A Five-co-ordinate Rhodium(0) Dimer: The Crystal and Molecular Structure of Tetrakis(triphenylphosphine)di-μ-carbonyl-dirhodium(o)–Bisdichloromethane Solvate

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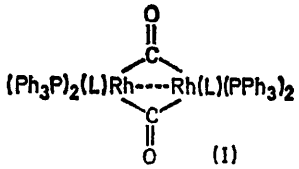
Summary $[(PPh_3)_2Rh(CO)]_2,2CH_2Cl_2$ is a five-co-ordinate dimer linked by two carbonyl bridges and a metal–metal bond, with a Rh–Rh separation of 2·630(2) Å.

Complexes of stoicheiometry $[(Ph_3P)_2(L)Rh(CO)]_2$, where L is dichloromethane or ethanol, were first reported by Wilkinson and his co-workers.[1] Since the i.r. spectra of the complexes showed bands attributable to bridging carbonyl groups but none attributable to terminal carbonyl, and since it was impossible to precipitate the complexes in the absence of dichloromethane or ethanol, these workers suggested that the complexes should be formulated as



$$\begin{array}{c} O \\ \| \\ C \\ (Ph_3P)_2(L)Rh\text{----}Rh(L)(PPh_3)_2 \\ C \\ \| \\ O \end{array}$$

(1)

dimers (I), but in the absence of crystallographic and magnetic data they were unable to present any compelling evidence for the presence of a Rh–Rh bond or for an interaction between the solvent molecules and the metal. We have undertaken a three-dimensional structural investigation of one of these complexes.

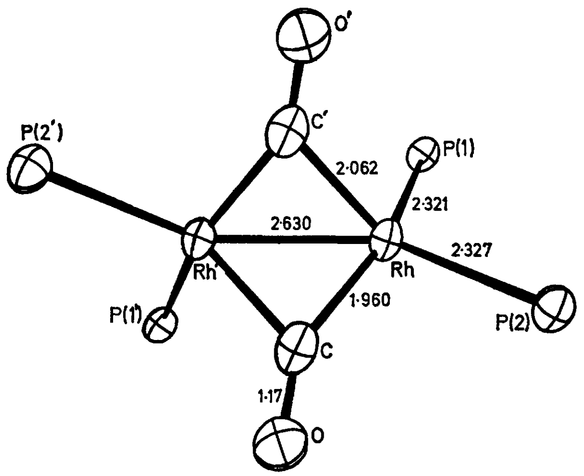


Figure. *The co-ordination about the* Rh^0 *atoms. Principal angles are:* C′–Rh–C = 88·9(3)°; C–Rh–P(1) = 151·9(3)°; C–Rh–P(2) = 96·8(2)°; C′–Rh–Rh′ = 50·9(2)°; C′–Rh–P(1) = 91·8(2)°; C′–Rh–P(2) = 131·3(2)°; C–Rh–Rh′ = 47·5(2)°; P(1)–Rh–P(2) = 103·7(1)°; P(1)–Rh–Rh′ = 112·2(1)°; P(2)–Rh–Rh′ = 144·0 (1)°; Rh–C–Rh′ = 81·6(3)°. *Atoms designated by a prime (′) are related to the reference atom by the twofold rotation.*

Dark red prismatic crystals of the dichloromethane complex were obtained by a minor modification of the method described.[1] *Crystal Data:* $C_{74}H_{60}O_2P_2Rh_2,2CH_2Cl_2$, M = 1480·9, monoclinic, a = 23·213(19), b = 13·171(6), c = 24·423(12) Å, β = 65·45(1)°, U = 6792 Å^3, D_m = 1·42(2) g cm^{-3}, Z = 4, D_c = 1·449 g cm^{-3}: space group $C2/c$; molecular symmetry $\bar{1}$(i) or 2(C_2), the latter being demonstrated by the structure analysis based on 5862 non-zero intensity data (Picker diffractometer, Mo-K_α radiation) and refined to R = 0·073.

Our study clearly indicates that the complex is dimeric and that there are two bridging carbonyl groups per dimer. The co-ordination geometry around the rhodium atoms is shown in the Figure. The Rh–Rh separation of 2·630(2) Å is in the range (2·618—2·796 Å) reported for other Rh–Rh bonds,[2–6] and confirms the existence of a rhodium–rhodium bond. As can be seen from the Figure, the rhodium(0) atoms are five-co-ordinated, but their co-ordination geometries are very different from either trigonal bipyramidal or tetragonal pyramidal. The geometry found here is quite different from that found in $Co_2(CO)_8$,[7] $[Rh(OAc)_2H_2O]_2$,[8] $[RhClO_2(PPh_3)_2]_2$,[9] or in any other binuclear complex.

There is clearly no interaction between the metal atoms and the solvent molecules, the shortest Rh–Cl approach being 5·695(5) Å. The complex is, therefore, co-ordinatively unsaturated, and this may explain its chemical properties.[1] The carbon atom of the solvent molecule is 3·13(2) Å from the nearest carbonyl oxygen atom in the dimer, which is approximately equal to the sum of the van der Waals radii of these atoms[2] and suggests that there may be a hydrogen-bonded interaction[10] between the dichloromethane molecules and the carbonyl bridges.

This complex is unique in that it represents an example of a five-co-ordinate binuclear rhodium(0) complex. While zerovalent rhodium complexes are not unknown, their occurrence in forms other than cluster compounds, such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$, is extremely uncommon.

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