Synthesis and Characterisation of Nona-osmium Carbonyl Clusters; Crystal and Molecular Structure of [(Ph$_3$P)$_2$N] [Os$_9$H(CO)$_{24}$]

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The anion [Os$_9$H(CO)$_{24}$]$^-$, **2** has been isolated in moderate yield by the vacuum pyrolysis of [Os$_3$(CO)$_{10}$(NCMe)$_2$], and has been shown by a single crystal X-ray structure analysis to contain the previously unobserved tricapped octahedral Os$_9$ metal core.

Extensive studies have been carried out on the structure and reactivity of high nuclearity osmium cluster compounds.[1–4] However, nona-osmium carbonyl clusters are extremely rare. The only report[5] of Os$_9$ species is the isolation of [Os$_9$(CO)$_{21}${CHC(R)CH}]$^-$ (R = Me or Et) from the thermolysis of [Os$_3$(CO)$_{12}$] in isobutyl alcohol or 2-methylbutan-1-ol, in very low yield (less than 2%).

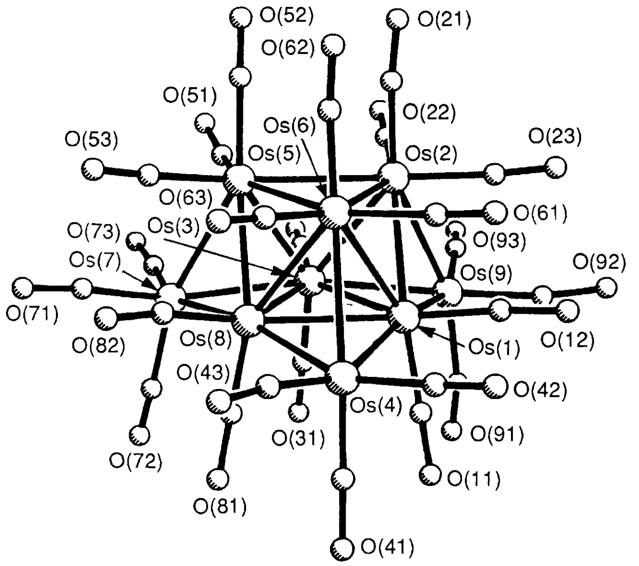

Fig. 1. The molecular structure of the [Os$_9$H(CO)$_{24}$]$^-$ **2** anion showing the atom numbering scheme. Principal bond distances (Å): Os(1)–Os(2), 2.815(3); Os(1)–Os(3), 2.892(3); Os(1)–Os(4), 2.738(3); Os(1)–Os(6), 2.816(3); Os(1)–Os(8), 2.886(3); Os(1)–Os(9), 2.735(3); Os(2)–Os(3), 2.831(3); Os(2)–Os(5), 2.924(3); Os(2)–Os(6), 2.942(3); Os(2)–Os(9), 2.938(3); Os(3)–Os(5), 2.822(3); Os(3)–Os(7), 2.739(3); Os(3)–Os(8), 2.874(3); Os(3)–Os(9), 2.745(3); Os(4)–Os(6), 2.960(3); Os(4)–Os(8), 2.729(3); Os(5)–Os(6), 2.946(3); Os(5)–Os(7), 2.936(3); Os(5)–Os(8), 2.813(3); Os(6)–Os(8), 2.823(3); Os(7)–Os(8), 2.741(3).

We now report a synthetic route to a series of new nona-osmium species [Os$_9$(H)$_2$(CO)$_{24}$] **1**, [Os$_9$H(CO)$_{24}$]$^-$ **2** and [Os$_9$(CO)$_{24}$]$^{2-}$ **3**. Vacuum pyrolysis of [Os$_3$(CO)$_{10}$(NCMe)$_2$] at 170 °C for 16 h gives a dark brown microcrystalline solid. The solid mixture of clusters is first extracted with CH$_2$Cl$_2$ to remove [Os$_5$(CO)$_{16}$] (3%), [Os$_6$(CO)$_{18}$] (18%), [Os$_7$(CO)$_{21}$] (8%) and [Os$_8$(CO)$_{23}$] (trace). The residue is then extracted with acetone to give a dark brown solution and a yellow powder of [Os$_3$(CO)$_{12}$] (22%). Separation of the brown solution by TLC on silica (eluent; acetone–hexane 1 : 1) gives the new [Os$_9$H(CO)$_{24}$]$^-$ **2** mono-anion (R_f ~0.6) in 20% yield. The stoichiometry of **2** was initially established by FAB MS† and ^{1}H NMR and has been confirmed by a single crystal X-ray structure analysis of the [(Ph$_3$P)$_2$N]$^+$ salt.‡ The molecular structure of **2**, together

