

Synthesis, Characterisation, and Reactivity of Transition Metal Carbonyl Clusters containing an Interstitial Phosphorus in a Trigonal Prismatic Co-ordination Environment: the X-Ray Structures of $[\text{PPh}_3\text{Me}][\text{Os}_6(\text{CO})_{18}\text{P}]$ and $[\text{Os}_6(\text{CO})_{18}\text{P}(\text{AuPPh}_3)]$

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Thermolysis of $[\text{Os}_6\text{H}_2(\text{CO})_{21}(\text{PH})]$ (**1**) or $[\text{Os}_6\text{H}(\text{CO})_{21}(\text{PH})]^-$ (**2**) results in the closing up of the cluster framework to afford the interstitial phosphide clusters $[\text{Os}_6\text{H}(\text{CO})_{18}\text{P}]$ (**3**) and $[\text{Os}_6\text{H}(\text{CO})_{18}\text{P}]^-$ (**4**), respectively; treatment of (**3**) with X^- ($\text{X} = \text{Cl}, \text{Br}$) also gives the anion (**4**), while both (**3**) and (**4**) react with $[\text{AuPPh}_3]^+$ to yield $[\text{Os}_6(\text{CO})_{18}\text{P}(\text{AuPPh}_3)]$ (**6**); X-ray analyses of (**4**) and (**6**) show that they contain a phosphide-centred trigonal prismatic metallic core.

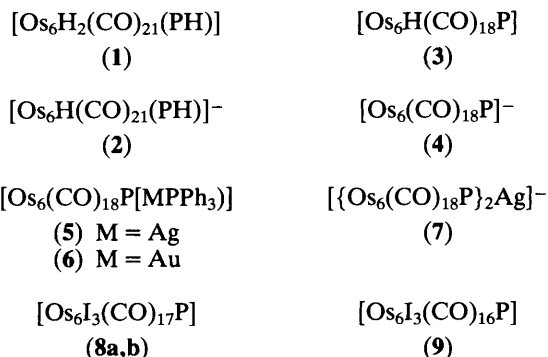
Although phosphorus atoms are found bridging transition metal atoms in many cluster complexes containing five or fewer metal atoms,¹ clusters with fully encapsulated, interstitial phosphorus atoms are rare. In $[\text{Rh}_9(\mu_9\text{-P})(\mu\text{-CO})_{12}(\text{CO})_9]^{2-}$ and $[\text{Rh}_{10}(\mu_{10}\text{-P})(\mu\text{-CO})_{12}(\text{CO})_{10}]^{3-}$ the phosphorus atoms are encapsulated in mono- and bi-capped square antiprismatic arrangements of Rh atoms, respectively.² In the

hexacobalt cluster anion $[\text{Co}_6(\mu\text{-CO})_2(\text{CO})_{14}\text{P}]^-$ the phosphide atom is only partially encapsulated.^{3†}

† Added in proof. The crystal structure of $[\text{Ru}_8(\mu_8\text{-P})(\mu_2\text{-}\eta^1, \eta^6\text{-CH}_2\text{C}_6\text{H}_5)(\mu\text{-CO})_2(\text{CO})_{17}]$ has appeared: L. M. Bullock, J. S. Fields, R. J. Haines, E. Marshall, D. N. Smit, and G. M. Sheldrick, *J. Organomet. Chem.*, 1986, **310**, C47.

Recently, we reported the stepwise synthesis of the hexa- osmium phosphinidene cluster $[\text{Os}_6\text{H}_2(\text{CO})_{21}(\text{PH})]$ (1) and its monoanion $[\text{Os}_6\text{H}(\text{CO})_{21}(\text{PH})]^-$ (2),⁴ in which the two Os_3 units are linked by a μ -PH group. We now report the next step in this reaction sequence, in which thermolysis of these clusters results in the closing up of the metal framework around the linking group to generate an interstitial phosphide in a trigonal prismatic environment.

The cluster $[\text{Os}_6\text{H}(\text{CO})_{18}\text{P}]$ (3) is isolated, as the only tractable product, in 35% yield, after prolonged heating of a xylene solution of $[\text{Os}_6\text{H}_2(\text{CO})_{21}(\text{PH})]$ (1) at reflux, and was characterised by spectroscopic techniques.[‡] The very low field shift for the P atom in the ^{31}P n.m.r. is indicative of the interstitial environment for this atom. Similar low field shifts have been reported for encapsulated main group atoms in other clusters.^{2,3,5,6} The position of the hydride signal in the ^1H n.m.r. suggests that the hydride occupies a μ_2 -site, and the i.r. spectrum is consistent with the presence of only terminal carbonyls. Cluster (3) is formally a 90-electron system, and this electron count is consistent with a trigonal prismatic metal arrangement with nine formal metal-metal bonds.



