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### Preliminary communication

## SYNTHESIS AND STRUCTURE OF $[\text{Rh}_4(\text{CO})_5(\mu\text{-PPh}_2)_5]^-$ , A COMPLETELY PHOSPHIDE BRIDGED TETRARHODIUM CLUSTER

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### Summary

The synthesis,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, and structure of the first completely phosphide bridged rhodium cluster is described. This novel complex has an arachno (or "butterfly") structure, with a dihedral angle of  $124^\circ$ , and contains only  $\text{PPh}_2^-$  groups as bridging ligands.

Treatment of a number of rhodium complexes with organophosphide ligands,  $\text{PR}_2^-$ , has resulted in the isolation and characterization of some new polynuclear complexes. Herein we describe the anion  $[\text{Rh}_4(\text{PPh}_2)_5(\text{CO})_5]^-$ , which is the first of a series of anionic, tetranuclear rhodium clusters.

Treatment of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  with  $\text{LiPPh}_2$  (1:2 ratio) in tetrahydrofuran produced a red-brown solution which yields air-sensitive, dark-brown crystals after addition of hexane [1]. The infrared spectrum (KBr pellet) showed bands at 1965(sh), 1950s, and 1910s  $\text{cm}^{-1}$ , indicating only terminal CO ligands in the solid. A crystal of dimensions 0.2 mm  $\times$  0.2 mm  $\times$  0.3 mm was obtained by cleaving a larger crystal, and it was coated with epoxy cement to inhibit decomposition. The crystal was subjected to a complete X-ray structure determination at  $T = -73^\circ\text{C}$ : Space group  $Cc$ ;  $a = 22.350(2)$ ,  $b = 15.334(2)$ ,  $c = 24.877(4)$  Å,  $\beta = 114.12(1)^\circ$ ,  $\lambda(\text{Mo-K}\alpha) = 0.71069$  Å,  $\rho_{\text{obs}}(\text{est}) \cong 1.6$ ,  $\rho_{\text{calc}} = 1.52$  for  $Z = 4$ ; 13900 reflections measured, of which 4075 ( $I \geq 3\sigma$  above background) have been used in the structure solution and refinement to date. Absorption corrections have not yet been made, but we expect no substantial changes in the preliminary results reported here. The structure was solved by direct methods [2], and refined by conventional Fourier and least squares techniques to a current  $R$  factor of 4.9%\*. Thermal parameters for all heavy atoms, except for phenyl carbon atoms, have been refined anisotropically. Contributions of 50 of the 82 hydrogen atoms have been included in the refinement\*\*. The structure of the

\* $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ; GOF =  $\Sigma \omega(F_o^2 - F_c^2)^2 / (n_o - n_p) = 1.88$ .

\*\*Because of the large number of atoms (182), 32 hydrogen atoms could not be included in the refinement at this time. We are currently modifying our programs to accommodate these remaining hydrogen atoms.

cluster is illustrated in Fig. 1, and important bond distances and angles are shown in Fig. 2. In accordance with electron counting rules for clusters, the complex adopts a "butterfly", or arachno configuration\*, in which the dihedral angle is  $124^\circ$ . Two of the rhodium atoms are equivalent (Rh(2), Rh(3)) and each bonded to three metal atoms, three phosphorus atoms, and one carbonyl ligand. The two remaining rhodium atoms (Rh(1), Rh(4)) are each bonded to two metal atoms and two phosphorus atoms; however, Rh(1) is bonded to two carbonyls, while Rh(4) is bonded only to one carbonyl ligand. The bridging phosphide groups assume an alternating up-down-up-down configuration around the periphery of the cluster.

