The First Nona-osmium Cluster Species; Synthesis and *X*-Ray Structure Analysis of $[Os_9(CO)_{21}\{CHC(R)CH\}]^-$ (R = Me or Et)

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When $Os_3(CO)_{12}$ is heated under reflux in isobutyl alcohol or 2-methylbutan-1-ol the novel cluster monoanions $[Os_9(CO)_{21}\{CHC(R)CH\}]^-$ (R = Me or Et respectively) are produced in low yield; *X*-ray analyses of the $[N(Ph_3P)_2]^+$ salts of both monoanions show that they both have the same unusual Os_9 core with 2 cluster valence-electrons less than the number predicted by the effective atomic number (E.A.N.) rule.

We recently reported that the anion $[HOs_8(CO)_{22}]^-$ is formed in low yield when the trinuclear cluster $Os_3(CO)_{12}$ is heated under reflux in isobutyl alcohol, the other products being $HOs_3(CO)_{10}(OBu^i)$, $H_4Os_4(CO)_{12}$, and $[Os_{10}C(CO)_{24}]^{2-}$.[1] We now find that the novel organo-osmium cluster $[Os_9(CO)_{21}\{CHC(Me)CH\}]^-$ (**1**) may also be isolated in very low yield from this reaction. The related monoanion $[Os_9(CO)_{21}\{CHC(Et)CH\}]^-$ (**2**) is also isolated in very low yield from the corresponding reaction in 2-methylbutan-1-ol. These new monoanions have been characterised† as their $[N(PPh_3)_2]^+$ salts by i.r., n.m.r., and fast atom bombardment mass spectroscopy and by *X*-ray structure analysis.‡

Cluster compounds with M_9 cores are very rare.[2] Although osmium species with up to eleven osmium atoms have been reported, several different core geometries being known for the species with six, seven, eight, and ten osmium atoms, there has been a gap in the sequence at nine.§

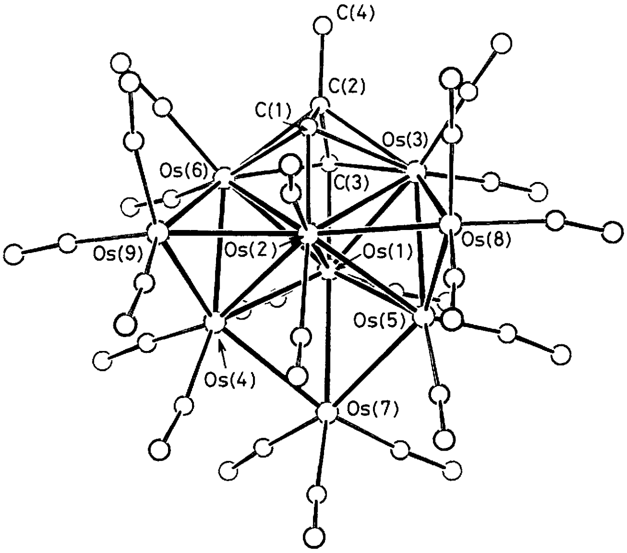

Figure 1. The structure of the monoanion $[Os_9(CO)_{21}\{CHC(Me)CH\}]^-$ (**1**). The Os–Os bond lengths (Å), with those for the equivalent bond lengths in (**2**) in parentheses, are: 1–2 2.852(2.867), 1–3 2.772(2.750), 1–4 2.705(2.682), 1–5 2.691(2.671), 1–6 2.757(2.758), 1–7 2.809(2.789), 2–3 2.767(2.768), 2–4 2.825(2.807), 2–5 2.820(2.820), 2–6 2.770(2.740), 2–8 2.818(2.826), 2–9 2.812(2.816), 3–5 2.776(2.751), 3–8 2.772(2.785), 4–6 2.773(2.754), 4–7 2.796(2.759), 4–9 2.639(2.639), 5–7 2.790(2.792), 5–8 2.648(2.608), 6–9 2.782(2.792); maximum e.s.d.s are 0.003 (**1**) and 0.008 (**2**).

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† ν(CO) (CH_2Cl_2): (**1**) and (**2**) 2077w, 2049sh, 2045s, 2012s, 1997s, and 1988ms cm^{-1}; ^1H n.m.r. τ: (**1**) 1.24 (d, 1H), 3.22 (d, 1H), and 5.76 (s, 3H); (**2**) 1.08 (d, 1H), 3.08 (d, 1H), 5.80 (q, 2H), and 8.32 (t, 3H); *m/z* 2353 for (**1**) and 2367 for (**2**) based on Os_9 = 1712.

