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THE CRYSTAL AND MOLECULAR STRUCTURE OF AN ω-CARBON BONDED COMPLEX, *cis*-CHLORO(BENZYLACETOACETATE)DIPYRIDINEPALLADIUM(II)

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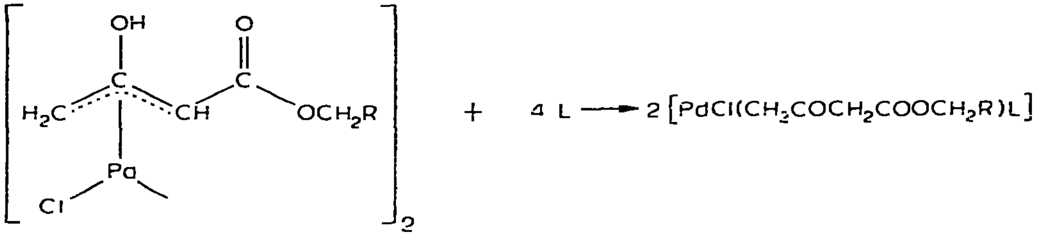
Summary

The molecular structure of *cis*-chloro(benzylacetoacetate)dipyridinepalladium(II) $[PdCl(CH_2COCH_2COOCH_2C_6H_5) \cdot (C_5H_5N)_2]$ has been determined by single-crystal X-ray diffraction. The crystal belongs to the triclinic system; a = 10.275(2), b = 11.849(3), c = 9.214(2) Å, α = 75.16(2), β = 96.70(3), γ = 100.02(4)°, U = 1064.8 Å^3, D_m = 1.54 g cm^{-3}, Z = 2, D_c = 1.532 g cm^{-3}, space group $P\bar{1}$. The structure was solved by the heavy atom method, and refined anisotropically by a least-squares procedure to R = 0.044 for 2812 independent (2689 non-zero) reflections.

The geometry around the palladium atom is square-planar: coordinated by the terminal carbon atom of the benzylacetoacetate [Pd—C = 2.051(8) Å], a chloride atom [Pd—Cl = 2.300(2) Å] and two pyridine molecules [Pd—N = 2.027(6) and 2.120(6) Å (*trans* to the carbon)]. The acetoacetate moiety in the benzylacetoacetate ligand is bent perpendicular to the coordination plane and the terminal benzyl group is again bent and its phenyl ring is roughly parallel to the coordination plane.

Introduction

Recently, there has been considerable interest in palladium(II) complexes containing the β-ketoester ligand [1, 2]. π-Allylic coordination of the β-ketoester ligand to the central palladium atom has been confirmed by X-ray structure analysis [2, 3]. Very recently, Shin'ichi Kawaguchi and his co-workers of the Osaka City University found that the addition of pyridine forced a change in coordination of the β-ketoester from π-allylic bonding to direct σ-bonding with its terminal carbon atom [4].



(1)

R = CH_3 and L = py or 2,2'-bipy ;

R = C_6H_5 and L = py, 4-mepy, 2,6-me$_2$py or 2,2'-bipy

This paper deals with the structure of *cis*-chloro(benzylacetoacetate)-dipyridinepalladium(II) [$PdCl(CH_2COCH_2COOCH_2C_6H_5)(C_5H_5N)_2$].

Experimental

Crystal data. $PdClC_{21}H_{21}N_2O_3$, mol. wt. = 491.3, triclinic, a = 10.275(2), b = 11.849(3), c = 9.214(2) Å, α = 75.15(2), β = 96.70(3), γ = 100.02(4)°, U = 1064.8(4) Å^3, D_m = 1.54 g cm^{-3}, Z = 2, D_c = 1.532 g cm^{-3}. Space group $P\bar{1}$ or $P1$, Mo-K_α radiation (λ = 0.71069 Å), μ = 10.04 cm^{-1}.

Recrystallization of the present complex from dichloromethane gives light yellow, polyhedral crystals, which decompose before melting at about 107°. The density was measured by flotation in an aqueous solution of zinc chloride at 17°.

Preliminary Weissenberg photographs showed that there was no symmetry other than that imposed by the Friedel condition, and the space group is either $P\bar{1}$ or $P1$. A Delaunay reduction failed to suggest the presence of hidden symmetry. Patterson solution showed that the space group was most probably $P\bar{1}$, and the structure has been successfully refined in this space group.

Unit-cell dimensions were determined by a least-squares fit of 2θ values of thirty independent reflections, each of which was obtained by measuring the differences of peak positions of hkl and $\bar{h}\bar{k}\bar{l}$ reflections.