Reaction of (3) with excess $[\text{PPh}_3\text{Me}]\text{Br}$ or $[(\text{PPh}_3)_2\text{N}]\text{Cl}$ gives the $[\text{PPh}_3\text{Me}]^+$ or $[(\text{PPh}_3)_2\text{N}]^+$ salt of the anion $[\text{Os}_6(\text{CO})_{18}\text{P}]^-$ (4).[‡] The reactions are essentially quantitative and are reversible. The addition of acids (CF_3COOH , $\text{HBF}_4\cdot\text{Et}_2\text{O}$) regenerates (3). The cluster anion is also generated as the main product after thermolysis of $[\text{Os}_6\text{H}(\text{CO})_{21}(\text{PH})]^-$ (2) as either the $[\text{PPh}_3\text{Me}]^+$ or $[(\text{PPh}_3)_2\text{N}]^+$ salt, in toluene at reflux, in 74% yield. The latter reaction is thus the preferred route to the hexa- osmium phosphide clusters. The overall yield of (4) from $[\text{Os}_3(\text{CO})_{12}]$ is 60%.

[‡] (3) I.r. spectroscopic data $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2): 2114w, 2081s, 2076vs, 2062s, 2042m, 2008w, 1979w. ^1H n.m.r. δ -21.36 (d, J_{PH} 21.3 Hz). ^{31}P n.m.r. [CD_2Cl_2 vs. $\text{P}(\text{OMe})_3$] 468.47 (d, J_{PH} 21.3 Hz) p.p.m. m/z 1668 - 18CO (for ^{192}Os). (4) I.r. spectroscopic data $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2): 2048s, 2034vs, 1985mw, 1977w. ^{31}P n.m.r. 522.92 (s) p.p.m. (5) I.r. spectroscopic data $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2): 2096w, 2064vs, 2053vs, 2047s, 2030mw, 2001m, 1983w. ^{31}P n.m.r. 506.2 (s, broad, J_{PAg} not resolved, $\text{Os}_6\text{-P}$) p.p.m. (6) I.r. spectroscopic data $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2): 2097w, 2065vs, 2054vs, 2047s, 2031w, 2001mw. ^{31}P n.m.r. 498.95 (d, J_{PP} 7.8 Hz, $\text{Os}_6\text{-P}$), -50.37 (d, J_{PP} 7.8 Hz, AuPPh_3) p.p.m. (7) I.r. spectroscopic data $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2): 2097w, 2064vs, 2053vs, 2047s, 2031mw, 2001m, 1985w, 1955vw. ^{31}P n.m.r. 489.67 (s, $\text{Os}_6\text{-P}$; J_{AgP} not resolved), -118.05 (m, $(\text{PPh}_3)_2\text{N}^+$) p.p.m. (8a) I.r. spectroscopic data $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2): 2113m, 2087vs, 2083s(sh), 2071vs, 2034m, 2023m, 2008w, 1971w. ^{31}P n.m.r. 195.16 (s, $\text{Os}_6\text{-P}$) p.p.m. m/z 2040 - 17CO. (8b) I.r. spectroscopic data $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2): 2113w, 2089vs, 2084vs, 2063m, 2034w(sh), 2028m, 1963w. ^{31}P n.m.r. 187.11 (s, $\text{Os}_6\text{-P}$) p.p.m. m/z 2040 - 17CO. (9) I.r. spectroscopic data $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2): 2108m, 2081ms, 2070vs, 2035m, 2014m, 1962w. ^{31}P n.m.r. 242.56 (s, $\text{Os}_6\text{-P}$) p.p.m. m/z 2012 - 16CO.

