The Crystal and Molecular Structure of (Acetylacetonato)(carboxymethyl)(triphenylphosphine)palladium(II)

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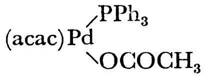
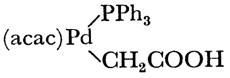
The molecular structure of (acetylacetonato)(carboxymethyl)(triphenylphosphine)palladium(II) [(acac)(PPh_3)$PdCH_2COOH$] has been determined by means of X-ray diffraction. The crystal belongs to the triclinic system, space group $P\bar{1}$, with two formula units in a cell with dimensions of $a=10.433(2)$, $b=12.746(2)$, $c=10.224(2)$ Å, $\alpha=106.62(1)$, $\beta=112.41(2)$, and $\gamma=75.13(2)°$. $R=0.032$ for 4972 non-zero reflections. The palladium atom, σ-bonded to the methylene group of the acetic acid moiety (Pd–C=2.063(4) Å), has a square-planar geometry. The molecule forms a dimer with the adjacent molecule related by a center of symmetry through an inter-molecular hydrogen bonding between acetic acid moieties, O–H···O=2.621(4) Å.

Recently, in a series of studies of palladium complexes (Scheme 1), palladium(II) C,O-chelates of acetic acid have been prepared by the reaction of ketene and triphenylphosphine with bis(acetylacetonato)palladium(I) by Kawaguchi and his co-workers of Osaka City University.[1)] In relation to this, the preparation of the following linkage isomers;


$(acac)Pd\begin{cases}PPh_3\\ OCOCH_3\end{cases}$

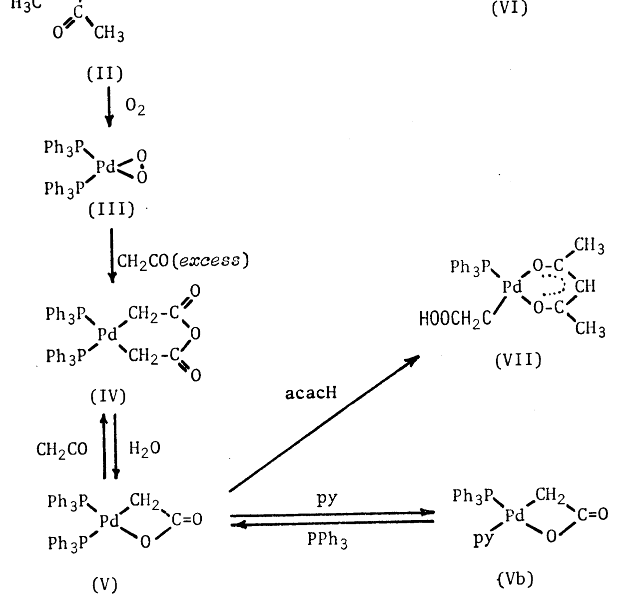
(VI)

and


$(acac)Pd\begin{cases}PPh_3\\ CH_2COOH\end{cases}$

(VII)

has also been reported.[3)] The molecular structure of II, IV, and Vb have been determined and reported.[2,4)] This paper will describe the molecular structure of VII. Interest in the Pd–C σ-bond also promoted this study.



Scheme 1.

Experimental

Pale yellow, polyhedral crystals of [(acac)(PPh_3)$PdCH_2COOH$] were kindly supplied by Professor Kawaguchi and his co-workers of Osaka City University. Preliminary photographic data showed that the crystals belong to the triclinic system. Accurate unit-cell dimensions were determined by a least-squares fit of the 2θ values of 24 high-order reflections as measured on a Rigaku automated, four-circle, single-crystal diffractometer.

Crystal Data: $C_{25}H_{25}O_4PPd$, *F.W.*=527.4, triclinic, space group $P\bar{1}$, $a=10.433(2)$, $b=12.746(2)$, $c=10.224(2)$ Å, $\alpha=106.62(1)$, $\beta=112.41(2)$, $\gamma=75.13(2)°$, $U=1187.6(3)$ Å^3, $D_m=1.48$ g·cm^{-3} (by flotation in carbon tetrachloride/hexane), $Z=2$, $D_x=1.47$ g·cm^{-3}, $\mu=8.57$ cm^{-1} (Mo$K\alpha_1$, $\lambda=0.70926$ Å).

