The Molecular Structure of Di-μ-chloro-bis-(μ-diphenylphosphido-tetracarbonylironpalladium)

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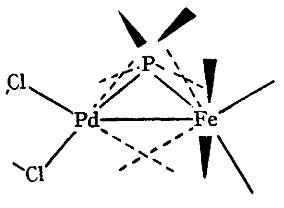
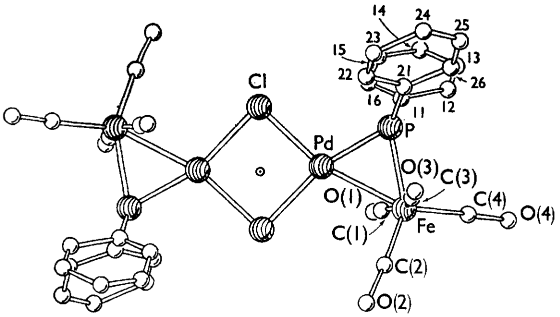
THE structure of di-μ-chloro-bis-(μ-diphenylphosphido-tetracarbonyliron palladium) (I), the preparation of which is described in the preceding communication,[1] has been determined by an X-ray crystal structure analysis and confirms that proposed. The complex (I) co-crystallizes with toluene in the monoclinic system; crystal data: $[(CO)_4Fe\ P(C_6H_5)_2\ PdCl]_2,PhMe$, $C_{39}H_{28}Cl_2Fe_2O_8P_2Pd_2$, $M = 1081$, $a = 20{\cdot}79$, $b = 11{\cdot}32$, $c = 18{\cdot}15$Å, $\beta = 94{\cdot}1°$, space group $C2/c$, $U = 4259$ Å^3 $D_m = 1{\cdot}69$ (flotation), $Z = 4$, $D_c = 1{\cdot}69$, Mo-K_α radiation, Picker single-crystal diffractometer data.

Standard methods were used to solve the structure and the present R value for 1001 reflections is 0·079. The palladium, iron, chlorine, and phosphorus atoms have been included with anisotropic and the light atoms with isotropic temperature factors. The position of the disordered toluene molecule has been found but not yet included in the refinement.



One molecule of the complex (I) itself is illustrated in the Figure; there is a crystallographic centre of symmetry at the midpoint between the bridging chlorines. The Figure shows a view perpendicular to the best plane through the five atoms, palladium, iron, phosphorus, and both chlorines; displacements out of this plane are Pd − 0·03, Fe + 0·10, P − 0·10, Cl + 0·08, Cl − 0·05, C(2) + 0·36, and C(4) − 0·22 Å.



FIGURE

The interatomic distances within the novel three-membered heterocyclic ring system of palladium, iron, and phosphorus are Pd–Fe 2·59 ± 0·01, Fe–P 2·24 ± 0·02, and P–Pd 2·15 ± 0·01 Å; the corresponding angles are P-Pd-Fe 55·5 ± 0·4°, Pd-Fe-P 52·2 ± 0·4, and Fe-P-Pd 72·3° ± 0·4°. (Other angles are Fe-Pd-Cl 161·3 ± 0·4°, Fe-Pd-Cl* 108·7 ± 0·4°, C(11)-P-C(21) 108 ± 2°, and C(2)-Fe-C(4) 104 ± 2°). Although depicted as a triangle, this three-membered ring is perhaps best represented by bent bonds. In this way square-planar co-ordination about palladium, approximate octahedral co-ordination around iron, and tetrahedral co-ordination around phosphorus are more closely approached.

The structure of (I) can be compared with the structures of the two complexes used in its preparation, π-allylpalladium chloride dimer[2] (II) and tetracarbonyldiphenylphosphineiron[3] (III). Of the two different Pd–Cl distances in complex (I), 2·42 ± 0·01 Å (*trans* to iron) and 2·45 ± 0·01 Å (*trans* to phosphorus) only the latter is definitely longer than the distances found in compound (II), 2·41 Å. The angles Cl-Pd-Cl, 89·5° ± 0·4 in (I) and 88·3° in (II) differ slightly.

In compound (I) iron is octahedrally co-ordinated whereas, in compound (III), it has a trigonal bipyramidal arrangement of ligands. The geometry of the present complex (I) is such that it is not easily possible to visualize the structural changes that resulted from the increase in co-ordination number. The phosphine in the mononuclear compound (III) is in an axial position, whereas the possible C-Fe-P axis in (I) is bent, C(2)-Fe-P 147·5°, suggesting a bent Fe–P bond. The apparent axis C(1)-Fe-C(3), with an angle of 162°, presumably arose from the insertion of the palladium ligand into the equatorial plane of the trigonal bipyramidal complex (III) and the opening out of a 120° equatorial angle.

An analogous change in co-ordination geometry around a metal atom, from 5 to 6 co-ordinate, was observed when cyclopentadienyldicarbonylcobalt reacted with mercuric chloride to form the adduct cyclopentadienyldicarbonylcobalt–mercuric chloride.[4] In the present case, however, the resulting complex (I) is not a simple adduct but was formed with elimination of propylene.

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[1] B. C. Benson, R. Jackson, K. K. Joshi, and D. T. Thompson, preceding communication.

[2] A. E. Smith, *Acta Cryst.*, 1965, **18**, 331.

[3] J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais, P. G. Owston, U. A. Raeburn, and D. T. Thompson, to be published.

[4] D. J. Cook and R. D. W. Kemmitt, *Chem. and Ind.*, 1966, 946; I. N. Nowell and D. R. Russell, *Chem. Comm.*, 1967, 817.