Remarkably, all the rhodium-rhodium bonds in  $[\text{Rh}_4(\mu\text{-PPh}_2)_5(\text{CO})_5]^-$  are bridged by phosphide ligands, even though both chloride and carbon monoxide (both possible bridging ligands) are present in the reaction mixture. Recent reports of phosphide bridged clusters reveal structures which contain  $\mu\text{-CO}$  ligands in addition to bridging phosphides, e.g.  $[\text{Co}_5(\mu\text{-CO})_3(\text{CO})_8(\mu\text{-P}(\text{CH}_3)_2)_3]$  [4],  $[\text{Pd}_3(\mu\text{-Cl})(\mu\text{-PPh}_2)_2(\text{PPh}_3)_3]^+$  [5] and  $[\text{Rh}_4(\mu\text{-PPh}_2)_4(\mu\text{-CO})_2(\text{CO})_3\text{PPh}_3]$  [6]. In our  $[\text{Rh}_4(\mu\text{-PPh}_2)_5(\text{CO})_5]^-$ , the rhodium-rhodium distances are long, but they are reasonable for assignment as single Rh-Rh bonds [7]. Further evidence for metal-metal bonding comes from the  $^{31}\text{P}$  NMR data. The phosphorus resonances are shifted far downfield (+275 ppm, +168 ppm from 85%  $\text{H}_3\text{PO}_4$ ), which is consistent with other  $^{31}\text{P}$  NMR data for phosphide ligands that bridge metal-metal bonds [5,8]. The rhodium-phosphorus distances are all reasonable for bridging phosphide groups. The variations of the Rh-P distances are probably due to intramolecular steric interactions of the phenyl groups; the geometries about the rhodium centers are thus fairly irregular. The rhodium-carbon distances average 1.82(1) Å, in good agreement with values for terminally bound carbon monoxide groups in polynuclear rhodium carbonyls [7]. The carbon-oxygen distances, at this stage of refinement, are unremarkable.

Attempts to isolate a series of similar clusters have led to substituted complexes of the general formula  $[\text{Rh}_4(\text{CO})_{5-x}(\mu\text{-PPh}_2)_5\text{L}_x]^-$ , where L is a neutral ligand. Such changes in the composition of the cluster are expected to lead to significantly altered reactivity. For example, for  $\text{L} = \text{PPh}_3$ , the resulting complex is significantly less reactive toward oxygen than the parent cluster; one may rationalize the lower oxygen sensitivity as being due to increased steric hindrance around the  $\text{Rh}_4$  frame.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the  $[\text{Rh}_4(\text{CO})_5(\mu\text{-PPh}_2)_5]^-$  cluster (Fig. 3) is complicated due to the presence of nine nuclei (five  $^{31}\text{P}$  and four  $^{103}\text{Rh}$ ) of spin 1/2. The multiplet at +168 ppm is due to P(5), and the resonances at +275 ppm and due to P(1), P(2), P(3), and P(4). This pattern appears to be characteristic of this type of cluster configuration [9]. Even though the complex has only  $C_1$  symmetry in the solid, the NMR spectrum exhibits resonances with mirror symmetry. This higher symmetry indicates an exchange process is occurring in solution and leads to equivalence of Rh(1) and Rh(4). A possible explanation would involve a "flapping" motion which brings Rh(1) and Rh(4) into close proximity,

\*With  $(\text{C}_6\text{H}_5)_2\text{P}^-$  considered as a formal four electron donor, the cluster has seven skeletal electron pairs, or  $(n + 3)$  pairs where  $n$  = number of vertices. This leads to the arachno configuration [3].

with a transfer of one CO group from Rh(1) to Rh(4). In the fast exchange limit, Rh(1) and Rh(4) would appear equivalent. At present, infrared and NMR evidence are inconclusive on this point, and further studies are in progress to define this behavior.

