Synthesis of the μ-PH Hexaosmium Clusters $[Os_6H_2(CO)_{20}L(\mu_3\text{-}PH)]$ (L = CO or MeCN) and their Reactions with Base: *X*-Ray Crystal Structures of $[Os_6H_2(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$ and $[Os_6H_3(CO)_{19}(CO_2Me)(\mu_3\text{-}PH)]$

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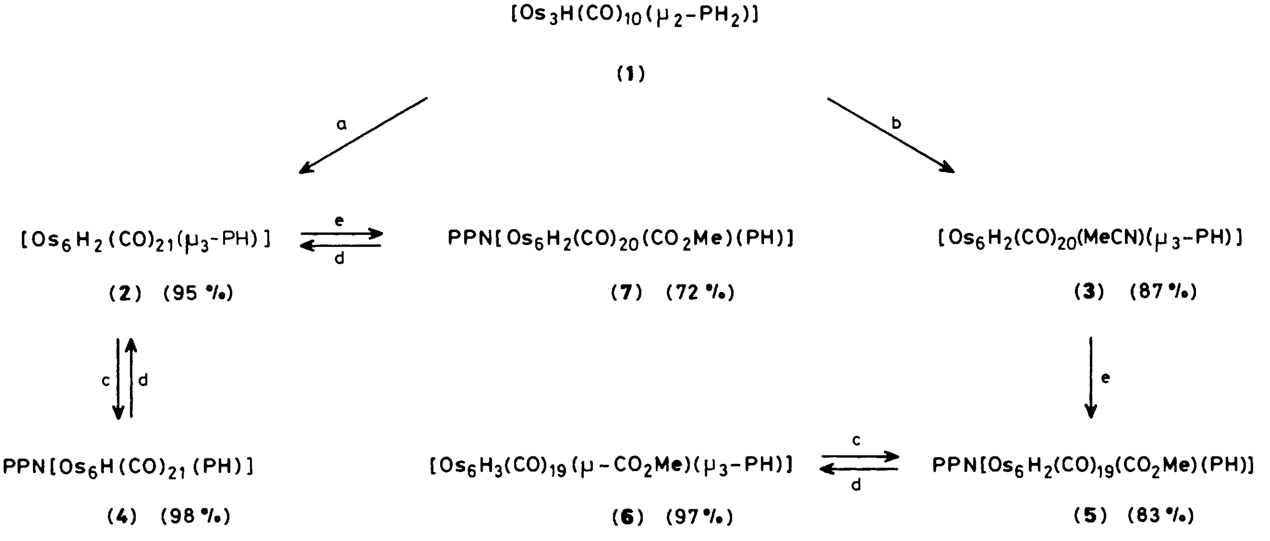
Mild heating of the phosphidotriosmium cluster $[Os_3H(CO)_{10}(\mu_2\text{-}PH_2)]$ (**1**) with $[Os_3(CO)_{12-n}(MeCN)_n]$ (*n* = 1 or 2) gives high yields of the (μ_3-PH) bridged hexaosmium clusters (**2**) and (**3**); reactions of (**2**) and (**3**) with bases and *X*-ray structure analyses of (**3**) and of (**6**), which was obtained from (**3**) and MeO^- followed by acid treatment are described.

Recently we reported coupling reactions of phosphido-osmium clusters $[Os_3H(CO)_{10}(PRH)]$ (R ≠ H) with $[M_3(CO)_{12}]$ (M = Os or Ru) at *high temperatures* to give higher nuclearity osmium and mixed osmium–ruthenium clusters having a bridging phosphinidene (μ-PR) ligand.[1] Higher nuclearity clusters containing the μ-PH group, which are of particular interest as potential intermediates in the synthesis of phosphide (μ-P) clusters, are not accessible *via* this route because of the thermal instability of $[Os_3H(CO)_{10}(PH_2)]$ (**1**).[2] A feature of reactions of $[Os_3(CO)_{12-n}(MeCN)_n]$ (*n* = 1 or 2) with compounds (organic, organometallic, and inorganic) containing 'acidic' hydrogen is the facile displacement of acetonitrile to give addition products containing a bridging hydride [equation (1)].[3] In this commun-



Scheme 1. (All the reactions are quantitative from i.r. spectra of the reaction mixtures; quoted yields in parentheses are for isolated products): *Reagents:* a, $[Os_3(CO)_{11}(MeCN)]$, cyclohexane 50 °C; b, $[Os_3(CO)_{10}(MeCN)_2]$, toluene 50 °C; c, [PPN]Cl (10 equiv.), CH_2Cl_2 or NEt_3, CH_2Cl_2 then [PPN]Cl (1 equiv.); d, CF_3CO_2H, CH_2Cl_2; e, Na_2CO_3, MeOH then [PPN]Cl (1 equiv.).

ication we report the products of the reactions of (**1**) with $[Os_3(CO)_{12-n}(MeCN)_n]$ and some reactions of these products with bases.

