$[HRu_6(CO)_{18}]^-$: a Ruthenium Anion Having an Interstitial H-Ligand. *X*-Ray Crystal Structures of Two Modifications†

By Colin R. Eady, Brian F. G. Johnson, Jack Lewis,* Maria Carlotta Malatesta
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Pella Machin
(*Rutherford Laboratory, Chilton, Didcot, Oxon* OX11 0QX)

and Mary McPartlin
(*Department of Chemistry, The Polytechnic of North London, London* N7 8DB)

Summary Reaction of $[Ru_3(CO)_{12}]$ with $[Mn(CO)_5]^-$ gives $[Ru_6(CO)_{18}]^{2-}$ which on acidification is converted into $[HRu_6(CO)_{18}]^-$; this monoanion has spectroscopic properties and an *X*-ray structure consistent with the H ligand lying at the centre of an octahedron (approximating to O_h symmetry) of ruthenium atoms.

$[HNb_6I_{11}]$ provides the only reported example of an H ligand occupying an interstice within a metal polyhedron;[1] evidence for such an H environment[2] in $[HMCo_3(CO)_{12}]$ (M = Fe, Ru) appears to be contradicted by an *X*-ray diffraction study on the phosphine derivative, $[HFeCo_3(CO)_9\{P(OMe)_3\}_3]$.[3] We report the preparation and characterization of the anion complex $[HRu_6(CO)_{18}]^-$ which shows spectroscopic properties consistent with the presence of an interstitial H-atom.

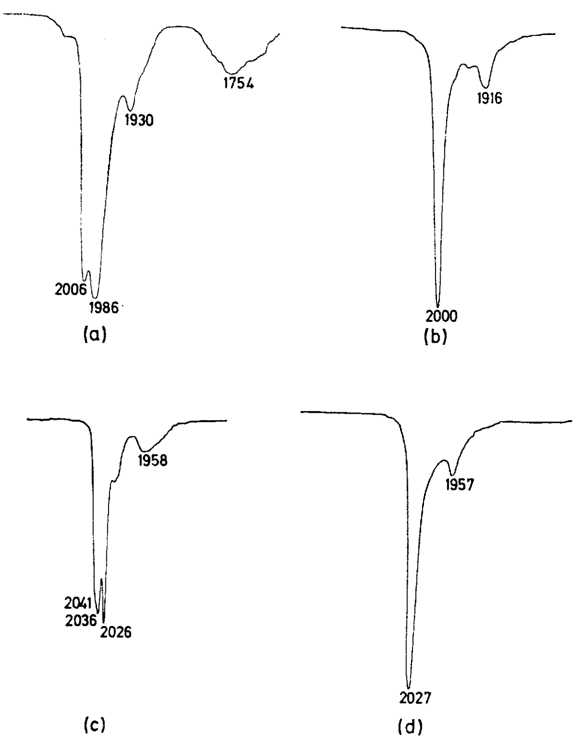

Figure 1. I.r. spectrum (ν_{CO}/cm^{-1} of (a) $[Ru_6(CO)_{18}]^{2-}$, (b) $[Os_6(CO)_{18}]^{2-}$, (c) $[HOs_6(CO)_{18}]^-$, and (d) $[HRu_6(CO)_{18}]^-$ in CH_2Cl_2

On heating $[Ru_3(CO)_{12}]$ with $[Na]^+[Mn(CO)_5]^-$ (equimolar) under reflux in tetrahydrofuran for 4 h the dianion $[Ru_6(CO)_{18}]^{2-}$ is produced. Addition of $[R]^+$ $[X]^-\{R = [(Ph_3P)_2N], [Me_4N]\}$ causes the formation of the brown salts, $[R^+]_2$ $[Ru_6(CO)_{18}]^{2-}$, which can be purified by t.l.c. and crystallization (yield 11%); the $[(Ph_3P)_2N]^+$ salt is the more stable. Elemental analysis is consistent with the given molecular formulae but i.r. spectra (ν_{CO}) of the salts differ from those of their osmium analogues (Figure 1) implying that, unlike $[Os_6(CO)_{18}]^{2-}$, $[Ru_6(CO)_{18}]^{2-}$ does not possess a metal geometry approximating to O_h symmetry.[4]

