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Preliminary Communication

REACTION OF $Os_3(CO)_{12}$ WITH ETHYLENE UNDER MODERATE PRESSURE; THE MOLECULAR STRUCTURES OF $[Os_4(CO)_{12}(C_2H_2)]$ AND $[Os_4(CO)_{12}(C_4H_6)]$

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Summary

The reaction of ethylene with $Os_3(CO)_{12}$ in hexane, at 20 atmospheres pressure yields the known complex $H_2Os_3(CO)_9C.CH_2$, and two new tetranuclear clusters $Os_4(CO)_{12}CH:CH$ (1) and $Os_4(CO)_{12}(HC:CEt)$ (2) which have been characterised by X-ray crystallography.

The reaction of ethylene with $Os_3(CO)_{12}$ at one atmosphere in refluxing octane yields $H_2Os_3(CO)_9C.CH_2$ [1]. In this communication we report the synthesis and molecular structures of two new osmium clusters obtained from the reaction of $Os_3(CO)_{12}$ with ethylene at moderate pressures and temperatures. Full synthetic and structural details will be published at a later date.

A solution of $Os_3(CO)_{12}$ in hexane was maintained under a 20 atmosphere pressure of ethylene at 160° for four hours. Chromatography of the resulting solution gave as the major product (ca. 60%) the known complex $H_2Os_3(CO)_9CCH_2$ [1]. An orange-yellow and an orange product were also isolated and characterised as $[Os_4(CO)_{12}(CH{:}CH)]$ (1) (yield ca. 10%) and $[Os_4(CO)_{12}(C_4H_6)]$ (2) (yield ca. 30%), respectively on the basis of analyses, i.r., ^1H n.m.r. and mass spectroscopic data (Table 1). The nature of the organic units and the overall molecular geometries of (1) and (2) were established by single-crystal X-ray analysis.

Both compounds were recrystallised from hexane.

TABLE 1: Spectroscopic Properties of (1) and (2)

Complex	m/e[a]	^1H n.m.r. $(\tau)^b$	ν_{CO} [c]/cm^{-1}
(1)	1130	-0.28(s)	2102w, 2075vs, 2049s, 2039s, 2018m, 2004m, 1973w.
(2)	1158	-1.0(s) 6.32 (q, J = 1Hz) 8.75 (t, J = 1Hz)	2099w, 2071vs, 2045s, 2038s, 2015m, 1998m, 1981w.

[a] measured on AEI MS12 [b] CD_2Cl_2 solvent [c] hexane solvent

Crystal data

(1) $C_{14}H_2O_{12}Os_4$, *M* 1122.96, monoclinic, *a* 7.758(2), *b* 17.173(4), *c* 15.649(5) Å, β 97.81(2)°, *U* 2065.5 Å^3, *Z* = 4, D_c = 3.61 g cm^{-3}; μ(Mo K_α) = 245.8 cm^{-1}, space group $P2_1/n$. 3134 intensities were recorded ($2\theta_{max}$ = 60.0°) on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo K_α radiation. These were averaged to

give 1980 unique observed intensities $[F > 5\sigma(F)]$. The residuals are R = 0.050, R_w $[=\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|]$ = 0.048.

(2) $C_{16}H_6O_{12}Os_4$, M 1151.01, monoclinic, a 23.008(5), b 9.156(7), c 31.685(9) Å, β 95.80°, U 6640.6 Å^3, Z = 12, D_c = 3.45 g cm^{-3}; μ(Mo K_α) = 229.4 cm^{-1}, space group $P2_1/c$. 4177 intensities (layers 0-h, 9, l) were recorded on a Stoe STADI-2 two-circle diffractometer using graphite-monochromated Mo K_α radiation. These were averaged to give 3571 unique observed intensities $[F>4\sigma(F)]$. The residuals are R = 0.042, R_w = 0.044.

The Os atoms in the two structures were located by multi-solution Σ_2 sign expansion, and the light atoms from subsequent electron-density difference syntheses. Structure (1) was refined by blocked cascade least-squares, and structure (2) by blocked full-matrix least-squares.

