The Preparation of an Unsaturated Hydrido Osmium Cluster by Hydrogenolysis of a Cyclometallated Phosphine; the *X*-Ray Structure of [$Os_3(CO)_8(H)_2(Ph_2PCH_2PPh_2)$]

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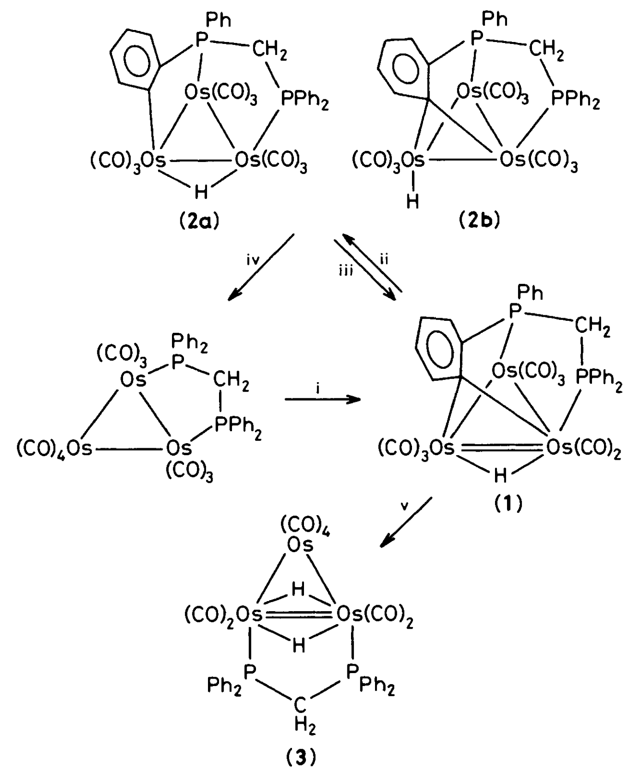
Treatment of [$Os_3(CO)_8(H)\{Ph_2PCH_2P(Ph)C_6H_4\}$] with H_2 affords a high yield of the unsaturated cluster [$Os_3(CO)_8(H)_2$-($Ph_2PCH_2PPh_2$)] which has been characterised by *X*-ray crystallography.

We recently reported the high yield synthesis of the unsaturated osmium cluster [$Os_3(CO)_8(H)\{Ph_2PCH_2P(Ph)C_6H_4\}$] (**1**) by the thermolysis of [$Os_3(CO)_{10}$(dppm)] (dppm = $Ph_2PCH_2PPh_2$) in refluxing toluene.[1] We also reported that (**1**) undergoes a facile, reversible addition reaction with CO, to give [$Os_3(CO)_9(H)\{Ph_2PCH_2P(Ph)C_6H_4\}$] (**2a**) or (**2b**) (see Scheme 1).[1] We now report that (**2**) undergoes further reaction with CO to regenerate the starting cluster [$Os_3(CO)_{10}$(dppm)], and that (**1**) undergoes a reaction with hydrogen to afford the unsaturated dihydrido osmium cluster [$Os_3(CO)_8(H)_2$(dppm)] (**3**) (see Scheme 1).

By bubbling CO through a toluene solution of (**1**), complete conversion into (**2**) is achieved after 2 h at 25 °C. It is not known at present whether (**2**) has the structure (**2a**) or (**2b**). Conversion of (**2**) back into (**1**) is achieved by refluxing (**2**) in toluene under N_2 for 4 h. However, if (**2**) is left standing under an atmosphere of CO at 25 °C for several days, quantitative conversion back to [$Os_3(CO)_{10}$(dppm)] occurs. This indicates that the cyclometallated phosphine group is readily demetallated by the transfer of the hydride from the osmium back to the phenyl ring of the phosphine.

A similar reaction occurs on treatment of (**1**) with hydrogen. Thus, on bubbling H_2 through a toluene solution of (**1**) at 80 °C, the solution changes colour from green to red over a



Scheme 1. i, Reflux in toluene, 5 h; ii, CO, 25 °C, 2 h; iii, reflux in toluene, 4 h; iv, CO, 25 °C, several days; v, H_2, 80 °C, 0.5 h.

