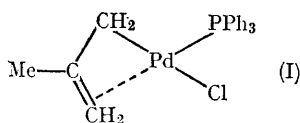


The Structure of Triphenylphosphinemethallylpalladium Chloride

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NUCLEAR MAGNETIC RESONANCE studies of the methallylpalladium chloride-triphenylphosphine system¹ have led to suggestions relating to the structures of intermediates in the conversion of π - into σ -allylpalladium complexes. An X-ray analysis of the structure of [PdCl (methallyl) PPh₃] fully confirms the view of Shaw *et al.*¹ that the bonding in this molecule is conveniently represented as (I).

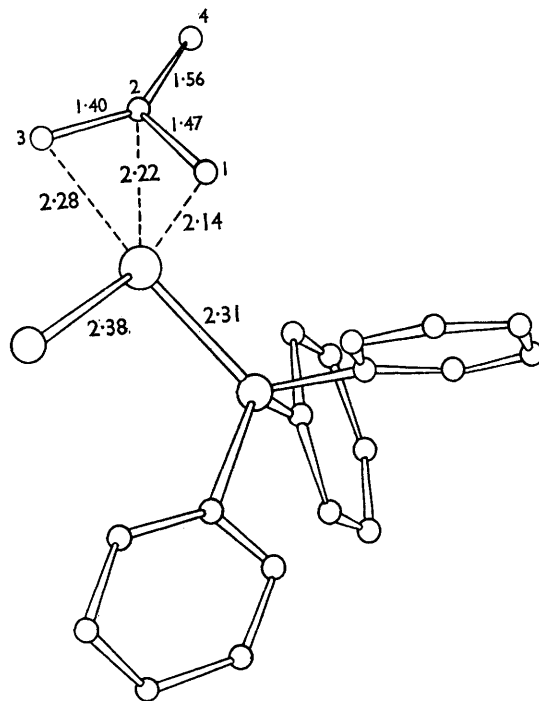


Some of the more important bond lengths (Å) in the molecule are given in the Figure and correspond to a present reliability index of 0.075 for 1129 independent reflexions.

Trans to the chloride ion, the palladium-carbon (C1) bond length of 2.14 Å ($\sigma = 0.03$ Å) is identical with that observed in π -allylpalladium chloride² but is significantly less (3–5 σ) than the Pd-(C2) and Pd-(C3) bond lengths. The carbon-carbon bond lengths, (C1)-(C2) and (C2)-(C3), while following the pattern expected on the basis of structure (I), are scarcely significantly different ($\Delta/\sigma = 1.7$). The standard deviation of the palladium-chlorine and palladium-phosphorus bond lengths is 0.01 Å, the phosphorus-carbon bond lengths averaging 1.81 Å ($\sigma = 0.02$ Å) and the phenyl carbon-carbon bond lengths averaging 1.42 Å ($\sigma = 0.04$ Å).

The dihedral angle between the plane defined by carbon atoms (C1), (C2), and (C3) and that defined by the palladium, phosphorus, and chlorine atoms is 116°, which is similar to the corresponding values found in π -allylpalladium chloride² and π -allylpalladium acetate.³ The methallyl ligand itself is significantly non-planar, the methyl group being displaced 0.5 Å out of the plane (C1)-(C2)-(C3) towards the metal. It will be of interest to compare this result in detail with the situation in the more symmetrical complex bismethallylnickel, a preliminary analysis of which has been reported.⁴

An alternative description of the angular relationship of the allyl group to the P-Pd-Cl plane, together with the observed non-planarity of the methallyl ligand, recognises the fact that the σ -bonded carbon atom, (C1), is coplanar, to within



FIGURE

0.04 Å, with the P-Pd-Cl system as is the centre of the formal double bond, (C2)-(C3); the dihedral angle between the respective planes containing (C2)-(C3)-(C4) and P-Pd-Cl is 119°. These conformations can be understood, in a general way, by an analysis of the metal-ligand overlap integrals.⁵

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¹ J. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Comm.*, 1965, 79.

² A. E. Smith, *Acta Cryst.*, 1965, **18**, 331; W. E. Oberhansli and L. F. Dahl, *J. Organometallic Chem.*, 1965, **3**, 43.

³ M. R. Churchill and R. Mason, *Nature*, 1964, **204**, 777.

⁴ H. Dietrich and R. Uttech, *Naturwiss.*, 1963, **50**, 613.

⁵ S. F. A. Kettle and R. Mason, *J. Organometallic Chem.*, in the press.