Journal of Organometallic Chemistry, 192 (1980) C42–C46

Preliminary communication

A NOVEL HYDRIDIC HIGH-NUCLEARITY RHODIUM CLUSTER: SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE ANION $[Rh_{14}H(\mu\text{-}CO)_{15}(CO)_{10}]^{3-}$

GIANFRANCO CIANI*, ANGELO SIRONI,
Istituto di Chimica Generale, Via G. Venezian 21, 20133-Milano (Italy)
and SECONDO MARTINENGO*
Centro del C.N.R. sui composti dei metalli di transizione nei bassi stati di ossidazione, Via G. Venezian 21, 20133-Milano (Italy)

(Received March 25th, 1980)

Summary

The novel anion $[Rh_{14}H(CO)_{25}]^{3-}$ has been obtained by reaction of the tetra-anion $[Rh_{14}(CO)_{25}]^{4-}$ with acids. Its structure can be related to that of the parent species, but there are differences in the cluster geometry and in the carbonyl stereochemistry. The metal atom polyhedron can be described as an array intermediate between a cubic body-centered packing and a cubic close-packed arrangement.

We are currently studying families of high-nuclearity clusters of rhodium which seem to play an important role as models of small metallic crystallites covered by ligands. The structures of the anions $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ (n = 2 [1], 3 [2]), containing a "twinned cubeoctahedron" of metal atoms, a portion of hexagonal close-packed lattice, have been described. We also recently reported the synthesis and structure of the $[Rh_{14}(CO)_{25}]^{4-}$ anion, which contains a portion of a body-centered cubic lattice, and on the related species $[Rh_{15}(CO)_{27}]^{3-}$, which has a metal atom cluster intermediate between a close-packed and a body-centered array [3].

We have now obtained the hydride $[Rh_{14}H(CO)_{25}]^{3-}$ by reaction of the tetraethylammonium salt of the $[Rh_{14}(CO)_{25}]^{4-}$ anion (Fig. 1) with acids:

$$[Rh_{14}(CO)_{25}]^{4-} + H^+ \rightarrow [Rh_{14}H(CO)_{25}]^{3-} \qquad (1)$$

The reaction is carried out in acetonitrile containing 10% of water by addition of a slight excess of a 0.7 *M* solution of 85% phosphoric acid in the same solvent. The product can be precipitated by addition of isopropanol and concentration in vacuum. Crystals suitable for the X-ray analysis were obtained from acetone-n-hexane by the slow diffusion technique.

