

Preliminary communication

SYNTHESIS AND MOLECULAR STRUCTURE OF $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_6(\text{PPh}_2\text{H})]$, AN UNUSUAL SIX-MEMBERED INORGANIC RING COMPLEX

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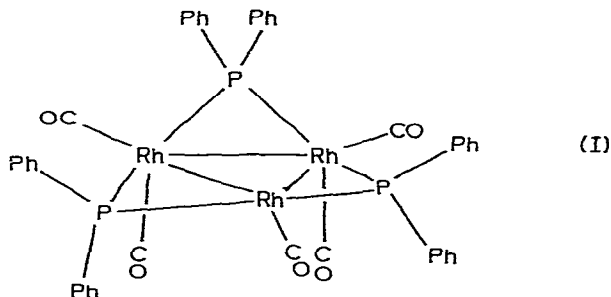
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Summary

Reaction of $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$ with PPh_2H in CO-saturated ethanol yields $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_6(\text{PPh}_2\text{H})]$, a red trinuclear cluster of rhodium containing a near-planar six-membered Rh_3P_3 ring; this compound reversibly undergoes elimination of CO and PPh_2H to afford $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$.

We have previously reported [1] that treatment of $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$ with PPh_2H in benzene in the presence of a base leads to the formation of a dark green trinuclear cluster of rhodium, $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ (I). An investigation of the properties of I has resulted in the isolation of



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$[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_6(\text{PPh}_2\text{H})]$ (II), obtained as a red microcrystalline solid either by passing CO through a methanolic solution of I containing free PPh_2H or by treatment of $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$ with a slight excess of PPh_2H in CO-saturated ethanol. II is stable in both the solid and the solution phases under an atmosphere of CO but rapidly decarbonylates under any other atmosphere or vacuum. Recrystallisation of II from a CO-saturated dichloromethane/methanol mixture yielded red crystals of the dichloromethane solvate of II, $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_6(\text{PPh}_2\text{H})]\cdot\text{CH}_2\text{Cl}_2$, with an IR spectrum indicating the presence of terminal carbonyl groups only ($\nu(\text{C}=\text{O})$: 2047m, 1996s, 1982s, 1948s and 1938s cm^{-1} , measured as a Nujol mull). A structure determination was undertaken to establish the geometry of this obviously unusual complex.

Crystal data: $[\text{Rh}_3(\text{PPh}_2)_3(\text{CO})_6(\text{PPh}_2\text{H})]\cdot\text{CH}_2\text{Cl}_2$, $M = 1\,303.5$, monoclinic, space group $P2_1/c$, $a\,12.515(5)$, $b\,11.843(5)$, $c\,37.102(5)$ Å, $\beta\,94.6(1)^\circ$, $U\,5481.4$ Å³, $Z=4$, $\mu(\text{Cu-K}\alpha)\,9.68$ mm⁻¹, final $R = 0.11^{**}$.

The molecular geometry of the compound is illustrated in Fig. 1. The three rhodium atoms are linked to each other through bridging diphenylphosphido ligands and together with the three phosphorus atoms occupy alternate vertices of a near-planar six-membered ring (deviations from the least squares plane range from 0.039 (Rh(3)) to 0.310 Å (P(2))). While two of the rhodium atoms have two terminal carbonyl groups coordinated to them and adopt geometries intermediate between square planar and tetrahedral the third has a diphenylphosphine as well as two carbonyl ligands coordinated to it and adopts a distorted trigonal bipyramidal geometry. In spite of a different coordination number for one of the rhodium atoms, the Rh_3P_3 ring contains an approximate three-fold axis, situated perpendicular to the ring (the internal angles at the phosphorus atoms are 83.3(1), 83.9(1) and 89.0(1) $^\circ$ while those at the rhodium atoms are 152.5(1), 155.2(1) and 150.8(1) $^\circ$). A range of compounds of the type $[\{\text{M}(\mu\text{-Y})\text{L}_n\}_3]$ ($\text{M} = \text{metal}$, $\text{Y} = \text{bridging ligands such as } \text{PPh}_2$, $\text{L} = \text{neutral ligand such as CO or } \text{PPh}_3$, $n = 1, 2, 3 \text{ or } 4$) with a planar M_3Y_3 skeleton is known [2] but the metal-metal distances in these complexes, in contrast to those in I ($\text{Rh}\cdots\text{Rh} = 3.118(2)$, $3.130(2)$ and $3.246(2)$ Å) are short and correspond, in a formal sense, to metal-metal bonds.

