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The Crystal and Molecular Structure of (Carboxymethyl)(pyridine)-(triphenylphosphine)palladium(II) Dichloromethane Solvate, $[Pd(C_2H_2O_2)(PPh_3)(py)]\cdot 0.6\,CH_2Cl_2$

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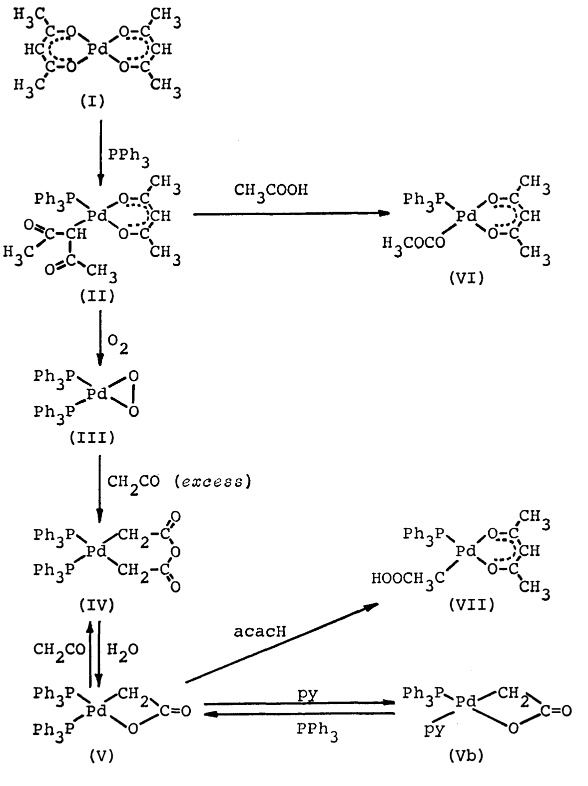
The molecular structure of carboxymethylpalladium(triphenylphosphine)pyridine has been determined by X-ray crystal structure analysis of its dichloromethane solvate, $[Pd(C_2H_2O_2)(PPh_3)(py)]\cdot 0.6\,CH_2Cl_2$. The crystal belongs to the monoclinic system, space group $P2_1/c$, with four formula units in a cell with dimensions of $a=8.791(4)$, $b=14.623(7)$, $c=19.862(5)$ Å, and $\beta=101.53(4)°$. $R=0.091$ for 2806 non-zero reflections. The feature of the structure is that the palladium atom is C,O-chelated by an acetic acid to form a four-membered ring [Pd–C=2.004 (16) and Pd–O=2.093 (11) Å], and the palladium atom has approximately square-planar geometry.

In a series of palladium complexes (Scheme) prepared by the reaction of ketene and triphenylphosphine with bis(acetylacetonate)palladium(II),[1] the molecular structures of I,[2] II,[3] IV,[4] and VII[5] have been determined by means of X-ray diffraction. The crystal structure analysis of V has been first attemped, however, all the crystals examined were decomposed by X-ray irradiation. Therefore, the more stable crystals of Vb, which is also a palladium C,O-chelate of acetic acid, has been selected. This paper deals with the structure of Vb, of which preriminary result has been reproted briefly.[6]



Experimental

Pale yellow, polyhedral crystals of $[Pd(C_2H_2O_2)(PPh_3)(py)]\cdot 0.6\,CH_2Cl_2$ were kindly supplied by Professor S. Kawaguchi and his coworkers of Osaka City University. Preliminary X-ray work showed that the crystals belong to the monoclinic system and that the space group is $P2_1/c$ (No. 14, absent reflections, $h0l$; $l=2n+1$ and $0k0$; $k=2n+1$). Unit-cell dimensions were determined by 2θ values of 12 strong reflections measured on a Rigaku automated, four-circle single crystal diffractometer.

Crystal Data. ($C_{25}H_{22}NO_2PPd+0.6\,CH_2Cl_2$), *F.W.*=556.8, monoclinic, space group, $P2_1/c$, $a=8.791(4)$, $b=14.623(7)$, $c=19.862(5)$ Å, $\beta=101.53(4)°$, $D_m=1.474$ g cm^{-3} (by flotation in aqueous solution of zinc bromide), $Z=4$, $D_c=1.478$ g cm^{-3}.

