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Preliminary communication

$[Rh_2(CO)_3\{(PhO)_2PN(Et)P(OPh)_2\}_2]$: A SUBSTITUTED DERIVATIVE OF HYPOTHETICAL $[Rh_2(CO)_7]$

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Summary

X-ray diffraction shows that $[Rh_2(CO)_3\{(PhO)_2PN(Et)P(OPh)_2\}_2]$, synthesised by reduction of $[\{RhCl(CO)(PhO)_2PN(Et)P(OPh)_2\}_2]$ with amalgamated zinc in the presence of carbon monoxide, has an unusual structure with one rhodium atom square planar and the other trigonal bipyramidal.

In contrast to its cobalt analogue, $[Rh_2(CO)_8]$ is unstable and has only been observed under high pressure of carbon monoxide and at low temperatures [1]. A number of bis-substituted derivatives of this binary carbonyl and in particular $[Rh_2(CO)_6L_2]$ ($L = PPh_3$, $P(p\text{-}MeC_6H_4)_3$ and $P(p\text{-}FC_6H_4)_3$) have been reported but, similar to their parent compound, these species readily rearrange to tetranuclear products in the absence of carbon monoxide [1]. Substituted derivatives of hypothetical $[Rh_2(CO)_6]$, viz. $[Rh_2(CO)_2(PPh_3)_4]$ and $[Rh_2(CO)_4(PBu^t_3)_2]$, obtained by decarbonylation of $[Rh_2(CO)_4(PPh_3)_4]$ and $[Rh_2(CO)_6(PBu^t_3)_2]$, respectively, have also been reported [2,3]. These reactions are reversible and in particular it has been established that treatment of $[Rh_2(CO)_2(PPh_3)_4]$ with CO at room temperature leads to the ready regeneration of $[Rh_2(CO)_4(PPh_3)_4]$ [2]. We now wish to report the synthesis of a substituted derivative of a third type of dinuclear binary carbonyl of rhodium, viz. $[Rh_2(CO)_3\{(PhO)_2PN(Et)P(OPh)_2\}_2]$ which can be considered as a derivative of hypothetical $[Rh_2(CO)_7]$.

Reduction of purple $[\{RhCl(CO)(PhO)_2PN(Et)P(OPh)_2\}_2]$ [4] with amalgamated zinc in methanol in the presence of carbon monoxide, led to the formation of the title compound in good yield. The solution infrared spectrum of this species reveals three carbonyl stretching peaks (ν(C—O) 2010m, 1995s and

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1945m cm^{-1}, measured in C_6H_{12}) all of which can be assigned to terminal carbonyl groups*. The room temperature ^{31}P-{^1H} NMR spectrum of this compound exhibits a single resonance of symmetrical pattern indicating that if the compound adopts an asymmetric structure it is fluxional in solution at this temperature. An X-ray analysis was carried out with the object of establishing the structure of this obviously unusual species.

Crystal data. Crystals are triclinic, space group $P\bar{1}$, a 10.76(1), b 16.50(2), c 16.27(2) Å, α 79.93(5), β 99.74(5), γ 101.12(5)°, V 2764.4 $Å^3$, $Z = 2$. Data were collected on a Philips PW1100 diffractometer (N.P.R.L., C.S.I.R., Pretoria) with graphite-monochromated Mo-K_α radiation to $\theta = 25°$. The structure was solved by standard Patterson and Fourier methods, and refined by block-diagonal least squares to $R = 0.078$ for 6545 observed data ($I > 2.0\sigma(I)$), rhodium atoms anisotropic.