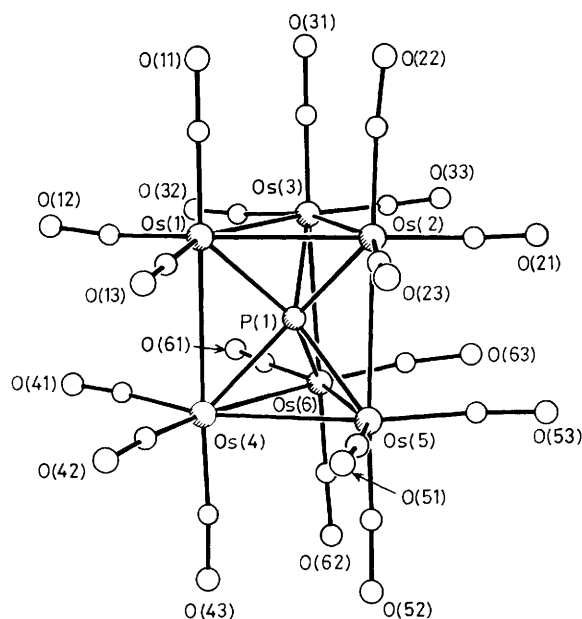


Figure 1. The structure of the $[\text{Os}_6(\mu_6\text{-P})(\text{CO})_{18}]^-$ anion, showing the atom numbering scheme adopted. Bond lengths [values for second molecule in square brackets]: Os(2)-Os(1), 2.941(2) [2.933(2)]; Os(3)-Os(1), 2.929(1) [2.949(2)]; Os(4)-Os(1), 3.151(1) [3.136(1)]; Os(3)-Os(2), 2.927(1) [2.923(2)]; Os(5)-Os(2), 3.144(1) [3.157(2)]; Os(6)-Os(3), 3.137(1) [3.138(1)]; Os(5)-Os(4), 2.933(1) [2.915(2)]; Os(6)-Os(4), 2.942(1) [2.917(2)]; Os(6)-Os(5), 2.932(1) [2.914(2)]; Os(1)-P(1), 2.299(6) [2.313(6)]; Os(2)-P(1), 2.320(7) [2.306(7)]; Os(3)-P(1), 2.316(7) [2.303(7)]; Os(4)-P(1), 2.300(7) [2.307(8)]; Os(5)-P(1), 2.311(6) [2.312(6)]; Os(6)-P(1), 2.312(6) [2.302(7)] Å.

The structure of the $[\text{PPh}_3\text{Me}]^+$ salt of the anion $[\text{Os}_6(\text{CO})_{18}\text{P}]^-$ (4) has been determined by a single crystal X-ray analysis.[§] The asymmetric unit contains two independent but structurally similar cations and anions. The structure of an anion is shown in Figure 1, together with selected bond lengths. This cluster is also formally a 90-electron system and, as expected, the cluster framework consists of an Os_6 trigonal prism containing an interstitial phosphorus atom that co-ordinates to all six metal atoms with

[§] *Crystal data* for (4): $\text{C}_{37}\text{H}_{18}\text{O}_{18}\text{Os}_6\text{P}_2$, $M = 1953.65$, monoclinic, space group $P2_1/a$ (No. 14), $a = 20.310(1)$, $b = 20.492(8)$, $c = 22.051(4)$ Å, $\beta = 95.83(2)^\circ$, $U = 9130.0$ Å³, $D_c = 2.842$ g cm⁻³, $Z = 8$, $F(000) = 6958$, Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu = 167.60$ cm⁻¹. Stoe-Siemens 4-circle diffractometer, 9890 measured reflections, 2θ range 5-41°, numerical absorption correction, 6493 unique observed reflections, $F > 4\sigma(F)$. Structure solved by random start tangent refinement and Fourier difference techniques. Refined by blocked full-matrix least squares with Os, and P atoms anisotropic; phenyl rings refined as rigid groups; phenyl-H AFIXed; converged $R = 0.053$, $R_w = 0.049$.

Crystal data for (6): $\text{C}_{36}\text{H}_{15}\text{AuO}_{18}\text{Os}_6\text{P}_2$, $M = 2135.59$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.778(3)$, $b = 14.645(3)$, $c = 16.041(5)$ Å, $\alpha = 63.67(2)$, $\beta = 83.15(3)$, $\gamma = 86.36(2)^\circ$, $U = 2252.7$ Å³, $D_c = 3.147$ g cm⁻³, $Z = 2$, $F(000) = 1880$, Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu = 202.18$ cm⁻¹. Stoe-Siemens 4-circle diffractometer, 6260 measured reflections, 2θ range 5-45°, numerical absorption correction, 4533 unique observed reflections, $F > 4\sigma(F)$. Structure solved by centrosymmetric direct methods and Fourier difference syntheses. Refined by blocked full-matrix least squares with Os, Au, and P atoms anisotropic; phenyl rings as rigid groups; phenyl-H AFIXed; converged $R = 0.053$, $R_w = 0.054$.

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, 1986.

