The Crystal and Molecular Structure of Oxydi(carboxymethyl)bis-(triphenylphosphine)palladium(II), [Pd($C_4H_4O_3$)(PPh_3)$_2$]

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The molecular structure of oxydi(carboxymethyl)bis(triphenylphosphine)palladium(II), [Pd($C_4H_4O_3$)(PPh_3)$_2$] has been determined by means of X-ray diffraction. The crystal belongs to the orthorhombic system, space group $P2_12_12_1$, with four formula units in a cell with dimensions of $a=16.320(2)$, $b=20.104(2)$, and $c=10.271(2)$ Å. $R=0.058$ for 4732 non-zero relfections. The feature of the structure is that the palladium atom is chelated by an acetic anhydride to form a six-membered ring [Pd–C=2.141(13) and 2.124(11) Å], and the palladium atom has a square-planar geometry.

Interesting studies on the synthesis and reactivity of a series of organopalladium complexes with the palladium–carbon σ-bond have been reported.[1–4] Stimulated by the stereochemical interests, X-ray molecular structures of [Pd($C_4H_4O_3$)(PPh_3)$_2$], [Pd($C_2H_2O_2$)(PPh_3)(py)],[2] [Pd(acac)$_2$(PPh_3)$_2$],[5] [Pd($C_6H_9O_3$)$_2$(MePy)$_2$][4], [PdCl($CH_2COCH_2COOCH_2Ph$)(Py)$_2$],[6] and [Pd(CH_2COOH)(acac)(PPh_3)][7] have been determined. This paper deals with the structure of [Pd($C_4H_4O_3$)(PPh_3)$_2$], of which preriminary result has been reported briefly.[2]

Experimental

Pale yellow, polyhedral crystal of [Pd($C_4H_4O_3$)(PPh_3)$_2$] were kindly supplied by Professor S. Kawaguchi and his co-workers of the Osaka City University. Preliminary X-ray work showed that the crystals belong to the orthorhombic system and that the space group is $P2_12_12_1$ (No. 16, absent reflections, $h00$; $h=2n+1$, $0k0$; $k=2n+1$, and $00l$; $l=2n+1$). Accurate unit-cell dimensions were determined by a least-squares fit using 2θ values of 20 strong reflections measured on a Rigaku automated, four-circle, single crystal diffractometer.

Crystal Data: $C_{40}H_{34}O_3P_2Pd$, *F. W.*=731.1, orthorhombic, space group, $P2_12_12_1$, $a=16.320(2)$, $b=20.104(2)$, $c=10.271(2)$ Å. $U=3369.8(8)$ Å^3, $D_m=1.41$ g·cm^{-3} (by flotation in aqueous solution of zinc iodide), $Z=4$, $D_c=1.44$ g·cm^{-3}, Mo $K\alpha_1$ ($\lambda=0.70926$ Å).

For the intensity measurement, a crystal with approximate dimensions of $0.18\times0.25\times0.30$ mm was used. Data were collected on the Rigaku diffractometer using graphite monochromatized Mo $K\alpha$ radiation. All data within a 2θ sphere of 60° ($\sin\theta/\lambda=0.70$) were measured using the θ-2θ scan technique. The integrated intensity was determined by scanning over the peak at a rate of 2°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 $\Delta(2\theta)=(1.6+0.7\tan\theta_c)°$, where θ_c is the calcualated Bragg angle for Mo $K\alpha_1$ ($\lambda=0.70926$ Å). A total of 5482 independent reflections was collected, of which the number of non-zero reflections was 4732. The intensities of three standard reflections (060, 004, and 3,18,2) were measured periodically; no intensity decrease in these reflections was observed during the experiment. Usual Lorentz and polarization corrections were made, but the absorption correction was ignored ($\mu=6.73$ cm^{-1} for Mo $K\alpha$).

