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Preliminary communication

RHODIUM CARBONYL CLUSTER CHEMISTRY UNDER HIGH PRESSURES OF CARBON MONOXIDE AND HYDROGEN

VIII*. SYNTHESIS AND STRUCTURE OF $[Rh_{15}(CO)_{30}]^{2-}$ (bcc array) AND ITS RELATIONSHIP TO $[Rh_{14}(CO)_{25}]^{4-}$ (incomplete bcc) AND $[Rh_{15}(CO)_{27}]^{3-}$ (hcp-bcc)

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Summary

The generation of $[Rh_{15}(CO)_{27}]^{3-}$ under high pressures of CO/H_2 (15 atm, 150°C, 3 h) from $Rh(CO)_2acac$ and $CsPhCO_2$ in 18-crown-6-alcohol solutions results in the formation, precipitation and isolation of single crystals of $[Rh_{15}(CO)_{30}]^{3-}$ with $[Cs(18\text{-crown-}6)_2]^+$ as a counterion. The new anion has a bcc array of metal atoms related to the distorted one in $[Rh_{15}(CO)_{27}]^{3-}$ (bcc-hcp) and derived from the incomplete bcc array in $[Rh_{14}(CO)_{25}]^{4-}$ by formal addition of a "$Rh(CO)_5{}^+$" group. These results are potentially relevant to the modeling of surfaces by clusters and to the steps involved in the detachment of mononuclear fragments from clusters by either CO or CO/H_2.

Rhodium carbonyl clusters serve as models for surfaces [1] and have been proposed as potential homogeneous catalysts [2]. Their ability to release smaller fragments (with halides, nitriles [3], or amines [4], CO [4], CO/H_2, H_2CO/H_2 but not with H_2 [4]) as seen with $[Rh_{15}(CO)_{27}]^{3-}$ may be relevant to both subjects. On the other hand, the addition of a "$Rh(CO)_2{}^+$" group to $[Rh_{14}(CO)_{25}]^{4-}$ gave the Rh_{15} hcp-bcc polyhedron of the former trianion instead of the expected isomeric Rh_{15} bcc polyhedron [3] (Scheme 1).

The transformation of $[Rh_{15}(CO)_{27}]^{3-}$ into $[Rh_{14}(CO)_{25}]^{4-}$ in the presence of carbon monoxide [4] suggested the intermediacy of a fifteen-rhodium atom cluster with more than 27 carbonyl ligands: a larger number of carbonyls

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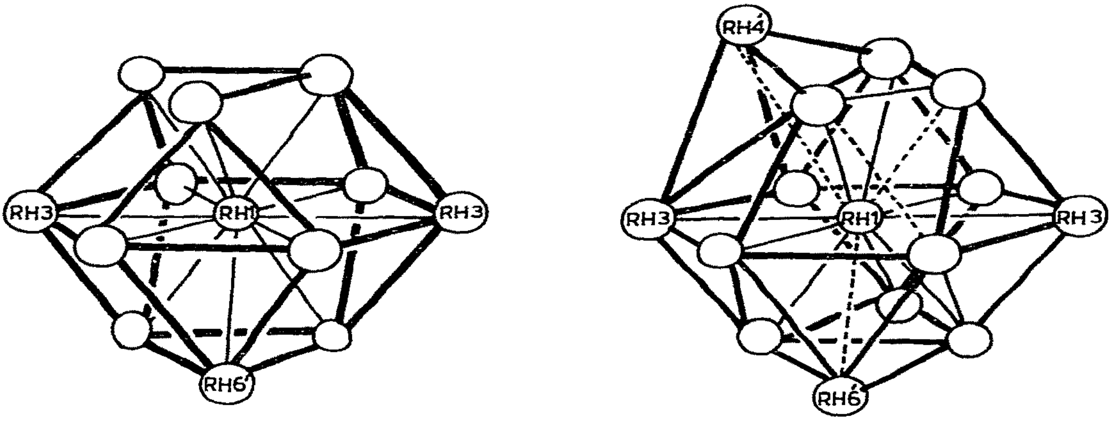
*For part VII see ref. 5.

