Oxidative Addition Reactions of Triphenylphosphine with Dodecacarbonyltriosmium(0) : Benzyne-, Phenyl-, and Related Complexes of Osmium

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Summary Reaction of $Os_3(CO)_{12}$ with PPh_3 in the mole ratio of 1 : 2 gives a mixture of nine products, three of which have been defined by *X*-ray crystallography as $HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$, $Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$, and $Os_3(CO)_7(PPh_2)_2(C_6H_4)$.

THE complexes $Os_3(CO)_{12-n}(PPh_3)_n$ ($n \leqslant 3$) can be prepared by the treatment of $Os_3(CO)_{12}$ with excess of PPh_3[1] or with $(Ph_3P)AuCl$.[2] The reaction of the dodecacarbonyl under reflux in xylene with PPh_3 in the mole ratio of 1 : 2 provided a mixture of nine products which could be separated by fractional crystallisation and chromatography on alumina columns. Three of these are the substituted species $Os_3(CO)_{12-n}(PPh_3)_n$, three appeared to be hydrides (i.r. and n.m.r.), and three were complexes whose analytical data indicated loss of phenyl groups. The general properties are given in the Table. Similar compounds were prepared by the reactions of tris-*p*-tolylphosphine and Ph_3As with $Os_3(CO)_{12}$. The new protonated species was $[HOs_3(CO)_9(PPh_3)_3]^+Br^-$, obtained by reaction of $Os_3(CO)_9(PPh_3)_3$ with gaseous hydrogen bromide in chloroform under reflux.

TABLE

Properties of the hydride and diphenylphosphide compounds

No	Compound	Colour	M.p. (°C)
(I)	$Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$	Orange	195
(II)	$Os_3(CO)_7(PPh_2)_2(C_6H_4)$	Red	238
(III)	$Os_3(CO)_8$"$(PPh_3)(PPh_2)$"	Yellow	217
(IV)	$HOs_3(CO)_8$"$(PPh_3)_2$"	Orange-red	198
(V)	$HOs_3(CO)_7(PPh_3)(PPh_2C_6H_4)$	Yellow	199
(VI)	$HOs_3(CO)_9$"$(PPh_3)_2$"	Yellow	210–220d
(VII)	$Os_3(CO)_8[P(C_6H_4Me)]_2[C_6H_4Me]$-$[(C_6H_4Me)P(C_6H_3Me)]$	Orange	204
(VIII)	$Os_3(CO)_7(AsPh_2)_2(C_6H_4)$	Red	238
(IX)	$[HOs_3(CO)_9(PPh_3)_3]^+Br^-$	Orange	146

d = decomposed.

X-Ray diffraction methods provide a clear characterisation of (I). The crystals are tetragonal with $a = b = 18{\cdot}818$ Å, $c = 41{\cdot}191$ Å; space group $I4_1/a$; $Z = 16$. The stereochemistry and certain interatomic distances are shown in Figure 1 and correspond to a structural analysis based on 2970 independent reflexion intensities [Mo-K_α, four-circle diffractometry; $F_0{}^2/\sigma(F_0{}^2) \gg 3{\cdot}0$; $R = 0{\cdot}049$ for absorption-corrected data; e.s.d.'s in bond lengths average 0·002 (Os–Os), 0·009 (Os–P), 0·03 (Os–C), and 0·04 Å(C–C) and (C–O)].

Apart from the eight terminal carbonyl groups, the cluster is held together by a variety of bridging ligands such that the average Os–Os distance is about 0·25 Å greater than that in $Os_3(CO)_{12}$.[3] Os(2)–Os(3) is bridged by a simple phosphide ligand. All three osmium atoms are further bridged by a phosphide ligand which has undergone oxidative addition of a C–H bond to give an intramolecular osmium-carbon σ-bond of length 2·16 Å. However, the novelty in the structure is the observation of a bridging phenyl group between Os(1) and Os(3); the plane of the phenyl ring (average C–C distance 1·41 Å; r.m.s. deviation of carbon atoms from a mean plane = 0·05 Å) is essentially orthogonal to the Os(1)–Os(3) bond direction with an Os–C–Os bond angle of 85·0°. The three-centre two-electron bond description of related phenyl-complexes such as Al_2Ph_6[4] is appropriate. The difference in the bond lengths to the bridging carbon atom from Os(1) and Os(3) is significant and may be associated with steric effects although it can be noted that the longer bond to Os(3) is roughly *trans* to the phosphorous atom, P(1), which will exert a strong *trans*-influence[5] in contrast to that of the carbonyl group which is positioned *trans* to the Os(1)–C(Ph) bond.