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† *Spectroscopic data* for **1**: IR ν(CO)/cm^{-1} (CH$_2$Cl$_2$) 2096w, 2087m, 2077s, 2070sh, 2042w and 2026w. For the [(Ph$_3$P)$_2$N]$^+$ salt of **2**: IR ν(CO)/cm^{-1} (CH$_2$Cl$_2$) 2057s, 2044s, 2020m, 2001m and 1990w sh; FAB MS M$^+$(obs.) *m/z* 2385 (calc.) 2385; ^{1}H NMR (CD$_2$Cl$_2$ δ −9.2 (s, 1H, MH) and 7.62 {m, 30H, [(Ph$_3$P)$_2$N]$^+$}. For the [(Ph$_3$P)$_2$N]$^+$ salt of **3**: IR ν(CO)/cm^{-1} (CH$_2$Cl$_2$) 2035s, 2023s, 1998m, 1975m and 1965w, sh; FAB MS M$^+$ (obs.) *m/z* 2384 (calc.) 2384.

‡ *Crystal data* for **2**: C$_{60}$H$_{31}$NO$_{24}$P$_2$Os$_9$, M = 2923.6, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$ No. 14), a = 12.001(2), b = 31.339(10), c = 17.602(3) Å, β = 90.57(2)°, U = 6620(3) Å^3, Z = 4, D_c = 2.933 g cm^{-3}, F(000) = 5216, Mo-Kα radiation, λ = 0.71069 Å, μ(Mo-Kα) = 173.52 cm^{-1}, 3770 observed diffractometer data [$F > 3\sigma(F)$]. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least-squares analysis (Os and P anisotropic) to R = 0.069, R_w = 0.063. Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

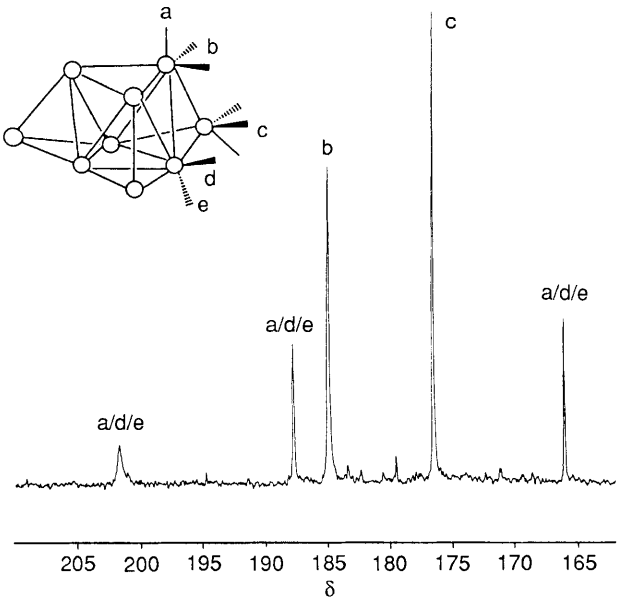
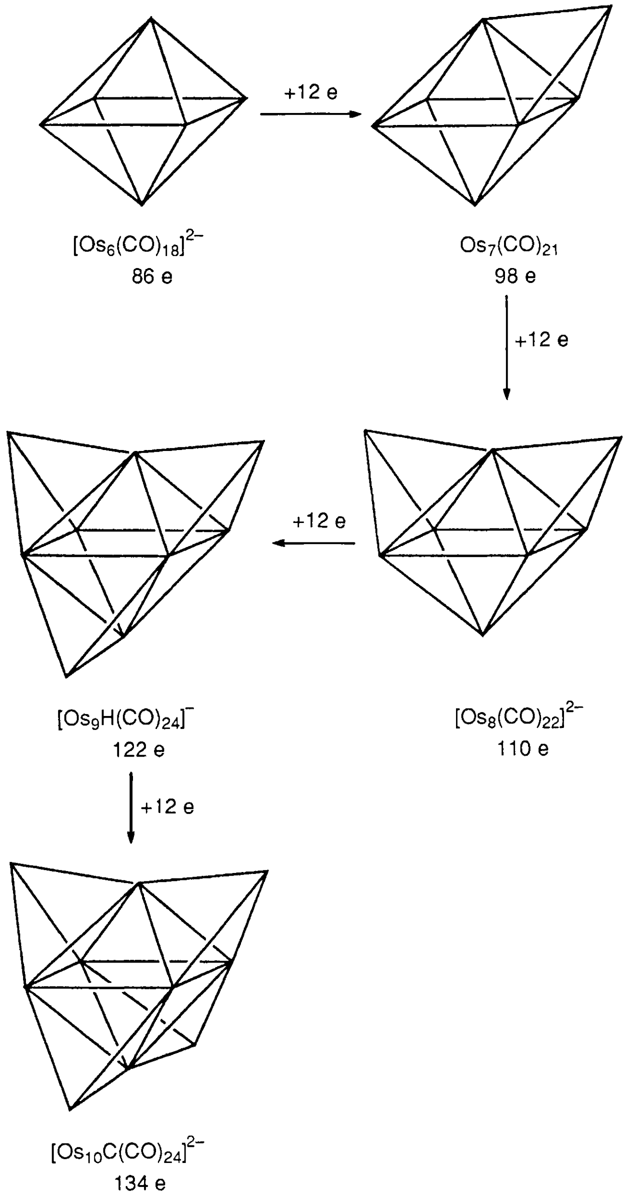