A crystal with approximate dimensions of $0.23\times0.35\times0.23$ mm was used. Data were collected at 20 °C on a Rigaku diffractometer, using graphite-monochromatized Mo$K\alpha$ radiation. All data within a 2θ sphere of 54° ($\sin\theta/\lambda=0.64$) were measured using the θ-2θ scan technique. The integrated intensity was determined by scanning over the peak at a rate of 4°/min and by subtracting the background obtained by averaging the two values measured for 5 s at both ends of a scan; the scan width of each reflection was: $\Delta\theta=1.0°+0.35°\tan\theta_c$, where θ_c is the calculated Bragg angle for λ(Mo$K\alpha_1$)$=0.70926$ Å. A total of 5207 reflections was collected, of which the number of independent, non-zero reflections was 4972. The intensities of three standard reflections (070, 444, and 500) were measured every 50 reflections; no intensity decrease in these reflections was observed during the experiment. Usual Lorentz and polarization corrections were made, but the absorption correction was ignored ($\mu=8.57$ cm^{-1} for Mo$K\alpha$).

Solution and Refinement of the Structure

The structure was established by the heavy-atom method. A three-dimensional Patterson function was computed and interpreted to give the coordinates of palladium and phosphorous atoms. The remaining non-hydrogen atoms were easily located on the successive Fourier maps.

The block-diagonal, unit weight, least-squares refinement was carried out using the HBLS-V program,[5)] the function minimized being $\sum(|F_o|-k\cdot|F_c|)^2$. Throughout the early stages of the refinement, the first set of data (4307 reflections of relatively lower

TABLE 1. FRACTIONAL ATOMIC COORDINATES (estimated standard deviations in parentheses)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	0.1305(1)	0.2160(1)	0.5227(1)	C(34)	0.2842(6)	0.1754(4)	1.1172(4)
P	0.0964(1)	0.3352(1)	0.7193(1)	C(35)	0.3593(5)	0.1619(4)	1.0276(5)
O(1)	−0.0646(2)	0.1712(2)	0.4537(2)	C(36)	0.3011(4)	0.2083(3)	0.9053(4)
O(2)	0.1732(2)	0.0987(2)	0.3513(2)	H(1A)	0.232(5)	−0.079(4)	0.197(5)
O(3)	0·4547(3)	0.0876(2)	0.6478(3)	H(1B)	0.105(5)	−0.111(4)	0.107(5)
O(4)	0.4622(3)	0.1226(2)	0.4505(3)	H(1C)	0.159(6)	−0.024(5)	0.080(7)
C(1)	0.1596(5)	−0.0560(3)	0.1596(5)	H(3)	−0.077(4)	−0.033(3)	0.195(4)
C(2)	0.0968(4)	0.0271(3)	0.2663(3)	H(5A)	−0.291(5)	0.034(4)	0.246(5)
C(3)	−0.0340(4)	0.0188(3)	0.2643(4)	H(5B)	−0.305(5)	0.139(4)	0.339(5)
C(4)	−0.1077(3)	0.0904(3)	0.3539(4)	H(5C)	−0.250(7)	0.014(6)	0.380(7)
C(5)	−0.2498(4)	0.0709(4)	0.3356(5)	H(6A)	0.363(4)	0.294(4)	0.686(5)
C(6)	0.3272(3)	0.2564(3)	0.5825(4)	H(6B)	0.324(4)	0.306(3)	0.523(4)
C(7)	0.4199(3)	0.1508(3)	0.5562(4)	H(O3)	0.494(5)	0.024(4)	0.623(5)
C(11)	−0.0890(3)	0.3824(3)	0.6989(3)	H(12)	−0.091(4)	0.543(3)	0.714(4)
C(12)	−0.1516(4)	0.4928(3)	0.7012(4)	H(13)	−0.341(5)	0.605(4)	0.685(5)
C(13)	−0.2956(4)	0.5250(4)	0.6812(4)	H(14)	−0.473(5)	0.470(4)	0.647(5)
C(14)	−0.3757(4)	0.4459(4)	0.6572(4)	H(15)	−0.365(4)	0.289(3)	0.645(4)
C(15)	−0.3139(4)	0.3370(4)	0.6551(5)	H(16)	−0.133(4)	0.230(3)	0.674(4)
C(16)	−0.1731(4)	0·3045(3)	0.6755(4)	H(22)	0.133(3)	0.478(3)	0.571(3)
C(21)	0.1708(3)	0.4621(2)	0.7759(3)	H(23)	0.229(4)	0.638(4)	0.639(5)
C(22)	0.1682(4)	0.5113(3)	0.6697(4)	H(24)	0.319(4)	0.725(3)	0.880(4)
C(23)	0.2199(5)	0.6089(3)	0.7065(4)	H(25)	0.323(5)	0.638(4)	1.051(5)
C(24)	0.2768(6)	0.6574(4)	0.8506(5)	H(26)	0.237(4)	0.478(3)	0.998(4)
C(25)	0.2822(6)	0.6084(4)	0.9562(5)	H(32)	0.000(4)	0.336(3)	0.956(4)
C(26)	0.2280(5)	0.5113(3)	0.9197(4)	H(33)	0.106(4)	0.244(3)	1.147(4)
C(31)	0.1684(4)	0.2727(2)	0.8782(3)	H(34)	0.321(5)	0.148(4)	1.200(5)
C(32)	0.0939(4)	0.2868(3)	0.9712(4)	H(35)	0.449(5)	0.125(4)	1.034(5)
C(33)	0.1531(6)	0.2370(4)	1.0895(4)	H(36)	0.351(4)	0.197(3)	0.840(4)

