Tetrazoles and Tetrazole Complexes. Part I. Crystal Structure of *cis*-Bis[dimethyl(phenyl)phosphine]bis-(5-methyltetrazolato)palladium(II)

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Crystals of the title compound are orthorhombic, $a = 16{\cdot}265$, $b = 10{\cdot}545$, $c = 13{\cdot}939$, space-group $P2_12_12_1$ with with $Z = 4$. The structure was refined by full matrix least-squares methods to R 0·042 for 1461 statistically significant reflections measured on a diffractometer. A distorted *cis*-square planar configuration is found around the palladium atom. If phenyl groups are excluded, a pseudo-two-fold axis exists along the line bisecting the two sets of nitrogen and phosphorus ligands. Both tetrazole rings are N(1) bonded, planar and almost regular pentagons with mean bond lengths of 1·33 Å. There are no unusually short intermolecular distances.

THE X-ray structure analysis of *cis*-bis[dimethyl(phenyl)phosphine]bis-(5-methyltetrazolato)palladium(II) (I) was carried out to confirm the assigned *cis*-configuration[1] and to determine whether the two tetrazole rings are bonded to the palladium through N(1) or N(2).

EXPERIMENTAL

Crystals of (I) were grown from nitrobenzene.

Crystal Data.—$C_{20}H_{28}N_8P_2Pd$, $M = 548{\cdot}5$, Orthorhombic, $a = 16{\cdot}265$ ($\pm 0{\cdot}010$), $b = 10{\cdot}545$ ($\pm 0{\cdot}010$), $c = 13{\cdot}939$ ($\pm 0{\cdot}010$), $U = 2390{\cdot}7$ Å^3, D_m (not enough sample available for measurement), $Z = 4$, $D_c = 1{\cdot}52$, $F(000) = 1120$. Space group $P2_12_12_1$ from systematic absences: $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, $\lambda(K_{\alpha 1}) = 1{\cdot}54050$, $\lambda(K_{\alpha 2}) = 1{\cdot}54434$ Å; $\mu(\text{Cu-}K_\alpha) = 79{\cdot}5$ cm^{-1}. Cell data were measured on a General Electric single-crystal orienter.

Intensity data (Cu-K_α) were collected on a 0·01° incrementing Datex automated diffractometer equipped with a scintillation counter and a pulse-height selector. The crystal was almost rectangular (0·009 × 0·012 cm cross-section) and elongated along the direction it was mounted (parallel to the b axis). Data were collected by the use of 3·66° 2θ scans with the computed 2θ at the middle of the scan. Background counts of 20 s were taken before and after a scan. A standard intensity and the setting of the crystal were checked at frequent intervals. No serious deterioration of the crystal was evident. However, during refinement it was noted that 26 of the lower-order $0kl$ intensities measured at low 2θ large χ and a constant ϕ values had consistently large F values. These and the $0k0$ values which were only measured once were thus refined with different scaling factors from those for the remaining data. Intensities were corrected for the usual Lorentz and polarization factors. Absorption corrections were applied by using the method described by Coppens.[2] Four planes were used to describe the cross-sectional area of the crystal and a 10 × 10 Gaussian grid was chosen. The four equivalent hkl, $\bar{h}k\bar{l}$, hkl, $\bar{h}kl$ F values were averaged. For the structure determination and subsequent refinement reflections were only included if $I(hkl) \geqslant 1{\cdot}5\sigma(I)$ [$\sigma(I) =$ (total count + total background)$^{\frac{1}{2}}$]. 1558 independent F values were measured.

Structure Analysis.—The co-ordinates of the palladium atom were found by solution of the three-dimensional Patterson function.[3] Positions of phosphorus and then all carbon and nitrogen atoms were found by applying the usual Fourier and least-squares[4] techniques. Isotropic refinement gave R 0·085. A difference Fourier synthesis was then computed and used to place hydrogen at the benzene and methyl positions. These were adjusted somewhat to give better trigonal and tetrahedral positions around the respective carbons (Table 1). They were assigned isotropic temperature factors of 6 Å^2 and were not refined during subsequent cycles of least-squares. Adjusting for scaling factor only reduced R to 0·084. For the remaining cycles all non-hydrogen atoms were refined anisotropically. To reduce computing time on each cycle, palladium and the phosphorus atoms were refined with two separate batches of fourteen nitrogen

