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Preliminary communication

STRUCTURAL CHARACTERIZATION OF THE ANIONS $[Rh_6(CO)_{15}X]^-$ $[X = COEt$ AND $CO(OMe)]$

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Summary

The anions $[Rh_6(CO)_{15}X]^-$, with X = COEt and CO(OMe), have been studied by single-crystal X-ray diffraction. They contain octahedral rhodium clusters, with mean metal—metal distances of 2.779 and 2.765 Å, respectively. The carbonyl stereochemistry in the two anions is similar to that of $Rh_6(CO)_{16}$, with one terminal CO group replaced by the X ligand. The Rh—C(carbomethoxy) bond distance (1.96(2) Å) is significantly shorter than the Rh—C(acyl) distance (2.06(2) Å).

We have undertaken a series of crystallographic determinations on the substitution products of $Rh_6(CO)_{16}$, with the aim of elucidating the nature of the cluster-ligand interactions when the ligands are small organic groups and of studying the associated distortions of the cluster and of the carbonyl stereochemistry.

We recently reported the synthesis and structure of the anion $[Rh_6(CO)_{14}(\eta^3\text{-}C_3H_5)]^-$ [1], and we now describe the structures of the anions $[Rh_6(CO)_{15}X]^-$ [X = COEt (I) and CO(OMe) (II)], whose syntheses were previously reported [2,3]. Crystals of the tetraphenylphosphonium, PPh_4^+, salts of anions I and II have been studied by single-crystal X-ray diffraction*.

The structures of the anions I and II are illustrated in Figs. 1 and 2, respectively. They are similar, both containing an octahedral cluster of rhodium atoms with 11 terminal and 4 face-bridging carbonyl ligands; the acyl (in I) and the carbomethoxy (in II) ligands are σ-bonded to the rhodium atom labelled Rh(6), and occupy the coordination site of the twelfth terminal CO ligand of the parent $Rh_6(CO)_{16}$.

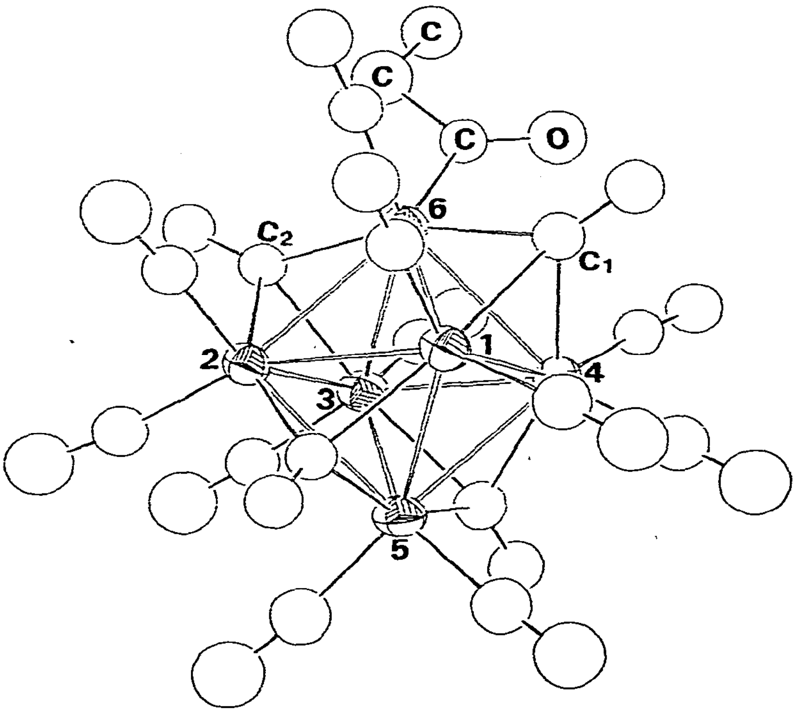

Fig. 1. A view of the anion $[Rh_6(CO)_{15}(COEt)]^-$. The metal—metal distances are: 1—2 2.710, 1—4 2.819, 1—5 2.750, 1—6 2.830, 2—3 2.828, 2—5 2.735, 2—6 2.829, 3—4 2.718, 3—5 2.790, 3—6 2.764, 4—5 2.768, 4—6 2.806 Å; e.s.d.'s are 0.001—0.002 Å.

The Rh—Rh bond lengths in I range from 2.710(1) to 2.830(2) Å, with a mean value of 2.779 Å, and in II range from 2.732(2) to 2.802(2) Å, with a mean value of 2.765 Å. These mean values are comparable, for instance, with those of $[Rh_6(CO)_{15}I]^-$ (2.746 Å) [4] and $Rh_6(CO)_{12}[P(OPh)_3]_4$ (2.789 Å) [5], which represent, respectively, the shorter and longer mean values found in octahedral carbonyl rhodium clusters. Taking into account the fact that $Rh_6(CO)_{16}$ has a mean Rh—Rh bond distance of 2.776 Å [6], no simple cor-

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*Crystal data. $[Rh_6(CO)_{15}(COEt)](PPh_4)$ (I), $M = 1434.0$, triclinic, space group $P\bar{1}$ (no. 2) $a = 12.996(7)$, $b = 14.484(7)$, $c = 12.748(7)$ Å, $\alpha = 89.75(5)°$, $\beta = 80.56(5)°$, $\gamma = 80.47(5)°$, $Z = 2$. $[Rh_6(CO)_{15}(CO(OMe))](PPh_4)$ (II), $M = 1436.0$, triclinic, space group $P\bar{1}$ (No. 2). $a = 14.918(4)$, $b = 12.357(4)$, $c = 13.099(4)$ Å, $\alpha = 100.36(4)°$, $\beta = 89.39(4)°$, $\gamma = 99.43(4)°$, $Z = 2$. Both structures were solved by conventional Patterson and Fourier methods, and refined by block-matrix least-squares, on the basis of 4533 (I) and 3727 (II) significant independent counter data, up to current conventional R values of 6.2% for I and 5.5% for II.