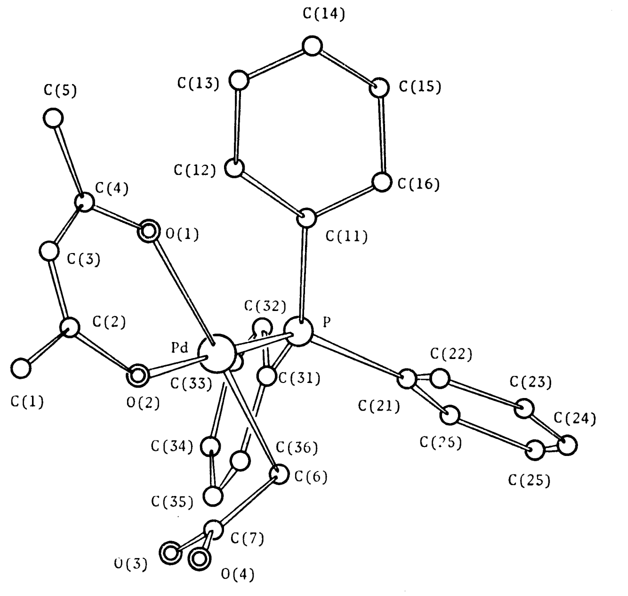


Fig. 1. Molecular structure of [(acac)(PPh$_3$)PdCH$_2$COOH] and numbering scheme of atoms.

diffraction angles) was used. After several cycles of isotropic refinement, $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o| =$ 0.068 for non-zero reflections. A further four cycles of refinement with anisotropic thermal parameters for all the non-hydrogen atoms reduced R_1 to 0.040. The difference synthesis could locate all the hydrogen atoms except the one attached to the carboxyl group; they were assigned to have equal thermal parameters, B=3.0 Å^2. The remaining 900 reflections were added to the first set of data. The difference Fourier map, computed after a few cycles of refinement, could locate the remaining hydrogen atom of the carboxyl group. Several cycles of refinement of all the atoms were carried out. The maximum shifts of the positional and thermal parameters for non-hydrogen atoms were about 0.14 σ and 0.08 σ respectively. The final R_1 is 0.032 ($R_2 = \{\Sigma||F_o|-|F_c||^2/\Sigma|F_o|^2\}^{1/2} = 0.041$) for 4972 non-zero reflections (R_1=0.037 for 5207 all reflections).

The atomic scattering factors used in all the calculations were those of Hanson *et al.*[6] The final positional and thermal parameters, along with their estimated standard deviations, are listed in Tables 1 and 2.*

Description of the Structure

Molecular Structure. The molecular structure of [(acac)(PPh$_3$)PdCH$_2$COOH] is shown in Fig. 1, which also indicates the numbering scheme. Figure 2 shows a stereoscopic view of the molecule, while the coordination geometry around the palladium atom is shown in

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* The Table of structure factors is kept as Document No. 7621 at the Chemical Society of Japan.

