A New Undecametal Rhodium Carbonyl Cluster consisting of Three Condensed Octahedral Units. Synthesis and Crystal Structure of the $[Rh_{11}(CO)_{23}]^{3-}$ Trianion

Alessandro Fumagalli,* Secondo Martinengo, Gianfranco Ciani,* and Angelo Sironi

C.N.R., Centro di studio sulla sintesi e la struttura dei composti dei metalli di transizione nei bassi stati di ossidazione, Via G. Venezian 21, 20133 Milano, Italy

The anion $[Rh_{11}(CO)_{23}]^{3-}$, obtained through oxidation of $[Rh_7(CO)_{16}]^{3-}$ or various redox condensations, contains a metal polyhedron of ideal D_{3h} symmetry which can be described as being the result of a face-to-face condensation of three octahedral sub-units.

We recently undertook studies to synthesize rhodium carbonyl clusters of medium nuclearity (8—12 metal atoms), which could be useful both for the development of rational stepwise syntheses of higher nuclearity species and for the understanding of the mechanism of cluster growth. These studies resulted in the isolation of the previously reported $[Rh_9(CO)_{19}]^{3-}$ anion[1] and we now report the isolation and *X*-ray characterization of a second species of this kind, the $[Rh_{11}(CO)_{23}]^{3-}$ anion.

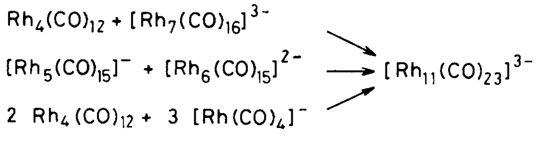
The $[Rh_{11}(CO)_{23}]^{3-}$ anion has been obtained as the main product of reactions performed on $[Rh_7(CO)_{16}]^{3-}$ [2] with reactants which can act as direct or indirect oxidants, such as Fe^{III} salts, mineral acids, and Au^{I} derivatives. The reaction with $FeCl_3$, in a slight excess with respect to the 1 : 1 molar ratio, is the most convenient way to produce the new anion but the redox condensations summarized in Scheme 1 may also be used. These reactions are performed in MeCN or tetrahydrofuran and are speeded up by evacuation or moderate heating, which favour CO evolution; prolonged heating must, however, be avoided, as it may cause further reaction to give $[Rh_{14}(CO)_{25}]^{4-}$ [3] and other products.

The i.r. spectrum of the $[NMe_4]^+$ salt shows a little solvent dependence: bands are observed at 2032vw, 1995s, and 1817m cm^{-1} in MeCN, and at 2028vw, 1991s, and 1819m cm^{-1} in acetone. No hydride signals were observed in the ^1H n.m.r. spectrum from τ −12 to +68, either at room temperature or at −80 °C.

The instability of $[Rh_{11}(CO)_{23}]^{3-}$ towards heating and the observation that this anion is present in the first stages of the pyrolytic treatment of solutions of $[Rh_{12}(CO)_{30}]^{2-}$ or $Rh_4(CO)_{12}$ plus OH^- mixtures which afford higher nuclearity clusters,[3–7] confirm its role of intermediate in cluster growth.

Crystals of the $[NMe_4]^+$ salt suitable for *X*-ray analysis were obtained from acetone by slow diffusion of propan-2-ol; they contain acetone-solvated molecules.†

A view of the novel cluster anion is reported in Figure 1. The metal skeleton, of ideal D_{3h} symmetry, is of a new type and consists of three condensed octahedral units (see Figure 2) having a common edge [Rh(1)–Rh(2)] coincident with the ideal three-fold axis. Each octahedron shares a triangular face with both of the adjacent octahedra. The array is not, therefore, a fragment of a metallic lattice, not being derived by superimposition of close-packed layers. It can instead be related to the recently characterized species $[Rh_9(CO)_{19}]^{3-}$,[1] containing two condensed face-sharing octahedra. The Rh_9 moiety is present here, somewhat distorted, in three different orientations (the three possible pairs of octahedra). Addition to such an Rh_9 array of an Rh_2 unit parallel to an edge of the central triangle followed by closure of six metal bonds would generate the third octahedron of the Rh_{11} cluster. Since octahedra are not space-filling polyhedra and the dihedral angle between the faces is of 109°28′ only, the necessity to attain 'ideal' dihedral angles of 120° around the common edge [Rh(1)–Rh(2)] leads to distortions of the octahedral units, as can be observed by an analysis of the metal–metal bonds. Of the 28 Rh–Rh bond lengths, 23, in the range 2.687(2)—2.865(1) Å (mean 2.765 Å), can be considered to be in the normal range of values for these interactions, with small differences between the 12 carbonyl-bridged (mean 2.772 Å) and the 11 unbridged edges (mean 2.758 Å). The other five unbridged metal–metal bonds [Rh(1)–Rh(2), Rh(3)–Rh(9), Rh(4)–Rh(9), Rh(7)–Rh(11), and Rh(8)–Rh(11)] are markedly longer, ranging from 2.958(2) to 3.062(2) Å (mean 2.988 Å), and their lengthenings are very probably related to the requirements mentioned above for the condensation of the three octahedra. From the point of view of the metal–metal connectivities, there are three types of metals with, respectively, seven [Rh(1) and Rh(2)], six [Rh(9), Rh(10), and Rh(11)], and four (the remaining Rh atoms) metal–metal bonds.



