

## Unusual Co-ordination of the Palladous Ion in the Structure of *trans*-Di-iodobis(dimethylphenylphosphine)palladium(II)

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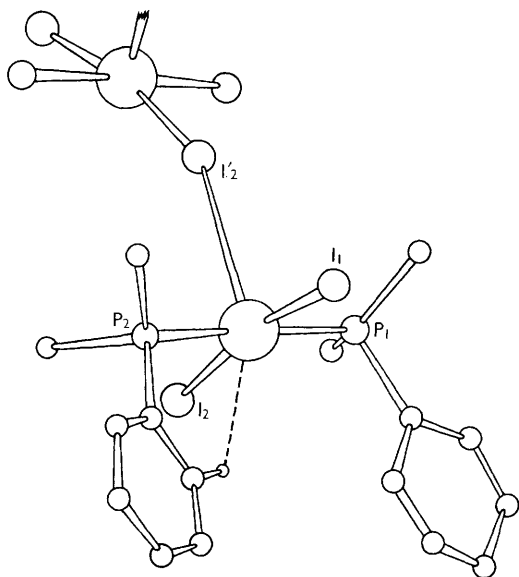
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THE reaction of dichlorobis(dimethylphenylphosphine)palladium(II) with sodium iodide in acetone gives the corresponding iodo-complex which on recrystallisation from methanol gives a mixture of dark red needles and yellow prisms. On heating this mixture to 120–130°, the yellow crystal modification undergoes a phase transformation to the red polymorph which in turn melts at 159–160° to give an orange liquid from which a yellow solid crystallises out on cooling (m.p. 144–146°). This yellow form when scratched at temperatures near to its melting point rapidly changes into the red form and the interconversion of red and yellow forms can be repeated indefinitely. Both crystal

forms dissolve in organic solvents to give yellow solutions and are monomeric in benzene. The yellow acetone solution becomes red-brown when treated with sodium iodide, probably as the result of the formation of  $[\text{PdI}_3(\text{PMe}_2\text{Ph})_2]^-$ . The dark red crystal modification is anomalous in so far as all compounds of the type *trans*- $[\text{PdI}_2(\text{PR}_3)_2]$  which have so far been reported are yellow or orange-yellow. Crystallographic studies of this system are now summarised.

The dark red crystals are orthorhombic, space group  $P2_12_12_1$ ; a least-squares analysis of the three-dimensional X-ray data has converged the discrepancy index to the present value of 0.13

when the average e.s.d. of the Pd-I and Pd-P bond lengths is 0.015 Å. Even at first sight, the co-ordination of the palladous ion (Figure) is interesting since it appears to be a distorted square pyramid with Pd-P bond lengths of 2.34 Å (average), two Pd-I bond lengths of 2.63 Å and an axial Pd-I bond of length 3.28 Å. This form of five-co-ordination results from the sharing of the iodine atom, (I)<sub>2</sub>, by successive palladium ions in a chain which runs throughout the crystal parallel to the "a" axis. A closer examination of interatomic distances shows, however, that the co-ordination of



the palladous ion is really a distorted octahedron, the sixth co-ordination site being occupied by a hydrogen on the  $\beta$ -carbon of the phenyl ring of the phosphine; the metal-hydrogen distance is only 2.8 Å as calculated from the co-ordinates of the phenyl-carbon atoms and assuming a C-H bond length of 1.1 Å. A similarly short (2.7 Å) metal-hydrogen distance occurs in dichlorotris(triphenylphosphine)ruthenium(II).<sup>1</sup>

These structural results are of interest in relation to the catalytic function of certain transition-metal complexes. Many tertiary phosphine complexes of the platinum metals are good catalysts for the migration of olefinic double bonds along carbon chains<sup>2</sup> and for homogeneous hydrogenation.<sup>3</sup> Chatt and Davidson<sup>4</sup> have shown recently that the complex of ruthenium(0), [Ru(PP)<sub>2</sub>] and the hydridoruthenium(II) complex, [RuH(CH<sub>2</sub>·PMe<sub>2</sub>·CH<sub>2</sub>·PMe<sub>2</sub>)(PP)] (PP = Me<sub>2</sub>P·CH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·PMe<sub>2</sub>) are in tautomeric equilibrium, a hydrogen readily migrating from the methyl group of the phosphine to the metal. Short metal-hydrogen distances such as we report here are, perhaps, essential to a facile intramolecular transfer of hydrogen from the alkyl or aryl groups of phosphine ligands and may also be an important factor in some hydrogen transfer reactions catalysed by metal complexes.

The yellow crystals of [PdI<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] are monoclinic with two molecules in a unit cell which has the space group  $P2_1/c$ ; the molecules are required to be strictly centrosymmetric (*trans*). The structural relationships between the monoclinic and orthorhombic polymorphs are under investigation.

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<sup>1</sup> J. A. Ibers, *Abst. Amer. Cryst. Assoc.*, 1965, B10.

<sup>2</sup> J. K. Nicholson and B. L. Shaw, unpublished work.

<sup>3</sup> J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Comm.*, 1965, 131.

<sup>4</sup> J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1965, 843.