Intensity data were collected at room temperature using the ω—2θ scan technique. The detailed procedure of intensity measurement has been described elsewhere [5]. A total of 2812 independent (2689 non-zero) reflections within a range of $(\sin\theta)/\lambda \leqslant 0.54$ was collected. A unique data set was first collected out to 2θ (Mo-$K_{\alpha 1}$) = 45°. A subsequent collection from 45 to 46.5° yielded relatively few intensities above background and so data collection was terminated. Intensities of three standard reflections 800, 003 and $\bar{1}1\bar{6}$ were measured every fifty reflections, and they decreased almost uniformly with time. About a 9 % decrease in the structure factor magnitude (average of three reflections) was observed at the end of the intensity data collection, and a linear correction was applied. The crystal used for intensity measurement had the dimensions of 0.21 × 0.17 × 0.10 mm, and the linear absorption coefficient of the specimen for Mo-K_α radiation is 10.04 cm^{-1}. No absorption correction was applied [$(\mu r)_{max}$ = 0.2].

Structure solution and refinement

The three-dimensional Patterson function unambiguously revealed the positions of the palladium and chlorine atoms. A subsequent Fourier synthesis immediately showed the locations of the remaining non-hydrogen atoms. Three cycles of block-diagonal least-squares refinement with isotropic temperature factors gave $R_1 = \Sigma\|F_o|-|F_c\|/\Sigma|F_o| = 0.11$. Anisotropic temperature factors were then introduced for all the non-hydrogen atoms, and six cycles of refinement lowered the values of R_1 to 0.054 and $R_2 = (\Sigma\|F_o|-|F_c\|^2/\Sigma|F_o|^2)^{1/2}$ to 0.064. The refinement was carried out by the HBLS program written by Dr. Ashida [6]. This program uses the block-diagonal approximation with a 2 × 2 matrix for a scale factor and an overall temperature factor and 9 × 9 matrix for each atom with anisotropic temperature factors and a 4 × 4 matrix for each atom with an isotropic temperature factor. The shift in an overall temperature factor B is calculated according to the equation, $\Delta B = \Delta B_{22} - \Delta B_{11}$, where ΔB_{22} and ΔB_{11} denote the shift from a 2 × 2 matrix and a 1 × 1 matrix respectively, and then it is added to the shift in the temperature factor of each atom. All the parameters were refined at the same time and the refinement was terminated when the largest shift did not exceed 0.10 σ.

A difference Fourier synthesis gave all the hydrogen peaks of methylene, pyridine and phenyl groups. Several cycles of refinement including hydrogen atoms with isotropic thermal parameters converged R_1 to 0.044 for non-zero (0.048 for all) reflections. The unit weight was given to each reflection. No weighting function other than unit weight was utilized, because of the average $w(\Delta F)^2$ for subsets of reflections, calculated as a function of both the size of $|F_o|$ and $(\sin\theta)/\lambda$, did not deviate significantly from unity. An anomalous dispersion correction was not applied. The neutral atomic scattering factors were taken from those of Hanson and his co-workers [7].

The final atomic coordinates and temperature factors are given in Tables 1, 2A and 2B respectively. A table of structure factors is available*.

Results and discussion

Molecular structure

The molecular structure is shown in Fig. 1, together with the numbering system for the atoms. Figure 2 shows a stereoscopic view of the molecule. Atoms are represented by thermal ellipsoids at 50% probability level for non-hydrogen ones and by spheres with radius of 0.1 Å for hydrogens. Table 3(A,B) shows bond lengths and bond angles. The *esd* on each parameter was calculated from the corresponding diagonal element of the inversion matrix of the normal equation coefficients. The maximum value among $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$, each denoting the *esd* along the cell edge, was assigned to the *esd* on the position of each atom, and used for the estimation of standard deviation on

