Stepwise Construction of $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$, a Hexanuclear Osmium Cluster Monoanion with Trigonal-prismatic Co-ordination for Phosphorus: *X*-Ray Crystal Structures of $[Os_6(\mu\text{-}H)_2(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$ and $[PPh_3Me][Os_6(CO)_{18}(\mu_6\text{-}P)]$ *

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Treatment of the labile cluster $[Os_3(CO)_{11}(MeCN)]$ with PH_3 affords the substituted product $[Os_3(CO)_{11}(PH_3)]$ (**1**) in high yield. Subsequent reaction of (**1**) with Na_2CO_3 in MeOH, followed by acidification, gives the hydrido phosphido cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ (**2**). When (**2**) is heated to 45—60 °C in the presence of $[Os_3(CO)_{11}(MeCN)]$ a hexanuclear complex with the formulation $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)]$ (**3**) is obtained. If this reaction is repeated using $[Os_3(CO)_{10}(MeCN)_2]$ instead of $[Os_3(CO)_{11}(MeCN)]$, an acetonitrile-containing product, $[Os_6(\mu\text{-}H)_2(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$ (**4**), is obtained. An *X*-ray analysis of (**4**) shows that two Os_3 triangular units are linked by a μ_3-phosphinidene ligand, which symmetrically bridges an Os–Os edge of one triangle and is terminally co-ordinated to one Os atom of the second triangle. When (**3**) is treated with a weak base, such as $[N(PPh_3)_2]Cl$ or $[PPh_3Me]Br$, deprotonation to the corresponding cluster monoanion $[Os_6(\mu\text{-}H)(CO)_{21}(\mu_3\text{-}PH)]^-$ (**5**) occurs. Treatment of (**5**) with a weak acid regenerates (**3**) in quantitative yield. Thermolysis of (**3**) leads to a closing up of the metal framework, affording the cluster $[Os_6(\mu\text{-}H)(CO)_{18}(\mu_6\text{-}P)]$, which readily deprotonates to give the anion $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$ (**7**) in the presence of $[N(PPh_3)_2]Cl$ or $[PPh_3Me]Br$. The same anion (**7**) may also be obtained by direct thermolysis of (**5**). An *X*-ray analysis of the $[PPh_3Me]^+$ salt of (**7**) confirms that the phosphorus occupies an interstitial site in a trigonal-prismatic hexaosmium framework, and co-ordinates to all six metal atoms with an average Os–P distance of 2.31 (1) Å. Proton and ^{31}P n.m.r. data on all the new clusters are presented, and the position of the phosphorus resonance in the ^{31}P n.m.r. spectrum is related to the changes in the environment of the phosphorus atom.

All elements except antimony, bismuth, and the inert gases form binary compounds with phosphorus.[1] In the 'metal-rich' phosphides the phosphorus atom is predominantly found co-ordinated by either a trigonal prism or capped trigonal prism of metal atoms.[1] Hoffmann[2,3] and others[4] have recently emphasised that 'there can be no real divergence between the bonding in a discrete molecule and that in an extended two- or three-dimensional solid,'[2] and that discrete cluster molecules with 'interstitial' atoms provide useful models for binary compounds.[2–4] However, as yet, no example of a cluster having an encapsulated phosphorus atom in a trigonal-prismatic environment has been reported. Indeed, only four phosphide–metal clusters with six or more metal atoms have been characterised. These are the interconvertible clusters $[Rh_9(\mu\text{-}CO)_{12}(CO)_9(\mu_9\text{-}P)]^{2-}$ and $[Rh_{10}(\mu\text{-}CO)_{12}(CO)_{10}(\mu_{10}\text{-}P)]^{3-}$ which contain encapsulated phosphorus atoms in mono- and bi-capped square-antiprismatic metal atom environments respectively,[5] $[Ru_8(\mu\text{-}CO)_2(CO)_{17}(\mu_8\text{-}P)(\mu\text{-}\sigma{:}\eta^6\text{-}CH_2C_6H_6)]$ which also has phosphorus atoms and in a square-antiprismatic metal environment,[6] and $[Co_6(\mu\text{-}CO)_2(CO)_{14}(\mu_6\text{-}P)]^-$ which contains partially encapsulated phosphorus atoms in an irregular metal environment.[7]

Given the current state of the art of cluster synthesis it seemed probable to us that hexaosmium carbonyl clusters with the requisite number of cluster valence electrons (c.v.e.), 90 electrons, to require an encapsulated phosphorus atom to be in a trigonal-prismatic geometry should be accessible. In this paper we report the stepwise construction and characterisation of two such clusters, $[Os_6(\mu\text{-}H)(CO)_{18}(\mu_6\text{-}P)]$ and its monoanion $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$. Preliminary accounts containing some of this work have appeared.[8–10]

Results and Discussion

Perhaps the most easily prepared, versatile reagent in osmium cluster chemistry is the acetonitrile-substituted trisomium cluster $[Os_3(CO)_{11}(MeCN)]$.[11] Starting from this weakly ligated cluster there are two obvious potential routes to clusters with 'naked' phosphorus atoms in an all metal environment: (*i*) substitution by a phosphorus trihalide followed by dehalogenation, and (*ii*) substitution by phosphine (PH_3) followed by sequential metallation of the P–H bonds. Although halogenophosphine derivatives are readily prepared from $[Os_3(CO)_{11}(MeCN)]$,[12] these are, in general, too unstable to warrant extensive investigation.

On the other hand, $[Os_3(CO)_{11}(MeCN)]$ reacts cleanly with phosphine in toluene to give a single isolable product $[Os_3(CO)_{11}(PH_3)]$ (**1**) (Scheme). I.r. spectroscopic and ^1H and ^{31}P n.m.r. data are presented in Tables 1 and 2, respectively.

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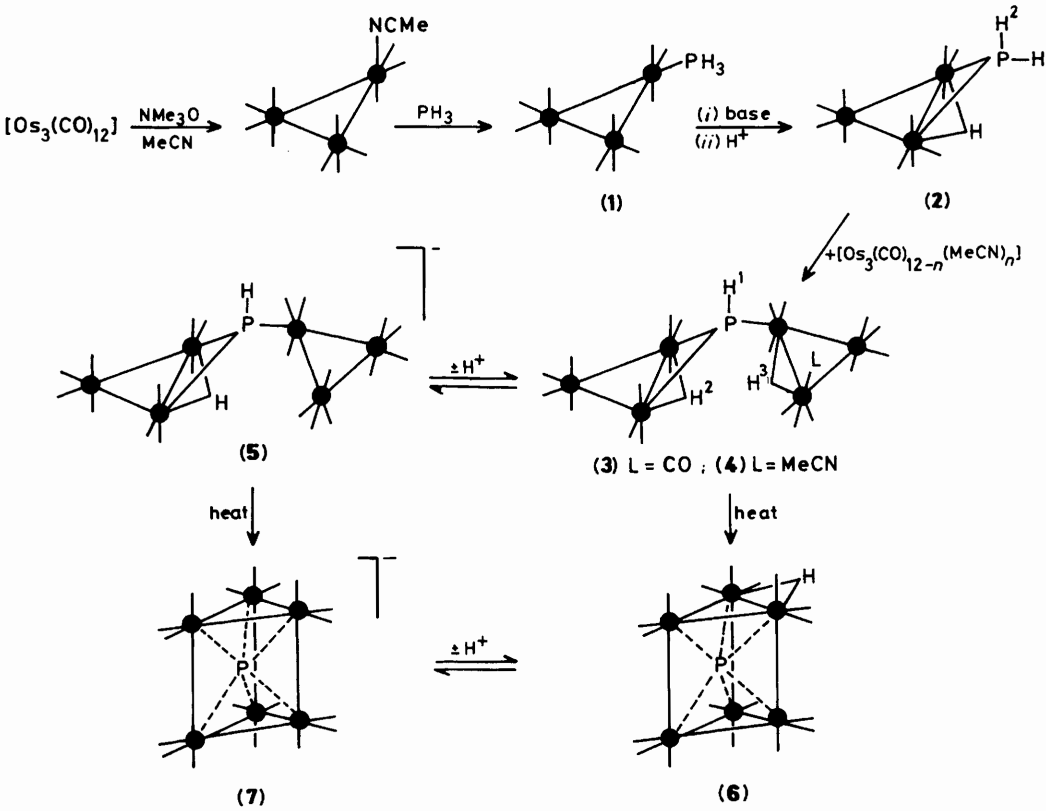
* 1,2-μ-[(2′-Acetonitrile-1′,1′,1′,2′,2′,2′,3′,3′,3′,3′-decarbonyl-1′,2′-μ-hydrido-*triangulo*-triosmio-$Os^{1'}$)hydrogenphosphido]-1,1,1,2,2,2,3,3,3,3-decarbonyl-1,2-μ-hydrido-*triangulo*-triosmium and methyltriphenylphosphonium μ_6-phosphido-*cyclo*-hexakis(tricarbonylosmate)(8 *Os–Os*) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