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

	x	y	z
Pd	0.09161(3)	0.02528(3)	0.08560(6)
P(1)	0.0590(1)	−0.0859(1)	0.0541(2)
P(2)	−0.0334(1)	0.0597(1)	0.1767(2)
O(1)	0.2499(4)	0.1201(4)	−0.0230(10)
O(2)	0.3246(4)	0.0560(4)	0.1071(12)
O(3)	0.1476(5)	0.1845(3)	−0.0905(10)
C(1)	0.2087(5)	0.0054(5)	−0.0002(13)
C(2)	0.2664(5)	0.0583(5)	0.0371(12)
C(3)	0.1718(6)	0.1461(4)	−0.0095(13)
C(4)	0.1307(6)	0.1251(4)	0.1122(11)
C(11)	−0.0070(4)	−0.0959(4)	−0.0873(8)
C(12)	−0.0280(6)	−0.0391(5)	−0.1571(8)
C(13)	−0.0803(7)	−0.0434(6)	−0.2667(10)
C(14)	−0.1110(6)	−0.1075(7)	−0.3024(10)
C(15)	−0.0865(7)	−0.1646(6)	−0.2343(10)
C(16)	−0.0365(5)	−0.1594(5)	−0.1277(8)
C(21)	0.1424(4)	−0.1453(4)	0.0208(8)
C(22)	0.1677(5)	−0.1567(5)	−0.1078(9)
C(23)	0.2321(7)	−0.2006(5)	−0.1293(11)
C(24)	0.2686(7)	−0.2344(6)	−0.0270(13)
C(25)	0.2453(8)	−0.2206(7)	0.0971(14)
C(26)	0.1805(6)	−0.1774(6)	0.1223(10)
C(31)	0.0117(5)	−0.1241(4)	0.1970(7)
C(32)	−0.0557(5)	−0.1679(4)	0.1883(9)
C(33)	−0.0833(6)	−0.1996(4)	0.3011(9)
C(34)	−0.0460(6)	−0.1886(4)	0.4201(10)
C(35)	0.0198(5)	−0.1436(5)	0.4275(8)
C(36)	0.0475(5)	−0.1110(4)	0.3171(8)
C(41)	−0.1198(5)	0.0028(4)	0.2028(8)
C(42)	−0.1659(5)	−0.0182(4)	0.0939(10)
C(43)	−0.2320(5)	−0.0611(5)	0.1077(11)
C(44)	−0.2523(5)	−0.0839(5)	0.2326(12)
C(45)	−0.2080(6)	−0.0645(5)	0.3386(11)
C(46)	−0.1404(5)	−0.0206(5)	0.3277(8)
C(51)	−0.0135(5)	0.0945(4)	0.3383(8)
C(52)	0.0507(6)	0.0667(5)	0.4079(11)
C(53)	0.0658(7)	0.0884(6)	0.5372(11)
C(54)	0.0208(7)	0.1383(5)	0.5928(12)
C(55)	−0.0426(8)	0.1664(6)	0.5221(11)
C(56)	−0.0599(6)	0.1453(5)	0.3933(11)
C(61)	−0.0856(5)	0.1256(3)	0.0855(8)
C(62)	−0.1625(5)	0.1492(5)	0.1224(9)
C(63)	−0.1980(6)	0.2026(5)	0.0582(10)
C(64)	−0.1596(7)	0.2299(5)	−0.0502(11)
C(65)	−0.0858(7)	0.2036(4)	−0.0946(10)
C(66)	−0.0490(6)	0.1519(4)	−0.0263(9)

Solution and Refinement of the Structure

The structure was solved by the heavy atom method. The palladium and two phosphorus atoms were located from a three-dimensional Patterson function. All the remaining non-hydrogen atoms were located by successive Fourier syntheses. The structure was refined by the block-diagonal least-squares procedure. The HBLS V program[8] was used, the function minimized being $(|F_o|-k|F_c|)^2$, where k is a single scale factor. Several cycles of isotropic refinement reduced the R_1 factor ($R_1=\sum||F_o|-|F_c||/\sum|F_o|$) to 0.092 for non-zero reflections, and no abnormal thermal parameter was observed. Anisotropic thermal parameters were introduced for palladium and phosphorus atoms for several cycles of refinement, and then for all the non-hydrogen atoms. The difference synthesis, based on the final atomic parameters, did not reveal any hydrogen atoms. Finally,

