Reactions of the Anionic Phenylphosphinidene Cluster $[Os_3(\mu\text{-}H)(\mu\text{-}PPh)(CO)_{10}]^-$ and Its Phenylphosphido Isomer $[Os_3(\mu\text{-}PHPh)(CO)_{10}]^-$ with Electrophiles. Crystal Structures of $[Os_3H(\mu\text{-}PMePh)(CO)_{10}]$ and $[\{Os_3H(PPh)(CO)_{10}\}_2Hg]$†

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Deprotonation of $[Os_3H(\mu\text{-}PHPh)(CO)_{10}]$ **3** gives the anion $[Os_3H(\mu\text{-}PPh)(CO)_{10}]^-$ **4** containing a nucleophilic phosphorus centre which reacts with H^+ to regenerate cluster **3** with the Ph group *exo* to the $Os(CO)_4$ group as in the starting material. However, MeI reacts with anion **4** at the most accessible side of the μ-PPh ligand to give $[Os_3H(\mu\text{-}PMePh)(CO)_{10}]$ **6** (X-ray structure reported) which has the Ph group *endo* and the Me group *exo* to the $Os(CO)_4$ group. Anion **4** reacts with $[AuCl(PMe_2Ph)]$ to give $[Os_3H(\mu\text{-}PhPAuPMe_2Ph)(CO)_{10}]$ **8** (Ph probably *endo*) but the thermally generated isomer of **4**, $[Os_3(\mu\text{-}PHPh)(CO)_{10}]^-$ **5**, reacts by the attack of gold at osmium atoms to give $[Os_3(\mu\text{-}AuPMe_2Ph)(\mu\text{-}PHPh)(CO)_{10}]$ **9** (Ph probably *endo*) which is isomeric with **8**. Compounds with P–Hg bonds are formed by the reaction of **4** with $[HgCl(R)]$ (R = Et, $PhCH_2$ or ferrocenyl) or with HgX_2 (X = Cl, Br or I). The X-ray structure of the Hg-bridged product, $[\{Os_3H(PPh)(CO)_{10}\}_2Hg]$, formed from anion **4** and HgX_2 or $[Fe(C_5H_5)(C_5H_4HgCl)]$, is described. Although the co-ordination of the Hg atom is closely linear [P–Hg–P 171.8(2)°], there are fairly close approaches of O atoms of axial CO ligands to this atom (Hg···O 2.88 and 2.85 Å). The conformations of the two μ_3-PPh groups are different.

The direct reaction of $[Os_3(CO)_{12}]$ **1** with PH_2Ph leads to fairly low yields of the phenylphosphido cluster $[Os_3H(\mu\text{-}PHPh)(CO)_{10}]$ along with the phenylphosphinidene cluster $[Os_3H_2(\mu_3\text{-}PPh)(CO)_9]$ and other products.[1,2] The problem with this route is that high temperatures are required for reaction. More recently high-yield routes have been developed.[3] The cluster $[Os_3(CO)_{11}(MeCN)]$ reacts rapidly with PH_2Ph to give $[Os_3(CO)_{11}(PH_2Ph)]$ **2** which is easily handled and can be isolated in good yield. Direct thermal decarbonylation of **2** might be expected to give $[Os_3H(\mu\text{-}PHPh)(CO)_{10}]$ **3** but a very effective and better way to decarbonylate is to deprotonate **2** with base to give $[Os_3(PHPh)(CO)_{11}]^-$ which quickly decarbonylates to $[Os_3(\mu\text{-}PHPh)(CO)_{10}]^-$. This decarbonylation is facile because the terminal phosphido ligand in the undecacarbonyl has a strong tendency to bridge and displace CO. Reprotonation of the decacarbonyl anion gives good yields of **3**. A very interesting feature of this chemistry is that the deprotonation of **3** leads to the kinetically controlled anion $[Os_3(\mu\text{-}H)(\mu\text{-}PPh)(CO)_{10}]^-$ **4** which persists in tetrahydrofuran (thf) solution at room temperature but which isomerises completely to $[Os_3(\mu\text{-}PHPh)(CO)_{10}]^-$ **5** on heating to $\geqslant 60$ °C.[3] We have studied the reactions of these anions with electrophiles {MeI, $[AuCl(PMe_2Ph)]$, HgX_2 or HgR(X) where R = Et or $PhCH_2$} with the intention of establishing the regioselectivity of addition (at metal or phosphorus atoms) and the stereochemistry of products of the general type $[Os_3(\mu\text{-}H)(\mu\text{-}PRPh)(CO)_{10}]$ and our results are presented here.

Results and Discussion

Reactions of Organic Electrophiles.—The cluster $[Os_3(\mu\text{-}H)(\mu\text{-}PHPh)(CO)_{10}]$ **3** was synthesised as reported briefly[3] by conversion of $[Os_3(CO)_{12}]$ **1** into $[Os_3(CO)_{11}(PH_2Ph)]$ **2** and subsequent deprotonation, decarbonylation and reprotonation of **2** to form **3**. Also, as reported, the deprotonation of **3** with dbu (1,8-diazabicyclo[5.4.0]undec-7-ene) in thf gave complete conversion into $[Os_3(\mu\text{-}H)(\mu\text{-}PPh)(CO)_{10}]^-$ **4**. Treatment of this with MeI (see Scheme 1) leads to a single TLC band containing a mixture of $[Os_3(\mu\text{-}H)(\mu\text{-}PMePh)(CO)_{10}]$ **6** and a minor amount of the starting material **3**. Repeat of this treatment on this mixture gave pure **6** as a single isomer, the stoichiometry of which was established by IR and ^1H and ^{31}P NMR data (Table 1). The $^{31}P\text{-}\{^1H\}$ NMR spectrum was a doublet (J_{PH} 16.2 Hz) because the proton-decoupling conditions we used did not extend as far as the hydride signal which remained coupled to phosphorus.