Table 2. Thermal parameters

a) Anisotropic thermal parameters ($\times 10^4$) expressed in the form: $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$ for non-hydrogen atoms (estimated standard deviations in parentheses)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	80.8(2)	48.8(1)	83.2(2)	−36.7(3)	57.2(4)	17.1(3)
P	84.3(8)	44.3(5)	74.5(8)	−34(1)	54(1)	20(1)
O(1)	92(3)	69(2)	121(3)	−61(3)	78(4)	−3(4)
O(2)	117(3)	72(2)	109(3)	−74(4)	106(5)	−20(4)
O(3)	131(3)	84(2)	133(3)	22(4)	123(5)	66(4)
O(4)	114(3)	87(2)	143(3)	−26(4)	144(5)	51(4)
C(1)	160(6)	75(3)	153(5)	−67(6)	160(9)	−39(6)
C(2)	121(4)	54(2)	97(4)	−40(5)	80(6)	17(4)
C(3)	121(4)	61(2)	125(4)	−76(5)	80(7)	−10(5)
C(4)	97(4)	60(2)	115(4)	−55(4)	55(6)	23(5)
C(5)	117(5)	100(4)	224(8)	−108(4)	133(10)	−38(8)
C(6)	87(3)	58(2)	136(4)	−41(4)	90(6)	18(5)
C(7)	74(3)	65(2)	117(4)	−44(4)	62(6)	23(5)
C(11)	92(3)	64(2)	80(3)	−36(4)	68(5)	15(4)
C(12)	105(4)	68(2)	110(4)	−23(5)	70(6)	30(5)
C(13)	108(4)	93(3)	149(5)	13(6)	78(8)	56(7)
C(14)	96(4)	129(4)	137(5)	−36(7)	76(8)	34(7)
C(15)	119(5)	110(4)	154(6)	−98(6)	115(8)	13(7)
C(16)	121(4)	75(3)	132(5)	−60(5)	123(7)	16(6)
C(21)	91(3)	49(2)	91(3)	−31(4)	63(5)	18(4)
C(22)	118(4)	60(2)	103(4)	−39(5)	60(6)	42(5)
C(23)	184(6)	69(3)	151(5)	−79(7)	114(9)	60(6)
C(24)	270(9)	76(3)	187(7)	−182(9)	147(13)	8(7)
C(25)	302(10)	112(4)	119(5)	−233(11)	118(12)	−37(7)
C(26)	193(6)	79(3)	96(4)	−126(7)	104(8)	−5(5)
C(31)	120(4)	48(2)	83(3)	−48(4)	44(6)	26(4)
C(32)	173(5)	71(3)	98(4)	−79(6)	102(8)	30(5)
C(33)	260(8)	87(3)	101(4)	−116(8)	131(10)	39(6)
C(34)	277(9)	83(3)	101(5)	−113(9)	26(10)	80(6)
C(35)	179(6)	89(3)	144(6)	−29(7)	4(10)	92(7)
C(36)	137(5)	78(3)	112(4)	−38(6)	50(7)	54(6)

b) Isotropic thermal parameters for hydrogen atoms (estimated standard deviations in parentheses)

Atom	B	Atom	B	Atom	B
H(1A)	4.9(12)	H(1B)	4.6(11)	H(1C)	7.8(16)
H(3)	2.6(8)	H(5A)	4.6(11)	H(5C)	4.6(11)
H(5C)	9.5(20)	H(6A)	3.3(9)	H(6B)	2.7(8)
H(O3)	5.2(12)	H(12)	1.7(7)	H(13)	3.6(10)
H(14)	4.4(11)	H(15)	3.1(9)	H(16)	1.9(7)
H(22)	0.6(6)	H(23)	3.4(9)	H(24)	2.7(9)
H(25)	5.0(12)	H(26)	2.3(8)	H(32)	2.7(9)
H(33)	3.1(9)	H(34)	3.8(10)	H(35)	3.8(10)
H(36)	1.9(12)				

Fig. 3. Tables 3 and 4 list the bond lengths and bond angles respectively. The least-squares best planes of several groups of atoms and the deviations of atoms from these planes are listed in Table 5.

