Synthesis and *X*-Ray Analysis of Unusual Planar Tetra- and Hexa-nuclear Osmium Clusters containing Trifluoroacetate Ligands

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The compounds $Os_6(CO)_{18}(O_2CCF_3)_2$ (**1**) and $Os_4(CO)_{12}(O_2CCF_3)_2$ (**2**), isolated in low yields from the reaction of $Os_6(CO)_{18}$ with $Hg(O_2CCF_3)_2$, have been found by *X*-ray analysis to have unusual planar arrangements of the metal atoms.

Ruthenium and osmium carbonyl complexes containing carboxylato ligands are of interest as potential model compounds[1,2] for the study of the metal catalysed decomposition of formic acid[3] and the production of alkyl formates from CO_2, H_2 and alcohols.[4] Despite this importance, examples of these complexes are still rare. This is especially true for osmium, where only dinuclear complexes of formula $Os_2(CO)_6(O_2CR)_2$[5] and trinuclear complexes of formula $Os_3(\mu\text{-}H)(CO)_{10}(O_2CR)$[1] have been structurally characterized. In addition, two isomers of $H_3Os_3(CO)_{10}(O_2CCF_3)$ have been recently characterized by n.m.r. and i.r. spectroscopic studies.[6] Here we report the synthesis and structural characterization of $Os_6(CO)_{18}(O_2CCF_3)_2$ (**1**) and $Os_4(CO)_{12}(O_2CCF_3)_2$ (**2**), new osmium carbonyl/carboxylato clusters with very unusual geometries (Figures 1 and 2, respectively).

Compound (**1**) is obtained as the initial product of the reaction of $Os_6(CO)_{18}$ with $Hg(O_2CCF_3)_2$ in CH_2Cl_2 or acetone. On standing, (**1**) converts to an as yet unidentified intermediate and finally to the insoluble (**2**). Compounds (**1**) and (**2**) have been formulated and characterized on the basis of *X*-ray structure analysis, i.r. spectroscopy, and, for (**1**) only, mass spectroscopy.[†][‡]

The metal core of (**1**) forms an unusual Os_6 'ladder' geometry. The six osmium atoms deviate markedly from strict

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[†] *Crystal data* for (**1**): $C_{22}F_6O_{22}Os_6$, $M = 1871.40$, monoclinic, space group $P2_1/n$ (alternative setting of $P2_1/c$, No. 14), $a = 24.867(4)$, $b = 12.140(3)$, $c = 11.696(3)$ Å, $\beta = 105.17(2)°$, $U = 3407.81$ Å^3, $F(000) = 3271$, $\mu(\text{Mo-}K_\alpha) = 223.70\ \text{cm}^{-1}$, $Z = 4$, $D_c = 3.657\ \text{g cm}^{-3}$.

For (**2**): $C_{16}F_6O_{16}Os_4$, $M = 1210.91$, monoclinic, space group $P2_1/n$ (alternative setting of $P2_1/c$, No. 14), $a = 9.070(2)$, $b = 17.035(3)$, $c = 8.181(2)$ Å, $\beta = 100.99(2)°$, $U = 1240.84$ Å^3, $F(000) = 1052$, $\mu(\text{Mo-}K_\alpha) = 204.79\ \text{cm}^{-1}$, $Z = 2$, $D_c = 3.241\ \text{g cm}^{-3}$. $R = 0.0482$ for (**1**) and 0.0965 for (**2**) for 1146 and 2860 absorption corrected data, respectively, with $I/\sigma(I) > 3.0$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Cystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] *Selected spectroscopic data* for (**1**): i.r. ν(CO) (CH_2Cl_2), 2118w; 2093s; 2061m; 2047w; 2027m; 2003s; 1971br.,v cm^{-1}.

For (**2**): i.r. ν(CO), (KBr pellet) 2101sh,w; 2096m; 2042m; 2021w; 2009sh,s; 2003s; 1996sh,m; 1958m cm^{-1}.