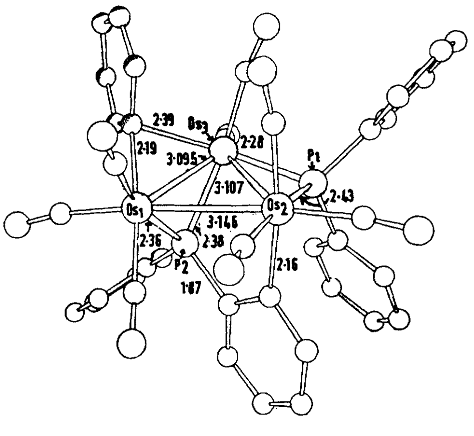

FIGURE 1. *Stereochemistry of* $Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$ (I).

The mass spectra of (I) and (II) are very similar and show the ions $Os_3(CO)_n$"$(PPh_2)_2Ph$"$^+$ (n = 0—7), the doubly charged ions $Os_3(CO)_n$"$(PPh_2)_2Ph$"$^{2+}$ (n = 0—6) and fragments of the Os_3"$(PPh_2)_2Ph$" cluster [the possibility that the compounds may have lost hydrogen atoms from the phenyl groups is suggested when writing the formulae, as *e.g.*, "$(PPh_2)_2Ph$" this possibility being clearly confirmed by the X-ray analysis of (I)].

The crystals of (II) have also been analysed by X-ray methods; they are orthorhombic with a = 18·031, b = 38·309, c = 10·354 Å; space group *Pbca*; Z = 8. Atomic parameters were defined by Patterson, Fourier, and least-square analysis of 3294 reflexions observed by four-circle automatic diffractometry (Mo-K_α). R is presently 0·05 and further refinement is underway with the absorption-corrected data.

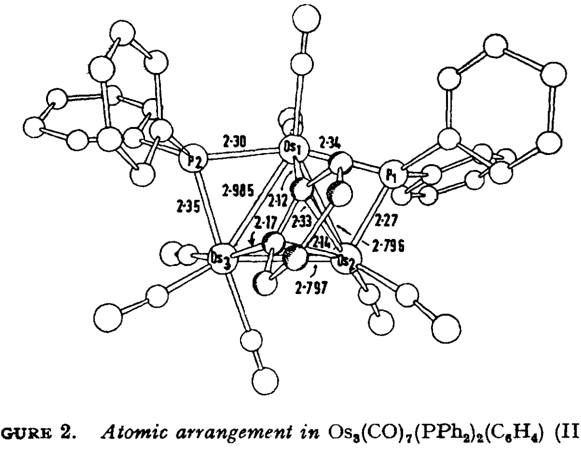

FIGURE 2. *Atomic arrangement in* $Os_3(CO)_7(PPh_2)_2(C_6H_4)$ (II).

The stereochemistry of the complex is shown in Figure 2. The osmium cluster has a very different geometry to that of (I). The seven terminal carbonyl ligands are supplemented by two simple phosphide bridging ligands but, additionally, the three osmium atoms are bridged by a benzyne fragment. At this stage of refinement, it would be premature to comment on the variation in the bond lengths between the osmium atoms and the carbon atoms of the ligands; the benzyne can be regarded as being attached to the cluster *via* a five-centre four-electron bond. The present work establishes unequivocally the possibility of stabilising a benzyne fragment by co-ordination to a metal and it is relatively easy to understand why this should have been achieved in a cluster rather than in a mononuclear complex.

