The Synthesis and *X*-Ray Structure Analysis of $Os_6(CO)_{17}(NC_5H_5)_2$: a Cluster Compound with an Unusual Mode of Metal–CO Bonding

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Reaction of the neutral hexaosmium cluster $Os_6(CO)_{18}$ with excess of pyridine (py) gives the pentanuclear dianion $[Os_5(CO)_{15}]^{2-}$ together with small amounts of a neutral hexanuclear cluster $Os_6(CO)_{17}(py)_2$ (**1**); *X*-ray analysis shows that (**1**) exhibits an unusual type of metal–carbonyl linkage.

Several different modes of bonding have been established for the carbonyl ligand.[1—3] In the course of our studies on the reactions of high nuclearity cluster compounds with small organic molecules we have isolated a bis(pyridine)hexaosmium cluster (**1**) in which there is an unusual type of carbonyl–metal linkage.

The reaction of $Os_6(CO)_{18}$ with excess of pyridine (py) in dichloromethane gives the pentanuclear dianion $[Os_5(CO)_{15}]^{2-}$ (**2**) as the major product, rather than $[Os_6(CO)_{18}]^{2-}$ as had been indicated by preliminary evidence.[4] The only neutral product is (**1**) which is formulated as $Os_6(CO)_{17}(py)_2$ on the basis of *X*-ray,† ¹H n.m.r., and i.r. spectroscopic data.‡

$$Os_6(CO)_{18} \xrightarrow{\text{pyridine}} \underset{(\mathbf{2})}{[Os_5(CO)_{15}]^{2-}} + \underset{(\mathbf{1})\ (10\%)}{Os_6(CO)_{17}(py)_2}$$

+ small amounts of unidentified compounds

X-Ray analysis has shown that the molecule (**1**) has a metal core consisting of a trigonal bipyramidal arrangement of five osmium atoms with the sixth, Os(6), bonded to an equatorial atom, Os(1), in a 'spike' arrangement (Figure 1). The most unusual feature of the structure is the presence of a novel CO linkage which may be envisaged as a μ_3-(CO) group [Os(1)–C(1) 1.98(2), Os(2)–C(1) 2.18(2), and Os(5)–C(1) 2.29(2) Å] acting as a ligand-bridge across the 'spike' bond Os(1)–Os(6), *via* σ-donation of 2e from the oxygen atom to Os(6)

