The Synthesis and *X*-Ray Structure Analysis of the Dianion $[Ru_{18}(C)_2(CO)_{42}Hg_3]^{2-}$, the First Octadecaruthenium Cluster

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The heterometallic dianion $[Ru_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ has been obtained from the decanuclear ruthenium carbido-dianion $[Ru_{10}C(CO)_{24}]^{2-}$ as its $[N(PPh_3)_2]^+$ salt by reaction with mercury(II) trifluoroacetate, and has been shown by *X*-ray single crystal analysis to be a dimer of two tricapped octahedral Ru_9 cluster fragments, linked by a bridging Hg_3 triangular unit.

High nuclearity metal clusters containing osmium have dominated the chemistry of large iron triad carbonyl compounds; these have included ten and eleven metal atom clusters with carbide and hydride ligands in interstitial sites in the metal frameworks, as well as a number of clusters with heterometal atoms.[1,2] Despite the well developed chemistry of hexaruthenium carbide species, there have been remarkably few reports of higher nuclearity clusters for this metal.

Recently the synthesis and *X*-ray structure determinations of the first tetracapped octahedral decaruthenium clusters,

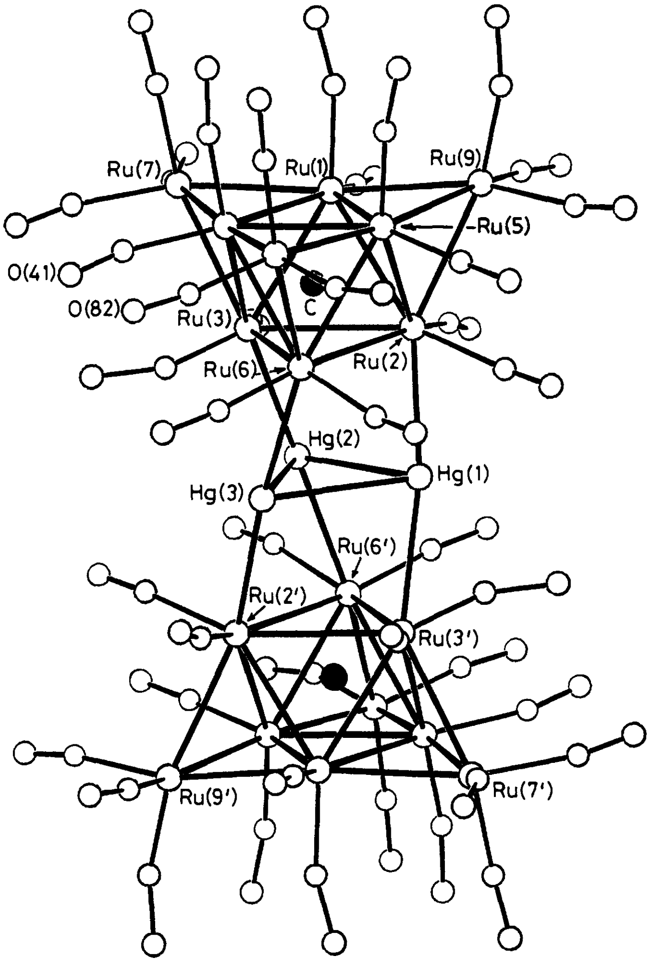

Figure 1. The molecular structure of $[Ru_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**3**); the first digit of each labelled carbonyl oxygen atom is the number of the ruthenium atom to which it is attached. Principal bond distances (Å): Ru–Ru: (1)–(2) 2.840(9), (1)–(3) 2.854(8), (1)–(4) 2.832(6), (1)–(5) 2.840(6), (1)–(7) 2.754(6), (1)–(9) 2.741(6), (2)–(3) 3.002(5), (2)–(5) 2.831(7), (2)–(6) 3.010(5), (2)–(9) 2.803(8), (3)–(4) 2.866(7), (3)–(6) 3.006(6), (3)–(7) 2.836(9), (4)–(5) 2.831(6), (4)–(6) 2.857(9), (4)–(7) 2.737(6), (4)–(8) 2.730(6), (5)–(6) 2.840(8), (5)–(8) 2.752(6), (5)–(9) 2.733(6), (6)–(8) 2.799(7); Ru–Hg: (2)–Hg(3) 2.712(8), (3)–Hg(1) 2.734(9), (6)–Hg(2) 2.691(9), (2′)–Hg(1) 2.660(6), (3′)–Hg(2) 2.640(6), (6′)–Hg(3) 2.698(6). Hg–Hg: Hg(1)–Hg(2) 2.934(6), Hg(1)–Hg(3) 2.919(5), Hg(2)–Hg(3) 2.922(5). Mean distances; Ru–C(carbonyl) 1.83(9), C–O(carbonyl) 1.17(9), Hg · · · C(carbonyl) 2.64(9).

$[Ru_{10}C(CO)_{24}]^{2-}$ (**1**)[3,4] and $[HRu_{10}C(CO)_{24}]^{-}$ (**2**)[4] were reported as their $[N(PPh_3)_2]^+$ salts; both are isostructural with their osmium analogues.