Scheme. Overall yield $[Os_3(CO)_{12}] \longrightarrow [Os_6(CO)_{18}(\mu_6\text{-}P)]^-$ (7) *ca.* 60%

Table 1. Infrared spectroscopic data (cm^{-1} in dichloromethane) for new compounds

Complex	
(1) $[Os_3(CO)_{11}(PH_3)]$	2 112w, 2 058ms, 2 038ms, 2 022vs, 1 989m
(2) $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$	2 107w, 2 066vs, 2 056s, 2 023s, 2 006ms, 1 998m (sh)
(3) $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)]$	2 143w, 2 101m, 2 092ms, 2 064vs, 2 050m, 2 041m, 2 014s, 1 979m, 1 969mw
(4) $[Os_6(\mu\text{-}H)_2(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$	2 112w, 2 092m, 2 076ms, 2 049s, 2 040ms, 2 026ms, 2 013s, 1 981m, 1 966m
(5) $[N(PPh_3)_2][Os_6(\mu\text{-}H)(CO)_{21}(\mu_3\text{-}PH)]$	2 084mw, 2 044vs, 2 004s, 1 974m
(6) $[Os_6(\mu\text{-}H)(CO)_{18}(\mu_6\text{-}P)]$	2 114w, 2 081s, 2 076vs, 2 062vs, 2 042m, 2 027w, 2 007w, 2 001w (sh), 1 980vw
(7) $[N(PPh_3)_2][Os_6(CO)_{18}(\mu_6\text{-}P)]$	2 048s, 2 034vs, 1 983mw, 1 974w (sh)

Compound (1) showed the resonances expected for the PH_3 ligand in its n.m.r. spectra {^{1}H: a doublet at 4.88 p.p.m. [*J*(PH) 380.5 Hz] and ^{31}P: a quartet at −336.8 p.p.m. [*J*(PH) 380.5 Hz]} (Table 2). The large phosphorus–hydrogen coupling constant is indicative of direct P–H bonding.[13]

Treatment of a suspension of (1) in methanol with anhydrous sodium carbonate gives a clear yellow solution which after acidification with CF_3COOH yields the hydrido phosphido triosmium cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ (2) in *ca.* 90% yield (Scheme). In the ^{1}H n.m.r. spectrum of (2) the two low-field multiplets with large PH couplings {at 5.24 [*J*(PH) 425.0] and 4.96 p.p.m. [*J*(PH) 397.0 Hz]} and the high-field multiplet {at −19.92 p.p.m. [*J*(PH) 16.0 Hz]} are assigned to two inequivalent hydrogen atoms in the PH_2 moiety and to the hydride ligand, respectively. A doublet [*J*(PH) 425.0 Hz] of doublets [*J*(PH) 397.0 Hz] of doublets [*J*(PH) 16.0 Hz] at −276.25 p.p.m. is observed for the phosphorus atom in the ^{31}P n.m.r. spectrum of (2). The deprotonation–protonation sequence from (1) to (2) appears to be general and has been used to give substituted-phosphido analogues of (2).[8]

Muller and Vahrenkamp[14] have demonstrated that dinuclear complexes with a bridging μ-PRH phosphido moiety will add oxidatively to sources of unsaturated metal fragments giving μ_3-PR phosphinidene-capped clusters as products. Given this, and that the weakly ligated triosmium clusters $[Os_3(CO)_{12-n}(MeCN)_n]$ (n = 1 or 2) readily react with compounds (organic, inorganic, and organometallic) containing 'acidic' hydrogen to give addition products [equation (1)],[1,15] it was decided to

$$[Os_3(CO)_{12-n}(MeCN)_n] + HX \longrightarrow [Os_3H(CO)_{12-n}(MeCN)_{n-y}X] + y\,MeCN \quad (1)$$

explore the reactions of these acetonitrile-substituted clusters with (2) as a possible way of both increasing cluster nuclearity and further metallating the phosphorus atom.

Accordingly, mild heating of (2) with $[Os_3(CO)_{11}(MeCN)]$ in toluene at 45—50 °C gives a bright yellow precipitate of $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)]$ (3) in *ca.* 95% yield. The analogous reaction of (2) with $[Os_3(CO)_{10}(MeCN)_2]$ in cyclohexane at 45—50 °C gives $[Os_6(\mu\text{-}H)_2(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$ (4) as a slightly darker yellow powder in *ca.* 90% yield (Scheme). Both (3) and (4) show a multiplet with a single large

Table 2. N.m.r. data for new compounds*

Complex	
(**1**) $[Os_3(CO)_{11}(PH_3)]$	^1H: 4.88 [d, J(PH) 380.5, PH_3] ^{31}P: −336.8 [q, J(PH) 380.5, PH_3]
(**2**) $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$	^1H: 5.24 [ddd, $J(PH^1)$ 425, $J(H^1H^2)$ 9.5, $J(H^1H^3)$ 5.0, PH], 4.96 [dd, $J(PH^2)$ 397, $J(H^1H^2)$ 9.5, PH], −19.92 [dd, $J(PH^3)$ 16.0, $J(H^1H^3)$ 5.0, OsH] ^{31}P: −276.25 [ddd, $J(PH^1)$, 425, $J(PH^2)$ 397, $J(PH^3)$ 16, PH_2]
(**3**) $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)]$	^1H: 6.26 [ddd, $J(PH^1)$ 337, $J(H^1H^2)$ 3.9, $J(H^1H^3)$ 0.9, PH], −17.92 [dd, $J(PH^2)$ 13.7, $J(H^2H^1)$ 3.9, OsH], −18.96 [dd, $J(PH^3)$ 10.6, $J(H^3H^1)$ 0.9, OsH] ^{31}P: −322.3 [d of t, $J(PH^1)$ 340, $J(PH^2) \sim J(PH^3)$ 12, PH]
(**4**) $[Os_6(\mu\text{-}H)_2(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$	^1H: 6.31 [ddd, $J(PH^1)$ 337, $J(H^1H^3)$ 4.0, $J(H^1H^2)$ 1.0, PH], 2.58 (s, CH_3CN), −16.18 [dd, $J(PH^2)$ 11.6, $J(H^2H^1)$ 1.0, OsH], −17.86 [dd, $J(PH^3)$ 13.6, $J(H^3H^1)$ 4.0, OsH] ^{31}P: −325.0 [ddd, $J(PH^1)$ 337, $J(PH^2)$ 12, $J(PH^3)$ 14, PH]
(**5**) $[N(PPh_3)_2][Os_6(\mu\text{-}H)(CO)_{21}(\mu_3\text{-}PH)]$	^1H: 7.6—7.3 {m, $[N(PPh_3)_2]^+$}, 6.78 [dd, J(PH) 328, J(HH) 3.6, PH], −17.67 [dd, J(PH) 12.8, J(HH) 3.6, OsH] ^{31}P: −118.1 {m, $[N(PPh_3)_2]^+$}, −316.3 [dd, $J(PH^1)$, 330, $J(PH^2)$, 4, PH]
(**6**) $[Os_6(\mu\text{-}H)(CO)_{18}(\mu_6\text{-}P)]$	^1H: −21.36 [d, J(PH) 21.3, OsH] ^{31}P: 468.47 [d, J(PH) 21.3, OsP]
(**7**) $[N(PPh_3)_2][Os_6(CO)_{18}(\mu_6\text{-}P)]$	^1H: 7.7—7.3 {m, $[N(PPh_3)_2]^+$} ^{31}P: 522.92 [s, OsP and satellites: doublet $J(P^{187}Os)$ 134.9], −117.97 {m, $[N(PPh_3)_2]^+$}

* Spectra in CD_2Cl_2; chemical shifts in p.p.m. [^1H relative to $SiMe_4$, ^{31}P relative to external $P(OMe)_3$]; coupling constants in Hz.

