Oxidative Addition of $Ph_3PCHCHO$ to $[Os_3(CO)_{10}(MeCN)_2]$†

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(Triphenylphosphoranylidene)ethanal ($Ph_3PCHCHO$) rapidly adds at room temperature or below to $[Os_3(CO)_{10}(MeCN)_2]$ to give the light-sensitive isomeric clusters $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PCCHO)(CO)_{10}]$ **1** (39%) and $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PCHCO)(CO)_{10}]$ **2** (34%) derived by C–H bond cleavage at the *CH*CHO and CH*CHO* positions respectively. Rates of oxidative addition are higher than for aldehydes or alkenes because of the greater nucleophilicity of this reagent; a reaction step involving co-ordination at osmium rather than subsequent C–H cleavage is probably rate-determining. Cluster **1** decarbonylates in daylight to give $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9]$ **3** containing the μ_3-ligand co-ordinated through an alkylidene bridge and a formyl group (X-ray structure). Cluster **3** is photochemically stable but thermally decarbonylates to give $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_4PPh_2CCHO)(CO)_8]$ **5** (X-ray structure) by orthometallation at one Ph ring of the triphenylphosphonium group. Like its isomer **1**, the decacarbonyl **2** also decarbonylates in visible light to give in this case two isomers of **3**, $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCO)(CO)_9]$ **4a** and **4b**, which differ only in the stereochemistry at the carbon atom Ph_3PCHCO. Selection of one crystal from a mixture of **4a** and **4b** allowed the crystal structure of isomer **4a** to be determined.

The cluster $[Os_3(CO)_{10}(MeCN)_2]$[1] and related compounds such as $[Os_3(CO)_{10}(C_8H_{14})_2]$[2] have a much higher reactivity towards oxidative addition than $[Os_3(CO)_{12}]$ because the acetonitrile or cyclooctene ligands are labile. An important type of reaction of these compounds is the oxidative addition of organic molecules (HX) with cleavage of C–H bonds to give $[Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$[3] where HX can be a wide range of organic species (such as alkenes,[4] aldehydes,[5] heterocyclics such as pyridine,[4,6] furan,[7] pyrrole[8] and others[9]). Some other molecules add with cleavage of other types of bond, for example selenophene adds with Se–C bond cleavage.[10] A common feature of these adding molecules is that they are all capable of co-ordinating prior to the C–H bond cleavage. However, even with a good ligand like pyridine (py) the first observed product is the oxidative-addition product, the 2-pyridyl complex $[Os_3(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_{10}]$, and the cluster $[Os_3(CO)_{10}(py)_2]$ is not observed. This indicates that the orthometallation is rapid if two co-ordination sites are accessible and simple pyridine complexes can only be obtained when there is just one labile ligand as in the reaction of $[Os_3(CO)_{11}(MeCN)]$ with pyridine.[6] This implies that the slow step in such reactions is the one in which MeCN is displaced by the adding molecule and that the C–H cleavage step that follows is rapid. In spite of the relative lability of the MeCN ligand, its displacement seems to be the rate-limiting step.

In this paper we describe some chemistry with a strong nucleophile ($Ph_3PCHCHO$) which has a major contribution from the zwitterionic form with a negative charge at the oxygen atom (Fig. 1). As expected from the above argument, rates of reaction with $[Os_3(CO)_{10}(MeCN)_2]$ and product yields are high, the acetonitrile ligand displacement and C–H bond-cleavage reactions occurring rapidly at well below room temperature because the co-ordination step is enhanced relative to less nucleophilic reagents. Only products in which C–H cleavage has occurred are observed. A communication of our work has appeared[11] and some related chemistry with ruthenium has been described by others.[12] Here we will emphasise the products of the decarbonylation reactions of the initial oxidative-addition products and their crystal structures.

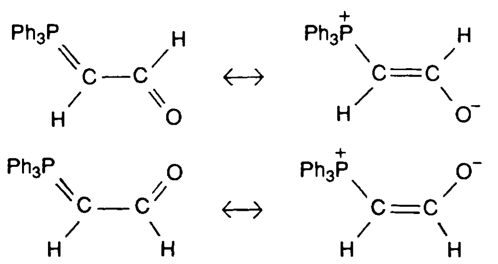

Fig. 1 Representations of the dipolar contributions to the electronic structures of $Ph_3PCHCHO$ in its *cis* and *trans* forms which are in equilibrium

Results and Discussion

Scheme 1 summarises the reactions and compounds described in this paper. Synthetic details are given in the Experimental section. When the reaction between $[Os_3(CO)_{10}(MeCN)_2]$ and $Ph_3PCHCHO$ was carried out in dichloromethane at room temperature an IR spectrum recorded immediately after mixing showed that reaction was complete. We have not measured rates but qualitatively the reaction is still rapid at 0 °C. The reaction, separation and isolation of products **1** and **2** were carried out in the dark because decarbonylation of both compounds in solution is induced by daylight. The crystals of each appear to be thermally and photochemically stable under the normal laboratory conditions.

The crystal structures of both compounds have been communicated.[11] We have been able to show that clusters **1** and **2** are derived by C–H cleavage at the *CH*CHO and CH*CHO* groups respectively. In both cases the oxygen atoms of the organic carbonyl groups are co-ordinated. The representations of **1** and **2** in Scheme 1 with P=C double bonds are, of course, extremes and the real situation will have delocalised π bonding along the PCCO chain and there will be significant positive charge at phosphorus. This corresponds to the situation for the free ligand (Fig. 1) and leads to the accumulation of negative charge at the metal atoms and a lowering of ν(CO) wavenumbers for the metal carbonyl ligands relative to those for related compounds derived from α,β-unsaturated