‡ Crystals of the $[N(Ph_3P)_2]^+$ salt of (**1**) and (**2**) were obtained by slow evaporation of the respective CH_2Cl_2–MeOH solutions. *Crystal data for* (**1**): $C_{61}H_{35}NO_{21}Os_9P_2$, $M = 2\,891.7$, monoclinic, space group $P2_1/n$, $a = 29.486(4)$, $b = 9.407(2)$, $c = 24.181(4)$ Å, $\beta = 95.07°$, $U = 6\,681.0$ Å^3, $F(000) = 5\,160$, $Z = 4$, $D_c = 2.87$ g cm^{-3}, Mo-K_α radiation $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 164.9 cm^{-1}. Current $R = 0.0595$ for 3337 reflections with $I > 3\sigma(I)$. *Crystal data for* (**2**): $C_{62}H_{37}NO_{21}Os_9P_2$, $M = 2\,907.7$, monoclinic, space group $P2_1/c$, $a = 18.484(4)$, $b = 19.417(4)$, $c = 18.991(4)$ Å, $\beta = 94.77°$, $U = 6\,792.3$ Å^3, $F(000) = 5\,192$, $Z = 4$, $D_c = 2.84$ g cm^{-3}, Mo-K_α radiation $\lambda = 0.71069$ Å, μ(Mo-K_α) = 162.2 cm^{-1}. Current $R = 0.0732$ for 1829 reflections with $I > 3\sigma(I)$. 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.

§ A species of formula $[HOs_9(CO)_{27}(CO_2)]$ is known but it consists of two individual cluster units $HOs_3(CO)_{10}$ and $Os_6(CO)_{17}$ linked by a CO_2 bridge (ref. 3).

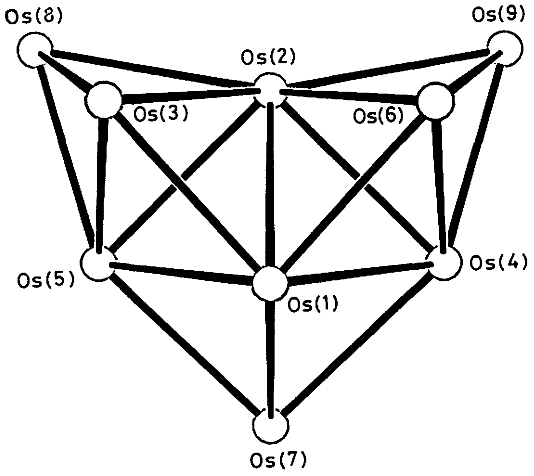

Figure 2. The structure of the Os_9 core in the clusters (**1**) and (**2**).

The structure of (**1**) is shown in Figure 1, and the structure of (**2**) is similar with the methyl group, C(4), being replaced by an ethyl group. The unusual core geometry present in both monoanions is shown in Figure 2. It may be described as a square pyramid fused at adjacent triangular faces to two trigonal bipyramidal units.

$[Os_9(CO)_{21}\{CHC(R)CH\}]^-$
(**1**) R = Me
(**2**) R = Et

Since the discovery of the first octahedral carbonyl cluster, with 86e rather than the 84e predicted by the effective atomic number (E.A.N.) rule, many theories have been used to rationalise the stoicheiometries of cluster compounds.[4,5] All the carbonyl clusters reported until now (with the exception of some Pt species) have either the number of electrons predicted by the E.A.N. rule or a number greater than that. The clusters (**1**) and (**2**) are unusual as they have only 120 valence electrons, two less than the 122e predicted by the E.A.N. rule. The possibility that the apparent deficit of 2e may be made up by the presence of two interstitial hydrogen atoms (the *X*-ray analysis shows no surface H-ligands) appears to be ruled out from the ^1H n.m.r. spectra of (**1**) and (**2**) which show no signals attributable to metal-linked hydrogen atoms in the range τ −50 to 50. In some small clusters such as $H_2Os_3(CO)_{10}$ the E.A.N. electron count is achieved by the presence of multiple M–M bonds,[6] and it may be relevant that in (**1**) and (**2**) there are some very short Os–Os bond lengths [minimum Os(4)–Os(9) 2.639 Å in both (**1**) and (**2**)]. However the shortest Os–Os bond so far observed (2.600 Å) is in $[HOs_8(CO)_{22}]^-$ which has an overall electron count in accord with the E.A.N. and a metal core geometry[1] which is readily rationalised by the latest skeletal electron counting procedures.[5]

The isolation of a hydrocarbon fragment on a high nuclearity cluster is very rare, and has not previously been observed for osmium compounds with more than six metal atoms. Such compounds are potential models of the interaction of hydrocarbons with metal surfaces. The bonding of the allylic fragments to all four atoms of the 'butterfly' indentation on the metal surface, a metal arrangement common for organic ligands in small clusters, may play an important role in stabilising this unusual structure.

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