For the intensity measurement, a crystal with approximate dimensions of $0.20\times0.175\times0.15$ mm was used. Intensity data were collected on the Rigaku diffractometer using Zr-filtered Mo $K\alpha$ radiation. All data within a 2θ sphere of 44° ($\sin\theta/\lambda=0.527$) were measured using the θ-2θ scan technique. The integrated intensity was determined by scanning over the peak at a rate of 4° min^{-1} and subtracting the background obtained by averaging the two values measured for 10 s at both ends of a scan; the scan width of each reflection was $\Delta(2\theta)=(2.0+0.7\tan\theta_c)°$, where θ_c is the calculated Bragg angle for Mo $K\alpha_1$ ($\lambda=0.70926$ Å). The intensities of two standard reflections (080 and 300) were measured after every 25 reflections. After about 2400 reflections with lower Bragg angles were measured, these standard reflections showed a sudden drop down in their intensities. Therefore, the second crystal with approximately the same dimensions was cut out from the same mother crystal as the first, which was then used to collect about 900 more reflections with high angles. A total of 3053 independent reflections was collected of which the number of non-zero reflections was 2806. Usual Lorentz and polarization corrections were made, but the absorption correction was ignored ($\mu=6.37$ cm^{-1} for Mo $K\alpha$).

Solution and Refinement of the Structure

The structure was solved by the heavy atom method. The palladium and phosphorus atoms were located from a three-dimensional Patterson function. The remaining non-hydrogen atoms of the $[Pd(C_2H_2O_2)(PPh_3)(py)]$ molecule were located by succesive Fourier syntheses. However, three low and broad peaks remained undefined, which could be assigned as non-hydrogen atoms of dichloromethane, the recrystallization solvent. The structure was then refined by the block-diagonal least-squares procedure. The HBLS-V program[7] was used, the function minimized being $\sum(|F_o|-k|F_c|)^2$, where k is a single scale factor. Several cycles of isotropic refinement followed by the several more cycles of anisotropic refinement reduced

TABLE 1. FRACTIONAL ATOMIC COORDINATES OF NON-HYDROGEN ATOMS
(estimated standard deviations in parentheses)

Atom	x	y	z	Atom	x	y	z
Pd	0.19485 (12)	0.03753 (7)	0.09744 (5)	C(34)	0.3170 (20)	−0.1962 (11)	0.3413 (8)
P	0.1323 (4)	0.0470 (2)	0.2006 (2)	C(35)	0.1806 (20)	−0.1513 (11)	0.3504 (8)
C(11)	−0.0730 (14)	0.0613 (8)	0.1991 (6)	C(36)	0.1196 (17)	−0.0797 (11)	0.3066 (8)
C(12)	−0.1302 (16)	0.0906 (10)	0.2558 (7)	N	0.1548 (13)	−0.1053 (8)	0.0765 (6)
C(13)	−0.2918 (17)	0.0961 (11)	0.2545 (9)	C(42)	0.0435 (17)	−0.1575 (10)	0.0950 (7)
C(14)	−0.3925 (16)	0.0693 (11)	0.1934 (9)	C(43)	0.0193 (19)	−0.2488 (11)	0.0777 (9)
C(15)	−0.3352 (15)	0.0423 (9)	0.1352 (8)	C(44)	0.1233 (19)	−0.2889 (10)	0.0450 (8)
C(16)	−0.1817 (16)	0.0380 (9)	0.1375 (8)	C(45)	0.2437 (20)	−0.2395 (12)	0.0251 (8)
C(21)	0.2196 (14)	0.1393 (8)	0.2564 (6)	C(46)	0.2532 (19)	−0.1491 (11)	0.0427 (8)
C(22)	0.1680 (18)	0.2294 (10)	0.2409 (7)	C(1)	0.3245 (17)	0.1515 (10)	0.0323 (8)
C(23)	0.2312 (21)	0.3029 (10)	0.2819 (8)	C(2)	0.2465 (17)	0.1702 (11)	0.0907 (8)
C(24)	0.3449 (19)	0.2869 (11)	0.3394 (8)	O(1)	0.4102 (14)	0.1994 (8)	0.0078 (6)
C(25)	0.3968 (18)	0.1999 (11)	0.3550 (8)	O(2)	0.2874 (12)	0.0673 (7)	0.0107 (5)
C(26)	0.3346 (16)	0.1264 (10)	0.3147 (8)	Cl(1S)	0.2649 (13)	0.4770 (6)	−0.0273 (4)
C(31)	0.1930 (14)	−0.0525 (9)	0.2546 (6)	Cl(2S)	0.2314 (14)	0.4312 (6)	0.1077 (5)
C(32)	0.3235 (16)	−0.0999 (10)	0.2439 (7)	C(S)	0.3304 (35)	0.4110 (17)	0.0462 (15)
C(33)	0.3822 (20)	−0.1719 (11)	0.2872 (8)				

