Two-electron Addition Reactions and Reversible Carbonylation of an Unsaturated Pentanuclear Osmium Complex; *X*-Ray Crystal Structure of $[Os_5(CO)_{13}H(PhNC_6H_4N)(PEt_3)]$

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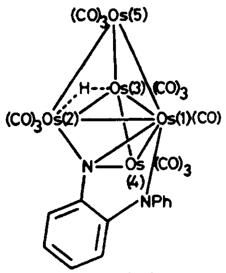
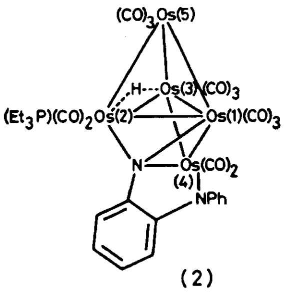
Summary Reaction of $[Os_5(CO)_{13}H(PhNC_6H_4N)]$ with L = PEt_3, $CNBu^t$, and CO yields 1:1 addition products of the type $[Os_5(CO)_{13}H(PhNC_6H_4N)L]$, the reaction with CO being reversible; the structure of the PEt_3 adduct has been established by an *X*-ray structural analysis.

WE have recently reported an *X*-ray diffraction study of $[Os_5(CO)_{13}H(PhNC_6H_4N)]$ (**1**) which revealed that the edge-bridged tetrahedron of metal atoms present in the molecule possesses two adjacent unusually short metal–metal bonds (2·60 Å).[1] We suggested on this basis that the molecule might constitute the first example of a cluster of nuclearity >3 with localised multiple metal–metal bonds, and we now present chemical and further structural evidence which substantiates this suggestion. Thus the reactions of (**1**) with PEt_3, $CNBu^t$, and CO demonstrate that (**1**) is co-ordinatively unsaturated, and an *X*-ray diffraction study of the 1:1 adduct with PEt_3 reveals that addition takes place without the ligand dissociation or modification of the metal atom skeleton which would have been expected in the absence of unsaturation. These features are typical of clusters such as $[Os_3(CO)_{10}H_2]$[2] and its substituted derivatives[3] in which the presence of localised metal–metal multiple bonds has been previously established.

The addition of a slight excess of PEt_3 to a hexane solution of (**1**) at room temperature gave one major product within minutes, which was separated by t.l.c. (CH_2Cl_2–hexane). The mass spectrum of this product (**2**) showed a parent ion at *m/e* 1624 (^{192}Os) indicative of the stoicheiometry $[Os_5(CO)_{13}H(PhNC_6H_4N)(PEt_3)]$ and the ^1H n.m.r.



(1)



(2)

spectrum showed a metal–hydride singlet resonance (δ $-20{\cdot}2$) shifted from that found for (**1**) (δ $-19{\cdot}07$). There were also marked changes in the i.r. spectrum of (**2**) [ν_{CO} (hexane) 2081vs, 2038s, 2033s, 2012s, 2003m, 1995m, 1998sh, 1972w, 1950w, 1942w, and 1914w] as compared to (**1**). The complex (**2**) was crystallised by slow cooling of a saturated solution in warm benzene to give square green-black plates in *ca.* 60% yield.

Crystal data: $C_{31}H_{25}N_2O_{13}Os_5P$, $M = 1\,621{\cdot}5$, monoclinic, space group $P2_1/c$, $a = 21{\cdot}146(5)$, $b = 11{\cdot}079(4)$, $c = 17{\cdot}779(5)$ Å, $\beta = 111{\cdot}44(2)^\circ$, $U = 3\,877{\cdot}0$ Å^3, $Z = 4$, $D_c = 2{\cdot}78$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 164{\cdot}17$ cm^{-1}. 5 848 intensities were recorded ($2\theta_{\max} = 50{\cdot}0^\circ$) on a Stoe 4-circle diffractometer using graphite-monochromated Mo-K_α radiation. Lorentz polarisation and numerical absorption corrections were applied and the data averaged to give 3 707 unique observed intensities [$F > 4\sigma(F)$]. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked full-matrix least squares [Os, N, P, and C(ethyl) anisotropic, ethyl and phenyl H riding 1·08 Å from the relevant C] to $R = 0{\cdot}050$ and $R_w = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o| = 0{\cdot}045$.†