The mass spectrum of (III) is very similar to those of (I) and (II) with the exception that the heavier ion, $Os_3(CO)_8$"$(PPh_3)(PPh_2)$"$^+$, was observed. Oxygen analytical data suggested the presence of a further carbonyl group but little further spectroscopic characterisation has been possible because the material is available only in very small quantities. The hydrides $HOs_3(CO)_8$"$(PPh_3)_2$" (IV) and $HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$ (V) have similar mass spectra to the non-hydridic complexes, (I) and (II); while most of the analytical data suggested the formula $HOs_3(CO)_8$"$(PPh_3)_2$", the oxygen analysis of (V) was consistent with a further carbonyl group, and (V) has been defined now by X-ray analysis as $HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$. The crystals are triclinic having the unreduced unit cell a = 13·059, b = 13·478, c = 12·156 Å, α = 82·45°, β = 94·80°, γ = 97·25°; Z = 2 in the space group $P\bar{1}$; R is presently 0·05 for the 3737 reflexions having $F^2_{obs}/\sigma(F^2_{obs}) \geqslant 3·0$; Mo-$K_\alpha$, four-circle diffractometry.

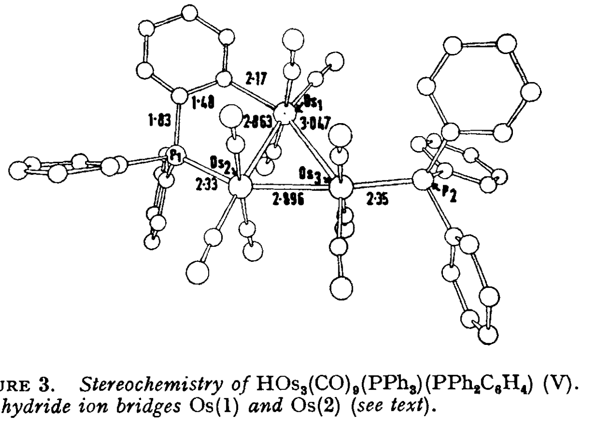

FIGURE 3. *Stereochemistry of* $HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$ (V). *The hydride ion bridges* Os(1) *and* Os(2) (*see text*).

The stereochemistry is shown in Figure 3. A carbon–hydrogen bond of one triphenylphosphine ligand has undergone oxidative addition to form a metal–carbon bond of length 2·17 Å and a five-membered chelate ring. In keeping with the rare-gas rule, the hydrogen atom can be reasonably assumed to bridge Os(1) and Os(2).

Compound (IV) is presently under study by X-ray methods. Its high field n.m.r. spectrum shows a hydride signal (1 : 1 : 1 : 1 quartet) at τ 27·31 (J_{P-H} 10, 17 Hz) while that of (V) is a 1 : 1 doublet at τ 30·36 (J_{P-H} 10 Hz). Integrated intensities of the n.m.r. spectra of mixtures of equal weights of (IV) and (V) and of (V) with $[HOs_3(CO)_8(PPh_3)_3]^+$ showed that both (IV) and (V) contain one hydride ligand. Whereas the $^1H-^{31}P$ spin–spin coupling pattern of (V) can be interpreted as proton coupling to one ^{31}P nucleus, that of (IV) appears to result from the coupling of a proton to two non-equivalent ^{31}P nuclei.

While the mass spectrum of (VI) is similar in most respects to the other complexes, the mass of the most abundant ion $[Os_3(CO)_7''PPh_3)(PPh_2)'']^+$ was 3 units lower than expected. The small amount of complex available has made it difficult to obtain good n.m.r. data. A weak high field signal (1 : 1 : 1 : 1 quartet) was observed at τ 19·55 (J_{P-H} 11, 15 Hz) but, since n.m.r. studies of mixtures with other hydrides could not be made, the number of hydride ligands has not been established.

All six complexes, together with a further unidentified yellow compound, can be obtained by the decomposition of $Os_3(CO)_{10}(PPh_3)_2$ in xylene under reflux. The yields of the hydrides decreased as the reaction time was increased suggesting that the decomposition proceeded *via* the hydrides to the diphenylphosphide complexes. This was confirmed by treating (IV) under similar conditions when a mixture of (II), (III), (VI), and the unidentified yellow compound was obtained.

Several of the remaining complexes are being examined by diffraction methods but our present results already extend views on oxidative addition and intramolecular aromatic substitution. While oxidative addition of a metal to an *ortho*-carbon–hydrogen bond of a tertiary-phosphine or -phosphite is well recognised,[6] a variety of new addition reactions can now be expected for polynuclear systems. A number of compounds such as the polynuclear triphenylphosphine complexes of platinum(o) may need to be re-examined. Most important, our observations can be reasonably assumed to bear a close relation to some of the initial reactions occuring during the chemisorption of unsaturated molecules on metal surfaces.

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