The First Non-carbido Decaruthenium Cluster; Synthesis and X-ray Structure Analysis of $[H_2Ru_{10}(CO)_{25}]^{2-}$

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The cluster dianion $[H_2Ru_{10}(CO)_{25}]^{2-}$ **1** may be synthesised by redox condensation of the anion $[HRu_6(CO)_{18}]^-$ **2** with $[Ru_3(CO)_{12}]$ **3** or by thermolysis of **3** in ethanol; it is the first high nuclearity ruthenium cluster not to contain an interstitial carbido-atom, and X-ray structure analysis shows that the cluster exhibits a unique metal core geometry which is clearly a fragment of the hexagonal close pack (hcp) system of metal atom packing.

We have recently reported on several new developments in high nuclearity ruthenium cluster chemistry,[1,2] and in most cases these parallel the structural patterns observed in the analogous chemistry of osmium. The observation that interstitial carbido-atoms appeared to be more prevalent in the chemistry of the lighter metal, and the importance of such atoms in reducing surface ligand overcrowding, emphasised their role in the stabilisation of large arrays of ruthenium atoms.[2] The isolation of the high nuclearity, non-carbido-dianion $[H_2Ru_{10}(CO)_{25}]^{2-}$ **1** is, therefore, significant.

In an attempt to synthesise the ruthenium analogue of the tetrahydrido-dianion, $[H_4Os_{10}(CO)_{24}]^{2-}$ {prepared by thermolysis of $[Os_3(CO)_{10}(OEt)_2]$ in 2-methylpropan-1-ol},[3] $[Ru_3(CO)_{12}]$ **3** was heated under reflux in ethanol. The initially orange solution became red over a period of several hours and IR spectroscopy indicated the formation of the known anion $[HRu_6(CO)_{18}]^-$ **2**. After 12 h a quantity of a black solid had been deposited and the solution had become dark brown. Separation of the mixture by column chromatography on silica (eluent: acetone–hexane 3 : 2) resulted in two products: the red monoanion **2**, and the new brown dianion **1**† (isolated in *ca.* 20% yield as its $[PPN]^+$ salt) in order of elution. The black solid was found to be insoluble in all common solvents. Significantly, it was found that **1** may also be generated by redox condensation of $[PPN][HRu_6(CO)_{18}]$ **2** with $[Ru_3(CO)_{12}]$ **3** at 140 °C in diglyme, thus indicating the intermediacy of **2** in the formation of **1** (Scheme 1). The new cluster dianion **1** was crystallised as its $[(PPh_3)_2N]^+$ salt from MeOH–CH_2Cl_2 at low temperature.

X-Ray single-crystal structure analysis shows that the

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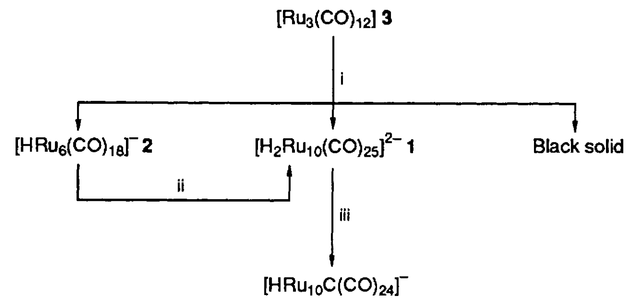
† *Spectroscopic data* for $[PPN]_2[H_2Ru_{10}(CO)_{25}]$ **1**: IR(CH_2Cl_2 solution); ν(CO) 2058 vw, 2015 s, sh, 2008 vs, 1992 m, sh, 1950 w, 1772 m, br cm^{-1}; ^1H NMR (CD_2Cl_2); δ 7.70 (multiplet, 30H), −14.20 (s, 2H) ppm; fast atom bombardment mass spectrum, M^+, *m/z* = 1713, $[(M)(PPN)]^+$ = 2251, M^{2+} = 856.