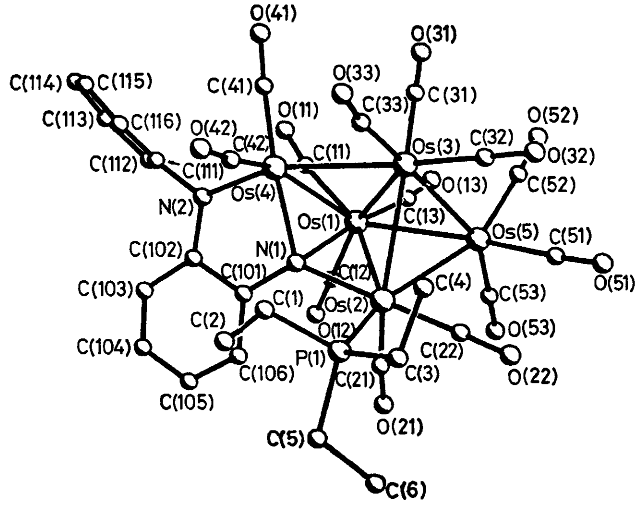


FIGURE 1. The molecular structure of $[Os_5(CO)_{13}H(PhNC_6H_4N)(PEt_3)]$, (**2**), including the atom numbering scheme. Bond lengths: Os(1)–Os(2), 2·785(2); Os(1)–Os(3), 2·831(2); Os(1)–Os(4), 2·836(2); Os(1)–Os(5), 2·823(2); Os(2)–Os(3), 2·926(2); Os(2)–Os(5), 2·833(2); Os(3)–Os(4), 2·826(2); Os(3)–Os(5), 2·767(2); Os(2)–P(1), 2·412(12); Os(1)–N(1), 2·25(3); Os(2)–N(1), 2·09(2); Os(4)–N(1), 2·11(2); Os(4)–N(2), 2·06(2) Å; bond angles: Os(1)–N(1)–Os(2), 79·7(8); Os(1)–N(1)–Os(4), 81·0(6); Os(2)–N(1)–Os(4), 121·2(8)°.

The structure of (**2**) is shown in Figure 1 whose caption includes some important bond parameters. The edge-bridged tetrahedron of Os atoms present in (**1**) is retained, but all the metal–metal distances are greater than 2·8 Å which indicates that no bonds of significant multiple character are present. The *o*-semidine-type ligand found in (**1**) has changed its orientation relative to the metal skeleton so that N(2), which was previously bound to Os(1), is now bound to Os(4) in a similar fashion. A transfer of a carbonyl group from Os(4) to Os(1) accompanies this change. The total number of electrons donated to the cluster by the organic ligand is presumably the same as in (**1**) and overall, therefore, a formal 2-electron addition reaction without major modification of the metal atom skeleton has occurred. The PEt_3 ligand is co-ordinated to Os(2), which has also transferred a carbonyl group to Os(1). The other structural features of (**1**) are essentially unchanged in the adduct (**2**).

The site at which attack by the nucleophile has occurred is not the expected one, since neither of the two shortest metal–metal bonds in (**1**) is associated with it. It could be that crowding round Os(1), the site of greatest unsaturation in (**1**), hinders the approach of the relatively bulky phosphine ligand.

The reaction of (**1**) with $CNBu^t$ in hexane proceeds in a similar manner to give one major product in *ca.* 50%

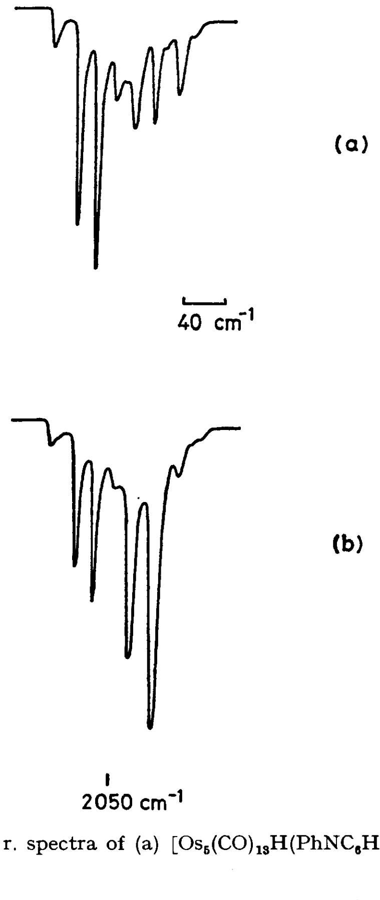


FIGURE 2. I.r. spectra of (a) $[Os_5(CO)_{13}H(PhNC_6H_4N)]$, (b) CO adduct.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

yield, of stoicheiometry [$Os_5(CO)_{13}H(PhNC_6H_4N)(CNBu^t)$] [*m/e* 1589 (^{192}Os)] and the ^{1}H n.m.r. spectrum of this complex shows an Os-*H* singlet resonance at δ −21·9 again shifted in position from the corresponding resonance in (**1**). The i.r. spectrum (ν_{CO} 2087m, 2060s, 2041m, 2035m, 2026m, 2009m, 1997w, 1989m, 1976w, and 1918w) shows a strong absorption at 2175 cm^{-1} due to ν_{NC}, confirming the presence of the Bu^{t}NC ligand, but is otherwise similar to that of (**2**), suggesting an analogous formulation.

When CO gas is passed through an octane solution of (**1**) for 2 h at room temperature, a single green product is obtained in quantitative yield. The i.r. spectrum of this product is identical to that of (**1**), except that the bands at 2021 and 1998 cm^{-1} show a marked increase in intensity relative to the remainder of the spectrum (Figure 2). Its formation is reversible and, when a stream of nitrogen is passed thraugh a solution of it or if it is allowed to stand in air for 2 h, the i.r. spectrum of the solution indicates complete reconversion into (**1**). Such reversible carbonylation is not a common process in cluster chemistry, but has been observed for [$Os_3(CO)_{10}H_2$],[4] and constitutes a further analogy between the chemistry of (**1**) and this molecule.

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