The X-ray structure of compound **6** (see later) showed that the phenyl ring is *endo* to the $Os(CO)_4$ unit, that is the structure is **6a** (Scheme 1) and it is very likely that this structure persists in solution. We needed a spectroscopic criterion to establish the *exo* or *endo* nature of similar compounds. The reported spectrum of the related compound $[Os_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_{10}]$ contains multiplets at δ 7.78 and 6.77 assigned to the *ortho*-hydrogen atoms of the two respective Ph rings.[4] The *ortho*-hydrogen atoms for compound **6** are at δ 7.77 so that an assignment of the signals in the PPh_2 complex would allow us to establish the stereochemistry in **6**. The corresponding PHPh cluster is known to have the Ph group *exo*, that is in the position corresponding to that in **6b**.[1,2] This configuration prevents unfavourable repulsions between the Ph group and an axial CO group of the $Os(CO)_4$ unit. The *ortho*-hydrogen atom signal is at δ 7.34 in this case, almost exactly the average of the two values for the PPh_2 compound. Assuming that the Ph groups of the

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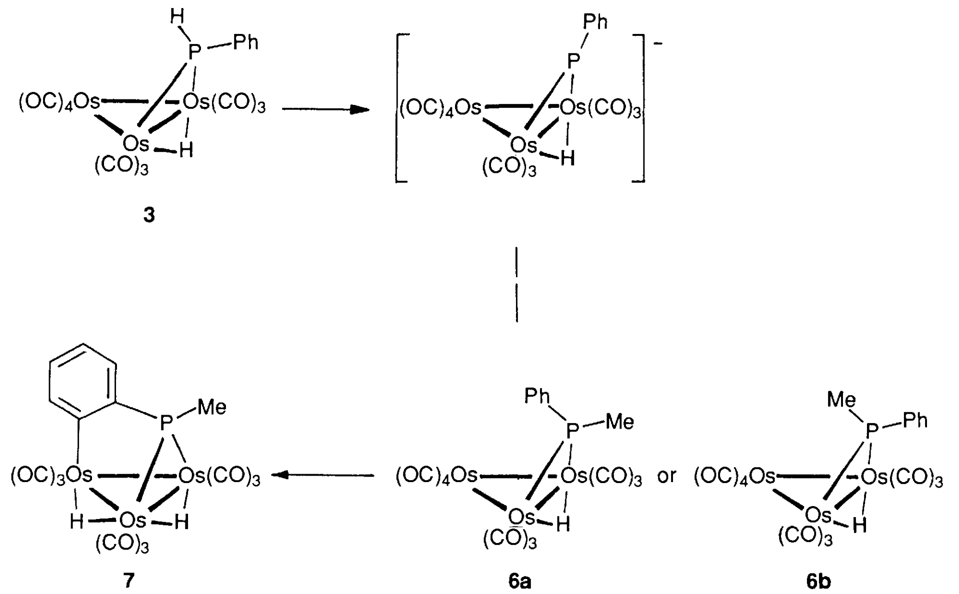
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



Scheme 1

Table 1 IR and NMR data for the complexes

Complex		ν(CO)/cm^{-1}	^{1}H NMR[a]	^{31}P NMR[b]
3	$[Os_3H(PHPh)(CO)_{10}]$	2108w, 2053m, 2036m, 2020s, 2002w, 1989m, 1976m[c]	7.34 (m, Ph), 7.05 (dd, PH, *J* 410, 4.4), −19.27 (dd, OsH, *J* = 17.2, 4.4)	38.26 (d, J_{PH} = 17.2)
6	$[Os_3H(PMePh)(CO)_{10}]$	2102m, 2060s, 2052s, 2020 (sh), 2017m, 2007w, 1992m, 1985m[d]	7.77 (m, Ph, *ortho*), 7.38 (m, Ph, *meta*, *para*), 1.92 (d, PMe, *J* 10.1), −18.65 (d, OsH, *J* 16.2)	84.72 (d, J_{PH} 16.2)
7	$[Os_3H_2(MePC_6H_4)(CO)_9]$	2105m, 2075s, 2048s, 2038m, 2022m, 2010s, 1995m, 1977m[c]	7.75 (m, *ortho* to Os), 6.94 (m, 3 H of C_6H_4), 2.13 (d, PMe, *J* 10.4), −17.12 (dd, OsH, *J* 1.6, 9.7), −17.26 (dd, OsH, *J* 1.6, 6.2)[e]	7.5 (br)
8	$[Os_3H(PhPAuPMe_2Ph)(CO)_{10}]$	2088m, 2043s, 2035m, 2004m, 1989m, 1974m[d]	7.74 (m, 2 H), 7.60 (m, 2 H), 7.52m (3 H), 7.17 (m, 3 H), 1.81 (dd, PMe, *J* 9.6, 2.0), −18.02 (dd, OsH, *J* 14.2, 2.1)	18.80 (d, *J* 327), 26.98 (dd, *J* 12.5, 327)
9	$[Os_3(AuPMe_2Ph)(PHPh)(CO)_{10}]$	2085m, 2031s, 2007m, 1998m, 1968w, 1960m[d]	7.71 (ddd, 2 H, *ortho*), 7.50 (m, 3 H), 7.46 (ddd, 2 H, *ortho*), 7.37 (dd, PH, *J* 394, 4.8), 7.30 (m, 3 H), 1.88 (d, *J* 9.6)	30.67 (d, *J* 10.2), 96.92 (d, *J* 10.2)
10	$[Os_3H(AuPMe_2Ph)(PPh)(CO)_9]$	2071m, 2050s, 2022s, 1997m, 1987m, 1975m, 1962w, 1942w[d]	7.93 (ddd, 2 H), 7.70 (m, 2 H), 7.48 (m, 3 H), 7.44 (m, 3 H), 1.94 (d, PMe, *J* 9.1), −23.25 (dd, *J* 11.4, 1.5)	
11	$[\{Os_3H(PPh)(CO)_{10}\}_2Hg]$	2094m, 2058s, 2047m, 2018m, 1988m, 1959[c]	7.40 (m, 2 H), 7.26 (m, 3 H), −18.69 (t, OsH)[f]	−10.6(t)[g]
12	$[Os_3H(PPhHgEt)(CO)_{10}]$	2092m, 2050s, 2039m, 2028m, 2010m, 1981s, 1965w[d]	7.44 (m, 2 H), 7.26 (m, 3 H), 1.72 (m, CH_2), 1.42 (dt, CH_3, J_{HH} 8.5, J_{PH} 10.5), −18.45 (d, *J* 15.1)	
13	$[Os_3H(PPhHgCH_2Ph)(CO)_{10}]$	2095m, 2055s, 2044m, 2018s, 1990s, 1962w[c]	7.4–7.0 (m, Ph_2), 2.97 (d, CH_2, *J* 7.5), −18.53 (d, *J* 15.5)	

[a] At 400 MHz in $CDCl_3$, *J* in Hz. [b] In $CDCl_3$ relative to H_3PO_4. [c] In thf. [d] In hexane. [e] At −55 °C, T_c *ca.* 27 °C. [f] Virtual triplet with outer peaks sharper and higher than broad central peak, $^{2}J_{PH} + {}^{4}J_{PH}$ = 12.0 Hz. [g] Virtual triplet, $^{2}J_{PH} + {}^{4}J_{PH}$ = 12 Hz.

PPh_2 compound are perpendicular as shown in Fig. 1 as found in closely related derivatives such as $[Os_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9\{P(OMe)_3\}]$,[4,5] the δ value for H^a would have a lower value than for the PHPh compound. This is because the H^a atom making a close approach to the face of the other phenyl group would be shielded (*i.e.* at low δ). Rotation about the P–C bonds would average the two sites for H^a so we examined the low-temperature ^{1}H NMR spectra of $[Os_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_{10}]$ but even at −80 °C rotation about the P–C bond is rapid. On the basis of the above arguments for the PPh_2 cluster we assign the signal at δ 6.77 to H^a and that at δ 7.78 to H^b. If there is only one phenyl group at phosphorus so that ring-current effects of one ring are not affecting another, the δ values for the *ortho*-hydrogen atoms of the *exo*- and *endo*-phenyl groups will be at around δ 7.3 and 7.8 respectively. This then requires cluster **6** to have structure **6a** in solution since the *ortho*-hydrogen atom signal is at δ 7.77. This is totally consistent with the crystallographic result.