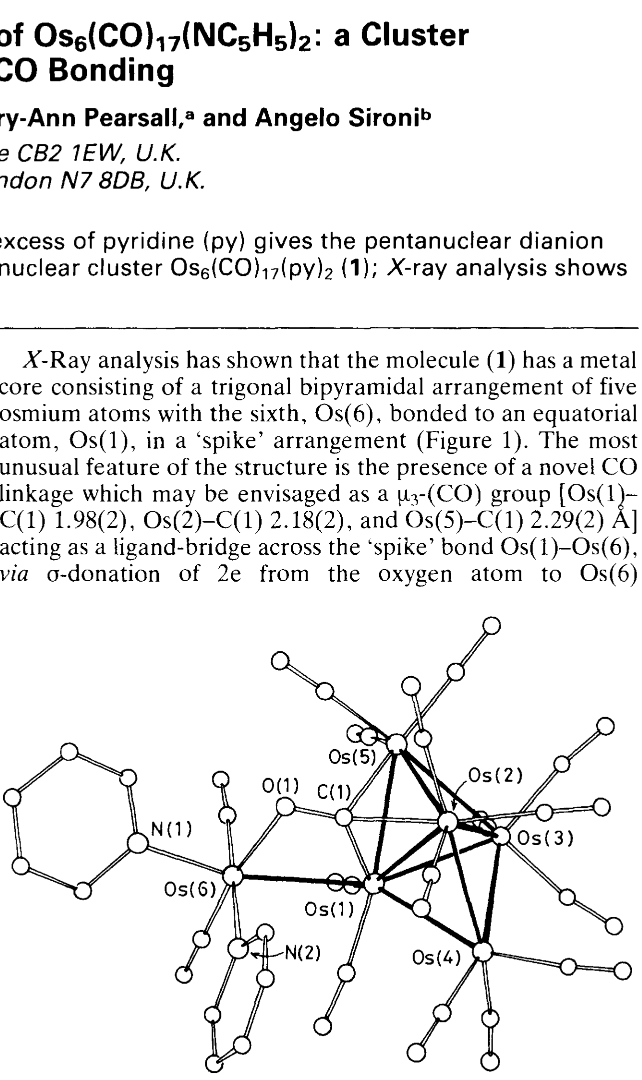

Figure 1. The structure of the $Os_6(CO)_{17}(py)_2$ molecule. The Os–Os bond lengths (Å) are: Os(1)–Os(2) 2.838, Os(1)–Os(3) 2.790, Os(1)–Os(4) 2.722, Os(1)–Os(5) 2.831, Os(1)–Os(6) 2.881, Os(2)–Os(3) 2.843, Os(2)–Os(4) 2.890, Os(2)–Os(5) 2.819, Os(3)–Os(4) 2.786, Os(3)–Os(5) 2.808, maximum e.s.d.s are 0.001. Other relevant bond distances are: Os(6)–O(1) 2.14(1) and C(1)–O(1) 1.28(2) Å.

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† *Crystal Data* for (**1**), $C_{27}H_{10}N_2O_{17}Os_6$; M = 1 775.6, monoclinic, space group $P2_1/c$ (from systematic absences), a = 12.358(2), b = 10.776(2), c = 26.373(4) Å, β = 93.16°, U = 3506.8 Å^3, $F(000)$ = 3 112, Z = 4, D_c = 3.36 g cm^{-3}, Mo-K_α radiation λ = 0.710 69 Å, (Mo-K_α) = 208.8 cm^{-1}. Current R value 0.035 for 2768 reflections with $I \geqslant 3\sigma(I)$. 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.

‡ ¹H N.m.r. (**1**) CD_2Cl_2: 8.71 (2H, dd, J 6.5, 1.4 Hz), 8.64 (2H, dd, J 6.5, 1.3 Hz), 7.93 (1H, tt, J 7.8, 1.3 Hz), 7.85 (1H, tt, J 7.7, 1.4 Hz), 7.47 (2H, m), and 7.39 (2H, m). ν(CO) (in CH_2Cl_2): 2083w, 2052s, 2033s, 2019ms, 1996m, 1977w, and 1949w cm^{-1}.

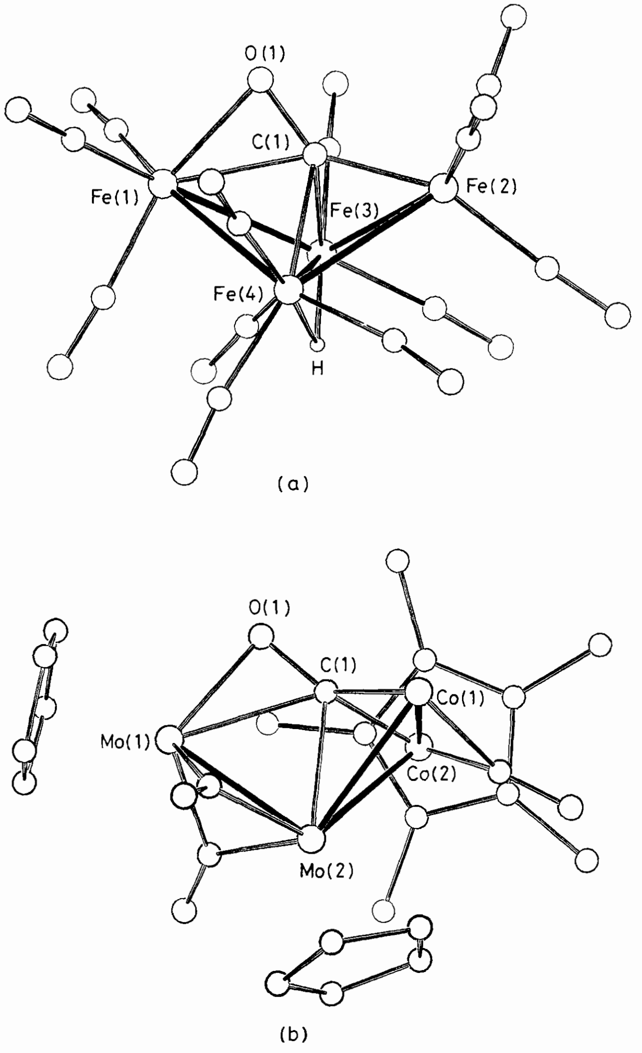
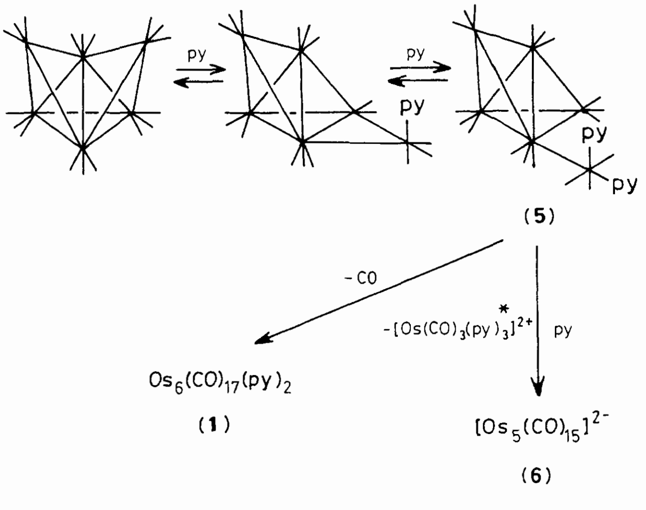