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TABLE 1

ATOMIC FRACTIONAL COORDINATES TOGETHER WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*
Pd	0.31837 (5)	0.24365 (4)	0.35037 (5)
Cl	0.5445 (2)	0.2635 (2)	0.4022 (2)
N(1)	0.1186 (5)	0.2257 (5)	0.3096 (6)
N(2)	0.3329 (5)	0.4262 (4)	0.2443 (6)
O(1)	0.1686 (6)	−0.0244 (5)	0.2667 (7)
O(2)	0.3500 (7)	−0.0580 (5)	0.0066 (7)
O(3)	0.3337 (6)	0.1286 (4)	−0.0040 (5)
C(1)	0.3001 (7)	0.0656 (6)	0.4441 (8)
C(2)	0.2785 (7)	0.0146 (6)	0.3118 (8)
C(3)	0.3977 (8)	0.0143 (6)	0.2300 (8)
C(4)	0.3595 (8)	0.0206 (6)	0.0678 (9)
C(5)	0.2984 (10)	0.1486 (8)	−0.1675 (9)
C(11)	0.0419 (7)	0.2355 (7)	0.4131 (8)
C(12)	−0.0937 (7)	0.2234 (7)	0.3901 (8)
C(13)	−0.1546 (7)	0.2004 (8)	0.2611 (9)
C(14)	−0.0780 (8)	0.1908 (10)	0.1555 (9)
C(15)	0.0571 (7)	0.2040 (9)	0.1815 (8)
C(21)	0.3443 (7)	0.5107 (7)	0.3172 (9)
C(22)	0.3572 (7)	0.6279 (7)	0.2484 (10)
C(23)	0.3582 (9)	0.6600 (6)	0.0968 (12)
C(24)	0.3507 (14)	0.5772 (8)	0.0173 (11)
C(25)	0.3346 (13)	0.4605 (7)	0.0968 (9)
C(31)	0.2109 (7)	0.2435 (6)	−0.2080 (7)
C(32)	0.0756 (8)	0.2186 (7)	−0.1991 (8)
C(33)	−0.0024 (9)	0.3032 (9)	−0.2386 (9)
C(34)	0.0521 (10)	0.4174 (9)	−0.2863 (10)
C(35)	0.1860 (9)	0.4488 (7)	−0.3000 (9)
C(36)	0.2673 (7)	0.3605 (8)	−0.2605 (8)
H(1a)	0.238 (5)	0.042 (5)	0.503 (6)
H(1b)	0.372 (7)	0.053 (6)	0.505 (8)
H(3a)	0.431 (7)	−0.054 (6)	0.270 (8)
H(3b)	0.463 (6)	0.082 (6)	0.240 (7)
H(5a)	0.243 (8)	0.065 (7)	−0.181 (9)
H(5b)	0.363 (12)	0.183 (11)	−0.276 (14)
H(11)	0.098 (7)	0.265 (6)	0.504 (8)
H(12)	−0.127 (7)	0.221 (6)	0.466 (8)
H(13)	−0.247 (6)	0.182 (5)	0.252 (7)
H(14)	−0.102 (8)	0.168 (7)	0.071 (9)
H(15)	0.115 (6)	0.207 (6)	0.116 (7)
H(21)	0.354 (10)	0.475 (9)	0.443 (11)
H(22)	0.393 (10)	0.682 (9)	0.316 (12)
H(23)	0.359 (7)	0.719 (6)	0.056 (8)
H(24)	0.375 (13)	0.610 (11)	−0.089 (14)
H(25)	0.322 (8)	0.394 (9)	0.055 (9)
H(32)	0.039 (7)	0.132 (7)	−0.182 (8)
H(33)	−0.111 (10)	0.277 (9)	−0.256 (12)
H(34)	−0.004 (10)	0.476 (9)	−0.334 (11)
H(35)	0.231 (8)	0.519 (7)	−0.332 (9)
H(36)	0.347 (7)	0.383 (7)	−0.275 (8)

the bond distances and bond angles. That means, each atom was treated independently.

The remarkable feature of the structure is that the benzylacetoacetate coordinates to the central palladium atom by its terminal carbon atom only.