TABLE 2. ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) EXPRESSED IN THE FORM:
$\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$
(estimated standard deviations in parentheses)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	117.6 (16)	39.1 (6)	20.5 (3)	−2.6 (15)	19.2 (11)	−3.3 (7)
P	95.5 (51)	32.1 (18)	19.0 (10)	7.0 (49)	12.4 (36)	−5.1 (22)
C(11)	94 (19)	28 (7)	20 (4)	9 (18)	28 (14)	−5 (8)
C(12)	125 (22)	42 (8)	25 (4)	29 (22)	20 (16)	0 (10)
C(13)	103 (22)	60 (10)	40 (6)	68 (24)	50 (18)	11 (12)
C(14)	79 (20)	47 (9)	51 (7)	24 (22)	40 (19)	12 (12)
C(15)	84 (20)	29 (7)	42 (6)	16 (19)	26 (17)	−8 (10)
C(16)	120 (22)	32 (7)	31 (5)	−7 (21)	11 (17)	10 (10)
C(21)	99 (19)	28 (6)	17 (4)	−10 (18)	29 (13)	−13 (8)
C(22)	158 (25)	47 (9)	24 (4)	4 (24)	11 (17)	−6 (10)
C(23)	241 (33)	35 (8)	33 (5)	18 (27)	70 (22)	−4 (11)
C(24)	187 (28)	57 (10)	27 (5)	−45 (27)	22 (19)	−55 (12)
C(25)	150 (26)	59 (10)	31 (5)	−31 (19)	−11 (19)	−16 (12)
C(26)	93 (20)	44 (8)	31 (5)	−15 (21)	1 (16)	−1 (10)
C(31)	98 (19)	34 (7)	17 (4)	−8 (19)	14 (14)	3 (8)
C(32)	132 (23)	39 (8)	24 (4)	29 (21)	34 (16)	−12 (9)
C(33)	210 (31)	49 (9)	31 (5)	85 (28)	33 (21)	−6 (11)
C(34)	209 (30)	43 (9)	27 (5)	46 (26)	−2 (19)	20 (11)
C(35)	210 (31)	50 (9)	26 (5)	−50 (27)	31 (20)	10 (11)
C(36)	124 (23)	53 (9)	26 (5)	−6 (24)	−3 (17)	5 (11)
N	137 (19)	39 (6)	21 (3)	−8 (18)	33 (13)	−1 (8)
C(42)	142 (24)	47 (9)	24 (5)	−4 (23)	16 (17)	−19 (10)
C(43)	175 (28)	41 (8)	36 (6)	−32 (25)	3 (20)	−10 (11)
C(44)	186 (28)	33 (8)	37 (6)	6 (24)	32 (20)	−8 (11)
C(45)	184 (29)	69 (11)	30 (5)	103 (30)	34 (20)	−6 (12)
C(46)	171 (27)	55 (9)	28 (5)	29 (26)	50 (19)	7 (11)
C(1)	155 (25)	40 (8)	28 (5)	13 (23)	39 (18)	9 (10)
C(2)	145 (25)	50 (9)	26 (5)	5 (24)	29 (17)	3 (10)
O(1)	231 (22)	64 (7)	35 (4)	−53 (21)	77 (15)	15 (9)
O(2)	196 (19)	52 (6)	19 (3)	19 (17)	54 (12)	6 (7)
Cl(1S)	512 (27)	62 (5)	26 (2)	162 (19)	121 (13)	33 (5)
Cl(2S)	486 (27)	78 (6)	42 (3)	168 (20)	204 (16)	27 (7)
C(S)	241 (56)	36 (14)	37 (10)	71 (46)	42 (38)	38 (19)