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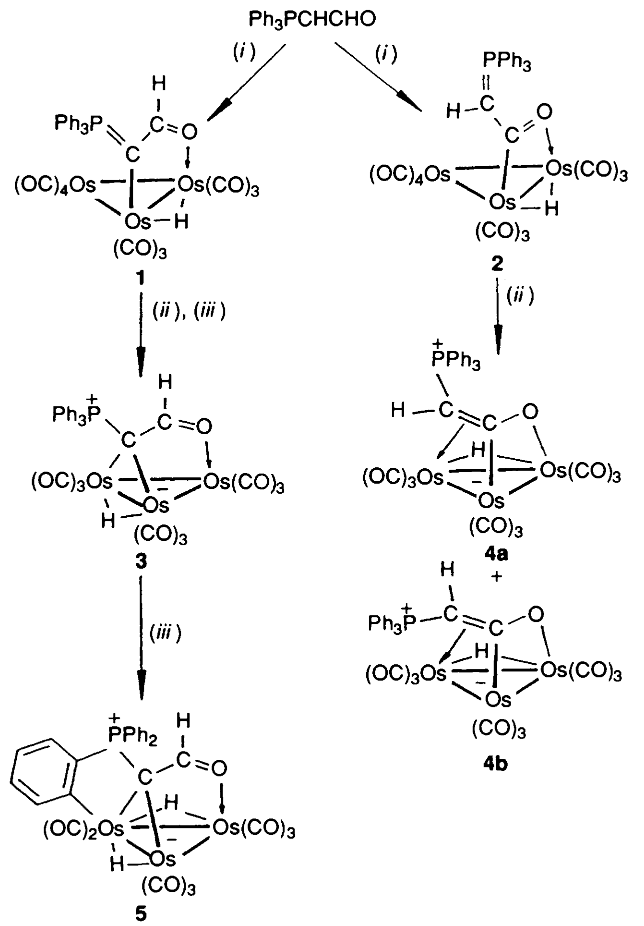
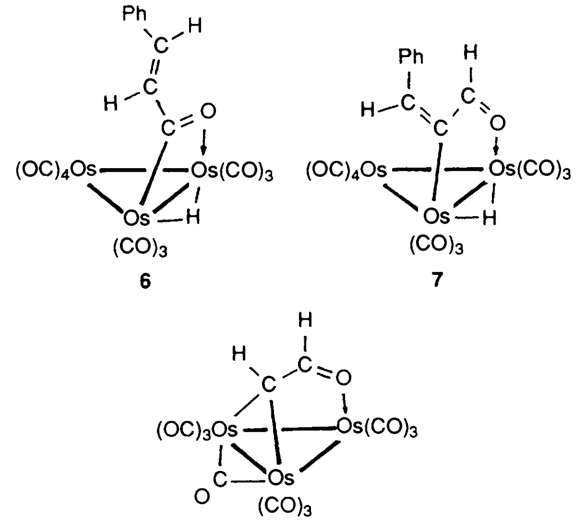
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 1 (*i*) $[Os_3(CO)_{10}(MeCN)_2]$, CH_2Cl_2, 20 °C; (*ii*) daylight, CH_2Cl_2, 20 °C; (*iii*) toluene at 100 °C or heptane at 96 °C



aldehydes. For example, the cluster $[Os_3(\mu\text{-H})(\mu\text{-PhCH=CH-CO})(CO)_{10}]$ **6** has ν(CO) wavenumbers 7–17 cm^{-1} higher than for cluster **2** while for $[Os_3(\mu\text{-H})(\mu\text{-PhCH=CCHO})(CO)_{10}]$ **7** they are 3–13 cm^{-1} higher than for cluster **1**.[13] Furthermore the length of the P–C bonds indicated as double in Scheme 1 are 1.73(1) Å for **1** and 1.75(1) Å for **2** compared with P–C bonds to phenyl which are normally in the range 1.80–1.83 Å. For the clusters **3**, **4a** and **5** (see later) the corresponding P–C distances are 1.80(1), 1.80(1) and 1.77(1) Å respectively, but in these cases the Ph_3P groups are regarded as fully developed phosphonium centres and the P–C bonds are believed to be single. Structures somewhere between **1a** and **1b** and between **2a** and **2b** (Fig. 2) are probably appropriate, there being some P–C multiple bonding together with a significant charge separation.

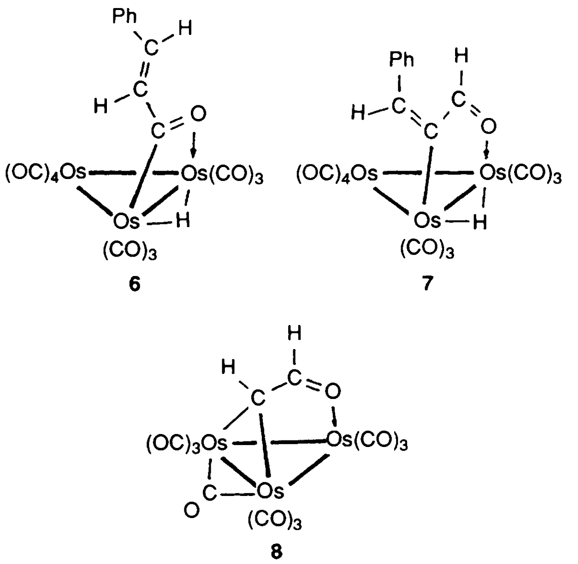


Fig. 2 Contributions **2a** and **2b** to the structure of cluster **2** and likewise contributions **1a** and **1b** to cluster **1**

Free $Ph_3PCHCHO$ exists as a mixture of *trans* and *cis* isomers as a result of multiple bonding in the central C–C bond (Fig. 1).[14] Clusters **1** and **2** also have the Ph_3P and O groups respectively *trans* and *cis* about the central C–C bond and it is tempting to deduce that each is formed from its respective isomer. However, although cluster **1** must have been formed from *trans*-$Ph_3PCHCHO$, **2** could have been formed from either isomer. *cis*–*trans* Interconversion should be very easy for cluster **2** and, since only the *cis* isomer is observed, this arrangement is the most stable. In view of the partial multiple P–C bonding we examined the reactions of **1** and **2** with aldehydes to see if any Wittig-type reactivity was present but, perhaps not surprisingly, no reaction was observed.

Unlike clusters **6** and **7** which are difficult to decarbonylate, **1** and **2** decarbonylate smoothly when dichloromethane solutions are kept in normal daylight in the laboratory, but not when kept in the dark at room temperature. Decarbonylation under similar conditions leads to good yields of the isomers $[Os_3(\mu\text{-H})(\mu_3\text{-}Ph_3PCCHO)(CO)_9]$ **3** and $[Os_3(\mu\text{-H})(\mu_3\text{-}Ph_3PCHCO)(CO)_9]$ **4** as shown in Scheme 1. The crystal structure of **3** has been determined and is shown in Fig. 3; selected bond lengths and angles are in Table 1. The μ_3-ligand is co-ordinated through the alkylidene bridging atom C(2) to Os(2) and Os(3) while a formyl group is co-ordinated through O(1) to Os(1). The C(1)–O(1) distance of 1.27(2) Å is consistent with this being a double bond. The structure is closely related to those of $[Os_3(\mu_3\text{-CHCHO})(CO)_{10}]$ **8**[15] and $[Os_3(\mu\text{-H})_2(\mu_3\text{-}C_6H_3\text{-}RO)(CO)_9]$ ($R = PhCH_2$).[16] The P–C(2) bond is single [1.80(1) Å] and therefore the phosphorus atom is part of a phosphonium group which in itself implies that the metal atoms carry a negative charge because the cluster is neutral overall. As expected the ν(CO) wavenumbers for the metal carbonyls are much lower (*ca.* 20–30 cm^{-1}) than for cluster **8**, for example. The hydride ligand is apparent from the ^1H NMR spectrum (δ −12.71) but was not located in the structure determination. Apart from the asymmetry of the PPh_3 group, the molecule has an approximate mirror plane. The Os(1)–Os(2) and Os(1)–Os(3) lengths are very similar [2.785(1) and 2.783(1) Å respectively] and it is highly unlikely that just one of these carries a hydride bridge. The Os–Os–C (carbonyl) angles are also very similar for these two edges and are smaller than those for the other edge, Os(2)–Os(3) (see Table 1). Hence we believe