Chemical reactivity also supports the stereochemistry **6a** since thermal decarbonylation leads to the ortho metallated compound **7** in Scheme 1. This assumes that inversion at phosphorus cannot occur at the reaction temperature (125 °C). Since it was important to have no doubt about the stereochemistry at phosphorus in compound **6**, a single-crystal X-ray structure determination was performed. The molecular structure is shown in Fig. 2 and selected bond lengths and angles

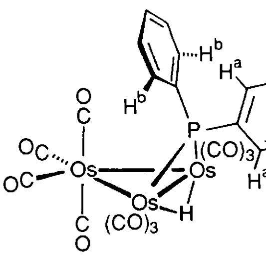


Fig. 1 Probable conformations of the phenyl rings in $[Os_3H(PPh_2)(CO)_{10}]$

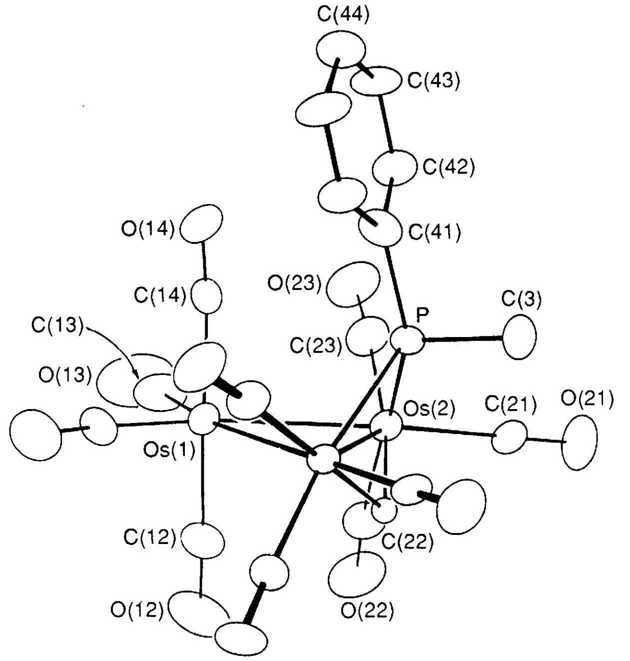


Fig. 2 Molecular structure of $[Os_3H(PMePh)(CO)_{10}]$ **6**. There is a crystallographic mirror plane through the molecule so unlabelled atoms have their labelled counterparts. The unlabelled Os atom is thus Os(2A)

Table 2 Selected bond lengths (Å) and angles (°) for $[Os_3H(PMePh)(CO)_{10}]$ **6**

Os(1)–Os(2)	2.8749(6)	Os(2)–Os(2A)	2.907(1)
Os(2)–P	2.368(3)	P–C(3)	1.83(2)
P–C(41)	1.77(2)	C(41)–C(42)	1.42(1)
C(42)–C(43)	1.37(2)	C(43)–C(44)	1.44(2)
Os(1)–Os(2)–Os(2A)	59.6(2)	Os(2)–Os(1)–Os(2A)	60.7(2)
Os(2)–P–Os(2A)	75.7(2)	Os(2)–P–C(3)	114.6(4)
Os(2)–P–C(41)	126.6(3)	C(3)–P–C(41)	99.2(7)
P–C(41)–C(42)	121.3(7)	Os(2)–Os(1)–C(12)	86.3(4)
Os(2)–Os(1)–C(14)	93.0(4)		

are in Table 2. The overall structure is as expected and the Ph group is shown to be *endo* to the $Os(CO)_4$ in contrast to its *exo* position in the starting material $[Os_3(\mu\text{-H})(\mu\text{-PHPh})(CO)_{10}]$ **3**. Apart from the different substituents at phosphorus, the overall geometry relates closely to those of similar compounds: $[Os_3H(PHPh)(CO)_{10}]$,[1] $[Os_3H(PPh_2)(CO)_9\{P(OMe)_3\}]$[4] and $[Os_3H_2(CF_3CO_2)(PPh_2)(CO)_9]$.[5] The dihedral angle between the ring Os(2)Os(2A)P and the Os_3 ring is 67.8° which is smaller than the 73.4° found in the PHPh analogue **3**. This reflects the effect of the repulsive interaction of the *endo*-Ph substituent in **6** with the adjacent axial CO ligand. The closest contacts between Ph and CO are C(41) ··· C(14) 3.11, C(41) ··· O(14) 2.94 and C(42) ··· O(14) 3.12 Å. The position of the axial CO also appears to have been affected by the close Ph group since angle Os(2)Os(1)C(14) is 93.0(4)°, larger than the corresponding angle for the CO *trans* to it which is 86.3(4)°.