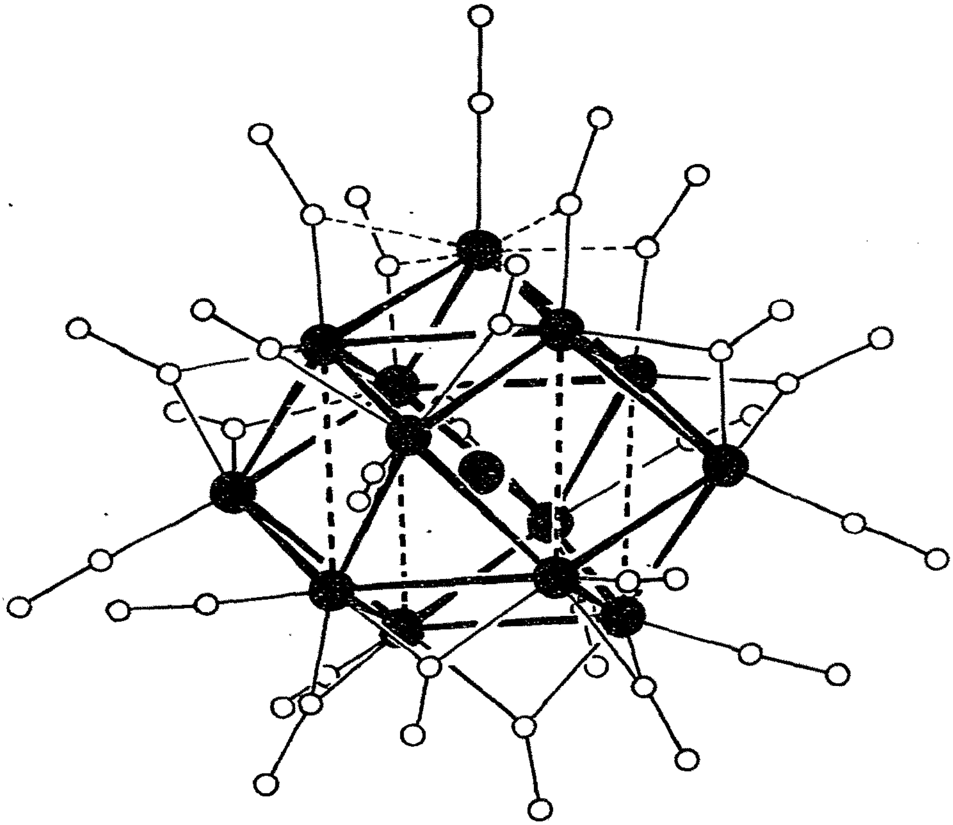

Fig. 1. Structure of the anion $[Rh_{14}(CO)_{25}]^{4-}$.

The $[Rh_{14}H(CO)_{25}]^{3-}$ anion can be deprotonated to the parent tetraanion with potassium t-butylate in acetonitrile.

The IR spectrum of the anion shows the expected shift at higher frequencies with respect to the parent tetraanion, and presents bands at 1988s and 1965(sh)w cm^{-1} in the terminal, and at 1835m and 1805(sh) cm^{-1} in the bridging COs stretching region in acetonitrile solution. The ^1H NMR spectrum in acetone shows a broad absorption at τ 41.3 at room temperature.

The same $[Rh_{14}H(CO)_{25}]^{3-}$ anion can be obtained [4] by reaction of $[NEt_4]_4[Rh_{13}H(CO)_{24}]$ with $[Rh(CO)_2(MeCN)_2]BF_4$ in acetonitrile:

$$[Rh_{13}H(CO)_{24}]^{4-} + [Rh(CO)_2(MeCN)_2]^+ \xrightarrow[25^\circ C]{MeCN} [Rh_{14}H(CO)_{25}]^{3-} + CO \quad (2)$$

This reaction is very important, as permits the stepwise growth from the Rh_{13} to the Rh_{14} and Rh_{15} clusters by the sequence of reaction 2 followed by reactions 3 and 4 [4]:

$$[Rh_{14}H(CO)_{25}]^{3-} + RO^- \xrightarrow[25^\circ C]{MeCN} [Rh_{14}(CO)_{25}]^{4-} + ROH \quad (3)$$

$$[Rh_{14}(CO)_{25}]^{4-} + [Rh(CO)_2(MeCN)_2]^+ \xrightarrow[25^\circ C]{MeCN} [Rh_{15}(CO)_{27}]^{3-} \quad (4)$$

Further details on the synthesis, reactivity, ^{1}H, ^{13}C, ^{103}Rh NMR and on ^{1}H{^{103}Rh} and ^{13}C{^{103}Rh} INDOR results will be reported elsewhere [4,5].

The $(NEt_4)^+$ salt of the $[Rh_{14}H(CO)_{25}]^{3-}$ anion has been investigated by X-ray diffraction*. Its structure, of C_s symmetry, is shown in Fig. 2, while the metal atom cluster is shown in Fig. 3. The metal—metal distances are reported in Table 1.