TABLE 1

Atomic co-ordinates of hydrogen atoms expressed as fractions of unit cell edges (× 10^4). Numbering denotes carbon atom to which the hydrogen is attached

	x	y	z
H(1*a*)	−350	−3229	−1255
H(1*b*)	−175	−3825	−131
H(1*c*)	179	−4596	−1129
H(2*a*)	1402	−4276	−1804
H(2*b*)	1937	−2956	−1882
H(2*c*)	2148	−4043	−1027
H(4)	1690	−1280	910
H(5)	2260	−1910	2530
H(6)	2200	−4130	3040
H(7)	1650	−5780	1990
H(8)	1110	−5200	0450
H(9*a*)	−933	−287	−1712
H(9*b*)	−1578	299	−874
H(9*c*)	−1467	−1320	−983
H(10*a*)	−167	−2237	945
H(10*b*)	−742	−1017	1474
H(10*c*)	−1166	−2073	638
H(12)	470	380	1560
H(13)	570	2400	2370
H(14)	−250	4150	1800
H(15)	−1140	4080	350
H(16)	−1250	1950	−450
H(18*a*)	1930	1228	159
H(18*b*)	1942	2799	377
H(18*c*)	2533	2186	−504
H(19*a*)	1297	411	−3091
H(19*b*)	1952	−277	−3872
H(19*c*)	1262	−1187	−3263

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[1] J. H. Nelson, D. L. Schmitt, R. A. Henry, D. W. Moore, and H. B. Jonassen, *Inorg. Chem.*, 1970, **9**, 2678.

[2] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **8**, 1035.

[3] J. Trotter, in 'World List of Crystallographic Computer Programs,' N.R.C., Ottawa, 2nd edn., 1966, p. 20.

[4] Computer program: ORFLS, A Fortran Crystallographic Least-Squares Program by W. R. Busing, K. O. Martin, and H. A. Levy, modified by W. C. Hamilton to correct for anomalous dispersion, Report ORNL TM 305, Oak Ridge National Laboratory, Tennessee.

and carbon atoms. Refinement was considered complete when all changes were $<\sigma$ (a lower value than if all 279 positional and thermal parameters had been varied together) and R and R' were 0·042 and 0·051 [refinement (*A*)]. Finally all positional parameters were refined together [refinement (*B*)]. After two cycles all changes were less than $0{\cdot}1\sigma$[4] and R and R' remained at 0·042 and 0·051 respectively. During all cycles of least-squares refinement a weighting scheme was adopted such that $w = 65/F_o$ for $F_o \geqslant 65$ and $w = 1$ for $F_o < 65$. Only 247 reflections with $F_o > 65$ were affected by this scheme which maintained $w\Delta^2$ constant for ranges of increasing F_o.

The final atomic co-ordinates and their estimated standard deviations are given in Table 2, anisotropic temperature factors and their standard deviations in Table 3. These were used to calculate orientations and magnitudes of the principal axes of the thermal ellipsoids shown in Figure 1.[5] Information about the most important planes is in Table 4. Bond lengths and angles with their estimated standard deviations are given in Figure 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20572 (6 pp., 1 microfiche).† The scattering factors for palladium, carbon, nitrogen, and hydrogen were taken from ref. 6; that for Pd was not corrected for anomalous dispersion. Of the 97 reflections regarded as small and statistically unreliable all gave a

TABLE 2

Final atomic fractional co-ordinates (Å) with their estimated standard deviations in patentheses (all $\times 10^4$)

Atom	*x*	*y*	*z*
Pd	901(8)	−713(7)	−863(8)
P(1)	982(32)	−2831(26)	−611(28)
P(2)	−331(29)	−453(29)	−142(31)
N(1)	846(96)	1211(77)	−1192(89)
N(2)	300(108)	1679(101)	−1831(102)
N(3)	425(133)	2923(99)	−1876(132)
N(4)	1032(121)	3245(104)	−1277(131)
N(5)	2050(83)	−760(91)	−1508(86)
N(6)	2744(94)	−954(93)	−1002(112)
N(7)	3350(103)	−938(117)	−1605(131)
N(8)	3070(94)	−762(123)	−2519(122)
C(1)	62(132)	−3753(122)	−776(151)
C(2)	1675(162)	−3614(132)	−1438(145)
C(3)	1373(112)	−3250(108)	565(125)
C(4)	1689(124)	−2308(118)	1154(116)
C(5)	1999(147)	−2647(150)	2060(138)
C(6)	1986(128)	−3879(125)	2363(137)
C(7)	1656(148)	−4801(135)	1764(141)
C(8)	1372(120)	−4508(106)	900(140)
C(9)	−1150(110)	−475(164)	−994(157)
C(10)	−648(161)	−1531(113)	785(170)
C(11)	−349(111)	1062(100)	460(108)
C(12)	158(129)	1197(125)	1268(122)
C(13)	168(147)	2312(182)	1735(152)
C(14)	−305(140)	3360(143)	1444(163)
C(15)	−773(128)	3241(123)	656(157)
C(16)	−800(118)	2083(111)	144(117)
C(17)	1291(115)	2190(105)	−855(147)
C(18)	1927(142)	2122(150)	−132(169)
C(19)	1665(152)	−451(181)	−3193(143)
C(20)	2262(112)	−656(130)	−2425(124)

