coupling indicate that the bulky phosphine in (**3**) occupies a site on one of the Os atoms associated with the phosphido- and hydrido-bridges. On heating, under reflux, in high-boiling solvents, complexes (**3**) and (**4**) decarbonylate and undergo metallation to give $[Os_3H_2(CO)_8L\{P(C_6H_4)Ph\}]$ [L = $P(C_6H_4Me$-*p*$)_3$ (**6**) or $P(OMe)_3$ (**7**)]. Complex (**6**) is isolated as a single isomer whereas (**7**) exists as a mixture of three isomers, the structures of which have been established by n.m.r. spectroscopy. In contrast, when complex (**5**) is heated in dichloromethane, under reflux, decarbonylation occurs, and metallation of the phosphine group, rather than of the phosphido-ligand, takes place to afford $[Os_3H_2(CO)_8(PPh_2)_2]$ (**8**) in good yield.

In transition-metal cluster chemistry bridging phosphorus ligands have received considerable attention because of their ability to maintain integrity in a polymetallic framework during chemical transformation.[1–5] It is, however, becoming clear that under forcing conditions the bridging ligands themselves often become involved in C–H and C–P bond cleavage reactions.[2]

We now report that cyclometallation of the triosmium cluster $[Os_3H(CO)_{10}(PPh_2)]$ (**1**) to give $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ (**2**) does not require forcing reaction conditions. On the contrary, in this and subsequent papers[3] it will be shown that this C–H bond cleavage is readily reversed and that (**2**) provides a rich entry to triosmium carbonyl clusters with a bridging diphenylphosphido moiety. Here the preparation and *X*-ray crystal structure of complex (**2**), reactions of (**2**) with phosphorus donor ligands to give substituted derivatives of (**1**), and the products from thermolyses of the latter complexes are described.

Results and Discussion

Invariably, the (diphenyl)phosphido-osmium (and-ruthenium) hydrido carbonyl clusters reported in the literature have been synthesised in low to moderate yields in direct thermal reactions of the appropriate carbonyl cluster and a primary or secondary phosphine.[4] We recently reported that hydridophosphidotriosmium clusters are most conveniently prepared by substitution of the weakly ligated cluster $[Os_3(CO)_{11}(MeCN)]$ with a primary or secondary phosphine, followed by a deprotonation–protonation sequence.[5] This route gave the diphenylphosphido-bridged triosmium cluster $[Os_3H(CO)_{10}(PPh_2)]$ (**1**), which is the precursor to all the compounds discussed below, in excellent overall yield ($\approx$90% Scheme).

$$\begin{tikzcd}
{[Os_3(CO)_{11}(MeCN)]} \arrow[r, "(i)"] & {[Os_3(CO)_{11}(PPh_2H)]} \arrow[d, "(ii)"] \\
{[Os_3H(CO)_{10}(PPh_2)]} & {[Os_3(CO)_{10}(PPh_2)]^-} \arrow[l, "(iii)"']
\end{tikzcd}$$

Scheme. (*i*) PPh_2H; (*ii*) dbu; (*iii*) CF_3CO_2H

Cyclometallation of complex (**1**) proceeded smoothly in refluxing n-octane to give high yields of $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ (**2**) which was obtained as pale yellow air-stable crystals. Infrared (Table 1), analytical, and mass spectroscopic data were consistent with the formulation of (**2**). The ^1H n.m.r. spectrum (Table 2) in the phenyl region is diagnostic of metallation of one of the PPh_2 phenyl groups at the *ortho* position.[6,7] The spectrum for (**2**) is reproduced in Figure 1, together with that of (**1**), for comparison. Each of the four well separated multiplets centred at δ 7.78, 6.88, 6.71, and 6.22

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

Table 1. Infrared data (cm^{-1})*

Compound	
(**1**) $[Os_3H(CO)_{10}(PPh_2)]$	2 104mw, 2 057vs, 2 021vs, 2 015m, 1 991ms, 1 978w
(**2**) $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$	2 108m, 2 078vs, 2 051vs, 2 039m, 2 028m, 2 011s, 1 999m, 1 986w, 1 980m
(**3**) $[Os_3H(CO)_9\{P(C_6H_4Me\text{-}p)_3\}(PPh_2)]$	2 084w, 2 053s, 2 022vs, 2 005s, 1 985m, 1 962m, 1 950mw
(**4**) $[Os_3H(CO)_9\{P(OMe)_3\}(PPh_2)]$	2 082w, 2 048s, 2 029mw, 2 003vs, 1 980m, 1 962w
(**5**) $[Os_3H(CO)_9(PPh_2H)(PPh_2)]$	2 079w, 2 044s, 2 029mw, 2 001vs, 1 982m, 1 975mw (sh), 1 961w
(**6**) $[Os_3H_2(CO)_8\{P(C_6H_4Me\text{-}p)_3\}$-$\{P(C_6H_4)Ph\}]$	2 077m, 2 042vs, 2 001s, 1 984s, 1 967m
(**7**) $[Os_3H_2(CO)_8\{P(OMe)_3\}\{P(C_6H_4)Ph\}]$	2 081s, 2 053, 2 043vs, 2 007vs, 1 989ms, 1 980w, 1 969s, 1 845mw
(**8**) $[Os_3H_2(CO)_8(PPh_2)_2]$	2 082m, 2 048vs, 2 022vs, 2 013s, 1 983ms, 1 961m

* ν(CO), 2 200—1 600 cm^{-1}, in hexane.

Table 2. N.m.r. data*

Compound	
(**1**) $[Os_3H(CO)_{10}(PPh_2)]$	^{1}H: 7.8—6.7 (m, PPh$_2$), −18.09 [d, J(PH) 19.8, OsH] ^{31}P-{^{1}H}: −74.14 (s, PPh$_2$)
(**2**) $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$	^{1}H: 7.78, 6.88, 6.71, 6.22 [complex multiplets, P(C$_6$H$_4$)], 7.7—7.1 (m, PPh), −17.10 (br s, 2OsH) ^{31}P-{^{1}H}: −99.07 [s, P(C$_6$H$_4$)Ph]
(**3**) $[Os_3H(CO)_9\{P(C_6H_4Me\text{-}p)_3\}(PPh_2)]$	^{1}H: 8.0—7.1 [m, PPh$_2$ and P(C$_6$*H*$_4$CH$_3$)$_3$], 2.45 [s, P(C$_6$H$_4$C*H*$_3$)$_3$], −18.86 [dd, J(PH) 10.3, J(P′H) 5.7, OsH] ^{31}P-{^{1}H}: −76.67 [d, J(PP′) 5.8, P(C$_6$H$_4$CH$_3$)$_3$], −147.64 [d, J(PP′) 5.8, PPh$_2$]
(**4**) $[Os_3H(CO)_9\{P(OMe)_3\}(PPh_2)]$	^{1}H: 7.9—6.8 (m, PPh$_2$), 3.64 [d, J(PH) 11.9, P(OCH$_3$)$_3$], −17.88 [dd, J(PH) 19.6, J(P′H) 3.5, OsH] ^{31}P-{^{1}H}: −42.44 [d, J(PP′) 7.5, P(OCH$_3$)$_3$], −123.32 [d, J(PP′) 7.5, PPh$_2$]
(**5**) $[Os_3H(CO)_9(PPh_2H)(PPh_2)]$	^{1}H: 8.0—6.7 (m, PPh$_2$ and P*Ph*$_2$H), 7.04 [d, J(PH) 380.5, PPh$_2$*H*], −17.67 [dd, J(PH) 19.9, J(P′H) 1.1, OsH] ^{31}P-{^{1}H}: −121.87 [d, J(PP′) 3.4, PPh$_2$], −166.52 [d, J(PP′) 3.4, PPh$_2$H]
(**6**) $[Os_3H_2(CO)_8\{P(C_6H_4Me\text{-}p)_3\}\{P(C_6H_4)Ph\}]$	^{1}H: 7.74, 6.88, 6.68, 6.16 [complex multiplets, P(C$_6$H$_4$)], 7.6—7.2 [m, P(C$_6$H$_4$CH$_3$)$_3$ and PPh], 2.45 [s, P(C$_6$H$_4$C*H*$_3$)$_3$], −15.82 [ddd, J(PH) 8.7, J(P′H) 8.2, J(HH′) 1.0, OsH], −17.67 [dd, J(PH) 7.4, J(P′H) 4.7, J(HH′) 1.0, OsH] ^{31}P-{^{1}H}: −103.07 [d, J(PP′) 140.5, P(C$_6$H$_4$CH$_3$)$_3$], −146.24 [d, J(PP′) 140.5, PPh]
(**7**) $[Os_3H_2(CO)_8\{P(OMe)_3\}\{P(C_6H_4)Ph\}]$	Peaks that may be attributed to three isomers (**a**)—(**c**) were observed ^{1}H: (**a**)—(**c**), 7.7—7.4 [complex multiplets, P(C$_6$H$_4$)], 7.7—7.4 (m, PPh); (**a**), 3.53 [d, J(PH) 12.0, P(OCH$_3$)$_3$], −17.14 [ddd, J(PH) 43.5, J(P′H) 9.5, J(HH′) 0.6, OsH], −17.38 [ddd, J(PH) 18.5, J(P′H) 6.6, J(HH′) 0.6, OsH]; (**b**), 3.75 [d, J(PH) 12.2, P(OCH$_3$)$_3$], −16.87 [ddd, J(PH) 12.7, J(P′H) 8.6, J(HH′) 1.2, OsH], −18.10 [ddd, J(PH) 12.8, J(P′H) 5.1, J(HH′) 1.2, OsH]; (**c**), 3.42 [d, J(PH) 11.8, P(OCH$_3$)$_3$]; hydrides not observed. Relative intensities for the phosphite signals of (**a**)—(**c**) were 7.3:3.1:1 ^{31}P-{^{1}H}: (**a**), −56.40 [s, P(CH$_3$)$_3$], −105.50 [s, P(C$_6$H$_4$)Ph]; (**b**), −38.89 [d, J(PP′) 221, P(CH$_3$)$_3$], −106.58 [d, J(PP′) 221, P(C$_6$H$_4$)Ph]; (**c**), −63.42 [s, P(CH$_3$)$_3$], −95.86 [s, P(C$_6$H$_4$)Ph]
(**8**) $[Os_3H_2(CO)_8(PPh_2)_2]$	^{1}H: 8.0—7.3 (m, PPh$_2$), −17.31 [t, J(PH) 13.7, 2OsH]

