# New Arrangements of Transition Metal Atoms in Carbido-carbonyl Clusters of Rhodium and Cobalt

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*Summary* New carbido-carbonyl cluster compounds of rhodium have been isolated and two of them, characterized by crystallographic methods, have been formulated as $Rh_8(CO)_{19}C$ and $[H_3O][Rh_{15}(CO)_{28}C_2]$; the synthesis of carbido-carbonyl clusters has been extended to cobalt for which the anion $[Co_6(CO)_{15}C]^{2-}$ has been obtained.

WE have previously reported the preparation and structure of the first carbido cluster of the cobalt subgroup, *i.e.* $[Rh_6(CO)_{15}C]^{2-}$ (I),[1] and we now describe new carbido-carbonyl compounds of rhodium and cobalt.

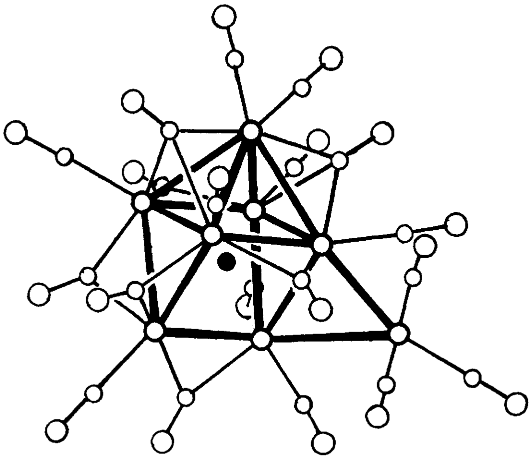
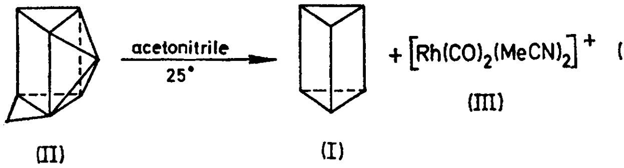


FIGURE 1. Perspective view of the $Rh_8(CO)_{19}C$ molecule. The rhodium atoms are joined by solid lines; the carbide atom is shown isolated in the centre of the prism.

Firstly we attempted the preparation of neutral derivatives of (I), and by oxidation of $K_2$ $[Rh_6(CO)_{15}C]$ in water under CO using ferric ammonium alum as a mild oxidant we have obtained a brown precipitate not characterized as yet. Solutions under CO of this product in toluene or $CH_2Cl_2$ slowly produce black diamagnetic crystals which have been identified by *X*-ray crystallographic methods as $Rh_8(CO)_{19}C$ (II).† The molecule, shown in Figure 1, contains a metal atom cluster derived from the prismatic unit present in the dianion (I) to which two extra atoms have been attached, one in a capping position on one rectangular face and the other in a bridging position on one base edge.



The Rh–Rh distances range from 2·699 to 2·913(3) Å, mean value 2·81 Å. The carbido carbon atom is situated in the centre of the prism with a mean Rh–C distance of 2·127 Å. Eleven of the nineteen CO groups are linearly bound, six of them are edge bridging, and two are face bridging. This molecule is a rare example of a completely asymmetric cluster, contradicting the common opinion that clusters are highly symmetrical units of close packed metal atoms.

The structural relationship between (I) and (II) has a chemical counterpart; in fact if (II) is dissolved in MeCN an immediate disproportionation takes place, and the dianion (I) is obtained ($\nu_{CO}$ = 2030sh, 1995vs, 1840s, and 1802m

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† Crystal data: $a = 9{\cdot}18(1)$, $b = 17{\cdot}76(2)$, $c = 10{\cdot}46(1)$ Å, $\alpha = 75°57'(6')$, $\beta = 69°3'(6')$, $\gamma = 92°21'(6')$, space group $P\bar{1}$, $Z = 2$.

$\text{cm}^{-1}$ in MeCN) together with the cation $[Rh(CO)_2(MeCN)_2]^+$ (III) ($\nu_{CO}$ = 2125 and 2065 $\text{cm}^{-1}$). The reaction can be schematized as in reaction (1). The $BF_4^-$ salt of the cation (III) has also been isolated in pure form starting from $AgBF_4$ and $Rh_2(CO)_4Cl_2$, and it is a strong electrolyte in acetonitrile ($\Lambda_e$ = 146 $\Omega^{-1}$ $\text{cm}^2$ $\text{mol}^{-1}$; $c_e = 3{\cdot}69 \times 10^{-3}$ M).