The most remarkable feature of the overall molecular configuration is that the palladium atom is σ-bonded to the methylene group of acetic acid, as is to be expected from the IR and NMR studies.[2] A second feature is that this compound is dimeric, with intermolecular hydrogen bonding between carboxylic acid moieties. The palladium atom has a square-planar geometry established by one phosphorus, two enolate oxygen (O(1) and O(2)), and one carbon (C(6) in acetic acid) atoms; the mean and maximum deviations from the least-squares plane are 0.04 and 0.05 Å respectively.

The acetic acid moiety (C(6), C(7), O(3) and O(4)) is approximately planar, nearly perpendicular to the coordination plane; the dihedral angle between these planes is 88.5° (Fig. 3). The Pd–C(6)–C(7) angle (105.5(3)°) is slightly smaller than the tetrahedral

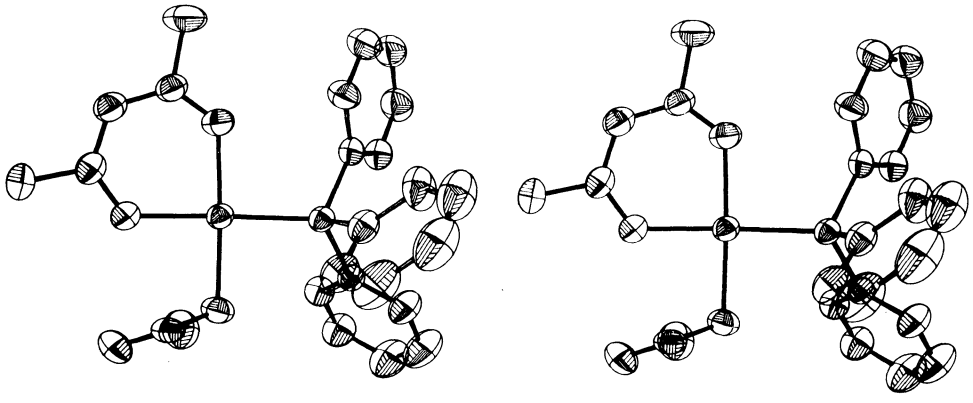

Fig. 2. Stereoscopic view of the molecule.

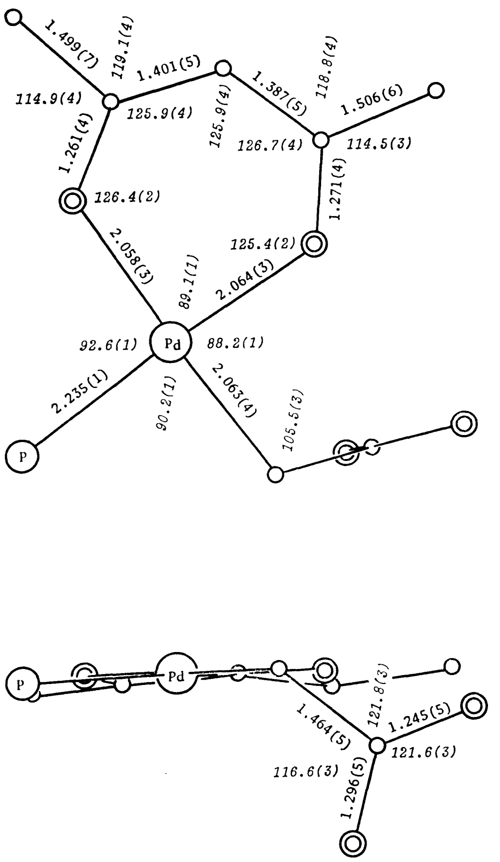

Fig. 3. The coordination geometry around the palladium atom.

