Crystal and Molecular Structure of Dichloro[bis(diphenylphosphino)ethylamine]palladium(II)

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The crystal structure of the title compound has been determined from *X*-ray diffraction data and refined by least-squares methods to *R* 0·109 for 2735 reflexions. Crystals are orthorhombic $a = 20{\cdot}90(4)$, $b = 17{\cdot}60(4)$, $c = 13{\cdot}87(4)$ Å, $Z = 8$, space group *Pbca*. The mean bond lengths are Pd–P 2·22, Pd–Cl 2·37, and P–N 1·72 Å; P–Pd–P is 71·4°, and P–N–P 97·7°.

A PRELIMINARY communication[1] reported the basic crystallographic information on dichloro[bis(diphenylphosphino)ethylamine]palladium(II). This compound was one of a number of complexes involving ambidentate ligands recently investigated. The aminophosphine ligand system here has three donor atoms (two phosphorus and one nitrogen) in juxtaposition.

EXPERIMENTAL

Preparation.—Bis(diphenylphosphino)ethylamine (8·68 g) in warm acetone (120 ml) and water (3 ml) was added dropwise to potassium tetrachloropalladate(II) (3·265 g) in water (100 ml) and acetone (4 ml). After this solution had been set aside a yellow crystalline solid (6·081 g, 67%) was obtained which could be recrystallised (m.p. 277 °C) from alcohol (Found: C, 53·1; H, 4·3; Cl, 10·8; N, 2·7; P, 10·2. $C_{26}H_{25}Cl_2NP_2Pd$ requires C, 52·8; H, 4·3; Cl, 12·0; N, 2·4; P, 10·5%).

Crystal Data.—The following were established by *X*-ray methods, by use of Cu-K_α-radiation ($\lambda = 1{\cdot}5418$ Å).

$C_{26}H_{25}Cl_2NP_2Pd$, $M = 591{\cdot}1$, Orthorhombic, $a = 20{\cdot}90(4)$, $b = 17{\cdot}60(4)$, $c = 13{\cdot}87(4)$ Å, $U = 5106$ Å^3, $D_m = 1{\cdot}56$, $Z = 8$, $D_c = 1{\cdot}54$. Space group, *Pbca* (No. 61); no molecular symmetry implied. μ(Cu-K_α) = 92 cm^{-1}.

Structure Analysis.—2735 Independent reflexions were recorded photographically for the nets $h0l$, $0kl$, and $hk0$—10. Their intensities were estimated visually, corrected in the usual way, and the derived relative values of $|F_o|$ were placed on an absolute scale, first by comparison with $|F_c|$, and later by refining a scale factor. The position of the Pd-atom was easily found from sharpened Patterson projections along each principal axis. The usual assumption of the heavy-atom method led directly to positions for all other atoms, except hydrogen.

Refinement was by least-square analysis, anisotropic vibrational parameters being introduced in the later stages. The weighting scheme in the final cycle was: $w = (P_1 + |F_o| + P_2|F_o|^2)^{-1}$, where $P_1 = 2 \times |F_o|_{\text{min.}}$ and $P_2 = 2/|F_o|_{\text{max.}}$ Atomic-scattering factors were taken from ref. 2. The block-diagonal least-square program for DEUCE was due to J. S. Rollett. The final *R* was 10·9%. No correction was made for absorption; with μr *ca.* 0·5 for the crystals used (r mean radius of crystal) neglect of absorption should not lead to serious errors in the positional parameters. Final

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† No reprints available.

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[1] J. A. A. Mokuolu, D. S. Payne, and J. C. Speakman, *Chem. Comm.*, 1965, 599; see also J. A. A. Mokuolu, Ph.D. Thesis, Glasgow, 1965.

[2] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

observed and calculated structure factors are listed in Supplementary Publication No. SUP 20726 (5 pp., 1 microfiche).*

