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THE CRYSTAL AND MOLECULAR STRUCTURE OF ACETYLACETONATO-ACETYLACETONYLTRIPHENYLPHOSPHINEPALLADIUM(II) BENZENE SOLVATE

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Summary

The molecular structure of acetylacetonatoacetylacetonyltriphenylphosphinepalladium(II) [Pd(acac)$_2$ (PPh$_3$)], has been determined by means of X-ray diffraction. The benzene solvate [Pd(acac)$_2$ (PPh$_3$)$\cdot$ 0.5 C_6H_6] forms yellow, monoclinic crystals; $a = 36.444(8)$, $b = 11.836(2)$, $c = 16.170(4)$ Å, and $\beta = 124.70(4)°$, space group $C2/c$ with $Z = 8$. The structure, solved by the conventional heavy-atom method, has been refined anisotropically by least-squares procedure to $R = 0.078$, for the 2806 independent non-zero reflections. The palladium atom takes a square-planar coordination. One of the acetylacetone ligands is bonded to the palladium via its oxygen atoms [Pd—O 2.048(10) and 2.062(10) Å] and the other by its γ-carbon atom [Pd—C 2.114(13) Å].

Introduction

Recently, Kawaguchi et al. of Osaka City University made an extensive study [1] of a series of palladium complexes as shown in Scheme 1. In cooperation with their studies, X-ray crystal structure determinations of complexes of II, IV, V and VII have been carried out. The molecular structures of IV and VII have been determined and communicated briefly [2]. The molecular structure of [Pt(O$_2$)(PPh$_3$)$_2$], the platinium analogue of III has also been determined [3, 4]. This paper describes the molecular structure of II. Interest in the coordination behavior of β-diketone derivatives to the palladium atom also promoted this study.

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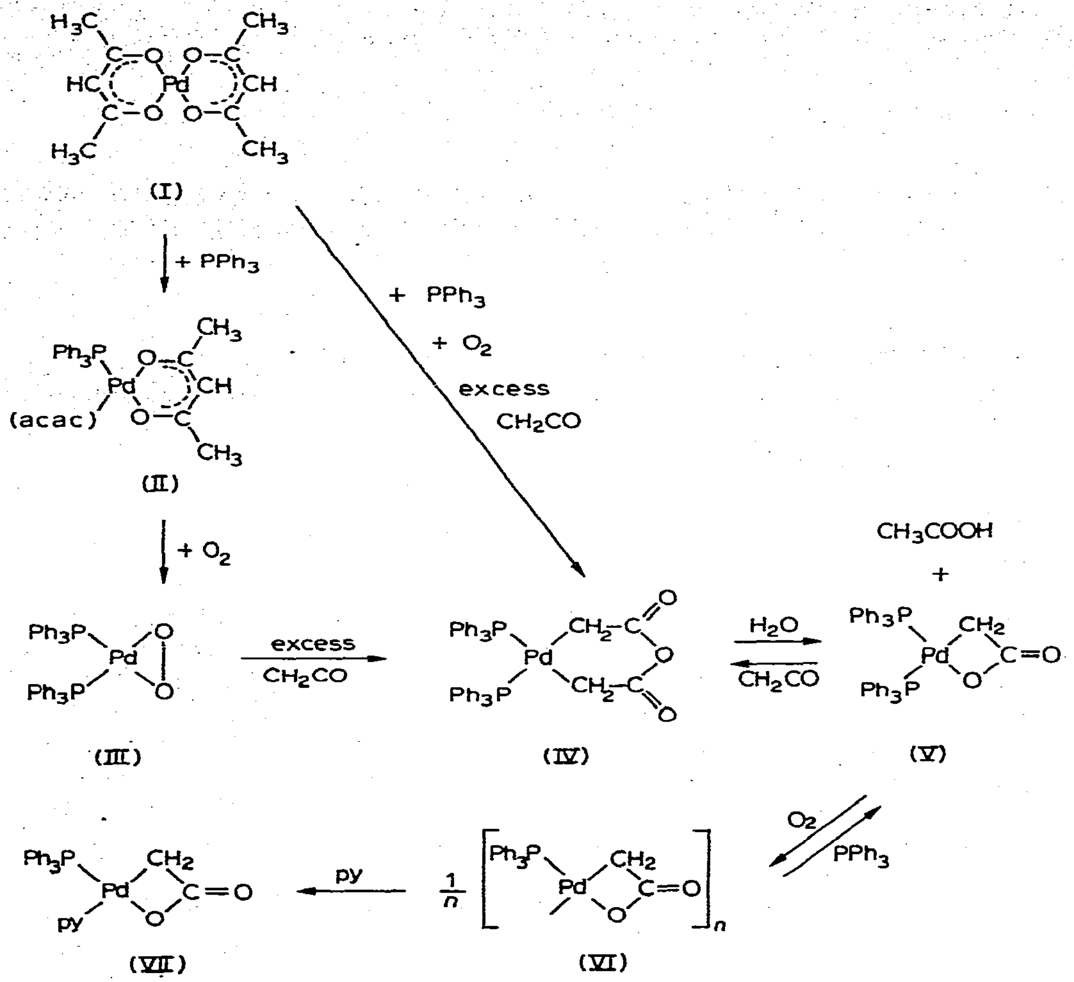
SCHEME 1



