Synthesis and *X*-Ray Structure of an Osmium Carbonyl Anion $[HOs_3(CO)_{10}{\cdot}O_2C{\cdot}Os_6(CO)_{17}]^-$ †

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Summary The reaction of $[Os_6(CO)_{18}]$ with $[Os_3(CO)_{11}H]^-$ gives the anion $[HOs_3(CO)_{10}{\cdot}O_2C{\cdot}Os_6(CO)_{17}]^-$ which has been fully characterized by a single crystal *X*-ray diffraction study on the $[(Ph_3P)_2N]^+$ salt.

TRIOSMIUM DODECACARBONYL, $[Os_3(CO)_{12}]$, reacts with potassium hydroxide in methanol giving the red anion, $[Os_3(CO)_{11}H]^-$, the $[Me_4N]^+$ and $[(Ph_3P)_2N]^+$ salts of which can be isolated in good yields (70—80%); these have been characterized by microanalysis, and i.r. [$\nu_{CO}(CH_2Cl_2)$, 2083w,

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† No reprints available.

2021s, 1996s, 1951ms, and 1667w,br cm^{-1}] and ^{1}H n.m.r. spectroscopy [τ 23·58 (CD_2Cl_2, 40 °C)]. On the basis of these data, $[Os_3(CO)_{11}H]^-$ is considered to be isostructural with its iron analogue, $[Fe_3(CO)_{11}H]^-$.[1] Both osmium salts are stable in the solid state but quickly decompose in solution. Acidification under anhydrous conditions with gaseous hydrogen chloride leads to $[Os_3(CO)_{11}H_2]$[2] whereas aqueous phosphoric acid transforms the anion into $[Os_3(CO)_{10}(OH)(H)]$.[3]

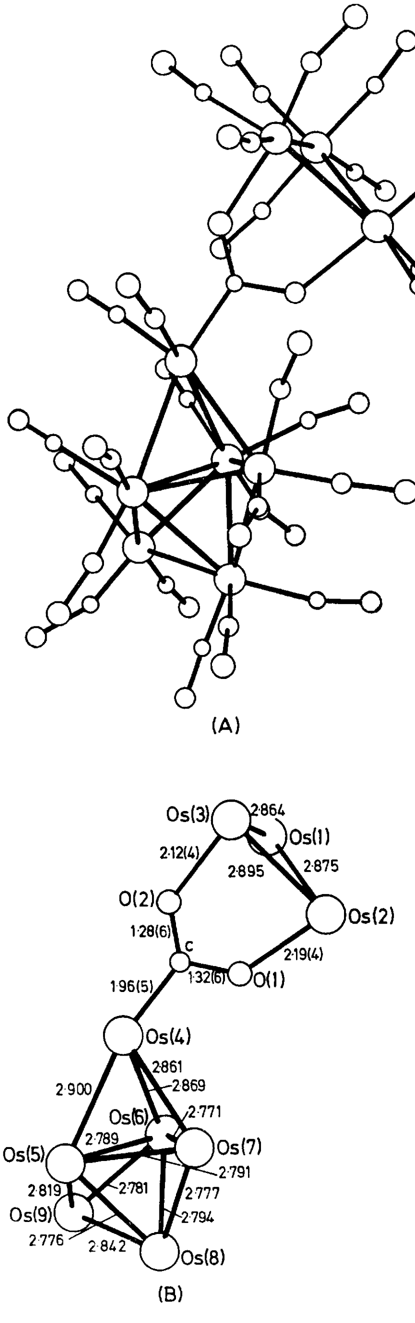

FIGURE. (A): Structure of $[HOs_3(CO)_{10}{\cdot}O_2C{\cdot}Os_6(CO)_{17}]^-$; (B): significant bond lengths (in Å) within the cluster, with CO groups omitted for clarity.