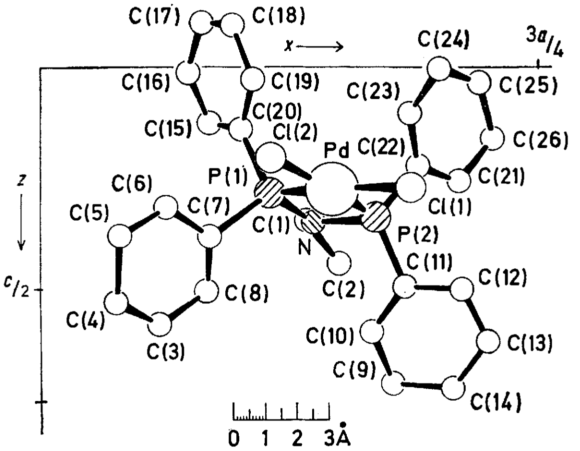

FIGURE 1 The structure in projection along the *b* axis

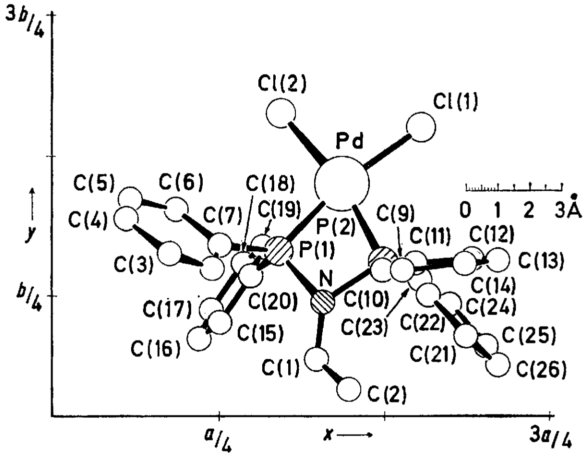

FIGURE 2 The structure in projection along the *c* axis

TABLE 1

Bond lengths (Å) with estimated standard deviations in parentheses

Pd–P(1)	2·22(0·004)	C(9)–C(10)	1·44(0·04)
Pd–P(2)	2·23(0·004)	C(9)–C(14)	1·46(0·04)
Pd–Cl(1)	2·37(0·005)	C(10)–C(11)	1·34(0·03)
Pd–Cl(2)	2·37(0·005)	C(11)–C(12)	1·40(0·03)
P(1)–N	1·73(0·01)	C(12)–C(13)	1·41(0·04)
P(1)–C(20)	1·79(0·02)	C(13)–C(14)	1·41(0·04)
P(1)–C(7)	1·79(0·02)	C(15)–C(16)	1·37(0·03)
P(2)–N	1·72(0·01)	C(15)–C(20)	1·37(0·03)
P(2)–C(22)	1·83(0·02)	C(16)–C(17)	1·42(0·03)
P(2)–C(11)	1·84(0·02)	C(17)–C(18)	1·35(0·03)
C(1)–N	1·45(0·02)	C(18)–C(19)	1·45(0·03)
C(1)–C(2)	1·50(0·03)	C(19)–C(20)	1·42(0·03)
C(3)–C(4)	1·42(0·03)	C(21)–C(22)	1·39(0·03)
C(3)–C(8)	1·40(0·03)	C(21)–C(26)	1·40(0·03)
C(4)–C(5)	1·33(0·03)	C(22)–C(23)	1·36(0·03)
C(5)–C(6)	1·38(0·03)	C(23)–C(24)	1·40(0·04)
C(6)–C(7)	1·41(0·03)	C(24)–C(25)	1·44(0·04)
C(7)–C(8)	1·40(0·03)	C(25)–C(26)	1·38(0·03)

RESULTS AND STRUCTURE

Figures 1 and 2 show the structure in different projections, as well as the numbering of atoms. Relevant bond lengths and angles are given in Tables 1 and 2. Table 3 gives information about the planarity of certain sets of atoms. Final co-ordinates (with standard deviations in parentheses) are listed in Table 4, and vibrational parameters (U_{ij}) in Table 5.

TABLE 2

Bond angles (°) (standard deviations are *ca.* 0·3° for angles at Pd, and 1·0 for other angles)

Cl(1)–Pd–Cl(2)	94·8	C(7)–C(8)–C(3)	119·4
P(1)–Pd–P(2)	71·4	C(8)–C(3)–C(4)	120·3
P(1)–N–P(2)	97·7	C(9)–C(10)–C(11)	121·6
Pd–P(1)–C(7)	117·6	C(10)–C(11)–C(12)	123·3
C(7)–P(1)–C(20)	103·5	C(11)–C(12)–C(13)	121·1
N–P(1)–C(20)	108·6	C(12)–C(13)–C(14)	114·6
Pd–P(1)–N	95·2	C(13)–C(14)–C(9)	126·4
N–P(1)–C(7)	111·2	C(14)–C(9)–C(10)	112·9
Pd–P(1)–C(20)	120·2	C(15)–C(16)–C(17)	120·6
Pd–P(2)–C(11)	118·5	C(16)–C(17)–C(18)	119·5
N–P(2)–C(11)	106·9	C(17)–C(18)–C(19)	118·7
Pd–P(2)–C(22)	115·5	C(18)–C(19)–C(20)	121·8
N–P(2)–C(22)	107·7	C(19)–C(20)–C(15)	115·9
Pd–P(2)–N	95·0	C(20)–C(15)–C(16)	123·3
C(11)–P(2)–C(22)	111·0	C(21)–C(22)–C(23)	121·2
C(3)–C(4)–C(5)	119·8	C(22)–C(23)–C(24)	120·5
C(4)–C(5)–C(6)	120·8	C(23)–C(24)–C(25)	117·9
C(5)–C(6)–C(7)	122·1	C(24)–C(25)–C(26)	121·1
C(6)–C(7)–C(8)	117·4	C(25)–C(26)–C(21)	118·6
		C(26)–C(21)–C(22)	120·5