Experimental

Deep yellow, polyhedral, crystals of [Pd(acac)$_2$(PPh$_3$)·0.5 C$_6$H$_6$] were kindly supplied by Kawaguchi et al. Single crystals of suitable size and shape were recrystallized from benzene/petroleum ether solution. Preliminary Weissenberg photographs (Cu-K_α) showed that the crystals belong to the monoclinic system, and the corresponding space group is either $C2/c$ or Cc (absent reflections, hkl: $h + k = 2n + 1$, $h0l$: $l = 2n + 1$). The unit-cell dimensions were precisely determined by a least-squares refinement using 21 2θ values of higher order reflections, each of which was obtained as a difference of peak positions of hkl and $\bar{h}\bar{k}\bar{l}$, measured on a G.E. single crystal orienter equipped on a Rigaku SG-2 Goniometer (Mo-K_{α_1}, $\lambda = 0.70926$ Å).

Crystal data: $a = 36.444(8)$, $b = 11.836(2)$, $c = 16.170(4)$ Å and $\beta = 124.70(4)$, $U = 5734(2)$ Å^3, $D_m = 1.40$ g·cm^{-3} (by flotation in an aqueous solution of ZnBr$_2$ at 10°C), $Z = 8$, $D_c = 1.40$ g·cm^{-3}.

For the intensity measurement, a crystal of approximate dimensions of $0.13 \times 0.21 \times 0.15$ mm^3 was used. Data were collected at 20°C using a Rigaku automatic, four-circle, single crystal diffractometer. Zirconium-filtered Mo-K_{α_1} radiation was used. All data within a 2θ sphere of 42° ($(\sin\theta)/\lambda = 0.5053$) were measured using $\omega - 2\theta$ coupled scanning. The asymmetric scan range $\Delta(2\theta)$ of each reflection was computed by the equation: $\Delta(2\theta) = 2.0° + 0.7° \tan\theta_c$. The starting angle of the scan is $(2\theta_c - 1.0)°$, where, θ_c is the calculated value of the Bragg angle using λ(Mo-K_{α_1}) (= 0.70926 Å), and the scanning speed was 4.0°/min. Corrections for background scattering and usual Lorentz and polarization effects were applied on a computer attached to the diffractometer. A total of 3152 reflections was collected, of which the number of independent non-zero reflections was 2806. During the intensity data collection the crystal decomposed gradually, and the intensities of three standard reflections, 040, 004, and 800 fell down to about 75% of their initial values. As they decreased almost uniformly with time, a linear correction was applied. Absorption correction was ignored ($\mu = 7.2$ cm^{-1} for Mo-K_{α_1}).

Solution and refinement of the structure

Approximate positions of palladium and phosphorus atoms were located from a three-dimensional Patterson function, from which the space group was determined to be centrosymmetric $C2/c$. The coordinates of the other non-hydrogen atoms were determined by the successive use of Fourier syntheses. The block-diagonal, unit-weight, least-squares refinement with isotropic thermal parameters was carried out using HBLS-V program [17]. After three cycles of refinement ($R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0| = 0.12$), the difference electron density map showed the existence of a solvating benzene molecule lying on a crystallographic two-fold axis. Three cycles of refinement with anisotropic thermal parameters for all the non-hydrogen atoms followed by three cycles of isotropic refinement, including carbon atoms of the solvating benzene, reduced R_1 to 0.078. The maximum positional shift was less than 0.1 σ and $R_2 = (\Sigma||F_0|-|F_c||^2)/\Sigma|F_0|^2 = 0.081$. The final difference synthesis, based on the final atomic parameters, did not show all hydrogen atoms and also any significant features. An attempt to find the exact position of the hydrogen atom attached to the C(8) atom by the technique of LaPlaca and Ibers [5] was not fully successful. Throughout the refinement neutral atomic scattering factors were taken from those given by Hanson et al. [6]. As mentioned above, no weighting function other than unit weight was utilized, because the average $w(\Delta F)^2$ for subsets of reflections, calculated as a function of both the size of $|F_0|$ and $(\sin\theta)/\lambda$, did not deviate significantly from unity. The final values of positional and thermal parameters are listed in Tables 1 and 2, while the observed and calculated structure factors are available*.

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* The table of structure factors has been deposited as NAPS Document No. 02377 with ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th Street, New York, New York 10017. A copy may be secured by citing the document numbers and remitting $1.50 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 1

FINAL ATOMIC FRACTIONAL COORDINATES (ESTIMATED STANDARD DEVIATIONS IN PARENTHESES)