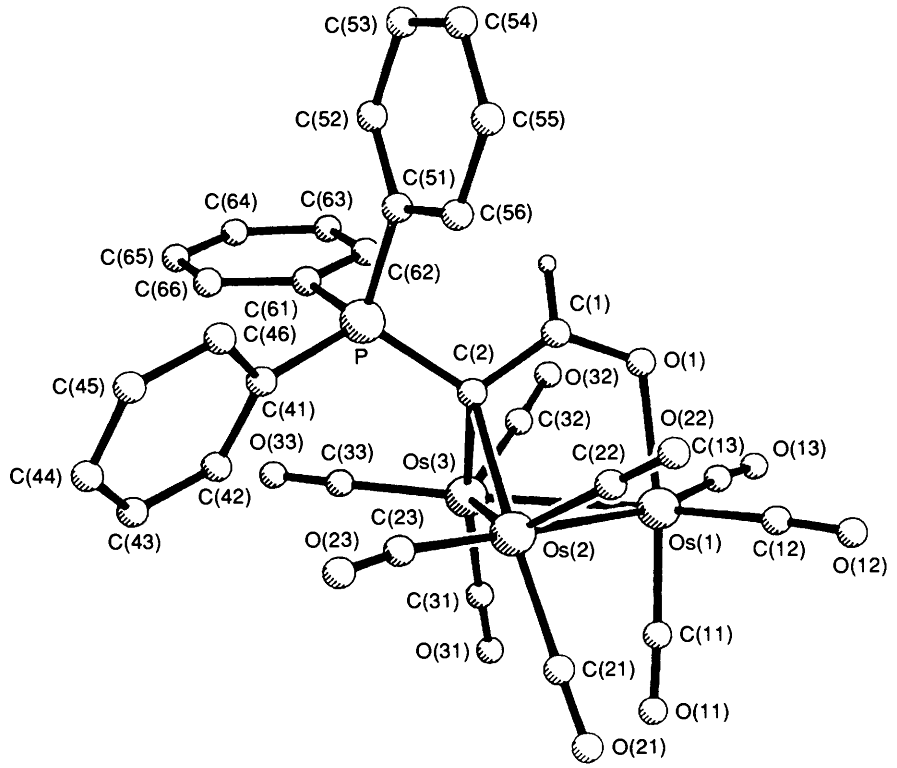


Fig. 3 Molecular structure of the cluster $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9]$ 3. The hydrogen atoms of the phenyl rings and the hydride are not shown; the hydride ligand bridges Os(2) and Os(3)

Table 1 Selected bond lengths (Å) and angles (°) for $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PCCHO)(CO)_9]$ **3**

Os(1)–Os(2)	2.785(1)	C(1)–O(1)	1.27(2)
Os(1)–Os(3)	2.783(1)	C(1)–C(2)	1.42(2)
Os(2)–Os(3)	2.811(1)	P–C(2)	1.80(1)
Os(2)–C(2)	2.25(1)	P–C(41)	1.80(1)
Os(3)–C(2)	2.24(1)	P–C(51)	1.83(1)
Os(1)–O(1)	2.14(1)	P–C(61)	1.83(1)
Os(2)–Os(1)–Os(3)	60.6(1)	C(1)–C(2)–P	110.0(9)
Os(1)–Os(2)–Os(3)	59.7(1)	Os(1)–Os(2)–C(22)	86.0(5)
Os(1)–Os(3)–Os(2)	59.7(1)	Os(1)–Os(2)–C(21)	90.1(4)
Os(2)–Os(3)–C(2)	51.5(3)	Os(1)–Os(3)–C(32)	83.1(4)
Os(3)–Os(2)–C(2)	51.1(4)	Os(1)–Os(3)–C(31)	92.4(4)
Os(1)–Os(3)–C(2)	76.9(3)	Os(2)–Os(1)–C(12)	97.7(6)
Os(1)–Os(2)–C(2)	76.7(3)	Os(2)–Os(1)–C(11)	91.3(4)
Os(3)–Os(1)–O(1)	83.7(2)	Os(3)–Os(1)–C(13)	103.0(4)
Os(2)–Os(1)–O(1)	83.6(2)	Os(3)–Os(1)–C(11)	89.8(4)
Os(2)–C(2)–Os(3)	77.5(4)	Os(2)–Os(3)–C(33)	120.3(5)
Os(1)–O(1)–C(1)	117.6(8)	Os(2)–Os(3)–C(31)	114.9(5)
O(1)–C(1)–C(2)	124(1)	Os(3)–Os(2)–C(23)	119.1(4)
Os(2)–C(2)–C(1)	111.0(7)	Os(3)–Os(2)–C(21)	113.1(5)
Os(3)–C(2)–C(1)	111.9(9)		

that the hydride bridges Os(2)–Os(3) and lies at the intersection of the vectors C(22)–Os(2) and C(32)–Os(3). The Os(2)–Os(3) bond is not as long [2.811(1) Å] as normally expected for hydride-bridged osmium atoms but this is commonly the case when there is an alkylidene bridge along the same edge. The effect of lengthening the Os–Os distance by the hydride is presumed to be limited by the presence of the alkylidene bridge. In the compounds $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9]$[17] and $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_3CH_2PhO)(CO)_9]$[16] where an alkylidene and a hydride bridge the same two osmium atoms these atoms are separated by 2.824(3) and 2.786(1) Å respectively, similar to the corresponding Os–Os distance of 2.811(1) Å in **3**.

Table 2 Selected bond lengths (Å) and angles (°) for $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_4PPh_2CCHO)(CO)_8]$ **5**