* In CDCl$_3$ or CD$_2$Cl$_2$; chemical shifts in p.p.m., coupling constants in Hz.

corresponds to one of the four protons of the metallated C$_6$H$_4$ group. In the high-field region of the spectrum, (**2**) showed a very broad peak at δ −17.10 indicating fluxional behaviour for the two inequivalent hydride ligands.[7,8] On cooling, changes in this signal, which are typical for an ABX spin system with A,B exchanging, were observed. Unfortunately, it was not possible to reach sufficiently low temperatures to obtain a limiting spectrum. A singlet at δ −99.07 p.p.m. was observed for the 'bridgehead' phosphorus atom in the ^{31}P-{^{1}H} n.m.r. spectrum of (**2**) [for comparison a singlet at −74.14 p.p.m. was observed for the precursor cluster (**1**)].

Several other triosmium clusters with the general formula $[Os_3H(CO)_{10}(EPh)]$ (E = NH or O and derivatives derived by substitution of the phenyl groups) have been reported to cyclometallate when heated.[7,9] Originally the cyclometallated product clusters $[Os_3H_2(CO)_9(EC_6H_4)]$ were ascribed structure (**i**) in Figure 2.[7] An *X*-ray crystal analysis subsequently showed that the benzyl-substituted alkoxo-derivative $[Os_3H_2(CO)_9O(C_6H_3CH_2Ph\text{-}3)]$ adopted structure (**ii**) in Figure 2.[9] Although the propensity for phosphido-groups to bridge might suggest that (**2**) adopts structure (**i**), the spectroscopic data do not enable a decision between either alternative structure. Consequently a single-crystal *X*-ray analysis of complex (**2**) was undertaken.

The crystal structure of (**2**) consists of discrete molecules of $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu\text{-}P(C_6H_4)Ph\}]$ separated by normal van der Waals distances. There are four crystallographically independent but structurally similar molecules in the asymmetric unit. The structure of one of these molecules is shown in Figure 3, while selected bond parameters are given in Table 3.

The three Os atoms in each independent molecule of (**2**) form an irregular triangle with the phosphorus atom of the metallated μ-P(C$_6$H$_4$)Ph moiety bridging the Os–Os edge of intermediate length [average phosphorus-bridged Os–Os distance 2.936(2) Å and average Os–P distance 2.354(7) Å]. The metallated phenyl ring in the μ-P(C$_6$H$_4$)Ph moiety in each case lies approximately perpendicular to the plane of the Os triangle [average dihedral angle 89.1(2)°] and is bound to the Os atom not bridged by the phosphorus atom. The osmium-metallated carbon bond lengths are unexceptional averaging 2.17(3) Å.

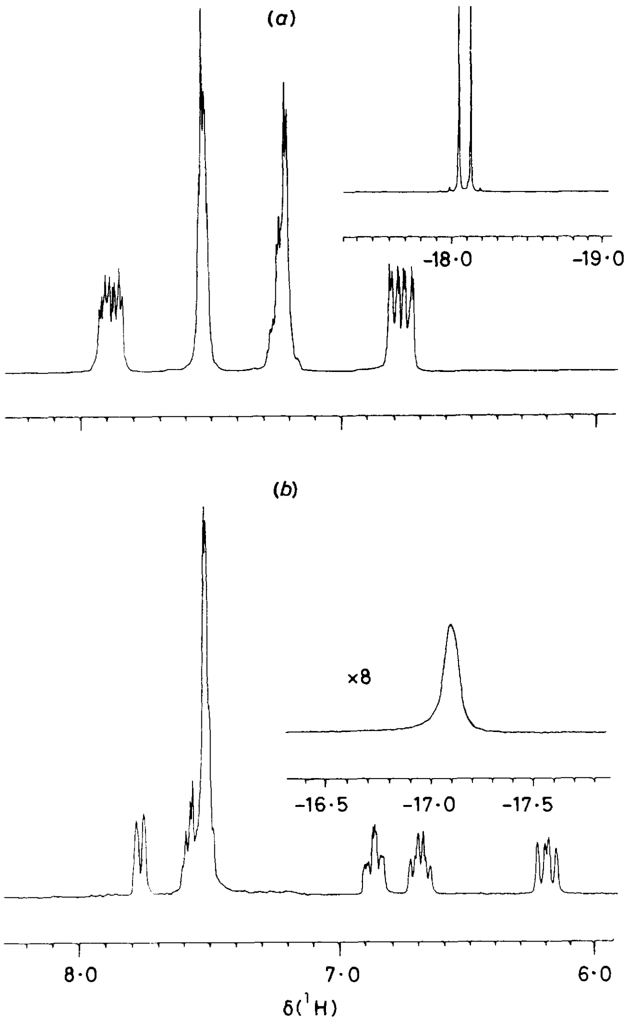
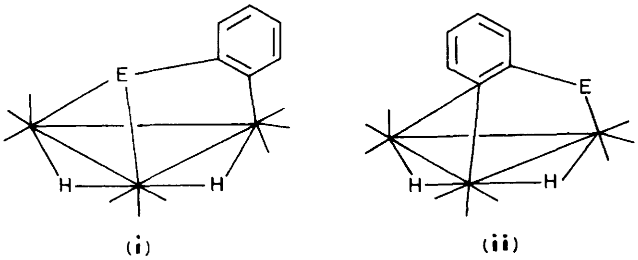


Figure 1. Proton n.m.r. spectra for clusters (**1**) (*a*) and (**2**) (*b*), showing that orthometallation of a phenyl ring in (**2**) has occurred



(i) (ii)

Figure 2. Possible structures for $[Os_3H_2(CO)_9(EC_6H_4)]$ (E = NH or O)

The non-metallated phenyl group in each independent molecule of (**2**) lies orientated away from the Os triangle and is approximately parallel to the Os–Os edge bridged by the phosphido-P atom.

Each of the osmium atoms has three essentially linear, terminal carbonyl ligands, two in equatorial and one in an axial site. The two hydride ligands on each independent molecule of (**2**) were not directly located in this analysis but in each molecule of one of the two Os edges not bridged by the phosphido-P atom [Os(1)–Os(3) in Figure 3] is longer [average 3.028(3) Å] than the other [average 2.869(3) Å], and may be compared with an Os–Os distance of 2.877(3) Å for $[Os_3(CO)_{12}]$[10]. The lengthening of this Os–Os edge is attributed to a bridging hydride ligand, a conclusion supported by the bending away of the carbonyl ligands from this edge (as compared to those carbonyl ligands about the other shorter Os edge). The conformation of the ligands about the Os atoms bridged by the phosphido-P atom suggests that the remaining hydride bridges the same edge, the lengthening effect of the bridging hydride atom being balanced by the shortening effect exerted by the μ-$P(C_6H_4)Ph$ moiety.

