Crystal Structure of *trans*-Chlorohydridobis(triethylphosphine)palladium

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The title compound crystallises in a monoclinic cell, space group $P2_1/c$, with a = 9·06, b = 13·83, c = 14·48 Å, β = 92·9°, Z = 4. The structure was solved by the heavy-atom method and refined by the method of least-squares to R 0·072 for 1807 observed reflections. The two phosphorus atoms, which are mutually *trans*, and the chlorine atom are situated at three of the corners of a distorted square, centred on the palladium, with the fourth site believed to be occupied by hydrogen. The Pd–Cl bond length (2·427 Å) is long compared with that (2·299 Å) observed in the $PdCl_4^{2-}$ ion, indicating the strong *trans*-influence of hydrogen, but is the same as the Pt–Cl distance (2·422 Å) in $(Ph_2EtP)_2Pt(H)Cl$.

THE compound *trans*-chlorohydridobis(triethylphosphine)palladium, $(Et_3P)_2Pd(H)Cl$, was the first hydridopalladium complex to be isolated and was prepared[1] by the reaction between *trans*-dichlorobis(triethylphosphine)palladium and trimethylgermane. The present study was undertaken to provide information about the *trans*-influence in this compound.

EXPERIMENTAL

Crystals of the complex were obtained directly from the reaction mixture as thick plates, elongated along *a* and with well developed {010} and {001} faces. They were mounted in thin-walled capillary tubes in an atmosphere of dry nitrogen since the compound decomposes readily in the air. On exposure to *X*-radiation, the crystals turned cherry red and a large crystal of dimensions 1·0 × 0·4 × 0·3 mm was accordingly used for data collection. Despite the change in appearance of the crystal, the extent of decomposition during data collection appeared to be small. This contrasts with the situation found[2] for the related compound, $(Et_3P)_2Pt(H)Br$, which is stable to air but decomposes rapidly on exposure to *X*-rays.

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[1] E. H. Brooks and F. Glockling, *J. Chem. Soc. (A)*, 1967, 1030.

[2] P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Cryst.*, 1960, **13**, 246.

Crystal Data.—$C_{12}H_{31}ClP_2Pd$, $M = 379\cdot18$, Monoclinic, $a = 9\cdot06(2)$, $b = 13\cdot83(2)$, $c = 14\cdot48(2)$ Å, $\beta = 92\cdot89(10)°$, $U = 1812$ Å^3, $D_m = 1\cdot37$, $Z = 4$, $D_c = 1\cdot39$, $\mu = 13\cdot04$ cm^{-1} for Mo-K_α radiation, $\lambda = 0\cdot7107$ Å. Space group $P2_1/c$.

Unit-cell dimensions were obtained from precession photographs of the *hk*0 and *h*0*l* nets recorded with Zr-filtered Mo-radiation. The nets *hk*0—6 and *h*0—5*l* were also recorded by the precession method. Intensities were estimated visually by comparison with a scale and were corrected for Lorentz and polarisation factors. The various layers were placed on the same scale by a least-square treatment[3] of the common reflections.

TABLE 1

Final positional parameters (fractional), with standard deviations in parentheses

	x	*y*	*z*
Pd	0·24360(11)	−0·06361(8)	−0·14762(6)
Cl	0·23838(64)	−0·21562(33)	−0·23148(28)
P(1)	0·22960(42)	0·03268(31)	−0·27811(23)
P(2)	0·25128(38)	−0·13327(26)	−0·00278(22)
C(1)	0·2942(24)	0·1602(14)	−0·2702(12)
C(2)	0·0410(21)	0·0519(19)	−0·3264(15)
C(3)	0·3269(25)	−0·0146(18)	−0·3779(12)
C(4)	0·2334(25)	0·2237(14)	−0·2033(16)
C(5)	−0·0447(23)	−0·0345(19)	−0·3478(19)
C(6)	0·4952(19)	−0·0292(19)	−0·3539(15)
C(7)	0·1247(21)	−0·2389(16)	0·0024(15)
C(8)	0·1982(26)	−0·0594(15)	0·0966(13)
C(9)	0·4221(21)	−0·1894(21)	0·0399(12)
C(10)	−0·0267(17)	−0·2153(15)	−0·0267(13)
C(11)	0·3001(26)	0·0314(16)	0·1096(13)
C(12)	0·4967(20)	−0·2529(15)	−0·0305(12)