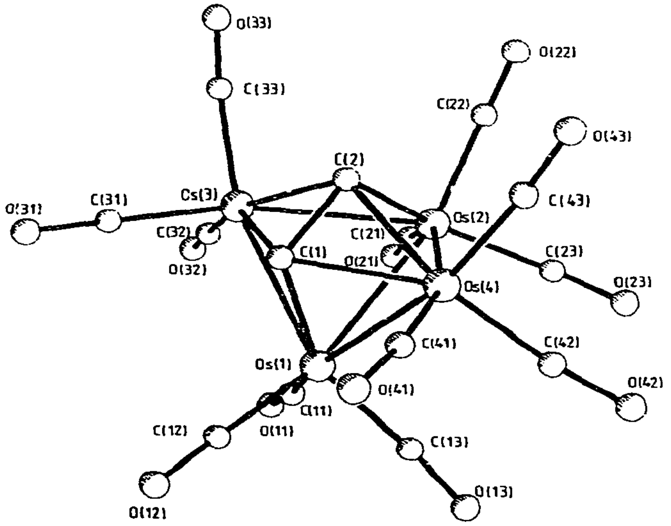

Fig. 1. The molecular structure of $[Os_4(CO)_{12}(HC{\vdots}CH)]$. Bond lengths: Os(1)-Os(2), 2.847(2); Os(1)-Os(3), 2.791(2); Os(1)-Os(4), 2.792(2); Os(2)-Os(3), 2.799(2); Os(2)-Os(4), 2.791(2); Os(1)-C(1), 2.19(3); Os(3)-C(1), 2.22(3); Os(4)-C(1), 2.22(3); Os(2)-C(2), 2.11(3); Os(3)-C(2), 2.16(3); Os(4)-C(2), 2.24(3); C(1)-C(2), 1.55(4) Å.

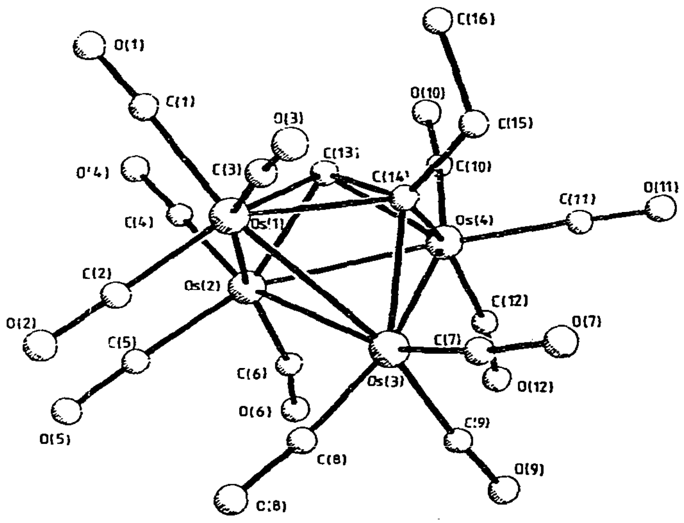

Fig. 2. The molecular structure of $[Os_4(CO)_{12}(HC\vdots CEt)]$. Average bond lengths: Os(1)-Os(2), 2.760(2); Os(1)-Os(3), 2.760(2); Os(2)-Os(3), 2.849(2); Os(2)-Os(4), 2.740(2); Os(3)-Os(4), 2.764(2); Os(1)-C(13), 2.23(3); Os(1)-C(14), 2.21(3); Os(2)-C(13), 2.17(3); Os(3)-C(14), 2.11(3); Os(4)-C(13), 2.21(3); Os(4)-C(14), 2.26(3); C(13)-C(14), 1.54(3) Å.

The structures of (1) and (2) are shown in Figs. 1 and 2 together with some important bond lengths.

In both structures the four Os atoms adopt the 'butterfly' configuration and three terminal carbonyl ligands are bonded to each metal. The acetylenic ligands lie over the 'butterfly' with the organic C-C bond parallel to the Os-Os 'hinge' bond. The acetylenic fragment is π-bound to the two 'wing-tip' metal atoms and σ-bound to the 'hinge' atoms to form a distorted octahedral core. The acetylenic C-C distances in both clusters suggest that the organic groups act as four electron donors. Although the acetylenic hydrogens were not located, the average C-C-C(ethyl) angle is 120.8° which suggests that both the hydrogen and ethyl groups bend away from the cluster core.

There are only two other examples of tetranuclear Os clusters displaying the 'butterfly' configuration, $[Os_4(CO)_{12}H_3I]$ [2] and $[Os_4(CO)_{12}H_4(OH)]^+$ [3,4]. A similar mode of coordination of the organic group has been observed in $[Co_4(CO)_{10}(EtC{:}CEt)]$ [5], $[Ru_4(CO)_{12}(PhC{:}CPh)]$ [6] and $[Ru_4(CO)_{11}(C_8H_{10})]$ [7]. In these complexes the C-C bond lengths of the bridging fragment lie in the range 1.43 - 1.46 Å and are considered to have formal double bond character. In (1) and (2) the equivalent C-C bonds have lengths close to the idealised single bond value, a situation not previously reported for acetylenic ligands bound to clusters [8].

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