Os(1)–Os(2)	2.805(1)	C(1)–O(1)	1.24(1)
Os(1)–Os(3)	2.993(1)	C(1)–C(2)	1.41(1)
Os(2)–Os(3)	2.823(1)	P–C(2)	1.76(1)
Os(2)–C(2)	2.22(1)	P–C(41)	1.773(8)
Os(3)–C(2)	2.240(9)	P–C(51)	1.82(1)
Os(1)–O(1)	2.144(8)	P–C(61)	1.80(1)
Os(3)–C(42)	2.11(1)		
Os(2)–Os(1)–Os(3)	58.2(1)	C(2)–P–C(51)	117.3(5)
Os(1)–Os(2)–Os(3)	64.3(1)	C(2)–P–C(61)	111.9(5)
Os(1)–Os(3)–Os(2)	57.6(1)	C(41)–P–C(51)	112.7(4)
Os(2)–Os(1)–O(1)	84.9(2)	C(41)–P–C(61)	107.5(4)
Os(3)–Os(1)–O(1)	80.4(2)	C(51)–P–C(61)	102.7(5)
Os(1)–Os(2)–C(2)	77.0(3)	P–C(41)–C(42)	115.2(7)
Os(1)–Os(3)–C(2)	72.8(3)	C(41)–C(42)–Os(1)	118.6(6)
Os(2)–Os(3)–C(2)	50.5(3)	Os(1)–Os(2)–C(22)	90.0(3)
Os(3)–Os(2)–C(2)	51.0(2)	Os(1)–Os(2)–C(21)	90.1(3)
Os(2)–Os(3)–C(42)	94.5(3)	Os(2)–Os(1)–C(11)	90.4(3)
Os(1)–O(1)–C(1)	116.2(6)	Os(2)–Os(1)–C(12)	90.4(3)
Os(3)–C(2)–P	106.7(4)	Os(2)–Os(3)–C(31)	118.4(3)
Os(2)–C(2)–P	120.4(5)	Os(3)–Os(2)–C(23)	106.2(3)
Os(3)–C(2)–C(1)	106.9(7)	Os(3)–Os(2)–C(21)	117.4(3)
Os(2)–C(2)–C(1)	117.0(8)	Os(1)–Os(3)–C(32)	107.5(3)
O(1)–C(1)–C(2)	127(1)	Os(1)–Os(3)–C(31)	105.5(3)
C(1)–C(2)–P	117.5(8)	Os(3)–Os(1)–C(13)	113.5(3)
C(2)–Os(3)–C(42)	85.5(3)	Os(3)–Os(1)–C(11)	92.4(3)
C(2)–P–C(41)	104.5(5)		

Cluster **3** is photochemically stable but decarbonylates further on heating in refluxing heptane (96 °C) to give a good yield of the dihydride $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_4PPh_2CCHO)(CO)_8]$ **5**. Another C–H bond must have been cleaved and the wide spread of ^1H NMR signals in the phenyl region (δ 6.9–8.2) (see Experimental section) indicates that a phenyl group is involved in an orthometallation reaction. The crystal structure was determined to confirm this (Fig. 4). Selected bond lengths and angles are given in Table 2. The ligand

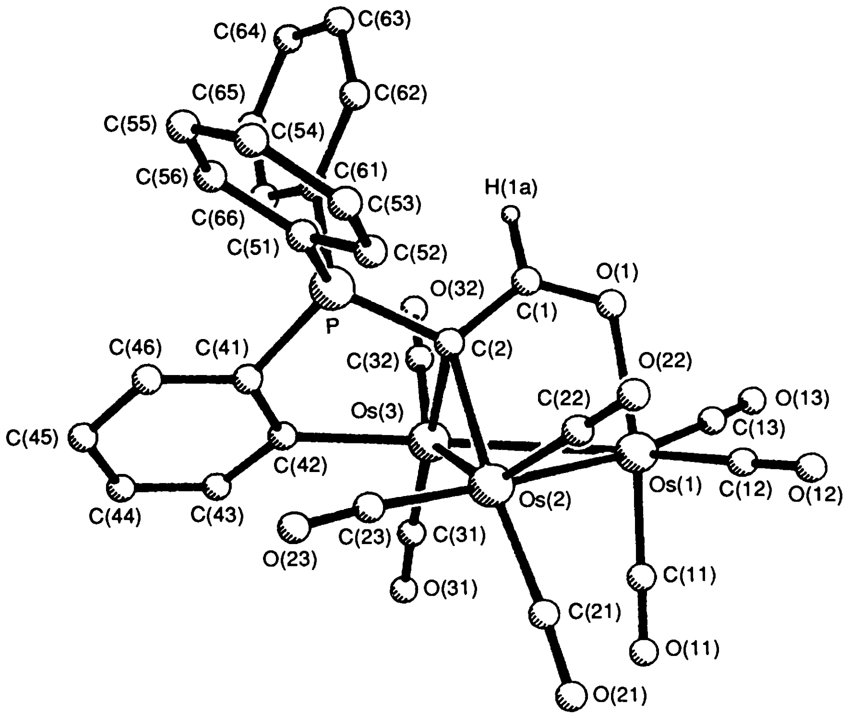


Fig. 4 Molecular structure of the cluster $[Os_3(\mu-H)_2(\mu_3-C_6H_4PPh_2CCHO)(CO)_8]$ **5**. The hydrogen atoms of the phenyl rings and the hydrides are not shown; one hydride ligand bridges Os(2) and Os(3) and the other Os(1) and Os(3)

Table 3 Selected bond lengths (Å) and angles (°) for $[Os_3(\mu-H)(\mu_3-Ph_3PCHCO)(CO)_9]$ **4a**

Os(1)–Os(2)	2.798(2)	Os(3)–C(1)	2.56(2)
Os(1)–Os(3)	3.031(2)	C(1)–O(1)	1.38(3)
Os(2)–Os(3)	2.775(2)	C(1)–C(2)	1.41(2)
Os(2)–C(1)	2.01(2)	P–C(2)	1.79(1)
Os(1)–C(2)	2.30(1)	P–C(41)	1.80(2)
Os(3)–O(1)	2.13(1)	P–C(51)	1.79(2)
Os(1)–C(1)	2.48(2)	P–C(61)	1.80(2)
Os(2)–Os(1)–Os(3)	56.7(1)	Os(2)–C(1)–O(1)	121(1)
Os(1)–Os(2)–Os(3)	65.9(1)	Os(2)–C(1)–C(2)	124(2)
Os(1)–Os(3)–Os(2)	57.4(1)	Os(1)–Os(2)–C(22)	96.0(7)
Os(2)–Os(3)–O(1)	73.3(3)	Os(1)–Os(2)–C(23)	99.9(6)
Os(1)–Os(3)–O(1)	76.7(3)	Os(2)–Os(1)–C(11)	90.2(7)
Os(3)–Os(2)–C(1)	62.2(7)	Os(2)–Os(1)–C(13)	89.5(6)
Os(1)–Os(2)–C(1)	59.4(6)	Os(2)–Os(3)–C(32)	88(1)
Os(2)–Os(1)–C(2)	72.3(2)	Os(2)–Os(3)–C(33)	95.9(8)
Os(3)–Os(1)–C(2)	83.7(3)	Os(3)–Os(2)–C(21)	97(1)
Os(3)–O(1)–C(1)	91(1)	Os(3)–Os(2)–C(23)	99.7(8)
O(1)–C(1)–C(2)	111(1)	Os(1)–Os(3)–C(31)	116.7(6)
C(1)–C(2)–P	123(1)	Os(1)–Os(3)–C(33)	93.3(7)
Os(1)–C(2)–P	122.9(7)	Os(3)–Os(1)–C(12)	117.7(7)
Os(1)–C(2)–C(1)	80(1)	Os(3)–Os(1)–C(13)	86.9(7)

$C_6H_4PPh_2CCHO$ is linked to the Os_3 cluster through three fused metallocycles (two five- and a three-membered ring). Other than the small distortions caused by the sideways pull of the Os–C(42) bond, the central O(1)C(1)C(2) bonding to the Os_3 is the same as in its parent, cluster **3**. The C(1)–O(1) distance of 1.24(1) Å is similar to that of **3**. Two hydride ^1H NMR signals are observed (δ −11.64 and −12.69) and, although the hydride ligands were not detected by the structure determination, we believe that these are positioned along the Os(1)–Os(3) [2.993(1) Å] and Os(2)–Os(3) [2.823(1) Å] edges. The Os(1)–Os(2) and Os(2)–Os(3) distances are fairly similar in compounds **3** and **5** but Os(1)–Os(3) has increased by 0.2 Å consistent with the introduction of the hydride at that edge. The Os–Os–C(carbonyl) angles have also increased at the Os(1)–Os(3) edge (see Table 2).