TABLE 2A

ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$) EXPRESSED IN THE FORM OF $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ FOR NON-HYDROGEN ATOMS. ESTIMATED STANDARD DEVIATIONS IN PARENTHESES.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	101.6 (0.5)	85.1 (0.4)	116.9 (0.7)	42.8 (0.8)	−7.9 (1.0)	−13.0 (0.9)
Cl	93 (2)	117 (2)	209 (3)	34 (3)	−46 (4)	−57 (4)
N(1)	108 (6)	110 (6)	119 (8)	43 (9)	17 (11)	4 (10)
N(2)	132 (7)	78 (5)	141 (8)	58 (9)	−7 (12)	−48 (10)
O(1)	162 (8)	137 (6)	287 (12)	−77 (11)	−94 (15)	−32 (14)
O(2)	303 (11)	114 (6)	326 (13)	191 (13)	−258 (19)	−239 (14)
O(3)	230 (8)	96 (5)	169 (8)	140 (10)	−99 (13)	−86 (10)
C(1)	132 (9)	96 (7)	174 (12)	3 (12)	1 (16)	69 (14)
C(2)	160 (10)	59 (6)	191 (12)	−3 (12)	−117 (17)	37 (13)
C(3)	168 (10)	86 (6)	195 (12)	103 (13)	−103 (18)	−69 (14)
C(4)	185 (11)	82 (6)	215 (13)	109 (14)	−113 (19)	−111 (15)
C(5)	286 (16)	148 (10)	164 (13)	210 (21)	−89 (23)	−93 (18)
C(11)	114 (8)	124 (8)	151 (11)	37 (13)	20 (15)	−25 (14)
C(12)	127 (9)	141 (9)	162 (12)	57 (14)	57 (16)	3 (16)
C(13)	89 (8)	180 (10)	207 (14)	57 (14)	25 (16)	51 (19)
C(14)	110 (9)	290 (16)	169 (13)	73 (19)	−54 (18)	−84 (23)
C(15)	112 (9)	265 (14)	118 (10)	114 (18)	−13 (15)	−96 (19)
C(21)	123 (9)	115 (7)	210 (13)	36 (13)	41 (17)	−121 (16)
C(22)	130 (9)	103 (7)	320 (18)	37 (13)	16 (20)	−171 (19)
C(23)	197 (13)	70 (7)	386 (22)	81 (15)	−221 (27)	−44 (19)
C(24)	529 (30)	96 (9)	188 (16)	59 (26)	−130 (34)	28 (19)
C(25)	484 (26)	82 (7)	153 (13)	72 (22)	−19 (29)	−53 (16)
C(31)	174 (10)	110 (7)	109 (9)	92 (14)	−39 (15)	−71 (13)
C(32)	163 (11)	136 (9)	160 (12)	−35 (15)	5 (18)	−80 (16)
C(33)	162 (12)	226 (13)	180 (14)	101 (20)	−3 (20)	88 (22)
C(34)	224 (14)	191 (12)	202 (15)	211 (22)	−16 (23)	69 (21)
C(35)	246 (14)	106 (8)	169 (13)	38 (17)	31 (21)	23 (16)
C(36)	120 (9)	166 (10)	158 (12)	18 (15)	−26 (16)	−83 (17)

TABLE 2B

ISOTROPIC TEMPERATURE FACTORS B(Å^2) FOR HYDROGEN ATOMS. ESTIMATED STANDARD DEVIATIONS IN PARENTHESES.

Atom	B	Atom	B	Atom	B
H(1a)	1.2(1.2)	H(1b)	3.8(1.7)	H(3a)	3.7(1.7)
H(3b)	3.0(1.5)	H(5a)	5.2(2.0)	H(5b)	12.8(3.9)
H(11)	3.7(1.7)	H(12)	4.7(1.9)	H(13)	2.5(1.4)
H(14)	5.6(2.1)	H(15)	3.1(1.5)	H(21)	8.7(2.9)
H(22)	9.9(3.2)	H(23)	4.2(1.8)	H(24)	13.6(4.2)
H(25)	5.5(2.0)	H(32)	4.7(1.9)	H(33)	9.5(3.1)
H(34)	9.0(2.9)	H(35)	6.1(2.2)	H(36)	4.8(1.9)

The geometry around the central palladium atom is square-planar, coordinated by the carbon atom of the terminal methylene of the benzylacetoacetate ligand, one chlorine atom and two nitrogen atoms of the pyridines. A slight distortion of the coordination plane toward a tetrahedral geometry is observed (Table 4).

The Pd—C(1) bond length of 2.051(8) Å is consistent with the expected Pd^{II}—C$_{sp^3}$ single bond length (Table 5).