Atom	*x*	*y*	*z*
Pd	0.16150(3)	0.14239(8)	0.64247(6)
P	0.1102(1)	0.2218(3)	0.6607(2)
O(1)	0.2084(3)	0.0741(8)	0.6253(6)
O(2)	0.1362(3)	0.2391(9)	0.5149(6)
O(3)	0.1442(3)	−0.1143(10)	0.7100(8)
O(4)	0.2692(3)	0.0411(10)	0.8566(7)
C(1)	0.2520(5)	0.0391(16)	0.5636(11)
C(2)	0.2150(4)	0.1027(14)	0.5582(10)
C(3)	0.1910(4)	0.1843(14)	0.4850(10)
C(4)	0.1540(5)	0.2476(14)	0.4666(11)
C(5)	0.1323(6)	0.3337(19)	0.3827(14)
C(6)	0.2152(5)	−0.1502(16)	0.7440(12)
C(7)	0.1811(4)	−0.0756(13)	0.7400(9)
C(8)	0.1901(4)	0.0454(11)	0.7753(8)
C(9)	0.2364(4)	0.0900(12)	0.8388(9)
C(10)	0.2406(5)	0.2029(15)	0.8850(11)
C(11)	0.0532(4)	0.1778(12)	0.5628(9)
C(12)	0.0427(4)	0.1583(13)	0.4671(10)
C(13)	−0.0020(5)	0.1339(15)	0.3894(11)
C(14)	−0.0360(5)	0.1373(16)	0.4046(11)
C(15)	−0.0244(5)	0.1516(16)	0.5011(12)
C(16)	0.0203(5)	0.1752(14)	0.5817(11)
C(21)	0.1145(4)	0.2027(12)	0.7789(9)
C(22)	0.1054(4)	0.0947(13)	0.7988(9)
C(23)	0.1102(5)	0.0770(15)	0.8924(11)
C(24)	0.1237(5)	0.1662(16)	0.9584(12)
C(25)	0.1341(5)	0.2706(15)	0.9406(11)
C(26)	0.1286(4)	0.2925(13)	0.8461(9)
C(31)	0.1086(4)	0.3756(11)	0.6464(8)
C(32)	0.0716(4)	0.4370(12)	0.6262(9)
C(33)	0.0724(5)	0.5563(14)	0.6218(11)
C(34)	0.1088(4)	0.6107(14)	0.6347(10)
C(35)	0.1458(5)	0.5478(14)	0.6552(10)
C(36)	0.1455(4)	0.4286(12)	0.6609(9)
C(41)	0.0260(7)	0.5352(21)	0.8385(15)
C(42)	0.0270(6)	0.4178(19)	0.8380(14)
C(43)	0.0	0.5906(23)	0.75
C(44)	0.0	0.3597(28)	0.75

Results and discussion

A perspective view and the numbering system of the molecule including crystalline benzene are shown in Fig. 1. An ORTEP drawing of the molecule is given in Fig. 2. Figure 3 shows the geometry around the palladium atom and the structure of the acetylacetonate ligands.

The remarkable feature of the structure is that one of the acetylacetonate ligands coordinates to the palladium atom by its γ-carbon atom whereas the other takes the usual enolate chelate type coordination, which is expected from spectroscopic studies [1]. The palladium atom is, therefore, four-coordinate, and a square-planar geometry is established by a phosphorus, two enolate oxygen (O(1) and O(2)) and the γ-carbon (C(8)) atoms. The mean and maximum deviations from the least-squares plane are 0.009 and 0.020 Å (Pd), respectively. (Table 3). The distortion of the coordination plane is slight, making the geo-

TABLE 2

FINAL ANISOTROPIC THERMAL PARAMETERS (X 10^4) EXPRESSED IN THE FORM $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$ (STANDARD DEVIATIONS IN PARENTHESES)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	9.9(1)	64.1(7)	45.0(5)	2.5(5)	25.7(4)	4(1)
P	8.2(4)	49(2)	47(2)	−2(2)	24(1)	−5(4)
O(1)	15(1)	70(7)	65(6)	18(5)	40(5)	25(11)
O(2)	15(1)	107(9)	65(6)	23(5)	46(5)	48(12)
O(3)	17(1)	79(9)	112(8)	−22(6)	47(6)	−31(13)
O(4)	11(1)	171(13)	90(8)	−3(6)	29(5)	−56(16)
C(1)	19(2)	141(18)	92(12)	40(11)	64(9)	27(24)
C(2)	16(2)	96(13)	60(9)	−27(8)	46(8)	−21(18)
C(3)	16(2)	94(13)	48(8)	9(8)	38(7)	13(17)
C(4)	17(2)	109(14)	59(9)	4(9)	47(8)	−7(19)
C(5)	25(3)	222(27)	127(16)	72(15)	82(13)	232(35)
C(6)	18(2)	58(11)	116(13)	14(9)	57(10)	−2(21)
C(7)	13(2)	69(11)	41(8)	−13(7)	22(6)	20(15)
C(8)	8(1)	46(9)	43(7)	−2(6)	22(5)	23(13)
C(9)	8(2)	114(14)	46(8)	−9(7)	24(6)	−7(17)
C(10)	18(2)	104(14)	75(11)	−23(9)	45(8)	−78(21)
C(11)	7(1)	40(9)	64(9)	−9(6)	16(6)	5(14)
C(12)	11(2)	105(14)	52(9)	−16(8)	17(7)	−27(18)
C(13)	12(2)	114(16)	83(11)	−1(9)	19(8)	−70(22)
C(14)	12(2)	71(12)	100(12)	18(8)	17(8)	−15(21)
C(15)	15(2)	64(12)	115(13)	−13(8)	39(9)	−8(21)
C(16)	9(2)	86(13)	88(11)	−3(7)	29(7)	0(19)
C(21)	6(1)	80(11)	59(8)	−2(7)	21(6)	−33(16)
C(22)	9(2)	100(13)	61(9)	7(7)	28(6)	36(18)
C(23)	15(2)	113(15)	91(12)	37(9)	51(9)	72(22)
C(24)	17(2)	127(17)	97(12)	26(10)	55(9)	62(24)
C(25)	13(2)	171(20)	66(10)	16(10)	27(8)	−22(24)
C(26)	7(1)	147(16)	34(8)	4(8)	12(7)	−27(18)
C(31)	9(1)	48(9)	38(7)	2(6)	19(5)	−9(13)
C(32)	10(2)	72(11)	55(8)	2(7)	22(6)	21(16)
C(33)	18(2)	58(11)	63(9)	8(8)	35(8)	10(17)
C(34)	14(2)	105(14)	66(9)	−16(9)	39(8)	5(19)
C(35)	14(2)	82(13)	74(10)	−11(8)	38(8)	−25(18)
C(36)	10(2)	69(11)	53(8)	−13(7)	33(6)	−10(15)
C(41)	24(3)	251(31)	123(17)	−41(17)	69(13)	−63(38)
C(42)	25(3)	252(29)	125(16)	85(16)	87(13)	156(36)
C(43)	33(6)	121(27)	169(29)	0	104(23)	0
C(44)	44(7)	203(38)	173(30)	0	155(27)	0