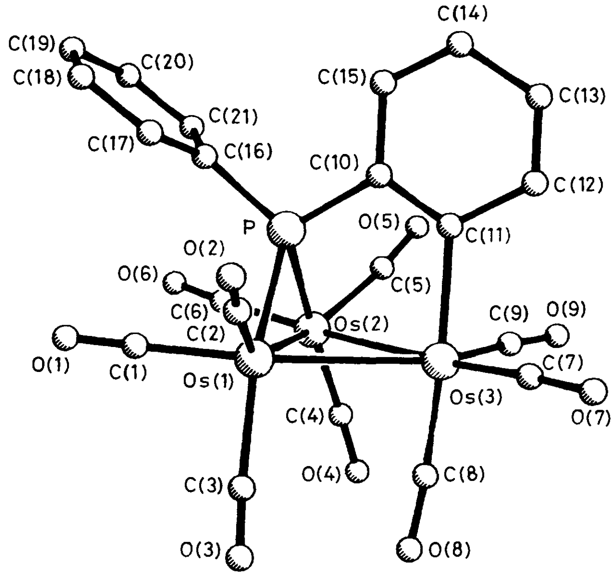


Figure 3. The molecular structure of $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ (**2**) showing the atom labelling scheme

Table 3. Selected bond lengths (Å) and angles (°) for $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ (**2**)

	Molecule 1	Molecule 2	Molecule 3	Molecule 4
Os(2)–Os(1)	2.937(2)	2.935(2)	2.936(2)	2.939(2)
Os(3)–Os(1)	3.028(2)	3.023(2)	3.023(2)	3.032(2)
Os(3)–Os(2)	2.870(2)	2.879(2)	2.867(2)	2.860(2)
P–Os(1)	2.375(9)	2.353(9)	2.353(9)	2.368(10)
P–Os(2)	2.357(5)	2.347(5)	2.350(5)	2.347(6)
P–C(10)	1.77(3)	1.77(3)	1.82(3)	1.80(3)
C(11)–Os(3)	2.17(3)	2.15(3)	2.18(2)	2.19(3)
P–C(16)	1.78(2)	1.84(2)	1.82(2)	1.83(2)
C(11)–C(10)	1.38(4)	1.42(4)	1.38(4)	1.45(4)
Os(3)–Os(1)–Os(2)	57.5(1)	57.8(1)	57.4(1)	57.2(1)
Os(3)–Os(2)–Os(1)	62.8(1)	62.6(1)	62.9(1)	63.0(1)
Os(2)–Os(3)–Os(1)	59.7(1)	59.6(1)	59.7(1)	59.8(1)
P–Os(1)–Os(2)	51.3(1)	51.3(1)	51.3(1)	51.1(1)
P–Os(1)–Os(3)	72.7(2)	72.7(2)	72.7(2)	72.7(2)
P–Os(2)–Os(1)	51.9(2)	51.4(2)	51.4(2)	51.8(2)
P–Os(2)–Os(3)	76.1(2)	75.6(2)	75.9(2)	76.4(2)
Os(2)–P–Os(1)	76.7(2)	77.3(2)	77.3(2)	77.1(2)
C(11)–C(10)–P	114(2)	115(2)	115(2)	112(2)
C(10)–C(11)–Os(3)	122(2)	119(2)	120(2)	121(2)

The overall structure of complex (**2**) is closely related to that of $[Os_3H_2(CO)_9(NHC_6H_3F)]$[11] where the NHC_6H_3F ligand caps the metal triangle in a similar mode to that of the $P(C_6H_4)Ph$ group in (**2**). However, the metal–metal distances do not follow the same trends as in (**2**). Notably, the Os–Os edge bridged by the nitrogen atom in $[Os_3H_2(CO)_9(NHC_6H_3F)]$[11] has a distance of only 2.808(4) Å compared to the average Os–Os distance of 2.936(2) Å for the phosphorus-bridged edge in (**2**). This presumably reflects the difference in size and electronic properties of the two 'bridgehead' atoms.

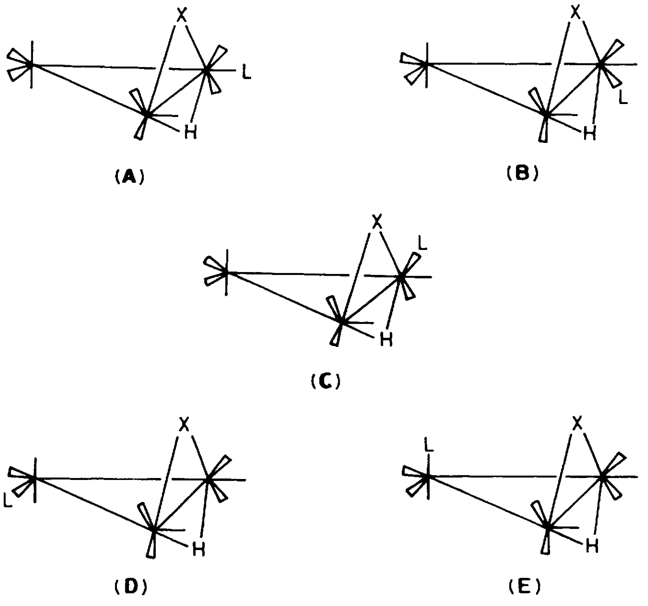


Figure 4. Possible positions of substitution in the clusters $[Os_3H(CO)_9L(X)]$

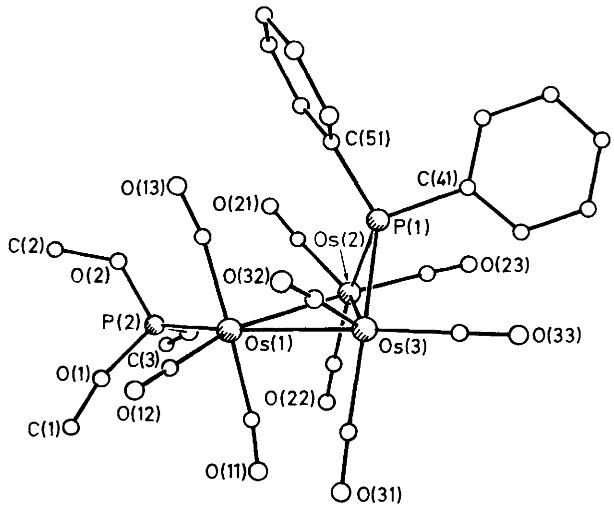


Figure 5. The molecular structure of $[Os_3H(CO)_9\{P(OMe)_3\}(PPh_2)]$ (**4**) showing the atom labelling scheme

Some comments about the effect of metallation on the phosphido-group are pertinent. First, the phosphido-group bends back towards the osmium triangle on metallation, *i.e.* in (**2**). This ligand orientation is also observed in the carbonylated form of the complex, $[Os_3(CO)_{10}\{P(C_6H_4)Ph\}]$.[12] Thus the average dihedral angle between the plane of the osmium triangle and the plane defined by the phosphorus atom and the two osmium atoms that it bridges is 93.4° in (**2**) compared with 110.8° in $[Os_3H(CO)_9\{P(OMe)_3\}(PPh_2)]$ (see below), 111° in $[Os_3H_2(CF_3CO_2)(CO)_9(PPh_2)]$,[3] and 107° in $[Os_3H(CO)_{10}(PPhH)]$.[4] Lastly, the relative orientations of the two phenyl groups is reversed in (**2**) compared to those in the three phosphido clusters listed above, such that the phenyl group orientated away from the osmium triangle lies parallel to the phosphido-bridged edge in (**2**) but perpendicular to this edge in the non-metallated phosphido clusters (this is most readily seen by inspection of Figures 3 and 5).