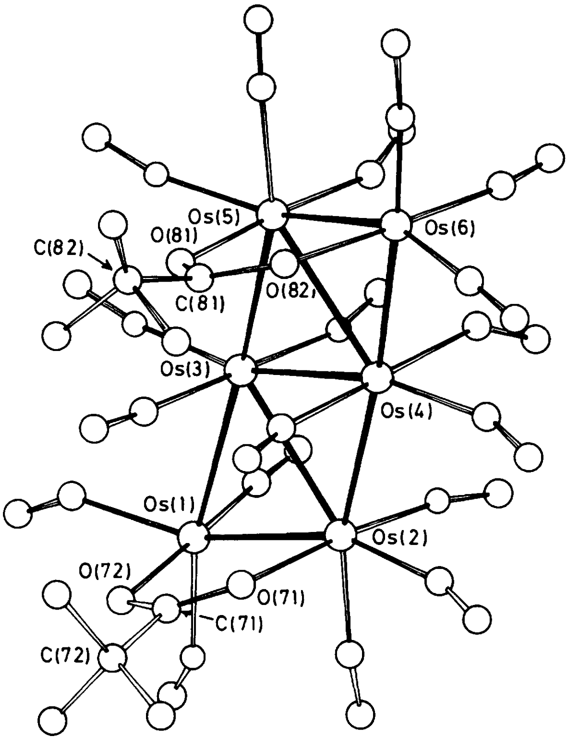

Figure 1. The structure of the molecule $Os_6(CO)_{18}(O_2CCF_3)_2$ (**1**). Principal bond lengths (Å) are: Os(1)–Os(2) 2.800, Os(1)–Os(3) 2.901; Os(2)–Os(3) 2.806, Os(2)–Os(4) 2.857, Os(3)–Os(4) 2.823, Os(3)–Os(5) 2.871, Os(4)–Os(5) 2.808, Os(4)–Os(6) 2.898, Os(5)–Os(6) 2.797, maximum e.s.d. 0.005 Å.

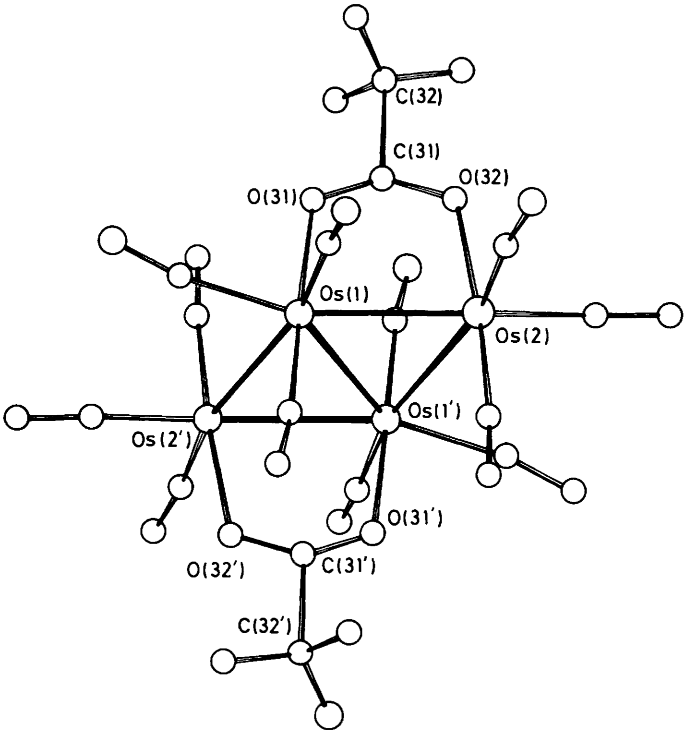

Figure 2. The structure of the molecule $Os_4(CO)_{12}(O_2CCF_3)_2$ (**2**). Principal bond lengths (Å) are: Os(1)–Os(2) 2.779, Os(1)–Os(1)′ 2.861, Os(1)–Os(2)′ 2.894, maximum e.s.d. 0.002 Å.

planarity; the central four osmium atoms are nearly co-planar [deviations Os(2) 0.025, Os(3) −0.025, Os(4) 0.025, and Os(5) −0.025 Å], but the two terminal metal atoms lie significantly out of the best plane through these atoms [deviations Os(1) 0.31 and Os(6) 0.26 Å]. Overall, the structure has virtual C_2 symmetry, with the bidentate carboxylato ligands approximately perpendicular to the terminal Os_3 triangles (mean dihedral angle 105.9°) and both projecting from the same side of the cluster. While most Os–Os distances are close to those expected for typical Os–Os single bonds [*cf.* 2.877 Å in $Os_3(CO)_{12}$],[7] the carboxylato bridged Os–Os distances and the Os(3)–Os(4) distance are significantly shorter. These short distances are probably due to the steric requirements of the bridging trifluoroacetate ligands, although the electonic influences of these ligands may also be important.

