

## Electronic Control of the Co-ordination Mode of an Alkyne to a Trimetallic Cluster; X-ray Crystal Structure of $\text{Os}_3(\text{CO})_7(\mu_3\text{-}\eta^2(\perp)\text{-PhC}\equiv\text{CPh})(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$

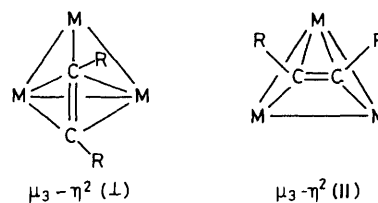
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Treatment of the unsaturated triosmium cluster  $\text{Os}_3(\mu\text{-H})(\text{CO})_8\{\mu\text{-Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}$  with diphenylacetylene leads to the formation of  $\text{Os}_3(\text{CO})_7(\text{PhC}\equiv\text{CPh})(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ , in which the alkyne ligand is bonded in a  $\mu_3\text{-}\eta^2(\perp)$  mode, as shown by an X-ray crystal structure determination.

The co-ordination mode of an alkyne to a triangular metal cluster has been shown to be dependent on both the metal and the substituents on the alkyne. Thus, the  $\mu_3\text{-}\eta^2(\perp)$  mode has been observed for  $\text{Fe}_3(\text{CO})_9(\text{RC}_2\text{R})^1$  and  $\text{Fe}_2\text{Ru}(\text{CO})_9(\text{RC}_2\text{R})^2$  while the  $\mu_3\text{-}\eta^2(\parallel)$  mode is observed in  $\text{Os}_3(\text{CO})_{10}(\text{RC}_2\text{R})^3$ ,  $\text{H}_2\text{M}_3(\text{CO})_9(\text{RC}_2\text{R})$  ( $\text{M} = \text{Ru}, \text{Os}$ ),<sup>4</sup> and several heterometallic cluster-alkyne complexes.<sup>5</sup> The reaction of terminal alkynes,  $\text{HC}\equiv\text{CR}$ , with trinuclear metal clusters usually leads to hydrogen transfer to the metal. We report here the first structurally characterised example of the  $\mu_3\text{-}\eta^2(\perp)$  co-ordination mode of an alkyne to an  $\text{Os}_3$  framework.

Treatment of the unsaturated cluster  $\text{Os}_3(\text{CO})_8(\text{H})\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}$  (I)<sup>6</sup> with diphenylacetylene in toluene at 80 °C for 24 h produced a red solution from which, after

