Synthesis and *X*-Ray Crystal Structure of the Cluster Compound $[Rh_{12}H_2(\mu_3\text{-}CO)_3(\mu\text{-}CO)_9(CO)_{13}]$ containing a Metallic Array formed by Three Superimposed Cofacial Octahedral Units

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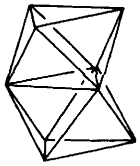
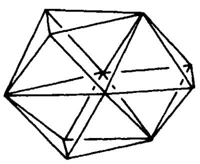
The neutral species $[Rh_{12}H_2(CO)_{25}]$, obtained by reaction of $[Rh_{14}(CO)_{25}]^{4-}$ with CF_3CO_2H in the presence of CO and chloride ions, contains a new Rh_{12} metallic array formed by superimposition of three face-sharing octahedral units, and in donor solvents readily gives the $[Rh_{12}H(CO)_{25}]^-$ monoanion.

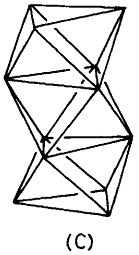
We are currently investigating the chemistry of medium-sized cluster compounds of rhodium (8—12 metal atoms), in order to understand the mechanism of cluster growth. For clusters of this size, in the absence of interstitial main group elements or when larger interstitial holes are not required, the skeletons are usually polycapped octahedra, as in $[Os_8(CO)_{22}]^{2-}$,[1] $[Re_8C(CO)_{24}]^{2-}$,[2] $[Os_{10}C(CO)_{24}]^{2-}$,[3] and $[Fe_6Pd_6H(CO)_{24}]^{3-}$.[4] Other geometries are possible, however, and we have already reported on two rhodium species based on condensed face-sharing octahedral units, namely $[Rh_9(CO)_{19}]^{3-}$,[5] type (A), and $[Rh_{11}(CO)_{23}]^{3-}$,[6] (B). A mixed-metal species with cluster geometry (B), *i.e.*



(A)



(B)



(C)

$[Pt_2Rh_9(CO)_{22}]^{3-}$, has also been described recently.[7] We report here the synthesis and characterization of a novel medium nuclearity rhodium cluster species, the neutral $[Rh_{12}H_2(CO)_{25}]$, which is based on the face-to-face condensation of octahedral units, geometry (C).

$[Rh_{12}H_2(CO)_{25}]$ (**1**) is formed together with $[Rh_6(CO)_{16}]$ when $[Rh_{14}(CO)_{25}]^{4-}$ is treated with chloride ions in an acid medium (CH_2Cl_2–CF_3CO_2H) in the presence of CO. The influence of CO is significant: in the absence of CO cracking of the cluster is hindered, while under pure CO fragmentation to $[Rh_6(CO)_{16}]$ completely occurs; the best yields were obtained by using a Cl^-/Rh_{14} ratio of two and operating under an atmosphere of CO–N_2 in a ratio of 1 : 6.†

$[Rh_{12}H_2(CO)_{25}]$
(**1**)

$[Rh_{12}H(CO)_{25}]^-$
(**2**)

Although we could not observe the ^1H n.m.r. spectrum of (**1**) because of the low solubility, its dihydric nature has been established on the following basis: (i) both in Nujol mull and in non basic solvents such as CH_2Cl_2, selected crystals of the product show i.r. bands which are assigned to terminal carbonyl groups at frequencies typical of neutral species;‡ (ii) in basic solvents such as THF, acetone, alcohols, or CH_2Cl_2 containing 1% THF, the crystals are soluble, but the i.r. bands shift to lower frequencies by *ca.* 12—15 cm^{-1},‡ in agreement with dissociation of one hydride ligand and formation of the corresponding monoanionic cluster; (iii) the n.m.r. spectrum of the acetone solution of selected crystals shows a sharp hydridic signal at δ −16.57 [septet, *J*(Rh–H) 14.45 Hz], thus indicating that the monoanion contains a hydride; this anionic species is assigned as $[Rh_{12}H(CO)_{25}]^-$ (**2**).[8] The neutral starting species is therefore a dihydride. This formulation has also been confirmed by potentiometric titration of the acidity evolved in basic solvents.[8]