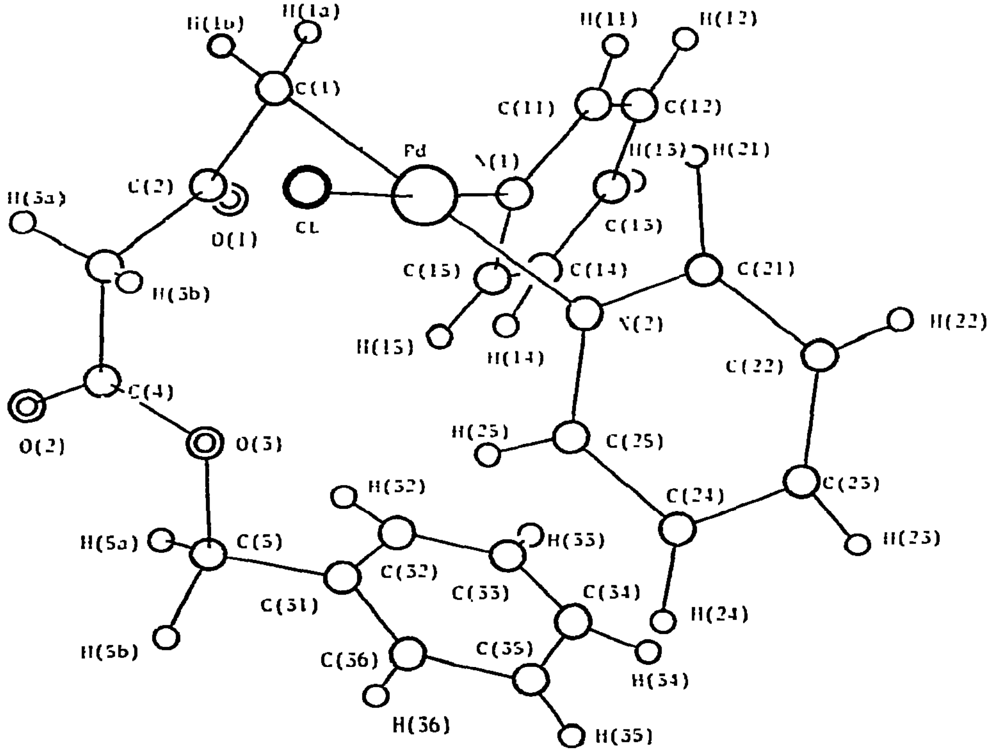

Fig. 1. Molecular structure with numbering system.

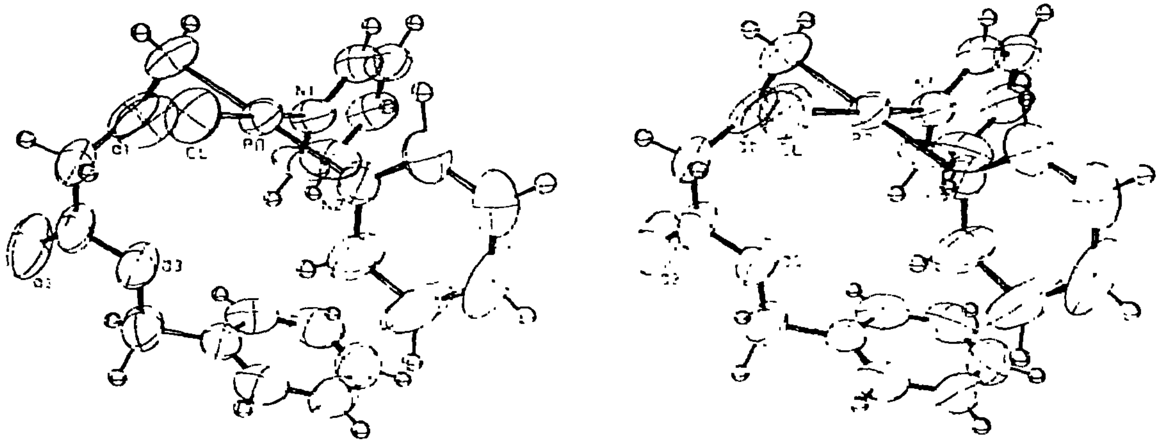

Fig. 2. Stereoscopic view of the molecule. Atoms are represented by thermal ellipsoids at 50% probability level for non-hydrogen ones and by spheres with radius of 0.1 Å for hydrogens.

The Pd—C(1)—C(2) bond angle is distorted in a similar way to that found in the γ-carbon bonded acetylacetonate ligand [8-10].

In the benzylacetoacetate ligand the acetoacetate moiety is bent approximately vertically to the coordination plane and the terminal benzyl group is again bent and its phenyl ring is roughly parallel to the coordination plane (Fig. 2). No abnormal value is found in bond lengths and bond angles. A