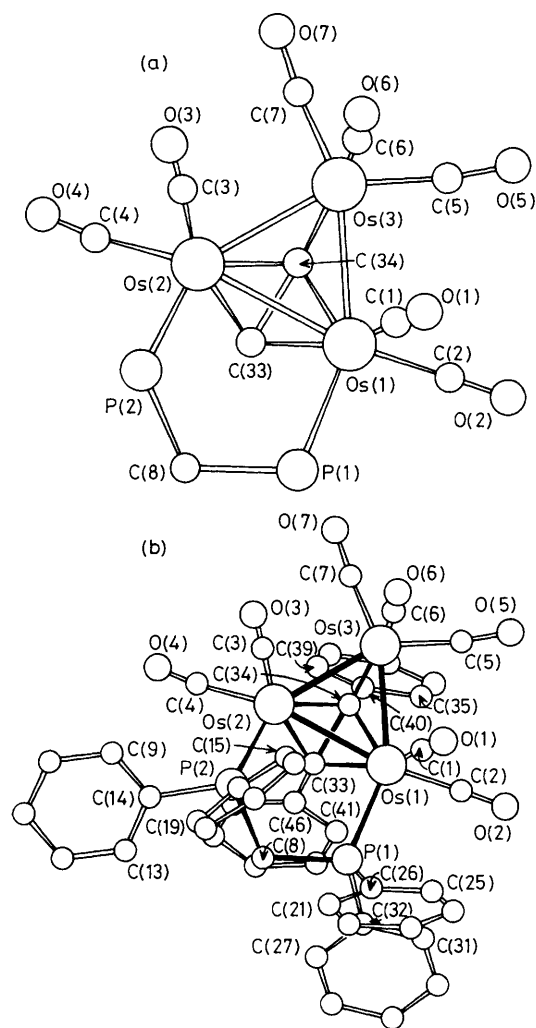


purification by t.l.c., a red crystalline solid,  $\text{Os}_3(\text{CO})_7(\text{Ph}_2\text{PCH}_2\text{PPh}_2)(\text{PhC}\equiv\text{CPh})$  (**2**), was obtained in 40% yield. The spectroscopic data for (**2**) [i.r.  $\nu_{\text{CO}}$  (in  $\text{CH}_2\text{Cl}_2$ ) 2052m, 1980s, 1960sh, and 1920sh  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  n.m.r., ( $\text{CDCl}_3$ ):  $\delta$  3.77 p.p.m. (s)] did not allow a full structural characterisation to be made, so an X-ray crystallographic study was carried out.† The structure of (**2**) is shown in Figure 1.

The X-ray structural analysis shows that the reaction of (**1**) with  $\text{PhC}\equiv\text{CPh}$  resulted in the de-metallation of the phenyl group on the phosphine ligand to regenerate co-ordinated  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm), and the co-ordination of the  $\text{PhC}\equiv\text{CPh}$  group in a  $\mu_3\text{-}\eta^2(\perp)$  mode to the  $\text{Os}_3$  triangle producing a stable, 46-electron cluster. The structure of (**2**) is analogous to those of  $\text{Fe}_3(\text{CO})_9(\text{PhC}\equiv\text{CPh})^1$  and  $\text{Fe}_2\text{Ru}(\text{CO})_9(\text{PhC}\equiv\text{CPh})^2$ . In particular, the two short Fe–Fe and Fe–Ru distances found in these latter complexes, suggested to be due to optimisation of the alkyne–cluster interaction, are paralleled in complex (**2**) by the two short Os–Os distances [Os(1)–Os(3) 2.680(1) and Os(2)–Os(3) 2.689(1) Å]. These Os–Os bond lengths are very similar to those found in the unsaturated clusters  $\text{Os}_3\text{H}_2(\text{CO})_{10}$  [Os–Os 2.681(1) Å]<sup>9</sup> and  $\text{Os}_3\text{H}_2(\text{CO})_8(\text{dppm})$  [Os–Os 2.681(1) Å],<sup>10</sup> and may be due, at least in part, to the fact that (**2**) is a 46-electron cluster, as well as to the requirements of co-ordination to the diphenylacetylene ligand.

The interaction between trinuclear clusters and alkynes has recently been the subject of a number of theoretical and spectroscopic studies.<sup>11–13</sup> The conclusions of these studies are that the preference for the perpendicular orientation of the alkyne ligand in 46-electron clusters is a consequence of the symmetry properties of the alkyne  $\pi$  orbitals and the cluster fragment levels,<sup>11</sup> with back-donation from the two equivalent metal atoms to the alkyne playing an important role,<sup>12</sup> such that for ruthenium and osmium, the previous failure to isolate stable complexes analogous to  $\text{Fe}_3(\text{CO})_9(\text{PhC}\equiv\text{CPh})$  can be related to the decreased back-donation ability of these metals compared to iron.<sup>2</sup> The preference for the formation of the 46-electron cluster of iron, in contrast to the 48-electron clusters for ruthenium and osmium, has been rationalised in terms of charge equilibration in the  $M_3$  triangle, and it has been suggested that the  $\mu_3\text{-}\eta^2(\parallel)$  mode may even be favoured for a 46-electron  $\text{Ru}_3$  compound.<sup>13</sup> This may explain the great difference in reactivity between the highly reactive  $\text{Os}_3(\text{CO})_9(\text{PhC}\equiv\text{CPh})^{14}$  (the structure of which is unknown) and the stable complex (**2**). If the co-ordination mode of the alkyne in  $\text{Os}_3(\text{CO})_9(\text{PhC}\equiv\text{CPh})$  is  $\mu_3\text{-}\eta^2(\parallel)$ , the cluster would have a low-lying LUMO leading to ready reaction to produce a 48-electron species. If the co-ordination mode is  $\mu_3\text{-}\eta^2(\perp)$ , poor back-donation from the osmium atoms to the alkyne would lead to an unstable structure and ready reaction with two-electron donors to give a 48-electron cluster where the  $\mu_3\text{-}\eta^2(\parallel)$  co-ordination mode is favoured.