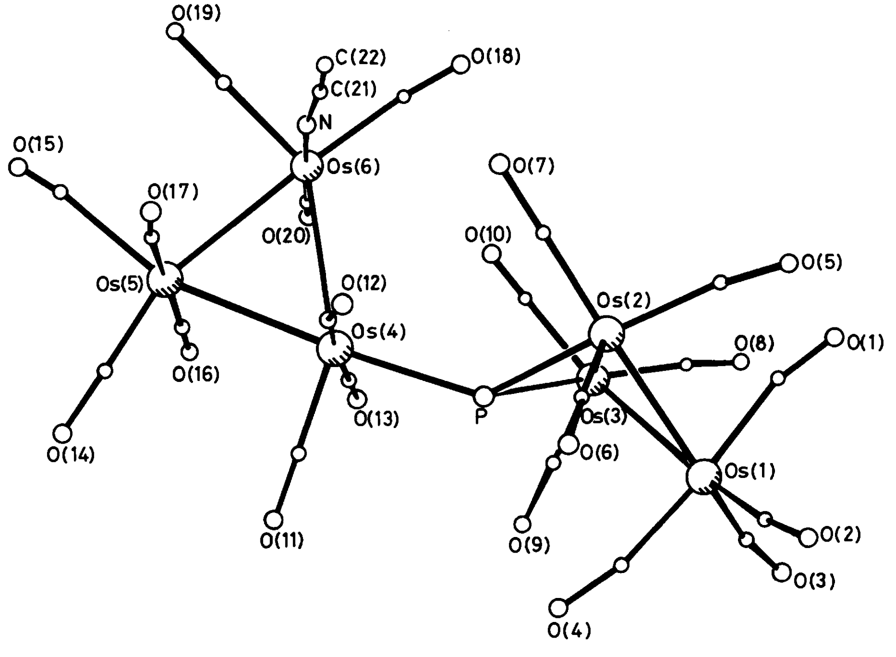


Figure 1. The molecular structure of $[Os_6(\mu\text{-}H)_2(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$ (**4**), showing the atom numbering scheme adopted

PH coupling {at −322.3 p.p.m. [J(PH) 340 Hz] for (**3**) and at −325.0 p.p.m. [J(PH) 337 Hz] for (**4**)} in their respective ^{31}P n.m.r. spectra, indicating that metallation of the μ-PH_2 bridge in (**2**) to give a μ_3-PH group in the hexanuclear clusters has occurred. This conclusion is supported by the ^1H n.m.r. spectra which show low-field multiplets at 6.26 p.p.m. for (**3**) and at 6.31 p.p.m. for (**4**) with the same large PH couplings as found in the respective ^{31}P n.m.r. spectrum and are therefore attributed to the μ_3-PH group in each case. Also, two high-field sets of peaks at −17.92 and −18.96 p.p.m. for (**3**) and at −16.18 and −17.86 p.p.m. for (**4**) are observed for the two inequivalent hydride ligands in each cluster. A single peak at 2.58 p.p.m. is also observed for the acetonitrile ligand of (**4**).

Compounds (**3**) and (**4**) have 96 c.v.e., an electron count associated with only six Os–Os bonds which suggests that the μ_3-PH group links two independent osmium triangles in each cluster. The fact that the two hydride ligands in both (**3**) and (**4**) couple to both atoms of the PH group, but not to one another, suggests that these ligands are distributed one per osmium triangle. To confirm this and definitively establish the formulation of (**4**), which did not show a parent molecular ion in its mass spectrum,* a single-crystal *X*-ray analysis on crystals of (**4**) was undertaken.

The molecular structure of $[Os_6(\mu\text{-}H)_2(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$ (**4**) is illustrated in Figure 1 and selected bond lengths and interbond angles listed in Table 3. In the solid state the discrete,

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* Compound (**4**) showed a molecular ion at m/z 1 718 corresponding to the formulation $[Os_6H_2(CO)_{19}(PH)]$. Failure to observe molecular ions is a common feature of cluster compounds with weakly co-ordinated ligand(s), see for example ref. 11, and the acetonitrile-substituted compounds in ref. 16.

Table 3. Bond lengths (Å) and angles (°) for $[Os_6(\mu\text{-}H)_2(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$ (**4**)

Os(1)–Os(2)	2.867(2)	Os(4)–Os(5)	2.891(2)
Os(1)–Os(3)	2.869(2)	Os(4)–Os(6)	3.022(2)
Os(2)–Os(3)	2.888(2)	Os(5)–Os(6)	2.881(2)
Os(2)–P	2.425(10)	Os(6)–N	2.10(3)
Os(3)–P	2.420(11)	N–C(21)	1.08(4)
Os(4)–P	2.411(12)	C(21)–C(22)	1.59(5)
Os(3)–Os(1)–Os(2)	60.5(1)	Os(5)–Os(4)–Os(6)	58.3(1)
Os(1)–Os(2)–Os(3)	59.8(1)	Os(4)–Os(5)–Os(6)	63.1(1)
Os(2)–Os(3)–Os(1)	59.7(1)	Os(4)–Os(6)–Os(5)	58.6(1)
Os(3)–P–Os(2)	73.2(3)	P–Os(2)–Os(1)	85.4(3)
Os(2)–P–Os(4)	128.4(5)	P–Os(2)–Os(3)	53.3(3)
Os(3)–P–Os(4)	127.6(4)	C(5)–Os(2)–P	88.3(12)
P–Os(3)–Os(1)	85.4(3)	C(6)–Os(2)–P	93.0(13)
P–Os(3)–Os(2)	53.5(2)	C(7)–Os(2)–P	170.4(12)
C(8)–Os(3)–P	86.6(12)	P–Os(4)–Os(5)	176.6(3)
C(9)–Os(3)–P	94.8(15)	P–Os(4)–Os(6)	118.3(6)
C(10)–Os(3)–P	168.4(13)	C(11)–Os(4)–P	84.0(15)
N–Os(6)–Os(4)	89.0(9)	C(12)–Os(4)–P	89.2(15)
N–Os(6)–Os(5)	90.6(9)	C(13)–Os(4)–P	90.5(20)
C(18)–Os(6)–N	178.7(16)	C(21)–N–Os(6)	172(4)
C(19)–Os(6)–N	88.5(15)	N–C(21)–C(22)	176(5)
C(20)–Os(6)–N	88.4(15)		

neutral molecules of (**4**) are separated by normal van der Waals distances.

The six metal atoms define two approximately perpendicular triangles, with a dihedral angle of 89° between the planes defined by Os(1)Os(2)Os(3) and Os(4)Os(5)Os(6), that are linked *via* a μ_3-phosphinidene (PH) group which symmetrically bridges Os(2) and Os(3), and co-ordinates to only Os(4) of the other triangle. An acetonitrile ligand is axially co-ordinated to Os(6),[16] and this ligand and all carbonyl ligands are essentially linear and do not deviate from linearity by more than 4σ. When no other groups span the same Os–Os bond, long distances are associated with the presence of bridging hydride ligands, and here the presence of a hydride ligand bridging the Os(4)Os(6) edge is confirmed by the bending away of the *cis* carbonyl ligand [C(20)O(20)] to this edge [C(20)–Os(6)–Os(4) is 118.4(1.3)° compared with an average angle for the other *cis* carbonyl ligands of Os(4), Os(5), and Os(6) of 92(2)°]. From the bending back of the carbonyl groups adjacent to the phosphinidene-bridged Os(2)–Os(3) edge {a ligand arrangement reminiscent of that found in $[Os_3H(CO)_{10}X]$ (X = 3-electron donor ligand) systems[17]} it may be inferred that the remaining hydride ligand also bridges this edge. Comparison of the Os(2)–Os(3) distance [2.888(2) Å] with the two other Os–Os distances in the same triangle [average 2.869(2) Å] reveals that the metal bond lengthening by the hydride ligand is largely offset by the shortening effect of the bridging PH group.

Thus, the molecular geometry of (**4**) is clearly derived from its two precursor clusters by oxidative addition of the equatorial P–H bond in the bridging PH_2 group of (**2**) to an unsaturated centre formed by loss of one acetonitrile ligand from $[Os_3(CO)_{10}(MeCN)_2]$. The linking phosphinidene (μ_3-PH) group and a further hydride ligand result. Other molecular features are essentially identical to those expected for the precursor clusters. The similarity of the spectroscopic data for (**3**) and (**4**) (Tables 1 and 2) suggests that (**3**) has an analogous structure (Scheme).