Table 3. Atomic parameters of hydrogen atoms (estimatimated standard deviations in parentheses)

	x	y	z	$B^{a)}$
H(12)	−0.055(14)	0.096(8)	0.299(6)	3.6
H(13)	−0.327(15)	0.114(9)	0.303(7)	4.8
H(14)	−0.506(15)	0.076(9)	0.188(7)	4.4
H(15)	−0.459(14)	0.035(9)	0.093(6)	3.7
H(16)	−0.115(14)	0.030(8)	0.100(6)	3.7
H(22)	0.096(14)	0.241(9)	0.199(6)	4.0
H(23)	0.191(16)	0.382(10)	0.263(7)	4.9
H(24)	0.397(15)	0.338(9)	0.373(7)	4.7
H(25)	0.497(15)	0.178(9)	0.397(7)	4.8
H(26)	0.356(14)	0.057(8)	0.325(6)	3.7
H(32)	0.368(14)	−0.089(8)	0.206(6)	3.5
H(33)	0.500(15)	−0.206(9)	0.282(7)	4.7
H(34)	0.369(15)	−0.251(9)	0.377(7)	4.3
H(35)	0.113(15)	−0.164(9)	0.379(7)	4.6
H(36)	0.031(14)	−0.034(9)	0.313(6)	4.1
H(42)	−0.025(14)	−0.118(9)	0.120(6)	3.9
H(43)	−0.060(15)	−0.296(9)	0.090(7)	4.6
H(44)	0.103(15)	−0.355(9)	0.040(7)	4.3
H(45)	0.316(16)	−0.268(10)	0.009(7)	5.0
H(46)	0.344(15)	−0.117(9)	0.029(7)	4.5
H(2A)	0.313(15)	0.195(9)	0.127(6)	4.3
H(2B)	0.158(15)	0.209(9)	0.078(6)	4.3

a) The isotropic temperature factors of each hydrogen atom is taken equal to that of equivalent temperature factor of its parent atom.

the R_1 factor ($R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$) to 0.090 for non-zero reflections. The difference Fourier synthesis, based on the atomic parameters at this stage, revealed all the hydrogen atoms except those of dichloromethane. Three cycles of refinement including those 22 hydrogen atoms gave $R_1=0.082$. However, equivalent isotropic thermal parameters of non-hydrogen atoms of the solvent molecule were exceptionally large, and the calculated density for four formula weights of $[Pd(C_2H_2O_2)(PPh_3)(py), CH_2Cl_2]$ per unit-cell [1.56 g cm^{-3}] is much larger than the observed value of 1.474 g cm^{-3}. These facts suggested a lower occupancy of dichloromethane than unity. Assuming the occupancy as 0.6. which gives the calculated density of 1.478 g cm^{-3} and a good fit with the observed values, the refinement converged: R_1 being 0.091 ($R_2=\Sigma||F_o|-|F_c||^2/\Sigma|F_o|^2=0.106$) for non-zero reflections. The atomic scattering factors used in the calculations were taken from International Tables for X-Ray Crystallography, Vol. IV.[8] The final atomic parameters of non-hydrogen atoms are listed in Tables 1 and 2, and those of hydrogen atoms in Table 3.†

Description of the Structure

Molecular Structure. The perspective view of the $[Pd(C_2H_2O_2)(PPh_3)(py)]$ and CH_2Cl_2 molecules are given in Fig. 1, with the numbering scheme of atoms. The stereoscopic drawing of the $[Pd(C_2H_2O_2)(PPh_3)(py)]$ molecule is given in Fig. 2. Bond lengths and bond angles are given in Table 4. Least-squares planes of some groups of atoms, deviations of atoms from, and dihedral angles between these planes are listed in Table 5.