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)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	21.6(1)	12.8(1)	84.5(5)	−2.8(3)	11.1(6)	−8.0(5)
P(1)	21.0(5)	11.6(4)	61(2)	−2.1(8)	2(2)	−2(1)
P(2)	22.3(6)	14.2(4)	65(2)	3.5(9)	5(2)	−3(2)
O(1)	36(3)	25(2)	284(16)	−13(4)	82(12)	2(9)
O(2)	31(3)	44(3)	304(18)	−4(5)	−32(13)	−59(13)
O(3)	63(4)	25(2)	204(12)	−4(4)	63(14)	46(9)
C(1)	27(3)	22(2)	231(18)	−20(4)	83(13)	−66(11)
C(2)	26(3)	23(2)	202(18)	−3(5)	64(13)	−5(11)
C(3)	33(4)	16(2)	201(17)	−18(4)	54(13)	−12(10)
C(4)	37(3)	14(2)	154(14)	−11(4)	22(12)	−29(8)
C(11)	23(2)	19(2)	59(6)	0(3)	−1(8)	−1(7)
C(12)	44(4)	30(3)	65(8)	17(6)	−5(9)	7(8)
C(13)	47(5)	45(4)	90(10)	30(7)	−13(12)	7(10)
C(14)	37(4)	56(5)	92(10)	−5(7)	−34(11)	−37(12)
C(15)	42(4)	41(3)	88(9)	−35(7)	6(12)	−21(10)
C(16)	31(3)	26(2)	76(8)	−14(5)	4(9)	−13(7)
C(21)	21(2)	14(2)	82(8)	4(3)	10(7)	−2(6)
C(22)	31(3)	28(2)	81(9)	1(5)	16(9)	−12(8)
C(23)	41(4)	32(3)	125(13)	5(6)	23(12)	−34(10)
C(24)	54(5)	39(4)	162(17)	55(8)	24(16)	−8(14)
C(25)	61(6)	57(5)	142(14)	86(9)	41(18)	59(16)
C(26)	42(4)	38(3)	102(11)	41(6)	−3(11)	4(10)
C(31)	27(3)	14(2)	61(7)	2(3)	0(7)	1(5)
C(32)	31(3)	17(2)	94(9)	−8(4)	−3(9)	−2(7)
C(33)	38(4)	18(2)	110(10)	−13(5)	5(11)	15(7)
C(34)	43(4)	21(2)	95(9)	4(5)	19(12)	18(9)
C(35)	36(3)	28(2)	62(7)	5(5)	−3(9)	15(8)
C(36)	29(3)	20(2)	76(8)	5(4)	−4(8)	−36(7)
C(41)	25(3)	14(2)	85(8)	11(3)	2(8)	−3(6)
C(42)	25(2)	23(2)	109(9)	−0(4)	−3(9)	11(9)
C(43)	31(3)	23(2)	142(13)	−2(5)	−13(11)	13(10)
C(44)	29(3)	22(2)	173(15)	−1(5)	20(12)	21(10)
C(45)	37(4)	25(3)	122(12)	2(5)	36(11)	30(9)
C(46)	31(3)	20(2)	93(8)	8(5)	28(9)	28(8)
C(51)	27(3)	18(2)	83(8)	−0(4)	−2(8)	−13(7)
C(52)	48(4)	33(3)	96(10)	26(6)	−20(13)	−50(10)
C(53)	60(6)	39(4)	108(11)	20(8)	−61(14)	−32(11)
C(54)	51(5)	32(3)	107(11)	1(6)	−1(14)	−30(11)
C(55)	62(6)	33(3)	112(12)	2(7)	6(15)	−59(11)
C(56)	37(4)	27(3)	127(12)	11(5)	4(12)	−51(10)
C(61)	30(3)	15(1)	72(6)	−2(4)	16(10)	5(6)
C(62)	32(3)	23(2)	99(10)	12(5)	−0(10)	10(8)
C(63)	45(4)	23(2)	105(11)	24(5)	−35(11)	−3(8)
C(64)	57(5)	21(2)	128(13)	9(6)	−36(14)	−4(9)
C(65)	57(4)	21(2)	85(8)	1(6)	−7(14)	7(8)
C(66)	37(4)	17(2)	87(9)	−0(4)	2(10)	1(7)