TABLE 3. BOND LENGTHS (l/Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Pd-P	2.235(1)	Pd-O(1)	2.058(3)
Pd-O(2)	2.064(3)	Pd-C(6)	2.063(4)
P-C(11)	1.820(3)	P-C(21)	1.822(3)
P-C(31)	1.829(4)	O(1)-C(4)	1.261(4)
O(2)-C(2)	1.271(4)	O(3)-C(7)	1.296(5)
O(4)-C(7)	1.245(5)	C(1)-C(2)	1.506(6)
C(2)-C(3)	1.387(5)	C(3)-C(4)	1.401(5)
C(4)-C(5)	1.499(7)	C(6)-C(7)	1.464(5)
C(11)-C(12)	1.389(5)	C(12)-C(13)	1.402(6)
C(13)-C(14)	1.381(7)	C(14)-C(15)	1.370(7)
C(15)-C(16)	1.370(6)	C(16)-C(11)	1.401(5)
C(21)-C(22)	1.389(5)	C(22)-C(23)	1.379(6)
C(23)-C(24)	1.380(8)	C(24)-C(25)	1.371(9)
C(25)-C(26)	1.387(8)	C(26)-C(21)	1.381(6)
C(31)-C(32)	1.391(6)	C(32)-C(33)	1.385(7)
C(33)-C(34)	1.360(8)	C(34)-C(35)	1.368(8)
C(35)-C(36)	1.394(7)	C(36)-C(31)	1.385(6)
O(3)-H(O3)	0.83(5)	C(1)-H(1A)	0.73(5)
C(1)-H(1B)	0.93(5)	C(1)-H(1C)	1.01(7)
C(3)-H(3A)	0.88(4)	C(5)-H(5A)	0.89(5)
C(5)-H(5B)	0.90(5)	C(5)-H(5C)	0.96(8)
C(6)-H(6A)	1.00(5)	C(6)-H(6B)	0.99(4)
C(12)-H(12)	0.96(4)	C(13)-H(13)	1.01(5)
C(14)-H(14)	0.96(5)	C(15)-H(15)	0.87(5)
C(16)-H(16)	0.93(4)	C(22)-H(22)	0.94(3)
C(23)-H(23)	0.92(5)	C(24)-H(24)	0.99(4)
C(25)-H(25)	0.91(5)	C(26)-H(26)	0.97(4)
C(32)-H(32)	1.00(4)	C(33)-H(33)	0.87(5)
C(35)-H(34)	0.91(5)	C(35)-H(35)	0.92(5)
C(36)-H(36)	0.96(4)		

angle, and the acetic acid moiety is bent away from the triphenylphosphine ligand. The Pd–C(6) bond length is 2.063(4)Å, which is a normal value and which is in agreement with the sum of the covalent radii (2.07 Å). The carboxyl group is hydrogen-bonded to the carboxyl group of the adjacent molecule related by the center of symmetry. These hydrogen bonds are moderately strong. The hydrogen bond distance is O(3)–H···O(4)=2.621(4) Å (H···O(4)=1.81(5) Å), which is comparable with those found in the majority of the carboxylic acid dimers. The C–O bond lengths are unequal (C(7)–O(3) 1.296(5) and C(7)–O(4) 1.245(5) Å), as is normally observed in most of the carboxylic acid dimers and also in $[(\pi\text{-}C_5H_5)Mo(CO)_3CH_2\text{-}COOH]$.[7)]

The acetylacetonate ligand takes a typical enolate-type coordination; the bond lengths and bond angles have normal values, implying that the π-electrons are completely delocalized, as are those in other metal chelates of acetylacetone. This ligand is approximately

Table 4. Bond angles (φ/°) with estimated standard deviations in parentheses

P-Pd-O (1)	92.6(1)	P-Pd-C (6)	90.2(1)
O (1)-Pd-O (2)	89.1(1)	O (2)-Pd-C (6)	88.2(1)
Pd-C (6)-C (7)	105.5(3)	C (6)-C (7)-O (3)	116.6(3)
C (6)-C (7)-O (4)	121.8(3)	O (3)-C (7)-O (4)	121.6(3)
Pd-O (1)-C (4)	126.4(2)	Pd-O (2)-C (2)	125.4(2)
O (2)-C (2)-C (1)	114.5(3)	O (2)-C (2)-C (3)	126.7(4)
C (1)-C (2)-C (3)	118.8(4)	C (2)-C (3)-C (4)	125.9(4)
O (1)-C (4)-C (3)	125.9(4)	O (1)-C (4)-C (5)	114.9(4)
C (3)-C (4)-C (5)	119.1(4)		
Pd-P-C (11)	112.7(1)	Pd-P-C (21)	116.3(1)
Pd-P-C (31)	112.3(1)	C (11)-P-C (21)	104.8(2)
C (11)-P-C (31)	104.4(2)	C (21)-P-C (31)	105.3(2)
P-C (11)-C (12)	122.3(3)	P-C (11)-C (16)	119.2(3)
C (12)-C (11)-C (16)	118.5(3)	C (11)-C (12)-C (13)	120.4(4)
C (12)-C (13)-C (14)	119.6(4)	C (13)-C (14)-C (15)	120.0(5)
C (14)-C (15)-C (16)	121.0(4)	C (11)-C (16)-C (15)	120.5(4)
P-C (21)-C (22)	118.4(3)	P-C (21)-C (26)	122.4(3)
C (22)-C (21)-C (26)	119.1(4)	C (21)-C (22)-C (23)	120.8(4)
C (22)-C (23)-C (24)	119.6(5)	C (23)-C (24)-C (25)	120.1(6)
C (24)-C (25)-C (26)	120.6(6)	C (21)-C (26)-C (25)	119.8(5)
P-C (31)-C (32)	122.1(3)	P-C (31)-C (36)	118.5(3)
C (32)-C (31)-C (36)	119.3(4)	C (31)-C (32)-C (33)	119.8(4)
C (32)-C (33)-C (34)	120.8(5)	C (33)-C (34)-C (35)	120.0(6)
C (34)-C (35)-C (36)	120.5(5)	C (31)-C (36)-C (35)	119.5(4)