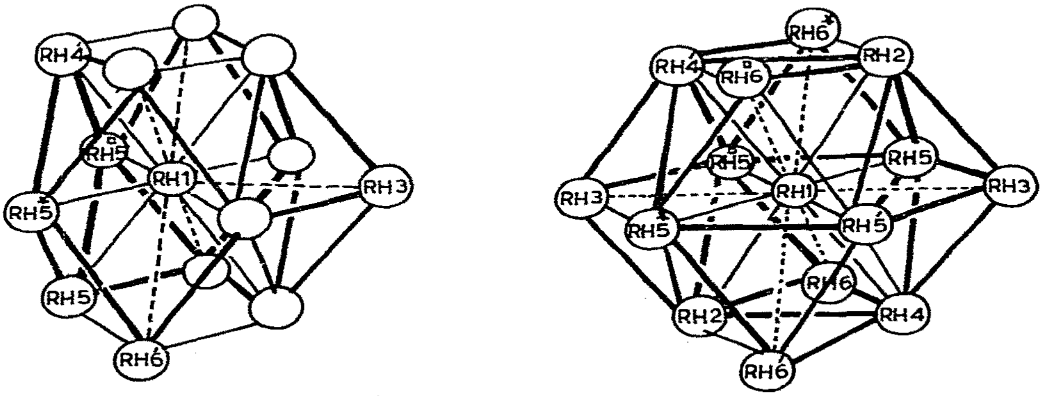


$[Rh_{13}(CO)_{24}Hx]^{(5-x)^-}$

hcp

$[Rh_{15}(CO)_{27}]^{3-}$

hcp — bcc



$[Rh_{14}(CO)_{25}]^{4-}$

Incomplete bcc

$[Rh_{15}(CO)_{30}]^{3-}$

bcc

SCHEME 1

than the former anion. The expectation that the isolation of such an intermediate would be facilitated under a high pressure of carbon monoxide, and by precluding its further transformation by precipitating it in situ, guided our studies.

$$\underset{\text{amine}}{\mathrm{Rh(CO)_2acac,\ CsPhCO_2}} \xrightarrow{<0.5\ \mathrm{h}} [\mathrm{Rh_{13}(CO)_{24}H_2}]^{3-} \xrightarrow{<2\ \mathrm{h}}$$

$$[\mathrm{Rh_{15}(CO)_{27}}]^{3-} \xrightarrow{\sim 24\ \mathrm{h}} [\mathrm{Rh_{14}(CO)_{25}}]^{4-}$$

The reagents, equipment and procedures employed in this work have been already described [5a—5c]. The reaction mixture below has been shown to serve as a suitable medium for the selective high pressure syntheses of $[\mathrm{Rh_{13}(CO)_{24}H_2}]^{3-}$ [5f], $[\mathrm{Rh_{15}(CO)_{27}}]^{3-}$ [4] and $[\mathrm{Rh_{14}(CO)_{25}}]^{4-}$ [5g]; It was expected that the addition of a precipitating agent such as a methanol/ethylene glycol mixture would facilitate the isolation of the desired intermediate. A solution of $\mathrm{Rh(CO)_2acac}$ (12.1 g, 46.9 mmol), cesium benzoate (3.00 g, 11.8 mmol), and *N*-methyl morpholine (12.2 g, 120.1 mmol) in a mixture of 18-crown-6 (500 ml) and ethylene glycol (60 ml) was charged to an autoclave purged with nitrogen. The reaction conditions were quickly adjusted to those required for the formation of $[\mathrm{Rh_{15}(CO)_{27}}]^{3-}$ [4] (15 atm of an equimolar mixture of $\mathrm{CO/H_2}$, 150°C) and the system was allowed to react for 4 hours. The stirrer was turned off, a mixture of methanol (170 ml) and ethylene glycol (30 ml) was added, and the system was allowed to rest for 48 hours. The solution was vented to ambient pressure and the reactor was washed with isopropanol and with acetone. The solids left in the reactor (1.35 g) were recovered under inert atmosphere and found to be soluble only in highly polar solvents (sulfolane, dimethyl sulfoxide). Their infrared spectrum (Fig. 1) is the one expected from the solid structure of the anion (vide

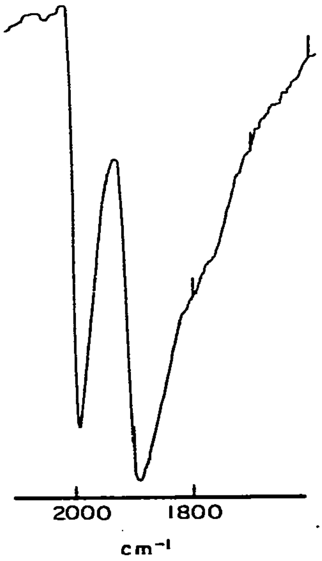


Fig. 1. Infrared spectra (in sulfolane or dimethyl sulfoxide solution) of $[\mathrm{Rh_{15}(CO)_{30}}]^{3-}$.