TABLE 3

Final anisotropic * thermal parameters ($\times 10^4$) with their estimated standard deviations in parentheses

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	30(0)	33(1)	45(0)	0(0)	2(0)	2(1)
P(1)	36(1)	33(2)	52(2)	−1(2)	−2(1)	0(2)
P(2)	30(1)	60(3)	52(2)	−4(2)	7(1)	0(2)
N(1)	36(4)	33(8)	57(6)	5(5)	0(5)	8(6)
N(2)	51(6)	83(11)	51(6)	10(7)	9(5)	14(8)
N(3)	72(7)	45(10)	99(9)	5(7)	0(7)	25(9)
N(4)	59(6)	71(11)	102(9)	4(8)	20(7)	5(8)
N(5)	35(4)	34(8)	50(6)	−1(6)	−4(4)	−4(7)
N(6)	35(5)	77(12)	83(8)	5(6)	−8(6)	−1(9)
N(7)	34(5)	101(15)	107(11)	−3(7)	3(7)	4(10)
N(8)	35(5)	115(13)	85(8)	8(8)	10(6)	−5(11)
C(1)	50(6)	73(13)	79(10)	−8(7)	−21(8)	2(10)
C(2)	75(9)	67(14)	72(10)	4(9)	20(8)	−18(10)
C(3)	46(5)	83(12)	100(10)	−1(7)	9(6)	−10(9)
C(4)	47(6)	69(13)	49(8)	−1(8)	−13(6)	−23(9)
C(5)	58(8)	121(18)	60(9)	−2(10)	−10(7)	15(11)
C(6)	45(6)	88(15)	63(9)	10(8)	−6(6)	4(10)
C(7)	59(8)	91(15)	65(9)	4(9)	−15(7)	46(11)
C(8)	46(5)	50(13)	71(8)	−6(7)	−3(7)	16(10)
C(9)	27(5)	177(22)	89(11)	−2(8)	−8(6)	−19(15)
C(10)	91(10)	40(12)	97(11)	−2(8)	45(10)	13(11)
C(11)	35(5)	43(11)	44(7)	−5(6)	5(5)	−7(7)
C(12)	44(6)	88(14)	48(7)	0(8)	−5(6)	−2(8)
C(13)	45(7)	196(25)	71(10)	−3(11)	−6(7)	−35(14)
C(14)	41(7)	103(17)	98(13)	3(10)	4(8)	−23(13)
C(15)	42(7)	76(14)	102(12)	12(9)	−2(8)	−17(11)
C(16)	33(5)	70(13)	60(8)	7(8)	4(6)	−7(9)
C(17)	39(5)	44(11)	76(9)	0(6)	2(7)	17(11)
C(18)	49(7)	114(18)	99(12)	6(9)	−4(8)	−34(13)
C(19)	54(7)	191(24)	61(9)	−10(11)	1(7)	12(13)
C(20)	36(6)	80(13)	65(9)	2(9)	6(6)	5(11)

* In the form: $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2(\beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$. Estimated standard deviations were computed during full-matrix positional and thermal refinement of two separate groups containing Pd, P(1), P(2), fourteen carbon and nitrogen atoms and overall scaling factors.