TABLE 3

Equations of mean planes in the form $lX + mY + nZ = p$ where X, Y, Z are co-ordinates in Å, and $X = ax$, $Y = by$, and $Z = cz$. Distances (Å) of atoms from the planes are given in square brackets

Plane (*a*): Pd, Cl(1), Cl(2), P(1), P(2)

$$0{\cdot}1808X - 0{\cdot}2475Y - 0{\cdot}9519Z = -3{\cdot}7348$$

[Pd −0·014, Cl(1) 0·021, Cl(2) −0·013, P(1) 0·026, P(2) −0·019, C(5) −2·257, C(6) −1·255, C(7) −1·281, C(9) −3·765, C(10) −2·600, C(11) −1·463, N −0·152, C(1) 0·206, C(20) 1·517, C(22) 1·552]

Plane (*b*): P(1), P(2), N, C(1)

$$0{\cdot}2082X - 0{\cdot}1829Y - 0{\cdot}9608Z = -3{\cdot}1580$$

[P(1) 0·050, P(2) 0·052, N −0·181, C(1) 0·079, Pd 0·157, C(2) −0·614]

Dihedral angle between planes (*a*) and (*b*): 178°.

DISCUSSION

The bidentate nature of the ligand through the two phosphorus atoms is clearly demonstrated and this is consistent with other evidence[3] and with expectations based on the likely electron availability in the P^{III}–N–P^{III} system. The bond angle at the nitrogen (97·7°) is considerably less than the tetrahedral or trigonal angle and indicates considerable strain in the PdP_2N ring, a feature common to other complexes involving ligands with a P–X–P system.[4] The related bond angle at the metal, P–Pd–P, is 71·4°, which represents considerable distortion from the 90° expected from a square-planar configuration. The bond length Pd–P, 2·22 Å, appears

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue (items less than 10 pp. are supplied as full size copies).

[3] G. Ewart, D. S. Payne, and A. P. Lane, *J. Chem. Soc.*, 1962, 3984.

[4] K. K. Cheung, T. F. Lai, and K. S. Mok, *J. Chem. Soc.* (*A*), 1971, 1644.

unaffected by this distortion; in somewhat comparable complexes values of 2·26,[5] 2·31,[6] and 2·33 Å [7] have been obtained and these are, if anything, somewhat larger. The sum of covalent radii gives a calculated Pd–P bond length of 2·31 Å. The relative shortness of the bond suggests that an effective orbital overlap is achieved despite the unusual positions of the two phosphorus atoms relative to the central palladium. In contrast the Pd–Cl bond length (2·37 Å) is very close to that observed elsewhere: 2·36 [5] and 2·38 Å,[6] but compared with the sum of covalent radii (2·30 Å) and with the value (2·29 Å) observed [8] for $PdCl_2(DMSO)_2$ (DMSO = dimethyl sulphoxide) is significantly longer, which is in general agreement with the probable *trans*-effect,[9] arising from the phosphine ligand. The palladium phosphorus and chlorine atoms lie very nearly in a plane (Table 3).

TABLE 4

Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atoms	*x*	*y*	*z*
Pd	3351(1)	5122(1)	2109(1)
Cl(1)	4273(2)	5902(3)	2089(4)
Cl(2)	2647(2)	6093(2)	1586(4)
P(1)	2627(2)	4201(2)	2175(4)
P(2)	3831(2)	4060(2)	2601(4)
N	3136(6)	3537(7)	2675(13)
C(1)	3055(10)	2717(11)	2651(17)
C(2)	3437(11)	2296(15)	3397(20)
C(3)	1363(9)	4176(10)	4439(16)
C(4)	866(10)	4645(12)	4065(18)
C(5)	909(11)	4916(12)	3177(18)
C(6)	1439(10)	4770(11)	2618(18)
C(7)	1941(8)	4295(10)	2937(15)
C(8)	1904(9)	4016(10)	3880(17)
C(9)	4076(11)	3961(14)	5540(19)
C(10)	3819(11)	3981(13)	4578(19)
C(11)	4199(9)	4045(11)	3804(17)
C(12)	4865(10)	4104(11)	3863(17)
C(13)	5179(12)	4098(15)	4760(19)
C(14)	4769(13)	4049(15)	5564(22)
C(15)	1938(10)	3277(12)	952(17)
C(16)	1697(9)	2994(11)	86(16)
C(17)	1857(10)	3383(12)	−776(17)
C(18)	2210(11)	4026(12)	−728(17)
C(19)	2443(11)	4274(12)	201(17)
C(20)	2299(8)	3870(9)	1061(14)
C(21)	4795(9)	3039(11)	2943(17)
C(22)	4350(8)	3600(10)	1710(15)
C(23)	4251(10)	3815(12)	777(17)
C(24)	4601(13)	3481(16)	28(20)
C(25)	5056(10)	2894(12)	275(17)
C(26)	5171(9)	2702(11)	1221(17)