Addition of phosphorus donor ligands caused reversal of the cyclometallation on (**2**) and gave good yields of the substituted hydridophosphidotriosmium clusters $[Os_3H(CO)_9L(PPh_2)]$ [L = $P(C_6H_4Me\text{-}p)_3$ (**3**), $P(OMe)_3$ (**4**), or PPh_2H (**5**)] isolated as moderately stable yellow solids. Other hydridotriosmium clusters with a bridgehead group 'X' and with the general formula $[Os_3H(CO)_9L(X)]$ have previously been reported.[13] In particular, it was shown that for a symmetrical bridging atom/group X there are five possible isomers for $[Os_3H(CO)_9L(X)]$ [obtained by substitution of the ligand L at positions (**A**)—(**E**) in Figure 4] and that each of the five isomers show characteristic, distinct ^1H n.m.r. data.[13]

The ^1H n.m.r. data for (**3**)—(**5**) showed that each compound was obtained as a single structural isomer (Table 2). However, the different i.r. profile for (**3**) compared with those for (**4**) and (**5**) is consistent with a different structure to the last two compounds (Table 1). Apart from resonances which are readily attributed to the PPh_2 moiety and to the phosphine ligand, the ^1H n.m.r. spectrum of (**3**) showed a high-field hydride multiplet at δ −18.86 [dd, *J*(PH) 10.3, *J*(P′H) 5.7 Hz]. It is not possible definitely to assign the coupling constants although the larger coupling might be expected to be between the phosphido-P atom and the hydride ligand. In any case, the magnitude of these phosphorus–hydrogen coupling constants is indicative of *cis* coupling between the nuclei,[13] eliminating (**C**)—(**E**) as possible structures for (**3**). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**3**) consists of two doublets [*J*(PP′) 5.8 Hz] at −76.67 and −147.64 p.p.m., which were assigned to the $P(C_6H_4Me\text{-}p)_3$ and PPh_2 phosphorus atoms respectively, from comparison of the n.m.r. data with those for the other diphenylphosphido-clusters (Table 2). The magnitude of the phosphorus–phosphorus coupling indicates that the two phosphorus atoms are *cis* to each other,[13] which eliminates (**B**) and leaves, by default, (**A**) as the structure of (**3**).

Compounds (**4**) and (**5**) showed in their respective ^1H n.m.r. spectra the resonances expected for the PPh_2 group and for the phosphorus donor, as well as a high-field doublet of doublets for the hydride ligand {at δ −17.88 [*J*(PH) 19.6, *J*(P′H) 3.5 Hz] for (**4**) and at δ −17.67 [*J*(PH) 19.9, *J*(P′H) 1.1 Hz] for (**5**)}. In each compound the larger phosphorus coupling for the hydride ligand is to the phosphido-P atom. In the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra doublets at −42.44 p.p.m. [*J*(PP′) 7.5 Hz] for (**4**) and at −166.52 p.p.m. [*J*(PP′) 3.4 Hz] for (**5**) are observed for the respective phosphorus donor ligands and doublets at −123.32 p.p.m. for (**4**) and −121.87 p.p.m. for (**5**) are observed for the PPh_2 group. Given that in an analogous series of compounds scalar couplings to phosphorus in phosphite derivatives are roughly double those in phosphine derivatives,[13] the very small couplings between the phosphorus atom of the P-donor ligands and both the PPh_2 and hydride ligands are consistent with structure (**D**) (in Figure 4) for both (**4**) and (**5**).

This conclusion was confirmed by an *X*-ray crystal structure determination carried out on pale yellow crystals of (**4**). The molecular structure of $[Os_3(\mu\text{-}H)(CO)_9\{P(OMe)_3\}(PPh_2)]$ (**4**) is shown in Figure 5 and selected bond lengths and interbond angles are given in Table 4. Normal distances separate discrete molecules of (**4**) in the crystal lattice.

The molecular structure of (**4**) is clearly derived from that found for clusters of the type $[Os_3H(CO)_{10}(\mu\text{-}X)]$[14] by substitution of an equatorial carbonyl ligand of the non-bridgehead osmium atom by the $P(OMe)_3$ ligand. Thus (**4**) consists of an approximate isosceles triangle of osmium atoms with two shorter bonds [Os(1)–Os(2) and Os(1)–Os(3)] and one longer bond [Os(2)–Os(3)]. The longer edge is symmetrically bridged by the diphenylphosphido-group such that a dihedral angle of 110.8° is observed between the planes Os(1),Os(2),Os(3) and Os(2),Os(3),P(1). This dihedral angle compares favourably with the comparable parameters in the other phosphidotriosmium clusters which have been characterised crystallographically (see above).[3,4] The equatorial

Table 4. Selected bond lengths (Å) and angles (°) for $[Os_3H(CO)_9\{P(OMe)_3\}(PPh_2)]$ (**4**)

Os(2)–Os(1)	2.894(1)	P(2)–Os(1)	2.283(3)
Os(3)–Os(1)	2.888(1)	P(1)–Os(2)	2.377(2)
Os(3)–Os(3)	2.922(1)	P(1)–Os(3)	2.378(2)
C(11)–Os(1)	1.926(11)	C(21)–Os(2)	1.882(11)
C(12)–Os(1)	1.888(14)	C(22)–Os(2)	1.912(12)
C(13)–Os(1)	1.963(12)	C(23)–Os(2)	1.915(10)
C(31)–Os(3)	1.961(12)	C(33)–Os(3)	1.903(12)
C(32)–Os(3)	1.867(13)		
Os(3)–Os(1)–Os(2)	60.7(1)	Os(3)–Os(2)–Os(1)	59.5(1)
P(2)–Os(1)–Os(2)	101.4(1)	P(1)–Os(2)–Os(1)	86.0(1)
P(2)–Os(1)–Os(3)	162.0(1)	P(1)–Os(2)–Os(3)	52.1(1)
Os(2)–Os(3)–Os(1)	59.7(1)	Os(3)–P(1)–Os(2)	75.8(1)
P(1)–Os(3)–Os(1)	86.1(1)	C(41)–P(1)–Os(2)	113.5(3)
P(1)–Os(3)–Os(2)	52.1(1)	C(41)–P(1)–Os(3)	116.0(3)
O(1)–P(2)–Os(1)	120.0(4)	C(51)–P(1)–Os(2)	126.4(3)
O(2)–P(2)–Os(1)	115.2(4)	C(51)–P(1)–Os(3)	123.5(3)
O(2)–P(2)–O(1)	104.7(6)	C(51)–P(1)–C(41)	101.4(4)
O(3)–P(2)–Os(1)	111.5(4)	O(3)–P(2)–O(2)	103.6(9)
O(3)–P(2)–O(1)	99.5(6)		

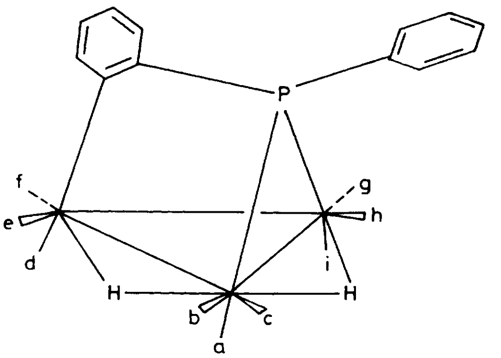


Figure 6. Possible isomeric positions of substitution in the clusters $[Os_3H_2(CO)_8L\{P(C_6H_4)Ph\}]$

$P(OMe)_3$ ligand [P(2) lies 0.10 Å out of the plane defined by Os(1),Os(2),Os(3)] bonds to Os(1), the distance Os(1)–P(2) being 2.283(3) Å. Each of the three osmium atoms is also co-ordinated to three terminal, and essentially linear, carbonyl groups. The hydride ligand was not directly located but the carbonyl ligand distribution indicates that it bridges the Os(2)–Os(3) edge.

Reflux of either complex (**3**) or (**4**) in a high-boiling solvent causes loss of a carbonyl ligand and formation of $[Os_3H_2(CO)_8L\{P(C_6H_4)Ph\}]$ [L = $P(C_6H_4Me\text{-}p)_3$ (**6**) or $P(OMe)_3$ (**7**)]. In these substituted cyclometallated clusters there are nine possible isomers corresponding to the nine possible positions for the ligand L (a—i in Figure 6). Compound (**6**) was isolated as a single isomer. In the ^1H n.m.r. spectrum, as well as the characteristic $P(C_6H_4)Ph$ moiety [see discussion for (**2**)] and $P(C_6H_4Me\text{-}p)_3$ ligand resonances, high-field doublets of doublets of doublets were observed for both the inequivalent hydride ligands at −15.82 [*J*(PH) 8.7, *J*(P′H) 8.2, *J*(HH′) 1.0 Hz] and at −17.67 [*J*(PH) 7.4, *J*(P′H) 4.7, *J*(HH′) 1.0 Hz]. It was not possible to assign individual couplings to a particular phosphorus atom but it should be noted that both hydride ligands show *cis* couplings to both the phosphine- and phosphido-P atoms, suggesting isomer (a) (in Figure 6) for (**6**). This assignment is substantiated by the large *trans* phosphorus–phosphorus coupling [*J*(PP′) 140.5 Hz] observed in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum between the phosphine (at −103.07 p.p.m.) and the $P(C_6H_4)Ph$ moiety (at −146.24 p.p.m.).