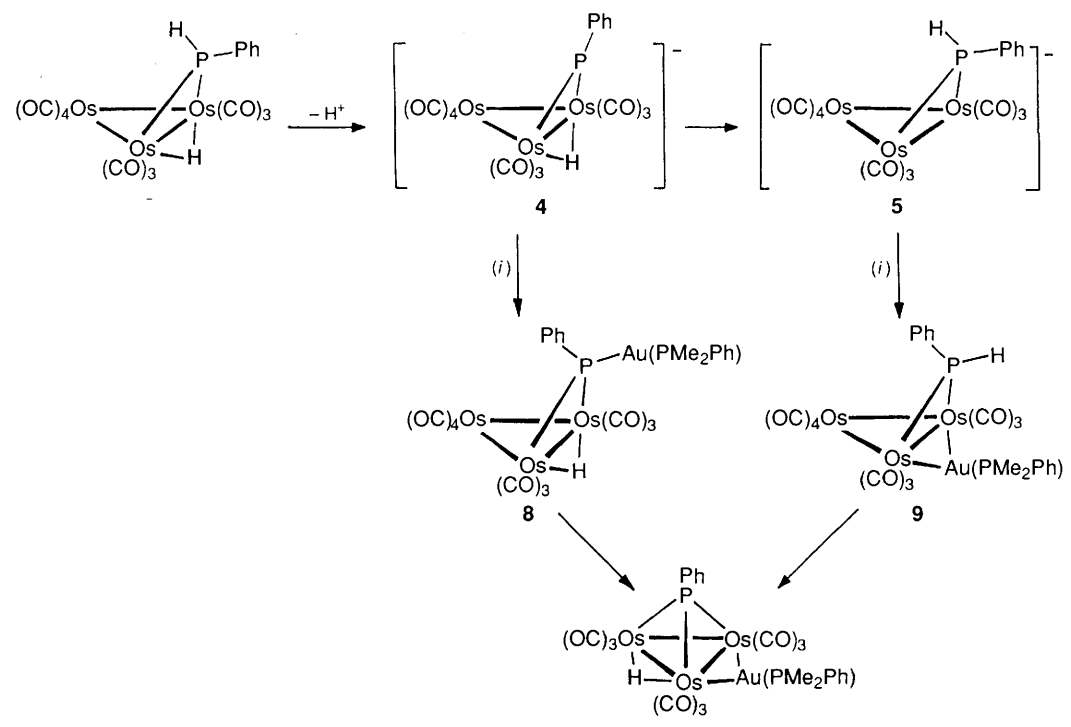
Whether the μ-phosphinidene in compound **4** is planar or pyramidal is still an open question. If it is pyramidal, deprotonation of **3** does not lead to any change in the number of electrons donated by phosphorus since there would be a stereochemically active 'lone pair'. In this case there must be an inversion from *exo*- to *endo*-phenyl before nucleophilic attack at methyl iodide takes place. If isomers of **4** with pyramidal phosphorus and with *exo*- and *endo*-Ph are in equilibrium, one would expect the *endo* isomer to be less populous but more nucleophilic since the lone pair is less crowded. This would react to give **6**. A planar phosphinidene would donate five electrons since one would expect this geometry to be achieved by π donation of the 'lone pair' at phosphorus. No Os–Os bond would be needed between the bridged atoms. The formation of compound **6** would occur by electrophilic addition from the less-crowded side. Protonation of **4** leads to the opposite isomer to that from methylation either because the protonation is reversible and the more stable isomer is then accessible or because protonation is less sterically restrictive and fast direct *endo* protonation is possible.

Reactions with Metallic Electrophiles.—Addition of dbu to cluster **3** followed by the addition of $[AuCl(PMe_2Ph)]$ as soon as the formation of anion **4** is complete gives the hydrido-cluster $[Os_3(\mu\text{-H})(\mu\text{-PhPAuPMe}_2Ph)(CO)_{10}]$ **8**. This is consistent with phosphorus being the most nucleophilic centre in **4**. From the $^{31}P\text{-}\{^1H\}$ NMR spectrum, J_{PP} was found to be 327 Hz, a value that is only consistent with both P atoms being bonded to Au. Furthermore there is no dynamic exchange. The chemical shift for the *ortho*-phenyl hydrogen atoms is δ 7.74, very similar to that in **6**, so we believe that the Ph group on phosphorus is *endo* to the $Os(CO)_4$ group. This requires a structure like **6b** with Me replaced by $AuPMe_2Ph$. Best yields of **8** were obtained by deprotonating **3** at −40 °C.

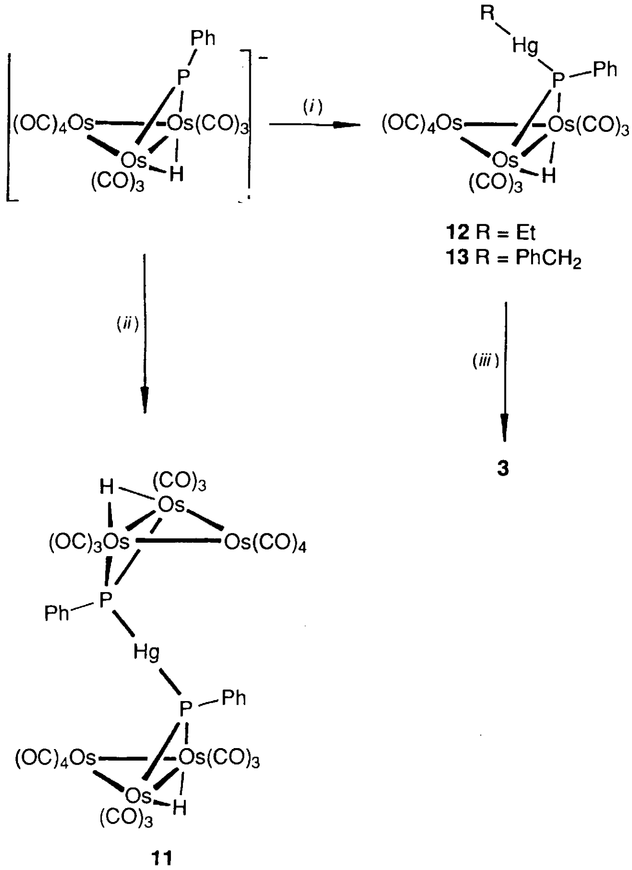
If, however, compound **3** is deprotonated with dbu in the thf and the mixture refluxed for 3 min to convert anion **4** to anion **5** before addition of $[AuCl(PMe_2Ph)]$, then an isomer of **8** is obtained, $[Os_3(\mu\text{-AuPMe}_2Ph)(\mu\text{-PHPh})(CO)_{10}]$ **9** (Scheme 2). The $^{31}P\text{-}\{^1H\}$ NMR spectrum now contains two doublets with J_{PP} = 10.2 Hz; this isomer does not have both P atoms bonded to the same metal atom; clearly **8** and **9** cannot be related as *exo* and *endo* isomers. Isomer **9** contains the PHPh ligand and no hydride (^1H NMR evidence, Table 1) so we believe that the $Au(PMe_2Ph)$ group is a μ ligand at osmium and behaves as a pseudo-hydride as described previously.[6] Again on the basis of the *ortho*-hydrogen chemical shift (δ 7.71 in this case) we believe that there is an *endo*-Ph group. Isomeric clusters **8** and **9** both decarbonylate thermally to the same compound, $[Os_3(\mu\text{-H})(\mu\text{-AuPMe}_2Ph)(\mu_3\text{-PPh})(CO)_9]$ **10**, formed by $AuPMe_2Ph$ or H migration respectively from P to Os atoms.

Anion **4** reacts similarly with the organomercury compounds $[HgBr(Et)]$ and $[HgBr(CH_2Ph)]$ to give the clusters **12** and **13** respectively (see Scheme 3) which were characterised by their spectra (Table 1). The stereochemistry with *exo*-phenyl groups is based on the chemical shifts of the *ortho*-protons (δ 7.44 for the ethyl compound) and comparison with the stereochemistry established for cluster **11**, see below. In contrast to these two organomercury compounds, anion **4** reacts with the ferrocenyl compound $[Fe(C_5H_5)(C_5H_4HgCl)]$ to give cluster **11** which does not contain the ferrocenyl group. The same compound was obtained from **4** and mercury(II) chloride, bromide, or iodide and was found to be halide-free. Compound **11** was shown to contain two Os_3 units since the ^1H NMR hydride signal is a virtual triplet characteristically appearing as a broad central peak and sharp outer peaks. Likewise the ^{31}P NMR spectrum, ^1H-decoupled except for the hydride, is also a virtual triplet. The phosphorus and hydride nuclei constitute a AA′XX′ set with a large J_{PP} value leading to virtual coupling.