When (**3**) is treated with weak bases such as NEt_3, $[N(PPh_3)_2]Cl$, or $[PPh_3Me]Br$ deprotonation to the corresponding cluster monoanion $[Os_6(\mu\text{-}H)(CO)_{21}(\mu_3\text{-}PH)]^-$ (**5**) occurs (the counter ion being $[NEt_3H]^+$, $[N(PPh_3)_2]^+$, or $[PPh_3Me]^+$, respectively) (Scheme). The formulation of (**5**) rests entirely on the fact that the deprotonation is reversible, the addition of CF_3COOH to (**5**) essentially quantitatively regenerates (**3**), and the similarities of the n.m.r. data for (**3**) and (**5**) (Table 2). Unlike (**3**), complex (**4**) did not react with weak bases such as $[N(PPh_3)_2]Cl$ or NEt_3 and with stronger bases such as MeOH–KOH or 1,5-diazabicyclo[4.3.0]non-5-ene only decomposition to mixtures of lower nuclearity products results. Apart from resonances expected for the counter ion, the cluster monoanion (**5**) shows in its ^1H n.m.r. spectrum a doublet of doublets at 6.78 p.p.m. [*J*(PH) 328, *J*(HH) 3.6 Hz] for the μ_3-PH group, and a high-field doublet of doublets at −17.67 p.p.m. [*J*(PH) 12.8, *J*(HH) 3.6 Hz] for the single hydride ligand, and in its ^{31}P n.m.r. a doublet of doublets at −316.3 p.p.m. with the expected PH couplings for the phosphorus atom of the μ_3-PH group. Each of these peaks has a corresponding resonance in the respective n.m.r. spectra of both the neutral clusters (**3**) and (**4**) that is largely unperturbed in both chemical shift and coupling constants. Given that the largest perturbation on going from (**3**) to (**4**) will be in the hydride ligand adjacent to the carbonyl ligand substituted by the acetonitrile ligand, then it may be deduced that this is the hydride ligand removed from (**3**) in forming (**5**) (see Scheme). This conclusion is also consistent with the observed differences in the acidity of this hydride ligand between (**3**) and (**4**).

Thermolysis of a cluster often causes loss of ligand(s) and as a consequence closure of the metallic framework (to accommodate the decrease in c.v.e.). Heating of (**3**) to reflux in *p*-xylene causes a smooth reaction to a new cluster product (**6**). There is a delicate balance between decomposition of the product (**6**) and thermolysis of (**3**) to this product, and the yield of (**6**) was optimised at *ca.* 20—35% by monitoring the i.r. of the reaction mixture. Infrared bands of an intermediate cluster in the thermolysis were observed after short reaction times but as yet this cluster has not been fully characterised.

Analytical, mass spectroscopic, ^1H and ^{31}P n.m.r. spectral data are all consistent with the formulation of (**6**) as $[Os_6(\mu\text{-}H)(CO)_{18}(\mu_6\text{-}P)]$ (Scheme). In the ^1H n.m.r. spectrum a doublet at −21.36 p.p.m. [*J*(PH) 21.3 Hz] is observed for the hydride ligand and in the ^{31}P n.m.r. spectrum a doublet at 468.47 p.p.m. is observed for the phosphorus atom. The extremely low-field phosphorus chemical shift is typical of an atom encapsulated within a metal framework.[5,18,19] While there are no related phosphide–metal clusters with the same electron count (90 c.v.e.) several isoelectronic carbido-[18] and nitrido-[19] clusters provide a precedent for (**6**) adopting a trigonal-prismatic metal arrangement. It was hoped to obtain evidence as to the exact symmetry of the phosphorus–metal environment *via* direct measurements of phosphorus–osmium couplings from the satellite ^{31}P n.m.r. spectrum of (**6**) (^{187}Os; $I = \frac{1}{2}$, 1.6% natural abundance), but the poor solubility of (**6**) precluded this experiment.

Excess $[PPh_3Me]Br$ or $[N(PPh_3)_2]Cl$ readily deprotonates (**6**) to the cluster monoanion $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$ (**7**). These reactions are almost quantitative and are reversible, addition of acid regenerates (**6**). The same monoanion (**7**) is prepared in better overall yield from (**3**) *via* thermolysis of (**5**) in toluene under reflux [77% yield of (**7**) from (**5**) and 69% direct from (**3**)]. Only resonances expected for the respective counter cations are observed in the ^1H n.m.r. spectrum of (**7**) and in the ^{31}P n.m.r. spectrum a low-field singlet at 522.92 p.p.m. consistent with an encapsulated phosphide atom is found. The $[PPh_3Me]^+$ and $[N(PPh_3)_2]^+$ salts of (**7**) are sufficiently soluble to obtain satellite ^{31}P n.m.r. spectra and about the phosphide peak a single doublet [$J(^{187}OsP)$ 134.9 Hz], shown for the $[PPh_3Me]^+$ salt of (**7**) in Figure 2, is observed as expected for a phosphide atom encapsulated by six equivalent osmium atoms.*

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* Fluxionality in an irregular metal framework rendering all six osmium atoms equivalent cannot be discounted from this evidence; see ref. 5.

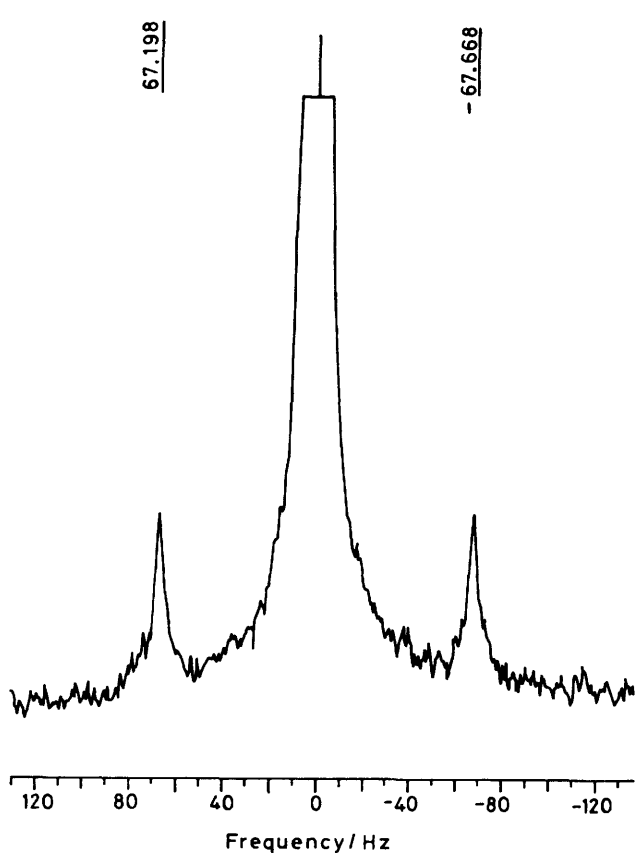

Figure 2. The ^{31}P n.m.r. spectrum of the anion $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$ (7) showing the $^{187}Os\text{-}P$ satellites

To establish unambiguously the molecular geometry of (7) [and by inference that of (**6**)], an *X*-ray crystal-structure analysis was undertaken on crystals of $[PPh_3Me][Os_6(CO)_{18}(\mu_6\text{-}P)]$. The crystal structure consists of discrete $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$ anions and $[PPh_3Me]^+$ cations that are separated by normal van der Waals contacts. Each asymmetric unit contains two independent but structurally similar cations and anions. The structure of one of the $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$ (7) anions is shown in Figure 3. Selected final bond lengths and interbond angles are given in Table 4.

The six osmium atoms in each monoanion are at the corners of a trigonal prism, so that each is bonded to three other metal atoms. The interstitial phosphorus atom lies at the centre of the prism and bonds all six metal atoms with an average P–Os distance of 2.31(1) Å. Each osmium atom also carries three terminal, essentially linear carbonyl ligands that lie approximately *trans* to the Os–Os vectors of the trigonal prism. Thus the cluster anion adopts the metal arrangement that its formal electron count (90 c.v.e.) predicts.

Some lengthening in the Os–Os distances over those that might be expected are observed in the monoanion of (7): within the basal triangles of the prism the Os–Os distances average 2.932(5) Å which is only slightly longer (*ca.* 0.06—0.07 Å) than the average distances of 2.877(3) Å in $[Os_3(CO)_{12}]$ and 2.863 Å in the octahedral dianion $[Os_6(CO)_{18}]^{2-}$,[17] whereas the three interbasal Os–Os distances average 3.140(3) Å. The latter distance is within the range of distances found for which there is no formal Os–Os bond,[17] and thus the three interbasal Os–Os distances are amongst the longest found in a cluster where a formal metal–metal bond is expected.