Figure 2. The reported structure of compounds with μ_4-η^2-(CO) ligands: (a) $[HFe_4(CO)_{13}]^-$ (**3**); (b) $Co_2Mo_2(CO)_4(C_5H_5)_2(C_5Me_5)_2$ (**4**) with a C_5Me_5 ring omitted for clarity.

[Os(6)–O(1) 2.139(13) Å]. This mode of CO bonding has not been reported before; a carbonyl ligand bridging four transition metals occurs in $[HFe_4(CO)_{13}]^-$ (**3**),[3] but in this monoanion [Figure 2(a)] the carbonyl C-atom is bonded to all four metal atoms of a 'butterfly' arrangement (Fe–C 1.81—2.17 Å), with the O-atom tilted towards a 'wingtip' Fe atom giving rise to a sideways π-donation from the CO-group to this metal atom. This type of η^2-bonding donation also occurs in the structure of $Co_2Mo_2(CO)_4(C_5H_5)_2(C_5Me_5)_2$ (**4**) [Figure 2(b)] in which the metal geometry closely resembles that in (**1**), with the CO ligand spanning a 'spike bond'.[5] In the structure of (**1**) the type of CO to metal π-bonding observed in (**3**) and (**4**) is ruled out by the large Os(6)–O(1)–C(1) angle of 95(1)° [*cf.* M(1)–O(1)–C(1) angles of 79° in (**3**) and 87.6(1)° in (**4**)] and the Os(6) to carbonyl-C(1) distance of 2.58(2) Å.

Donation of 2e from the carbonyl O-atom to Os(6) brings the total number of electrons in the valence shell of Os(6) to eighteen. The trigonal bipyramidal arrangement of the remaining five osmium atoms is consistent with a σ-donation of 2e from the Os atom of the $Os(CO)_2(py)_2$ group, Os(6), to this unit giving it a total of 72e, the required electron count for this geometry.



* not identified

Scheme 1

The structure of the pyridine complex is in complete agreement with the mechanism for attack of nucleophiles on the $Os_6(CO)_{18}$ core which we have previously suggested involves primary attack at a capping atom.[6] We now propose the following mechanism for the pyridine-induced decapping of $Os_6(CO)_{18}$ to give (**2**). Initial attack by two pyridine molecules at a capping Os atom causes successive reversible breaking of two Os–Os bonds to give the proposed intermediate $Os_6(CO)_{18}(py)_2$ (**5**) as shown in Scheme 1. Two alternative irreversible reactions are then envisaged. Firstly, donation of two more electrons by a third pyridine ligand would sever a third Os–Os bond causing the splitting off of the 'spike' Os to give the pentanuclear dianion (**6**). Alternatively, intramolecular attack on the 'spike' Os atom by the oxygen atom of a carbonyl group on an adjacent osmium atom to displace a CO ligand would give the carbonyl-bridged molecule (**1**). This mechanism is consistent with the enhanced yield (20%) of the hexanuclear cluster (**1**) that is obtained if one equivalent of Me_3NO, which promotes CO loss, is added to the reaction mixture.

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