During attempts to obtain higher nuclearity clusters by reaction of the dianion (**1**) with cationic metallic species,[2] it was found that with mercury(II) trifluoroacetate it gave a very large cluster dianion (**3**) together with a small quantity of an uncharacterized precipitate. *X*-Ray structure analysis of this new species shows it to be the giant fused cluster dianion $[Ru_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ (**3**) (Figure 1). The cluster may be envisaged as being formed from two decaruthenium clusters each of which has lost a capping $Ru(CO)_3$ group, generating two nonaruthenium tricapped octahedral fragments which are

Figure 2. The 100.6 MHz ^{13}C n.m.r. spectrum of $[Ru_{18}(C_2)(CO)_{42}Hg_3]^{2-}$ (**3**) in CD_2Cl_2 solution at 293 K showing the significant broadening at the base of the resonance at δ 203.7, assigned to the carbonyl ligands of the ruthenium atoms adjacent to the mercury atoms, due to unresolved coupling between carbon and ^{199}Hg. The single resonance due to the two carbide ligands is observed at δ 371.4.

fused by a doubly face-capping μ_6-η^3-Hg_3 unit.† The tricapped octahedral geometry exhibited by the ruthenium subclusters has not been previously reported for any cluster of the iron triad metals. Mercury has been noted previously for its ability to bridge between small metal aggregates to form larger clusters,[5] as in for example $[Hg_2Ru_7(CO)_{22}(\mu_3\text{-}C_2Bu^t)_2]$[6] and $[M_3(CO)_{11}Hg]_3$ (M = Ru and Os).[7]

In the solid state the dianion (**3**) has virtual C_3 symmetry, and the mean twist angle of 30° between the central Hg_3 triangle and the two adjacent Ru_3 triangles (which together form a 'spiral' linking unit) results in the two faces Ru(2)–Ru(3)–Ru(6) and Ru(2′)–Ru(3′)–Ru(6′) of the Ru_9 units

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† *Crystal data* for (**3**): $C_{116}H_{60}N_2O_{42}P_4Ru_{18}Hg_3\cdot CH_2Cl_2$, $M = 4697.12$ (4782.05 with CH_2Cl_2), triclinic, space group $P\bar{1}$ (no. 2), $a = 19.042(4)$, $b = 15.729(3)$, $c = 15.197(3)$ Å, $\alpha = 115.59(2)$, $\beta = 68.51(2)$, $\gamma = 115.46(2)°$, $U = 2983.18$ Å^3, $F(000) = 2240$, $\mu(\text{Mo-}K_\alpha) = 48.48\ cm^{-1}$, $Z = 1$, $D_c = 2.66\ g\ cm^{-3}$. Data were collected using a crystal mounted in a Lindemann capillary to prevent the rapid loss of solvent of crystallisation, on a Philips PW1100 diffractometer in the θ-range 3—21°, with a scan width of 0.8°; final R 0.0756 and R_w 0.0733 for 2761 reflections with $I/\sigma(I) > 3.0$. A random distribution of 'left-handed' and 'right-handed' molecules in the crystal results in a disorder of the central Hg_3 triangle in the *X*-ray structure analysis, the top and bottom Ru_9 units being related by a crystallographically imposed inversion centre. Atomic co-ordinates, bond lengths and angles, and thermal parmeters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

being exactly staggered with a total twist angle of 60° between them.† In solution the simple i.r. spectrum in the CO stretch region is consistent with C_3 symmetry of the dianion. At 25 °C, the ^{13}C n.m.r. spectrum shows only four sharp resonances in the region δ 210—190 in the intensity ratio 1:1:2:3 which is expected from inspection of the solid-state structure, assuming rotation of the $Ru(CO)_3$ groups. The resonance due to the carbide ligands in this cluster is observed at δ 371.4 (Figure 2).‡ The resonance of relative intensity 2 at δ 203.7 is considerably broadened at its base; this may be attributed to the presence of unresolved satellite resonances due to coupling to ^{199}Hg (16.8% natural abundance), since this resonance may be assigned to the twelve carbonyl ligands equatorially disposed above and below the Hg_3 plane. It is relevant that the crystal structure analysis shows six very short contact distances between the mercury atoms and the carbon atoms of these ligands [mean Hg · · · C(carbonyl) 2.64 Å] indicating significant interaction consistent with the observable Hg · · · C coupling in the ^{13}C n.m.r. spectrum; the alternative of mercury–carbonyl coupling through ruthenium would be expected to be small in comparison. This is the first reported example of a mercury–carbonyl interaction observed. Overall the fused cluster unit shows remarkable stability to degradation to smaller cluster species.

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‡ *Spectroscopic data* for (**3**): i.r. (CH_2Cl_2) ν(CO): 2065s, 2055vs, 2002s cm^{-1}; ^1H n.m.r. (CD_2Cl_2): δ 7.70 {m, $[N(PPh_3)_2]^+$}; ^{13}C n.m.r. (CD_2Cl_2): δ 371.4 (μ_6-carbide), 210.6, 208.2, 203.7, 190.6; negative ion fast atom bombardment mass spectrum M^+ (obs.) *m/z* 3623, (calc.) 3618.

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