Cluster **2** also decarbonylates photochemically in daylight to give $[Os_3(\mu-H)(\mu_3-Ph_3PCHCO)(CO)_9]$, as a mixture of isomers **4a** and **4b**. The mixture was inseparable by TLC but a single crystal selected from a mass of crystals was shown to have structure **4a** (Scheme 1). The structure is shown in Fig. 5 and selected bond lengths and angles are given in Table 3. The μ_3-ligand is bonded through atoms C(1), C(2) and O(1) to the metal atoms. The hydrogen atoms of the phenyl rings and at C(2) were included in the model in idealised positions; it is clear from the geometry of C(2) that this atom does carry a hydrogen atom. Isomer **4b** is believed to have the alternative stereochemistry at C(2). The hydride ligand bridges the Os(1)–Os(3) edge [3.031(2) Å] rather than the others, which are shorter [Os(1)–Os(2) 2.798(2) and Os(2)–Os(3) 2.775(2) Å]. The equatorial Os–Os–C(carbonyl) angles at the Os(1)–Os(3) edge [116.7(6) and 117.7(7)°] are bigger than those at the other edges [90.2(7), 96.0(7), 97(1) and 88(1)°] as expected for the hydride positioned close to the Os_3 plane on the Os(1)–Os(3) edge near to the intersection of the Os(1)–C(11) and Os(3)–C(32) directions.

Vahrenkamp and co-workers[12] have reported the formation of the ruthenium analogue; $[Ru_3(CO)_{12}]$ reacts with $Ph_3P{=}CH_2$ in tetrahydrofuran (thf) at −20 °C to give some of the compound $[Ru_3(\mu-H)(\mu_3-Ph_3PCHCO)(CO)_9]$ **9**, the structure of which was determined. Cluster **9** decarbonylates thermally to $[Ru_3(\mu-H)_2(\mu_3-CPPh_3)(CO)_9]$ **10**. Clusters **9** and **10** were also obtained by reaction of $[Ru_3(CO)_{12}]$ with $Ph_3PCHCHO$ in refluxing cyclohexane (Scheme 2). The reaction was believed to go *via* the species **11**, analogous to cluster **2**, but the ruthenium cluster was not observed. The reaction of $[Ru_3(CO)_{10}(MeCN)_2]$ with Ph_3CHCHO was not described but we expect this to give cluster **11** at low temperatures under conditions that it might be expected to be detected or isolated. We originally reported cluster **4a** in a communication and described this as having structure **a** (Fig. 6), whereas the ruthenium analogue **9** was described by Vahrenkamp and co-workers as having structure **b**. It is clear, now that both structures are known, that clusters **9** and **4a** are directly comparable. Descriptions **a**–**c** in Fig. 6 should all be considered and the actual structure probably lies somewhere between these.

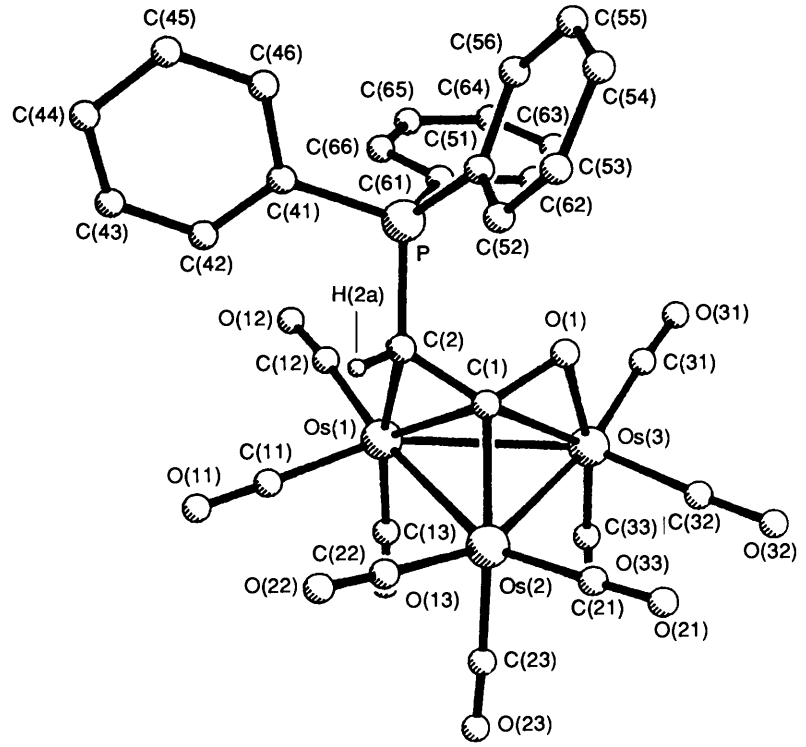
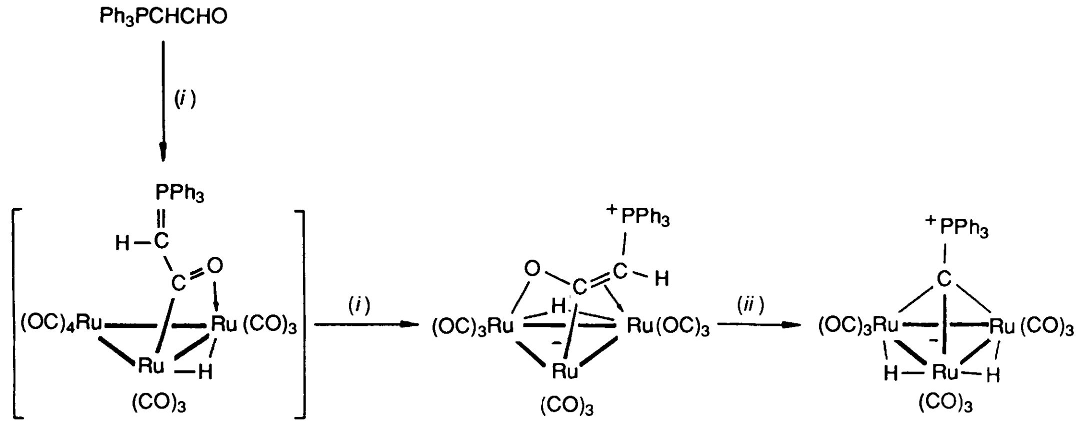