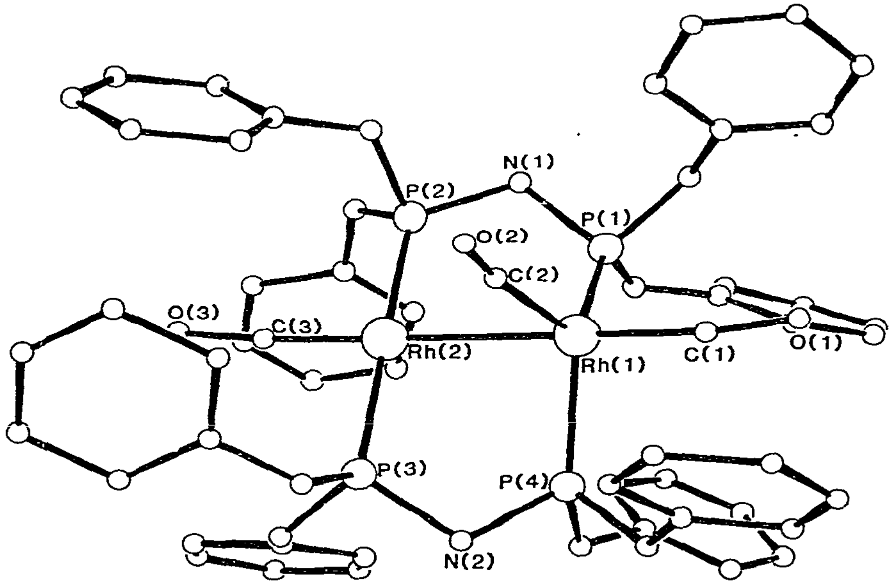

Fig. 1. The molecular stereochemistry of $[Rh_2(CO)_3\{(PhO)_2PN(Et)P(OPh)_2\}_2]$ (ethyl groups omitted). Bond lengths and angles: Rh(2)—Rh(1), 2.724; Rh(1)—P(1), 2.267; Rh(1)—P(4), 2.261; Rh(2)—P(2), 2.247; Rh(2)—P(3), 2.248 ± 0.005 Å; Rh(1)—C(1), 1.88; Rh(1)—C(2), 1.86; Rh(2)—C(3), 1.80 ± 0.01 Å; Rh(2)—Rh(1)—C(1), 170; Rh(2)—Rh(1)—P(1), 89.2; Rh(2)—Rh(1)—C(2), 69; Rh(2)—Rh(1)—P(4), 86.4; P(1)—Rh(1)—C(2), 112; C(2)—Rh(1)—P(4), 115; P(4)—Rh(1)—P(1), 127.5; Rh(1)—Rh(2)—C(3), 174; Rh(1)—Rh(2)—P(3), 90.8; Rh(1)—Rh(2)—P(2), 89.9; P(2)—Rh(2)—P(3), 177.7; P(4)—Rh(1)—Rh(2)—P(3), 27; P(1)—Rh(1)—Rh(2)—P(2), —23°.

The molecular geometry of this compound is illustrated in Fig. 1. The two rhodium atoms are not only bridged by two diphosphazane ligands but are joined by a formal metal—metal bond (Rh(1)—Rh(2) 2.724 Å). The three carbonyl groups are essentially terminal with two being coordinated to one rhodium atom and the third to the other. Two of these carbonyls are approximately colinear with the rhodium—rhodium vector (Rh(2)—Rh(1)—C(1) 170°; Rh(1)—Rh(2)—C(3) 174°) while the third subtends an angle of 69° with it, leaning towards Rh(2). This Rh(2)—Rh(1)—C(2) bond angle might be inter-

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*The lowest energy peak could alternatively be assigned to a semi-bridging carbonyl group.

preted in terms of this carbonyl group being a semi-bridging one. However, the Rh(2)—C(2) distance of 2.68 Å and the difference between this distance and that between Rh(1) and C(2) (1.86 Å) are basically too large for this carbonyl to warrant a description beyond that of a slightly disturbed carbonyl group [5].

As can be observed from Fig. 1, Rh(2) with a coordination number of four has a square planar geometry whereas Rh(1) with a coordination number of five adopts an approximately trigonal bipyramidal configuration. Both rhodium atoms have the same formal oxidation number of zero but because of the different coordination numbers, Rh(1) is an 18-electron system while Rh(2) is a 16-electron system. As also illustrated in Fig. 1 the underside and top of Rh(2) are blocked by the phenyl rings of P(2) and P(3), respectively. This will explain why a second carbonyl group does not coordinate to Rh(2) to afford a substituted derivative of $[Rh_2(CO)_8]$ in spite of the reduction being effected in the presence of an excess of carbon monoxide.

The structure of $[Rh_2(CO)_3\{(PhO)_2PN(Et)P(OPh)_2\}_2]$ contrasts with that proposed for recently reported $[Rh_2(CO)_3\{Ph_2PCH_2PPh_2\}_2]$ which, on the basis of IR spectroscopic evidence, is thought to be symmetrical with the rhodium atoms bridged by a single carbonyl group as well as by two diphosphine ligands [6].

Other dinuclear rhodium(0) compounds analogous to the title compound have been obtained by reduction of $[Rh_2Cl_2(\mu\text{-}CO)(CO)\{(MeO)_2PN(Et)P(OMe)_2\}_2]$ [7] and $[\{RhCl(CO)(Pr^iO)_2PN(Me)P(OPr^i)_2\}_2]$ under the same experimental conditions as those employed for $[\{RhCl(CO)(PhO)_2PN(Et)P(OPh)_2\}_2]$.

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