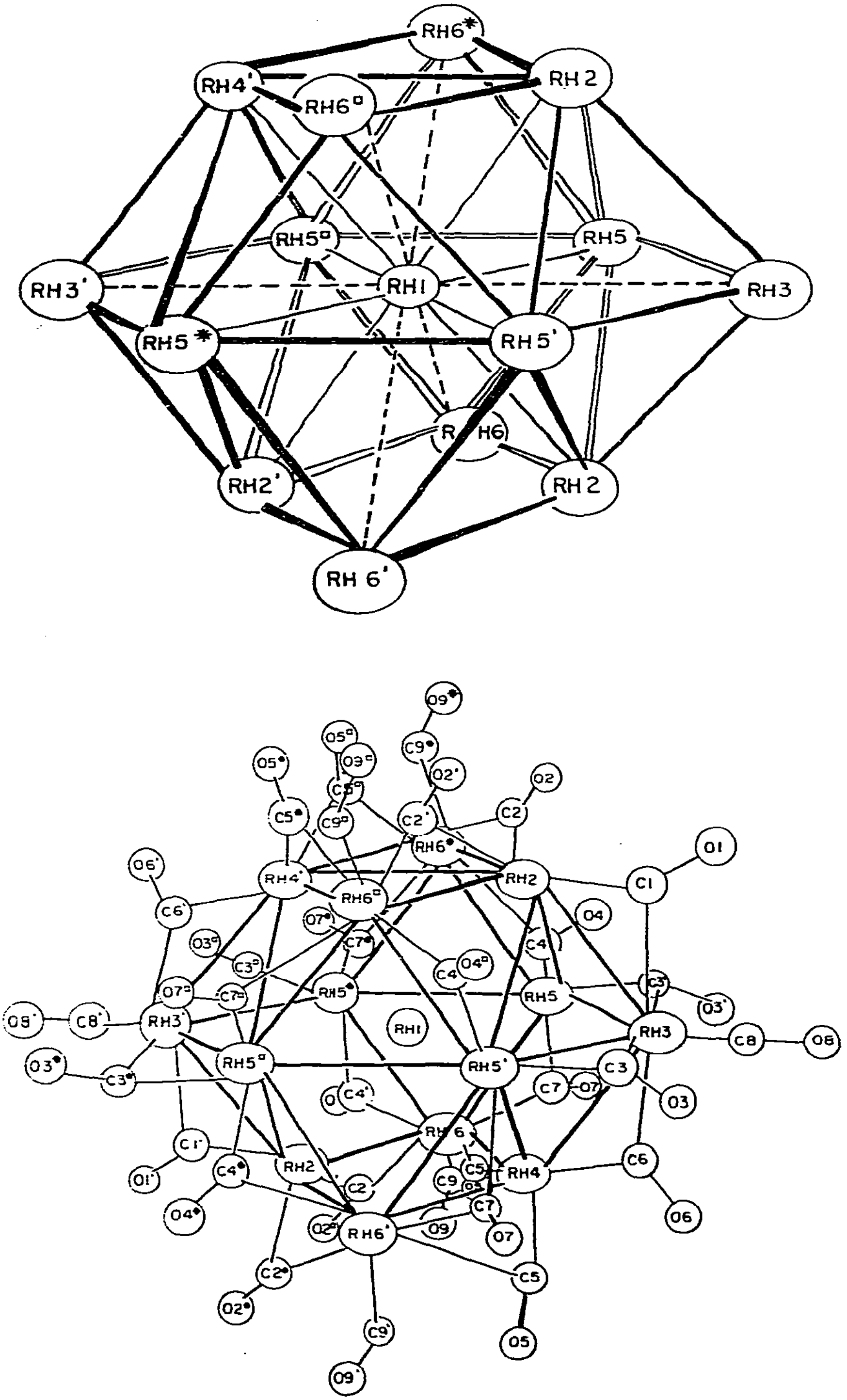


Fig. 2. ORTEPS of $[Rh_{15}(CO)_{30}]^{3-}$ (a) without the carbonyl ligands and (b) the complete anion.

infra). Close examination of the material showed the existence of single crystals suitable for X-rays diffraction studies. The same product was isolated upon heating the solution above (or one prepared using ethylene glycol as solvent) at 175°C for 10 days under a fast flow of carbon monoxide at 1 atm).

The anion, $[Rh_{15}(CO)_{30}]^{3-}$, was isolated as the cesium-18-crown-6 salt. The crystal selected for the study (0.15 × 0.25 × 0.35 mm) was very mosaic and it belonged to the monoclinic space group $I2/M$ (a = 18.995(6), b = 22.410(8), c = 17.940(5) Å; β = 109.69(2)°; V = 7190.0 Å^3; Z = 2). The structure* was solved by direct methods with final agreement factors of 0.076 and 0.092. The poor quality of the crystal resulted in high temperature factors and precluded the complete localization of all the non-hydrogen atoms in the 18-crown-6 molecules found around the cesium atoms. Instead, the cluster has been characterized as a fifteen-atom rhodium trianion containing thirty carbonyl ligands. The absence of metal-bonded hydrogen atoms in this cluster is suggested by our inability to detect the expected ^{1}H NMR resonances (sulfolane solution, 35°C). The metal polyhedron of the new cluster (Fig. 2) resembles that observed in $[Rh_{15}(CO)_{27}]^{3-}$ [3] but with important differences. The new cluster has (i) five mirror planes for an idealized D_{4h} symmetry; (ii) the central rhodium atom is surrounded by eight close neighboring rhodium atoms (average length, 2.604 Å) (Table 1), and six rhodium atoms placed