Table 3. Bond lengths and bond angles (estimated standard deviations in parentheses)

Bond lengths [l/Å]			
Pd–P(1)	2.320(2)	Pd–P(2)	2.349(2)
P(1)–C(11)	1.818(8)	P(1)–C(21)	1.844(8)
P(1)–C(31)	1.828(8)	P(2)–C(41)	1.836(8)
P(2)–C(51)	1.830(9)	P(2)–C(61)	1.832(9)
Pd–C(1)	2.141(13)	Pd–C(4)	2.124(11)
C(1)–C(2)	1.473(18)	C(3)–C(4)	1.479(17)
C(2)–O(2)	1.192(18)	C(3)–O(3)	1.202(17)
C(2)–O(1)	1.412(16)	C(3)–O(1)	1.386(17)
C(11)–C(12)	1.390(13)	C(12)–C(13)	1.415(16)
C(13)–C(14)	1.432(18)	C(14)–C(15)	1.403(18)
C(15)–C(16)	1.369(14)	C(16)–C(11)	1.426(12)
C(21)–C(22)	1.404(12)	C(22)–C(23)	1.390(15)
C(23)–C(24)	1.387(18)	C(24)–C(25)	1.359(20)
C(25)–C(26)	1.394(18)	C(26)–C(21)	1.375(14)
C(31)–C(32)	1.412(12)	C(32)–C(33)	1.397(13)
C(33)–C(34)	1.382(14)	C(34)–C(35)	1.406(14)
C(35)–C(36)	1.387(12)	C(36)–C(31)	1.390(11)
C(41)–C(42)	1.413(13)	C(42)–C(43)	1.387(15)
C(43)–C(44)	1.402(17)	C(44)–C(45)	1.365(16)
C(45)–C(46)	1.416(14)	C(46)–C(41)	1.408(12)
C(51)–C(52)	1.386(14)	C(52)–C(53)	1.421(16)
C(53)–C(54)	1.367(17)	C(54)–C(55)	1.385(17)
C(55)–C(56)	1.418(17)	C(56)–C(51)	1.392(14)
C(61)–C(62)	1.394(13)	C(62)–C(63)	1.388(14)
C(63)–C(64)	1.390(15)	C(64)–C(65)	1.392(16)
C(65)–C(66)	1.390(14)	C(66)–C(61)	1.399(12)
Bond angles [ϕ/°]			
P(1)–Pd–P(2)	98.05(7)	P(1)–Pd–C(1)	88.1(4)
P(2)–Pd–C(4)	86.0(3)	C(1)–Pd–C(4)	87.8(5)
C(2)–O(1)–C(3)	117.6(11)	Pd–C(1)–C(2)	109.2(9)
C(1)–C(2)–O(1)	113.6(11)	C(1)–C(2)–O(2)	129.6(13)
O(1)–C(2)–O(2)	116.8(12)	C(4)–C(3)–O(1)	113.2(11)
C(4)–C(3)–O(3)	128.3(12)	O(1)–C(3)–O(3)	118.3(12)
Pd–C(4)–C(3)	107.3(8)		
Pd–P(1)–C(11)	110.8(3)	Pd–P(1)–C(21)	118.7(3)
Pd–P(1)–C(31)	113.0(3)	C(11)–P(1)–C(21)	102.5(4)
