Synthesis of $[Os_5(CO)_{15}]^{2-}$, $[HOs_5(CO)_{15}]^-$, and $[H_2Os_5(CO)_{15}]$; *X*-Ray Crystal Structure of $[(Ph_3P)_2N]^+[HOs_5(CO)_{15}]^-$ †

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Summary The complex $[Os_6(CO)_{18}]$ reacts with methanolic potassium hydroxide to produce $[Os_5(CO)_{15}]^{2-}$ which, upon acidification, gives $[HOs_5(CO)_{15}]^-$ and $[H_2Os_5(CO)_{15}]$; single crystal *X*-ray diffraction and ^{13}C n.m.r. studies show the presence, within the anionic pentaosmium clusters, of trigonal bipyramidal metal arrangements.

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† No reprints available.

THE reactions of base with metal carbonyl clusters often lead to anion formation together with CO loss[1] as shown in reaction (1). Invariably a mixture of products is obtained,

$$[Ru_6(CO)_{17}C] \xrightarrow[\text{MeOH}]{\text{KOH}} [Ru_6(CO)_{16}C]^{2-} \qquad (1)$$

relative yields being sensitive to the reaction conditions employed, *i.e.* nature of the base, solvent, and N_2 or CO atmosphere.[2] In contrast, $[Os_6(CO)_{18}]$,[3] when treated with methanolic potassium hydroxide, leads almost quantitatively to $[Os_5(CO)_{15}]^{2-}$.

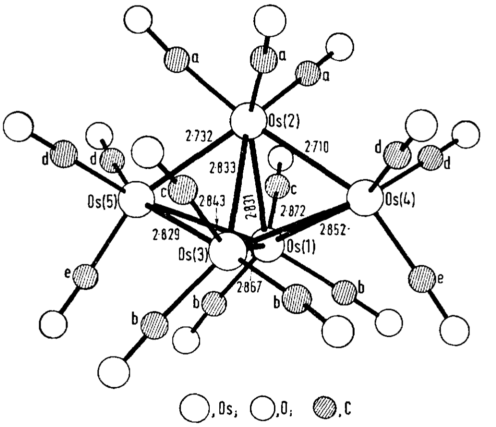

FIGURE 1. Structure of $[HOs_5(CO)_{15}]^-$ with Os–Os bond lengths in Å; a, b, c, d, and e refer to ^{13}C n.m.r. resonances in Figure 2 (iv).

The complex $[Os_6(CO)_{18}]$ is only slightly soluble in MeOH, but addition of KOH (in a 100:1 mole ratio) with rapid stirring under nitrogen at room temperature, leads to its complete dissolution within minutes and the formation of an intense red solution. The anion $[Os_5(CO)_{15}]^{2-}$ can be isolated from this solution as its $[Me_4N]^+$, $[Bu^n{}_4N]^+$, or $[(Ph_3P)_2N]^+$ salts. The $[(Ph_3P)_2N]^+$ salt, on recrystallization from MeCN–Et_2O, gives deep purple crystals (yield 97%). The salts were characterized by microanalysis, conductivity measurements, and n.m.r. and i.r. (ν_{CO}) spectroscopy. The ^{13}C (CO) n.m.r. spectrum of this compound (^{13}CO, *ca.* 40%) over the temperature range 0 to −110 °C showed just two signals [δ(CD_2Cl_2, 0 °C, 25·2 MHz) 191·2 and 183·9 p.p.m. (downfield from Me_4Si)] of intensity ratio 3:2. These data are consistent with an idealized trigonal bipyramidal (D_{3h}) arrangement of osmium atoms with three terminal carbonyl groups bonded to each metal atom. This contrasts with the structure observed for the isoelectronic $[Os_5(CO)_{16}]$ which has three different types of osmium atoms associated with a distorted trigonal bipyramid.[4]

Acidification of $[Os_5(CO)_{15}]^{2-}[(Ph_3P)_2N]_2{}^+$ with an excess of sulphuric acid in acetonitrile gave initially $[HOs_5(CO)_{15}]^-$ and finally a precipitate (quantitative) of $[H_2Os_5(CO)_{15}]$.[5] This transformation, together with the acid nature of $[H_2Os_5(CO)_{15}]$ [reaction (2)], is similar to that reported for

$$\begin{aligned}[H_2Os_5(CO)_{15}] \rightleftharpoons [HOs_5(CO)_{15}]^- + H^+ \\ \rightleftharpoons [Os_5(CO)_{15}]^{2-} + 2H^+ \qquad (2)\end{aligned}$$

$[H_2Os_6(CO)_{18}]$.[6] The composition of the two Os_5 hydridoclusters, after purification by t.l.c., was confirmed by microanalysis, and mass, n.m.r., and i.r. (ν_{CO}) spectroscopy; in particular the ^1H Fourier transform n.m.r. spectra at room temperature (80 MHz) showed sharp singlets in the high field region {$[HOs_5(CO)_{15}]^-$, τ (CD_3CN) 32·66; $[H_2Os_5(CO)_{15}]$, τ (CD_2Cl_2) 31·03, unaltered on cooling to −70 °C}. Treatment of $[Os_6(CO)_{18}]$ with an excess of isopropylamine provides a more effective route to $[HOs_5(CO)_{15}]^-$. The structure of $[HOs_5(CO)_{15}]^-$ $[(Ph_3P)_2N]^+$ was determined by single crystal *X*-ray diffraction (Figure 1).

