

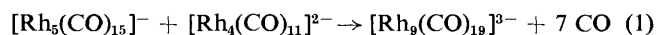
Synthesis and X-Ray Structure of the Anion $[\text{Rh}_9(\mu_3\text{-CO})_3(\mu\text{-CO})_9(\text{CO})_7]^{3-}$ containing a Cofacial Bioctahedral Rhodium Cluster

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The novel anion $[\text{Rh}_9(\text{CO})_{19}]^{3-}$, obtained by condensation between the anions $[\text{Rh}_4(\text{CO})_{11}]^{2-}$ and $[\text{Rh}_5(\text{CO})_{15}]^-$, contains a Rh_9 metal-atom cluster formed by two condensed octahedra sharing a face.

In the field of high-nuclearity carbonyl cluster compounds of Rh, without interstitial main-group elements, there is, at present, a certain discontinuity in the nuclearity of the known compact species. A seven-metal cluster, namely $[\text{Rh}_7(\text{CO})_{16}]^{3-}$,^{1,2} and various close-packed species with between 13 and 22 metal atoms are now known, but no such compound with 8–12 metal atoms has yet been isolated. We have attempted to isolate such species, which can be useful in understanding the mechanism of cluster growth, and also furnish suitable intermediates for a rational stepwise synthesis of the higher-nuclearity clusters. We report here the synthesis and characterization of the first species we have isolated, the enneametal carbonyl cluster anion $[\text{Rh}_9(\text{CO})_{19}]^{3-}$.



The $[\text{Rh}_9(\text{CO})_{19}]^{3-}$ anion was synthesized in high yield by condensation of the $[\text{Rh}_5(\text{CO})_{15}]^-$ anion³ with the $[\text{Rh}_4(\text{CO})_{11}]^{2-}$ dianion⁴ at room temperature according to reaction (1).[†] Formation of the $[\text{Rh}_9(\text{CO})_{19}]^{3-}$ anion has been observed in the decomposition of the $[\text{Rh}_5(\text{CO})_{14}\text{X}]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) anions^{5,6} and in the reaction of the $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ anion with excess of chloride ions;⁷ however in these cases the yields are highly dependent on both the solvent and the counterion.⁸

The i.r. spectrum of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ (PPN) salt in MeCN solution shows bands at 2020vw, 1990m, 1968vs, and 1957vs

cm^{-1} in the terminal, and 1822ms, 1790sh, and 1770sh cm^{-1} in the bridging CO stretching regions. No hydride bands were observed in the ^1H n.m.r. spectrum either at room temperature or at -76°C . ^{13}C , ^{103}Rh , and $^{13}\text{C}\{^{103}\text{Rh}\}$ INDOR n.m.r. studies are in progress.⁸

The $[\text{Rh}_9(\text{CO})_{19}]^{3-}$ anion reacts slowly with CO in MeCN solution to give quantitatively the $[\text{Rh}_9(\text{CO})_{15}]^{2-}$ anion.¹

Only the Cs^+ salt, of a variety of cations studied, gave crystals suitable for X-ray analysis.[‡]

The structure of the novel anion $[\text{Rh}_9(\text{CO})_{19}]^{3-}$ is illustrated in Figure 1. It contains an Rh_9 metal-atom cluster formed by two condensed octahedra sharing a triangular face. This metallic array, of idealized D_{3d} symmetry, has been found previously only in the nickel species $[\text{Ni}_9(\text{PEt}_3)_6\text{S}_9]^{2+}$,⁹ which does not contain carbonyl groups; it can also be described as a hexagonal close-packed fragment formed by three superimposed triangles with a sequence *aba*. It differs from another nine-metal-atom cluster present in the anion $[\text{Pt}_9(\text{CO})_{18}]^{2-}$, in which three-metal-atom triangles are superimposed with small relative rotations in a tube-like structure, and which is related to simple hexagonal packing.¹⁰

The 21 Rh–Rh bond lengths are in the range 2.712(1)–2.852(1) Å, with an overall mean value of 2.759 Å, the shortest bonds being associated with the Rh atoms of the central triangular layer. These three metal atoms have six Rh–Rh

[†] A mixture of $[\text{PPN}]_2[\text{Rh}_4(\text{CO})_{11}]$ [0.12 g, PPN = $(\text{Ph}_3\text{P})_2\text{N}$] and $[\text{PPN}][\text{Rh}_5(\text{CO})_{15}]$ (0.10 g) dissolved under nitrogen in MeCN (6 ml) reacted immediately to give a brown solution which was evaporated to dryness *in vacuo*. The tacky residue was dissolved in acetone (4 ml) and precipitated by addition of propan-2-ol (20 ml) and concentration *in vacuo*. The PPN salt was filtered off, washed with propan-2-ol and dried *in vacuo* (yield: 80–90%). The caesium salt was obtained by metathesis with NaBPh_4 in acetone, evaporation to dryness, extraction with water, addition of KBr, filtration to remove $[\text{PPN}]\text{BPh}_4$ and KBPh_4 , and precipitation by addition of CsCl ; yields: ca. 50%.