Fig. 5 Molecular structure of isomer **4a** of the cluser $[Os_3(\mu-H)(\mu_3-PPh_3CHCO)(CO)_9]$ **4**. The hydrogen atoms of the phenyl rings and the hydride are not shown; the hydride ligand bridges Os(1) and Os(3)



Scheme 2 (*i*) thf, −20 °C, $MeOSO_2CF_3$; (*ii*) refluxing cyclohexane

The C(1)–O(1) distance in **4a** is 1.38(3) Å and the corresponding distance in **9** is 1.31(3) Å. These distances are only slightly longer than those expected for double bonds. However, both C(1) and C(2) are bonded to Os(1) [Os(1)–C(1) 2.48(2) and Os(1)–C(2) 2.30(1) Å] so that the dihapto vinyl description also has validity. Even structure **c** has some possible contribution since the C(1)O(1) group could be considered to be dihapto to Os(3), albeit highly unsymmetrically co-ordinated [Os(3)–O(1) 2.13(1) and Os(3)–C(1) 2.56(2) Å]. None of the descriptions **a**–**c** is exclusively correct.

Experimental

Chromatographic separations were carried out using TLC on silica (HF_{254} type 60, E. Merck) prepared as an aqueous slurry, spread on glass sheets and dried at 100 °C. The light petroleum used as eluent had a boiling temperature <40 °C. (Triphenylphosphoranylidene)ethanal was obtained from Aldrich and used as obtained. The compound $[Os_3(CO)_{10}(MeCN)_2]$ was prepared as reported.[1]

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ *with* $Ph_3PCHCHO$.—A solution of $Ph_3PCHCHO$ (0.054 g, 0.18 mmol) in dichloromethane (2 cm^3) was added to a solution of the acetonitrile compound (0.150 g, 0.16 mmol) in dichloromethane (25 cm^3) in apparatus wrapped in aluminium foil. The reaction, work-up, TLC separation and isolation of products were carried out in the dark. After 15 min the solvent was removed under reduced pressure and the residue redissolved in CH_2Cl_2 and separated by TLC (eluent: CH_2Cl_2–light petroleum, 3:17 v/v) to give two yellow bands. The faster band was extracted with CH_2Cl_2 and gave $[Os_3(\mu-H)(\mu-Ph_3PCHCO)(CO)_{10}]$ **2** as yellow crystals (0.0721 g, 34%) from a CH_2Cl_2–hexane mixture (Found: C, 31.65; H, 1.5. $C_{30}H_{17}O_{11}Os_3P$ requires C, 31.2; H, 1.5%). IR ν(CO)/cm^{-1} (hexane): 2097m, 2055s, 2046s, 2012s, 2007s, 1994m, 1984(sh), 1979m, 1974(sh) and 1964m. ^1H NMR (200 MHz, $CDCl_3$): δ 7.6–7.4 (m, Ph), 4.20 [d, CHCO, *J*(PH) 29.3

Hz], and −14.45 (s, OsH). The slower band gave the isomer $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PCCHO)(CO)_{10}]$ **1** as yellow crystals (0.0827 g, 39%) from the same solvent mixture (Found: C, 32.7; H, 1.85). IR ν(CO)/cm^{-1} (CH_2Cl_2): 2097m, 2058s, 2042s, 2009s, 2003s, 1980m and 1956w. ^{1}H NMR (200 MHz, $CDCl_3$, 27 °C): δ 8.10 [d, CCHO, *J*(PH) 14.8 Hz], 7.7–7.5 (m, Ph) and −12.85 (s, OsH). These products are photochemically sensitive in solution but not as crystals.

Photolysis of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PCCHO)(CO)_{10}]$ **1**.—A clear yellow solution of cluster **1** (0.0954 g, 0.083 mmol) in dichloromethane (25 cm^3) was stirred under natural London daylight under nitrogen for 3 d to give a bright clear orange solution. The IR spectrum of the solution showed that no cluster **1** remained. TLC work-up [eluent: CH_2Cl_2–light petroleum (1:9 v/v)] gave one main orange band yielding $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9]$ **3** as orange crystals from a CH_2Cl_2–hexane mixture (0.0745 g, 80%), stable in the light at room temperature (Found: C, 31.9; H, 1.7. $C_{29}H_{17}O_{10}Os_3P$ requires C, 30.9; H, 1.5%). IR ν(CO)/cm^{-1} (CH_2Cl_2): 2071m, 2036vs, 2015s, 1985m and 1955m. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.65 [d, CCHO, *J*(PH) 7.0 Hz], 7.8–7.1 (m, Ph) and −12.71 (s, OsH).

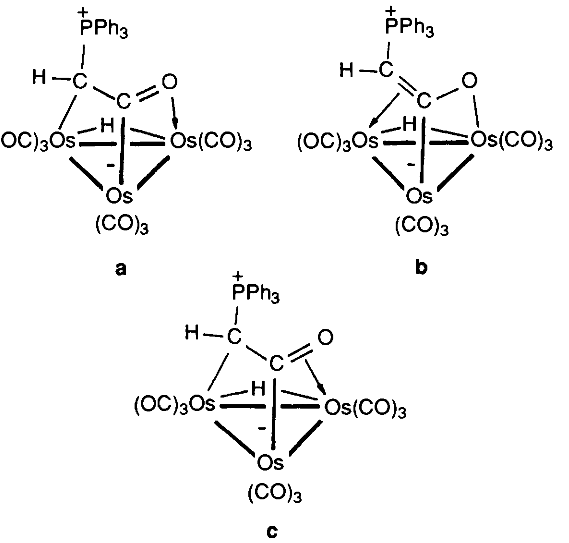


Fig. 6 These descriptions of the bonding in the cluster **4a** (see Fig. 5) which are considered; note that the carbon atom Ph_3PCHCO could be considered to be within bonding distance of all three metal atoms

Photolysis of $[Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PCHCO)(CO)_{10}]$ **2**.—A clear yellow solution of cluster **2** (0.090 g, 0.078 mmol) in dichloromethane (30 cm^3) was treated similarly with daylight for 3 d. TLC work-up eluting with light petroleum, then CH_2Cl_2–light petroleum (1:3 v/v), gave after repeated elutions two yellow bands. The faster band gave some starting material and the slower one gave a isomeric mixture of $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCO)(CO)_9]$ **4** which was deposited as yellow crystals (0.0658 g, 75%) from a CH_2Cl_2–heptane mixture. IR ν(CO) (CH_2Cl_2), mixture of **4a** and **4b**: 2078s, 2047vs, 2011s, 1995m and 1981m. ^{1}H NMR (200 MHz, $CDCl_3$): isomer **4a**, δ 7.7–7.3 (m, Ph), 3.07 [dd, CHCO, *J*(PH) 14.8, *J*(HH) 1.1], and −15.50 [t, OsH, *J*(PH) = *J*(HH) = 1.1]; isomer **4b**, δ 7.7–7.3 (m, Ph), 2.90 [d, CHCO, *J*(PH) 17.7 Hz] and −12.92 (s, OsH). Careful slow rechromatography gave no detectable separation or enrichment of isomers. A good-quality single crystal was chosen from the mixed sample for structure determination.

