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**Preliminary communication**

# SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE ANION $[Rh_6(CO)_{14}(\eta^3\text{-}C_3H_5)]^-$

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## Summary

The anion $[Rh_6(CO)_{14}(C_3H_5)]^-$, obtained by reaction of $[Rh_6(CO)_{15}]^{2-}$ with allyl chloride, contains an octahedral rhodium cluster with a mean metal—metal distance of 2.753 Å. The structure of the carbonyls resembles that of $Rh_6(CO)_{16}$, with the two terminal CO groups of one metal atom replaced by a $\pi$-bonded allyl group.

Following our work on the substitution products of carbonyl compounds such as $Rh_6(CO)_{16}$ which gives complexes of the type $[Rh_6(CO)_{15}X]^-$ [1,2], and in the light of the possibility that some of the latter complexes may be intermediates in catalytic processes [2], we have undertaken X-ray structural investigations on two examples, namely, the carboalkoxy $[Rh_6(CO)_{15}(COOMe)]^-$ and the acyl $[Rh_6(CO)_{15}(COEt)]^-$ derivatives [3]. We have also synthesized a related species, i.e. the $\pi$-allyl $[Rh_6(CO)_{14}(C_3H_5)]^-$ anion, and describe below its chemical and structural characterization.

This new anion was obtained by reaction of the $[Rh_6(CO)_{15}]^{2-}$ dianion with allyl chloride in THF at room temperature, according to 1:

$$[Rh_6(CO)_{15}]^{2-} + C_3H_5Cl \xrightarrow[25^\circ C]{THF} [Rh_6(CO)_{14}(C_3H_5)]^- + Cl^- + CO \quad (1)$$

The reaction is fast, and the product can be isolated from the orange-brown solution by precipitation as the $PPh_4^+$ salt. Crystals suitable for the X-ray analysis were obtained from THF n-hexane by the slow diffusion technique. (The same

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$[Rh_6(CO)_{14}(C_3H_5)]^-$ anion is also formed, together with other by-products, by reaction of allyl chloride with the $[Rh_7(CO)_{16}]^{3-}$ and $[Rh_{12}(CO)_{30}]^{2-}$ anions [4].

The IR spectrum in THF solution shows bands at 2065w, 2030vs and 1995w cm$^{-1}$ in the terminal, and at 1775m and 1765(sh) cm$^{-1}$ in the triple-bridging CO's stretching region, in agreement with the X-ray structure (see below).

The $^1H$ NMR spectrum in $CDCl_3$ at room temperature shows a complex multiplet centered at $\delta$ 4.82 ppm, a doublet at 3.55 ppm ($J$ 7 Hz) and a doublet of doublets at 2.28 ppm ($J$ 11.4 Hz, $J'$ 1.5 Hz) attributable to the central, *syn*- and *anti*-hydrogens of the allyl group, respectively; the 1.5 Hz splitting of the *anti*-hydrogens doublet can be attributed to a weak coupling with the rhodium atom. More details of the synthesis, reactions, catalytic properties, IR, $^{13}C$ and $^{103}Rh$ NMR spectra will be reported later [4].

The structure of the $[Rh_6(CO)_{14}(C_3H_5)]^-$ anion, determined by X-ray diffraction*, is illustrated in Fig. 1. It contains an octahedral cluster of metal atoms bearing 10 terminal and 4 face-bridging carbonyl groups. The allyl ligand is $\pi$-bonded to Rh(6). The stereochemistry is formally obtained by removing two terminal CO groups of one rhodium atom of $Rh_6(CO)_{16}$ [5] and replacing them by the allyl group.