The Rh_{14} polyhedron is related to that of the parent $[Rh_{14}(CO)_{25}]^{4-}$ anion of C_{4v} idealized symmetry (see Fig. 1) so that only one of the original mirror planes is retained. The main distortions are as follows: (i) in the tetraanion the central metal atom exhibited 8 short bonds with the nearest neighbours (mean 2.64 Å), 4 intermediate bonds with the lateral capping atoms (mean 3.08 Å) and 1 long bond with the apical capping atom (3.38 Å) resulting in a distorted body-centered cubic environment; in the present case there are still 8 short bonds (mean 2.65 Å) and the long bond with the apical Rh(9) atom (3.39 Å), but of

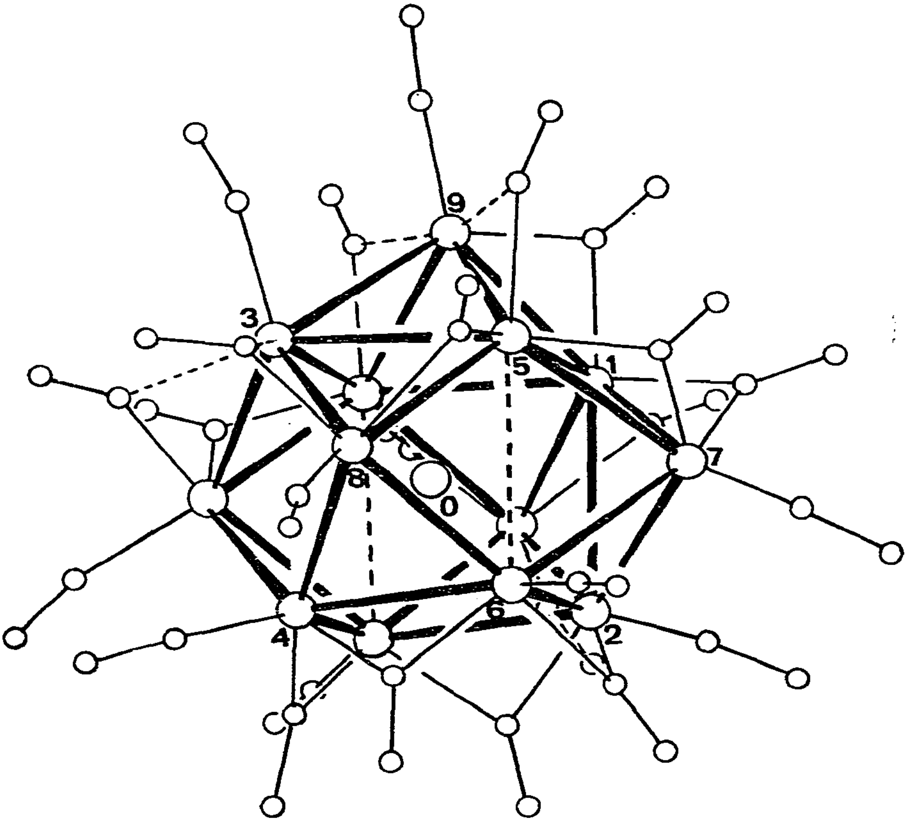

Fig. 2. A view of the anion $[Rh_{14}H(CO)_{25}]^{3-}$.

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*Crystal data. $C_{49}H_{61}N_3O_{25}Rh_{14}$, mol. wt. 2532.7, monoclinic crystals, space group $P2_1/m$ (No. 11), with a 13.656(3), b 18.321(4), c 15.387(3) Å, β = 103.32(2)°, Z = 2, U = 3746 Å^3. The structure was solved by conventional Patterson and Fourier methods and refined by block-matrix least-squares, on the basis of 2811 significant independent reflections, up to an actual R value of 10.1%. The anion was found to lie on a crystallographic mirror plane; one of the cations lies in a general position, while another one is located on the mirror plane and leads to considerable disorder.

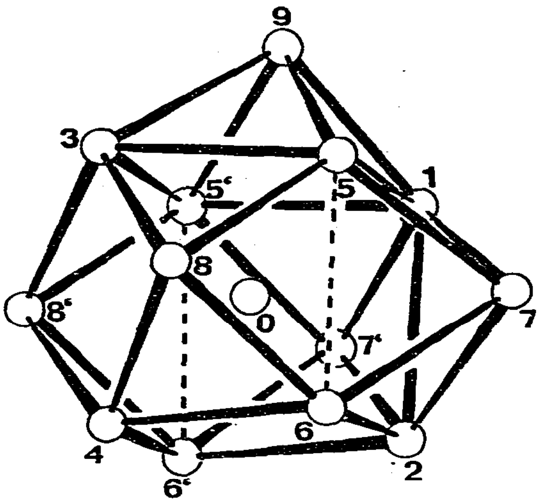

Fig. 3. The metal atom cluster of the anion $[Rh_{14}H(CO)_{25}]^{3-}$ with the atom numbering.

