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Preliminary communication

CARBIDE CLUSTER CHEMISTRY IN THE COBALT SUB-GROUP

XI*. SYNTHESIS OF THE DODECANUCLEAR CARBIDO CARBONYL CLUSTER ANIONS $[Rh_{12}C_2(CO)_{23}]^{n-}$ ($n = 3, 4$) AND X-RAY CHARACTERIZATION OF THE $[Rh_{12}C_2(\mu\text{-}CO)_{10}(CO)_{13}]^{3-}$ TRIANION

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Summary

The new $[Rh_{12}C_2(CO)_{23}]^{n-}$ (n = 3, 4) anions have been obtained by reduction of $[Rh_{12}C_2(CO)_{24}]^{2-}$. The trianion is paramagnetic and rather unstable; an X-ray crystal structure determination shows that it has the same metal framework as the parent dianion.

In studies of carbido-carbonyl clusters of rhodium with nuclearity higher than 6 we isolated a series of neutral or anionic species such as $[Rh_8C(CO)_{19}]$, $[Rh_{15}C_2(CO)_{28}]^-$ and $[Rh_{12}C_2(CO)_{25}]$ [1—3], for which it is very difficult to develop a chemistry without affecting the metal cluster because of the ready breakdown on contact with most common basic solvents. Recently we also isolated the $[Rh_{12}C_2(CO)_{24}]^{2-}$ dianion (I) which in contrast is stable towards such solvents [4]. In view of the interest in developing derivatives of this cluster fragment which could possibly be involved in catalytic mechanisms, we began a study of the chemistry of this anion, and we report here the synthesis of two new derivatives of it, the paramagnetic $[Rh_{12}C_2(CO)_{23}]^{3-}$ trianion (II) and the $[Rh_{12}C_2(CO)_{23}]^{4-}$ tetraanion (III). The crystal structure of II is reported.

The paramagnetic trianion II is formed with other products in the reduction under nitrogen or hydrogen of the dianion I by addition of NaOH in MeOH until

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*For part X see ref. 4.

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the original IR bands at 2016 and 1847 cm^{-1} are replaced by new bands at 1995 and 1820 cm^{-1}; generally under nitrogen an excess of about 20 moles/mole of I is required, while under hydrogen a 1/1 ratio is enough. From magnetic measurements on the crude reaction product and the assumption that II has one unpaired electron and taking into account the diamagnetic contributions, the conversion to the paramagnetic trianion is about 35—40%; the main by-product is a diamagnetic species which, on the basis of an IR spectrum very similar to that of II and of the presence in the NMR spectrum of a hydridic signal at τ 25.25, is thought possibly to be the $[HRh_{12}C_2(CO)_{23}]^{3-}$ trianion. The retention of the parent $Rh_{12}C_2$ cluster frame in this hydridic anion as well as in the other products, is supported by the clean conversion to the tetraanion (see below) on addition of more NaOH.

Compound II is rather unstable, as indicated by the decay of the ESR signals (g_1 = 2.282, g_2 = 2.198, g_3 = 2.038 at 120 K [5]) which almost disappear after a few days in solution. The decomposition products are mainly diamagnetic species, along with traces of other paramagnetic species; this makes it difficult to isolate II in a pure state and prevents reliable magnetic moment measurements.

The tetraanion III can be obtained in the same way by use of a very large excess of KOH under nitrogen (about 200 moles/mole of I) or by prolonged pyrolysis of $K_2[Rh_6C(CO)_{15}]$ [6,7] in refluxing propan-2-ol (yields 70—80%). The tetraanion III reacts with acids under CO with partial hydrogen evolution to give initially a mixture of products including the trianion II, then, with excess of acid, the dianion I. Stoichiometric addition of oxidants such as iodine to the tetraanion III in acetonitrile immediately gives a clean solution of II, which decomposes on standing.

The IR spectrum of II in MeCN shows bands at 1998s, 1823m and 1800sh cm^{-1} and that of III at 1972s, 1795m and 1770sh cm^{-1}, consistent with the increase in the negative charge.

Both anions have been isolated as tetrapropylammonium salts by metathesis with NPr_4Br in alcohol. Crystals suitable for X-ray analysis were obtained by slow diffusion of diisopropylether into MeCN solutions. During the crystallization of II there is considerable decomposition to give a brown powder, and only few crystals were obtained, these were shown by ESR and IR spectroscopy still to be the paramagnetic species.