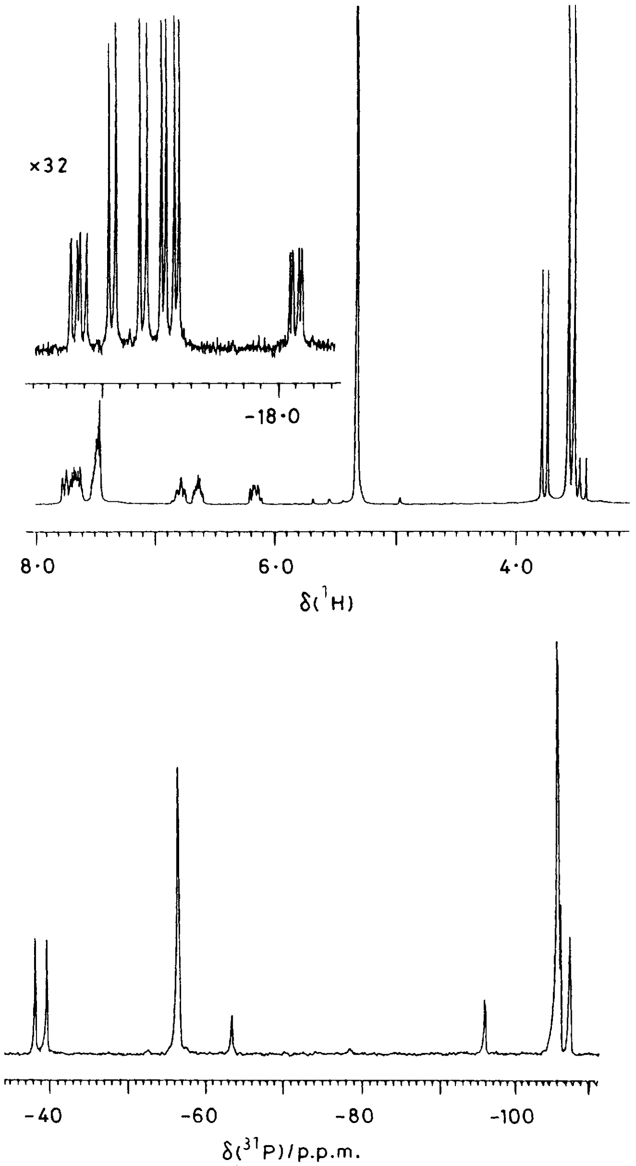


Figure 7. N.m.r. spectra for complex (**7**) showing the presence of isomers

On the other hand, compound (**7**) was isolated as a mixture of three isomers (**a**)—(**c**). These were inseparable by conventional chromatographic techniques and the same isomer ratio was obtained from several different preparations, suggesting that (**7a**)—(**7c**) form an equilibrium mixture. The ^1H n.m.r. spectrum showed a common set of peaks for the cyclometallated $\mu\text{-}P(C_6H_4)Ph$ moiety and three sets of doublets [*J*(PH) ≈ 12 Hz], relative intensities 1:3.1:7.3 between 3.8 and 3.4 p.p.m. corresponding to the $P(OMe)_3$ ligand in each isomer (see insert, Figure 7). The high-field hydride region is more complex and only the peaks from the two more abundant isomers are clearly discernible (Figure 7). In the most abundant isomer (**7a**) the hydride ligand at −17.14 shows a large *trans* coupling [*J*(P′H) = 43.5 Hz] to one phosphorus atom and a *cis* coupling [*J*(P′H) = 9.5 Hz] to the other, whereas the hydride at −17.38 shows *cis* couplings [*J*(PH) 18.5, *J*(P′H) 6.6 Hz] to both the phosphite- and phosphido-P atoms. Clearly this coupling scheme requires that the $P(OMe)_3$ ligand has moved from the non-bridgehead osmium atom in (**4**) to the bridgehead osmium atom that bonds both hydride ligands (see Figure 6) in forming (**7a**). The large *trans* coupling to phosphorus suggests that the

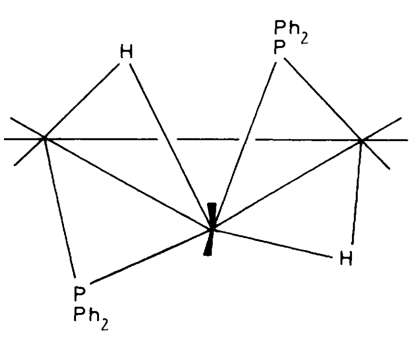


Figure 8. The structure of $[Os_3H_2(CO)_8(PPh_2)_2]$ (**8**)

phosphite ligand is at either of positions b or c in Figure 6. The other isomer for which the hydride peaks were clearly discernible, (**7b**), shows *cis* couplings to both of the phosphite- and phosphido-P atoms for both hydride atoms (Table 2), suggesting that the $P(OMe)_3$ ligand has again moved osmium atoms on cyclometallation and that the phosphite is at position b or c in Figure 6. Given that (**7a**)—(**7c**) appear to be in equilibrium at room temperature and that transfer of phosphite between metals is a high-energy process, it seems likely that (**7c**) results from substitution of the $P(OMe)_3$ at position b or c [whichever (**7b**) is not]. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (reproduced in Figure 7) is consistent with this interpretation. Peaks due to the phosphido- and phosphite-P atoms in each of the three isomers are observed. For both (**7a**) and (**7c**) phosphorus–phosphorus coupling was not resolved (resolution of spectrum ≈ 10 Hz) whereas a large *trans* coupling [J(PP′) 221 Hz] was observed as expected between the phosphido- and phosphite-P atoms in (**7b**).

In contrast to (**3**) and (**4**), heating the PPh_2H-substituted cluster (**5**) in refluxing dichloromethane led to carbonyl loss and metallation of the phosphine ligand rather than the PPh_2 group, and gave the dihydridobis(diphenylphosphido)triosmium cluster $[Os_3H_2(CO)_8(PPh_2)_2]$ (**8**) in good yield. No cyclometallated products were observed from the reaction. Compound (**8**) has been previously isolated as a product of the decompositon of $[Os_3(CO)_{10}(PPh_2H)_2]$, and its molecular structure was determined to be that shown in Figure 8.[15]

Experimental

With the exception of chromatography, all operations were carried out with the exclusion of air. Solvents were dried and distilled from appropriate reagents immediately prior to use. Except where stated, product separation was achieved using thin-layer chromatography (t.l.c.) on plates precoated to 0.25 mm thickness with Merck Kieselgel 60 F_{254}. Hexane with just sufficient dichloromethane added to achieve separation was used as eluant. The complex $[Os_3(CO)_{11}(MeCN)]$ was prepared by the literature method.[16] All other reagents were commercial products and were used as supplied.

Infrared spectra were recorded between 2 200 and 1 600 cm^{-1} on Perkin-Elmer 983 spectrometers and n.m.r. spectra on Bruker 80, 250, and 400 instruments using deuteriated solvents as both lock and internal reference [^1H, ^{13}C, $SiMe_4$ ($\delta = 0$); ^{31}P, 1% $P(OMe)_3$ in C_6D_6 ($\delta = 0$); downfield positive]. Mass spectra were recorded on an A.E.I. MS12 spectrometer with *ca.* 70 eV (1.12×10^{-17} J) ionising potential at 100—150 °C; tris(perfluoroheptyl)-*s*-triazine was used as a reference.