To characterise compound **11** properly we determined its



Scheme 2 (*i*) [AuCl(PMe$_2$Ph)]



Scheme 3 (*i*) [HgBr(R)]; (*ii*) HgX$_2$ (X = Cl, Br or I); (*iii*) HCl

single-crystal X-ray structure which established the formula, [{Os$_3$(μ-H)(μ$_3$-PPh)(CO)$_{10}$}$_2$Hg]. Fig. 3 shows that the dinuclear unit is held together by a P–Hg–P bridge. The Ph groups in each cluster are *exo* to the Os(CO)$_4$ unit and the *ortho* protons have a ^{1}H NMR signal at δ 7.40 as expected for this *exo* arrangement. The P–Hg–P angle is 171.8(2)° (Table 3). There is a fairly close approach of axial CO groups to the Hg atom [Hg $\cdots$ O(14) 2.88 and Hg $\cdots$ O(42) 2.85 Å]. Although the Hg is essentially two-co-ordinate and linear, the O(14) and O(42) atoms cause a slight distortion towards a tetrahedral geometry. In spite of the rather open appearance of compound **11** in Fig. 3, the two Os$_3$ clusters are closely compacted and this has a consequence on the phenyl conformations. All known structures of similar type have Ph groups perpendicular to the Os$_3$ plane and bisecting two equatorial CO ligands. However, in **11** the Ph group at P(2) has this perpendicular conformation while the other at P(1) has the ring roughly parallel to the Os$_3$ plane. We think that there is only room for one Ph group to adopt the perpendicular arrangement since the Os$_3$ clusters tilt with respect to each other to make space on one side of the molecule for the perpendicular Ph group. Fig. 4 shows the crowding in this molecule. Because of these different conformations, the Os$_3$ units are different but NMR spectra at room temperature and even down to −75 °C show them to be equivalent; an AA′XX′ spectrum is observed for the phosphorus and hydride ligands. The most likely explanation is that the solid-state structure persists in solution but a rapid fluxional exchange of the clusters is occurring.

Experimental

The compounds [AuCl(PMe$_2$)Ph)][7] and [Fe(C$_5$H$_5$)(C$_5$H$_4$HgCl)][8] were prepared as described in the literature. The mercury compounds, [HgCl(Et)] and [HgCl(CH$_2$Ph)], and dbu were used as purchased from Aldrich. Light petroleum (b.p. 30–40 °C) was used as eluent for TLC and SiO$_2$ (HF$_{254}$ type 60, Merck) as the support.

Synthesis of [Os$_3$H(PHPh)(CO)$_{10}$] **3**.—Using a method similar to that indicated earlier,[3] a solution of [Os$_3$(CO)$_{12}$] **1** (0.366 g) in dichloromethane (400 cm^3) and acetonitrile (4 cm^3) was treated with a solution of Me$_3$NO·2H$_2$O (0.142 g) in methanol (1 cm^3). The mixture was stirred for 30 min at room temperature and filtered through a small silica column (60–120 mesh). The resulting solution of [Os$_3$(CO)$_{11}$(MeCN)] was treated directly with PH$_2$Ph (0.044 g) and stirred for 60 min.

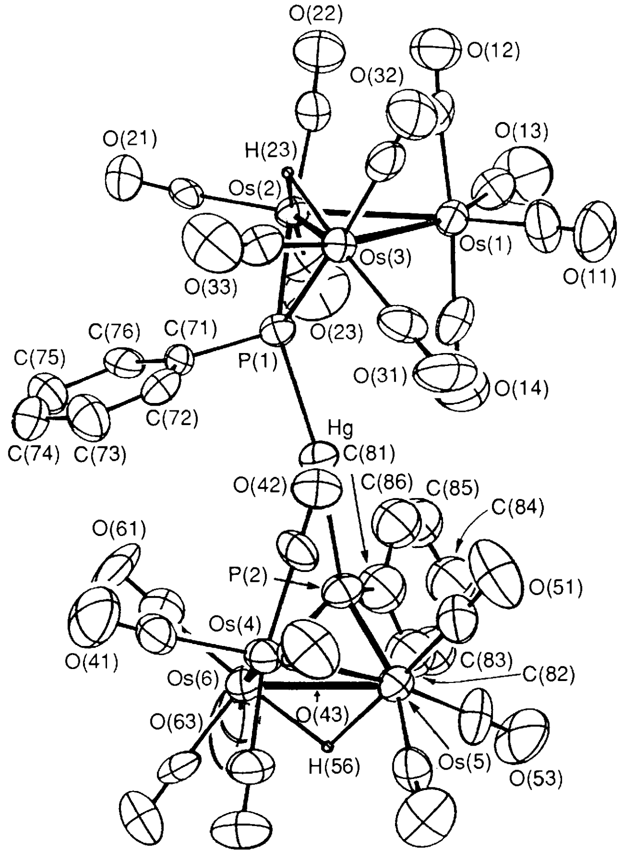


Fig. 3 Molecular structure of $[\{Os_3H(PPh)(CO)_{10}\}_2Hg]$ **11**

Table 3 Selected bond lengths (Å) and angles (°) for $[\{Os_3H(PPh)(CO)_{10}\}_2Hg]$ **11**

Os(1)–Os(2)	2.870(1)	Os(4)–Os(5)	2.873(1)
Os(2)–Os(3)	2.8956(9)	Os(5)–Os(6)	2.900(1)
Os(1)–Os(3)	2.875(1)	Os(4)–Os(6)	2.897(1)
Os(2)–P(1)	2.388(4)	Os(5)–P(2)	2.421(4)
Os(3)–P(1)	2.389(4)	Os(6)–P(2)	2.403(5)
Hg–P(1)	2.402(4)	Hg–P(2)	2.390(4)
P(1)–C(71)	1.84(2)	P(2)–C(81)	1.81(2)
C(71)–C(72)	1.36(2)	C(81)–C(82)	1.41(4)
C(72)–C(73)	1.42(3)	C(82)–C(83)	1.47(7)
C(73)–C(74)	1.38(3)	C(83)–C(84)	1.36(5)
C(74)–C(75)	1.43(3)	C(84)–C(85)	1.18(5)
C(75)–C(76)	1.41(3)	C(85)–C(86)	1.60(8)
C(71)–C(76)	1.38(2)	C(81)–C(86)	1.40(5)
Os(1)–Os(2)–Os(3)	59.81(2)	Os(4)–Os(5)–Os(6)	60.25(3)
Os(1)–Os(3)–Os(2)	59.65(2)	Os(4)–Os(6)–Os(5)	59.41(3)
Os(2)–Os(1)–Os(3)	60.54(2)	Os(5)–Os(4)–Os(6)	60.34(3)
Os(1)–Os(2)–P(1)	87.5(1)	Os(4)–Os(5)–P(2)	86.8(1)
Os(1)–Os(3)–P(1)	87.4(1)	Os(4)–Os(6)–P(2)	86.6(1)
Os(2)–P(1)–Os(3)	74.6(1)	Os(5)–P(2)–Os(6)	73.9(1)
Os(2)–P(1)–Hg	132.7(2)	Os(5)–P(2)–Hg	128.9(2)
Os(3)–P(1)–Hg	124.5(2)	Os(6)–P(2)–Hg	120.4(2)
Os(2)–P(1)–C(71)	117.9(5)	Os(5)–P(2)–C(81)	117.3(5)
Os(3)–P(1)–C(71)	117.4(5)	Os(6)–P(2)–C(81)	115.8(5)
Hg–P(1)–C(71)	92.5(5)	Hg–P(2)–C(81)	100.3(5)
P(1)–Hg–P(2)	171.8(2)		