Treatment of (**1**) with $[Os_3(CO)_{11}(MeCN)]$ in cyclohexane (50 °C) gives a bright yellow precipitate (**2**) formulated from analytical and spectroscopic data† as $[Os_6H_2(CO)_{21}(PH)]$ (Scheme 1). The analogous reaction of (**1**) with $[Os_3(CO)_{10}(MeCN)_2]$ in toluene (50 °C) gives a yellow precipitate (**3**) which shows a 'parent' ion in its mass spectrum corresponding to the formulation $[Os_6H(CO)_{19}(PH)]$. However, analytical data and the similarity of chemical shift and coupling constants for the two hydride and one PH signals in the ^1H and ^{31}P n.m.r. spectra† of (**2**) and (**3**) suggest that the correct formulation for (**3**) is $[Os_6H_2(CO)_{20}(MeCN)(PH)]$. To confirm this and to establish the molecular geometries of (**2**) and (**3**), an *X*-ray analysis of (**3**) was undertaken on yellow crystals grown from ethyl acetate–hexane solution.‡ The structure (shown in Figure 1 along with some important bond parameters) consists of two perpendicular osmium triangles linked by a μ_3-PH group. Presumably the PH group is formed by concomitant displacement of acetonitrile from $[Os_3(CO)_{10}(MeCN)_2]$ and metallation of the μ_2-PH_2 group of (**1**).[4] The bridging hydrides were not directly located but the distribution of carbonyl ligands and the osmium bond lengths indicate that they bridge the Os(2)–Os(3) and Os(4)–Os(6) edges. In terms of electron counting, this complex is a 96-electron system which is consistent with the 6 observed Os–Os bonds. (**3**) is the first compound containing a μ_3-PH ligand to be structurally characterised. $\{[(C_5Me_5)_2M(OMe)]_2(PH)\}$ (M = U or Th),[5] $[Co_2Cr(CO)_{11}(PH)]$,[6] and $[Fe_4H(CO)_{10}\{(PPr)_2CH_2\}(PPrMe)(PH)]$[7] are the only other known compounds containing the μ_n-PH group.

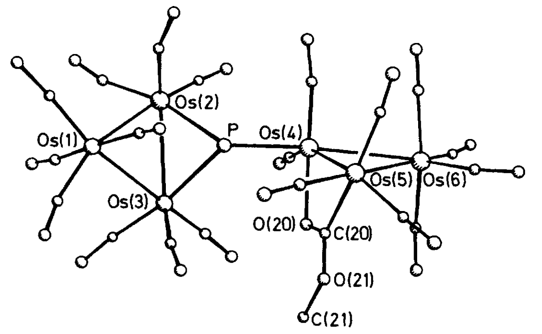


Figure 1. Molecular structure of $[Os_6H_2(CO)_{20}(MeCN)(\mu_3\text{-}PH)]$ (**3**). Selected bond distances and angles are: Os(1)–Os(2) 2.867(2), Os(1)–Os(3) 2.869(2), Os(2)–Os(3) 2.888(2), Os(4)–Os(5) 2.891(2), Os(4)–Os(6) 3.022(2), Os(5)–Os(6) 2.881(2), Os(2)–P 2.425(10), Os(3)–P 2.420(10), Os(4)–P 2.411(12) Å: Os(2)–P–Os(3) 73.2(3), Os(2)–P–Os(4) 128.4(5), Os(3)–P–Os(4) 127.6(4)°.

$$[Os_3(CO)_{12-n}(MeCN)_n] + HA \rightarrow [Os_3(\mu\text{-}H)_{12-n}(MeCN)_{n-x}(A)] + x[MeCN] \quad (1)$$

Weak bases such as NEt_3 and [PPN]Cl $\{PPN^+ = [N(PPh_3)_2]^+\}$ readily deprotonate (**2**) to its monoanion $[PPN][Os_6H(CO)_{21}(PH)]$ (**4**)† (Scheme 1). This deprotonation is reversible, the addition of CF_3CO_2H to (**4**) regenerating (**2**). Unlike (**2**), (**3**) does not react with either NEt_3 or [PPN]Cl and with the stronger bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or MeOH–KOH only decomposition to give mixtures of lower nuclearity products occurs. However, (**3**) does react with Na_2CO_3–MeOH, a mild source of the nucleophilic base NaOMe, to give $[PPN][Os_6H_2(CO)_{19}(CO_2Me)(PH)]$ (**5**) which is reversibly protonated by acid to give $[Os_6H_3(CO)_{19}(CO_2Me)(PH)]$ (**6**) (Scheme 1). The formulations of (**5**) and (**6**) were confirmed by spectroscopic and analytical data,† and *X*-ray analysis of (**6**) performed on yellow crystals obtained from ethyl acetate solution.‡