metry around the palladium atom somewhat square-pyramidal. The two Pd—O bond lengths between the palladium and coordinated oxygens of 2.048(10) and 2.062(10) Å are identical, as are those in acetylacetonato(π-pentamethylbicyclo[2,2,0]-hexa-2,5-dienylmethyl)palladium(II), $[Pd(acac)(C_{12}H_{17})]$ (2.050(10) and 2.077(9) Å) [7] and in acetylacetonato(cycloocta-2,4-dienyl)-palladium, $[Pd(acac)(C_8H_{11})]$ (2.080(8) and 2.089(8) Å) [8]. However, in $[K^+ \cdot \{Pt(acac)_2\}^-]$ it seems that a bonded γ-carbon of an acetylacetone ligand causes the two Pt—O distances to differ (Pt—O = 1.968(14) and 2.072(14) Å) [14]. The bond length between the palladium and γ-carbon (C(8)) atom is 2.114(13) Å. It is shorter than the Pd—C distance in *trans*-bromo(5-methoxy-nortricyclo-3-enyl)dipyridine palladium, $[Pd(C_7H_8OMe)(py)_2Br]$ (2.16(5) Å) [9], but rather longer than those in $[Pd(PPh_3)(py)(C_2H_2O_2)]$ (2.03(2) Å) [10], the azobenzene complex of palladium(II), $[Pd(PEt_3)_2(C_{12}H_9N_2)Cl]$ (1.998(13) Å) [11], and 1,1′-dichloropallado-2,5-bis(methylamino)-3,4-di-azacyclopentadiene, $[Pd(Me_2C_2N_4H_4)Cl_2]$ (1.948(5) Å) [12]. The Pd—P

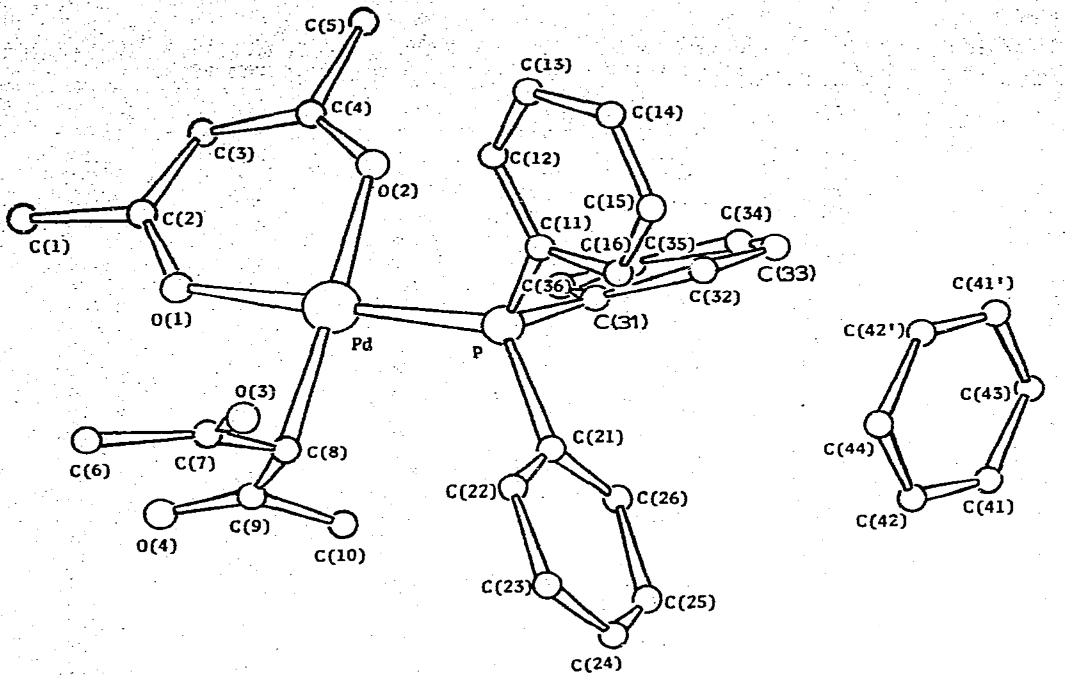

Fig. 1. Perspective view of the molecule, including crystalline benzene, showing the numbering system.

