A Pentanuclear Osmium Complex with Two Adjacent, Unusually Short Metal–Metal Bonds: The *X*-Ray Crystal Structure of $[HOs_5(CO)_{13}(PhNC_6H_4N)]$

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Summary The new complex $[HOs_5(CO)_{13}(PhNC_6H_4N)]$ has been prepared, its *X*-ray crystal structure shows the presence of an edge-bridged tetrahedron of metal atoms with two short Os–Os bonds

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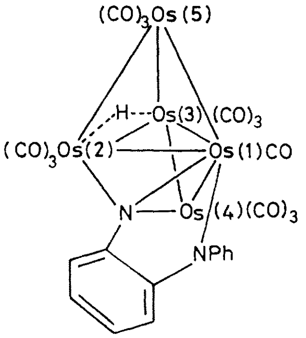
There are relatively few polynuclear metal carbonyl complexes which may be thought of as possessing localised multiple metal–metal bonds The best studied complex of this type is $[Os_3(CO)_{10}H_2]$, in which the evidence for the presence of a multiple metal–metal bond is provided both by the short Os–Os distance between two of the metal atoms[1] and by the ability of the complex to react with electron-donor molecules without metal–metal bond fission or ligand dissociation [2] Other related dimeric[3,4] and trimeric[5] complexes have been prepared, but in higher-nuclearity clusters (>3) any unsaturation which, on the basis of electron counting rules, may be thought of as being present is not generally reflected by the presence of multiple metal–metal bonds between particular metal atoms Thus the *X*-ray crystal structure of $[H_4Re_4(CO)_{12}]$, a complex which requires two double bonds to satisfy the E A N rule, does not reveal any significant variation in the lengths of the six metal–metal bonds which are present [6]

We now report the *X*-ray crystal structure of a pentanuclear osmium complex, $[HOs_5(CO)_{13}(PhNC_6H_4N)]$ (**1**), in which two adjacent, short Os–Os bonds {shorter than the short Os–Os bond in $[Os_3(CO)_{10}H_2]$} are present in the molecule



(1)

The complex was prepared from the reaction of $[Os_3(CO)_{10}H_2]$ and azobenzene in refluxing octane under N_2. After overnight reflux the solution was taken to dryness and the products separated by t.l.c. using 10% CH_2Cl_2–hexane as eluant. A green band was extracted and crystallised from hot hexane to give green-black needles of (**1**) in *ca.* 20—30% yield. The i.r. spectrum of (**1**) showed ν(CO) absorptions at 2096(m), 2071(s), 2054(s), 2037(m), 2026(sh), 2020(m), 2001(m), 1990(w), 1977(m), 1973(sh), and 1965(w) and the ^1H n.m.r. spectrum showed a singlet at δ −19·07 in addition to peaks in the region δ 6·65—7·38 due to aromatic H atoms. The mass spectrum of (**1**) showed a parent ion at m/e 1506 (^{192}Os).

Crystal data: $C_{25}H_{10}N_2O_{13}Os_5$, M 1497·35, triclinic, a = 9·144(5), b = 10·459(6), c = 17·634(8) Å, α = 96·31(2), β = 110·85(2), γ = 98·67(2)°, U = 1 533·4 Å^3, Z = 2, D_c = 3·24 g cm^{-3}; graphite monochromated Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 207·01 cm^{-1}; space group $P\bar{1}$. The Os atoms were located by multisolution Σ_2 sign expansion and the remaining non-hydrogen atoms from a subsequent electron density difference-synthesis. The structure was refined by blocked-cascade least-squares (Os anisotropic), using 2447 unique observed intensities $[F > 5\sigma(F)]$ recorded on a Stoe A.E.D. four-circle diffractometer with an ω/θ scan technique. The aromatic hydrogen atoms were placed in geometrically idealised positions (C–H, 1·08 Å; C–C–H, 120·0°) and assigned a common isotropic temperature factor. The current residuals are R = 0·051 and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0|]$ = 0·051. The weighting scheme employed was $w = [\sigma^2(F) + 0{\cdot}002\,F^2]^{-1}$.