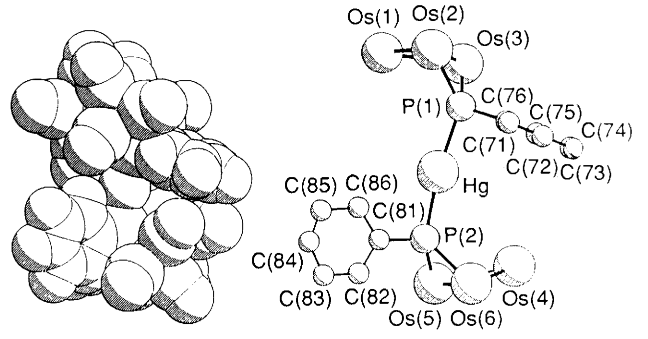


Fig. 4 Orientations of the phenyl rings in compound **11** showing that one phenyl is perpendicular and the other parallel to the Os_3 planes. The space-filling picture shows the close approach of the perpendicular ring to the CO ligands of the other cluster component and that there is insufficient space for both phenyl rings to be perpendicular

The solvent was removed under reduced pressure and the residue separated by TLC [eluent: light petroleum–dichloromethane (90:10 v/v)] to give a small amount of **1** near the solvent front and a major following band yielding $[Os_3(CO)_{11}(PH_2Ph)]$ **2** as bright yellow crystals (0.306 g, 76%) characterised by its spectrum; ν(CO) (thf) 2108w, 2053m, 2036m, 2020s, 2002w, 1989m and 1976m(br) cm^{-1}. A sample of compound **2** (0.117 g) in dry thf (50 cm^3) was treated with the base dbu (0.018 cm^3) to give an immediate change from pale yellow to deep orange as $[Os_3(PHPh)(CO)_{11}]^-$ is formed. The solution quickly became pale yellow as decarbonylation to $[Os_3(\mu\text{-}PHPh)(CO)_{10}]^-$ **5** occurred and this was treated with HCl gas. The solution quickly became cloudy and the IR spectrum confirmed the formation of **3**. The solvent was removed and TLC of the yellow residual oil as above gave one main yellow band which gave compound **3** as yellow crystals (0.074 g, 65%) characterised by data in Table 1.

Synthesis of $[Os_3(\mu\text{-}H)(\mu\text{-}PMePh)(CO)_{10}]$ **6**.—A solution of $[Os_3H(PHPh)(CO)_{10}]$ **3** (0.0609 g) in dry thf (50 cm^3) was treated with dbu (0.0144 cm^3) at room temperature and the IR spectrum indicated complete formation of the anion **4**. A large excess of methyl iodide (0.4 cm^3) was added and the solution stirred for 30 min and the solvent removed. TLC work-up [eluent: light petroleum–dichloromethane (95:5 v/v)] gave one major yellow band yielding a yellow oil (0.055 g) containing starting material **3** (minor) and product **6** (major). Retreatment of the oil with dbu then MeI as above and a similar work-up gave pure **6** as deep yellow crystals from a dichloromethane–hexane mixture (Found: C, 20.95; H, 0.95; P, 3.15. $C_{17}H_9O_{10}Os_3P$ requires C, 20.9; H, 0.7; P, 3.3%).

Decarbonylation of Cluster **6**.—A solution of compound **6** (0.020 g) in octane (20 cm^3) was refluxed under nitrogen. After 45 min the IR spectrum showed complete reaction and the yellow oil after the removal of the solvent was separated by TLC [eluent: light petroleum–dichloromethane (80:20 v/v)]. The leading band gave a very low yield of $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_9]$ and the major band gave $[Os_3(\mu\text{-}H)_2(\mu\text{-}MePC_6H_4)(CO)_9]$ **7** as yellow crystals (0.011 g, 56%).

Reactions of $[Os_3(\mu\text{-}H)(\mu\text{-}PHPh)(CO)_{10}]$ **3** *with Base followed by* $[AuCl(PMe_2Ph)]$.—(*a*) A solution of cluster **3** (0.0147 g) in dry thf (25 cm^3) was treated with dbu (0.0023 cm^3) at room temperature under argon. As soon as the IR spectrum showed that deprotonation was complete, $[AuCl(PMe_2Ph)]$ (0.0056 g) in thf (2 cm^3) was added leading to an immediate change from pale to deep yellow. The solvent was removed and the residue separated by TLC (eluent: light petroleum–dichloromethane (90:10 v/v)] to give a small amount of fast moving **3** and the major band which gave $[Os_3(\mu\text{-}H)(\mu\text{-}PhPAuPMe_2Ph)(CO)_{10}]$ **8** as orange crystals (0.010 g, 53%).

(*b*) By a similar procedure but allowing 10 min between complete deprotonation and the addition of the gold complex, two closely moving bands were resolved by TLC. One was the hydride **8** and the other its non-hydridic isomer $[Os_3(\mu\text{-}AuPMe_2Ph)(\mu\text{-}PHPh)(CO)_{10}]$ **9**. Cooling a hexane solution of **8** at −20 °C gave a pure sample of cluster **8** as orange crystals

Table 4 Crystallographic details* for $[Os_3(\mu\text{-H})(\mu\text{-PMePh})(CO)_{10}]$ **6** and $[\{Os_3(\mu\text{-H})(\mu_3\text{-PPh})(CO)_{10}\}_2Hg]$ **11**

	Compound **6**	Compound **11**
Formula	$C_{17}H_9O_{10}Os_3P$	$C_{32}H_{12}HgO_{20}Os_6P_2$
M	974.83	2120.18
Crystal system	Orthorhombic	Triclinic
Space group	*Pnma*	$P\bar{1}$
a/Å	15.401(3)	13.739(2)
b/Å	14.241(3)	18.908(2)
c/Å	10.090(3)	8.947(2)
α/°	90	89.77(2)
β/°	90	75.79(2)
γ/°	90	73.41(1)
U/Å^3	2213(2)	2154(1)
Z	4	2
D_c/g cm^{-3}	2.93	3.27
$F(000)$	1736	1860
μ/cm^{-1}	173.3	213.5
Collection temperature/°C	25 ± 1	−50 ± 1
2θ range/°	4–68	4–50
Unique data	5008	7572
Data with $F_o \geqslant 3\sigma(F_o)$	2839	6485
Parameters refined	155	520
R	0.0477	0.0474
R'	0.0560	0.0509
Largest shift/e.s.d.	0.04	0.03

* In common: Scan type $\omega - 2\theta$; Patterson solution method; $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 4F_o^2/[\sigma(F_o)^2]^2$; highest peak in final difference map 1.43 e Å^{-3}.