TABLE 3A

BOND LENGTHS (Å) TOGETHER WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Pd—Cl	2.300 (2)	Pd—N(1)	2.027 (6)
Pd—N(2)	2.120 (6)	Pd—C(1)	2.051 (8)
N(1) —C(11)	1.346(10)	N(1)—C(15)	1.334(13)
C(11)—C(12)	1.374(12)	C(12)—C(13)	1.343(13)
C(13)—C(14)	1.360(16)	C(14)—C(15)	1.372(17)
N(2) —C(21)	1.324(10)	N(2) —C(25)	1.319(15)
C(21)—C(22)	1.362(13)	C(22)—C(23)	1.349(15)
C(23)—C(24)	1.355(19)	C(24)—C(25)	1.381(21)
O(1) —C(2)	1.211(10)	O(2) —C(4)	1.190(11)
C(1) —C(2)	1.475(11)	C(2) —C(3)	1.513(11)
C(3) —C(4)	1.485(12)	C(4) —O(3)	1.336(10)
O(3) —C(5)	1.476(12)	C(5) —C(31)	1.509(13)
C(31) —C(32)	1.377(12)	C(32) —C(33)	1.339(14)
C(33)—C(34)	1.354(16)	C(34)—C(35)	1.373(15)
C(35)—C(36)	1.403(14)	C(36)—C(31)	1.388(12)
H(1a)—C(1)	0.85 (6)	H(1b)—C(1)	0.87 (7)
H(3a)—C(3)	0.91 (7)	H(3b)—C(3)	0.96 (7)
H(5a)—C(5)	1.09 (8)	H(5b)—C(5)	1.19 (13)
H(11)—C(11)	1.06 (7)	H(12)—C(12)	0.82 (8)
H(13)—C(13)	0.95 (7)	H(14)—C(14)	0.88 (8)
H(15—C(15)	0.89 (7)	H(21)—C(21)	1.13 (10)
H(22)—C(22)	0.98 (11)	H(23)—C(23)	0.71 (8)
H(24)—C(24)	0.99 (13)	H(25)—C(25)	0.95 (8)
H(32)—C(32)	1.01 (8)	H(33)—C(33)	1.11 (11)
H(34)—C(34)	0.96 (10)	H(35)—C(35)	0.87 (9)
H(36)—C(36)	0.83 (8)		

TABLE 3B

BOND ANGLES (DEG) TOGETHER WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Cl—Pd—N(1)	178.8(0.2)	N(2)—Pd—C(1)	177.5(0.3)
Cl—Pd—N(2)	90.3(0.2)	N(1)—Pd—N(2)	90.0(0.2)
Cl—Pd—C(1)	91.1(0.2)	N(1)—Pd—C(1)	88.6(0.3)
Pd—N(1)—C(11)	120.3(0.5)	Pd—N(1)—C(15)	122.7(0.6)
C(11)—N(1)—C(15)	117.1(0.7)	N(1)—C(11)—C(12)	122.1(0.7)
C(11)—C(12)—C(13)	120.3(0.8)	C(12)—C(13)—C(14)	118.2(1.0)
C(13)—C(14)—C(15)	120.1(1.1)	C(14)—C(15)—N(1)	122.3(1.0)
Pd—N(2)—C(21)	124.2(0.5)	Pd—N(2)—C(25)	119.3(0.7)
C(21)—N(2)—C(25)	116.5(0.8)	N(2)—C(21)—C(22)	123.7(0.8)
C(21)—C(22)—C(23)	118.4(0.9)	C(22)—C(23)—C(24)	120.2(1.1)
C(23)—C(24)—C(25)	117.2(1.3)	C(24)—C(25)—N(2)	123.9(1.2)
Pd—C(1)—C(2)	102.9(0 5)	C(1)—C(2)—C(3)	118.2(0.7)
O(1)—C(2)—C(1)	121.6(0.7)	O(1)—C(2)—C(3)	120.2(0.7)
C(2)—C(3)—C(4)	110.7(0.7)	C(3)—C(4)—O(3)	110.5(0.7)
O(2)—C(4)—C(3)	126.5(0.8)	O(2)—C(4)—O(3)	123.0(0.8)
C(4)—O(3)—C(5)	116.4(0.7)	O(3)—C(5)—C(31)	106.7(0.8)
C(5)—C(31)—C(32)	122.3(0.8)	C(5)—C(31)—C(36)	119.3(0.8)
C(32)—C(31)—C(36)	118.4(0.8)	C(31)—C(32)—C(33)	122.3(0.9)
C(32)—C(33)—C(34)	119.9(1.0)	C(33)—C(34)—C(35)	121.2(1.0)
C(34)—C(35)—C(36)	119.0(0.9)	C(35)—C(36)—C(31)	119.3(0.8)

TABLE 4

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

Equation of the plane is of the form $AX + BY + CZ + D = 0^{a}$. Atoms marked by * are not included. in the least-squares plane calculation.