The molecular structure of the trianion II was determined by the single crystal X-ray method*. It is similar to that of the dianion I [4] (Fig. 1). The metal atom polyhedron is unaltered, and can be represented as a three layer sequence, square-rhomb-square, stacked in such a way as to generate two prismatic cavities en-

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*Crystal data: $C_{61}H_{84}N_3O_{23}Rh_{12}$, M = 2546.8, monoclinic, space group $P2_1/c$, a 26.351(3), b 26.162(3), c 26.712(3) Å, β 118.95(2)°, Z = 8, U 16114 $Å^3$, D_c 2.10, D_m 2.15 g cm^{-3}, μ(Mo-K_α) 22.38 cm^{-1}, $F_0/\sigma(F_0) > 5.0$, present R factor 0.12 for 5585 reflections; 15046 diffraction data were collected in the θ range 2—20° on a Philips PW1100 diffractometer. Solution and refinement of the structure turned out to be very difficult because of the presence of two isooriented anions in the asymmetric unit. An additional difficulty was the exceedingly high number of atoms to be refined, 198, half of which are chemically irrelevant.

Atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, Great Britain. Any request should be accompanied by a full literature citation for this communication.

capsulating two carbon atoms. The idealized symmetry of the anion decreases from D_{2h} in I to C_{2v} in II as a result of the loss of CO from an equatorial vertex. Sixteen CO groups are coordinated around the outer squares with the same geometry as that in the dianion I, i.e. eight are terminal and eight edge-bridging. The remaining seven ligands are bonded to the equatorial atoms and, unlike the parent dianion, form two asymmetric bridges towards the vertex from which the CO has left.

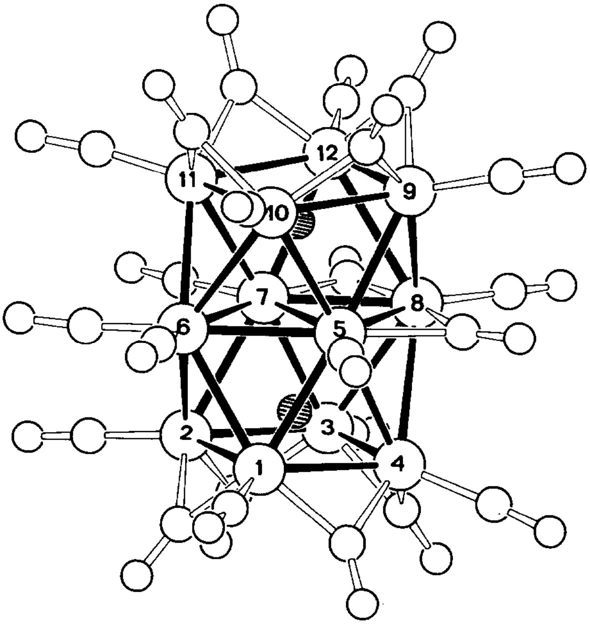

Fig. 1. The structure of the trianion $[Rh_{12}C_2(CO)_{23}]^{3-}$, showing the numbering of the rhodium atoms. Important bond lengths are:
Rh—Rh*: (1)—(2) 2.746, (1)—(4) 2.846, (1)—(5) 2.753, (1)—(7) 3.030, (2)—(3) 2.843, (2)—(6) 2.775, (2)—(7) 3.082, (3)—(4) 2.732, (3)—(6) 2.786, (3)—(8) 2.882, (4)—(5) 2.778, (4)—(8) 2.917, (5)—(6) 2.742, (5)—(7) 2.741, (5)—(8) 2.771, (5)—(10) 2.772, (5)—(11) 2.883, (6)—(7) 2.753, (6)—(8) 2.774, (6)—(9) 2.780, (6)—(12) 2.880, (7)—(11) 2.948, (7)—(12) 2.812, (8)—(9) 2.982, (8)—(10) 2.910, (9)—(10) 2.730, (9)—(12) 2.855, (10)—(11) 2.820, (11)—(12) 2.765; maximum e.s.d. 0.002 Å; mean Rh—C(carbide) 2.125 Å. *Average values computed from the two independent anions.

The mean Rh—C(carbide) distance is 2.125 Å; the Rh—Rh values range from 2.660(2) to 3.157(2) Å with mean 2.831 Å. From a comparison of these mean values with the corresponding values in I (2.120, 2.81 Å) it can be inferred that the extra electron goes into a delocalized antibonding cluster orbital, causing a slight swelling of the metal core.

Preliminary X-ray data for III indicate that it has the same cluster structure as II. Further work is in progress to isolate and structurally characterize the other species formed as by-products in the synthesis of II.

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