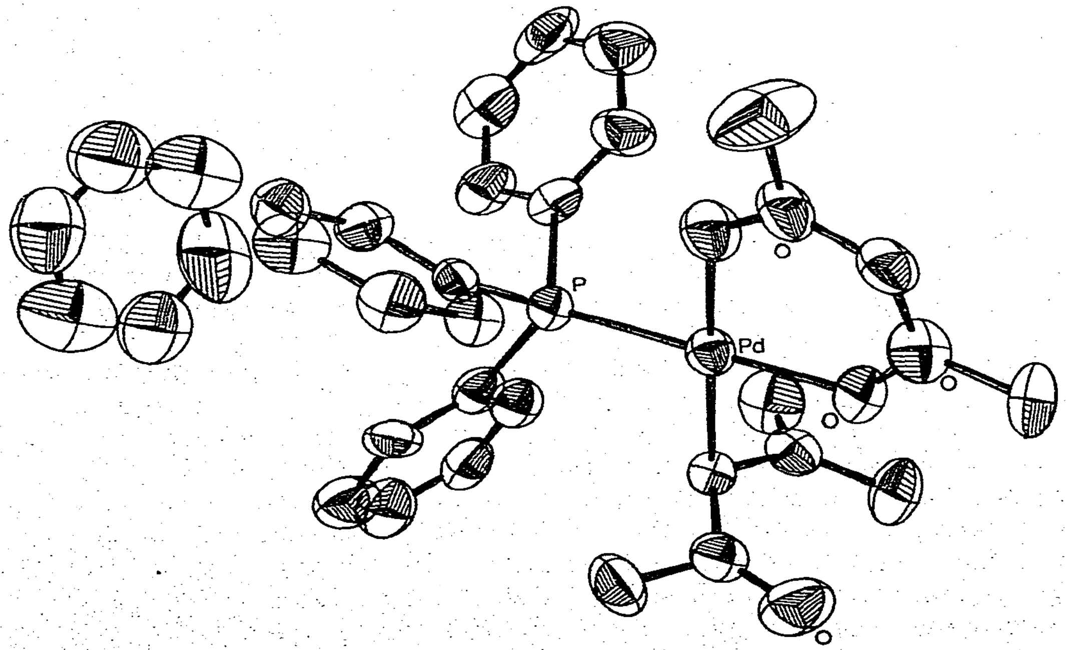

Fig. 2. An ORTEP drawing of the molecule. Nonhydrogen atoms are represented by thermal ellipsoids at 50% probability levels.

