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Preliminary communication

SYNTHESIS AND MOLECULAR STRUCTURE OF $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$, AN EDGE-BRIDGED TRIANGULAR CLUSTER OF RHODIUM

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Summary

The reaction of $[\{Rh(CO)_2Cl\}_2]$ with PPh_2H in benzene in the presence of a base affords a green product $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$, the structure of which has been determined by X-ray crystallography.

The thermal decomposition of $[RhH(CO)(PPh_3)_3]$ in nonane at 120°C has recently been reported to yield trinuclear $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$ in the absence of carbon monoxide [1] but tetranuclear $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2\text{-}(CO)_3(PPh_3)]$ in the presence of a 1/1 mixture of CO and H_2 at 4 atmospheres pressure [2]. The trinuclear compound has a triangular structure with the one rhodium atom being coordinatively unsaturated.

We now report that the parent compound of this species is readily obtained by reaction of $[\{Rh(CO)_2Cl\}_2]$ with PPh_2H under mild conditions. Specifically, treatment of the rhodium dimer with a twice molar amount of this secondary phosphine in benzene in the presence of a base such as diethylamine affords a green species, characterised as $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$ (I) by means of X-ray crystallography.

The compound crystallised in the monoclinic space group $P2_1/c$: a 14.003(5), b 17.471(5), c 16.523(5) Å, β 103.76(1)°, $Z = 4$. The structure was solved using 5346 unique $(I > \sigma(I))$ reflections. Direct methods were used to locate the three rhodium atoms and the remaining non-hydrogen atoms appeared in a difference Fourier synthesis. Initially, phenyl rings were refined as rigid perfect hexagons with individual isotropic temperature factors and hydrogen atoms were included at calculated positions. In a final two cycles of refinement, the rigid group constraints were removed. All other atoms were refined anisotropically. R converged to 0.067. R_w was 0.044 with a weighting scheme of $w = 0.461/\sigma^2(F)$*,**.

The molecular geometry of I is illustrated in Fig. 1 and 2. The complex adopts a triangular structure very similar to that of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3\text{-}(PPh_3)_2]$. Thus P(1) and P(2) as well as CO(3) are essentially coplanar with the trirhodium plane (Fig. 1) whereas P(3) is almost orthogonal to it, dihedral angle between planes Rh(1)Rh(2)Rh(3) and Rh(1)Rh(3)P(3) 97.2° (Fig. 2). The carbonyl groups on Rh(1) and Rh(3) are slightly staggered with respect to each other as revealed by the C(2)—Rh(1)—Rh(3)—C(5) torsion angle of 17.6° (Fig. 2). The essentially planar configuration of the "five-coordinate" Rh(1) and the shorter Rh(2)—P(2) and Rh(2)—P(1) distances compared with Rh(3)—P(2) and Rh(1)—P(1) is obviously a result of this rhodium atom being a 16 electron system. A similar geometry has been observed for the unique rhodium atom in $[Rh_3Fe(\mu\text{-}PPh_2)_3(\mu\text{-}CO)_2(CO)_6]$ [3]. The coordination unsaturation of Rh(2) can be attributed to the presence of a phenyl group on P(3) blocking a coordination site (Fig. 1).