(Found: C, 22.25; H, 1.15; P, 5.25. $C_{24}H_{17}AuO_{10}Os_3P$ requires C, 22.3; H, 1.3; P, 4.75%).

(*c*) An improved yield of compound **8** was obtained by carrying out the deprotonation at −40 °C and adding the gold complex immediately.

(*d*) A better yield of compound **9** was obtained by refluxing a mixture of **3** (0.014 g) and dbu (0.003 cm^3) in thf (20 cm^3) for 3 min by which time anion **4** had been totally converted into anion **5** (IR evidence). The solution was cooled to room temperature and the gold complex (0.0056 g) in thf (1 cm^3) was added. The solution turned deep orange immediately and a TLC work-up as above gave a little of cluster **3** but mainly cluster **9** which crystallised from hexane at −20 °C (Found: C, 22.05; H, 1.05. $C_{24}H_{17}AuO_{10}Os_3P$ requires C, 22.3; H, 1.3%).

Reactions of $[Os_3(\mu\text{-H})(\mu\text{-PPh})(CO)_{10}]^-$ **4**.—*With mercury*(II) *chloride*. A solution of cluster **3** (0.024 g) in thf (25 cm^3) at −40 °C was treated with dbu (0.0038 cm^3). There was an immediate change to deep yellow-orange on addition of mercury(II) chloride (0.0068 g). The mixture was stirred for 30 min under argon and the oily residue after the removal of solvent was separated by TLC [eluent: light petroleum–dichloromethane (80:20 v/v)] to give cluster **3** (trace) and a slow-moving band which gave yellow microcrystals (0.0095 g) from a dichloromethane–hexane mixture at −20 °C. The product was characterised by its IR spectrum and an X-ray structure determination as $[\{Os_3(\mu\text{-H})(\mu_3\text{-PPh})(CO)_{10}\}_2Hg]$ **11**. Similar reactions using mercury(II) bromide or iodide gave the same product.

With alkylmercury(II) *halides*. [HgBr(Et)]. A solution of cluster **3** (0.028 g) in thf (25 cm^3) was treated with dbu (0.005 cm^3) at −30 °C. Then [HgBr(Et)] (0.009 g) was added and the solution was stirred at this temperature until there was no further change in the IR spectrum. Since cluster **3** was still observed to be present, more of the mercury compound (0.101 g in total) was added until all of **3** had been consumed. TLC of the residue after removal of the solvent [eluent: light petroleum–dichloromethane (75:25 v/v)] gave one broad diffuse band which gave deep orange crystals of $[Os_3(\mu\text{-H})(\mu\text{-PPhHgEt})(CO)_{10}]$ **12** (0.025 g, 75%) (Found: C, 19.2; H, 0.85; P, 3.15. $C_{18}H_{11}HgO_{10}Os_3P$ requires C, 18.2; H, 0.95; P, 2.6%).

Table 5 Fractional atomic coordinates for the cluster $[Os_3(\mu\text{-H})(\mu\text{-PMePh})(CO)_{10}]$ **6**

Atom	x	y	z
Os(1)	0.270 97(4)	0.250	0.040 48(6)
Os(2)	0.138 44(2)	0.147 93(3)	0.180 16(4)
P	0.164 6(2)	0.250	0.361 1(4)
O(12)	0.148(1)	0.250	−0.199(1)
O(13)	0.369 7(7)	0.086 0(7)	−0.079(1)
O(14)	0.398 6(7)	0.250	0.271(1)
O(21)	−0.009 8(6)	0.056 1(6)	0.325 6(9)
O(22)	0.075 7(6)	0.061 8(7)	−0.079 2(9)
O(23)	0.275 0(5)	−0.000 6(6)	0.233(1)
C(12)	0.193(1)	0.250	−0.108(2)
C(13)	0.334 2(9)	0.149(1)	−0.030(1)
C(14)	0.347 9(9)	0.250	0.190(1)
C(21)	0.043 4(6)	0.090 1(7)	0.273(1)
C(22)	0.100 4(7)	0.094 8(7)	0.013(1)
C(23)	0.223 0(7)	0.055 7(8)	0.217(1)
C(41)	0.257(1)	0.250	0.466(2)
C(42)	0.296 2(8)	0.164 8(8)	0.508(1)
C(43)	0.367 1(7)	0.164 2(9)	0.591(1)
C(44)	0.403(1)	0.250	0.635(2)
C(3)	0.079(1)	0.250	0.488(2)

$[HgBr(CH_2Ph)]$. A similar procedure using compound **3** (0.031 g), dbu (0.0049 cm^3), thf (30 cm^3) and $[HgBr(CH_2Ph)]$ (0.12 g) gave $[Os_3(\mu\text{-H})(\mu\text{-PPhHgCH}_2\text{Ph})(CO)_{10}]$ **13** as orange crystals (0.027 g, 60%) (Found: C, 23.2; H, 1.15; P, 2.55. $C_{23}H_{13}HgO_{10}Os_3P$ requires C, 22.1; H, 1.05; P, 2.5%).

$[Fe(C_5H_5)(C_5H_4HgCl)]$. A similar treatment using compound **3** (0.0406 g), dbu (0.0064 cm^3), thf (30 cm^3) and $[Fe(C_5H_5)(C_5H_4HgCl)]$ (0.0177 g) gave a single yellow TLC band which gave yellow crystals (0.012 g, 27%) of cluster **11**, spectroscopically identical to samples obtained from mercury(II) halides. Recrystallisation from a dichloromethane–hexane mixture gave crystals suitable for single-crystal X-ray structure determination (see below). No evidence was obtained for any product analogous to **12** or **13**.

Treatment of Clusters $[Os_3(\mu\text{-H})(\mu\text{-PPhHgR})(CO)_{10}]$ **12** *and* **13** *with Dry* HCl *Gas*.—A sample of compound **12** or **13** (*ca.* 0.005 g) in thf (5 cm^3) was treated with HCl gas until the IR spectrum showed that the reaction was complete. Proton NMR and IR measurements showed a total conversion into $[Os_3(\mu\text{-H})(\mu\text{-PHPh})(CO)_{10}]$ in each case.