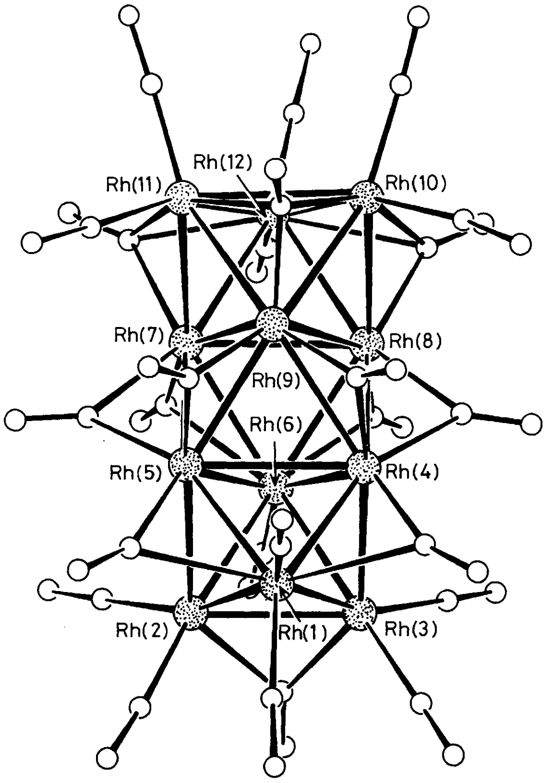


Figure 1. The *X*-ray crystal structure of (**1**).

The structure of the novel compound (**1**) is shown in Figure 1.§ It contains a Rh_{12} cluster of idealized D_{3d} symmetry, derived by three superimposed face-sharing octahedral units. It is a fragment of hexagonal close-packing formed by the stacking of four triangles, with an *abab* sequence.

As in the case of the metal cluster of the anion $[Rh_9(CO)_{19}]^{3-}$ (D_{3h} symmetry, *aba* sequence of triangles) the cluster shows alternation of staggered triangles, giving rise to octahedral subunits, in contrast to the situation in the $[Pt_3(CO)_6]^{2-}{}_n$ (n = 3—5) family, in which the triangles are superimposed in an almost eclipsed manner (with small

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† $[NEt_4]_4[Rh_{14}(CO)_{25}]$ (0.325 g) with $[(Ph_3P)_2N]Cl$ (0.139 g) in CH_2Cl_2 (20 ml) under a CO–N_2 (ratio 1 : 6) atmosphere were treated with CF_3CO_2H (14.5 ml), and after stirring left to stand for 1 week. The crystalline product containing (**1**) and $[Rh_6(CO)_{16}]$ was filtered, washed first with CF_3CO_2H, then with hexane, and dried *in vacuo*. Crystals suitable for *X*-ray analysis were found directly from this mixture. Yields (20—30%) were determined after extraction with tetrahydrofuran (THF) which left undissolved the $[Rh_6(CO)_{16}]$. The i.r. spectrum of the THF extract was identical with the i.r. spectrum of selected crystals of (**1**) in THF.

‡ I.r. data for (**1**): selected crystals (Nujol) ν 2075vs, 2030(sh), 2010(sh), 1910m, 1890mw, 1870m, and 1800w cm^{-1}; in CH_2Cl_2: 2083(sh), 2074s, 2062s, 2047(sh), 1912w, 1881mw, 1860mw, and 1809mw cm^{-1}; in THF: 2062s, 2049s, 1956w, 1890mw, 1858mw, and 1807mw cm^{-1}. In all the spectra the bridging CO bands are broad.