Thermolysis of $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9]$ **3**.—A suspension of cluster **3** (0.0444 g, 0.041 mmol) in heptane (11 cm^3) gave an orange solution on warming which was heated under reflux under nitrogen for 125 min. Solvent was removed under reduced pressure and the residue separated by TLC eluting with CH_2Cl_2–light petroleum (3:17 v/v) to give one major band yielding $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_4PPh_2CCHO)(CO)_8]$ **5** as yellow crystals (0.0366 g, 85%) from a dichloromethane–heptane mixture (Found: C, 32.9; H, 1.9. $C_{28}H_{17}O_9Os_3P$ requires C, 30.6; H, 1.6%) which were difficult to free from hydrocarbon impurity. IR ν(CO) (heptane): 2082s, 2044s, 2013vs, 1992s, 1973m, and 1944s. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.73 (dd, CCHO, *J* 6.8, 1.3), 8.22 (m, *ortho*-H of C_6H_4), 7.9–6.9 (m, C_6H_4 + Ph), −11.64 (d, OsH, *J* 5.3 Hz) and −12.69 (s, OsH). The sample contained traces of residual heptane

Table 4 Crystallographic data* for compounds $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9]$ **3**, $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCO)(CO)_9]$ **4a**, and $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}C_6H_4PPh_2CCHO)(CO)_8]$ **5**

	3	**4a**	**5**
Formula	$C_{29}H_{17}O_{10}Os_3P$	$C_{29}H_{17}O_{10}Os_3P$	$C_{28}H_{17}O_9Os_3P$
M	1127.03	1127.03	1099.02
Crystal size/mm	0.40 × 0.35 × 0.30	0.20 × 0.20 × 0.05	0.11 × 0.16 × 0.18
a/Å	10.222(2)	9.809(3)	10.290(3)
b/Å	11.014(2)	10.200(4)	11.173(3)
c/Å	14.454(3)	16.513(7)	13.290(4)
α/	79.05(2)	85.80(3)	83.29(2)
β/	86.67(2)	88.35(3)	88.02(2)
γ/	74.86(2)	67.46(3)	72.49(2)
U/Å^3	1542(1)	1522(1)	1447.2(7)
D_c/g cm^{-3}	2.49	2.46	2.52
μ(Mo-Kα)/cm^{-1}	124.2	126.1	132.6
F(000)	1028	1028	1000
No. orientation reflections, 2θ range/	25, 12 ⩽ 2θ ⩽ 30	19, 6 ⩽ 2θ ⩽ 22	29, 8 ⩽ 2θ ⩽ 26
Unique data	5466	5282	5108
Rejection criterion	$I_o < 3\sigma(I_o)$	$I_o < 1.5\sigma(I_o)$	$I_o < 1.5\sigma(I_o)$
Reflections used	4454	3512	4331
Parameters refined	388	295	370
R	0.0481	0.0664	0.0363
R'	0.0458	0.0568	0.0363
g	0.000 267	0.000 397	0.000 415
Maximum residual peak/e Å^{-3} (close to Os)	3.5	1.8	1.0

* For each compound: data recorded on a Nicolet R3v/m diffractometer using Mo-Kα radiation, λ = 0.710 73 Å; yellow crystal; crystal system, triclinic; space group $P\bar{1}$; *Z* = 2; scan mode ω 2θ, 2θ collection range 5 50 ; $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|]^{\frac{1}{2}}$ where $w = [\sigma^2(F_o) + g(F_o^2)]^{-1}$; maximum shift/e.s.d in final refinement <0.001.

Table 5 Fractional atomic coordinates (× 10^4) for $[\mathrm{Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCCHO)(CO)_9}]$ **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	3 320(1)	7 359(1)	2 183(1)	O(32)	6 420(13)	5 477(12)	1 019(8)
Os(2)	2 213(1)	5 587(1)	3 389(1)	C(33)	6 098(15)	3 273(13)	3 328(10)
Os(3)	4 974(1)	4 955(1)	2 888(1)	O(33)	6 911(12)	2 352(10)	3 525(9)
P	3 239(3)	2 860(3)	2 279(2)	C(41)	2 792(14)	1 997(11)	3 385(8)
C(1)	2 914(13)	5 235(11)	1 350(8)	C(42)	3 568(14)	1 818(13)	4 198(9)
C(2)	3 244(13)	4 497(10)	2 264(7)	C(43)	3 233(17)	1 111(13)	5 025(10)
O(1)	2 877(10)	6 418(8)	1 117(6)	C(44)	2 164(17)	573(13)	5 070(10)
C(11)	3 780(15)	7 986(12)	3 206(10)	C(45)	1 425(19)	717(15)	4 289(11)
O(11)	4 107(13)	8 328(10)	3 832(8)	C(46)	1 726(16)	1 433(13)	3 428(10)
C(12)	1 688(21)	8 697(15)	1 942(13)	C(51)	2 025(14)	2 799(11)	1 422(8)
O(12)	772(16)	9 537(13)	1 816(15)	C(52)	2 450(15)	2 086(14)	733(9)
C(13)	4 496(15)	8 132(14)	1 327(11)	C(53)	1 498(18)	2 081(17)	72(11)
O(13)	5 165(14)	8 662(12)	839(8)	C(54)	159(18)	2 807(18)	117(12)
C(21)	1 802(15)	6 705(13)	4 298(9)	C(55)	−187(17)	3 499(17)	788(12)
O(21)	1 564(14)	7 359(12)	4 799(9)	C(56)	718(14)	3 542(14)	1 450(10)
C(22)	592(17)	6 409(14)	2 766(11)	C(61)	4 890(13)	1 923(11)	1 947(8)
O(22)	−442(13)	6 905(13)	2 396(10)	C(62)	5 591(14)	2 471(12)	1 208(8)
C(23)	1 480(14)	4 327(13)	4 217(10)	C(63)	6 858(15)	1 800(14)	966(10)
O(23)	907(13)	3 758(10)	4 749(8)	C(64)	7 429(16)	575(16)	1 466(11)
C(31)	6 094(17)	5 658(13)	3 530(11)	C(65)	6 702(17)	43(14)	2 185(11)
O(31)	6 753(14)	6 107(12)	3 889(10)	C(66)	5 441(14)	690(12)	2 428(10)
C(32)	5 882(14)	5 295(12)	1 737(10)				