We therefore rationalise the formation of (**2**) in terms of the presence of the good  $\sigma$ -donor, poor  $\pi$ -acceptor phosphine



**Figure 1.** The structure of  $\text{Os}_3(\text{CO})_7(\text{PhC}\equiv\text{CPh})(\text{dppm})$  (**2**): (a) with phenyl rings omitted and (b) with H atoms omitted. Important bond lengths (Å) and angles ( $^\circ$ ): Os(1)–Os(2) 2.850(1), Os(1)–Os(3) 2.680(1), Os(2)–Os(3) 2.689(1), Os(1)–P(1) 2.333(5), Os(2)–P(2) 2.311(5), Os(1)–C(33) 2.116(16), Os(2)–C(33) 2.100(16), Os(1)–C(34) 2.199(15), Os(2)–C(34) 2.260(15), Os(3)–C(34) 2.205(15); Os(1)–Os(2)–Os(3) 57.8(1), Os(1)–Os(3)–Os(2) 64.1(1), Os(2)–Os(1)–Os(3) 58.1(1), C(46)–C(33)–C(34) 124.8(14), C(40)–C(34)–C(33) 119.4(13).

groups providing osmium atoms Os(1) and Os(2) with sufficient electron density to allow them to act as good back-donors to the alkyne ligand, and thus stabilise the  $\mu_3\text{-}\eta^2(\perp)$  co-ordination mode and achieve charge equilibration on the  $\text{Os}_3$  triangle. Certainly there appear to be no steric constraints on the co-ordination mode of the alkyne. This indicates that it is possible to control the co-ordination mode of an alkyne to a metal framework (metal surface) by modifying the electronic properties of the ligands attached to the metal atoms involved in the interaction with the alkyne.

The unsaturated cluster (**1**) appears to undergo de-metallation reactions readily, allowing the addition of two or four electrons to the cluster framework to occur under mild conditions, and is proving to be a useful starting material for a number of substituted  $\text{Os}_3$  clusters. For example, we have also found that (**1**) reacts smoothly with  $\text{P}(\text{OMe})_3$  to produce  $\text{Os}_3(\text{CO})_8(\text{dppm})\{\text{P}(\text{OMe})_3\}_2$ .<sup>15</sup>

† Crystal data for (**2**):  $\text{C}_{46}\text{H}_{32}\text{O}_7\text{Os}_3\text{P}_2$ ,  $M = 1329$ , monoclinic, space group  $P2_1/n$ ,  $a = 10.972(2)$ ,  $b = 19.216(2)$ ,  $c = 20.325(3)$  Å,  $\beta = 100.013(17)^\circ$ ,  $U = 4220$  Å<sup>3</sup>, Mo– $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $Z = 4$ ,  $D_c = 2.09$  g  $\text{cm}^{-3}$ ,  $D_o = 2.20$  g  $\text{cm}^{-3}$ ,  $\mu(\text{Mo–}K_\alpha) = 92.0$   $\text{cm}^{-1}$ . The structure was solved by Patterson and heavy atom phased Fourier methods (SHELX)<sup>7</sup> using 5908 reflections with  $F > 6\sigma(F)$ . Least-squares refinement with anisotropic Os, P and O atoms, and an empirical absorption correction,<sup>8</sup> converged to  $R = 0.063$ . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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