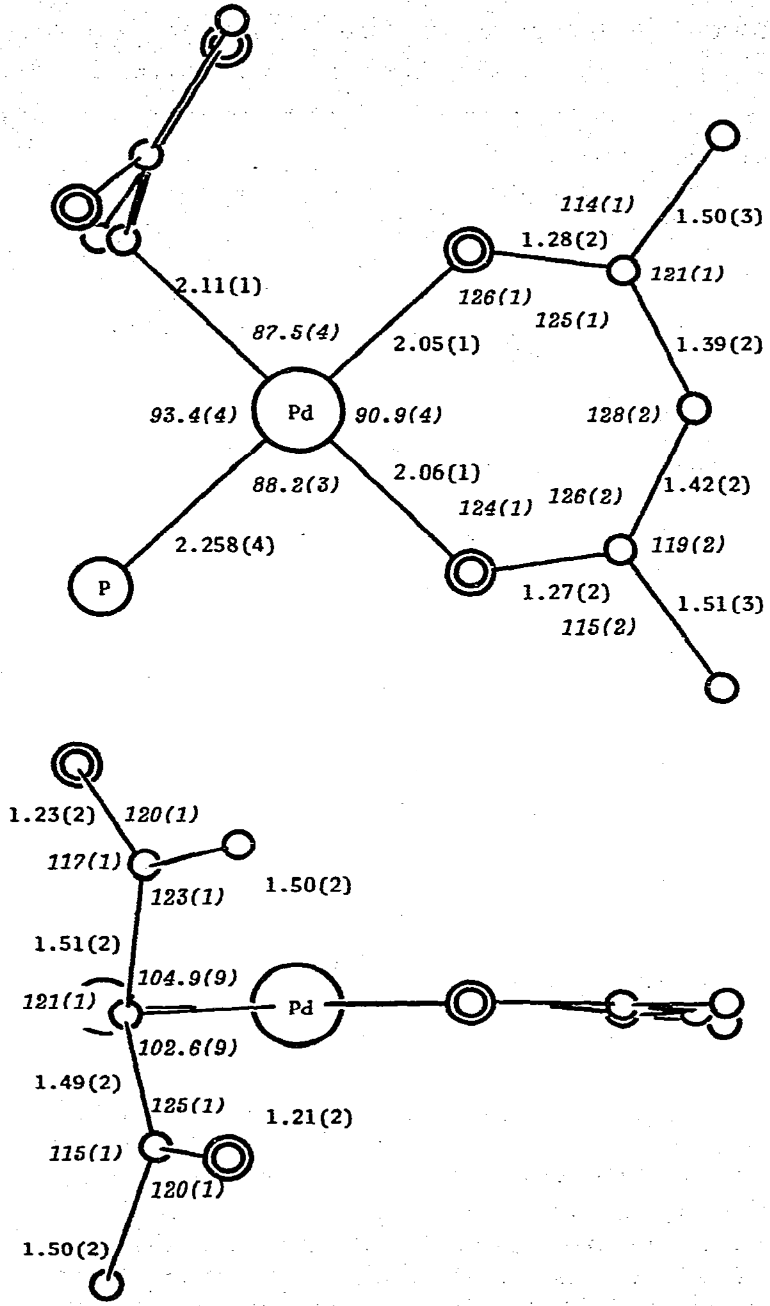

Fig. 3 Geometry around the palladium atom and the structure of the acetylacetone ligands. (e.s.d.'s in parentheses).

bond length of 2.258(4) Å is equal to that of *cis*-dichlorobis(dimethylphenylphosphine)palladium(II) (2.260(2) Å) [13].

The bond lengths of two C_β—C_γ bonds C(8)—C(7) = 1.51(2) and C(8)—C(9) = 1.49(2) Å are equal, which are normal C(sp^2)—C(sp^3) single bond lengths. Intramolecular atomic contacts between Pd and O(2), O(3), C(6), C(7), C(9)

TABLE 3

LEAST-SQUARES PLANES THROUGH VARIOUS GROUPS OF ATOMS AND DEVIATIONS OF ATOMS FROM THE PLANE

Equation of the plane is of the form AX + BY + CZ + D = 0.0 where X, Y, Z and D are measured in Å units: $X = ax + cz \cos\beta$, $Y = by$, $Z = cz \sin\beta$.

(a) Coordination around Pd

−0.39662X − 0.74175Y − 0.54083Z + 5.87844 = 0.0

Pd	0.020	P	0.001	C(1)[a]	−0.102	C(2)[a]	−0.107
O(1)	0.001	O(2)	−0.011	C(3)[a]	−0.217	C(4)[a]	−0.172
C(8)	−0.011			C(5)	−0.318		

(b) O-coordinated acetylacetone

−0.33721X − 0.70592Y − 0.62287Z + 6.37948 = 0.0

O(1)	−0.039	O(2)	0.043	C(1)	0.039	C(2)	−0.011
C(3)	−0.019	C(4)	0.004	C(5)	−0.016		

(c) C_γ-coordinated acetylacetone

0.32192X + 0.38908Y − 0.86312Z + 8.94723 = 0.0

O(3)	−0.139	O(4)	−0.074	C(6)	0.039	C(7)	0.038
C(8)	0.192	C(9)	0.024	C(10)	−0.073		

(d) Phenyl ring 1 (C(11)—C(16))

0.05193X − 0.98031Y + 0.19050Z + 0.79451 = 0.0

C(11)	−0.011	C(12)	−0.001	C(13)	0.037	C(14)	−0.035
C(15)	0.019	C(16)	−0.005	P[a]	−0.213		

(e) Phenyl ring 2 (C(21)—C(26))

−0.86326X + 0.27156Y − 0.42549Z + 1.17559 = 0.0

C(21)	0.008	C(22)	−0.008	C(23)	−0.001	C(24)	0.014
C(25)	−0.020	C(26)	0.008	P[a]	−0.065		

(f) Phenyl ring 3 (C(31)—C(36))

0.18483X − 0.05993Y − 0.98094Z + 9.06488 = 0.0

C(31)	0.000	C(32)	0.006	C(33)	−0.010	C(34)	0.007
C(35)	−0.001	C(36)	−0.003	P[a]	−0.091		

(g) Phenyl ring 4 (solvated molecule)

0.99155X − 0.00017Y − 0.12974Z + 8.13999 = 0.0

C(41)	−0.020	C(42)	0.019	C(43)	−0.000	C(44)	0.000
C(41)[b]	0.020	C(42)[c]	−0.019				

[a] Not included in the least-squares calculation. [b] C(41) = C(41) (−x, y, 1.5−z). [c] C(42) = C(42) (−x, y, 1.5−z).