Preparations.—$[Os_3H(CO)_{10}(PPh_2)]$ (**1**). The cluster $[Os_3(CO)_{11}(MeCN)]$ (500 mg) and excess of PPh_2H (*ca.* 0.5 cm^3) were stirred together in dichloromethane (50 cm^3) until the i.r. spectrum showed complete conversion into $[Os_3(CO)_{11}(PPh_2H)]$ [ν(CO): 2 108w, 2 054m, 2 034m, 2 020vs, 1 980mw, and 1 958ms (sh) cm^{-1}]. The dichloromethane was then removed *in vacuo*, the residue redissolved in tetrahydrofuran (40 cm^3), and excess of dbu (*ca.* 0.6 cm^3) added. A rapid colour change from pale yellow to an intense red followed by slower decolorisation back to yellow occurred. At this point the solution shows i.r. bands from $Hdbu^+$ and $[Os_3(CO)_{10}(PPh_2)]^-$ [ν(CO): 2 059w, 2 003s, 1 990vs, 1 970s, and 1 920m cm^{-1}]. The anion was then protonated by adding trifluoroacetic acid until the solution was acidic, the solvents removed *in vacuo*, and the residue passed down a silica column eluting with hexane. Bright orange crystals of complex (**1**) were obtained from recrystallisation of the single yellow band (yield 557 mg, 96%) (Found: C, 25.00; H, 1.00%; M^+ at m/z 1 042. Calc. for $C_{22}H_{11}O_{10}Os_3P$: C, 25.4; H, 1.1%).

$[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ (**2**). A suspension of complex (**1**) (238 mg) in n-octane (40 cm^3) was heated at reflux until the i.r. spectrum of the solution showed all the carbonyl bands of the reactant to have been replaced by those of the product (**2**) (≈ 1 h). Removal of the solvent followed by chromatography on silica eluting with dichloromethane–hexane (20:80) gave a single pale yellow band which afforded (**2**) (230 mg, 97%) (Found: C, 25.20; H, 1.25; P, 3.05%; M^+ at m/z 1 014. Calc. for $C_{21}H_{11}O_9Os_3P$: C, 24.9; H, 1.1; P, 3.05%).

$[Os_3H(CO)_9\{P(C_6H_4Me\text{-}p)_3\}(PPh_2)]$ (**3**). The cluster (**2**) (53 mg) and excess of $P(C_6H_4Me\text{-}p)_3$ (*ca.* 10 mg) were stirred together at 80 °C in 1,2-dichloroethane (20 cm^3) until the bands of the reactants disappeared from the i.r. spectrum (≈ 2 h). Removal of the solvent, followed by t.l.c., gave complex (**3**) (46.5 mg, 87%) (Found: C, 39.75; H, 2.80; P, 4.55%; M^+ at m/z 1 321. Calc. for $C_{33}H_{31}O_9Os_3P_2$: C, 38.3; H, 2.4; P, 4.7%).

$[Os_3H(CO)_9\{P(OMe)_3\}(PPh_2)]$ (**4**). A mixture of complex (**2**) (80 mg) and excess of $P(OMe)_3$ (*ca.* 0.5 cm^3) in dichloromethane (30 cm^3) was heated at reflux for ≈ 1 h. Removal of the solvent and t.l.c. afforded complex (**4**) (73 mg, 92%) (Found: C, 25.35; H, 1.65; P, 5.60; M^+ at m/z 1 138. Calc. for $C_{24}H_{20}O_{12}Os_3P_2$: C, 25.3; H, 1.7; P, 5.45%).

$[Os_3H(CO)_9(PPh_2H)(PPh_2)]$ (**5**). Cluster (**2**) (72 mg) and excess of PPh_2H (0.2 cm^3) were stirred at room temperature in dichloromethane (40 cm^3) for 0.5 h. Removal of the solvent and then t.l.c. gave complex (**5**) (59 mg, 82%) [Found: C, 33.30; H, 1.80; P, 5.25%; M^+ at m/z 1 172. Calc. for $C_{24}H_{21}O_9Os_3P_2$: C, 33.0; H, 1.8; P, 5.2%; M^+ (^{192}Os) at m/z 1 200].

Thermolyses.—Compound (**3**) (35 mg) was heated at reflux in xylenes (30 cm^3) for 1 h. Removal of the solvent followed by t.l.c. gave $[Os_3H_2(CO)_8\{P(C_6H_4Me\text{-}p)_3\}\{P(C_6H_4)Ph\}]$ (**6**) (28 mg, 79%) (Found: C, 40.40; H, 3.00; P, 4.80. Calc. for $C_{42}H_{32}O_9Os_3P_2\text{·}0.5C_6H_{14}$: C, 39.9; H, 2.9; P, 4.6%).

Compound (**4**) (61 mg) was heated at 100 °C in toluene (40 cm^3) for 2 h. Removal of the toluene followed by t.l.c. afforded $[Os_3H_2(CO)_8\{P(OMe)_3\}\{P(C_6H_4)Ph\}]$ (**7**) (44 mg, 72%); M^+ at m/z 1 138.

Compound (**5**) (45 mg) was heated at reflux in dichloromethane (25 cm^3) for 3 h. T.l.c. of the residue from the reaction gave $[Os_3H_2(CO)_8(PPh_2)_2]$ (**8**) (30 mg, 67%); M^+ at m/z 1 172.

Crystal-structure Determination of $[Os_3H_2(CO)_9\{P(C_6H_4)Ph\}]$ (**2**).—Crystals of complex (**2**) were grown by slow evaporation of a dichloromethane–hexane mixture, and a suitable single crystal was mounted on a glass fibre.

Crystal data. $C_{21}H_{11}O_9Os_3P$, $M = 1\,008.87$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.394(1)$, $b = 17.421(2)$, $c = 21.862(2)$ Å, $\alpha = 109.90(1)$, $\beta = 92.20(1)$, $\gamma = 112.52(1)°$, $U = 4\,995.4$ Å^3 (by least-squares refinement of diffractometer angles from 50 automatically centred reflections in the range $15 < 2\theta < 25°$, $\lambda = 0.710\,69$ Å), $Z = 8$, $D_c = 2.68$ g cm^{-3}, D_m not measured, $F(000) = 3\,688$. Yellow platelet. Crystal dimensions (distance from centre): 0.182 (010, 0$\bar{1}$0) $\times$ 0.177 (100, $\bar{1}$00) $\times$ 0.067 ($\bar{1}$02,

$10\bar{2}$) × 0.181 ($1\bar{1}2$, $\bar{1}1\bar{2}$) × 0.194 ($4\bar{1}2$, $\bar{4}1\bar{2}$) mm, μ(Mo-K_α) = 153.18 cm^{-1}.

Data collection and processing.[17] Stoe-Siemens diffractomer, 24-step ω—θ scan mode with ω scan width 0.04°, scan speed ranging from 0.5 to 2.0 s per step, graphite-monochromated Mo-K_α radiation, 13 452 reflections measured ($5.0 < 2\theta < 45°$, $\pm h$, $\pm k$, $+l$), 13 041 unique [merging R = 0.024 after absorption correction (maximum, minimum transmission factors 0.140, 0.032)], giving 8 126 with $F > 5\sigma(F)$. Three check reflections showed no significant variation during data collection.

Structure analysis and refinement. Random start direct methods (Os atom) followed by normal heavy-atom procedures. Full matrix least-squares refinement (in four blocks for final cycles) with Os and P atoms anisotropic. Phenyl rings refined as rigid bodies with C–C fixed at 1.395 Å and C–C–C 120°. The weighting scheme $w = 4.6632/[\sigma^2(F) + 0'0008F_o^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final R and R' values were 0.056 and 0.056. Highest peak in final difference map 1.9 e Å^{-3} close to Os atom position. A list of final fractional atomic co-ordinates is presented in Table 5.