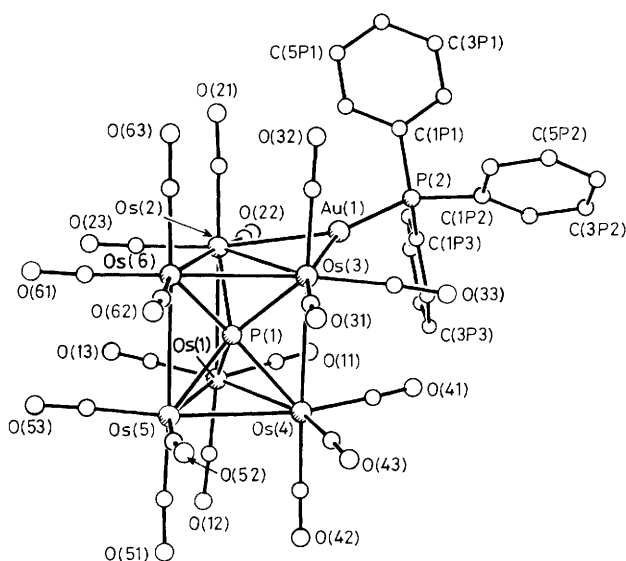


Figure 2. The molecular structure of $[\text{Os}_6(\mu_6\text{-P})(\text{CO})_{18}(\text{AuPPh}_3)]$, showing the atom numbering scheme adopted. Bond lengths: Os(2)–Os(1), 3.101(1); Os(4)–Os(1), 2.932(1); Os(5)–Os(1), 2.942(1); Os(3)–Os(2), 3.093(1); Os(6)–Os(2), 2.925(1); Os(4)–Os(3), 3.114(1); Os(6)–Os(3), 2.936(1); Os(5)–Os(4), 2.926(1); Os(6)–Os(5), 3.126(1); Os(2)–Au(1), 2.793(1); Os(3)–Au(1), 2.775(1); P(2)–Au(1), 2.315(5); Os(1)–P(1), 2.297(6); Os(2)–P(1), 2.340(5); Os(3)–P(1), 2.327(5); Os(4)–P(1), 2.283(6); Os(5)–P(1), 2.290(5); Os(6)–P(1), 2.331(7) Å.

an average P–Os distance of 2.31(1) Å. Each metal atom is also bonded to three terminal carbonyl ligands that lie approximately *trans* to the Os–Os vectors. The overall idealised anion symmetry is D_{3h} . The six Os–Os distances within the Os_3 basal triangles average 2.930(5) Å, whereas considerable lengthening is observed for the three inter-basal Os–Os edges [average 3.140(5) Å]. Trigonal prismatic co-ordination of interstitial carbon and nitrogen atoms has been observed in clusters with metals of the cobalt subgroup⁵ but the anion $[\text{Os}_6(\text{CO})_{18}\text{P}]^-$ is the first crystallographically characterised cluster with this geometry for phosphorus. This is also the first cluster of the iron triad to contain an interstitial atom encapsulated by a trigonal prism of metal atoms.

Both (3) and (4) readily react with $[\text{MPPH}_3][\text{PF}_6]$ ($\text{M} = \text{Ag}, \text{Au}$) to give $[\text{Os}_6(\text{CO})_{18}\text{P}(\text{MPPH}_3)]$ [$\text{M} = \text{Ag}$ (5), Au (6)].[‡] Treatment of the anion (4) with half an equivalent of Ag^+ gives the bridged complex $[\{\text{Os}_6(\text{CO})_{18}\text{P}\}_2\text{Ag}]^-$ (7). An X-ray analysis[§] of the gold complex (6) shows that the centred trigonal prismatic Os_6P core of the anion (4) is retained, and

the gold atom of the AuPPh_3 group bridges an Os–Os triangular edge. The molecular structure of (6) is shown in Figure 2, which includes selected bond parameters. This structure is presumably closely related to that of (3), with the AuPPh_3 group in (6) occupying the same bridging site as the hydride in (3). The introduction of the bridging Au atom causes small perturbations of the Os_6 framework compared to that in $[\text{Os}_6(\text{CO})_{18}\text{P}]^-$ (4). The bridged Os(2)–Os(3) edge is *ca.* 0.16 Å longer than the average Os–Os distance [2.932(5) Å] for the other Os–Os triangular edges. The inter-basal Os–Os distances are similar in (4) and (6). The structure of (6) contrasts with those obtained from the ‘capping’ reactions of the trigonal prismatic clusters $[\text{M}_6(\text{CO})_{15}\text{E}]^{n-}$ ($\text{M} = \text{Co}, \text{Rh}$; $\text{E} = \text{C}, n = 2$; $\text{E} = \text{N}, n = 1$) in which the incoming metal fragment, including $[\text{AuPPh}_3]^+$, always adds to either a trigonal or square face of the parent cluster.⁵

The reaction of the anion (4) with excess iodine initially gives two isomeric products which have been spectroscopically characterised[‡] as $[\text{Os}_6\text{I}_3(\text{CO})_{17}\text{P}]$ (8a,b). With increasing reaction times a product $[\text{Os}_6\text{I}_3(\text{CO})_{16}\text{P}]$ (9) is obtained, which corresponds to the loss of CO from (8a,b).

We thank the S.E.R.C. for financial support.

Received, 7th August 1986; Com. 1131

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