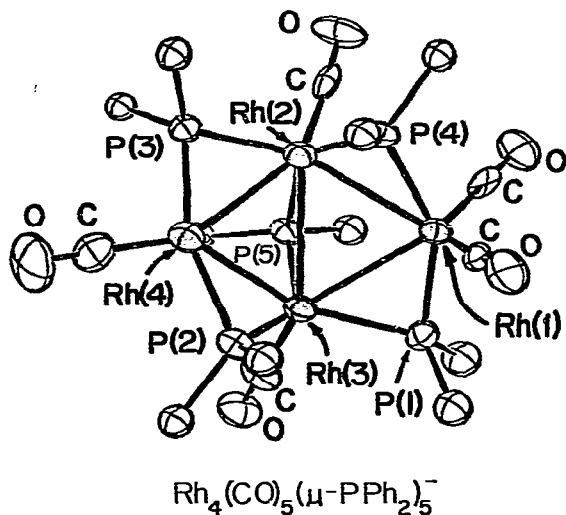


Fig. 1. ORTEP diagram showing the arachno arrangement of the title cluster anion and the conformation of the phosphide bridges.

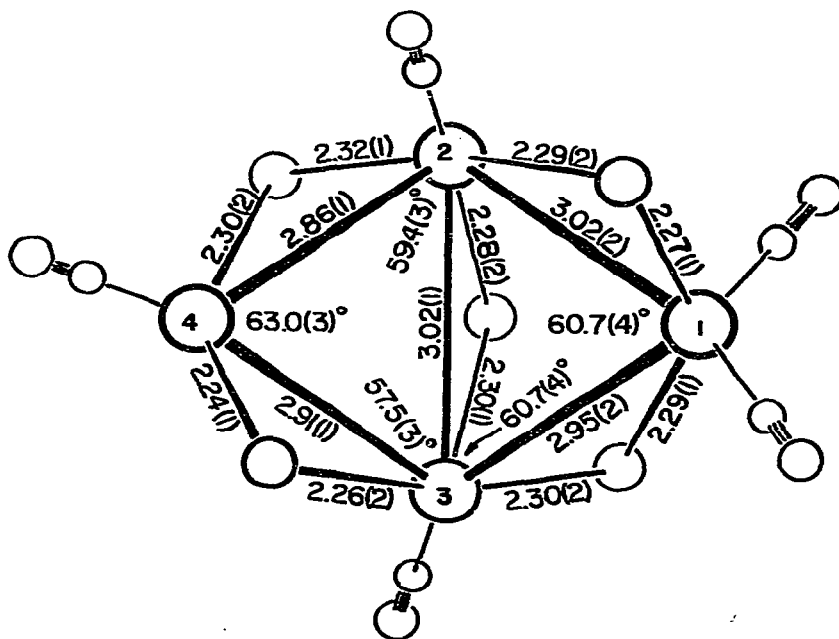


Fig. 2. Bond distances (Å) and angles (degrees) for the cluster frame.

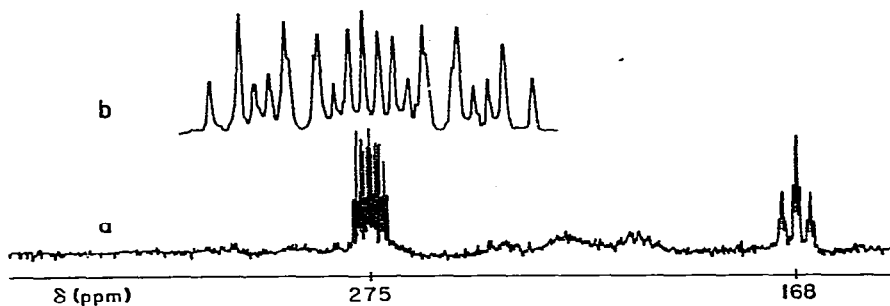


Fig. 3.  $^{31}\text{P}$  NMR spectrum of a tetrahydrofuran solution of the title complex at  $T = 23^\circ\text{C}$ . Chemical shifts are relative to an external standard of 85%  $\text{H}_3\text{PO}_4$ ; positive values are downfield from the standard. The resonances at 275 ppm are shown at 10X expanded scale in b.

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### References and notes

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