Scheme 1

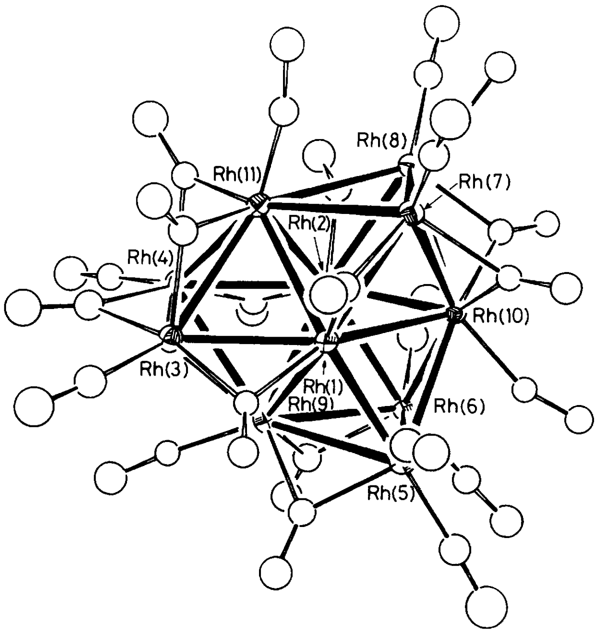


Figure 1. A view of the anion $[Rh_{11}(CO)_{23}]^{3-}$.

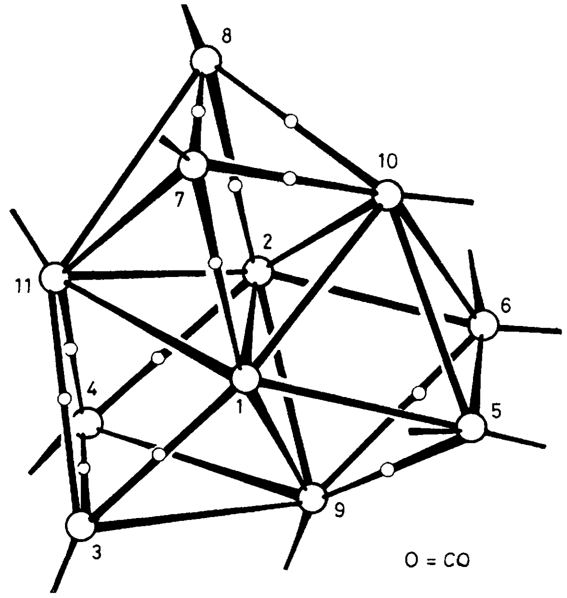


Figure 2. A scheme of the metal atom array, showing also the metal–carbonyl connectivity (edges with small circles are carbonyl-bridged). Individual Rh–Rh bond lengths are: (1)–(2) 2.965, (1)–(3) 2.721, (1)–(5) 2.687, (1)–(7) 2.734, (1)–(9) 2.797, (1)–(10) 2.732, (1)–(11) 2.766, (2)–(4) 2.722, (2)–(6) 2.703, (2)–(8) 2.702, (2)–(9) 2.749, (2)–(10) 2.738, (2)–(11) 2.762, (3)–(4) 2.727, (3)–(9) 2.958, (3)–(11) 2.844, (4)–(9) 2.974, (4)–(11) 2.836, (5)–(6) 2.709, (5)–(9) 2.834, (5)–(10) 2.865, (6)–(9) 2.840, (6)–(10) 2.828, (7)–(8) 2.742, (7)–(10) 2.760, (7)–(11) 2.982, (8)–(10) 2.799, (8)–(11) 3.062 Å. E.s.d's 0.001—0.002 Å.

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† *Crystal data:* $C_{38}H_{42}N_3O_{24}Rh_{11}$, M = 2056.7, monoclinic, space group $P2_1/n$ (No. 14), a = 12.296(3), b = 19.999(5), c = 24.006(8) Å, β = 104.35(3)°, Z = 4. The structure was solved by direct methods and refined by block-matrix least-squares, on the basis of 7745 significant $[I > 2.5\sigma(I)]$ data, up to a current R value of 0.065.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The geometry of the 23 carbonyl ligands on the cluster surface is such as to distribute the electronic density equally over the various metal atoms, but their stereochemistry drastically lowers to C_s the ideal D_{3h} cluster symmetry; only an approximate mirror plane, passing through the atoms Rh(9), Rh(10), and Rh(11) is maintained. There are twelve symmetric edge-bridging groups (Figure 2) with mean Rh–C and C–O bonds of 2.01 and 1.19 Å, respectively. Eleven carbonyls are terminally bonded so that Rh(5) and Rh(6) bear two such ligands each, Rh(1) and Rh(2) do not possess terminal groups, and the other seven ligands are bound to the remaining metals, one per rhodium atom. The mean values of the Rh–C and C–O bond lengths for these groups are 1.86 and 1.16 Å, respectively. However, one of the CO groups bound to Rh(5) shows a weak interaction with Rh(1) of 2.46(2) Å [*cf.* Rh(5)–C = 1.89(2) Å], which is also reflected in the Rh(5)–C–O angle of 156(2)°. Three other terminal CO's also show a tendency to interact with neighbouring metals, but to a lesser extent.

The anion possesses 148 valence electrons, corresponding to 74 cluster valence molecular orbitals, one more than the value of $6N$(metals) $+7$, previously suggested as the more probable value for metal clusters which are fragments of a compact close-packed lattice;[8] this increase is justified by the lowering of compactness of the present metallic array.

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