Single-crystal X-Ray Structure Determinations of $[Os_3(\mu\text{-H})(\mu\text{-PMePh})(CO)_{10}]$ **6** *and of* $[\{Os_3(\mu\text{-H})(\mu_3\text{-PPh})(CO)_{10}\}_2Hg]$ **11**.—A yellow crystal of compound **6** with dimensions 0.23 × 0.30 × 0.53 mm was obtained by cooling a hexane solution and a yellow-orange crystal of **11** with dimensions 0.07 × 0.11 × 0.33 mm was obtained by evaporation of a dichloromethane–hexane solution at room temperature. Crystals were mounted on glass fibres on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.709 30 Å). Details of crystal data and intensity data collection, structure solution and refinement for **6** and **11** are in Table 4. Intensity data were collected at 25 ± 1 °C for **6** and at −50 ± 1 °C for **11** in the 2θ ranges given in Table 4.

In each case the intensities of two representative reflections were measured at intervals during the data collections and a linear decay correction applied. Lorentz and polarisation corrections and empirical absorption corrections based on ψ scans were made.

The solutions were solved with SHELX 86[9] using the Patterson heavy-atom method which revealed the positions of

Table 6 Fractional atomic coordinates for the cluster $[\{Os_3(\mu\text{-}H)(\mu_3\text{-}PPh)(CO)_{10}\}_2Hg]$ **11**

Atom	*x*	*y*	*z*
Hg	0.518 43(5)	0.225 86(3)	0.169 77(8)
Os(1)	0.148 86(5)	0.306 74(4)	0.204 85(8)
Os(2)	0.212 42(5)	0.357 70(3)	0.456 80(7)
Os(3)	0.264 09(5)	0.413 63(3)	0.154 86(7)
Os(4)	0.827 54(5)	0.238 64(4)	−0.147 04(9)
Os(5)	0.780 80(5)	0.103 93(4)	−0.202 93(8)
Os(6)	0.841 07(6)	0.127 62(4)	0.077 24(9)
P(1)	0.382 9(3)	0.336 6(2)	0.285 3(5)
P(2)	0.670 5(4)	0.124 9(2)	0.058 9(5)
O(11)	0.113(1)	0.298 5(9)	−0.118(2)
O(12)	−0.048(1)	0.441 2(8)	0.306(2)
O(13)	0.023(1)	0.207 2(9)	0.370(2)
O(14)	0.350(1)	0.174 7(9)	0.122(3)
O(21)	0.250(1)	0.445 2(8)	0.711(1)
O(22)	−0.018(1)	0.401 8(9)	0.638(2)
O(23)	0.271(1)	0.205 7(8)	0.573(2)
O(31)	0.384(1)	0.326 4(9)	−0.150(2)
O(32)	0.086(1)	0.516 5(8)	0.039(2)
O(33)	0.353(1)	0.544 9(7)	0.139(2)
O(41)	0.866(1)	0.344 9(8)	0.076(2)
O(42)	0.589(1)	0.308 2(7)	−0.079(2)
O(43)	0.829(1)	0.329 1(8)	−0.432(2)
O(44)	1.062(1)	0.163 8(9)	−0.294(2)
O(51)	0.611(1)	0.180 7(9)	−0.361(2)
O(52)	0.958(1)	0.082 7(7)	−0.501(2)
O(53)	0.766(1)	−0.050 2(7)	−0.261(2)
O(61)	0.756(1)	0.242 2(9)	0.352(2)
O(62)	1.071(1)	0.122(1)	0.041(2)
O(63)	0.878(2)	−0.001 0(9)	0.278(2)
C(11)	0.127(1)	0.302(1)	0.005(2)
C(12)	0.023(1)	0.393(1)	0.269(2)
C(13)	0.073(1)	0.243(1)	0.305(2)
C(14)	0.275(2)	0.227(1)	0.154(2)
C(21)	0.243(1)	0.412 0(9)	0.615(2)
C(22)	0.066(1)	0.385(1)	0.568(2)
C(23)	0.248(2)	0.263(1)	0.536(2)
C(31)	0.339(1)	0.363(1)	−0.041(2)
C(32)	0.149(1)	0.478 7(9)	0.089(2)
C(33)	0.323(1)	0.492(1)	0.146(2)
C(41)	0.851(1)	0.306(1)	−0.008(2)
C(42)	0.678(1)	0.280(1)	−0.094(2)
C(43)	0.829(1)	0.293 4(9)	−0.330(3)
C(44)	0.976(1)	0.188(1)	−0.231(2)
C(51)	0.676(1)	0.151(1)	−0.302(2)
C(52)	0.896(1)	0.091(1)	−0.390(2)
C(53)	0.773(2)	0.005(1)	−0.241(3)
C(61)	0.789(2)	0.199(1)	0.247(2)
C(62)	0.986(2)	0.125(1)	0.051(2)
C(63)	0.857(2)	0.047(1)	0.210(2)
C(71)	0.476(1)	0.376 2(9)	0.345(2)
C(72)	0.534(1)	0.413 0(9)	0.247(2)
C(73)	0.611(1)	0.438(1)	0.294(3)
C(74)	0.628(1)	0.426(1)	0.439(2)
C(75)	0.567(1)	0.387(1)	0.540(2)
C(76)	0.492(1)	0.362 4(9)	0.490(2)
C(81)	0.628(1)	0.048 4(9)	0.143(2)
C(82)	0.691(3)	−0.025(2)	0.104(4)
C(83)	0.663(4)	−0.088(3)	0.182(6)
C(84)	0.565(2)	−0.072(1)	0.280(3)
C(85)	0.499(4)	−0.015(3)	0.320(7)
C(86)	0.527(4)	0.054(3)	0.235(6)

three metal atoms in compound **6** and seven in **11**. The remaining atoms were located in successive Fourier syntheses and least-squares refinements. HYDEX[10] was used to calculate positions of hydride ligands and HYDRO[11] was used for the remaining hydrogen-atom positions. Hydrogen atoms were included in calculations for **6** but not for **11**. All non-H atoms were refined anisotropically. Anomalous dispersion effects were included in F_c; $\Delta f'$ and $\Delta f''$ and scattering factors were obtained from standard sources.[12]

Compound **6** has a crystallographic mirror plane passing through the Os(1) and P atoms and bisecting Os(2) and its symmetry-related counterpart. Compound **11** contains asymmetric molecules with non-equivalent $Os_3(\mu\text{-}H)(\mu\text{-}PPh)(CO)_{10}$ units differing notably in the conformations of the phenyl ligands. The phenyl group on P(1) refined well with normal thermal parameters for all the carbon atoms. That on P(2) shows a degree of disorder apparent from the high thermal parameters for C(82), C(83), C(85) and C(86). This indicates disorder with slightly different conformations about the P(2)–C(81) bond being present; normal thermal parameters were obtained for C(81) and C(84).

All calculations were performed on a MicroVax II computer using SDP/VAX.[11]

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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