Scheme 1 *Reagents and conditions*: i, reflux in EtOH, 12 h; ii, $[Ru_3(CO)_{12}]$ **3** in diglyme at 140 °C; iii, $[Ru_3(CO)_{12}]$ **3** in diglyme at 162 °C

dianion **1** has the structure illustrated in Fig. 1.‡ The metal core geometry may be envisaged as the fusion of a bicapped octahedron with a bicapped square pyramid through a planar array of five metal atoms [Ru(1)–Ru(4)–Ru(5)–Ru(9)–Ru(10)]. This type of metal framework, of virtual C_s symmetry, has not previously been reported, but is closely related to that of $[Rh_{10}(CO)_{21}]^{2-}$.[4] The asymmetric distribution of the 25 carbonyl ligands, including four bridging (μ_2-), reduces the overall symmetry to C_1. The observed electron count of 134 is in agreement with that predicted from extended Hückel MO calculations,[5] and the same value may be derived from electron counting procedures.[6] Interestingly, the metal core of **1** may be envisaged as a fragment of the recently reported non-carbido-cluster $[Os_{17}(CO)_{36}]^{2-}$ (Fig. 2),[7] and may formally be generated by successive decapping of this structure. The formation of even larger ruthenium clusters by redox condensation of **1** with reactive $Ru(CO)_x$ fragments under thermolysis, therefore, seems possible. However, attempts to obtain such a product by reaction of **1** with **3** in diglyme at 162 °C failed, and surprisingly only the carbido-anion $[HRu_{10}C(CO)_{24}]^-$ was generated.

The best known decanuclear clusters of ruthenium and osmium have the tetracapped octahedral geometry of T_d symmetry and may formally be regarded as being derived from a face centred cubic (fcc) unit cell of metal atoms,[1,2,3,8] which is in contrast to the hcp arrangement found in the bulk metals, and the bis-octahedral dicarbido-dianion, $[Ru_{10}C_2(CO)_{24}]^{2-}$, has only two close packed layers of metal atoms.[9] The structure of the new dianion $[H_2Ru_{10}(CO)_{25}]^{2-}$ **1**, although nominally derived from an octahedron by multiple capping, shows clear ABA ordering of metal atom layers, and the cluster may, therefore, be regarded as containing hexagonally close packed metal atoms.

It has previously been a general observation that thermolytic syntheses of ruthenium clusters result in the formation of carbido-containing species, usually *via* the cleavage of a CO ligand,[2,10] and the synthesis of **1**, therefore, sets a precedent. The reason for the non-formation of the carbido-atom in this case is presumably due to the use of the relatively acidic solvent, ethanol, which may liberate protons to fulfil the