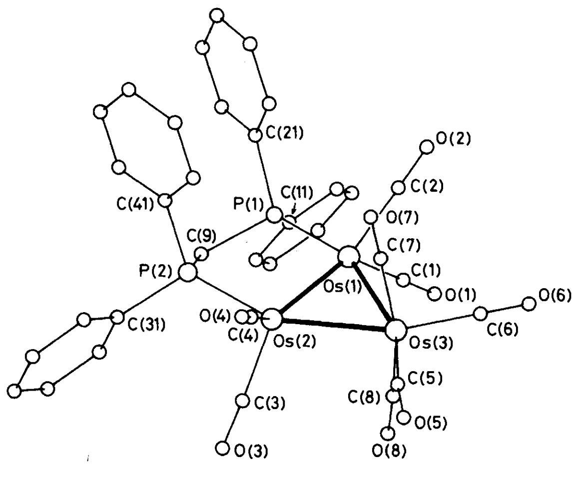


Figure 1. The structure of $[Os_3(CO)_8(H)_2(dppm)]$ (**3**) with H atoms omitted. Important bond lengths (Å) and angles (°) are Os(1)–Os(2) 2.681(1), Os(1)–Os(3) 2.820(1), Os(2)–Os(3) 2.812(1), Os(1)–P(1) 2.347(5), Os(2)–P(2) 2.323(5), Os(1)–C(1) 1.872(19), Os(1)–C(2) 1.903(22), Os(2)–C(3) 1.880(24), Os(2)–C(4) 1.894(22), Os(3)–C(5) 1.921(21), Os(3)–C(6) 1.946(21), Os(3)–C(7) 1.919(20), Os(3)–C(8) 1.840(21), P(1)–C(9) 1.865(17), P(2)–C(9) 1.825(17); Os(2)–Os(1)–Os(3) 61.424(1), Os(1)–Os(2)–Os(3) 61.736(1), Os(1)–Os(3)–Os(2) 56.840(1), C(1)–Os(1)–Os(2) 133.1(6), C(2)–Os(1)–Os(2) 132.2(7), C(3)–Os(2)–Os(1) 131.7(7), C(4)–Os(2)–Os(1) 134.7(7), Os(2)–Os(1)–P(1) 95.3(1), Os(1)–Os(2)–P(2) 93.4(1), Os(1)–P(1)–C(9) 110.6(6), Os(2)–P(2)–C(9) 110.4(6), P(1)–C(9)–P(2) 112.0(9).

period of 0.5 h, and $[Os_3(CO)_8(H)_2(dppm)]$ (**3**) may be isolated as large red crystals on cooling the solution (75% yield). The spectroscopic data for (**3**) {ν(CO) (in CH_2Cl_2) 2068s, 2005vs, 1982vs, 1954m, and 1943m cm^{-1}; n.m.r., $^{31}P\{^1H\}$ ($CDCl_3$): δ −0.53 p.p.m. (s, relative to 85% H_3PO_4); ^1H ($CDCl_3$): δ 7.27(m,Ph), 4.23[t, *J*(PH) 10.5 Hz], −10.22[t, *J*(PH) 10.25 Hz]} did not allow a full structural characterisation to be made, so an *X*-ray crystallographic study was carried out.† The structure was solved by Patterson and heavy atom phased Fourier methods (SHELX[2]) using 4090 unique reflections with $F > 4\sigma(F)$. Least squares refinement with anisotropic Os, P, O, and carbonyl C atoms converged to a current *R* 5.1%. The structure of (**3**) is shown in Figure 1.

The reaction of (**1**) with H_2 has thus led to a hydrogenolysis reaction in which the demetallation of the phenyl ring to reform the dppm ligand occurs, and this dppm ligand now bridges the formal Os=Os double bond, [Os(1)–Os(2)], the phosphine groups occupying equatorial co-ordination sites. The hydride ligands were not located directly but the distribution of the carbonyl ligands indicates that they also bridge the Os=Os double bond, above and below the Os_3 plane [C(1)–Os(1)–Os(2) 133.1(6), C(2)–Os(1)–Os(2) 132.2(7); C(3)–Os(2)–Os(1) 131.7(7), and C(4)–Os(2)–Os(1) 134.7(7)°]. The formal double bond character of the Os(1)–Os(2) interaction is indicated by the bond length [Os(1)–Os(2) 2.681 (1) Å] which is significantly shorter than the other two Os–Os bonds [2.820(1) and 2.812(1) Å] and comparable with the Os=Os double bond length in $[Os_3(CO)_{10}H_2]$ [2.681(1) Å].[3]

The reversibility of the *ortho*-metallation reaction, well-known in mononuclear metal complexes,[4,5] has been previously observed in cluster carbonyl complexes. For example, $[Os_3(CO)_9(H)_2(HNC_6H_4)]$, a complex containing an *ortho*-metallated aniline ligand, reacts with CO at 125 °C to give the aniline complex $[Os_3(CO)_{10}(H)(HNPh)]$.[6] However, the present reaction suggests that the treatment of cluster complexes containing metallated ligands with hydrogen can provide a convenient route to hydrido cluster complexes. It is notable that preliminary studies indicate the reaction of $[Os_3(CO)_{10}(H)_2]$ with dppm does not lead to the formation of (**3**).

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† *Crystal data:* $[Os_3(CO)_8(H)_2(Ph_2PCH_2PPh_2)]$ (**3**), $C_{33}H_{24}O_8Os_3P_2$, $M = 1181$, orthorhombic, space group *Pbca*, $a = 16.405(7)$, $b = 16.906(2)$, $c = 25.370(3)$ Å, $U = 7036$ Å^3, Mo-K_α radiation, $\lambda = 0.7107$ Å, $Z = 8$, $D_c = 2.24$ g cm^{-3}, $D_m = 2.16$ g cm^{-3}, μ(Mo-K_α) = 110.29 cm^{-1}. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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