(a) Coordination plane

$$0.23618X - 0.40505Y - 0.88326Z + 3.64186 = 0.0$$

Pd	−0.006 Å	Cl	−0.027	N(1)	−0.030	N(2)	0.031
C(1)	0.033						

(b) Pyridine ring 1

$$0.07056X - 0.91037Y + 0.40774Z + 1.87165 = 0.0$$

N(1)	0.002 Å	C(11)	0.001	C(12)	−0.004	C(13)	0.005
C(14)	−0.002	C(15)	−0.002	Pd*	0.017		

(c) Pyridine ring 2

*

$$-0.99317X - 0.07150Y - 0.09225Z + 2.85845 = 0.0$$

N(2)	0.000 Å	C(21)	−0.007	C(22)	−0.0001	C(23)	0.014
C(24)	−0.020	C(25)	0.014	Pd*	−0.063		

(d) Phenyl ring

$$-0.00959X + 0.34359Y + 0.93907Z + 0.94232 = 0.0$$

C(31)	0.007	C(32)	0.000	C(33)	−0.008	C(34)	0.009
C(35)	−0.003	C(36)	−0.005	C(5)*	−0.013		

[a] The orthogonal axes, X, Y and Z refer to the triclinic axes through the following transformation:

$X = ax \cdot \sin\gamma + cz(\cos\beta - \cos\alpha \cdot \cos\gamma)/\sin\gamma$

$Y = by + ax \cdot \cos\gamma + cz \cdot \cos\alpha$

$Z = cz\ \{(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha \cdot \cos\beta \cdot \cos\gamma)/\sin^2\gamma\}^{1/2}$.

TABLE 5

Pd—C σ BOND LENGTHS (Å)

1.95(1)	sp^2	$PdCl_2(C_2H_4N_4Me_2)$
1.97(2) 2.00(1)	sp	$[Pd(CN)]_4{}^{2-}$
1.98(2) 2.00(2)	sp^2	$PdCl(C_{12}H_9N_2)(PEt_3)_2$
1.99(3)	sp^2	$PdBr(PPh_3)_2[C_4(COOMe)_4H]$
2.03(2)	sp^3	$Pd(C_2H_2O_2)(Py)(PPh_3)$
2.05(1)	sp^3	$PdCl(C_4H_6O_3 \cdot CH_2Ph)(Py)_2$
2.11(1)	sp^3	$Pd(acac)_2PPh_3$
2.16(5)	sp^3	$PdBr(C_7H_8OMe)(Py)_2$
2.20(9) 2.22(8)	sp^3	$Pd(C_4H_4O_3)(PPh_3)_2$

localization of π-electrons in carbonyl and ester group is observed. Both carbonyl and ester oxygen atoms are far away from the palladium atom, Pd · · · O distances being 3.51, 5.42 and 3.88 Å for O(1), O(2) and O(3), respectively. Among the intermolecular nonbonded distances between the phenyl carbon and pyridine carbon atoms the shortest one is C(15) · · · C(32) (3.5 Å). Thus the benzylacetoacetate ligand is completely free in the molecule.

The Pd—Cl bond length of 2.300(2) Å agrees well with that of 2.30(1) Å in dichloro(tetrahydrogenoethylenediaminetetraacetato)palladium(II) $[PdCl_2\{CN(CH_2CO_2H)\}_2]$ [11]. The coordination of the chlorine atom is not sterically hindered.

Two pyridine ligands coordinate to the palladium atom with a rather unstable *cis*-configuration in the crystalline state although the co-existence of *cis* and *trans* isomers is suggested in solution [4]. Both the pyridine rings are approximately perpendicular to the coordination plane. The dihedral angles between the coordination plane and pyridine rings (*trans* to chlorine and *trans* to methylene respectively) are 88.6 and 97.1°. The steric hindrance between pyridine rings and the other ligands is minimal. Furthermore, according to Chatt and Shaw's discussion [12] the overlap between delocalized π^*-orbitals of each pyridine ring and the $4d_{xy}$ orbital of the palladium atom is a maximum in this situation and, therefore, the energy level of the highest occupied orbital, $4d_{xy}$, is lowered and the difference between the highest occupied and the lowest unoccupied energy levels becomes large. (Here the xy plane is the coordination plane.) This fact may contribute partly to the stabilization of the complex.