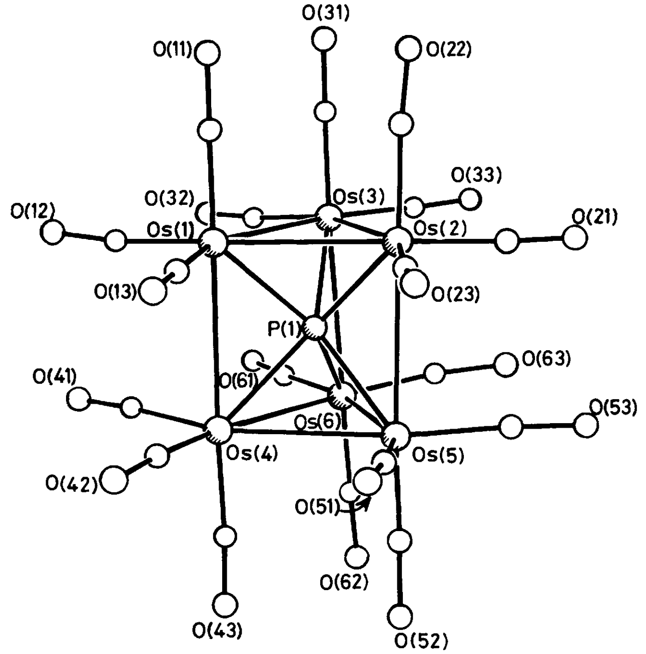

Figure 3. The molecular structure of the $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$ (7) anion, showing the atom numbering scheme adopted

It is tempting to attribute the lengthening in the Os–Os distances in the anion of (7) to the size requirements of the interstitial phosphorus atom. However, in *all* the clusters with a trigonal-prismatic metal framework to have been characterised structurally, lengthening of the interbasal metal distances over those within the basal triangles is observed.[18–20] These examples include the cluster dianion $[Pt_6(CO)_{12}]^{2-}$ which does not have an interstitial atom.[20] Further, evidence has been presented for the fact that an intersititial atom can to some extent 'expand' or 'contract' to meet the size requirements of the metal cavity in which it is encapsulated. For example, on heating the trigonal-prismatic cluster anion $[Co_6N(CO)_{15}]^-$ (90 c.v.e.) two carbonyl ligands are lost to give the octahedral cluster anion $[Co_6N(CO)_{13}]^-$ (86 c.v.e.) with, as a consequence, the apparent radius of the interstitial nitrogen atom decreasing from 0.67 Å in the larger trigonal prismatic cavity to 0.54 Å in the octahedral cavity.[21]

Experimental

Although none of the compounds reported here is particularly air-sensitive, all the manipulations (reactions, chromatography, and recrystallisations) described below were carried out under inert atmospheres of either dinitrogen or argon.

Proton and ^{31}P n.m.r. data were obtained on Bruker WM250 or WH400 instruments at 20 °C using deuteriated solvent as internal lock and reference (^1H, ^{13}C: $SiMe_4$, $\delta = 0$; ^{31}P: 1% $P(OMe)_3$ in C_6D_6, $\delta = 0$; downfield positive). Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer and mass spectra were obtained on an AEI MS12 spectrometer with *ca.* 70 eV (1.12×10^{-17} J) ionizing potential at 100—150 °C. Tris(perfluoroheptyl)-*s*-triazine was used as reference.

The compounds $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$ were prepared by the literature methods.[11] All other reagents were commercial grade and used as obtained.

Table 4. Bond lengths (Å) and angles (°) for the $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$ anion (**7**)

Molecule 1				Molecule 2			
Os(1)–Os(2)	2.941(2)	Os(5)–Os(6)	2.932(1)	Os(10)–Os(20)	2.933(2)	Os(50)–Os(60)	2.914(2)
Os(1)–Os(3)	2.929(1)	Os(1)–P(1)	2.299(6)	Os(10)–Os(30)	2.949(2)	Os(10)–P(10)	2.313(6)
Os(1)–Os(4)	3.151(1)	Os(2)–P(1)	2.320(7)	Os(10)–Os(40)	3.136(1)	Os(20)–P(10)	2.306(7)
Os(2)–Os(3)	2.927(1)	Os(3)–P(1)	2.316(7)	Os(20)–Os(30)	2.923(2)	Os(30)–P(10)	2.303(7)
Os(2)–Os(5)	3.144(1)	Os(4)–P(1)	2.300(7)	Os(20)–Os(50)	3.157(2)	Os(40)–P(10)	2.307(8)
Os(3)–Os(6)	2.942(1)	Os(5)–P(1)	2.311(6)	Os(30)–Os(60)	3.138(1)	Os(50)–P(10)	3.312(6)
Os(4)–Os(5)	2.933(1)	Os(6)–P(1)	2.312(6)	Os(40)–Os(50)	2.915(2)	Os(60)–P(10)	3.302(7)
Os(4)–Os(6)	2.942(1)			Os(40)–Os(60)	2.917(2)		
Os(3)–Os(1)–Os(2)	59.8(1)	P(1)–Os(3)–Os(6)	47.3(2)	Os(30)–Os(10)–Os(20)	59.6(1)	P(10)–Os(30)–Os(60)	47.0(2)
Os(4)–Os(1)–Os(2)	91.3(1)	P(1)–Os(4)–Os(1)	46.7(1)	Os(40)–Os(10)–Os(20)	89.8(1)	P(10)–Os(40)–Os(10)	47.3(2)
Os(4)–Os(1)–Os(3)	88.6(1)	P(1)–Os(4)–Os(5)	50.7(2)	Os(40)–Os(10)–Os(30)	89.8(1)	P(10)–Os(40)–Os(50)	50.9(2)
Os(3)–Os(2)–Os(1)	59.9(1)	P(1)–Os(4)–Os(6)	50.5(2)	Os(30)–Os(20)–Os(10)	60.5(1)	P(10)–Os(40)–Os(60)	50.7(2)
Os(5)–Os(2)–Os(1)	88.4(1)	P(1)–Os(5)–Os(2)	47.4(2)	Os(50)–Os(20)–Os(10)	89.9(1)	P(10)–Os(50)–Os(20)	46.8(2)
Os(5)–Os(2)–Os(3)	91.3(1)	P(1)–Os(5)–Os(4)	50.3(2)	Os(50)–Os(20)–Os(30)	89.6(1)	P(10)–Os(50)–Os(40)	50.8(2)
Os(2)–Os(3)–Os(1)	60.3(1)	P(1)–Os(5)–Os(6)	50.6(2)	Os(20)–Os(30)–Os(10)	59.9(1)	P(10)–Os(50)–Os(60)	50.7(2)
Os(6)–Os(3)–Os(1)	91.4(1)	P(1)–Os(6)–Os(3)	47.4(2)	Os(60)–Os(30)–Os(10)	89.6(1)	P(10)–Os(60)–Os(30)	47.0(2)
Os(6)–Os(3)–Os(2)	88.6(1)	P(1)–Os(6)–Os(4)	50.2(2)	Os(60)–Os(30)–Os(20)	90.2(1)	P(10)–Os(60)–Os(40)	50.8(2)
Os(5)–Os(4)–Os(1)	88.4(1)	P(1)–Os(6)–Os(5)	50.6(2)	Os(50)–Os(40)–Os(10)	90.6(1)	P(10)–Os(60)–Os(50)	51.0(2)
Os(6)–Os(4)–Os(1)	90.9(1)	Os(2)–P(1)–Os(1)	79.1(2)	Os(60)–Os(40)–Os(10)	90.2(1)	Os(20)–P(10)–Os(10)	78.8(2)
Os(6)–Os(4)–Os(5)	59.9(1)	Os(3)–P(1)–Os(1)	78.8(2)	Os(60)–Os(40)–Os(50)	60.0(1)	Os(30)–P(10)–Os(10)	79.4(2)
Os(4)–Os(5)–Os(2)	91.5(1)	Os(3)–P(1)–Os(2)	78.3(2)	Os(40)–Os(50)–Os(20)	89.7(1)	Os(30)–P(10)–Os(20)	78.7(2)
Os(6)–Os(5)–Os(2)	88.4(1)	Os(4)–P(1)–Os(1)	86.5(2)	Os(60)–Os(50)–Os(20)	90.0(1)	Os(40)–P(10)–Os(10)	85.5(2)
Os(6)–Os(5)–Os(4)	60.2(1)	Os(4)–P(1)–Os(2)	141.1(3)	Os(60)–Os(50)–Os(40)	60.0(1)	Os(40)–P(10)–Os(20)	136.6(3)
Os(4)–Os(6)–Os(3)	88.7(1)	Os(4)–P(1)–Os(3)	134.1(3)	Os(40)–Os(60)–Os(30)	90.4(1)	Os(40)–P(10)–Os(30)	137.6(3)
Os(5)–Os(6)–Os(3)	91.3(1)	Os(5)–P(1)–Os(1)	134.0(3)	Os(50)–Os(60)–Os(30)	90.2(1)	Os(50)–P(10)–Os(10)	137.1(3)
Os(5)–Os(6)–Os(4)	59.9(1)	Os(5)–P(1)–Os(2)	85.5(2)	Os(50)–Os(60)–Os(40)	60.0(1)	Os(50)–P(10)–Os(20)	86.3(2)
P(1)–Os(1)–Os(2)	50.8(2)	Os(5)–P(1)–Os(3)	139.6(3)	P(10)–Os(10)–Os(20)	50.5(2)	Os(50)–P(10)–Os(30)	136.7(3)
P(1)–Os(1)–Os(3)	50.9(2)	Os(5)–P(1)–Os(4)	79.0(2)	P(10)–Os(10)–Os(30)	50.1(2)	Os(50)–P(10)–Os(40)	78.3(2)
P(1)–Os(1)–Os(4)	46.8(2)	Os(6)–P(1)–Os(1)	140.8(3)	P(10)–Os(10)–Os(40)	47.2(2)	Os(60)–P(10)–Os(10)	136.8(3)
P(1)–Os(2)–Os(1)	50.1(1)	Os(6)–P(1)–Os(2)	132.3(3)	P(10)–Os(20)–Os(10)	50.7(2)	Os(60)–P(10)–Os(20)	137.6(3)
P(1)–Os(2)–Os(3)	50.8(2)	Os(6)–P(1)–Os(3)	85.4(2)	P(10)–Os(20)–Os(30)	50.6(2)	Os(60)–P(10)–Os(30)	85.9(3)
P(1)–Os(2)–Os(5)	47.1(2)	Os(6)–P(1)–Os(4)	79.3(2)	P(10)–Os(20)–Os(50)	46.9(2)	Os(60)–P(10)–Os(40)	78.5(2)
P(1)–Os(3)–Os(1)	50.3(2)	Os(6)–P(1)–Os(5)	78.7(2)	P(10)–Os(30)–Os(10)	50.5(2)	Os(60)–P(10)–Os(50)	78.3(2)
P(1)–Os(3)–Os(2)	50.9(2)			P(10)–Os(30)–Os(20)	50.7(2)		