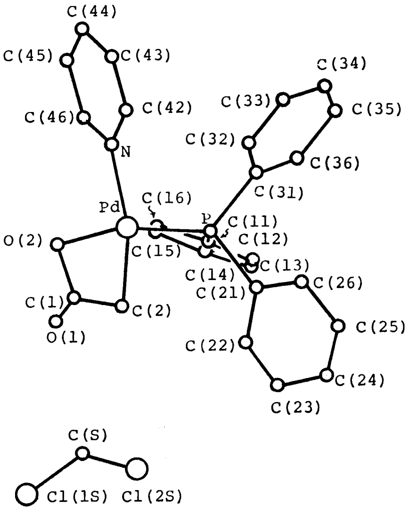


Fig. 1. Perspective view of the $[Pd(C_2H_2O_2)(PPh_3)(py)]$ and CH_2Cl_2 molecules with the numbering scheme of atoms.

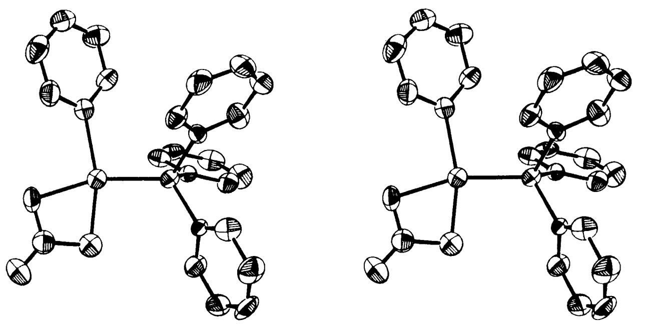


Fig. 2. A stereoscopic view of the $[Pd(C_2H_2O_2)(PPh_3)(py)]$ molecule. Non-hydrogen atoms are represented by the thermal ellipsoids at 50% probability level.

The remarkable feature of the molecular structure is that this complex contains a C,O-chelate ring of acetic acid (Fig. 1). The palladium atom has an approximately square-planar geometry coordinated by an oxygen and an sp^3 carbon atoms of the chelate ring and a phosphorus and a nitrogen stoms; the mean and maximum deviations of atoms from the best plane being 0.057 and 0.078 Å, however, the planarity is not so good as that of IV, a C,C′-chelate of acetic anhydride.[4]

The Pd–C(2) bond lengths [2.004(16) Å] is much shorter than those in IV [2.141(13) and 2.124(11) Å], which is probably the shortest of the observed Pd–C σ-bond. The Pd–O(2) length [2.093(11) Å] is longer than those of O,O′-chelate of acetylacetone [1.989(2) and 1.986(2) Å],[2b] which is considered as due to trans-influence of the pyridine ligand. The C(2)–Pd–O(2) angle [67.3(5)°] is much smaller than 90°.

The Pd–P bond [2.230(4) Å] is equal in length to that of 2.235(1) Å in VII,[5] and this is shorter than that

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† The tables of observed and calculated structure factors are kept as Document No. 7914 at the Chemical Society of Japan.

TABLE 4. BOND LENGTHS AND BOND ANGLES (estimated standard deviations in parentheses)