TABLE 2

Final thermal parameters,* with standard deviations in parentheses

	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
Pd	166(1)	46(1)	35(1)	3(1)	20(1)	−6(2)
Cl	419(12)	59(3)	48(2)	−23(5)	35(8)	−18(9)
P(1)	174(5)	57(2)	39(2)	10(4)	14(5)	3(6)
P(2)	152(5)	46(2)	34(1)	5(4)	27(4)	1(5)
C(1)	383(42)	65(11)	76(11)	−26(23)	170(35)	−32(37)
C(2)	200(30)	165(24)	98(14)	39(33)	−37(32)	−27(43)
C(3)	344(41)	116(18)	64(10)	27(27)	88(34)	18(45)
C(4)	367(46)	63(12)	110(15)	56(25)	−34(42)	11(35)
C(5)	235(35)	142(21)	148(21)	9(40)	−91(43)	−121(45)
C(6)	164(25)	170(22)	100(13)	−1(34)	49(29)	107(39)
C(7)	221(30)	106(16)	116(15)	69(31)	−17(35)	−81(36)
C(8)	381(44)	91(15)	64(10)	−13(24)	103(34)	−63(41)
C(9)	239(32)	206(26)	70(10)	61(31)	66(29)	247(50)
C(10)	166(25)	107(15)	90(12)	−36(25)	29(27)	−71(30)
C(11)	403(46)	83(13)	67(10)	−48(26)	−60(36)	−54(42)
C(12)	231(28)	98(14)	74(10)	−5(24)	62(27)	135(24)

* Anisotropic temperature factors are in the form:

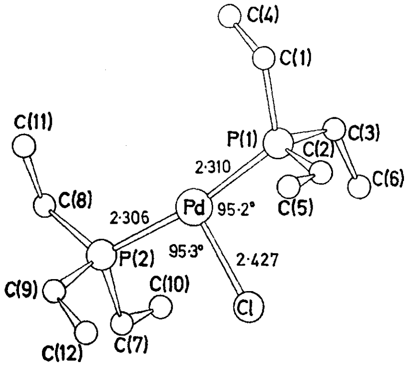
$$\exp\,[-10^{-4}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}])]$$

Structure Determination and Refinement.—The position of the palladium atom was found from the Patterson function and those of the other non-hydrogen atoms by Fourier methods. The atomic parameters were refined by the method of least squares using the block-diagonal approximation. A difference-Fourier map calculated at the end of the refinement showed one peak of height 1 eÅ^{-3} at a position related to that of the palladium atom. The remaining peaks were small and none could be convincingly assigned to any of the hydrogen atoms. For the 1807 observed reflections, the final *R* was 0·072.

In the final cycle of refinement, the parameter shifts were all $<\frac{1}{3}\sigma$ and the weighting was given by: $\sqrt{w} = 1\cdot0/(15\cdot07 + |F_o| + 0\cdot007|F_o|^2)^{\frac{1}{2}}$. Unobserved reflections were given zero weight in the refinement. Scattering factors were those given in ref. 4 and the real part of the dispersion correction was applied in the case of palladium. Final positional parameters are shown in Table 1 and thermal parameters in Table 2. The observed and calculated structure factors are listed in Supplementary Publication No. SUP 20576 (7 pp.).*

RESULTS AND DISCUSSION

As expected, the palladium atom has a square planar environment (Figure). The phosphorus atoms are mutually *trans* and together with the chlorine atom are situated at three corners of a distorted square. The hydrogen atom is presumed to occupy the fourth site, *trans* to chlorine. There is a small but significant departure from coplanarity in respect of the central atoms. The equation of the weighted least-squares mean plane through the palladium, chlorine, and phosphorus atom is $-0\cdot9999X - 0\cdot0084Y - 0\cdot0075Z + 2\cdot2868 = 0$ where *X*, *Y*, *Z* are in Å and refer to the orthogonal axes *a*, *b*, *c**. The deviations from this plane are: Pd −0·0044(10), Cl 0·0085(58), P(1) 0·030(4), and P(2) 0·024(3) Å. In addition (Table 3), the two P–Pd–Cl angles (95·2 and 95·3°) are increased over the ideal value of 90°. Similar features were found[5] in the related platinum compound, $(Ph_2EtP)_2Pt(H)Cl$, whereas in $(Et_3P)_2PtCl_2$ the platinum and its co-ordinated atoms were strictly coplanar.[6]



Molecular structure, showing the numbering of the atoms

The phosphine groups are in a staggered arrangement with respect to one another and their dimensions are similar to those found in related compounds. However, the Pd–P–C angles are greater than the tetrahedral

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* For details, see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[3] J. E. Monahan, M. Shiffer, and J. P. Shiffer, *Acta Cryst.*, 1967, **22**, 322.

[4] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[5] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 773.

[6] G. G. Messmer and E. L. Amma, *Inorg. Chem.*, 1965, **5**, 1775.