Table 5. Atomic co-ordinates (× 10^4) for [$Os_3H_2(CO)_9\{P(C_6H_4)Ph\}$] (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Molecule 1							
Os(1)	4 087(1)	7 231(1)	1 473(1)	O(1)	3 790(16)	7 127(15)	2 816(12)
Os(2)	2 065(1)	6 700(1)	958(1)	C(2)	5 336(19)	8 182(17)	1 843(13)
Os(3)	3 398(1)	7 077(1)	102(1)	O(2)	6 074(14)	8 773(13)	2 040(10)
P(1)	3 247(5)	8 153(4)	1 603(3)	C(3)	4 541(23)	6 215(21)	1 189(16)
C(10)	3 539(18)	8 875(16)	1 166(12)	O(3)	4 806(18)	5 705(16)	1 013(13)
C(11)	3 609(18)	8 474(16)	519(13)	C(4)	1 352(23)	5 519(21)	352(16)
C(12)	3 829(19)	9 034(17)	115(13)	O(4)	986(18)	4 756(17)	−36(13)
C(13)	3 937(18)	9 895(16)	383(13)	C(5)	1 363(18)	7 131(16)	573(12)
C(14)	3 881(22)	10 309(19)	1 077(15)	O(5)	832(15)	7 403(13)	388(11)
C(15)	3 654(18)	9 807(16)	1 453(12)	C(6)	1 342(27)	6 608(24)	1 674(19)
C(16)	3 181(14)	8 783(11)	2 422(7)	O(6)	974(20)	6 604(18)	2 087(14)
C(17)	4 007(14)	9 251(11)	2 914(7)	C(7)	4 302(21)	7 404(19)	−393(15)
C(18)	3 961(14)	9 707(11)	3 566(7)	O(7)	4 854(17)	7 560(15)	−747(12)
C(19)	3 088(14)	9 695(11)	3 725(7)	C(8)	3 212(20)	5 855(19)	−206(14)
C(20)	2 262(14)	9 226(11)	3 233(7)	O(8)	3 177(15)	5 095(14)	−351(11)
C(21)	2 308(19)	8 770(17)	2 581(14)	C(9)	2 373(17)	6 878(15)	−495(12)
C(1)	3 911(19)	7 166(17)	2 316(14)	O(9)	1 798(14)	6 771(13)	−915(10)
Molecule 2							
Os(21)	3 094(1)	3 435(1)	1 497(1)	O(201)	4 120(15)	3 698(14)	346(11)
Os(22)	1 071(1)	2 909(1)	992(1)	C(202)	3 876(22)	3 026(19)	1 850(15)
Os(23)	1 763(1)	3 066(1)	2 361(1)	O(202)	4 316(16)	2 740(14)	2 068(11)
P(21)	1 899(5)	1 992(4)	864(3)	C(203)	3 728(20)	4 645(19)	2 098(14)
C(210)	1 608(14)	1 274(12)	1 309(7)	O(203)	4 194(16)	5 354(15)	2 489(12)
C(211)	1 540(14)	1 681(12)	1 979(7)	C(204)	681(21)	3 834(18)	1 282(15)
C(212)	1 359(14)	1 137(12)	2 371(7)	O(204)	456(15)	4 444(13)	1 425(11)
C(213)	1 322(14)	256(12)	2 069(7)	C(205)	−180(21)	1 962(19)	668(14)
C(214)	1 380(14)	−103(12)	1 458(7)	O(205)	−931(15)	1 425(14)	483(10)
C(215)	1 507(14)	370(12)	1 054(7)	C(206)	1 248(21)	2 957(19)	152(14)
C(216)	1 938(13)	1 324(11)	19(7)	O(206)	1 402(15)	3 023(14)	−345(11)
C(217)	2 820(13)	1 363(11)	−138(7)	C(207)	2 807(21)	3 284(19)	2 965(15)
C(218)	2 866(13)	869(11)	−780(7)	O(207)	3 366(15)	3 306(13)	3 348(11)
C(219)	2 032(13)	337(11)	−1 264(7)	C(208)	1 935(22)	4 276(20)	2 648(15)
C(220)	1 150(13)	298(11)	−1 106(7)	O(208)	2 070(15)	5 005(14)	2 851(11)
C(221)	1 103(13)	792(11)	−465(7)	C(209)	782(19)	2 756(16)	2 854(13)
C(201)	3 764(19)	3 585(17)	777(11)	O(209)	259(15)	2 545(14)	3 149(11)
Molecule 3							
Os(31)	7 087(1)	6 372(1)	2 974(1)	O(301)	5 868(17)	5 499(15)	3 821(11)
Os(32)	9 086(1)	6 877(1)	3 524(1)	C(302)	6 365(19)	6 931(19)	2 784(15)
Os(33)	8 523(1)	7 162(1)	2 304(1)	O(302)	5 883(16)	7 291(14)	2 691(11)
P(31)	8 179(5)	7 722(5)	3 813(3)	C(303)	6 544(22)	5 303(19)	2 206(16)
C(310)	8 564(17)	8 689(15)	3 576(12)	O(303)	6 140(18)	4 657(16)	1 728(13)
C(311)	8 674(17)	8 501(15)	2 926(12)	C(304)	9 558(22)	6 046(19)	3 091(15)
C(312)	8 907(23)	9 218(20)	2 708(16)	O(304)	9 854(15)	5 515(13)	2 815(10)
C(313)	8 944(24)	10 081(21)	3 116(17)	C(305)	10 296(19)	7 857(18)	4 001(13)
C(314)	8 830(23)	10 194(21)	3 736(16)	O(305)	10 970(15)	8 431(14)	4 310(11)
C(315)	8 608(22)	9 513(20)	4 002(16)	C(306)	8 772(23)	6 503(20)	4 214(16)
C(316)	7 983(14)	8 039(12)	4 661(7)	O(306)	8 613(17)	6 280(15)	4 664(12)
C(317)	7 051(14)	7 822(12)	4 778(7)	C(307)	7 545(23)	7 103(21)	1 730(17)
C(318)	6 897(14)	8 097(12)	5 427(7)	O(307)	7 007(17)	7 100(16)	1 344(12)
C(319)	7 675(14)	8 589(12)	5 958(7)	C(308)	8 441(19)	5 953(17)	1 799(13)
C(320)	8 607(14)	8 806(12)	5 840(7)	O(308)	8 458(16)	5 285(14)	1 507(11)
C(321)	8 761(14)	8 531(12)	5 192(7)	C(309)	9 535(20)	7 657(18)	1 947(14)
C(301)	6 338(20)	5 849(18)	3 495(14)	O(309)	10 164(17)	8 008(15)	1 664(12)

Table 5 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Molecule 4							
Os(41)	2 059(1)	6 283(1)	5 455(1)	O(401)	768(15)	5 399(14)	6 268(11)
Os(42)	4 068(1)	6 926(1)	6 071(1)	C(402)	1 266(23)	6 690(20)	5 179(16)
Os(43)	3 494(1)	7 118(1)	4 808(1)	O(402)	768(17)	7 051(15)	5 097(12)
P(41)	3 049(5)	7 676(5)	6 295(4)	C(403)	1 597(23)	5 195(21)	4 665(17)
C(410)	3 317(18)	8 621(16)	6 055(12)	O(403)	1 302(17)	4 541(16)	4 202(12)
C(411)	3 495(20)	8 420(16)	5 384(14)	C(404)	3 817(19)	6 485(17)	6 755(13)
C(412)	3 673(21)	9 090(19)	5 114(15)	O(404)	3 591(16)	6 233(14)	7 195(11)
C(413)	3 674(24)	9 876(21)	5 509(17)	C(405)	5 233(20)	7 935(18)	6 616(14)
C(414)	3 507(24)	10 105(21)	6 178(17)	O(405)	5 897(17)	8 528(15)	6 936(12)
C(415)	3 330(21)	9 453(19)	6 448(15)	C(406)	4 790(21)	6 138(19)	5 635(15)
C(416)	2 856(14)	8 023(13)	7 147(7)	O(406)	5 165(17)	5 771(15)	5 434(12)
C(417)	1 936(14)	7 734(13)	7 288(7)	C(407)	7 545(20)	7 103(28)	1 730(21)
C(418)	1 809(14)	8 016(13)	7 943(7)	O(407)	7 007(18)	7 100(16)	1 344(13)
C(419)	2 602(14)	8 587(13)	8 457(7)	C(408)	841(23)	5 953(20)	1 799(16)
C(420)	3 522(14)	8 876(13)	8 317(7)	O(408)	8 458(19)	5 285(17)	1 507(13)
C(421)	3 649(14)	8 594(13)	7 662(7)	C(409)	10 164(22)	8 008(20)	1 664(16)
C(401)	1 255(19)	5 727(18)	5 913(13)	O(409)	8 441(21)	5 953(19)	1 799(16)

