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## Preliminary communication

# SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF TETRA-$\mu_3$-CARBONYLHEXACARBONYLTRIS[BIS(DIPHENYLPHOSPHINO)METHANE]-HEXARHODIUM

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## Summary

The title compound $Rh_6(CO)_{10}(DPM)_3$ (DPM = bis(diphenylphosphino)-methane), obtained by heating $Rh_6(CO)_{16}$ and DPM in toluene, contains an octahedral rhodium cluster, with a mean Rh—Rh bond length of 2.783 Å, which bears four triple bridging and six terminal carbonyl ligands, and three DPM molecules chelating pairs of adjacent metal atoms (mean Rh—P 2.307 Å). Thus each Rh atom is connected to one phosphorous atom and to one terminal and two triple-bridging carbonyl ligands.

Substituted derivatives of tetranuclear carbonyl clusters, $M_4(CO)_{12}$ (M = Co, Rh, Ir) have been described for a wide variety of ligands [1] and several structures have been determined [2—5]. However, few examples of neutral substituted derivatives of $Rh_6(CO)_{16}$ are known [6—9] and only one structure has been described [10], in spite of the special interest in such compounds as catalysts which arises from their high stability during a catalytic cycle [9]. As part of our study of the reactivity of hexanuclear carbonyl clusters $M_6(CO)_{16}$ (M = Co, Rh, Ir) toward phosphorus-donor ligands we now report the preparation, IR spectrum and X-ray structure determination of $Rh_6(CO)_{10}(DPM)_3$ (DPM = bis(diphenylphosphino)methane).

Heating $Rh_6(CO)_{16}$ and DPM in a molar ratio 1/3, at 80°C for 3 h in toluene, gave a hexasubstituted species $Rh_6(CO)_{10}(DPM)_3$. Recrystallization from toluene/isopropanol gave dark-red crystals which were studied by X-ray

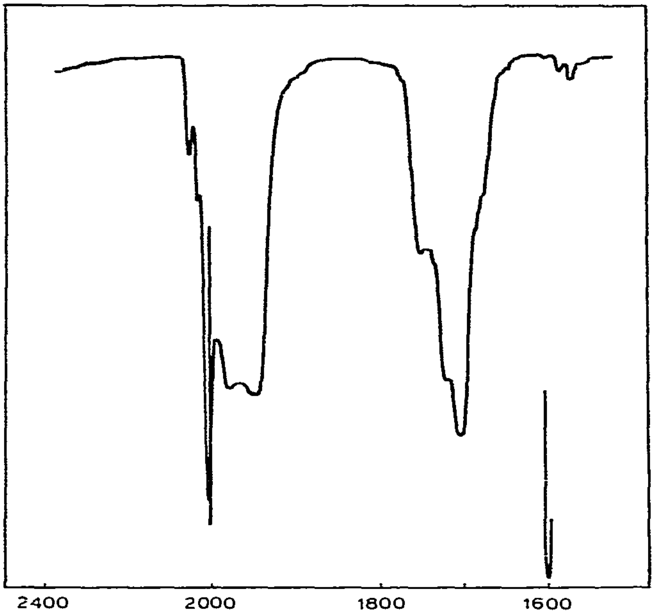

Fig. 1. Infrared spectrum in the CO stretching region of $Rh_6(CO)_{10}(DPM)_3$ in THF solution.

diffraction*. The infrared spectrum (in THF) of the compound in the carbonyl stretching region is shown in Fig. 1 and is consistent with the structure found in the solid state. Thus it shows two sets of bands, one due to the terminal and the other to face-bridging carbonyls, shifted to lower frequencies with respect to $Rh_6(CO)_{16}$ as expected as a result of the poorer $\pi$-acceptor ability of the DPM ligands. The structure of the $Rh_6(CO)_{10}(DPM)_3$ molecule is formally derived from that of the parent $Rh_6(CO)_{16}$ [11] by replacing six terminal carbonyl ligands by the six phosphorus atoms of the three DPM ligands, giving an environment of $C_3$ overall idealized symmetry (see Fig. 2). It consists of two triangular moieties of rhodium atoms stacked to form an essentially regular octahedron, surrounded by six terminal (one for each rhodium atom) and four face bridging carbonyl groups (one on the upper triangular moiety and the others bridging the three interbasal faces formed by one upper and two lower rhodium atoms) and three DPM ligands bridging on three alternating interbasal edges. A structure of this type was previously suggested by Lewis for the similar species $Rh_6(CO)_{10}(DPE)_3$ (DPE = bis(diphenyl phosphino)ethane) [8].