Addition of excess of sulphuric acid to the initial tetrahydrofuran solution (*vide supra*) yields $[HRu_6(CO)_{18}]^-$ which may be isolated as the $[(Ph_3P)_2N]^+$, $[Bu^n{}_4N]^+$ and $[Me_4N]^+$ salts. These deep red complexes, which can be purified by t.l.c. and crystallization, are obtained in low yields (15%), the major acidification products being $[H_4Ru_4(CO)_{12}]$ and $[H_2Ru_4(CO)_{13}]$. Significantly, further acidification of the monoanion with sulphuric acid in chloroform gives $[H_2Ru_6(CO)_{18}]$[5] in quantitative yield.

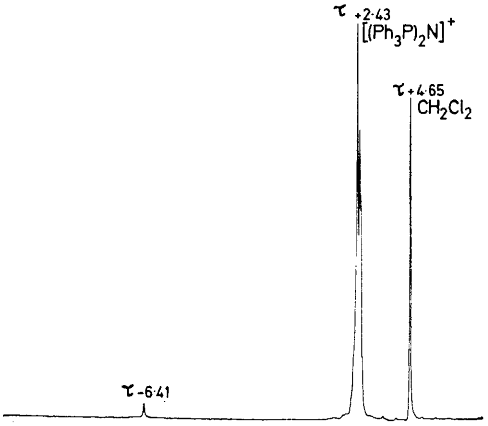

Figure 2. ^1H F.t. n.m.r. spectrum of $[(Ph_3P)_2N]^+[HRu_6(CO)_{18}]^-$ in CD_2Cl_2 at 40 °C (CH_2Cl_2 as internal calibrant).

The salts of $[HRu_6(CO)_{18}]^-$ were characterized by microanalysis, n.m.r., i.r., and *X*-ray studies. Thus ^1H Fourier transform (F.t.) n.m.r. spectroscopy $\{[(Ph_3P)_2N]^+$ salt$\}$

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† No reprints available.

over the range τ −40 to +100 using a 30 s pulse delay showed a singlet at τ −6·41 together with the expected cation multiplet at τ +2·4 of relative intensity *ca.* 1:30 (Figure 2). A similar ^{1}H F.t. n.m.r. spectrum of $[DRu_6(CO)_{18}]^-$ prepared by addition of D_2SO_4 to $[Ru_6(CO)_{18}]^{2-}$ in CD_2Cl_2 shows only a very weak absorption at τ −6·41. It is reasonable therefore to assign the resonance to the H-ligand; its occurrence at such a low-field position indicated a highly unusual environment. The use of a 30 s pulse delay under F.t. n.m.r. conditions in order to observe the τ −6·41 resonance is supported by its relaxation time (T_1) study which gives a value of 20 ± 3 s. By comparison the related $[HOs_6(CO)_{18}]^-$ shows a characteristic high-field hydride resonance in its ^{1}H n.m.r. spectrum at τ 21·26 (CD_2Cl_2, + 40 °C); single crystal *X*-ray diffraction and ^{13}C n.m.r. studies are consistent with a face bridging hydride within this osmium cluster.[4,6] The highly unusual H-ligand environment within $[HRu_6(CO)_{18}]^-$ as revealed by ^{1}H n.m.r. studies is demonstrated further by other spectroscopic studies. Thus, solution i.r. spectra (ν_{CO}) show just one broad band (Figure 1); this is significantly different to that of $[HOs_6(CO)_{18}]^-$ but closely resembles (in pattern) $[Os_6(CO)_{18}]^{2-}$ which possesses a metal geometry of approximate O_h symmetry.[4,6b] Moreover, a variable temperature ^{13}C (CO) n.m.r. study on $[HRu_6(CO)_{18}]^-$ (^{13}CO, *ca.* 40%) reveals a sharp singlet which remains unchanged over the temperature range 0 to −104 °C (^{1}H–^{13}C coupling could not be detected). Despite the greater fluxionality observed in ruthenium rather than osmium systems, these ^{13}C n.m.r. spectra, together with other data including an *X*-ray diffraction study, are consistent with an octahedral arrangement (O_h symmetry or approximating to) of metal atoms within $[HRu_6(CO)_{18}]^-$, with three terminal carbonyl groups per ruthenium atom and the H-ligand lying at the centre of the octahedron.