Preparation of $[Os_3(CO)_{11}(PH_3)]$ (**1**).*—A suspension of $[Os_3(CO)_{11}(MeCN)]$ (200 mg) in toluene (30 cm^3) was heated to 40 °C under an atmosphere of phosphine gas. The progress of the reaction was monitored by the uptake of phosphine. After *ca.* 1 h all the reagent cluster had dissolved and no further uptake of phosphine occurred. The reaction mixture was cooled to room temperature (r.t.) and purged of excess phosphine. Removal of the solvent *in vacuo* gave a quantitative yield of (**1**) as a fine yellow powder of sufficient purity for the syntheses described below. Analytically pure (**1**) was obtained by recrystallisation from toluene–hexane mixtures at −80 °C (yield 150 mg, 75%) (Found: C, 14.45; H, 0.45. Calc. for $C_{11}H_3O_{11}Os_3P$: C, 14.5; H, 0.3%; M^+ m/z 918).

Preparation of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}PH_2)]$ (**2**).—Excess anhydrous Na_2CO_3 (500 mg) was added to a suspension of (**1**) (500 mg) in methanol (60 cm^3). The reaction mixture was stirred until all of (**1**) dissolved and the i.r. spectrum showed complete conversion of (**1**) to $Na[Os_3(CO)_{10}(PH_2)]$ [ν(CO) (MeOH): 2 070w, 2 009s, 1 997vs, 1 986s, 1 968m, and 1 933m cm^{-1}]. The excess of Na_2CO_3 was filtered off and CF_3COOH added dropwise until the solution was acidic. The solvent was then removed and the residue subjected to column chromatography on silica using hexane as eluant. Removal of the solvent from the single yellow band gave (**2**) as a yellow powder (yield 434 mg, 89%); M^+ m/z 890.

Preparation of $[Os_6(\mu\text{-}H)_2(CO)_{21}(\mu_3\text{-}PH)]$ (**3**).—$[Os_3(CO)_{11}(MeCN)]$ (320 mg) was added to a solution of (**2**) (300 mg) in toluene (50 cm^3). The mixture was then heated to 50 °C {the compound $[Os_3(CO)_{11}(MeCN)]$ rapidly dissolved} and as the reaction proceeded a fine yellow precipitate formed. Heating was continued until the i.r. spectrum of the reaction mixture showed no bands attributable to either starting cluster (*ca.* 30 h). Filtration of the precipitate, and repeated washing with toluene and then hexane gave (**3**) (yield 556 mg, 94%); M^+ m/z 1 774.

Preparation of $[Os_6(\mu\text{-}H_2)(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$ (**4**).—Using an exactly analogous procedure to that described above for (**3**), but with cyclohexane rather than toluene as solvent, $[Os_3(CO)_{10}(MeCN)_2]$ (210 mg) and (**2**) (200 mg) gave (**4**) (yield 342 mg, 89%) (Found: C, 14.7; H, 0.3%; M^+ m/z 1 718. Calc. for $C_{22}H_6O_{20}Os_6P$: C, 14.7; H, 0.3%; ^{192}Os m/z 1 787).

Preparation of the $[N(PPh_3)_2]^+$ *Salt of* $[Os_6(\mu\text{-}H)(CO)_{21}(\mu_3\text{-}PH)]^-$ (**5**).—Compound (**3**) (300 mg) was stirred in dichloromethane (30 cm^3) with a large excess of $[N(PPh_3)_2]Cl$ (600 mg) for 20 h at which stage the i.r. spectrum of the solution showed only ν(CO) bands from the product cluster (**5**). After concentration (to *ca.* 5 cm^3) the solution was passed through a silica plug (10 × 5 cm) eluting with dichloromethane–hexane (70:30) to remove the excess $[N(PPh_3)_2]Cl$. Removal of the solvent from the single yellow band gave (**5**) (yield 375 mg, 96%).

The $[PPh_3Me]^+$ salt of (**5**) was prepared from the analogous reaction of (**3**) with excess $[PPh_3Me]Br$.

Preparation of $[Os_6(\mu\text{-}H)(CO)_{18}(\mu_6\text{-}P)]$ (**6**) *via Thermolysis of* (**3**).—A suspension of compound (**3**) (50 mg) in xylene (25

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* **CAUTION**: The experimenter should be familiar with the use of phosphine (which is an extremely toxic and inflammable gas) before undertaking this preparation!

cm^3) was heated to reflux. After 10—15 min the cluster had dissolved and the solution darkened from yellow to deep orange. The i.r. spectrum of the solution showed the clean formation of an uncharacterised intermediate product [ν(CO): 2 124w, 2 085m, 2 067vs, 2 056s, 2 013m, and 1 981w cm^{-1}]. As reflux was continued the solution turned dark brown and the above i.r. bands were gradually replaced by those of the product cluster (**6**). After 16 h the reaction was adjudged to be completed, was cooled and the solvent removed *in vacuo*. Chromatography on silica eluting with dichloromethane–hexane (50:50) gave a single yellow-orange band from which orange crystals of (**6**) were obtained (yield 16 mg, *ca.* 35%) (Found: C, 13.1; H, 0.1%; M^+ m/z 1 688. Calc. for $C_{18}HO_{18}Os_6P$: C, 12.9; H, 0.1%).

Preparation of the $[N(PPh_3)_2]^+$ *Salt of* $[Os_6(CO)_{18}(\mu_6\text{-}P)]^-$ (**7**) via *Thermolysis of* (**5**).—Compound (**5**) (250 mg) was heated at reflux in toluene (300 cm^3). As reflux proceeded the solution darkened from yellow to brown-orange. Accompanying changes were observed in the solution i.r. spectrum; after a short time (*ca.* 1 h) the carbonyl bands from (**5**) were replaced by those of an uncharacterised cluster species [ν(CO): 2 048vs, 2 011m, 1 992m, and 1 969m cm^{-1}] and then more slowly by those of the product cluster (**7**) (some of the product precipitated from solution at this point). The reflux was continued until the i.r. spectrum of the reaction mixture showed only bands from the product (**7**) (no further change in the i.r. occurs), the mixture cooled, and the toluene removed *in vacuo*. Column chromatography on silica eluting with dichloromethane gave a single major yellow orange band (several minor brown bands followed), and recrystallisation of the residue of this band from dichloromethane–hexane gave orange crystals of $[N(PPh_3)_2][Os_6(CO)_{18}(\mu_6\text{-}P)]$ (**7**) (yield 184 mg, 77%) (Found: C, 29.1; H, 1.4. Calc. for $C_{54}H_{30}NO_{18}Os_6P$: C, 29.3; H, 1.4%).