Fig. 2 $^{13}C\{^1H\}$ NMR spectrum of 50% ^{13}C enriched $[(Ph_3P)_2N]^+[Os_9H(CO)_{24}]^-$ (CD_2Cl_2, 298 K)

with some important bond parameters is shown in Fig. 1. The metal core can be described as a tricapped octahedron and may be viewed as being derived from the Os_{10} framework in $[Os_{10}H_4(CO)_{24}]^{2-}$ by the removal of one cap.[6] The capping $Os(CO)_3$ groups are asymmetric with one long and two short bonds [2.940(10) and 2.739(5) Å] to the central octahedron so that the atoms Os(4), Os(7) and Os(9) lie below the plane defined by Os(1), Os(3) and Os(8) with average deviation 0.30 Å from the plane. This feature is not observed in $[Os_{10}H_4(CO)_{24}]^{2-}$ where the four Os_6 frameworks, defining the tetrahedron faces, are planar.[6] The mono-anion **2** exhibits an approximate C_{3v} symmetry. All carbonyl ligands are terminally bonded and essentially linear. The position of the hydride could not be determined directly by X-ray analysis, but potential energy calculations[7] suggest that the hydride atom μ_3-bridges Os(1), Os(3), Os(8) face. At 25 °C, the $^{13}C\{^1H\}$ NMR spectrum shows five resonances in the region δ 205–165 with intensity ratio 1:1:2:3:1 which is consistent with the solid state structure assuming the turnstile rotation of the carbonyls on Os(2), Os(5) and Os(6) is restricted, see Fig. 2.

Reaction of **2** with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) gives the dianion **3** in quantitative yield which can be isolated as $[(Ph_3P)_2N]^+$, $[Ph_4P]^+$ or $[Bu_4P]^+$ salts. A preliminary X-ray analysis§ of $[Ph_4P]^+$ salt of **3** reveals an identical metal core to that found in **2**. However, the poor crystal quality and severe absorption effect of the crystal precluded the determination of ligand positions. Protonation of **3** with CF_3CO_2H in CH_2Cl_2 gives **2** and further protonation can be achieved by HBF_4 to give **1** which dissociates easily back to **2** in CH_2Cl_2.

Both **2** and **3** contain 122 valence electrons and the observed structures represent the first examples of the simple tricapped octahedral geometry of M_9-cluster. In the light of electron counting and structural relation of transition metal clusters, they fit in the capping principle based on the Wade[8] and Mingos[9] approaches, see Scheme 1.



Scheme 1 The relationship between structure and the total polyhedral electron count for osmium cluster species

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§ *Crystal data* for **3**: $C_{72}H_{40}O_{24}P_2Os_9$, M = 3062.9, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$ No. 14), a = 13.168(9), b = 20.473(5), c = 27.033(9) Å, β = 94.46(4)°, U = 7265.7 Å^3, Z = 4, 2351 observed diffractometer data [$F > 3\sigma(F)$] with current R factor 0.198.