Compound (**1**) is the first example of a 90-electron hexanuclear cluster adopting a 'ladder' geometry rather than the typical giant equilateral triangular raft geometry.[8] For (**1**), the 'ladder' geometry has several advantages to the triangular geometry. In the triangular rafts each osmium atom is bound to an even number (2 or 4) of osmium atoms, whereas in the 'ladder' raft two osmium atoms are bound to an odd number (*i.e.* 3) of osmium atoms. Thus the two trifluoroacetate ligands, which are three-electron donors, are more readily incorporated into a 'ladder' raft. The 'ladder' geometry of (**1**) has previously been seen in the 92-electron clusters $Os_6(CO)_{20}[CC(H)R]$, where the CC(H)R ligands cap one of the terminal Os_3 triangles.[9] Unlike (**1**), the perimeter of the $Os_6(CO)_{20}[CC(H)R]$ clusters exhibit two unusually long Os–Os distances (*ca.* 3.18 Å). Theoretical studies are currently underway to determine the extent to which the extra pair of electrons present in these compounds is responsible for these long distances.

Compound (**2**) crystallizes as discrete centrosymmetric tetramers in which the four metal atoms are strictly planar and form a parallelogram with one long and one short diagonal. Each osmium atom is co-ordinated by three carbonyl ligands, and alternating pairs of osmium atoms are bridged by the trifluoroacetate groups. The five membered Os–O–C–O–Os rings are approximately perpendicular to the plane of the four osmium atoms (mean dihedral angle O_2C_2/Os_4 98.6°) and project from opposite sides of the metal plane. The distances about the perimeter of the metal parallelogram alternate between 2.779 Å along the bridged edges and 2.890 Å along the non-bridged edges. Again we attribute these short Os–Os distances primarily to the steric requirements of the bridging trifluoroacetate ligands.

In general, 62-electron tetranuclear clusters adopt a butterfly geometry.[10] Only a few tetranuclear osmium containing clusters are planar or nearly so. Of these, $Os_4(CO)_{14}L$ (L = PMe_3[11] or CO[12]) and $HOs_3Re(CO)_{15}$[13] are the most closely related to (**1**). In $Os_4(CO)_{14}L$ one osmium atom is co-ordinated by three carbonyl ligands and the other three osmium atoms are co-ordinated by four ligands. As in (**1**), the length of the short diagonals are those expected for Os–Os single bonds while the perimeters of the parallelograms are composed of two long (2.98—3.00 Å) and two short (2.77—2.78 Å) bonds. However, in $Os_4(CO)_{14}L$ the two short edges are adjacent to one another rather than across from one another as in $Os_4(CO)_{12}(O_2CCF_3)_2$. These distances in $Os_4(CO)_{14}L$ were rationalized in terms of two-centre three-electron bonds, giving bond orders of one-half and three-halves. Using this bonding scheme each osmium atom achieves an 18-electron configuration.[11a,12] In contrast, the M–M distances about the periphery of $HOs_3Re(CO)_{15}$ are essentially identical (2.944—2.957 Å). It is noteworthy that in planar $Re_4(CO)_{16}{}^{2-}$ the M–M distances about the periphery of the cluster are also virtually equal.[14]

Transformation of $Os_6(CO)_{18}$ to (**1**) involves a two-electron oxidation and an addition of two trifluoroacetate ligands. Overall, six electrons are added to the cluster, resulting in the breakage of three Os–Os bonds and an 'unfolding' of the bicapped tetrahedral metal framework. Hg(II) is the most likely oxidant as $Os_6(CO)_{18}$ will not react with HO_2CCF_3 in the absence of Hg(II) and small amounts of mercury metal are deposited during these reactions. Formation of (**2**) from (**1**) occurs *via* an unknown intermediate and involves cluster breakdown.

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