Table 6. Atomic co-ordinates (× 10^4) for $[Os_3H(CO)_9\{P(OMe)_3\}(PPh_2)]$ (**4**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	1 537(1)	1 591(1)	2 479(1)	C(12)	−361(15)	1 596(11)	1 851(10)
Os(2)	4 423(1)	2 443(1)	3 556(1)	C(13)	2 059(12)	1 260(9)	1 088(9)
Os(3)	2 609(1)	3 897(1)	2 713(1)	C(21)	4 976(12)	1 138(9)	3 048(8)
P(1)	4 688(3)	3 414(2)	2 117(2)	C(22)	3 897(12)	1 914(10)	4 790(9)
P(2)	1 348(3)	−208(2)	2 638(2)	C(23)	6 292(11)	3 118(8)	4 278(8)
O(1)	−62(10)	−846(8)	2 889(10)	C(31)	1 050(13)	4 049(10)	3 514(9)
O(2)	1 698(14)	−923(7)	1 710(10)	C(32)	1 510(13)	3 859(10)	1 402(10)
O(3)	2 419(12)	−394(9)	3 586(11)	C(33)	3 281(12)	5 423(10)	2 916(8)
O(11)	621(9)	1 883(7)	4 639(6)	C(41)	6 283(10)	4 489(8)	2 363(7)
O(12)	−1 477(10)	1 660(11)	1 449(9)	C(42)	6 585(11)	5 206(8)	3 280(8)
O(13)	2 174(10)	971(8)	257(7)	C(43)	7 812(13)	6 013(10)	3 499(9)
O(21)	5 381(10)	360(6)	2 743(7)	C(44)	8 754(14)	6 086(11)	2 788(10)
O(22)	3 675(9)	1 593(8)	5 550(6)	C(45)	8 494(12)	5 391(10)	1 876(9)
O(23)	7 391(8)	3 455(7)	4 756(6)	C(46)	7 263(11)	4 573(9)	1 665(8)
O(31)	163(10)	4 170(8)	3 973(7)	C(51)	4 714(9)	2 833(7)	780(6)
O(32)	797(10)	3 855(8)	608(6)	C(52)	4 182(11)	3 326(9)	−34(8)
O(33)	3 666(11)	6 330(6)	3 023(8)	C(53)	4 269(12)	2 930(9)	−1 053(9)
C(1)	−1 450(20)	−688(15)	2 838(13)	C(54)	4 897(11)	2 029(9)	−1 262(8)
C(2)	1 094(18)	−1 993(15)	1 246(13)	C(55)	5 949(12)	755(10)	−756(9)
C(3)	2 486(16)	−1 301(13)	4 105(11)	C(56)	5 326(11)	1 934(8)	565(8)
C(11)	1 017(12)	1 834(9)	3 853(8)				

Programs and computers used and sources of scattering factor data are given in ref. 15.

Crystal-structure Determination of $[Os_3H(CO)_9\{P(OMe)_3\}(PPh_2)]$ (**4**).—Crystals of (**4**) were grown by slow evaporation of a hexane solution, and a suitable single crystal was mounted on a glass fibre.

Crystal data. $C_{24}H_{20}O_{12}Os_3P_2$, $M = 1\,132.94$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.586(1)$, $b = 12.605(1)$, $c = 13.023(1)$ Å, $\alpha = 96.81(1)$, $\beta = 98.10(1)$, $\gamma = 99.17(1)°$, $U = 1\,521.9$ Å^3 (by least-squares refinement of diffractometer angles from 50 automatically centred reflections in the range $15 < 2\theta < 25°$, $\lambda = 0.710\,69$ Å), $Z = 2$, $D_c = 2.47$ g cm^{-3}, D_m not measured, $F(000) = 1\,036$. Pale yellow plates. Crystal dimensions (distance to faces from centre): 0.080 (010, $0\bar{1}0$) × 0.040 ($0\bar{1}1$, $01\bar{1}$) × 0.285 (100, $\bar{1}00$) × 0.266 ($\bar{1}10$, $1\bar{1}0$) mm, μ(Mo-K_α) = 126.31 cm^{-1}.

Data collection and processing.[15] Stoe-Siemens diffractometer, 24-step ω—θ scan mode with ω scan width 0.05°, ω scan speed ranging from 0.5 to 0.2 s per step, graphite-monochromated Mo-K_α radiation; 4 497 reflections measured ($5.0 < 2\theta < 45°$, $-h$, $\pm k$, $\pm l$), 3 985 unique [merging $R = 0.011$ after numerical absorption correction (maximum, minimum transmission factors 0.425, 0.076)], giving 3 617 with $F > 4\sigma(F)$. Three check reflections showed no significant variation during data collection.

Structure analysis and refinement. Patterson synthesis (Os atoms) followed by normal heavy-atom procedures. Full-matrix least-squares refinement with Os, P, and O atoms anisotropic, and phenyl H atoms in calculated positions (C–H 1.08 Å and C–C–H 120°) with a fixed overall thermal parameter of 0.09 Å^2. The weighting scheme $w = 1.7726/[\sigma^2(F) + 0.0005F_o^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final R and R' values were 0.036 and 0.038. Highest peak in final difference map 1.8 e Å^{-3} close to the Os atom positions. Final fractional atomic co-ordinates are presented in Table 6. Programs and computers used and sources of scattering factor data are given in ref. 15.

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

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References

1 E. Sappa, A. Tiripicchio, and P. Braunstein, *Coord. Chem. Rev.*, 1985, **65**, 219; O. J. Schener, *Angew. Chem., Int. Ed. Engl.*, 1984, **24**, 925 and refs. therein.

2 P. E. Garrou, *Chem. Rev.*, 1985, **85**, 717; C. Bergounhou, J-J. Bonnet, P. Fompeyrine, G. Lavigne, N. Lugan, and F. Mansilla, *Organometallics*, 1986, **5**, 60; N. Lugan, J-J. Bonnet, and J. A. Ibers, *J. Am. Chem. Soc.*, 1985, **107**, 4484; D. J. Brauer, G. Hasselkuss, S. Hietkamp, H. Sommer, and O. Stelzer, *Z. Naturforsch., Teil B*, 1985, **40**, 961; D. J. Brauer, S. Hietkamp, H. Sommer, and O. Stelzer, *ibid.*, p. 1977; J. A. Clucas, M. M. Harding, and A. K. Smith, *J. Chem. Soc., Chem. Commun.*, 1985, 1280; J. A. Clucas, D. F. Foster, M. M. Harding, and A. K. Smith, *ibid.*, 1984, 949; M. I. Bruce, O. B. Shawkataly, and M. L. Williams, *J. Organomet. Chem.*, 1985, **287**, 127.

3 S. B. Colbran, P. T. Irele, B. F. G. Johnson, P. T. Kaye, J. Lewis, and P. R. Raithby, following paper.

4 F. Iwasaki, M. J. Mays, P. R. Raithby, P. L. Taylor, and P. J. Wheatley, *J. Organomet. Chem.*, 1981, **213**, 185; K. Natarajan, L. Zsolnai, and G. Huttner, *ibid.*, **220**, 365; M. J. Mays, F. Pavelcik, P. R. Raithby, P. L. Taylor, and P. J. Wheatley, *Acta Crystallogr., Sect. B*, 1981, **37**, 2228.

5 S. B. Colbran, B. F. G. Johnson, J. Lewis, and R. M. Sorrell, *J. Organomet. Chem.*, 1985, **296**, C1.

6 R. P. Ferrari, G. A. Vaglio, O. Gambino, and G. Cetini, *J. Chem. Soc., Dalton Trans.*, 1972, 1998.

7 K. A. Azam, A. J. Deeming, R. E. Kimber, and P. R. Shukla, *J. Chem. Soc., Dalton Trans.*, 1976, 1853; C. C. Yin and A. J. Deeming, *ibid.*, 1974, 1013.

8 See, for instance, W. G. Jackson, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, 1975, **90**, C13; A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1974, 1415.

9 K. A. Azam, A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and L. New, *J. Chem. Soc., Chem. Commun.*, 1978, 1086.

10 M. R. Churchill and B. C. DeBoer, *Inorg. Chem.*, 1978, **16**, 878.

11 K. A. Azam, A. J. Deeming, J. P. Rothwell, M. B. Hursthouse, and J. D. J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.*, 1981, 2039.

12 A. J. Deeming, S. E. Kabir, N. I. Powell, P. G. Bates, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1987, 1529.

13 E. J. Ditzel, B. E. Hanson, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1987, 1285; E. J. Ditzel, B. F. G. Johnson, and J. Lewis, *ibid.*, pp. 1289, 1293.

14 P. R. Raithby, 'Transition Metal Clusters,' ed. B. F. G. Johnson, Wiley, New York, 1980.

15 V. D. Patel, A. A. Cherkas, D. Nucciarone, N. J. Taylor, and A. J. Carty, *Organometallics*, 1985, **4**, 1792.

16 B. F. G. Johnson, J. Lewis, and D. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407.

17 B. F. G. Johnson, J. Lewis, P. R. Raithby, S. N. A. B. Syed-Mustaffa, M. J. Taylor, K. H. Whitmire, and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1984, 2111.

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