Bond length [l/Å]			
Pd-P	2.230(4)	Pd-N	2.144(12)
C(1)-C(2)	1.487(22)	C(1)-O(2)	1.322(19)
C(1)-O(1)	1.201(20)		
Pd-O(2)	2.093(11)	Pd-C(2)	2.004(16)
P-C(11)	1.811(13)	P-C(21)	1.816(13)
P-C(31)	1.822(13)		
C(11)-C(12)	1.376(19)	C(11)-C(16)	1.435(20)
C(12)-C(13)	1.421(22)	C(13)-C(14)	1.409(25)
C(14)-C(15)	1.405(24)	C(15)-C(16)	1.343(22)
C(21)-C(22)	1.408(20)	C(21)-C(26)	1.389(20)
C(22)-C(23)	1.396(24)	C(23)-C(24)	1.380(25)
C(24)-C(25)	1.367(24)	C(25)-C(26)	1.385(23)
C(31)-C(32)	1.392(19)	C(31)-C(36)	1.383(20)
C(32)-C(33)	1.392(23)	C(33)-C(34)	1.361(25)
C(34)-C(35)	1.410(25)	C(35)-C(36)	1.398(23)
N-C(42)	1.349(19)	N-C(46)	1.358(20)
C(42)-C(43)	1.384(23)	C(43)-C(44)	1.356(24)
C(44)-C(45)	1.402(25)	C(45)-C(46)	1.365(24)
C(S)-Cl(1S)	1.749(33)	C(S)-Cl(2S)	1.661(33)
Bond angle [ϕ/°]			
P-Pd-N	100.2(3)	P-Pd-C(2)	95.8(4)
P-Pd-O(2)	162.1(3)	N-Pd-C(2)	163.9(5)
N-Pd-O(2)	96.8(4)	C(2)-Pd-O(2)	67.2(5)
Pd-C(2)-C(1)	91.1(9)	C(2)-C(1)-O(1)	129.3(15)
Pd-O(2)-C(1)	92.2(9)	C(2)-C(1)-O(2)	107.6(13)
O(1)-C(1)-O(2)	123.1(14)		
Pd-P-C(11)	114.8(4)	Pd-P-C(21)	117.1(4)
Pd-P-C(31)	113.2(4)	C(11)-P-C(21)	102.9(6)
C(11)-P-C(31)	106.0(6)	C(21)-P-C(31)	101.3(6)
P-C(11)-C(12)	123.1(10)	P-C(11)-C(16)	118.6(10)
C(12)-C(11)-C(16)	118.3(12)	C(11)-C(12)-C(13)	122.6(14)
C(12)-C(13)-C(14)	116.4(15)	C(13)-C(14)-C(15)	121.4(16)
C(14)-C(15)-C(16)	120.6(15)	C(11)-C(16)-C(15)	120.7(14)
P-C(21)-C(22)	118.9(10)	P-C(21)-C(26)	123.8(10)
C(22)-C(21)-C(26)	117.3(12)	C(21)-C(22)-C(23)	121.3(14)
C(22)-C(23)-C(24)	119.5(16)	C(23)-C(24)-C(25)	119.9(16)
C(24)-C(25)-C(26)	121.1(15)	C(21)-C(26)-C(25)	120.9(14)
P-C(31)-C(32)	117.5(10)	P-C(31)-C(46)	123.0(11)
C(32)-C(31)-C(36)	119.5(13)	C(31)-C(32)-C(33)	119.9(14)
C(32)-C(33)-C(34)	121.5(16)	C(33)-C(34)-C(35)	118.9(16)
C(34)-C(35)-C(36)	119.9(16)	C(31)-C(36)-C(35)	120.2(14)
N-C(46)-C(45)	124.8(15)	C(42)-C(43)-C(44)	116.9(15)
C(43)-C(44)-C(45)	122.1(16)	C(44)-C(45)-C(46)	116.0(16)
N-C(42)-C(43)	124.2(14)	C(42)-N-C(46)	115.8(13)
Cl(1S)-C(S)-Cl(2S)	112.5(18)		

of 2.267(1) Å in [PdCl(CH_2SCH_3)(PPh_3)].[9] The Pd–N bond length [2.144(12) Å] is comparable to those in [PdCl($CH_2COCH_2COOCH_2Ph$)(py)$_2$] [2.027(6) and 2.120(6) Å]. The P–Pd–N angle of 100.2(3)° is much larger than 90° because of steric interaction between the triphenylphosphine and pyridine ligands.

In the C,O-chelate ring of acetic acid, the C(1)–C(2) bond length of 1.487(22) is equal to those in IV of 1.473(18) and 1.479(19) Å, which can be compared with those observed in C–C=O moieties in many organic compounds [av 1.506(5) Å]. The C(1)–O(2) bond length [1.322(19) Å] is shorter than those in IV [1.412(16) and 1.386(17) Å]. The C(1)=O(1) double bond length of 1.201(20) is equal to those of 1.192(18) and 1.202(17) Å in IV, which is normal value in aldehydes and ketones [av 1.215(5) Å],[10] and α-oxalic acid [1.207(1) Å].[11] Both the Pd–C(2)–C(1) and Pd–O(2)–C(1) angles are around 90° [91.1(9) and 92.9(9)°, respectively]. The C(2)–C(1)–O(2) angle [107.6(13)°] is much smaller, whereas the C(2)–C(1)–O(1) angle [129.3(15)°] is much larger than 120°. However, the sum of the three angles around