Table 5. Least-squares planes through various groups of atoms and the deviations (l/Å) of the atoms from the plane

Equation of the plane is of the form $AX+BY+CZ+D=0$, where X, Y, Z and D are measured in Å unit. (Atoms marked by * are not included in the least-squares calculation.)

(a) Coordination around Pd							
		$-0.0058X+0.8397Y-0.5430Z+1.2894=0$					
Pd	0.027	P	−0.050	O (1)	0.037	O (2)	−0.044
C (6)	0.034	C (1)*	−0.362	C (2)*	−0.212	C (3)*	−0.276
C (4)*	−0.130	C (5)*	−0.200	C (7)*	−0.886		
(b) Acetic acid moiety							
		$-0.7640X-0.3323Y-0.5530Z+5.1556=0$					
O (3)	0.001	O (4)	0.001	C (7)	−0.003	C (6)	0.001
Pd*	1.923						
(c) Acetylacetone moiety							
		$-0.3242X+0.7569Y-0.6528Z+1.7571=0$					
O (1)	−0.005	O (2)	0.005	C (1)	0.004	C (2)	0.001
C (3)	−0.017	C (4)	0.004	C (5)	0.008	Pd*	−0.170
(d) Phenyl ring 1 (C (11)-C (16))							
		$0.1603X+0.0513Y-0.9857Z+6.5805=0$					
C (11)	0.002	C (12)	0.005	C (13)	−0.003	C (14)	0.002
C (15)	0.00	C (16)	−0.002	P*	0.056		
(e) Phenyl ring 2 (C (21)-C (26))							
		$0.8373X-0.5468Y+0.0062Z+1.9984=0$					
C (21)	0.002	C (22)	0.007	C (23)	−0.008	C (24)	0.002
C (25)	0.006	C (26)	−0.008	P*	−0.022		
(f) Phenyl ring 3 (C (31)-C (36))							
		$-0.4242X-0.7203Y-0.5489Z+5.2825=0$					
C (31)	−0.005	C (32)	−0.005	C (33)	0.006	C (34)	0.003
C (35)	−0.012	C (36)	0.013	P*	−0.011		

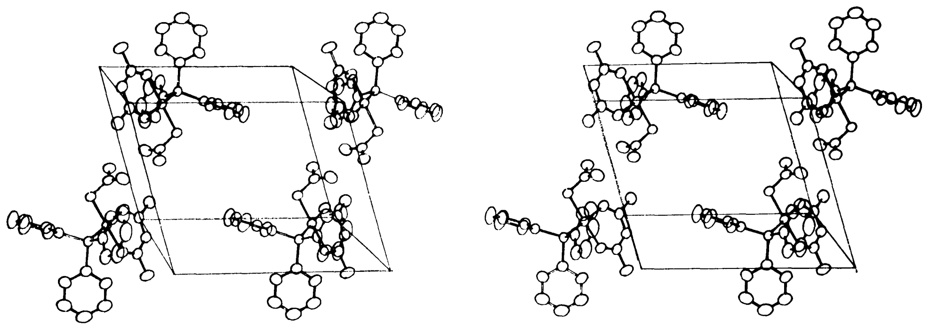

Fig. 4. Stereo drawing of the molecular packing in the unit cell.