TABLE 1

METAL—METAL DISTANCES (Å) WITHIN THE ANION $[Rh_{14}H(CO)_{25}]^{3-}$

Rh—Rh distances from the central metal atom			
Rh(0)—Rh(1)	2.616(4)	Rh(2)—Rh(6)	2.790(4)
Rh(0)—Rh(2)	2.680(5)	Rh(2)—Rh(7)	2.803(4)
Rh(0)—Rh(3)	2.696(5)	Rh(3)—Rh(5)	3.003(4)
Rh(0)—Rh(4)	2.681(5)	Rh(3)—Rh(8)	2.730(5)
Rh(0)—Rh(5)	2.612(4)	Rh(3)—Rh(9)	2.843(5)
Rh(0)—Rh(6)	2.658(4)	Rh(4)—Rh(6)	2.794(4)
Rh(0)—Rh(7)	3.225(3)	Rh(4)—Rh(8)	2.749(5)
Rh(0)—Rh(8)	2.861(4)	Rh(5)—Rh(6)	3.352(5)
Rh(0)—Rh(9)	3.389(5)	Rh(5)—Rh(7)	2.718(4)
		Rh(5)—Rh(8)	2.696(4)
Rh—Rh surface distances		Rh(5)—Rh(9)	2.765(4)
		Rh(6)—Rh(7)	2.804(3)
Rh(1)—Rh(2)	3.101(5)	Rh(6)—Rh(8)	2.738(4)
Rh(1)—Rh(5)	2.952(4)	Rh(3) ··· Rh(4)	3.697(5)
Rh(1)—Rh(7)	2.697(3)		
Rh(1)—Rh(9)	2.724(5)		

the other four contacts two become shorter (mean 2.86 Å) and two longer (mean 3.22 Å). (ii) The Rh—Rh surface distances are similar in the two cases except for two contacts: Rh(1)—Rh(2) and Rh(3)—Rh(4) are equivalent in the tetraanion (3.33 Å) while in the present anion the former is shorter (3.10 Å) and the latter is longer, and definitely non-bonding (3.70 Å).

These distortions result in a structure which can be described as intermediate between a bcc array (atoms Rh(0), Rh(1), Rh(2), Rh(7), Rh(7′), Rh(5), Rh(5′), Rh(6), Rh(6′) and Rh(9)) and a ccp array (two layers: Rh(5), Rh(5′), Rh(6), Rh(6′), Rh(9), Rh(0) and Rh(3), Rh(4), Rh(8), Rh(8′)).

Differences are present also in the carbonyl stereochemistries of the two anions. In the hydridic species there are 10 terminal CO groups, 11 symmetric edge-bridging groups and 4 asymmetric edge-bridging groups (between Rh(3) and Rh(8), Rh(3) and Rh(8′), short Rh—C 1.84 Å, long Rh—C 2.24 Å; between

Rh(9) and Rh(5), Rh(9) and Rh(5′), short Rh—C 2.04 Å, long Rh—C 2.31 Å). The mean values of the Rh—C and C—O bonds for the terminal groups are 1.76 and 1.18 Å, and for the symmetric bridging groups are 1.97 and 1.21 Å.

Although we have no direct evidence for the position of the hydridic atom, we suggest that it is located on the face Rh(3,4,8,8′) i.e. in a distorted (100) surface hole of the ccp moiety, as can be inferred from the lengthening of the Rh(3)—Rh(4) contact with respect to the parent species. The observed bcc→ccp interconversion can be related to the presence of this interstitial hydride atom, since similar transformations occur also in binary hydrides of transition metals [6].

Acknowledgements

We thank the Italian C.N.R. for financial support, and Professor P. Chini for his interest in this work.

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