and C(10) are all longer than 2.8 Å, and no interaction with Pd is observed. However, considerable distortions are observed in the bond angles around the γ-carbon atom. The C(7)—C(8)—C(9) angle (121(1)°) is larger than the tetrahedral angle, whereas two Pd—C_γ—C_β angles (104.9(0.9)° and 102.6(0.9)°) are slightly smaller. The two C_β—O bond lengths (1.23(2) and 1.21(1) Å) are both equal to the usual C=O double bond length. The structure of acetylacetonyl ligands coordinated by the γ-carbon to the platinum atom is compared in Fig. 4 with that of the present complex. The corresponding C_β—C_γ, and C_β=O bond lengths and C_β—C_γ—C_β bond angles of three complexes agree well with each other. The dihedral angles between two C_α—C_β—C_γ moieties are 9.5, 27.6 and 15.19° in $[K^+ \cdot \{Pt(acac)_2Cl\}^-]$ [14], $[Me_3Pt(acac)(bipy)]$ [15] and the present complex, respectively. The two carbonyl groups are not parallel in $[Me_3Pt(acac)(bipy)]$ and the present complex in contrast to the complex

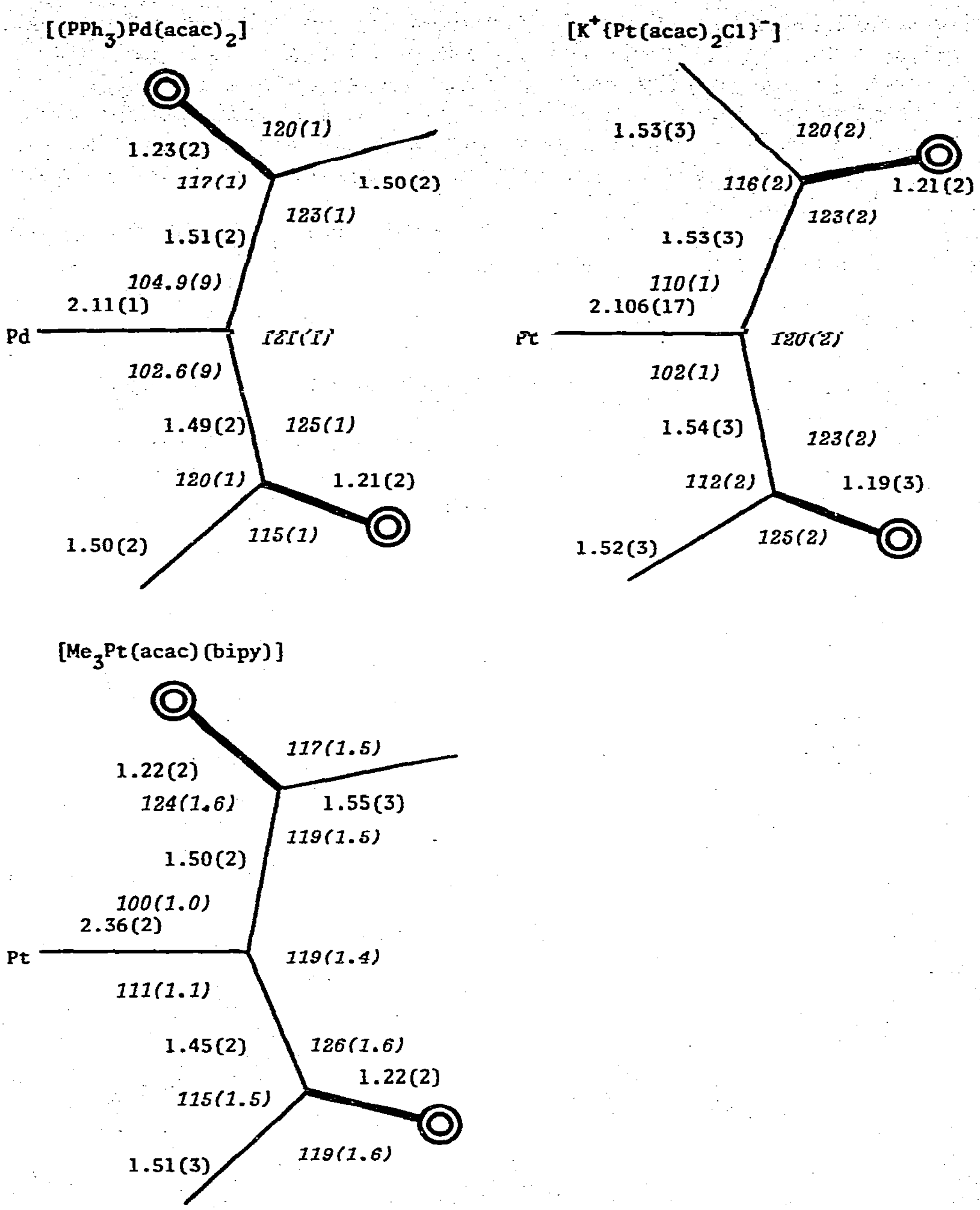

Fig. 4. Structure of acetylacetonyl ligands. Oxygen atoms are shown by double circles.

[K$^+$· {Pt(acac)$_2$ Cl}$^-$]. Interactions between two carbonyl oxygens and the potassium cation in the crystalline state probably affect the parallel position of the two carbonyl groups and the dihedral angles between two C_α—C_β—C_γ moieties in [K$^+$· {Pt(acac)$_2$ Cl}$^-$].

The bond lengths and bond angles in the enolate type acetylacetone ligand show normal values, which implies that π-electrons are delocalized completely, and the bonding is consistent with that of various metal chelates of acetylacetone. This ligand is approximately planar (Table 3), the maximum deviation from the least-squares plane being 0.04 Å, and has a pseudo C_{2v} symmetry around the Pd—C(3) axis. The dihedral angle between least-squares planes of the ligand and the coordination planes is 6.2°.