On a larger scale, from $[Os_3(CO)_{12}]$ (2.0 g) and using the sequence of reaction steps $[Os_3(CO)_{12}]$ → (**1**) → (**2**) → (**3**) → (**5**) → (**7**), we have routinely obtained $[N(PPh_3)_2][Os_6(CO)_{18}(\mu_6\text{-}P)]$ {1.4—1.6 g, 57—65% based on $[Os_3(CO)_{12}]$}.

Reaction of (**6**) *with Excess* $[N(PPh_3)_2]Cl$ *to give* (**7**).—Compound (**6**) (10 mg) was dissolved in dichloromethane (10 cm^3), excess $[N(PPh_3)_2]Cl$ (15 mg) added and the solution stirred until its i.r. spectrum showed only the carbonyl bands of (**7**). Work-up gave (**7**) (12 mg, 92%).

Protonation of (**7**).—Trifluoroacetic acid (*ca.* 0.2 cm^3) was added dropwise to (**7**) (200 mg) in dichloromethane (20 cm^3) until the solution i.r. spectrum showed only the bands of the product cluster (**6**). Much of the slightly soluble product precipitated out as the acid was added and the remainder was precipitated out by the addition of isopropyl alcohol (30 cm^3) to the solution. The precipitate was filtered off, washed successively with isopropyl alcohol and then hexane, and then dried *in vacuo* to give the cluster (**6**) as an orange powder (148 mg, 98%).

X-*Ray Structural Analysis of* $[Os_6(\mu\text{-}H)_2(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$ (**4**).—Crystals of (**4**) were obtained from ethyl acetate–hexane solution.

Crystal data. $C_{22}H_6NO_{20}Os_6P$, M = 1 776.45, orthorhombic, a = 12.358(3), b = 22.473(5), c = 25.559(16) Å, U = 7 098.3 Å^3 (by least-squares refinement on diffractometer angles for 52 automatically centred reflections, λ = 0.710 69 Å), space group *Pbca* (no. 61), D_m not measured, Z = 8, D_c = 3.31 g cm^{-3}, $F(000)$ = 6 208. Yellow elongated rectangular blocks. Crystal dimensions (distance to faces from centre): 0.055 (001, 00$\bar{1}$) × 0.108 (1$\overline{21}$, $\bar{1}$21) × 0.093 (1$\bar{2}$1, $\bar{1}$2$\bar{1}$) × 0.150 (12$\bar{1}$,$\overline{121}$) mm, μ(Mo-K_α) = 215.11 cm^{-1}.

Data collection and processing.[22] Stoe-Siemens four-circle diffractometer, 24 step ω/θ scan mode with scan step 0.05°, scan time 0.5—2.0 s per step, graphite monochromated Mo-K_α radiation; 10 355 reflections measured ($5.0 \leqslant 2\theta \leqslant 45°$, $+h + k \pm l$), 4 638 unique [merging R = 0.120 after absorption correction (max., min. transmission factors = 0.131, 0.029)], giving 3 202 with $F > 4\sigma(F)$. No significant decay during data collection.

Structure analysis and refinement. Direct methods (Os atoms)

Table. 5. Atomic co-ordinates (× 10^4) for (**4**)

Atom	*x*	*y*	*z*
Os(1)	2 046(1)	854(1)	3 040(1)
Os(2)	2 795(1)	369(1)	4 012(1)
Os(3)	2 964(1)	1 630(1)	3 813(1)
Os(4)	1 499(1)	1 359(1)	5 336(1)
Os(5)	1 356(1)	1 603(1)	6 444(1)
Os(6)	3 492(1)	1 434(1)	6 017(1)
P	1 734(9)	1 151(4)	4 417(5)
O(1)	−260(26)	1 110(13)	3 448(15)
O(2)	1 301(27)	−316(13)	2 528(16)
O(3)	1 919(31)	1 792(15)	2 170(17)
O(4)	4 481(26)	643(13)	2 727(14)
O(5)	756(28)	−435(14)	3 987(15)
O(6)	3 803(26)	−2(14)	5 059(15)
O(7)	4 152(26)	−526(13)	3 379(14)
O(8)	1 269(23)	2 604(12)	3 650(13)
O(9)	4 268(25)	2 227(12)	4 660(14)
O(10)	4 497(26)	2 056(13)	2 949(15)
O(11)	1 732(21)	2 652(11)	4 980(12)
O(12)	−836(25)	1 415(13)	5 179(13)
O(13)	1 326(24)	29(12)	5 510(12)
O(14)	1 244(26)	270(13)	6 698(14)
O(15)	−1 052(24)	1 658(13)	6 532(13)
O(16)	1 919(30)	1 884(14)	7 544(18)
O(17)	1 309(25)	2 917(13)	6 120(14)
O(18)	3 788(26)	2 756(14)	5 837(15)
O(19)	4 435(22)	1 614(11)	7 122(12)
O(20)	5 589(25)	1 245(12)	5 489(13)
N	3 382(26)	516(13)	6 147(15)
C(1)	570(39)	1 036(19)	3 294(21)
C(2)	1 547(33)	152(16)	2 723(17)
C(3)	1 846(42)	1 442(20)	2 507(25)
C(4)	3 698(36)	709(18)	2 869(20)
C(5)	1 463(35)	−155(17)	4 033(19)
C(6)	3 435(35)	146(17)	4 646(18)
C(7)	3 772(32)	−154(17)	3 621(18)
C(8)	1 838(21)	2 219(16)	3 709(17)
C(9)	3 772(36)	1 999(18)	4 329(20)
C(10)	3 971(37)	1 860(18)	3 257(21)
C(11)	1 582(36)	2 157(18)	5 122(20)
C(12)	109(33)	1 388(18)	5 237(18)
C(13)	1 318(47)	582(23)	5 467(25)
C(14)	1 298(42)	750(22)	6 621(23)
C(15)	−104(33)	1 644(17)	6 485(18)
C(16)	1 655(51)	1 690(25)	7 135(20)
C(17)	1 336(33)	2 422(17)	6 212(18)
C(18)	3 625(36)	2 256(18)	5 899(19)
C(19)	4 027(30)	1 518(16)	6 703(17)
C(20)	4 843(31)	1 304(16)	5 708(17)
C(21)	3 383(35)	35(18)	6 164(19)
C(22)	3 454(36)	−667(17)	6 220(19)