TABLE 3

(*a*) Bond lengths (Å) and their standard deviations

Pd–Cl	2·427(5)	C(1)–C(4)	1·44(3)
		C(2)–C(5)	1·45(4)
Pd–P(1)	2·310(4)	C(3)–C(6)	1·56(3)
Pd–P(2)	2·306(3)	C(7)–C(10)	1·45(3)
Mean Pd–P	2·308	C(8)–C(11)	1·56(3)
		C(9)–C(12)	1·53(3)
P(1)–C(1)	1·86(2)	Mean C–C	1·50
P(1)–C(2)	1·83(2)		
P(1)–C(3)	1·85(2)		
P(2)–C(7)	1·86(2)		
P(2)–C(8)	1·85(2)		
P(2)–C(9)	1·81(2)		
Mean P–C	1·84		

(*b*) Bond angles (deg.) and their standard deviations

Cl–Pd–P(1)	95·24(15)	C(1)–P(1)–C(2)	99·8(9)
Cl–Pd–P(2)	95·28(15)	C(1)–P(1)–C(3)	102·9(9)
Mean Cl–Pd–P	95·26	C(2)–P(1)–C(3)	103·0(10)
		C(7)–P(2)–C(8)	102·6(9)
P(1)–Pd–P(2)	169·35(14)	C(7)–P(2)–C(9)	99·6(10)
		C(8)–P(2)–C(9)	102·9(10)
Pd–P(1)–C(1)	119·5(6)	Mean C–P–C	101·8
Pd–P(1)–C(2)	114·0(7)		
Pd–P(1)–C(3)	115·2(7)	P(1)–C(1)–C(4)	119·4(15)
Pd–P(2)–C(7)	112·0(7)	P(1)–C(2)–C(5)	116·1(17)
Pd–P(2)–C(8)	118·7(7)	P(1)–C(3)–C(6)	111·8(15)
Pd–P(2)–C(9)	118·4(7)	P(2)–C(7)–C(10)	112·7(14)
Mean Pd–P–C	116·3	P(2)–C(8)–C(11)	111·2(14)
		P(2)–C(9)–C(12)	114·7(15)
		Mean P–C–C	114·3

(*c*) Some intramolecular non-bonding contacts (Å)

Cl · · · P(1)	3·500	Cl · · · C(6)	3·95
Cl · · · P(2)	3·498	Cl · · · C(7)	3·60
Cl · · · C(3)	3·61	Cl · · · C(10)	3·91
Cl · · · C(5)	3·91	Cl · · · C(12)	3·68

(*d*) Intermolecular non-bonding contacts (Å) <4 Å

Cl · · · C(7^{III})	3·99	C(6) · · · C(11^{I})	3·91
Cl · · · C(8^{III})	3·99	C(6) · · · C(12^{III})	3·95
C(4) · · · C(9^{I})	3·85	C(10) · · · C(2^{II})	3·86
C(4) · · · C(10^{I})	3·90	C(10) · · · C(11^{I})	3·71
C(4) · · · C(5^{II})	3·84	C(11) · · · C(12^{I})	3·78

Superscripts in Roman numerals refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $-x, -y, -z$

II $-x, \frac{1}{2} + y, \frac{1}{2} - z$

III $x, \frac{1}{2} - y, \frac{1}{2} + z$

value and the C–P–C angles less. The Pd–P distances (2·310 and 2·306 Å) are the same but smaller than the sum [7] of the covalent radii, in agreement with there being some degree of multiple bonding between the metal and phosphorus atoms.

The Pd–Cl bond length (2·427 Å) is considerably greater than that found (2·299 Å) in the $PdCl_4^{2-}$ ion [8] or given by the sum (2·30 Å) of the covalent radii [7] and this increase can be attributed to the strong *trans*-influence of the hydrogen atom. A very similar distance (2·422 Å) was found for the Pt–Cl bond in $(Ph_2EtP)_2PtHCl$ and the direct comparison can be made since the covalent radii of platinum and palladium are the same.

The *trans*-influence of ligands in square planar and octahedral transition-metal complexes has been discussed in terms of the σ-donor ability of the ligand [9,10] but it has also been considered, at least in part, in terms of its π-acceptor properties.[10] In the present case, the hydrogen and metal atoms are linked by σ bonds and the extent of π bonding between chlorine and the metal, if this is present, is believed to be small. A strong *trans*-influence is to be expected, and the *trans*-influence of hydrogen acting through palladium is found to be as strong as that through platinum.

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[2/1732 *Received, 24th July*, 1972]

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[11] F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, NRC Crystallographic programs for the I.B.M. 360 system, World List of Crystallographic Computer Programs, 2nd edn., Appendix p. 52.