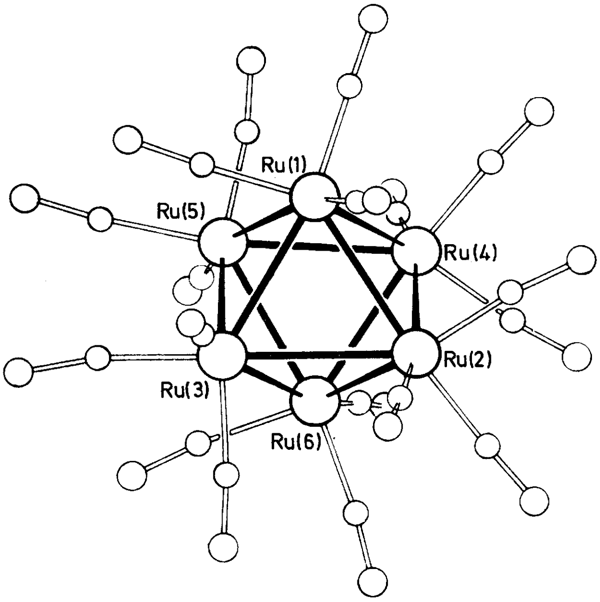

FIGURE 3. The structure of $[HRu_6(CO)_{18}]^-$. Mean Ru–Ru bond length = 2·87(1) Å.

Recrystallisation by slow diffusion techniques from CH_2Cl_2–cyclohexane gave two crystalline modifications of $[(Ph_3P)_2N]^+[HRu_6(CO)_{18}]^-$ which from i.r. spectroscopy (ν_{CO}) appeared to be chemically identical.‡ They pose an unusual crystallographic problem having different space groups with two and three formula units, respectively, per equivalent position. The data were collected using a Philips PW1100 diffractometer and Mo-K_α radiation. All non-hydrogen atoms have been located in (I) but, owing to computing problems associated with the large amount of data (9165 reflections) and the large number of independent atoms (162 non-hydrogen), the refinement is still at an early stage. However, the overall structure of the complex is clearly established and is shown in Figure 3. For (II) only a small proportion of low-angle data were collected in order to locate the metal atoms. There are three separate Ru_6 octahedra in the asymmetric unit, which is consistent with the spectroscopic evidence that (I) and (II) are modifications of the same compound. The carbonyl distribution in $[HRu_6(CO)_{18}]^-$ (Figure 3) has a marked resemblance to that in $[Os_6(CO)_{18}]^{2-}$ but is quite unlike that of the $[HOs_6(CO)_{18}]^-$ anion.[4]

This work establishes that the complexes, $[H_2M_6(CO)_{18}]$, $[HM_6(CO)_{18}]^-$, and $[M_6(CO)_{18}]^{2-}$ (M = Ru, Os) are not isostructural. An interstitial carbido ruthenium complex $[Ru_6(CO)_{17}C]$ is known[7] and significantly we again find the ruthenium system showing a preference for an interstitial arrangement.

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‡ *Crystal data:* (I) triclinic, space group $P\bar{1}$, a = 18·083, b = 19·101, c = 19·238 Å, α = 117·70, β = 78·13, γ = 97·05°, Z = 4, $I/\sigma(I) \geqslant 3{\cdot}0$, range 3—25°, present *R*-value = 0·10 for 9165 reflections; (II) monoclinic, space group $P2_1/c$, a = 33·82, b = 52·55, c = 9·832 Å, β = 92·66°, Z = 12, $I/\sigma(I) \geqslant 3{\cdot}0$, range 3—15°, present *R*-value = 0·23 (Ru only) for 1480 reflections.

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