C(11)–P(1)–C(31)	110.2(4)	C(21)–P(1)–C(31)	100.8(4)
Pd–P(2)–C(41)	122.8(3)	Pd–P(2)–C(51)	108.6(3)
Pd–P(2)–C(61)	114.4(3)	C(41)–P(2)–C(51)	104.0(4)
C(41)–P(2)–C(61)	99.6(4)	C(51)–P(2)–C(61)	105.6(4)
P(1)–C(11)–C(12)	117.8(7)	P(1)–C(11)–C(16)	122.1(6)
C(12)–C(11)–C(16)	120.1(8)	C(11)–C(12)–C(13)	120.7(9)
C(12)–C(13)–C(14)	117.9(11)	C(13)–C(14)–C(15)	120.6(12)
C(14)–C(15)–C(16)	120.5(11)	C(11)–C(16)–C(15)	120.1(9)
P(1)–C(21)–C(22)	119.8(6)	P(1)–C(21)–C(26)	119.8(7)
C(22)–C(21)–C(26)	120.3(8)	C(21)–C(22)–C(23)	118.3(9)
C(22)–C(23)–C(24)	121.2(11)	C(23)–C(24)–C(25)	119.3(12)
C(24)–C(25)–C(26)	120.9(13)	C(21)–C(26)–C(25)	119.7(11)
P(1)–C(31)–C(32)	122.7(6)	P(1)–C(31)–C(36)	117.1(6)
C(32)–C(31)–C(36)	120.2(7)	C(31)–C(32)–C(33)	118.9(8)
C(32)–C(33)–C(34)	121.2(9)	C(33)–C(34)–C(35)	119.2(9)
C(34)–C(35)–C(36)	120.6(8)	C(31)–C(36)–C(35)	119.9(8)
P(2)–C(41)–C(42)	118.7(7)	P(2)–C(41)–C(46)	121.7(6)
C(42)–C(41)–C(46)	119.7(8)	C(41)–C(42)–C(43)	121.2(9)
C(42)–C(43)–C(44)	118.8(11)	C(43)–C(44)–C(45)	120.7(11)
C(44)–C(45)–C(46)	121.9(10)	C(41)–C(46)–C(45)	117.8(8)
P(2)–C(51)–C(52)	116.6(7)	P(2)–C(51)–C(56)	123.5(7)
C(52)–C(51)–C(56)	119.8(9)	C(51)–C(52)–C(53)	119.4(10)
C(52)–C(53)–C(54)	121.4(11)	C(53)–C(54)–C(55)	118.9(11)
C(54)–C(55)–C(56)	121.0(11)	C(51)–C(56)–C(55)	119.4(10)
P(2)–C(61)–C(62)	121.7(7)	P(2)–C(61)–C(66)	119.6(6)
C(62)–C(61)–C(66)	118.6(8)	C(61)–C(62)–C(63)	120.7(9)
C(62)–C(63)–C(64)	119.8(10)	C(63)–C(64)–C(65)	120.2(10)
C(64)–C(65)–C(66)	119.6(10)	C(61)–C(66)–C(65)	120.8(9)

TABLE 4. 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; $X=ax$, $Y=by$, and $Z=cz$.
(Atoms marked by * are not included in the least-squares calulation.)