The Pd—N(1) bond (2.027(6) Å) is significantly shorter than the corresponding Pd—N(2) bond (2.120(6) Å). The values of 2.018(8) and 2.068(6) Å are found in chloro[methylbis-{(6-methyl-2-pyridyl)methyl} amine]palladium(II) chloride [13]. Pd^{II}—N lengths found in square-planar palladium(II) complexes, in which the Pd—N bond is neither sterically hindered nor *trans* to a very strong *trans*-influencing ligand, are in the range of 1.99 to 2.04 Å [14]. The Pd—N(1) bond length in the present complex falls within this range, while that of Pd—N(2) is rather longer. The Pd—N(2) length is rather close to the value of 2.20(2) Å in chloro(2-methoxycycloocta-1,5-dienyl)-pyridineplatinum [Pt(MeO—COD)(py)Cl] [16], and of 2.148(7) Å in isothi-

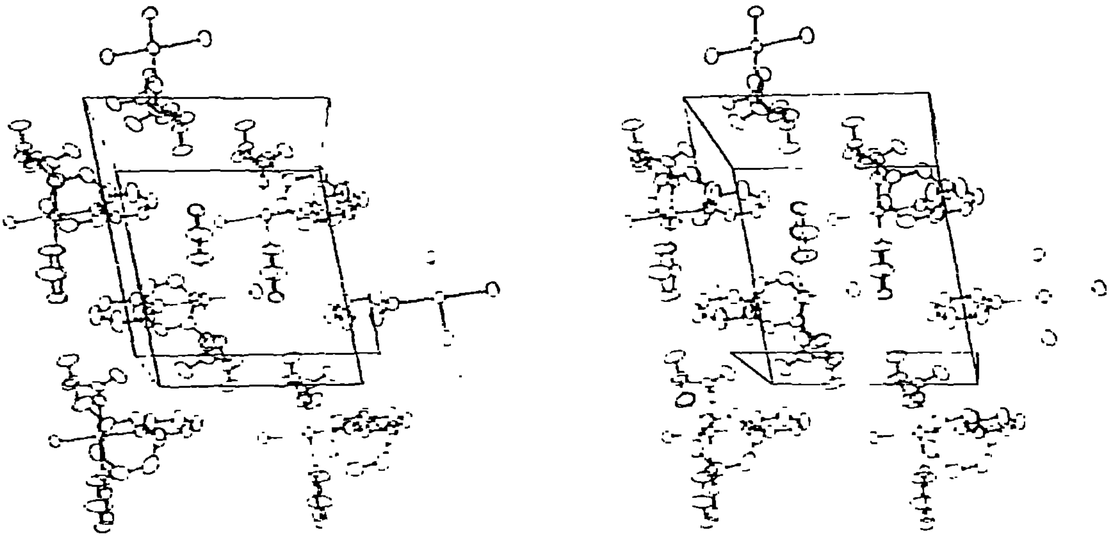

Fig. 3. Crystal structure projected along the c* axis. Atoms are represented by thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted.

ocyanatothiocyanato(1-diphenylphosphino-3-dimethylaminopropane)palladium(II) [$Pd(SCN)_2\{PPh_2(CH_2)_3NMe_2\}$] [14]. The elongation of the Pd—N(2) bond length can therefore be ascribed to the *trans* carbon atom (C(1)) which has a stronger σ-donor power than the chlorine atom. Such a situation as described above has already been suggested by Pidcock, Richard and Venanzi [17] in their discussion of the *trans*-lengthening effect of the hydrido ligand in [$PtHCl(Et_2PhP)_2$] [15].

Bond lengths and bond angles in the pyridine rings have normal values. However, it seems that the pyridine ring *trans* to the chlorine atom is less distorted that that *trans* to the σ-bonded terminal methylene carbon, though it is not fully significant. The four pyridine ring carbon atoms which are near to the phenyl ring of benzylacetoacetate show larger thermal vibrations than the others, as is seen in Fig. 2.

Molecular packing

A stereoscopic projection of the packing of molecules along the c^* axis

TABLE 6

INTERMOLECULAR ATOMIC CONTACTS LESS THAN 3.5 Å

Distance (Å)	
O91) — C(32)[a]	3.215(11)
O(2) — C(14)[a]	3 348(14)
O(2) — C(23)[b]	3.243(13)
O(2) — O(2)[c]	3.151(14)
O(2) — O(3)[c]	3.498 (9)
O(2) — C(3)[c]	3.464(11)
O(2) — C(4)[c]	3.071(11)
C(4) — C(4)[c]	3.430(17)

[a] $-x, -y, -z$. [b] $x, -1 + y, z$. [c] $1 - x, -y, -z$.

is shown in Fig. 3. Hydrogen atoms are omitted in the drawing. The atoms are represented in the same manner as in Fig. 2 at 30% probability level. Table 6 lists all the intermolecular atomic contacts less than 3.50 Å. Some of them are short enough to suggest significant deviations from normal van der Waals' interaction.

Computations throughout the present study were carried out on a Neac 2200-700 computer at Osaka University. Figures 2 and 3 were drawn on a Numericon 7000 system at Osaka University with a local version of ORTEP [18].

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