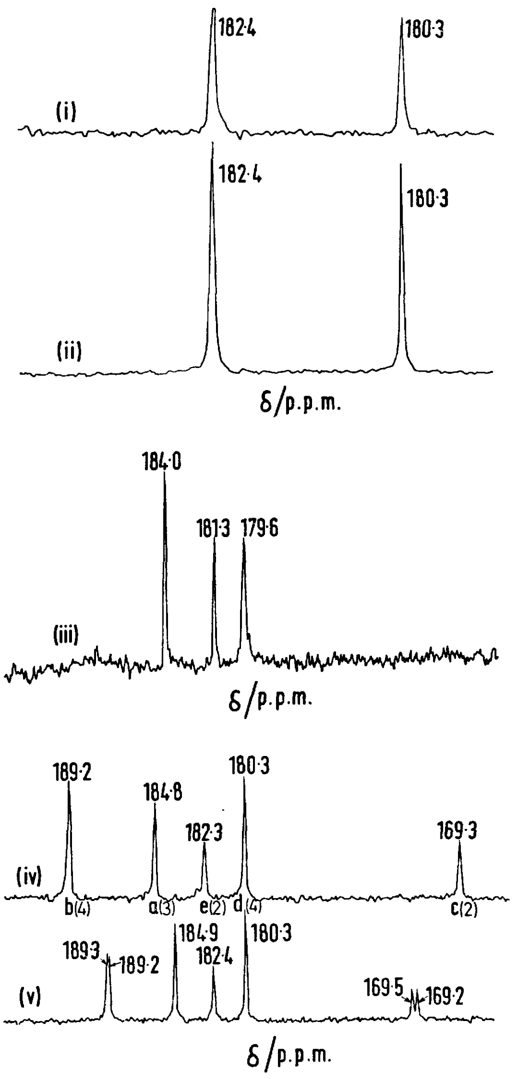

FIGURE 2. ^{13}C N.m.r. spectra of $[HOs_5(CO)_{15}]^-$. (i): +55 °C, no ^1H spin decoupling; (ii): +55 °C, ^1H spin decoupling; (iii): −50 °C, ^1H spin decoupling; (iv): −108 °C, ^1H spin decoupling; (v): −108 °C, no ^1H spin decoupling.

Crystal data: $C_{51}H_{31}NO_{15}Os_5P_2$, *M* 1910·7, monoclinic, space group $C2/c$, $a = 21{\cdot}98(1)$, $b = 15{\cdot}76(1)$, $c = 31{\cdot}01(2)$ Å, $\beta = 99{\cdot}3(1)°$, $Z = 8$, $U = 10596{\cdot}4$ Å^3, $\mu = 116{\cdot}2$ cm^{-1} for Mo-K_α. Data were collected using a Syntex $P2_1$ 4-circle diffractometer with graphite-monochromated Mo-K_α radiation. The osmium atom positions were located by multisolution sigma-2 sign expansion and light atoms were found by subsequent electron density difference syntheses, after numerical absorption corrections had been applied.

The structure was refined by the blocked cascade least-squares method to $R_w = 0{\cdot}059$ for the 6001 reflections with $F > 4\sigma(F)$. Molecular dimensions for the cation, refined with constrained phenyl rings, were normal [P–N 1·55(2), 1·59(2) Å; ∠P–N–P 144·5(10)°]. The Os–C and C–O bond lengths are all essentially equal with mean values of 1·89 and 1·13 Å, respectively. The hydride ligand cannot be unambiguously positioned on the basis of the Os–Os bond distances. However, examination of the polyhedron designated by the CO groups indicates a close similarity to the 16 CO polyhedron found for $[Os_5(CO)_{16}]$ but with one vertex missing. If it is assumed that the H-ligand occupies this vacant site, then it would bridge the edge Os(1)–Os(3) in agreement with the n.m.r. data given below.

Figure 2 shows the ^{13}C (*ca.* 40% ^{13}CO) n.m.r. spectra of $[HOs_5(CO)_{15}]^-$ over a range of temperatures. These can be interpreted on the basis of a structure in which the hydride ligand is placed on the edge Os(1)–Os(3) with carbonyl assignments according to Figure 2 (iv). ^1H Spin decoupling confirms a symmetrical edge-bridging hydride [Figure 2 (v)]. On warming to −50 °C the two resonances coupled to the hydride ligand collapse completely [Figure 2 (iii)] indicating local CO scrambling on Os(1) and Os(3). Further warming leads to collapse of the three remaining resonances; Figure 2 (ii) shows the spectrum at +55 °C which is similar to that of $[Os_5(CO)_{15}]^{2-}$. This spectrum can be interpreted in terms of the hydride ligand moving rapidly around all three edges of the trigonal plane [Os(1)–Os(2)–Os(3)]. This is supported by ^1H spin decoupling [Figure 2 (i)]. Our data are unable to show the CO scrambling processes on Os(2) (at −108 °C) or Os(4) and Os(5) (at +55 °C).

The complex $[H_2Os_5(CO)_{15}]$ could have a structure similar to that of $[HOs_5(CO)_{15}]^-$ with the second hydride ligand occupying a similar edge-bridging position.

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