The triphenylphosphine ligand takes the usual configuration in which bond lengths and bond angles have normal values.

Crystal structure

Figure 5 depicts the molecular packing in a half of a unit cell projected along the b axis. Each crystalline benzene molecule is located in a void in the molecular network and lies on the 2-fold axis. Intermolecular atomic contacts less than 3.5 Å are given in Table 4. Some of them are short enough to suggest significant deviations from normal Van der Waals' interactions.

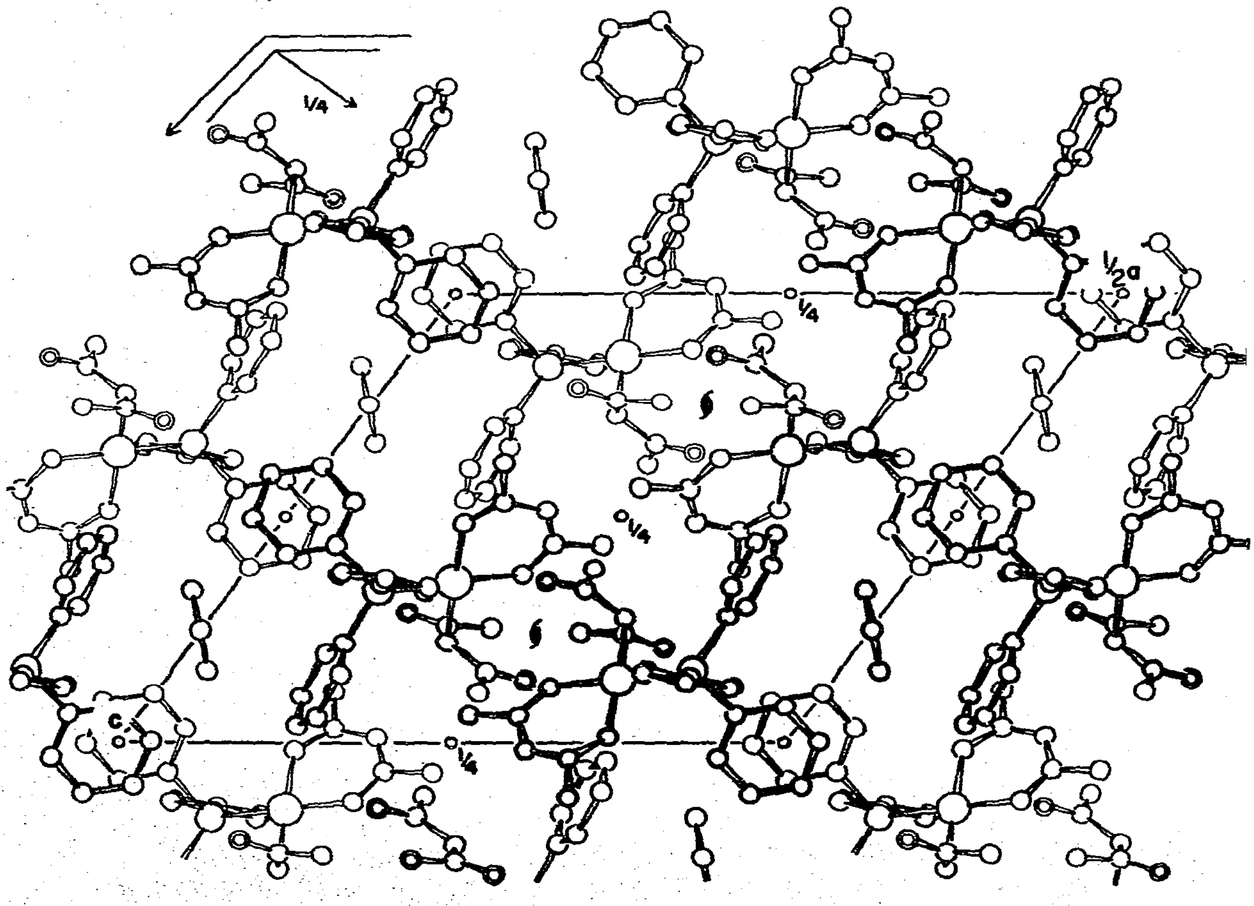

Fig. 5. Crystal structure projected along the *b* axis. A half of the unit cell is shown.

TABLE 4

INTERMOLECULAR ATOMIC CONTACTS LESS THAN 3.5 Å

Distance	
O(3) —C(34) [a]	3.457(20) Å
C(35)—O(4) [b]	3.210(20) Å
O(3) —C(14) [c]	3.277(22) Å

[a] $x, -1 + y, z$. [b] $\frac{1}{2} - x, \frac{1}{2} - z, \frac{3}{2} - z$, [c] $-x, -y, 1 - z$.

Computations throughout the present study were carried out on a NEAC 2200-700 computer at Osaka University and also on a FACOM 230-60 at Kyoto University. Figure 2 was drawn on a NUMERICON 7000 system at Osaka University with a local version of ORTEP [16].

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