In an attempt systematically to increase the cluster size by treating $[Os_6(CO)_{18}]$ with osmium carbonyl anions a stoicheiometric amount of $[Os_3(CO)_{11}H]^-$ was added to $[Os_6(CO)_{18}]$ in CH_2Cl_2 under N_2. A rapid reaction occurred and an anion of approximate composition $[Os_9(CO)_{\sim 28}H]^-$ was isolated in almost quantitative yield as the $[(Ph_3P)_2N]^+$ salt. This salt, which is stable in all common organic solvents apart from acetonitrile, was purified from traces of unchanged reagents by t.l.c. [eluant, cyclohexane–CH_2Cl_2 (10 : 90)] and recrystallized as brown-black air-stable crystals from a mixture of the same solvents. It was characterized by microanalysis, ^{1}H n.m.r. [τ 20·24, (CD_2Cl_2, 40 °C)] and i.r. spectroscopy [ν_{CO} (CH_2Cl_2), 2111vw, 2082mw, 2074m, 2062mw, 2047m, 2028ms, 2013s, 1971vw, and 1961vw cm^{-1}], and a single crystal X-ray diffraction study (see Figure).

Crystal data: $C_{64}H_{31}NO_{29}Os_9P_2$, M = 3051·6, monoclinic, space group $P2_1/c$, a = 18·75(1), b = 15·20(1), c = 28·41(2) Å, β = 114·5(1)°, Z = 4, D_m = 2·756 g cm^{-3}; D_c = 2·751 g cm^{-3}, U = 7367·8 Å^3, μ (Mo-K_α) = 150·0 cm^{-1}. Data were collected using a Syntex $P2_1$ 4-circle diffractometer with graphite-monochromated Mo-K_α radiation. Numerical absorption corrections were applied and the osmium atom positions were determined by multisolution Σ_2 sign expansion. The light atoms were found by difference Fourier techniques and the structure refined to R_w = 0·072, with anisotropic osmium atoms and isotropic light atoms, for the 3274 reflections with $F > 4\sigma(F)$. The assignment of the carbon and oxygen atoms in the CO_2 bridge was the only model for which temperature factors of these three atoms refined to acceptable values. Dimensions of the cation refined to values similar to those previously reported[4] for the $[(PPh_3)_2N]^+$ cation [P–N 1·57(5), 1·60(5) Å; ∠P–N–P 139(4)°].

The X-ray diffraction study did not show the formation of an Os_9 cluster but rather a complex anion containing discrete Os_6 and Os_3 units linked together by a CO_2 bridge. The Os–Os distances within the Os_6 fragment (σ, 0·005 Å) are similar to those observed for $[Os_6(CO)_{18}]$[5] apart from those associated with Os(4) which are *ca.* 0·05 Å longer. ^{13}C N.m.r. spectra of the anion (*ca.* 40% ^{13}CO) with and without proton decoupling are consistent with the hydride ligand being located on the Os_3 rather than the Os_6 fragment in either a face- or edge-bridging position. The $[HOs_3(CO)_{10}]$ fragment is connected to the $[Os_6(CO)_{17}]$ fragment through an O_2C group forming a ring described by Os(2)–O(1)–C–O(2)–Os(3) with which some electron delocalization and thermodynamic stability could be associated. The mean plane of this ring (maximum deviation 0·07 Å) is almost perpendicular to the plane described by Os(1)–Os(2)–Os(3) (interplanar angle 100·5°). It may be possible to consider the carbon atom of this five membered ring which is bonded to Os(4) as a carbene and within the limits of experimental accuracy appropriate bond lengths satisfy the now well established criteria.[6] Alternatively $[O_2C{\cdot}Os_6(CO)_{17}]$ may be bonded to the $[HOs_3(CO)_{10}]$ fragment as a carboxylato ligand.

As far as we are able to judge this is the first example in which two metal clusters are linked together by what is formally a carbon dioxide group. Further evidence in support of this linkage group is provided by three observations: (a) the i.r. spectrum as a Nujol mull of the $[Me_4N]^+$

salt‡ shows an intense broad absorption at 1270 cm^{-1} consistent with the expected stretching vibration of a C–O single bond; (b) aqueous acidification produces $[Os_3(CO)_{10}(OH)(H)]$ and $[Os_6(CO)_{18}]$; (c) the i.r. spectrum as a KBr disc shows no O–H stretching vibrations.

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‡ The i.r. spectrum of the $[(PPh_3)_2N]^+$ salt is complicated by cation absorptions. The $[Me_4N]^+$ salt was synthesized in a similar manner to that described for the imino-salt but using acetone as solvent and 2:1 CH_2Cl_2–acetone as t.l.c. eluant.

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