

The High Yield Synthesis of an Unsaturated Osmium Cluster; the X-Ray Crystal Structure of $[\text{Os}_3(\text{CO})_8(\text{H})\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$

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Thermolysis of $[\text{Os}_3(\text{CO})_{10}(\text{dppm})]$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) in refluxing toluene affords a high yield of the unsaturated cluster $[\text{Os}_3(\text{CO})_8(\text{H})\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$ which has been characterised by X-ray crystallography, and which undergoes a facile reversible reaction with CO.

The use of transition metal cluster complexes in catalysis requires that co-ordinative unsaturation is present or readily generated on the cluster without breakdown of the metal atom framework. Although unsaturated clusters are becoming less uncommon among the Group 8 metals, high yield syntheses of such unsaturated clusters are very limited. The much studied

unsaturated osmium cluster $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$ shows, however, that such species can be catalytically active, and provide starting materials for a wide range of cluster derivatives.¹ This communication reports the high yield (>70%) synthesis of a new unsaturated osmium cluster.

Treatment of a benzene solution of an equimolar mixture of

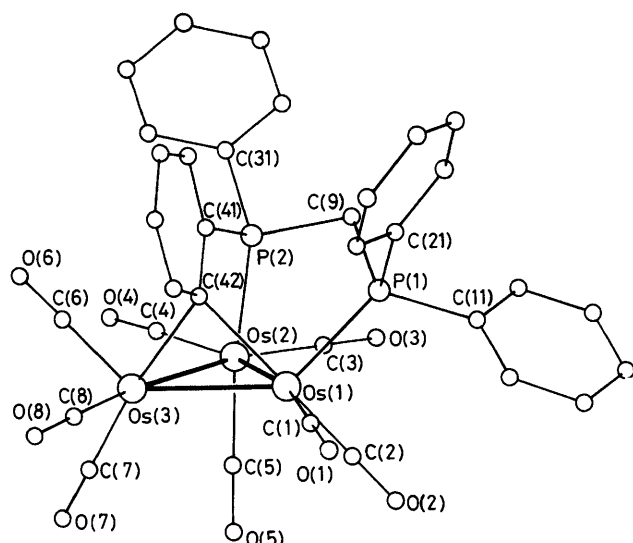
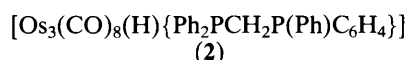
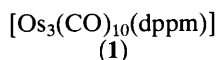


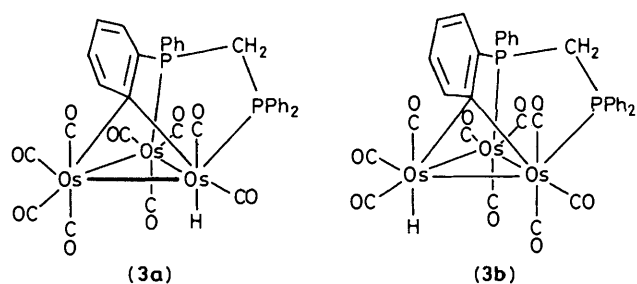
Figure 1. The structure of $[\text{Os}_3(\text{CO})_8(\text{H})\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$ with H atoms omitted. Important bond lengths (Å) and angles ($^\circ$) are Os(1)–Os(2) 2.844(1), Os(1)–Os(3) 2.747(1), Os(2)–Os(3) 2.834(1), Os(1)–P(1) 2.324(4), Os(2)–P(2) 2.329(4), Os(1)–C(42) 2.283(13), Os(3)–C(42) 2.297(15), Os(1)–C(1) 1.896(14), Os(1)–C(2) 1.864(14), Os(2)–C(3) 1.915(15), Os(2)–C(4) 1.911(18), Os(2)–C(5) 1.910(15), Os(3)–C(6) 1.884(16), Os(3)–C(7) 1.908(19), Os(3)–C(8) 1.911(16); Os(1)–C(42)–Os(3) 73.7(4), C(42)–Os(1)–Os(2) 84.7(4), C(42)–Os(3)–Os(2) 84.7(3), P(1)–Os(1)–Os(3) 133.2(1), P(2)–Os(2)–Os(1) 76.2(1), C(7)–Os(3)–Os(1) 120.8(5), C(2)–Os(1)–Os(3) 121.1(5).

$[\text{Os}_3(\text{CO})_{12}]$ and dppm (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) with $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (2 equiv.) in methanol at 60 $^\circ\text{C}$ affords $[\text{Os}_3(\text{CO})_{10}(\text{dppm})]$ (**1**) in 74% yield. By comparison with $[\text{Ru}_3(\text{CO})_{10}(\text{dppm})]$,² the spectroscopic data of (**1**) $\{\nu(\text{CO})$ (in CH_2Cl_2) 2090m, 2026sh, 2006vs, 2000vs, 1971m, 1954m, and 1944m cm^{-1} ; n.m.r., $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2): δ -27.0 p.p.m. [s , relative to 85% H_3PO_4]; ^1H (CD_2Cl_2): δ 5.09 [t, $J(\text{PH})$ 10.7 Hz] indicate that the dppm ligand bridges two Os atoms and that each phosphine group occupies an equatorial site.