The molecular structure of (**1**) is shown in the Figure together with some important bond parameters. The five Os atoms define an edge-bridged tetrahedron with two short metal–metal bonds, Os(1)–Os(4) and Os(1)–Os(5). This overall geometry of the metal skeleton has been observed previously in $[Os_5(CO)_{16}H_2]$[7] and the iodide and phosphite derivatives.[8]

The azobenzene molecule has rearranged to give a *o*-semidine type ligand. Similar rearrangements have been observed with complexes of other metals (*e.g.* Fe,[9] Rh,[10] and Ru[11]). This is the first complex to be reported, however, in which all three of the nitrogen-bound hydrogen atoms are absent. The nitrogen atom, N(1), has a distorted tetrahedral geometry capping one edge of the Os_4 tetrahedron [Os(1)–Os(2)] and one edge of the bridging Os_3 triangle [Os(1)–Os(4)]. The second nitrogen atom, N(2), is formally sp^2-hybridised and is bonded to Os(1) by an Os–N bond which is short compared with the Os–N distance of 2·156(6) Å reported for the sp^2 nitrogen in $[Os_3(CO)_{10}H(\mu\text{-}p\text{-}MeC_6H_4NC(H)O)]$.[12]

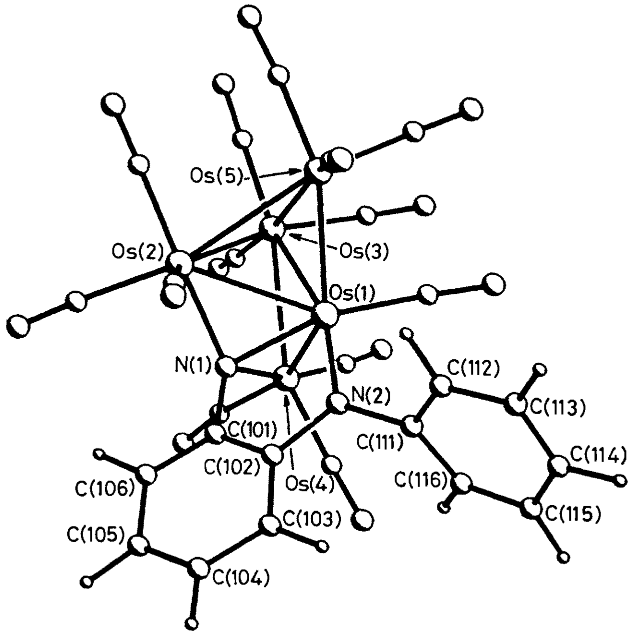


FIGURE. The molecular structure of $[HOs_5(CO)_{13}(PhNC_6H_4N)]$. Bond lengths: Os(1)–Os(2), 2·724(3); Os(1)–Os(3), 2·847(3); Os(1)–Os(4), 2·606(3); Os(1)–Os(5), 2·601(3); Os(2)–Os(3), 2·900(3); Os(2)–Os(5), 2·961(3); Os(3)–Os(4), 2·846(3); Os(3)–Os(5), 2·838(3); Os(1)–N(1), 2·03(2); Os(1)–N(2), 1·94(3); Os(2)–N(1), 2·09(3); Os(4)–N(1), 2·13(3) Å.

The most striking feature of the structure is, perhaps, the co-ordination of Os(1), which is bonded to only one carbonyl group. Two of the Os–Os bonds emanating from Os(1) [Os(1)–Os(4) and Os(1)–Os(5)] are, at 2·60 Å, the shortest Os–Os bonds yet reported in a carbonyl cluster. Os(1)–Os(2) at 2·72 Å is also relatively short but Os(1)–Os(3) and all other Os–Os bonds in the molecule are ⩾2·84 Å. It is possible that Os(1)–Os(2) and Os(1)–Os(4) are shortened to some degree by the presence of the bridging N(1) atom, but there are no such constraints on Os(1)–Os(5) and an explanation must therefore be sought on electronic grounds. Assuming that the $(PhNC_6H_4N)$ ligand is a 5-electron donor [4e from N(1) and 1e from N(2)] and that all the Os–Os bonds are single and non-dative in character, then (**1**) is overall 2 electrons short of the number required to satisfy the E.A.N. rule. On a more localised basis Os(1) is $1\frac{2}{3}$ electrons short of the required number [assuming N(1) donates $1\frac{1}{3}$ electrons to Os(1)] whereas Os(5) and Os(4), to which Os(1) forms its shortest bonds, are respectively 1 electron and $\frac{2}{3}$ electron short. Whilst these considerations suggest that the formation of multiple metal–metal bonds involving Os(1) is a possibility it should be noted that the lone pair of electrons on N(2) may also relieve the electron deficiency of Os(1), and the planar geometry of N(2) together with the short Os(1)–N(2) bond length strongly suggests that some multiple bond character is indeed present between these atoms.

The hydride ligand in (**1**) was not located in the *X*-ray analysis, but the configuration of the thirteen terminal carbonyl groups suggests that it bridges the Os(2)–Os(3) edge †

An orange product isolated from the same reaction as (**1**) has been identified by its spectroscopic properties and by an *X*-ray analysis[13] as the *ortho*-metallated complex $[(PhNNC_6H_4)_2Os(CO)_2]$ in which the carbonyl ligands are *cis* and the co-ordinated N atom of one azobenzene is *trans* to a co-ordinated C atom of the other

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† 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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