Table 6 Fractional atomic coordinates (× 10^4) for $[\mathrm{Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PCHCO)(CO)_9}]$ **4a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	2 632(1)	6 560(1)	6 401(1)	O(32)	6 068(23)	3 410(22)	9 229(14)
Os(2)	3 763(1)	3 794(1)	7 132(1)	C(33)	6 235(27)	5 483(22)	7 395(15)
Os(3)	4 431(1)	5 751(1)	7 952(1)	O(33)	7 346(17)	5 273(17)	7 116(12)
P	−581(6)	7 734(5)	7 688(3)	C(41)	−2 151(21)	8 345(19)	7 025(13)
C(1)	2 087(22)	5 343(19)	7 649(13)	C(42)	−1 973(27)	8 240(23)	6 187(15)
C(2)	819(12)	6 282(12)	7 229(8)	C(43)	−3 203(28)	8 630(25)	5 712(18)
O(1)	2 301(12)	5 896(12)	8 352(8)	C(44)	−4 598(27)	9 149(24)	5 994(16)
C(11)	1 853(26)	5 921(26)	5 536(14)	C(45)	−4 782(24)	9 307(21)	6 850(14)
O(11)	1 352(20)	5 576(20)	5 016(11)	C(46)	−3 565(22)	8 924(21)	7 348(14)
C(12)	1 767(21)	8 536(23)	6 049(13)	C(51)	−1 172(21)	7 094(20)	8 618(13)
O(12)	1 319(21)	9 681(18)	5 780(12)	C(52)	−974(22)	5 697(20)	8 739(13)
C(13)	4 408(24)	6 189(22)	5 849(14)	C(53)	−1 589(32)	5 236(33)	9 425(19)
O(13)	5 481(17)	6 027(16)	5 476(10)	C(54)	−2 253(29)	6 218(27)	10 017(18)
C(21)	4 294(33)	2 372(29)	7 953(16)	C(55)	−2 455(29)	7 607(29)	9 873(18)
O(21)	4 574(23)	1 467(19)	8 486(12)	C(56)	−1 912(25)	8 107(25)	9 185(15)
C(22)	2 620(30)	3 093(25)	6 526(16)	C(61)	−139(22)	9 242(20)	7 878(13)
O(22)	1 874(23)	2 672(22)	6 185(14)	C(62)	763(27)	9 122(26)	8 548(16)
C(23)	5 557(26)	2 996(21)	6 508(15)	C(63)	1 050(33)	10 324(30)	8 685(20)
O(23)	6 620(19)	2 530(19)	6 107(12)	C(64)	512(30)	11 532(30)	8 183(18)
C(31)	4 397(21)	7 271(25)	8 565(15)	C(65)	−266(33)	11 606(32)	7 548(20)
O(31)	4 469(20)	8 181(20)	8 932(12)	C(66)	−653(26)	10 438(24)	7 413(16)
C(32)	5 424(28)	4 275(31)	8 714(18)				

Table 7 Fractional atomic coordinates (× 10^4) for $[\mathrm{Os_3(\mu\text{-}H)(\mu_3\text{-}C_6H_4PPh_2CCHO)(CO)_8}]$ **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	7 180(1)	4 479(1)	1 672(1)	C(32)	7 438(10)	7 823(10)	476(8)
Os(2)	6 009(1)	5 879(1)	3 269(1)	O(32)	8 145(8)	8 147(8)	−128(6)
Os(3)	6 295(1)	7 306(1)	1 422(1)	C(41)	6 244(9)	9 193(9)	2 913(7)
P	7 827(3)	8 042(2)	3 225(2)	C(42)	5 633(9)	9 061(9)	2 022(7)
C(1)	8 907(10)	5 812(9)	2 436(8)	C(43)	4 545(10)	10 082(9)	1 630(8)
C(2)	7 696(10)	6 666(9)	2 762(7)	C(44)	4 066(12)	11 144(10)	2 160(9)
O(1)	9 030(7)	4 798(6)	2 098(5)	C(45)	4 652(11)	11 258(10)	3 044(9)
C(11)	5 455(13)	4 423(10)	1 298(8)	C(46)	5 754(11)	10 270(10)	3 432(8)
O(11)	4 410(9)	4 390(9)	1 081(7)	C(51)	8 275(10)	7 921(10)	4 554(7)
C(12)	7 527(11)	2 935(10)	2 571(9)	C(52)	8 328(11)	6 839(11)	5 209(8)
O(12)	7 751(9)	2 010(8)	3 080(7)	C(53)	8 693(12)	6 785(13)	6 217(9)
C(13)	8 071(12)	3 747(11)	484(10)	C(54)	9 002(12)	7 754(15)	6 541(9)
O(13)	8 613(11)	3 345(10)	−245(8)	C(55)	8 952(13)	8 836(12)	5 912(9)
C(21)	4 589(12)	5 122(10)	3 357(8)	C(56)	8 571(12)	8 934(11)	4 905(9)
O(21)	3 674(9)	4 723(10)	3 409(7)	C(61)	9 144(11)	8 600(10)	2 584(8)
C(22)	7 119(11)	4 598(10)	4 209(8)	C(62)	10 533(11)	8 027(10)	2 881(9)
O(22)	7 785(9)	3 824(8)	4 763(6)	C(63)	11 529(11)	8 483(11)	2 367(10)
C(23)	5 170(11)	7 067(11)	4 188(8)	C(64)	11 185(14)	9 459(13)	1 620(10)
O(23)	4 606(9)	7 733(9)	4 775(7)	C(65)	9 834(12)	10 023(12)	1 332(9)
C(31)	4 835(10)	7 797(9)	484(7)	C(66)	8 832(12)	9 586(10)	1 811(8)
O(31)	3 935(8)	8 046(8)	−46(6)				

(^{1}H NMR evidence). Refluxing solutions of **5** in heptane are indefinitely stable under nitrogen but cluster **5** slowly decomposes in refluxing nonane solution.

Crystal-structure Determinations for Clusters **3**, **4a** *and* **5**.—Yellow crystals of each compound were obtained by evaporation of dichloromethane–heptane mixtures. Details of the data collections, structure solutions and refinements for each are given in Table 4. Each crystal was fixed to a glass fibre mounted on a goniometer head on a Nicolet R3v/m diffractometer. Autoindexing and least-squares refinement of orientation reflections gave a triclinic cell in each case. Intensity data were collected at 23 ± 2 °C. Lorentz, polarization and empirical absorption (azimuthal-scan method) corrections were made.

Structures were solved by direct methods in the space group $P\bar{1}$. All non-H atoms were refined anisotropically for clusters **3** and **5**, and all except those of the phenyl rings for cluster **4a**. All hydrogen atoms except the metal-bonded hydrides were included in each model in idealised positions (C–H 0.96 Å, U_{iso} = 0.080 Å^2) and were allowed to ride on the carbon atoms but their positions were not refined. The metal-bonded H atoms were not included.

Calculations were carried out using a MicroVax II computer running SHELXTL PLUS.[18] Fractional atomic coordinates for clusters **3**, **4a** and **5** are given in Tables 5, 6 and 7 respectively.

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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