§ *Crystal data:* $2[Rh_{12}H_2(CO)_{25}] \cdot 3\,CH_2Cl_2$, $C_{53}H_{10}Cl_6O_{50}Rh_{24}$, M = 4129.1, monoclinic, space group $P2_1/c$ (No. 14), with a = 18.570(8), b = 25.694(8), c = 20.013(8) Å, β = 106.12(4)°, U = 9173.5 $Å^3$, Z = 4, D_c = 2.99 g cm^{-3}, μ(Mo-K_α) = 43.9 cm^{-1}, Mo-K_α radiation (λ = 0.71073 Å). The intensity data were collected on an Enraf–Nonius CAD4 automated diffractometer by the ω-scan method, within the limits $3 < \theta < 23.5°$. An empirical absorption correction was applied to the intensities (normalized transmission factors in the range 0.50—1.0). The structure was solved by direct methods, which showed the presence of two independent cluster molecules (*A* and *B*) and of three solvated CH_2Cl_2 molecules (affected by disorder, as indicated by very high thermal parameters and by the presence of some vicinal residual peaks in the difference-Fourier maps). In one of the two cluster molecules (*A*) a terminal carbonyl ligand, bound to Rh(12), was found doubled by some disorder and was treated as a pair of half carbonyl groups, very close together. The refinements were carried out by full-matrix least-squares, on the basis of 5768 significant independent reflections [$I > 3\,\sigma(I)$], up to current values of R and R_w of 0.040 and 0.047, respectively.

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

relative rotations), resulting in tube-like structures of piled face-sharing trigonal prisms.[9]

There is a wide range of metal–metal bond distances but the corresponding interactions in the two independent molecules compare very well. The ranges of values are 2.692(2)—2.918(2) Å in one molecule, and 2.682(2)—2.929(2) Å in the second one. The Rh–Rh bonds within the stacked triangular layers are significantly longer than the inter-layer ones. The metal–metal bond lengths can be assigned to the following classes: (i) within the triangle Rh(1,2,3), mean 2.775 Å; (ii) connecting the Rh(1,2,3) and the Rh(4,5,6) triangles, mean 2.725 Å; (iii) within the Rh(4,5,6) triangle, mean 2.857 Å; (iv) connecting the Rh(4,5,6) and the Rh(7,8,9) triangles, mean 2.744 Å; (v) within the Rh(7,8,9) triangle, mean 2.857 Å; (vi) connecting the Rh(7,8,9) and the Rh(10,11,12) triangles, mean 2.743 Å; and (vii) within the Rh(10,11,12) triangle, mean 2.904 Å.

The six rhodium atoms of the central octahedral unit each exhibit six metal–metal connections, while the six atoms of the outer triangles show only four such connections. The compound can be viewed as being derived from two interconnected Rh_6 octahedra. In contrast to the dimeric $[Rh_{12}(CO)_{30}]^{2-}$ with only one Rh–Rh inter-octahedral bond,[10] in (**1**) there are six such connections.

The carbonyl stereochemistry reduces the overall idealized symmetry of the molecule to C_s, the ideal mirror plane passing through atoms Rh(1), Rh(6), Rh(9), and Rh(12). Of the 25 carbonyl groups 13 are terminally bonded, nine are edge bridging (four markedly asymmetric), and three are asymmetrically face bridging.

With respect to the location of the hydrides, one hydride is probably inside the central octahedral hole, in accord with the lengthening of the Rh–Rh bonds within the two central triangles with respect to the basal Rh(1,2,3) one (mean 2.857 *vs.* 2.775 Å). This hydride, which should be less exposed to external influences, is probably that retained in the monoanion (**2**), and its interstitial nature is confirmed, provided that the CO ligands are fluxional, by the septet observed in the n.m.r. spectrum, which arises on coupling with the six surrounding equivalent Rh atoms. The second, more weakly bonded, hydride ligand is probably in the upper part of the cluster, either inside the Rh(7,8,9,10,11,12) octahedron, or, more likely, in a triple bridging location on the Rh(10,11,12) triangle, as suggested by the particularly long Rh–Rh bond lengths within it (mean 2.904 Å) and by the stereochemistry of the terminal carbonyl groups bound to these atoms.

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