(a)	Coordination plane						
	$-0.3546X+0.2240Y-0.9078Z+1.2106=0$						
	Pd	−0.004	P(1)	−0.021	P(2)	0.026	C(1)	0.029
	C(4)	−0.027	C(2)*	−0.414	C(3)*	0.963	O(1)*	0.520
(b)	Plane defined by C(1), C(2), O(1), and O(2)						
	$-0.5838X+0.2492Y+0.7727Z+1.9597=0$						
	C(1)	−0.003	C(2)	0.009	O(1)	−0.003	O(2)	−0.004
(c)	Plane defined by C(3), C(4), O(1), and O(3)						
	$-0.3942X-0.7739Y-0.4956Z+3.3519=0$						
	C(3)	0.022	C(4)	−0.007	O(1)	−0.007	O(3)	−0.009
(d)	Phenyl ring 1 (C(11)—C(16))						
	$-0.4947X+0.1173Y+0.5956Z+0.6837=0$						
	C(11)	0.013	C(12)	−0.006	C(13)	−0.009	C(14)	0.020
	C(15)	−0.016	C(16)	−0.001	P(1)*	0.048		
(e)	Phenyl ring 2 (C(21)—C(26))						
	$0.6570X+0.7505Y+0.0714Z+0.6470=0$						
	C(21)	−0.004	C(22)	0.003	C(23)	0.015	C(24)	−0.030
	C(25)	0.021	C(26)	−0.004	P(1)*	0.023		
(f)	Phenyl ring 3 (C(31)—C(36))						
	$-0.6369X+0.7527Y+0.1666Z+1.6461=0$						
	C(31)	−0.017	C(32)	0.007	C(33)	0.007	C(34)	−0.010
	C(35)	−0.001	C(36)	0.015	P(1)*	−0.173		
(g)	Phenyl ring 4 (C(41)—C(46))						
	$0.6120X-0.7812Y-0.1232Z+1.4936=0$						
	C(41)	−0.004	C(42)	0.017	C(43)	−0.012	C(44)	0.001
	C(45)	0.003	C(46)	0.001	P(2)*	−0.001		
(h)	Phenyl ring 5 (C(51)—C(56))						
	$0.6336X+0.6829Y-0.3636Z+0.1006=0$						
	C(51)	−0.004	C(52)	0.017	C(53)	−0.012	C(54)	0.001
	C(55)	−0.005	C(56)	0.007	P(2)*	−0.084		
(i)	Phenyl ring 6 (C(61)—C(66))						
	$-0.4768X-0.6575Y-0.5834Z+1.4762=0$						
	C(61)	−0.030	C(62)	0.035	C(63)	−0.010	C(64)	−0.020
	C(65)	0.020	C(66)	0.007	P(2)*	−0.112		

four cycles of refinement converged to $R_1=0.058$ ($R_2=0.070$) for 4732 non-zero reflections. The largest shifts in positional and thermal parameters were about 0.02σ and 0.3σ, respectively. The atomic scattering factors used in the calculations were those of Hanson and co-workers.[9] The final positional and thermal parameters are listed in Tables 1 and 2.**

Description of the Structure

Molecular Structure. The perspective view of the $[(Pd(C_3H_4O_3)(PPh_3)]$ molecule is given in Fig. 1, with numbering scheme of atoms. A stereoscopic drawing of the molecule and the coordination geometry around the palladium atom are given in Figs. 2 and 3, respectively. Bond lengths and bond angles are given in Table 3. Least-squares planes of various groups of atoms and

** The Table of observed and calculated structure factors are kept as Document No. 7820 at the Chemical Society of Japan.

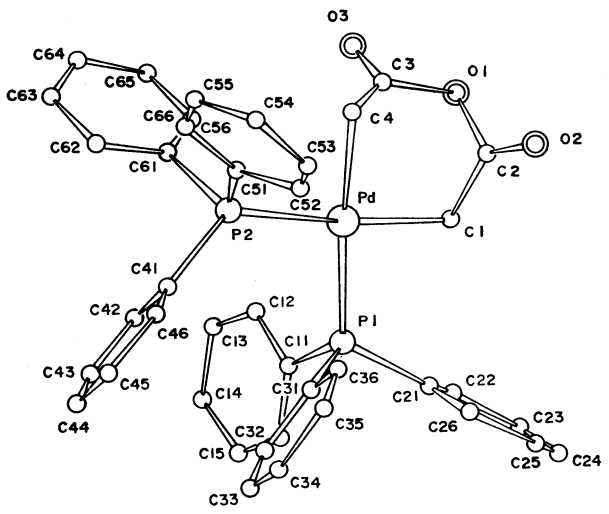

Fig. 1. Perspective view of the molecule with the numbering scheme of atoms.