[‡] Crystal data: $\text{C}_{19}\text{Cs}_9\text{O}_{19}\text{Rh}_9$, $M = 1857.1$, monoclinic, space group $P2_1/n$ (No. 14), with $a = 9.415(1)$, $b = 19.297(3)$, $c = 19.152(3)$ Å, $\beta = 90.61(1)^\circ$, $U = 3479.4$ Å³, $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares, on the basis of 5267 significant independent counter data, to a current conventional R value of 0.033. The atomic co-ordinates for this work are available on request from Prof. Dr G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

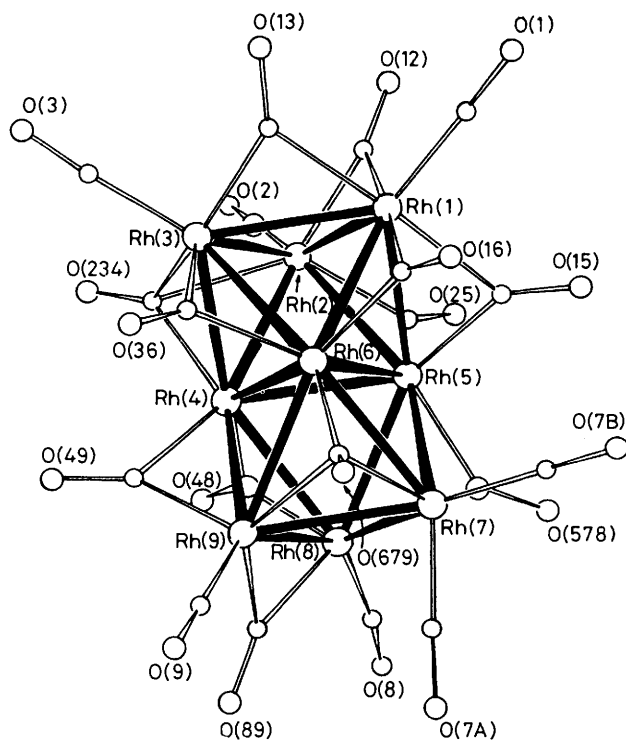


Figure 1. A view of the anion $[\text{Rh}_9(\text{CO})_{19}]^{2-}$. The individual Rh–Rh bond lengths are as follows: (1)–(2) 2.822, (1)–(3) 2.823, (1)–(5) 2.770, (1)–(6) 2.762, (2)–(3) 2.836, (2)–(4) 2.727, (2)–(5) 2.725, (3)–(4) 2.712, (3)–(6) 2.742, (4)–(5) 2.725, (4)–(6) 2.716, (4)–(8) 2.745, (4)–(9) 2.733, (5)–(6) 2.742, (5)–(7) 2.769, (5)–(8) 2.733, (6)–(7) 2.733, (6)–(9) 2.752, (7)–(8) 2.852, (7)–(9) 2.765, and (8)–(9) 2.758 Å; e.s.d.s 0.001 Å.

connections, while the remaining rhodium atoms have only four metal–metal connections.

The carbonyl stereochemistry reduces the overall idealized symmetry of the anion to C_s , the ideal mirror plane passing through Rh(1), Rh(4), and Rh(7). Of the 19 carbonyl groups

7 are terminally bonded to the Rh atoms of the external triangles, one per metal atom except for Rh(7) which bears two such ligands. The Rh atoms of the central triangle, Rh(4), Rh(5), and Rh(6), do not possess terminal CO groups. The mean values of the Rh–C and C–O distances for these ligands are 1.86 and 1.15 Å, respectively. There are 9 edge-bridging CO groups; four of these, bound to Rh(1), are asymmetric [mean Rh(1)–C, Rh–C, and C–O 2.16, 1.94, and 1.18 Å] and five are almost symmetric (mean Rh–C and C–O 2.04 and 1.18 Å). Three CO groups are triply bridging, on faces Rh(2,3,4), Rh(5,7,8), and Rh(6,7,9); these groups are all asymmetric, with Rh–C distances ranging from 1.934(8) to 2.512(8) Å.

The anion possesses 122 valence electrons, corresponding to 61 cluster valence molecular orbitals (CVMOs). This corresponds exactly to the number of $6N_{\text{metals}} + 7$ CVMOs, previously suggested as the more probable for a compact closest-packed cluster.¹¹

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