The molecule has an intrinsic chirality but crystallizes in a racemic form. Although the rhodium atoms are not all equivalent with respect to the idealized point group symmetry they are all stereochemically equivalent, each being bonded to one phosphorous atom (of the DPM ligand) and to one terminal and two face-bridging carbonyl groups. The three Rh—Rh edges bridged by the DPM ligand are significantly shorter than the other unbridged nine, the

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**Crystal data.* $C_{85}H_{66}O_{10}P_6Rh_6$, $M$ = 2050.7, monoclinic crystals, space group $P2_1/c$ (No. 14), $a$ = 16.277(4), $b$ = 20.550(5), $c$ = 27.192(6) Å, $\beta$ = 91.96(3)°, $Z$ = 4. The structure was solved by conventional Patterson and Fourier methods and refined by least-squares, on the basis of 8790 independent significant counter data, up to a current $R$ value of 5.9%.

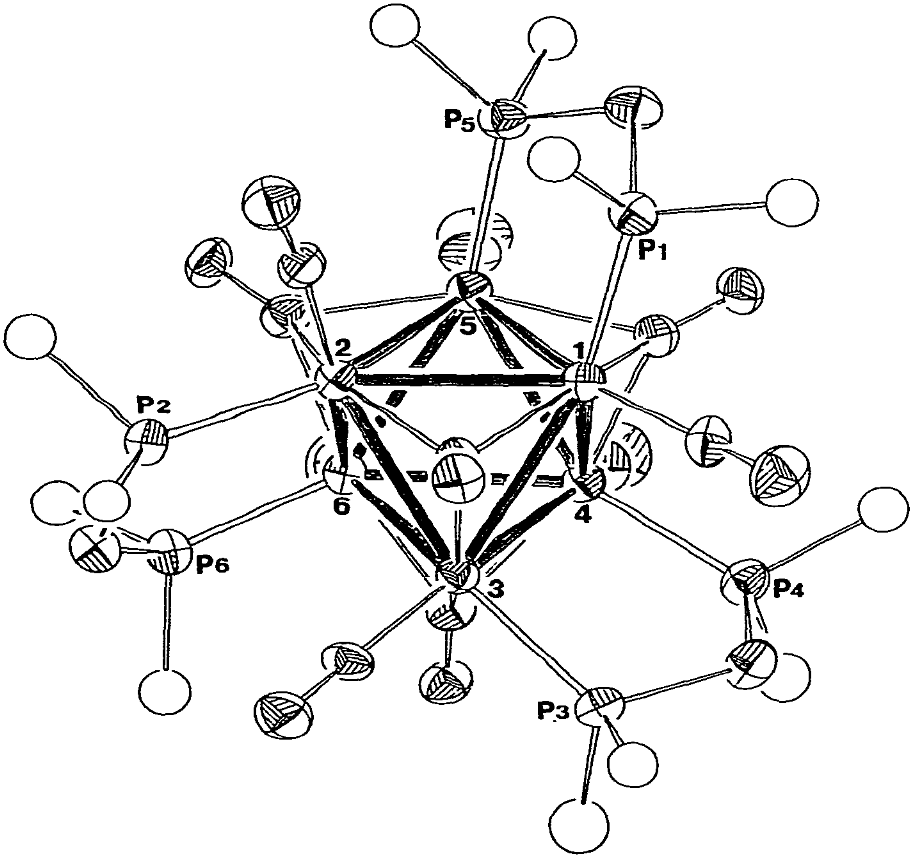

Fig. 2. A view of $Rh_6(CO)_{10}(DPM)_3$. The phenyl rings are illustrated for clarity only by the first carbon atom. The Rh atoms are indicated with their sequence number. The Rh—Rh distances are: 1—2 2.795, 1—3 2.837, 1—4 2.778, 1—5 2.748, 2—3 2.813, 2—5 2.795, 2—6 2.758, 3—4 2.756, 3—6 2.805 4—5 2.786, 4—6 2.766 and 5—6 2.760 Å, esd's 0.001 Å. The Rh—P distances are Rh(1)—P(1) 2.325, Rh(2)—P(2) 2.304, Rh(3)—P(3) 2.330, Rh(4)—P(4) 2.291, Rh(5)—P(5) 2.305 and Rh(6)—P(6) 2.286 Å, esd's 0.004 Å.

mean values being 2.754 and 2.793 Å, respectively. The overall mean 2.783 Å is intermediate between those found for $Rh_6(CO)_{16}$ [11] and $Rh_6(CO)_{12}$-$\{P(OPh)_3\}_4$ [10], 2.776 and 2.789 Å, respectively.

The Rh—P bond lengths (mean 2.307 Å) are comparable with those in similar systems, e.g. in $Rh_4(CO)_8(DPM)_2$ (mean 2.30 Å) [3]. All the Rh—C and C—O bonding parameters in the present compounds are normal with average values of Rh—$C_t$ 1.86, Rh—$C_b$ 2.18, C—O (terminal) 1.14, C—O (bridging) 1.17 Å. A small amount of asymmetry is present in the face-bridging carbonyl ligands and this is clearly due to the bulky DPM ligands. For instance, the three interbasal face-bridging carbonyl groups are all pushed away from the triangular edge bridged by the DPM ligand. Preliminary $^{13}C$, $^{31}P$, $^{103}Rh$ NMR studies suggest that the basic structure is maintained in solution from −120°C to room temperature.

Further studies on related species are in progress.

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