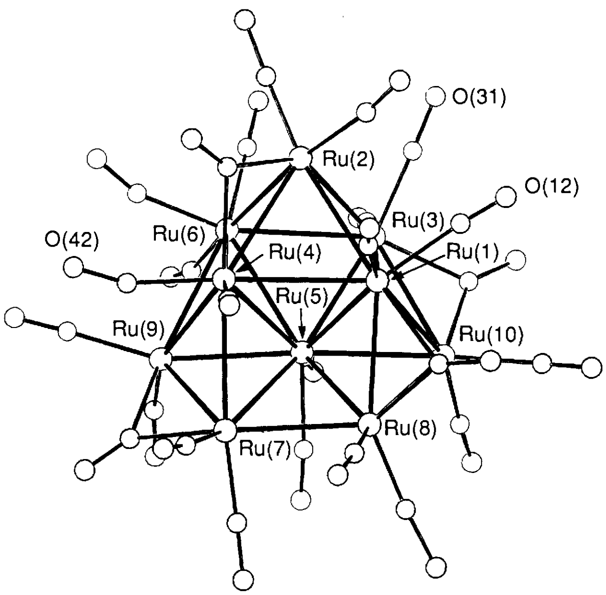


Fig. 1 The molecular structure of the dianion $[H_2Ru_{10}(CO)_{25}]^{2-}$ **1**; principal bond distances (Å) are: Ru(1)–Ru(2) 2.903, Ru(1)–Ru(3) 2.895, Ru(1)–Ru(4) 3.001, Ru(1)–Ru(5) 2.815, Ru(1)–Ru(8) 2.791, Ru(1)–Ru(10) 2.802, Ru(2)–Ru(3) 2.956, Ru(2)–Ru(4) 2.853, Ru(2)–Ru(6) 2.871, Ru(3)–Ru(5) 2.793, Ru(3)–Ru(6) 2.886, Ru(3)–Ru(10) 2.796, Ru(4)–Ru(5) 2.845, Ru(4)–Ru(6) 2.898, Ru(4)–Ru(7) 2.908, Ru(4)–Ru(9) 2.909, Ru(5)–Ru(6) 2.901, Ru(5)–Ru(7) 2.872, Ru(5)–Ru(8) 2.767, Ru(5)–Ru(9) 2.761, Ru(5)–Ru(10) 2.803, Ru(6)–Ru(9) 2.863, Ru(7)–Ru(8) 2.845, Ru(7)–Ru(9) 2.826, Ru(8)–Ru(10) 2.860 maximum esds 0.003 Å

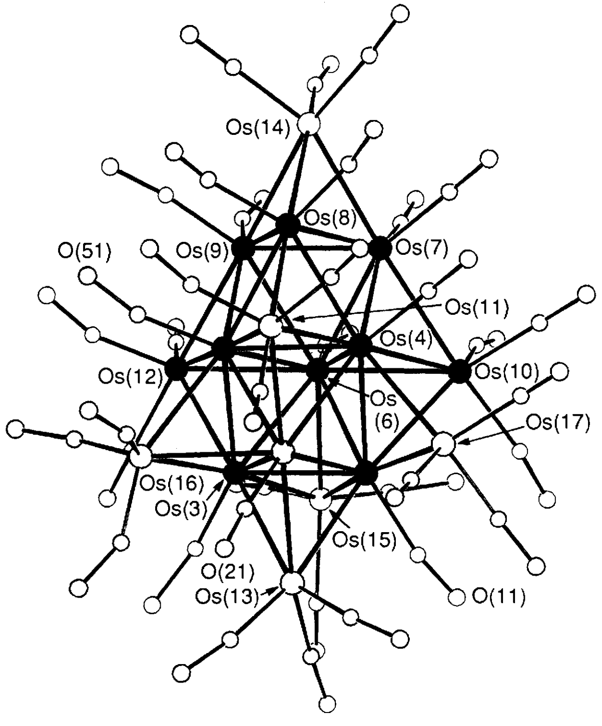


Fig. 2 The structure of the dianion $[Os_{17}(CO)_{36}]^{2-}$ showing the relationship to the metal framework of **1** (shaded atoms)

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‡ *Crystallographic data* for $[PPN]_2[H_2Ru_{10}(CO)_{25}]$ **1**: $C_{97}H_{62}N_2O_{25}P_4Ru_{10}$, $M = 2790.15$, triclinic, space group $P\bar{1}$ (No. 2), $a = 17.244(4)$, $b = 20.487(5)$, $c = 16.769(4)$ Å, $\alpha = 92.07(2)$, $\beta = 115.26(2)$, $\gamma = 67.66(2)°$, $U = 4898.92$ Å^3, $Z = 2$, $D_c = 1.891$ g cm^{-3}, $F(000) = 2716$, $R = 0.0730$ for 7443 reflections with $I/\sigma(I) > 3.0$ corrected for absorption μ(Mo-Kα) = 14.74 cm^{-1}. Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

electronic role of the carbon atom in stabilising intermediate structures. The carbonyl ligand distribution is rather asymmetric in **1** and neither potential energy minimisation,[11] computer graphics techniques[12] or comparison of Ru–Ru bond lengths indicated suitable H-ligand locations on the cluster surface. It seems probable that both of these ligands are in interstitial or semi-interstitial sites in the metal framework. Significantly, the hydride in the monoanion $[HRu_6(CO)_{18}]^-$ **2**,[13] and one of those in the structurally related dihydride $[H_2Ru_8(CO)_{21}]^{2-}$,[14] are known to reside in interstitial octahedral positions.

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