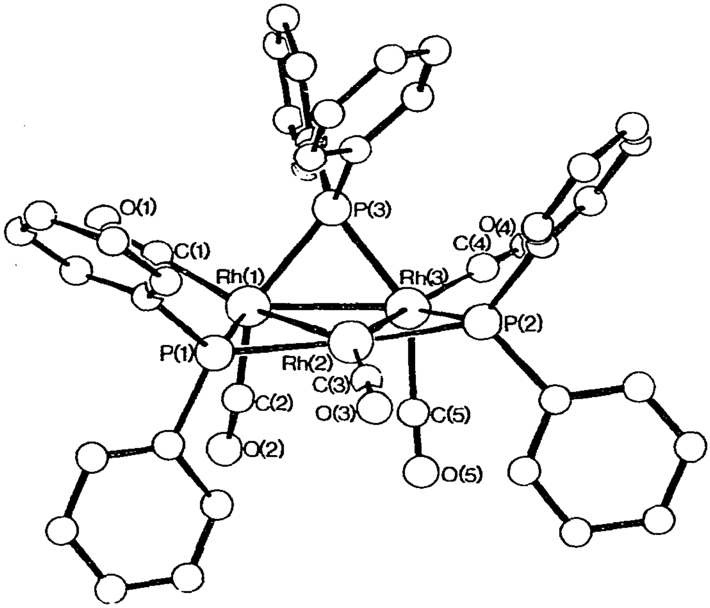

Fig. 1. The molecular stereochemistry of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$. Important bond lengths (in Å) are: Rh(1)—Rh(2), 2.793(1); Rh(1)—Rh(3), 2.698(1); Rh(2)—Rh(3), 2.806(1); Rh(1)—P(1), 2.288(2); Rh(2)—P(1), 2.269(2); Rh(2)—P(2), 2.263(2); Rh(3)—P(2), 2.295(2); Rh(3)—P(3), 2.285(2); Rh(1)—P(3), 2.291(2).

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*A dark green prismatic crystal, 0.32 × 0.2 × 0.12 mm was used. Data were collected on a Philips four-circle PW1100 diffractometer (N.P.R.L., C.S.I.R., Pretoria) with a graphite-monochromated Mo-K_α radiation (λ 0.7107 Å) in the $\omega - 2\theta$ scan mode. 5712 reflections were measured of which 5346 unique reflections had $I > \sigma(I)$. No crystal decomposition was observed by monitoring three reference reflections. Lorenz polarisation, but not absorption, corrections were applied. All calculations were performed on the University of South Africa's Burroughs B6800 computer.

**Supplementary material is available from the authors.

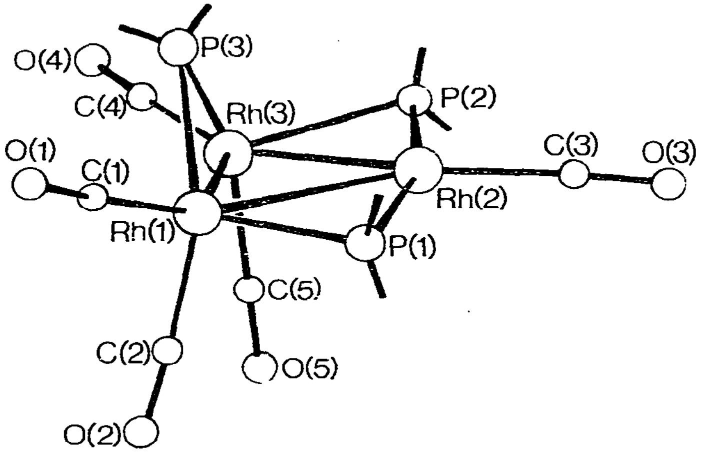

Fig. 2. An alternative view of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_5]$, phenyl groups omitted.

The similarity of the structure of I to that of $[Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2]$ indicates that the formation of the latter in preference to *trans*-$[\{Rh(\mu\text{-}PPh_2)(CO)(PPh_3)\}_2]$ cannot necessarily be attributed to steric interactions between the phenyl groups on the terminal triphenylphosphine ligands and those on the bridging diphenylphosphino groups as previously proposed [1].

Compound I reacts readily and reversibly with carbon monoxide to produce a yellow compound characterised as $[\{Rh(\mu\text{-}PPh_2)(CO)_x\}_y]$ ($x = 3$, y is probably 2); the ready degradation of this species to compound I in solution prevented its molecular weight determination. Compound I undergoes a slow decarbonylation and rearrangement in solution to afford $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_4]$, the structure of which [4] is very similar to that of $[Rh_4(\mu\text{-}PPh_2)_4(\mu\text{-}CO)_2(CO)_3(PPh_3)]$ [2].

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