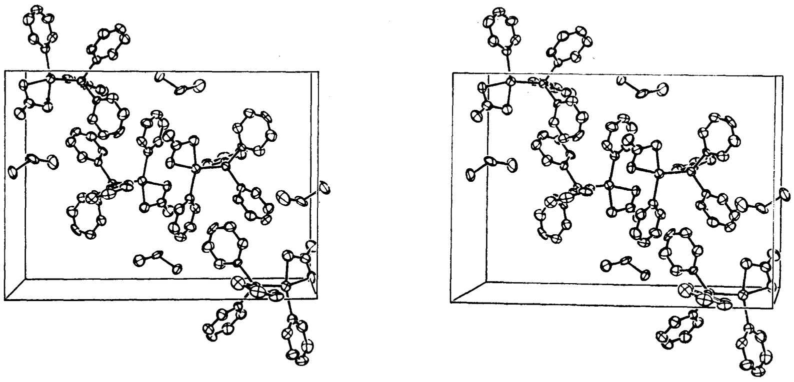

Fig. 3. A stereoscopic drawing of the molecular packing in the unit cell.

Table 5. Least-squares planes, deviations (l/Å) of atoms from the plane, and dihedral angles [ϕ/°]

Equation of the plane is of the form: $AX+BY+CZ+D=0$, where X, Y, Z, and D are measured in Å units: $X=ax+cz\cos\beta$, $Y=by$, $Z=cz\sin\beta$. (Atoms marked by * are not in the least-squares plane calculation.)

(a) Coordination plane
$-0.8594X+0.1982Y-0.4714Z+1.959=0$
Pd 0.035 P −0.060 N 0.045
C(2) 0.068 O(2) −0.078 C(1)* −0.239
O(1)* −0.606

(b) Plane defined by C(1), C(2), O(1), and O(2)
$-0.6749X+0.3618Y-0.6431Z+1.451=0$
C(1) 0.010 C(2) −0.003 O(1) −0.004
O(2) −0.003 Pd* −0.465

(c) Plane defined by Pd, C(2), and O(2)
$-0.8326X+0.1707Y-0.5270Z+2.010=0$

Dihedral angle between (a) and (b): 17.3
Dihedral angle between (b) and (c): 15.7

the C(1) atom is 360.0°; the planarity around the C(1) being good (Table 5). The dihedral angle between the planes defined by Pd, C(2), and O(2) and C(1), C(2), O(1), and O(2), is 15.7°.

Similar to those in IV the phosphorus atom show a deviation from the tetrahedral geometry: the C(11)–P–C(21), C(11)–P–C(31), and C(21)–P–C(31) [102.9(6), 106.0(6), and 101.3(6)°] being much smaller, whereas Pd–P–C(11), Pd–P–C(21) and Pd–P–C(31) [114.8(4), 117.1(4), and 113.2(4)°] being larger than th tetrahedral angle. Three P–C bond lengths are equal [1.811(13), 1.816(13), and 1.822(13) Å]. Three phenyl rings in triphenylphosphine group have normal structure [C–C(av)=1.392 Å and C–C–C(av)=120.0°]. The pyridine ring coordinated to palladium atom also has normal geometry [C–C(av)=1.377, C–N(av)=1.354 Å, C–N–C=115.8°, and C–C–C(av)=120°].

Crystal Structure. Figure 3 shows a stereoscopic drawing of the molecular packing in the unit-cell along the c axis. All intermolecular atomic contacts are considered to be normal van der Waals distances, the shortest contact being 3.285(21) Å (C(24)(x, y, z)⋯O(1)(x, $0.5-y$, $0.5+z$)).

Computations throughout the present study were carried out on a NEAC 2200-700 computer at the Osaka University. Figures 2 and 3 were drawn on the NUMERICON 7000 system at Osaka University with a local version of ORTEP.[12]

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