Thermolysis of (**1**) in refluxing toluene produces a change in colour of the solution from orange to green, from which a dark green crystalline solid (**2**) may be obtained in 77% yield. The spectroscopic data of (**2**) $\{\nu(\text{CO})$ (in CH_2Cl_2) 2066s, 2020s, 1991vs, and 1928m cm^{-1} ; n.m.r., $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2): δ -18.0 (d) and -20.2 p.p.m. [d , $J(\text{PP})$ 69.6 Hz]; ^1H (CD_2Cl_2): δ 5.05 [ddd, $J(\text{HH})$ 14.2, $J(\text{PH})$ 11.4, $J(\text{P}'\text{H})$ 9.0 Hz], 4.20 [ddd, $J(\text{HH})$ 14.2, $J(\text{PH})$ 11.4, $J(\text{P}'\text{H})$ 7.4 Hz], and -13.43 [dd, $J(\text{PH})$ 28.9, $J(\text{P}'\text{H})$ 12.1 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 direct

† *Crystal data:* $[\text{Os}_3(\text{CO})_8(\text{H})\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$ (**2**), $\text{C}_{33}\text{H}_{22}\text{O}_8\text{Os}_3\text{P}_2$, $M = 1179$, monoclinic, space group $P2_1/c$, $a = 19.546(6)$, $b = 12.386(3)$, $c = 14.022(4)$ Å, $\beta = 103.28(3)^\circ$, $U = 3304$ Å³, Mo- K_α radiation, $\lambda = 0.7107$ Å, $Z = 4$, $D_c = 2.37$ g cm^{-3} , $\mu(\text{Mo-}K_\alpha) = 1.34$ 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.



methods and a heavy atom phased Fourier series (SHELX³) using 4437 unique reflections with $F > 4\sigma(F)$. Least squares refinement with anisotropic Os and P atoms converged to a current R 4.3%. This study shows that (**2**) is $[\text{Os}_3(\text{CO})_8(\text{H})\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$, the structure of which is shown in Figure 1.

Thermolysis of (**1**) has thus led to the loss of two CO ligands and the metallation of one of the phenyl groups of the dppm ligand, the metallated phenyl group adopting a bridging position between two Os atoms. This metallation has forced the phosphorus atom [P(2)] into an axial co-ordination site. The hydride ligand was not located directly but the distribution of the carbonyl groups indicates that it bridges the Os(1)–Os(3) edge {Os(1)–Os(3)–C(7) 120.8 $^\circ$, Os(3)–Os(1)–C(2) 121.1 $^\circ$ }. The bond length between the two Os atoms bridged by the metallated phenyl group and the hydride ligand [Os(1)–Os(3) 2.747(1) Å] is significantly shorter than the other two Os–Os bonds [2.844(1) and 2.834(1) Å], indicative of the formal double bond character of the Os(1)–Os(3) interaction. By comparison, in the cluster $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$, the Os=Os double bond length is 2.681(1) Å,⁴ suggesting that the bridging phenyl group and/or the phosphine ligands† cause some lengthening of the Os=Os bond in (**2**).

The co-ordinative unsaturation of (**2**) is demonstrated by its facile reversible addition reaction with CO. Thus, by bubbling CO through a toluene solution of (**2**), complete conversion into the yellow $[\text{Os}_3(\text{CO})_9(\text{H})\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$ (**3**) is achieved after 2 h at 25 $^\circ\text{C}$. Conversion of (**3**) back into (**2**) is achieved by refluxing (**3**) in toluene under N_2 for 4 h. The spectroscopic data for (**3**) $\{\nu(\text{CO})$ (CH_2Cl_2) 2079s, 2047s, 2018vs, 2006sh, 1976s, 1955sh, and 1935sh cm^{-1} ; n.m.r., $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2): δ -13.5 (d) and -22.4 p.p.m. [d , $J(\text{PP})$ 70.9 Hz]; ^1H (CD_2Cl_2): δ 5.50 (m), 3.64 (m), and -16.52 [dd, $J(\text{PH})$ 9.3, $J(\text{P}'\text{H})$ 1.14 Hz] indicate that (**3**) has the structure (**3a**) or (**3b**).

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† An increase in M–M bond lengths is generally observed when a carbonyl cluster is substituted by phosphine ligands. This has been attributed to both electronic and steric effects. See for example, R. D. Adams, I. T. Horváth, B. E. Segmüller, and L.-W. Yang, *Organometallics*, 1983, **2**, 144, and references therein.