The molecular geometry of (**6**) (Figure 2) is best considered as being derived from that of (**3**) by methoxide attack at C(18) (Figure 1) to give a transitory intermediate anion having a terminal methoxycarbonyl ligand bound to Os(6).[8] Loss of acetonitrile from this intermediate anion is accompanied by bridging of the methoxycarbonyl ligand between Os(6) and Os(4), and movement of a carbonyl from Os(4) to Os(6) to give (**5**). Protonation then gives (**6**) in which the hydrides, although not directly located in the *X*-ray analysis, are believed from potential energy calculations to lie along the Os(2)–Os(3), Os(4)–Os(5), and Os(4)–Os(6) edges.

Reaction of (**2**) with Na_2CO_3–MeOH gives a mildly unstable monoanion which we assign as $[PPN][Os_6H_2(CO)_{20}(CO_2Me)(PH)]$ (**7**) from spectroscopic data† alone (Scheme 1). We believe that the reversible protonation of (**7**)

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† Selected spectroscopic data (i.r. in CH_2Cl_2, ^1H and ^{31}P n.m.r. in $CDCl_3$ or CD_2Cl_2; *J* values in Hz): (**2**) ν(CO): 2143w, 2101m, 2092ms, 2064vs, 2050m, 2041m, 2014s, 1979m, and 1969mw cm^{-1}; ^1H n.m.r.: δ 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], and −18.96 [dd, $J(PH^3)$ 10.6, $J(H^3H^1)$ 0.9, OsH]; ^{31}P n.m.r.: δ −322.3 [d of t, $J(PH^1)$ 340, $J(PH^2)$ ~$J(PH^3)$ = 12, PH] p.p.m.; M^+: *m/z* 1774. (**3**) ν(CO): 2112w, 2092m, 2076ms, 2049s, 2040ms, 2026ms, 2013s, 1981m, and 1966m cm^{-1}; ^1H n.m.r.: δ 6.31 [ddd, $J(PH^1)$ 337, $J(H^1H^3)$ 4.0, $J(H^1H^2)$ 1.0, PH], 2.58 (s, MeCN), −16.18 [dd, $J(PH^2)$ 11.6, $J(H^2H^1)$ 1.0, OsH], and −17.86 [dd, $J(PH^3)$ 13.6, $J(H^3H^1)$ 4.0, OsH]; ^{31}P n.m.r.: δ −325.0 [ddd, $J(PH^1)$ 337, $J(PH^2)$ 12, $J(PH^3)$ 14, PH] p.p.m.; M^+: *m/z* 1718 {calc. (^{192}Os) for $[Os_6H_2(CO)_{19}(PH)]$ 1718}. (**4**) ν(CO): 2084mw, 2044vs, 2004s, and 1974m cm^{-1}; ^1H n.m.r.: δ 7.6—7.3 [m, $(Ph_3P)_2N^+$], 6.78 [dd, *J*(PH) 328, *J*(HH) 3.6, PH] and −17.67 [dd, *J*(PH) 12.8, *J*(HH) 3.6, OsH]; ^{31}P n.m.r.: δ −118.1 [m, $(Ph_3P)_2N^+$] and −316.3 [dd, $J(PH^1)$ 330, $J(PH^2)$ 4, PH] p.p.m. (**5**) ν(CO): 2092w, 2078m, 2045vs, 2004, 1978m, and 1924w cm^{-1}; ^1H n.m.r.: δ 7.6—7.3 [m, $(Ph_3P)_2N^+$], 6.39 [ddd, $J(PH^1H^3)$ 4.6, PH], 3.72 (s, CO_2CH_3), −13.41 [dd, $J(PH^2)$ 9.5, $J(H^2H^1)$ 2.2, OsH], and −17.61 [dd, $J(PH^3)$ 13.0, $J(H^3H^1)$ 4.6, OsH]; ^{31}P n.m.r.: δ − 117.9 [m, $(Ph_3P)_2N^+$] and −234.68 [ddd, $J(PH^1)$ 308, $J(PH^2)$ 9.5, $J(PH^3)$ 13.0, PH] p.p.m. (**6**) ν(CO): 2132mw, 2097m, 2085m, 2058vs, 2014m, and 2000m cm^{-1}; ^1H n.m.r. δ 6.16 [dddd, $J(PH^1)$ 342, $J(H^1H^2)$ 3.6, $J(H^1H^3)$ 1.4, $J(H^1H^4)$ 4.2, PH], 3.85 (s, CO_2CH_3), −14.53 [ddd, $J(PH^2)$ 8.4, $J(H^2H^1)$ 3.6, $J(H^2H^3)$ 1.3, OsH], −15.10 [ddd, $J(PH^3)$ 15.2, $J(H^3H^1)$ 1.4, $J(H^3H^2)$ 1.3, OsH], and −18.16 [dd, $J(PH^4)$ 14.9, $J(H^4H^1)$ 4.2, OsH]; $^{31}P\{^1H\}$ n.m.r.: δ −266.8 (s, PH) p.p.m.; M^+: *m/z* 1776. (**7**) ν(CO): 2101w, 2092m, 2064s, 2048vs, 2037vs, 2018vs, 2008s, and 1971m cm^{-1}; ^1H n.m.r.: δ 7.6—7.4 [m, $(Ph_3P)_2N^+$], 6.27 [ddd, $J(PH^1)$ 331, $J(H^1H^2)$ 4.0, $J(H^1H^3)$ 1.5, PH], 3.25 (s, CO_2Me), −17.77 [dd, $J(PH^2)$ 13.5, $J(H^2H^1)$ 4.0, OsH], and −21.08 [dd, $J(PH^3)$ 12.4, $J(H^3H^1)$ 1.5, OsH]. Satisfactory analyses were obtained for (**2**), (**3**), and (**6**).