TABLE 4

Plane	Mean planes						
1	Atoms	Pd	P(1)	P(2)	N(1)	N(5)	
	Deviation/Å $\times 10^3$	10	−44	53	−4	45	
	Equation of plane	$0{\cdot}444x + 0{\cdot}189y + 0{\cdot}876z + 0{\cdot}555 = 0$					
2	Atoms	N(1)	N(2)	N(3)	N(4)	C(17)	
	Deviation/A $\times 10^3$	−2	2	−1	0	1	
	Equation of plane	$-0{\cdot}665x + 0{\cdot}136y + 0{\cdot}734z + 1{\cdot}960 = 0$					
3	Atoms	N(5)	N(6)	N(7)	N(8)	C(20)	
	Deviation/A $\times 10^3$	6	−7	6	−2	−2	
	Equation of plane	$0{\cdot}095x + 0{\cdot}989y + 0{\cdot}116z + 0{\cdot}724 = 0$					
4	Atoms	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
	Deviation/Å $\times 10^3$	0	5	−2	−4	9	−7
	Equation of plane	$-0{\cdot}906x + 0{\cdot}145y + 0{\cdot}398z + 2{\cdot}208 = 0$					
5	Atoms	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)
	Deviation/Å $\times 10^3$	−14	8	5	−11	4	9
	Equation of plane	$0{\cdot}760x + 0{\cdot}304y - 0{\cdot}575z + 0{\cdot}446 = 0$					

Interplanar angles	1,2;	1,3;	1,4;	1,5;	2,3;	2,4;	2,5;
	68·1	70·7	91·5	96·2	81·0	23·9	152·4
	3,4;	3,5;	4,5;				
	84·1	72·2	150·8				

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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).

[5] C. K. Johnson, ORTEP, Report ORNL 3794, Oak Ridge National Laboratory, Tennessee, 1965.

[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1968.

small F_c by use of positional and thermal co-ordinates from refinement (B).

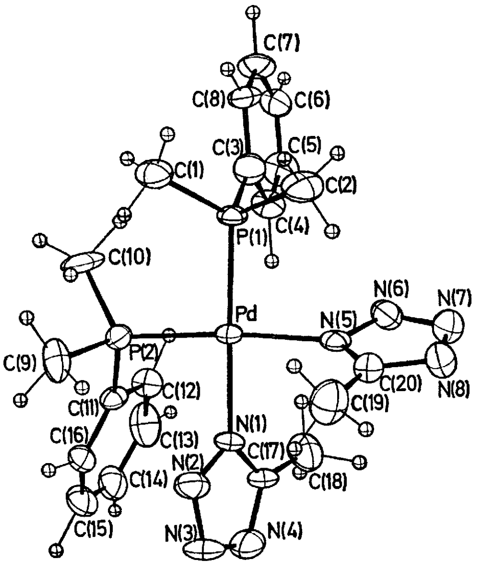

FIGURE 1 The molecules viewed down the c axis then rotated 20° around the x and 7° around the b axes (x axis horizontal, b axis vertical). Thermal ellipsoids are shown with 35% probability