Table. 6. Atomic co-ordinates ($\times 10^4$) for (7)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	5 981(1)	9 840(1)	7 830(1)	Os(10)	3 716(1)	5 178(1)	7 551(1)
Os(2)	5 544(1)	10 894(1)	6 978(1)	Os(20)	4 665(1)	4 561(1)	6 812(1)
Os(3)	4 970(1)	10 768(1)	8 137(1)	Os(30)	4 284(1)	3 889(1)	7 892(1)
Os(4)	4 839(1)	8 920(1)	7 259(1)	Os(40)	4 890(1)	5 853(1)	8 349(1)
Os(5)	4 488(1)	9 928(1)	6 339(1)	Os(50)	5 841(1)	5 239(1)	7 624(1)
Os(6)	3 839(1)	9 912(1)	7 467(1)	Os(60)	5 443(1)	4 577(1)	8 698(1)
P(1)	4 948(3)	10 035(4)	7 336(3)	P(10)	4 805(3)	4 879(4)	7 820(3)
P(4)	2 013(3)	2 816(4)	275(3)	P(5)	2 931(3)	7 078(4)	4 557(3)
C(14)	2 376(11)	3 631(14)	114(11)	C(15)	2 871(11)	7 170(13)	3 750(11)
C(24)	2 234(9)	2 605(10)	1 050(6)	C(25)	3 712(6)	7 354(8)	4 893(7)
C(34)	1 775	2 583	1 478	C(35)	4 049	7 066	5 408
C(44)	1 984	2 448	2 088	C(45)	4 654	7 323	5 656
C(54)	2 653	2 335	2 268	C(55)	4 921	7 867	5 390
C(64)	3 112	2 357	1 839	C(65)	4 583	8 154	4 875
C(74)	2 903	2 493	1 230	C(75)	3 979	7 898	4 627
C(84)	1 120(5)	2 875(9)	110(7)	C(85)	2 860(10)	6 234(9)	4 743(10)
C(94)	788	3 456	206	C(95)	3 143	5 768	4 387
C(104)	101	3 487	86	C(105)	3 088	5 106	4 522
C(114)	−255	2 937	−129	C(115)	2 752	4 910	5 012
C(124)	77	2 356	−224	C(125)	2 470	5 376	5 368
C(134)	764	2 325	−105	C(135)	2 524	6 038	5 233
C(144)	2 334(8)	2 232(10)	−200(8)	C(145)	2 294(8)	7 525(10)	4 869(9)
C(154)	2 466	2 422	−783	C(155)	2 420	7 803	5 447
C(164)	2 727	1 973	−1 169	C(165)	1 917	8 134	5 706
C(174)	2 856	1 334	−973	C(175)	1 290	8 187	5 388
C(184)	2 724	1 144	−390	C(185)	1 165	7 908	4 811
C(194)	2 463	1 594	−3	C(195)	1 667	7 577	4 551
O(11)	7 074(10)	10 715(11)	8 392(9)	O(110)	2 571(10)	4 458(13)	6 921(10)
O(12)	6 114(10)	8 958(12)	8 953(10)	O(120)	3 503(9)	6 363(12)	6 716(9)
O(13)	6 874(10)	9 190(11)	7 009(9)	O(130)	2 878(9)	5 599(11)	8 536(9)
O(21)	4 659(9)	12 023(11)	6 554(9)	O(210)	5 527(11)	3 470(14)	6 443(11)
O(22)	6 586(9)	11 851(11)	7 511(9)	O(220)	3 495(11)	4 012(12)	6 069(10)
O(23)	6 342(8)	10 593(10)	5 937(8)	O(230)	4 782(12)	5 598(15)	5 869(13)
O(31)	6 044(9)	11 650(11)	8 742(8)	O(310)	3 223(12)	3 127(14)	7 134(11)
O(32)	4 727(10)	10 103(13)	9 318(11)	O(320)	3 578(11)	3 670(13)	8 998(11)
O(33)	4 017(9)	11 878(12)	8 071(9)	O(330)	5 199(11)	2 722(13)	7 833(11)
O(41)	4 871(9)	8 220(11)	8 460(10)	O(410)	4 003(10)	5 954(12)	9 383(10)
O(42)	5 881(8)	8 098(10)	6 709(8)	O(420)	5 976(9)	6 540(11)	9 162(9)
O(43)	3 751(9)	8 049(11)	6 677(9)	O(430)	4 693(11)	7 012(15)	7 509(12)
O(51)	5 502(9)	9 466(11))	5 491(9)	O(510)	5 858(14)	6 301(18)	6 700(14)
O(52)	3 461(9)	9 047(11)	5 697(9)	O(520)	7 002(10)	5 844(12)	8 391(10)
O(53)	3 865(9)	11 105(12)	5 667(9)	O(530)	6 713(14)	4 206(17)	7 195(14)
O(61)	3 463(9)	9 584(11)	8 713(9)	O(610)	6 573(10)	5 166(11)	9 520(9)
O(62)	2 692(10)	9 127(12)	6 884(10)	O(620)	6 234(12)	3 339(16)	8 543(12)
O(63)	3 120(11)	11 164(14)	7 120(11)	O(630)	4 677(10)	4 308(11)	9 754(10)
C(11)	6 641(13)	10 361(16)	8 167(12)	C(110)	3 014(15)	4 764(18)	7 170(14)
C(12)	6 044(13)	9 286(16)	8 478(14)	C(120)	3 617(12)	5 883(15)	7 057(12)
C(13)	6 521(12)	9 438(15)	7 339(12)	C(130)	3 213(13)	5 447(16)	8 135(13)
C(21)	5 006(13)	11 570(16)	6 708(13)	C(210)	5 220(15)	3 973(18)	6 576(14)
C(22)	6 193(12)	11 461(15)	7 324(12)	C(220)	4 002(15)	4 289(18)	6 388(14)
C(23)	6 032(11)	10 690(14)	6 343(11)	C(230)	4 801(16)	5 196(22)	6 234(17)
C(31)	5 623(13)	11 285(16)	8 491(12)	C(310)	3 632(13)	3 499(16)	7 437(12)
C(32)	4 818(13)	10 350(16)	8 829(13)	C(320)	3 886(14)	3 708(17)	8 590(14)
C(33)	4 367(13)	11 426(16)	8 121(13)	C(330)	4 862(13)	3 212(16)	7 856(12)
C(41)	4 849(13)	8 510(16)	8 030(14)	C(410)	4 343(14)	5 916(16)	8 956(14)
C(42)	5 492(11)	8 437(13)	6 933(11)	C(420)	5 561(12)	6 237(15)	8 827(12)
C(43)	4 189(12)	8 410(15)	6 889(12)	C(430)	4 691(13)	6 554(17)	7 867(14)
C(51)	5 102(13)	9 673(16)	5 800(13)	C(510)	5 883(18)	5 812(22)	7 036(18)
C(52)	3 873(13)	9 428(15)	5 978(12)	C(520)	6 561(12)	5 587(15)	8 065(12)
C(53)	4 123(13)	10 655(16)	5 948(13)	C(530)	6 348(19)	4 661(24)	7 348(18)
C(61)	3 606(13)	9 692(16)	8 237(14)	C(610)	6 123(14)	4 927(17)	9 205(14)
C(62)	3 180(15)	9 444(17)	7 119(14)	C(620)	5 918(15)	3 856(18)	8 633(14)
C(63)	3 424(16)	10 641(19)	7 317(16)	C(630)	4 946(15)	4 381(17)	9 341(15)

followed by Fourier-difference syntheses. Full-matrix least-squares refinement with Os anisotropic, P, O, and C isotropic. The weighting scheme $w = 4.594/[\sigma^2(F_o)]$ gave satisfactory agreement analyses. Final *R* and *R'* values are 0.078 and 0.056. Programs and computers used and scattering factor data are given in ref. 23. Final atomic co-ordinates are listed in Table 5.

X-*Ray structural analysis of* $[PPh_3Me][Os_6(CO)_{18}(\mu_6\text{-}P)]$ (7).—Crystals of (7) were obtained from CH_2Cl_2–hexane solution.

Crystal data. $C_{37}H_{18}O_{18}Os_6P_2$, M = 1 953.65, monoclinic, a = 20.310(1), b = 20.492(8), c = 22.051(4) Å, β = 95.83(2)°, U = 9 130.0 Å^3 (by least-squares refinement on diffractometer angles for 48 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/a$ (alt. $P2_1/c$, no. 14), D_m not measured, $Z = 8$, $D_c = 2.842$ g cm^{-3}, $F(000) = 6\,958$. Orange blocks. Crystal dimensions (distance to faces from centre): 0.054 (010, 0$\bar{1}$0) × 0.086 (1$\bar{1}$0, $\bar{1}$10) × 0.087 (110, $\overline{110}$) × 0.182 (00$\bar{1}$, 001) mm, μ(Mo-K_α) = 167.60 cm^{-1}.

Data collection and processing.[22] Stoe-Siemens four-circle diffractometer, 24 step ω/θ scan mode with step width = 0.05°, scan time 0.75—3.0 s per step, graphite monochromated Mo-K_α radiation, 9 890 reflections measured ($5.0 \leqslant 2\theta \leqslant 41.0°$, $\pm h - k + l$), 9 120 unique [merging $R = 0.030$ after absorption correction (max., min. transmission factors = 0.217, 0.049)], giving 6 493 with $F > 4\sigma(F)$. No significant decay during data collection.

Structure analysis and refinement. Direct methods (Os atoms) followed by Fourier-difference techniques. Blocked full-matrix least-squares refinement with Os, P, and O atoms assigned anisotropic thermal parameters. Phenyl rings refined as rigid groups with C–C fixed at 1.395 Å and C–C–C at 120°. The weighting scheme $w = 2.103/[\sigma^2(F_o) + 0.000\,412\ F_o^2]$, with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Final R and R' values are 0.053 and 0.049. Programs and computers used and scattering factors are given in ref. 23. Final atomic co-ordinates are presented in Table 6.

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