If the whole oxidation process of (I) is carried out under nitrogen a new black crystalline species is formed which has been examined by a crystallographic study. This new compound is diamagnetic and a non-electrolyte in $CH_2Cl_2$ ($\Lambda_e$ *ca.* 1 $\Omega^{-1}$ $\text{cm}^2$ $\text{mol}^{-1}$) and it is presently formulated as $[H_3O][Rh_{15}(CO)_{28}C_2]$(IV).‡ The diamagnetism and the presence in the Fourier map of an electron density peak attributable to the cation are the strongest evidences in favour of the formulation of (IV) as an oxonium salt. Unfortunately the low solubility of (IV) in inert solvents and its high reactivity towards Lewis basic solvents, such as methanol and tetrahydrofuran, have hindered further proof of the ionic character of the compound. The molecular structure of the anion is shown in Figure 2. The molecule possesses $C_{2v}$ idealized symmetry and the $Rh_{15}$ cluster can be described as a centred tetracapped pentagonal prism, or alternatively as a system of two octahedra sharing one vertex (the central atom), plus four other atoms forming tetrahedra fused with the octahedra and with themselves; the Rh–Rh distances are scattered in the range 2·738—3·332(3) Å.§ It is worthwhile pointing out the highly metallic situation of the central rhodium atom which is linked to twelve other metal atoms (mean distance 2·90 Å) and to both carbide carbon atoms which occupy the centres of the octahedra with mean Rh–C distance 2·06 Å. The twenty-eight CO ligands are arranged as follows: fourteen in terminal positions, one per metal atom, and the remaining are bridging edges of the metal atom polyhedron (Figure 2).

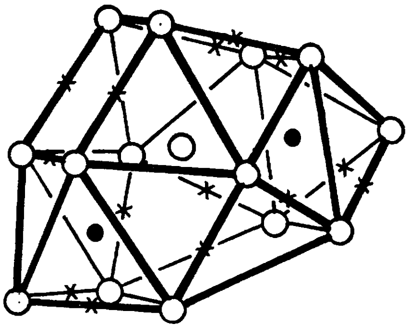

FIGURE 2. Schematic representation of the $Rh_{15}(CO)_{28}C_2^-$ anion. Only the least distances among the surfacial metal atoms are drawn; small circles indicate the carbide atoms. The terminal CO groups are not shown, and the location of the fourteen edge bridging carbonyl groups are indicated by crosses.

These new structural features are reflected in the different behaviour of (IV) and (II) towards MeCN. Complex (IV) reacts with MeCN to give a new anionic species ($\nu_{CO}$ = 2020s, 1865sh, 1840m, and 1805sh, $\text{cm}^{-1}$) which is presently under investigation, together with the same cationic species (III) formed in reaction (1).

By carrying out the whole oxidation process of (I) under different experimental conditions other cluster compounds have been obtained, and their structural characterisation is presently under way.

We have extended the syntheses of carbido-clusters to cobalt. Reaction of $[Co(CO)_4]^-$ with the chloromethynyl derivative $Co_3(CO)_9CCl$ in THF at 70 °C (or propan-2-ol at 25 °C) gives (40—50% yields) the dianion $[C_6(CO)_{15}C]^{2-}$. It has been obtained in pure crystalline form as the black trimethylbenzylammonium salt (V) which is strictly isomorphous with the corresponding salt of (I). The i.r. spectrum of (V) in the CO stretching region ($\nu_{CO}$ 2015w, 1975s, 1855m, 1820s, and 1810s $\text{cm}^{-1}$ in THF) is very similar to that of (I). Both these facts indicate that (V) and (I) are isostructural. The characteristic different behaviour towards carbon monoxide in cluster carbonyl compounds of cobalt and rhodium is maintained,[2] and CO causes the decomposition of the species (V) at atmospheric pressure.

The analogous reaction between $[Rh(CO)_4]^-$ and $CO_3(CO)_9CCl$ gives an anion formulated as $[Co_2Rh_4(CO)_{15}C]^{2-}$ (VI). The trimethylbenzylammonium salt of (VI) is isomorphous with the corresponding salts of (I) and (V), implying that the three anions are isostructural. At present however it is not clear if (VI) is a mixed anion or a mixture of (I) and (V).

All these compounds [except (IV)] formally obey the noble gas rule, but this does not explain the bonding situation of the carbide atoms in the centre of the clusters that can be described only in terms of delocalized molecular orbitals.

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‡ Crystal data: *a* = 15·01(2), *b* = 17·34(2), *c* = 18·85(2) Å, space group *Pbca*, Z = 4.

§ The bond lengths of 31 out of 33 edges are in the range 2·738—3·091(3) Å, and only two edges (connecting the two square faces which contains the carbon atoms) span distances of 3·332(3) Å.

[1] V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J.C.S. Dalton*, 1973, 651.
[2] S. Martinengo and P. Chini, *Gazzetta*, 1972, **102**, 344, and references therein.