The Preparation and Crystal Structure of Tristriphenylphosphinetriphenylarsinerhodium(I) Hydride, $(Ph_3P)_3(Ph_3As)HRh^I,\frac{1}{2}C_6H_6$

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Summary Crystals of tristriphenylphosphinetriphenylarsinerhodium(I) hydride are isomorphous with those of tetrakistriphenylphosphinerhodium(I) hydride with the arsenic and phosphorus atoms randomly occupying the four tetrahedral heavy-atom-ligand positions and the hydrogen atom *trans* to both arsenic and phosphorus.

THE stereochemistry of univalent low-spin complexes of Co, Rh, and Ir is of special interest because they may be either 4- or 5-co-ordinate and in the latter case might be either square-pyramidal, trigonal-bypyramidal, or tetrahedral with the fifth atom approximately in one tetrahedral face.

In extending earlier studies of structures of rhodium hydrido-complexes[1] we have prepared a new 5-co-ordinate complex $(Ph_3P)_3(Ph_3As)HRh^I,\frac{1}{2}C_6H_6$ by addition of Ph_3As to a benzene solution of $(Ph_3P)_3RhH$. At first yellow hexagonal plates crystallised from the solution, which upon standing for several days in the mother-liquor recrystallised to light orange cubo-octahedra of $(Ph_3P)_3(Ph_3As)HRh^I,\frac{1}{2}C_6H_6$. This preparation is entirely analogous to the preparation of $(Ph_3P)_4RhH$.[2] In the phosphine–arsine compound, however, two rhodium–hydrogen stretching bands at 2125 and 2180 cm^{-1} are observed in the i.r. spectrum compared to one band at 2140 cm^{-1} observed in the tetrakisphosphine compound.[2] We interpret the two bands of the phosphine arsine compound to indicate that the H atom is *trans* to both P and As atoms.

Results of the refinement of various structures of $(Ph_3P)_3(Ph_3As)HRh^I\ \frac{1}{2}C_6H_6$. *In all cases the refinement involved seven cycles of full-matrix least-squares using isotropic thermal parameters.*

As on 3	P in general	$R = 0{\cdot}132$	$B(P) = -0{\cdot}35$	$B(As) = 8{\cdot}32$
P on 3	As in general	$R = 0{\cdot}142$	$B(P) = 0{\cdot}08$	$B(As) = 6{\cdot}43$
$\frac{1}{4}$As + $\frac{3}{4}$P in all positions		$R = 0{\cdot}073$	$B(3) = 4{\cdot}29$	B(general) = 2·69

Multiplicity refinement	Mult.	σ	Theoretical for $\frac{1}{4}$As + $\frac{3}{4}$P
Three-fold As	0·06	0·01	0·083
Three-fold P	0·22	0·02	0·25
General As	0·24	0·03	0·25
General P	0·74	0·05	0·75

Crystals of $(Ph_3P)_3(Ph_3As)HRh^I.\frac{1}{2}C_6H_6$ are light orange cubo-octahedra, isometric, space-group T_h^6–$Pa3$, $a =$ 2293(1) pm, $Z = 8$. One octant of three-dimensional diffraction data in the range $\theta < 23°$ using Mo-K_α radiation resulted in 925 measurements which reduced to 241 unique observed $[I > 3\sigma(I)]$ diffraction maxima. Starting parameters for refinement of the structure were those determined for $(Ph_3P)_4HRh^I,\frac{1}{2}C_6H_6$. In these crystals three of the four tetrahedral heavy-atom-ligand positions are related to each other by a crystal three-fold axis and the fourth position lies on the three-fold axis. In the Table are shown refinement results for three forms of order and disorder of the fourth heavy-atom ligands. It is clear from the refinement results that each of the four heavy-atom-ligand positions is occupied at random by three P atoms and one As atom, ignoring the possible order of the crystal with the three P atoms in the general position of the space-group and the As atom in the special position on the three-fold axis. The Rh–P/As distances of 236(6) and 239(3) pm are not significantly different from those observed in tetrakistriphenylphosphine rhodium(I) hydride of 234(5) and 239(3) pm.[1] As in that compound, the presence of the

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H atom does not affect the regular tetrahedral arrangement of the heavy atom ligands.

We cannot tell whether the H atom lies in the regular crystallographic position on the three-fold axis or whether it too occupies a random position *trans* to any of the four heavy-atom ligands. Both possibilities satisfy the i.r. and diffraction evidence available at present. Though the triphenylphosphine and triphenylarsine groups are sterically equivalent in terms of the crystal, their bonding properties must be different to give two rhodium–hydrogen stretching frequencies in the i.r. $(Ph_3P)_4HRh$ cannot be in the present crystals because there is no evidence for the characteristic rhodium–hydrogen frequency of this compound at 2140 cm^{-1}.

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[1] R. W. Baker and P. J. Pauling, *Chem. Comm.*, 1969, 1495.

[2] B. Ilmaier and R. S. Nyholm, *Naturwiss.*, 1969, **56**, 415 and 635.