The Preparation and Spectroscopic and *X*-Ray Crystallographic Determination of the Structure of $H_2Ru_6(CO)_{18}$: a New Octahedral Cluster Compound Containing Triply-bridging Hydride Ligands

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Summary $H_2Ru_6(CO)_{18}$ has been synthesized and characterized by spectroscopic and *X*-ray diffraction methods: the metal atoms define an octahedron, each ruthenium bearing three terminal carbonyl groups; hydride ligands occupy triply-bridging positions on two opposite faces of the octahedron.

SEVERAL polynuclear hydrido-carbonyls of ruthenium and osmium have been obtained by acidification of the products formed on reduction of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ with reducing agents such as hydroxide and borohydride ions. These include the tetranuclear complexes $H_4M_4(CO)_{12}$ and $H_2M_4(CO)_{13}$ (M = Ru or Os) as well as the trinuclear $H_2Os_3(CO)_{10}$.[1]

We have found that reduction of $Ru_3(CO)_{12}$ in tetrahydrofuran with the mononuclear carbonyl anions, $[Mn(CO)_5]^-$ or $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ follows a different course, and that a hexanuclear hydrido-carbonyl complex $H_2Ru_6(CO)_{18}$,† can be isolated in low yield by extraction of the reaction mixture with dichloromethane after acidification. The known tetranuclear hydrido-complexes are also present but can be removed by a preliminary extraction with petroleum. The new air-stable hexanuclear complex, which is only sparingly soluble in organic solvents, was obtained as deep-violet crystals by recrystallisation of the crude product from dichloromethane at −20°.

The mass spectrum of the complex shows the molecular ion together with ions formed by loss of carbonyl and hydride ligands. The presence of two hydrogen atoms was confirmed by the preparation of the deuteride, $D_2Ru_6(CO)_{18}$, for which the *m/e* value of the molecular ion is two units higher. Only 3 carbonyl stretching absorptions are observed in the i.r. spectrum of the hydride complex and all are in the terminal carbonyl region [ν(C–O) (CCl_4) 2060s, 2054s, 2008m cm^{-1}] Little change in the frequencies of these absorptions was observed in the corresponding deuterio-complex. The i.r. spectrum therefore suggests a highly symmetrical structure for the molecule.

In order to ascertain the molecular stereochemistry unequivocally, an *X*-ray crystallographic investigation of the material was undertaken.

Crystal data: $C_{18}H_2O_{18}Ru_6$, $M = 1112{\cdot}63$, monoclinic, $a = 16{\cdot}63(2)$, $b = 9{\cdot}58(1)$, $c = 19{\cdot}45(2)$ Å, $\beta = 120° 35(3)'$, $U = 2667$ Å^3, $D_m = 2{\cdot}80(2)$, $D_c = 2{\cdot}77$ g/cm^3, $Z = 4$; space group $P2_1/c$ (C_{2h}^5, No. 14). Diffraction data complete to $\sin\theta = 0{\cdot}38$ (Mo-K_α radiation) were collected on a 0·01°-incrementing Supper-Pace "Buerger Automated Diffractometer" and were corrected for absorption ($\mu = 33{\cdot}1$ cm^{-1}), The structure was solved by reiterative application of Sayre's relationships[2] to the 283 reflections with $E \geqslant 1{\cdot}6$ and was refined by difference-Fourier and least-squares techniques. All non-hydrogen atoms have been accurately located. Using anisotropic thermal parameters, the final discrepancy index is $R = 5{\cdot}72\%$ for 2779 independent non-zero reflections.

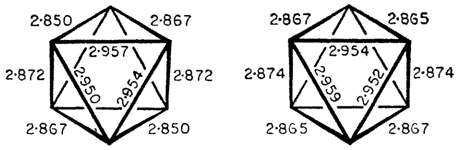

FIGURE 1. *Bond distances* ($\sigma = 0{\cdot}003$ Å) *within the two octahedral* Ru_6 *clusters.*

The unit-cell contains two sets of symmetry-unrelated $H_2Ru_6(CO)_{18}$ molecules which occupy the special positions 2(*c*) and 2(*b*) of space group $P2_1/c$.[3] However, the two sets of molecules are stereochemically equivalent, each molecule having precise C_i symmetry (and approximate D_{3d} symmetry) with its six ruthenium atoms defining a distorted

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† Correct analysis for carbon.

octahedron (see Figure 1). Each ruthenium atom is associated with three terminal carbonyl ligands.

Although the two hydride ligands have not been detected directly, their most probable positions may be derived by extension of the argument used to find hydride ligand positions in the $H_2Re_3(CO)_{12}^-$ ion:[4] *viz.* (i) Ru–Ru distances within two opposite faces of each octahedron range from 2·950—2·959 Å as opposed to values of 2·850—2·874 Å for all other Ru–Ru bonds. (ii) Three carbonyl groups lie almost vertically above each of the six small octahedral faces, but carbonyl ligands are spread away from truly axial positions above the two large faces of the Ru_6 octahedron (see Figure 2).

The symmetrically increased bond distances and the symmetrical distortion of carbonyl ligands from truly axial positions above the large triangular faces of the octahedron thus lead us to postulate that the undetected hydride ligands occupy positions above the centres of these large "open" faces, and are each directly bonded to three ruthenium atoms.

The $H_2Ru_6(CO)_{18}$ molecule is isoelectronic with the known species $Rh_6(CO)_{16}$[5] and $Ru_6C(CO)_{17}$.[6,7]

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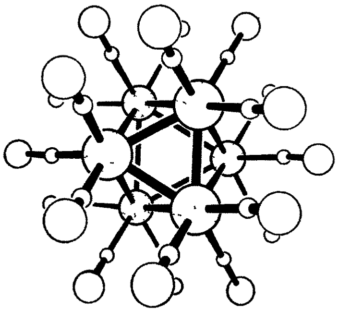

FIGURE 2. *An* $H_2Ru_6(CO)_{18}$ *molecule, projected onto one of its large "open" faces.*

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[1] B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2856; B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc.* (*A*), 1968, 2859.

[2] D. Sayre, *Acta Cryst.*, 1952, **5**, 60.

[3] "International Tables for X-Ray Crystallography, Volume 1," The Kynoch Press, Birmingham, 1965, p. 99.

[4] M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Amer. Chem. Soc.*, 1968, **90**, 7135.

[5] E. R. Corey L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

[6] B. F. G. Johnson, R. D. Johnston, and J. Lewis, *Chem. Comm.*, 1967, 1057.

[7] A. Sirigu, M. Bianchi, and E. Benedetti, *Chem. Comm.*, 1969, 596.