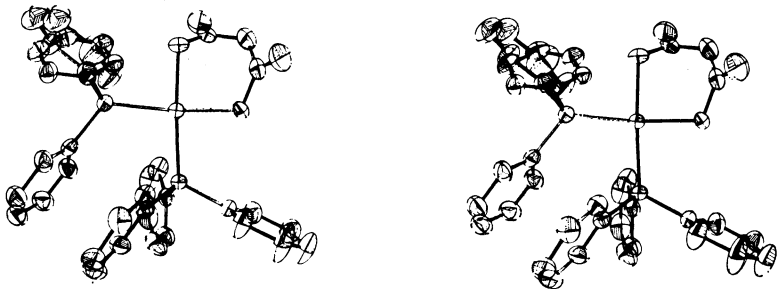

Fig. 2. A stereoscopic view of the molecule. Non-hydrogen atoms are represented by the thermal ellipsoids at 50% probability level.

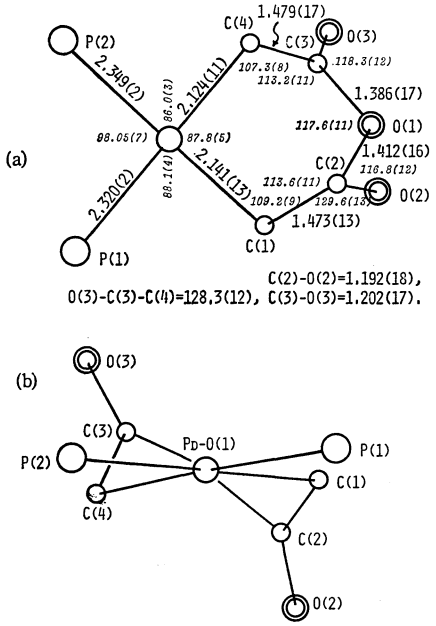

Fig. 3. The coordination geometry around the palladium atom. (a) Selected bond lengths [l/Å] and bond angles [ϕ/°]. (b) Viewed down along the Pd···O(1).

deviations of atoms from these planes are listed in Table 4.

The remarkable feature of the molecular structure is that this complex contains a carbon-bonded chelated ring of acetic anhydride (Fig. 1). The palladium atom has a square-planar geometry coordinated by two sp^3 carbon atoms (C(1) and C(4)) of the chelate ring and two phosphorus atoms: the mean and maximum deviations of atoms from the best plane being 0.023 and 0.029 Å.

The bond lengths between the palladium and two carbon atoms (C(1) and C(4)) are equal: 2.141(13) and 2.124(11) Å, which are longer ones of the Pd(II)–C-(sp^3) bonds.[6] The C(1)–Pd–C(4) angle [87.8(5)°] is slightly smaller than 90°.

The Pd–P bond lenghts [2.320(2) and 2.349(2) Å] are not equal, and these values are slightly longer than those of 2.232(3) Å in $[Pd(C_2H_2O_2)(PPh_3)(py)]$,[2] 2.235(1) Å in $[Pd(CH_2COOH)(acac)(PPh_3)]$,[7] and 2.258(4) Å in $[Pd(acac)_2(PPh_3)]$.[5] The P(1)–Pd–P(2) angle of 98.05(7)° is larger than 90° because of steric interaction between two triphenylphosphine ligands.