‡ *Crystal Data:* (**3**), $C_{22}H_6NO_{20}Os_6P$, *M* = 1776.45, orthorhombic, space group *Pbca* (No. 61), *a* = 12.358(3), *b* = 22.473(5), *c* = 25.559(16) Å, *U* = 7098.3 Å^3, D_c = 3.32 g cm^{-3}, *Z* = 8, *F*(000) = 6208, $\mu(Mo\text{-}K_\alpha)$ = 215.11 cm^{-1}, $F > 4\sigma(F)$, 2θ range 5—45°, *R* = 0.078, R_w = 0.056 for 3191 observed, absorption-corrected diffractometer data.

Crystal Data: (**6**), $C_{22}H_7O_{21}Os_6P$, *M* = 1779.45, monoclinic, space group *C*2/*c* (No. 15), *a* = 26.128(3), *b* = 9.553(2), *c* = 28.645(4) Å, β = 99.87(1)°, *U* = 7044.0 Å^3, D_c = 3.36 g cm^{-3}, *Z* = 8, *F*(000) = 6224, $\mu(Mo\text{-}K_\alpha)$ = 216.78 cm^{-1}, $F > 4\,\sigma(F)$, 2θ range 5—40°, *R* = 0.083, R_w = 0.070 for 2671 observed, absorption-corrected diffractometer data. The atomic co-ordinates bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

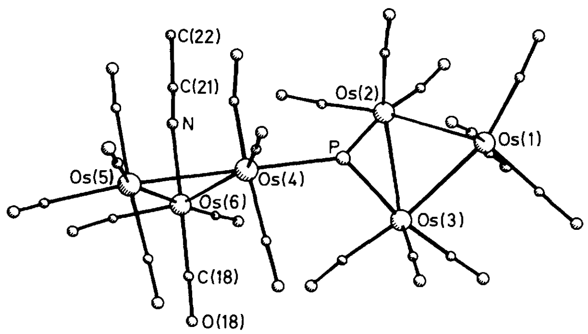

Figure 2. Molecular structure of [$Os_6H_3(CO)_{19}(\mu\text{-}CO_2Me)(\mu_3\text{-}PH)$] (**6**). Selected bond distances and angles are: Os(1)–Os(2) 2.873(4), Os(1)–Os(3) 2.869(3), Os(2)–Os(3) 2.904(4), Os(4)–Os(5) 3.081(3), Os(4)–Os(6) 2.955(3), Os(5)–Os(6) 2.890(3), Os(2)–P 2.401(14), Os(3)–P 2.387(14), Os(4)–P 2.372(13), Os(4)–O(20) 2.14(3), Os(6)–C(20) 1.85(6) Å; Os(2)–P–Os(3) 74.7(4), Os(2)–P–Os(4) 129.3(6), Os(3)–P–Os(4) 125.9(6), Os(4)–O(20)–C(20) 108.3(6), Os(6)–C(20)–O(20) 120(4), Os(6)–C(20)–O(21) 121(4)°.

to regenerate (**2**) indicates that the methoxycarbonyl ligand in (**7**) is terminal. Complete characterisation of this product and further reactions of the new osmium μ-PH clusters detailed here will be reported later.

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