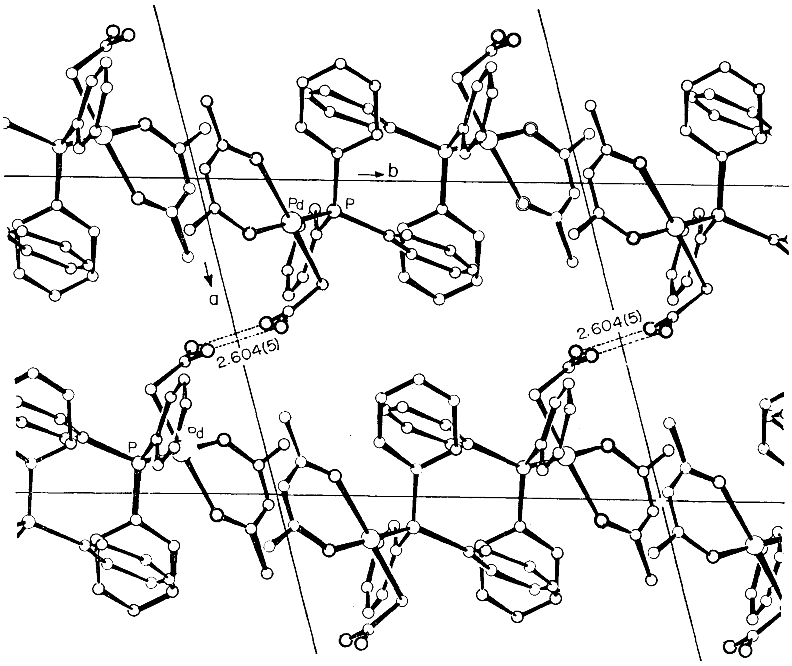

Fig. 5. Crystal structure projected along the c axis. Hydrogen bonds are shown by dotted lines.

TABLE 6. INTERMOLECULAR ATOMIC CONTACTS WITHIN 3.5Å

O(3)···O(4)[a]	2.621(4) Å	(Hydrogen bond)	
O(3)···C(7)[a]	3.422(5)		
O(3)···O(3)[a]	3.499(6)	Code for superscript	
O(4)···C(7)[a]	3.374(5)	a)	$1-x, -y, 1-z$
C(12)···C(33)[b]	3.496(7)	b)	$-x, 1-y, 2-z$
O(3)···C(5)[c]	3.373(6)	c)	$-x, -y, 1-z$
O(1)···C(23)[d]	3.381(6)	d)	$-x, 1-y, 1-z$

planar, and has a pseudo-symmetry of C_{2v} with the unique direction along the Pd–C(3) axis. The dihedral angle between the least-squares planes of this ligand and the coordination plane is 8.0 °. Two Pd–O bond lengths are approximately equal, 2.058(3) and 2.064(3) Å; they are also equal, within the limits of error, to those found in [Pd(acac)$_2$(PPh$_3$)] (2.048(10) and 2.062(10) Å).[4]

The Pd–P bond length is 2.235(1) Å, which is close to those in [Pd($C_2H_2O_2$)(PPh$_3$)(py)][2,8] (2.232(3) Å) and [Pd(acac)$_2$(PPh$_3$)][4] (2.258(4) Å). However, the values are different from those in [Pd($C_4H_4O_3$)(PPh$_3$)$_2$][2,9] (2.320(2) and 2.349(2) Å). The bond angles around the phosphorus atom are much distorted from the tetrahedral angle. Similar distortions are generally observed in triphenylphosphine complexes.

Crystal Structure. Figure 4 shows a stereoscopic view of the molecular packing along the c axis. In Fig. 5, the crystal structure projected along the same c axis is given; the intermolecular hydrogen bonds being shown by the dotted lines. The crystal is composed of hydrogen-bonded dimers related by the center of symmetry. Intermolecular atomic short contacts within 3.5 Å are listed in Table 6; some of them are slightly shorter than the usual van der Waals distances.

Computations throughout the present study were carried out on a NEAC 2200-700 computer at Osaka University. Figures 2 and 4 were drawn on a NUMERICON 7000 system at Osaka University with a local version of ORTEP.[10]

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