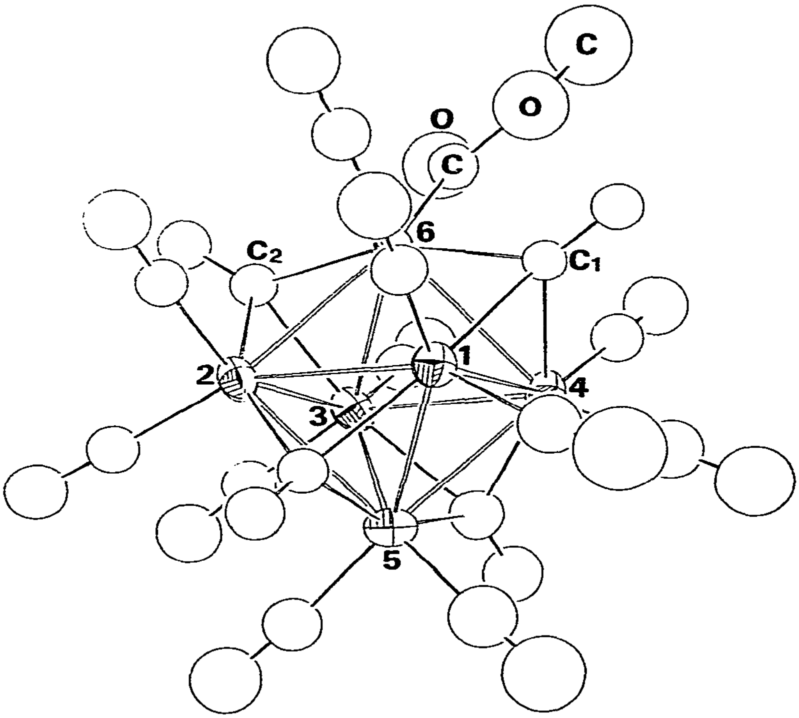
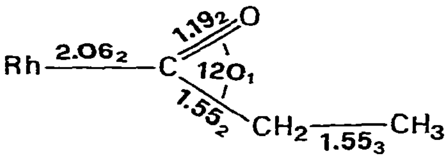


Fig. 2. A view of the anion $[Rh_6(CO)_{15}(CO(OMe))]^-$. The metal—metal distances are: 1—2 2.741, 1—4 2.802, 1—5 2.743, 1—6 2.797, 2—3 2.786, 2—5 2.760, 2—6 2.760, 3—4 2.732, 3—5 2.769, 3—6 2.767, 4—5 2.769, 4—6 2.759 Å; e.s.d.'s are 0.002 Å.

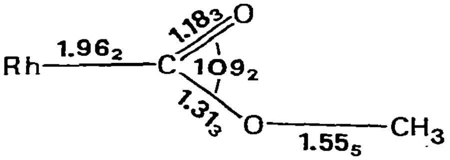
relation can be found between the net negative charge on the cluster and the mean metal—metal bond distance.

The Rh—C bond lengths for the terminal CO groups have mean values of 1.86 Å in I and 1.85 Å in II. In both the anions the triple bridging carbonyls bound to the metal atom, Rh(6), bearing the X ligand, are markedly asymmetric, a feature frequently observed in this class of compounds [1,4,5,7]. In fact, the mean Rh(6)—C(1,2) bond length is 2.06 Å in I and 2.11 Å in II, while the mean Rh(1,2,3,4)—C(1,2) bond length is 2.30 Å in I and 2.22 Å in II. The other two triple bridging carbonyls show only a little asymmetry. They have the same mean Rh—C bond length of 2.16 Å in the two anions. The C—O(terminal) bond lengths (mean 1.15 Å in both anions) are, as expected, shorter than the C—O(bridging) ones (mean 1.20 Å in both anions). Typical e.s.d.'s for the Rh—C and C—O bond lengths are 0.02 Å.

The acyl group and, particularly, the carbomethoxy group are rather uncommon ligands in mononuclear rhodium species, and only a few structures containing them are known. Bond parameters for these groups are illustrated below. The Rh—C(acyl) bond length, 2.06(2) Å, is significantly longer than the Rh—C(carbomethoxy) one, 1.96(2) Å, as expected for the presence in the second ligand of the more electronegative OCH_3 group in place of C_2H_5 in the former, which increases the drift of π electrons from the metal atom [8]. These bond lengths can be compared with those of Rh^{III}—C(acyl) in



(I)



(II)

Rh(CO-n-Pr)(PEt$_3$)$_2$(mnt), 2.002(7) Å, [9] and in [RhI(COEt)(PPh$_3$)(mnt)]$^-$, 2.006(14) Å [10] (mnt = maleonitriledithiolate).

Considering the overall geometries of the two anions, we observe that II shows smaller distortions from Rh$_6$(CO)$_{16}$ than I, i.e. a less scattered range of Rh—Rh bond lengths and lower asymmetries of the μ_3-CO groups. These results are in line, taking into account the above mentioned better π-acidity of the CO(OMe) ligand, with the hypothesis that larger distortions in these derivatives can be related to the poorer π-accepting ability of the substituent ligands.

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