TABLE 1

RHODIUM—RHODIUM DISTANCES (Å) IN $[Rh_{15}(CO)_{30}]^{3-}$

Rh(1)—Rh(2)	2.619(3)
Rh(1)—Rh(3)	3.271(3)
Rh(1)—Rh(4)	2.601(3)
Rh(1)—Rh(5)	2.598(2)
Rh(1)—Rh(6)	3.239(2)
Rh(1)—Rh(6)	3.240(2)
Rh(2)—Rh(3)	2.571(4)
Rh(2)—Rh(4)	3.046(4)
Rh(2)—Rh(5)	3.007(3)
Rh(2)—Rh(6)	2.749(3)
Rh(2)—Rh(6)	2.753(3)
Rh(3)—Rh(4)	2.744(4)
Rh(3)—Rh(5)	2.752(3)
Rh(3)—Rh(5)	2.748(3)
Rh(4)—Rh(5)	2.980(3)
Rh(4)—Rh(5)	2.981(3)
Rh(4)—Rh(6)	2.745(3)
Rh(4)—Rh(6)	2.749(3)
Rh(5)—Rh(5)	3.024(3)
Rh(5)—Rh(6)	2.748(3)
Rh(5)—Rh(6)	2.766(3)

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*See NAPS Document No. 03852 for 66 pages of supplementary material. Order from NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only. $ 16.50 for photocopies or $3.00 for microfiche. Outside the U.S. and Canada add postage of $3 for photocopy and $1 for microfiche. The supplementary material includes descriptions of data collection and reduction, structure solution and refinements and tables with experimental details concerning crystal data, intensity measurements, structure solution and refinement; tables of positional and thermal parameters, general temperature factor expressions (B's and U's), root-mean-square (rms) amplitudes of thermal variation, bond distances and angles, torsion angles, least-squares planes, intensity data and ORTEPS of single molecule showing 5% probability ellipsoids.

farther away (average length, 3.250 Å), (iii) equal values for Rh(2)—Rh(4) and Rh(5)—Rh(5) contacts (average length, 3.035 Å), and (iiii) a symmetrical array of the capping rhodium atoms (Rh(3), Rh(3′), Rh(6), Rh(6′), Rh(7), Rh(7′)) around the cluster (average Rh(capp)—Rh(cluster) length, 2.751 Å).

Thus, the array of metal atoms in $[Rh_{15}(CO)_{30}]^{3-}$ corresponds to a bcc packing [6] which contrasts with the hcp-bcc packing in $[Rh_{15}(CO)_{27}]^{3-}$. The former configuration is related to that of $[Rh_{14}(CO)_{25}]^{4-}$ which has, rigorously, an incomplete bcc packing. A formal comparison of both structures suggests that addition of a hypothetical "$Rh(CO)_5{}^+$" group to the basal square face of $[Rh_{14}(CO)_{25}]^{4-}$ will complete the octahedral hole given the new cluster. Thus, the series of rhodium clusters modeling the close packing of metal atoms is now completed (Scheme 1).

The cluster has also a unique array of carbonyls with six terminals (average lengths, Rh—C = 1.85 Å; C—O = 1.04 Å) and twenty-four asymmetric edge-bridging (average lengths, Rh—C = 1.91 and 2.21 Å; C—O = 1.22 Å) ligands. The ratio of bridging to terminal carbonyls (24:6) is the largest ever found in a cluster although the carbonyl:Rh surface ratio (2.14) is only slightly larger than the usual value for anions of this type (1.80—2.00) [7,8]. This suggests, in contrast to previous expectations [8,9], that the curvatire of the cluster could be more important than size for the terminal → bridging carbonyl realignment.

The structures of these clusters (Scheme 1) suggest that the atom released in the formation of $[Rh_{14}(CO)_{25}]^{4-}$ from $[Rh_{15}(CO)_{27}]^{3-}$ may be Rh(6′) (Fig. 2), and that coordination of CO or CO/H_2 to this center and to the other atoms in the octahedral hole (Rh(2), Rh(4), Rh(5′), Rh($5^{\square}$)) could well be the initial step in that reaction.

Acknowledgement

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