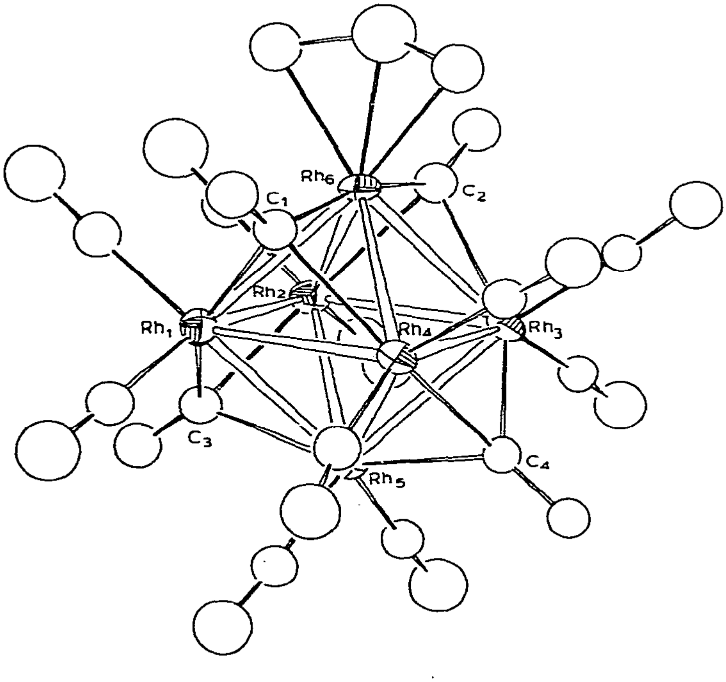

Fig. 1. A view of the anion $[Rh_6(CO)_{14}(C_3H_5)]^-$. The Rh—Rh bond distances are: 1—2 2.703, 1—4 2.822, 1—5 2.752, 1—6 2.743, 2—3 2.804, 2—5 2.760, 2—6 2.758, 3—4 2.706, 3—5 2.737, 3—6 2.765, 4—5 2.736, 4—6 2.753 Å (e.s.ds 0.001—0.002 Å).

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*Crystal data. $[Rh_6(CO)_{14}(C_3H_5)](PPh_4)\cdot(C_4H_8O)$, Mol. wt. 1462.2, monoclinic, space group $P2_1/m$ (No. 11) with $a$ 15.952(3), $b$ 9.942(2), $c$ 15.168(3) Å, $\beta$ 95.87(2)° and $Z = 4$. The intensities were collected on an automatic diffractometer with Mo-$K_\alpha$ radiation within the limit $2\vartheta \leq 50°$. The structure was solved by Patterson and Fourier methods. It showed the presence of one solvated molecule of THF in the asymmetric unit. The refinements were carried out by block-matrix least-squares, on the basis of 4165 independent significant reflections, up to a current $R$ value of 4.8%.

The Rh—Rh bond distances range from 2.703(1) to 2.822(1) Å. Their mean value, 2.753 Å, is shorter than that in $Rh_6(CO)_{16}$ (2.776 Å) [5], in $Rh_6(CO)_{12}[P(OPh)_3]_4$ (2.789 Å) [6] and in $[Rh_{12}(CO)_{30}]^{2-}$ (2.787 Å) [7], but a little longer than that in $[Rh_6(CO)_{15}I]^-$ (2.746 Å) [8].

The Rh—C bond distances for the terminal carbonyl ligands have a mean value of 1.85 Å. Of the four face-bridging CO groups the two having in common the metal atom bearing the allyl ligand (Rh(6)) are markedly asymmetric (mean Rh(6)—C(1,2) 2.03 Å, mean Rh(1,2,3,4)—C(1,2) 2.29 Å). The other two also show a small, though significant, asymmetry (mean Rh(5)—C(3,4) 2.21 Å, mean Rh(1,2,3,4)—C(3,4) 2.14 Å). The especially short Rh(6)—C(1,2) bond lengths are related to the good $\sigma$ and $\pi$ donor ability of the allyl ligand [9], and the distortions in the overall $\mu_3$-CO system show that it is involved in charge delocalization from Rh(6) to all the other cluster atoms. The C—O(bridging) bond distances (mean 1.18 Å) are, as expected, longer than the C—O(terminal) ones (mean 1.15 Å).

As previously observed by various mono- and di-nuclear structures, the allyl ligand shows asymmetry in the bonding mode: the Rh(6)—C(central) bond, 2.11(2) Å, is significantly shorter than the Rh(6)—C(external) ones, 2.18(2) and 2.21(2) Å. The C(external)—C(central)—C(external) angle, 137(3)°, is, to our knowledge, the largest found in a $\eta^3$-$C_3H_5$ moiety coordinated to a metal atom [9,10]. The two C(central)—C(external) bonds, 1.38(3) and 1.33(3) Å, can be considered equivalent.

The study of this anion as well as that of the $[Rh_6(CO)_{15}X]^-$ species [3] shows that a metal cluster compound is at least able to bind the organic functional groups involved in a catalytic reaction and, moreover, the examination of a series of related species may elucidate the nature of the small distortions occurring both in the organic moieties and in the cluster fragment. Further investigations on these compounds are in progress.

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