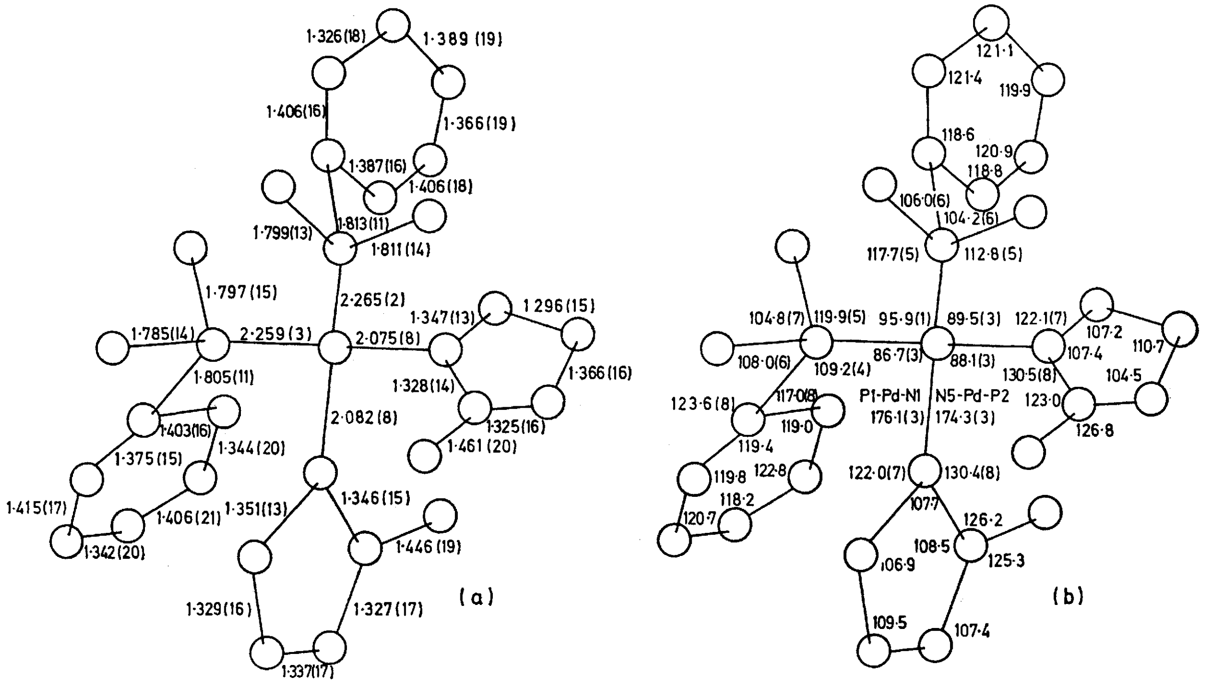

FIGURE 2 (a) Bond lengths and (b) bond angles in the molecule with estimated errors. The standard deviation of the bond lengths and angles were calculated from the formula given by G. A. Jeffrey and D. W. Cruickshank, *Quart. Rev.*, 1953, **7**, 335. Those for bond angles in the phenyl group are 1·1—1·3 and 1·0—1·4, and in the tetrazole group, 0·9—1·2 and 0·8—1·2° The following angles are not shown: C(9)–P(2)–C(10) 104·8(7), C(9)–P(2)–Pd 111·4(5), C(1)–P(1)–C(2) 100·9(7), and C(3)–P(1)–Pd 113·6(4)°

DISCUSSION AND DESCRIPTION OF THE STRUCTURE

The palladium atom has an approximately *cis*-square-planar environment. There is, however, a significant opening of the P(1)–Pd–P(2) angle to 95·9° from the theoretical value of 90° and a corresponding closure of angle N(1)–Pd–N(5) to 88·1°. Pd, P(1), P(2), N(1), and N(5) deviate by $<0\cdot06$ Å from plane (1). Pd–P values of 2·265 and 2·259 Å are in close agreement with the (2·260 Å) value for dichlorobis[dimethyl(phenyl)phosphine]palladium(II)[7] (II). The P–Pd–P geometry in these compounds is also similar. The two P–N bonds are 2·082 and 2·075 Å and within 1σ. The Pd–P value is less than the sum of the covalent radii (1·28 + 1·10 Å)[8] whilst the P–N value is greater than this sum (1·28 + 0·70 = 1·98 Å). This is expected and is due to a strong *trans*-effect where the strongly *trans*-directing phosphorus ligand causes *trans*-bonded tetrazole nitrogens to be weakly bonded and therefore somewhat longer than the sum of their covalent radii. Similar effects have been noted in (II). In (II) there is steric interaction between the two phenyl groups which are related by a two-fold axis. A similar two-fold axis is absent in this compound and there is no evidence for overcrowding and the attendant similar interaction. The P(1)–C(3)–C(6) and P(2)–C(11)–C(14) angles are 179·4 and 177·0° showing little distortion from the theoretical value of 180° and compare with the corresponding angle of 174·6° in (II). The opening of the P(1)–Pd–P(2) angle by 5·9° from the theoretical value may be attributed to the bulky *trans*-bonded phosphorus ligands arranging themselves to minimize

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[7] L. L. Martin and R. A. Jacobson, *Inorg. Chem.*, 1971, **10**, 1975.

[8] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960.

such interaction. If the phenyl groups are excluded from the molecule, however, there is a pseudo-two-fold axis in the direction of the line bisecting P(1) · · · P(2) and N(1) · · · N(5). The carbon atoms in the two phenyl rings show no significant deviations from the least-squares planes (4,5) through them (the largest being 0·014 Å). The angles within the ring are all within 3σ of the normal value of 120°. Bond distances agree fairly well with the expected value of 1·396 Å, except for C(8)–C(7), C(12)–C(13), and C(14)–C(15) which are slightly short.