Decarbonylation of II is accompanied by a loss of PPh_2H to produce $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ (I) which has a structure related to that of II but with Rh-Rh distances of 2.698, 2.793 and 2.806 Å. This process is reversible and an obvious intermediate in the formation of II from I is $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$. It has not been possible thus far to isolate and structurally characterise this particular compound but it is assumed that it will contain a Rh_3P_3 framework

*A red prismatic crystal, $0.10 \times 0.07 \times 0.07$ mm was used. Data were collected on a Philips four-circle PW1100 diffractometer (N.P.R.L., C.S.I.R., Pretoria) with graphite-monochromated $\text{Cu-K}\alpha$ radiation ($\lambda\,1.5418$ Å) in the ω - 2θ scan mode. 8930 reflections were measured of which 5587 unique reflections had $I > \sigma(I)$. Some crystal instability was evinced by a drop off of reference reflection intensity of between 7% (at $\theta\,4.8^\circ$) and 25% (at $\theta\,40.4^\circ$) during the 240 h collection; however no corrections were applied to compensate for this decrease. Lorentz polarization, but no absorption, corrections were applied. The final value of R was 0.11. All calculations were performed on the University of South Africa's Burroughs B6800 computer.

**Supplementary material is available from the authors.

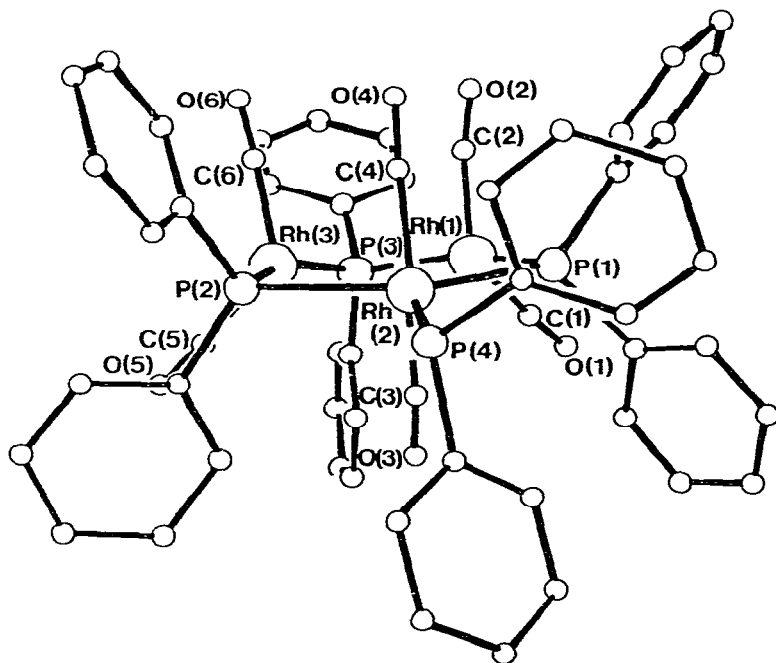


Fig. 1. The molecular stereochemistry of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_6(\text{PPh}_2\text{H})]$. Important bond lengths (in Å) are Rh(1)—P(1), 2.289(4); Rh(2)—P(1), 2.401(4); Rh(2)—P(2), 2.393(4); Rh(3)—P(2), 2.288(4); Rh(3)—P(3), 2.315(4); Rh(1)—P(3), 2.315(4); Rh(2)—P(4), 2.355(4).

structurally analogous to that in I, with Rh—Rh distances of the order of 2.8 Å, on the basis that the Co_3P_3 skeleton in a corresponding tricobalt cluster, $[\text{Co}_3(\mu\text{-PMe}_2)_3(\text{CO})_6]$, adopts a similar conformation and that the Co—Co distances in this complex range from 2.514 to 2.673 Å [3]. Addition of two electrons to $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_6]$, by coordination of a donor ligand, would thus appear to result in the population of a singly-degenerate orbital which is anti-bonding with respect to the three metal atoms. Studies in this direction are continuing.

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