Within the bis(diphenylphosphino)ethylamine ligand the mean P–N bond length of 1·72 Å is closer to the normally accepted [10] single-bond value of 1·77 Å than to the values of *ca.* 1·6 Å found for the cyclic P–N bond lengths in the phosphazenes.[11] It is also significantly longer than the values of 1·650—1·658 Å found in $PO(NH_2)_3$ [12] and the values of exocyclic P–N bonds in various phosphazenes, 1·68,[13] 1·67,[14] and 1·63 Å,[15] and thus appears to involve comparatively little p_π–d_π bonding. The intramolecular non-bonded distances are quite normal with the exception of the P–P distance across the PdP_2N ring (2·71 Å), which is short when compared to the sum of the van der Waal's radii. The data relating to the phenyl ring and the P–C distances show no deviation from expected values.

TABLE 5

Anisotropic thermal parameters, U_{ij} ($10^3 \times$ Å^2)

Atoms	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Pd	26	25	43	−0	−2	3
Cl(1)	34	46	74	0	−11	−21
Cl(2)	46	36	48	4	2	24
P(1)	22	27	51	4	−5	4
P(2)	24	26	37	7	−1	3
N	39	23	26	24	−3	−4
C(1)	56	38	58	29	−7	−7
C(2)	66	21	142	66	−45	2
C(3)	32	32	73	−24	11	−17
C(4)	36	63	63	−23	23	−34
C(5)	53	57	53	−8	5	10
C(6)	34	46	73	23	−14	34
C(7)	42	35	31	4	−17	−9
C(8)	41	56	17	−4	10	−20
C(9)	68	72	26	−10	2	19
C(10)	62	44	82	11	−17	20
C(11)	52	44	33	−9	−25	6
C(12)	44	41	57	−18	−23	−22
C(13)	67	62	73	−7	−42	7
C(14)	98	50	82	−4	−57	14
C(15)	43	40	93	−4	6	5
C(16)	37	47	52	−7	−46	6
C(17)	45	63	34	−36	6	34
C(18)	49	56	55	1	−9	6
C(19)	54	65	37	1	4	8
C(20)	31	31	38	22	−17	11
C(21)	25	50	78	−6	−1	4
C(22)	35	35	42	−3	6	8
C(23)	54	56	40	−15	−15	8
C(24)	81	75	68	−14	14	−33
C(25)	51	53	63	−13	9	−28
C(26)	49	40	59	−8	1	12

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[5] L. L. Martin and R. A. Jacobson, *Inorg. Chem.*, 1971, **10**, 1795.

[6] D. L. Weaver, *Inorg. Chem.*, 1970, **9**, 2257.

[7] P. Groth, *Acta Chem. Scand.*, 1970, **24**, 2785.

[8] M. J. Bennett, F. A. Cotton, and D. L. Weaver, *Acta Cryst.*, 1967, **23**, 788.

[9] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 1955, 4456.

[10] D. W. J. Cruickshank, *Acta Cryst.*, 1964, **17**, 671.

[11] D. E. C. Corbridge, *Topics in Phosphorus Chem.*, 1966, **3**, 323.

[12] G. J. Bullen, F. S. Stephens, and R. J. Wode, *J. Chem. Soc.* (*A*), 1969, 1804.

[13] G. J. Bullen, *J. Chem. Soc.*, 1962, 3193; J. Trotter, *J. Chem. Soc.* (*A*), 1969, 2309.

[14] G. J. Bullen and P. R. Mollinson, *J.C.S. Dalton*, 1972, 1412; A. J. Wagner and A. Vos, *Acta Cryst.*, 1968, **B24**, 1412.

[15] J. B. Faught, T. Moeller, and I. C. Paul, *Inorg. Chem.*, 1970, **9**, 1656.