The Crystal and Molecular Structure of Tetrakistriphenylphosphinerhodium(I) Hydride

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Summary Crystals of tetrakistriphenylphosphinerhodium(I) hydride, $(Ph_3P)_4HRh^I.\frac{1}{2}C_6H_6$, are isometric, spacegroup $T_h^6 - Pa3$, $a = 2284{\cdot}5(1)$ pm, $Z = 8$: the rhodium atom and one phosphorus atom lie on a three-fold axis, the arrangement of the four phosphorus atoms being regularly tetrahedral to within experimental error, and, though the position of the hydrogen atom has not been determined in this analysis, to be consistent with the crystal symmetry, the hydrogen atom must also lie on the three-fold axis.

IT has been suggested by Dewhurst, Keim, and Reilly[1] that the co-ordination polyhedron of a novel compound of rhodium(I), tetrakistriphenylphosphinerhodium(I) hydride, $(Ph_3P)_4HRh^I$, be trigonal bipyramidal analogous to that of $(Ph_3P)_3(CO)HRh^I$) as analysed by La Placa and Ibers.[2] The preparation and properties of this substance have been reported by Ilmaier and Nyholm,[3] who have discussed the evidence for a hydride. The chemical analysis of the crystalline substance is consistent with $(Ph_3P)_4HRh.\frac{1}{2}(C_6H_6)$

Crystals of tetrakistriphenylphosphinerhodium(I) hydride crystallised from benzene are well developed orange cubo-octahedra, of the isometric system, Laue group $m3$, spacegroup $T_h^6 - Pa3$, $a = 2284{\cdot}5(1)$ pm, $Z = 8$, $D_m = 1369$ (by Dr. B. Ilmaier), D_c for $(Ph_3P)_4HRh$ (M 1153) = 1284, for $(Ph_3P)_4HRh.\frac{1}{2}(C_6H_6) = 1326$, and for $(Ph_3P)_4HRh.(C_6H_6) = 1371$ kg m^{-3}. One octant of 2047 three-dimensional diffraction data measured on a computer-controlled[4] Stoe four-circle diffractometer with Cu-K_α radiation in the range $2\theta = 1 \rightarrow 60°$ resulted in 287 independent observed $[I \geqslant 3\sigma(I)]$ diffraction maxima. The structure was analysed by Patterson and Fourier methods and refined by full-matrix least-squares analysis with all atoms isotropic, to a present value of the residual R of 0·061. The standard deviations derived from the least-squares matrix of the carbon atom positions are about 7, those of the phosphorus atoms about 4, and that of the rhodium atom 2 pm.

The rhodium atom and one of the phosphorus atoms [P(1)] lie on a three-fold axis of the crystal (position 8*c*3 of spacegroup *Pa*3) and the other three phosphorus atoms [P(2)] are related to each other by this three-fold axis. Interatomic distances and angles with standard deviations of the heavy atom co-ordination complex are given in the Figure. The rhodium–phosphorus distances of this analysis and other known compounds of rhodium are given in the Table. There is no significant difference in this distance in changing from rhodium(I) to rhodium(III), or in changing the co-ordination polyhedron. To within experimental error (2σ) the phosphorus atoms in this compound are at the vertices of a regular tetrahedron around the rhodium atom. The average phosphorus–carbon distance is 194(7) pm, the average rhodium–phosphorus–carbon angle is 119(2)°.

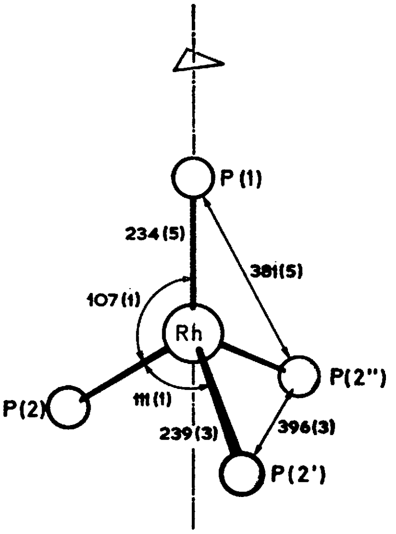

FIGURE. *The phosphorus co-ordination polyhedron of tetrakistriphenylphosphinerhodium*(I) *hydride. Interatomic distances and angles are given in picometers and degrees with standard deviations in brackets in terms of the least significant digit given.*

TABLE. *A comparison of observed rhodium–phosphorus bond lengths*

	Distance	Molecule	Co-ordination polyhedron
Rh^I–P(1)	234(5)	$(Ph_3P)_4HRh^I$	tetrahedral
Rh^I–P(2)	239(3)	,,	,,
Rh^I–P	234(1)	$(Ph_3P)_3(CO)HRh^I$	trigonal bipyramidal[2]
Rh^I–P	234	$(Ph_3P)_2ClCSRh^I$	square[5]
Rh^{III}–P	235	$(Ph_3P)_2I_2MeRh^{III}$	square pyramidal[6]

The hydride hydrogen atom of this compound was not seen in the observed and difference Fourier syntheses calculated at $R = 0{\cdot}061$. If the hydride hydrogen atom is in a position consistent with the spacegroup symmetry, it must lie on the three-fold axis through P(1) and the rhodium atom, more or less in the tetrahedral face formed by the three P(2) atoms. It is possible that the hydrogen atom occupies at random a position more or less in any of the tetrahedral faces or, in fact, anywhere. Such a random occupation would not observably destroy the macroscopic isometric symmetry.

Although the density of the compound measured by Dr. B. Ilmaier is most closely consistent with one molecule of benzene of crystallization per molecule of co-ordination compound, only one half a molecule of benzene of crystallisation per molecule of co-ordination compound is observed in the crystals in location $4b\bar{3}$ of spacegroup $Pa3$ at $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$.

We thank Dr. Bernard Ilmaier for crystals of the compound and the density measurement, Miss Margaret Dellow for programming assistance, Mr. John Cresswell for the Figure, and the S.R.C. for support of this work.

(*Received, October* 23*rd*, 1969; *Com.* 1608.)

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