In the chelate ring of acetic anhydride, the C(1)–C(2) and C(3)–C(4) bond lenghts of 1.473(18) and 1.479(19) Å are compared with those ovserved in C–C=O moieties in many organic compounds [av 1.506(5) Å].[10] The C(2)=O(2) and C(3)=O(3) bond lengths are 1.192(18) and 1.202(17) Å, respectively, which are equal to those in aldehydes and ketones [av 1.215(5) Å],[10] and that in α-oxalic acid [1.207(1) Å].[11] The C(2)–O(1) and C(3)–O(1) bond lengths [1.412(16) and 1.386(17) Å] have intermediate values between those observed in saturated [av 1.426(5) Å] and conjugated heterocyclic C–O bonds [1.371(16) Å (in furan)].[12] The C(1)–C-(2)–O(1) and C(4)–C(3)–O(1) angles [113.6(11) and 113.2(11)°] are much smaller, whereas the C(1)–C(2)–O(2) and C(4)–C(3)–O(3) angles [129.6(13) and 128.3-(12)°] are much larger than 120°. However, the C(1), C(2), O(1), and O(2) atoms and C(3), C(4), O(1), and O(3) atoms respectively lie on a plane: the dihedral angles between these planes being 69.8°. The dihedral angles between these planes and the coordination plane are 64.0 and 65.4°, respectively: the O(2) and O(3) atoms being above and below the coordination plane

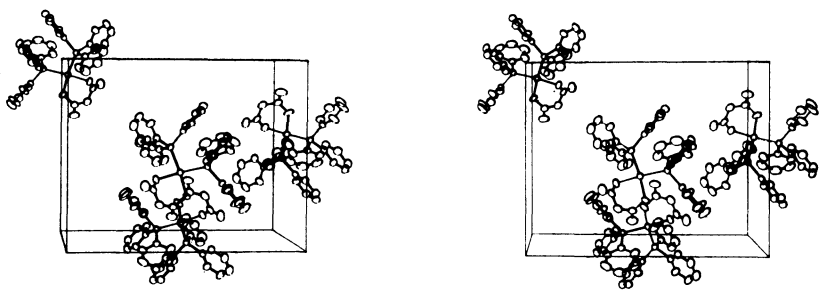

Fig. 4. A stereoscopic drawing of the molecular packing in the unit cell.

TABLE 5. INTERMOLECULAR ATOMIC CONSTANTS WITHIN 3.5 Å

O(2)–C(53)[a]	3.48(2) Å	Code for superscript
O(1)–C(64)[b]	3.44(2)	a) $0.5-x$, $-y$, $-0.5+z$
O(3)–C(63)[b]	3.41(2)	b) $0.5+x$, $0.5-y$, $-z$

(Fig. 3(b)). The Pd–C(1)–C(2) and Pd–C(4)–C(3) angles [109.2(9) and 107.3(8)°] have normal tetrahedral values.

Both phosphorus atoms show deviations from the tetrahedral geometry: the C(11)–P(1)–C(21) and C(21)–P(1)–C(31) [102.5(4), and 100.8(4)°] and C(41)–P(2)–C(51), C(41)–P(2)–C(61), and C(51)–P(2)–C(61) angles [104.0(4), 99.6(4), and 105.6(4)°] being much smaller, whereas Pd–P(1)–C(21) and Pd–P(1)–C(31) [118.7(3) and 113.0(3)°] and Pd–P(2)–C(41) angle [122.8(3) Å] being larger than the tetrahedral angle. Six phenyl rings attached to the phosphorus atoms heve normal structure [C–C (av)=1.395 Å and C–C–C (av)=120.0°].

Crystal Structure. Figure 4 shows a stereoscopic view of the molecular packing in the unit-cell along the c axis. The intermolecular atomic contacts less than 3.5 Å are listed in Table 5: no short interatomic distance being found.

Computations throughout the present study were carried out on a NEAC 2200-700 computer at the Osaka University. Figures 2 and 4 were drawn on the NUMERICON 7000 system at Osaka University with a local version of ORTEP.[13]

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