All P–C distances are in excellent agreement with each other, ranging from 1·785 to 1·813 Å, and with those in (II) (1·82 Å) and the two isomers of di-iodobis-[dimethyl(phenyl)phosphine]palladium(II) (III) [9] (1·79—1·84 and 1·79—1·88 Å).

Both tetrazole rings are co-ordinated through N(1) and are planar. They are related by the pseudo-two-fold axis described above. No ring atom deviates from the mean planes (2,3) by $>0·007$ Å. Of the various possible tetrazole configurations around the palladium to be discussed by Nelson *et al.*[1] the one found here was considered by them to be the most likely. The planes make angles of 68·1 and 70·7° with the mean plane through Pd, P(1), P(2), N(1), and N(5). Bond lengths appear to be almost identical and equal, mean 1·338 and 1·333 Å in both rings. There is no significant difference between C–N and N–N values. Only N(6)–N(7) (1·296 Å) and N(7)–N(8) (1·366 Å) deviate slightly here and even these are within 3σ of the mean for the ring. These values are indicative of partial double-bonding between all atoms and of the ring being aromatic. These may be compared with other values for tetrazoles.[10–16] Although quite similar, it is likely that values are sensitive to substituents on the ring, however.

There is a marked difference between these values and ring co-ordinated through N(2) in bis[2-(5-perfluoromethyltetrazolato)]-μ-1,2-bis(diphenylphosphino)-ethane-bis[1,2-bis(diphenylphosphino)ethane]dicopper(I) [17] where the combination of N(2) bonding to copper and the substitution of perfluoromethyl at the 5-position results in an unsymmetrical bond pattern in the tetrazole ring with distances ranging from 1·119 to 1·482 Å. The C–C(methyl) distances of 1·446 and 1·461 Å are considerably less than the value for a paraffinic single bond (1·54 Å). This is no doubt due to the presence of adjacent partial double-bonding on the tetrazole ring. Ring angles are close to that expected for a regular pentagon 108°. Neither tetrazole ring is attached symmetrically to the Pd atom. In both cases the methyl groups [C(18) and C(19)] have opened the respective C(tetrazole ring)–N–Pd angles from the idealized value (126°) to 130·4 and 130·5°, with corresponding closure of the N–N–Pd angles from 126 to 122·0 and 122·1°. There is some evidence for hydrogen interaction with the octahedral sites of palladium. At the approximate position of one site the Pd · · · HC(4) distance is 2·85 Å with HC(4) · · · Pd–P(1), HC(4) · · · Pd–P(2), HC(4) · · · Pd–N(1), HC(4) · · · Pd–N(5) angles of 68·4, 92·2, 114·5, and 88·0°. At approximately the other side H(18*a*) · · · Pd is 3·00 Å. H(18*a*) · · · Pd–P(1), H(18*a*) · · · Pd–P(2), H(18*a*) · · · Pd–N(1), H(18*a*) · · · Pd–N(2) angles are 124·5, 101·6, 62·2, and 57·6°. It must be emphasized that hydrogen positions were not refined and H(18*a*) may be in more error than HC(4) since it is attached to a methyl carbon. Similar Pd · · · H interactions have been discussed for (II).[9] If such an interaction exists, however, the P(1)–C(3)–C(4) and P(1)–C(3)–C(8), P(1)–C(3)–C(6) angles (119·4, 122·0, and 179·4°) show little of the expected distortion [9,18] from the theoretical values (120, 120, and 180°).

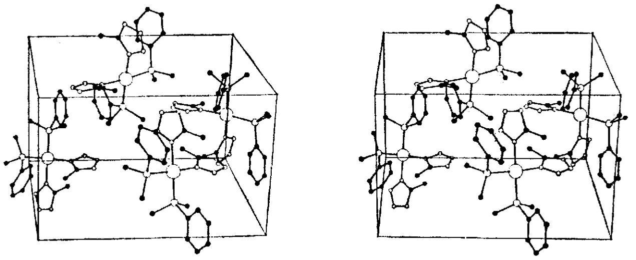

FIGURE 3 A stereoscopic view of the structure as seen by looking in the directions described in the caption to Figure 1

The thermal motion of the palladium is not very anisotropic. However, the slight maximum direction is as expected and within 12° of the normal to Plane (1). The phosphorus atoms are quite isotropic and consistent with their symmetric environment. All intermolecular distances are large enough to suggest there are van der Waals separations between the molecules. The packing of the molecules is shown in Figure 3.[5]

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