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Crystal and Molecular Structure of Di-μ-chloro-bis(π-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II)

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The crystal and molecular structures of di-μ-chloro-bis-(π-1-ethoxycarbonyl-2-hydroxyallyl)-dipalladium, $(C_6H_9O_3PdCl)_2$ have been determined from the three-dimensional data. The crystals are triclinic; space group $P\bar{1}$; with one dimeric molecule per unit-cell; $a=4.80$, $b=10.31$, $c=10.64$ Å, $\alpha=117.4$, $\beta=102.3$, and $\gamma=84.1°$. The final discrepancy index is 14.0% for 1208 reflections. The two palladium atoms are joined by two chlorine bridges to form a square planar arrangement. The molecule possesses a center of symmetry which coincides with a crystallographic center of symmetry in the crystal; the overall coordination scheme of the palladium atom is similar to that established for the π-allyl palladium chloride dimer. The dihedral angle between the plane of four atoms [Pd, Pd′, Cl, and Cl′] and the π-allyl plane is 108. There are intermolecular hydrogen-bonds between the enolic hydroxyl group of one molecule and the carbonyl-group of the other molecule related by the center of symmetry.

A number of π-allylic complexes have been synthesized from palladium(II) chloride and various mono-olefins or conjugated di-olefins.[1] However, few complexes have been synthesized from unsaturated ketones and esters.

The ethanolysis of diketene is accelerated by the addition of sodium tetrachloropalladate(II).[2] The yellow crystals separated at the end of this reaction were identified as di-μ-chloro-bis-(π-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II) on the basis of the analytical data, the molecular weight, and the infrared spectrum. The same complex was also prepared directly by the reaction of palladium(II) chloride with ethyl acetoacetate in water.

The IR data reveal that, instead of the usual chelate structure, the complex may have a π-allylic linkage. The stretching absorption bands of O–H and C=O groups are both shifted to lower frequency, indicating the existence of intra- or intermolecular hydrogen-bonding.

Proton magnetic resonance spectra are frequently utilized as one of the most powerful tools in the structural study of π-allylic metal complexes. Unfortunately, however, no suitable inert solvents are available for the present complex. Thus, the three-dimensional X-ray analysis of this complex was carried out in order to determine the exact structure; a preliminary report has already been reported.[3]

Experimental

Di-μ-chloro-bis-(π-1-ethoxycarbonyl-2-hydroxyallyl)-dipalladium, $(C_6H_9O_3PdCl)_2$, was recrystallized as yellow needles in a dark place from a benzene solution. The complex is easily decomposed by the irradiation of the benzene solution by visible light.

By the use of Cu$K\alpha$ radiation, the unit-cell dimensions were determined from ($hk0$), ($h0l$), and ($0kl$) Weissenberg photographs, on which the powder patterns of tungsten ($a=3.16535$ Å) were superposed for the calibration. In the least-squares refinement of the cell dimensions, 26 high angle reflections were used.

$$a = 4.80\pm0.01\text{ Å}, \quad \alpha = 117.4\pm0.2°,$$
$$b = 10.31\pm0.06\text{ Å}, \quad \beta = 102.3\pm0.1°,$$
$$c = 10.64\pm0.06\text{ Å}, \quad \gamma = 84.1\pm0.3°.$$

The volume of the unit cell, U, is 457 Å^3; $D_m=1.96$ (by flotation in an aqueous solution of $ZnBr_2$); with $Z=1$ (as a dimeric molecule $(C_6H_9O_3PdCl)_2$; $M=542.0$) $D_c=1.97$ g·cm^{-3}. There was no symmetry in the X-ray photographs except that imposed by the Friedel condition, and the space group is either $P1$ or $P\bar{1}$.

Nickel-filtered Cu$K\alpha$ radiation was used to collect equi-inclination Weissenberg data for the layers from

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1) For example, M. L. H. Green and P. L. I. Nagy, "Advances in Organometallic Chemistry," Vol. 2, ed. by F. G. A. Stone and R. West, Academic Press, New York (1964), p. 325.

2) Y. Tezuka, T. Ogura and S. Kawaguchi, This Bulletin, **42**, 443 (1969).

3) K. Oda, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, Y. Tezuka, T. Ogura and S. Kawaguchi, *Chem. Commun.*, **1968**, 989.

(0*kl*) through (3*kl*) and from (*hk*0) through (*hk*4) by the multiple-film technique. In all, 1323 independent reflections were obtained, but the refinement was carried out by using 1208 reflections with 2θ less than 120°. The relative intensities were estimated visually, and then corrected for Lorentz and polarization factors. As the dimensions of the crystal used in the experiment were about $0.05\times0.08\times0.10$ mm, the absorption correction was ignored ($\mu=98$ cm^{-1}).

Determination and Refinement of the Structure

In the three-dimensionsl Patterson function, the vectors of Pd-Pd′, Pd-Cl, and Pd-Cl′ lie on the same plane, and a centro-symmetrical arrangement of two palladium and two chlorine atoms was easily derived. Therefore, the space group was assumed to be $P\bar{1}$, the structure has been determined satisfactorily in this space group. The other non-hydrogen atoms were found on the three-dimensional electron density map based on the positions of the palladium and chlorine atoms. The positional and isotropic thermal parameters were then refined by a block-diagonal least-squares procedure. After four cycles, the residual, *R*, was reduced to 0.167 for 1068 non-zero reflections. The isotropic thermal parameters for palladium and chlorine atoms were then expressed in their anisotropic form, using the expression:

$$T = \exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{13}hl)\},$$

and the least-squares refinement was continued. After a further five cycles of refinement, *R* was 0.140 ($R=0.170$ for all reflections). At this stage, the refinement was assumed to be finished, since the maximum shift of coordinates was less than 1% of the estimated standard deviation. Hydrogen atoms could not be located on the three-dimensional difference-synthesis, and their contributions to the calculated structure factors have not been estimated.

Throughout the refinement, the neutral atomic scattering factors were taken from those given by Hanson *et al.*[4] The Patterson function was calculated on a NEAC-2200 computer of this university, with the program written by one of the present authors (N.Y.). The least-squares refinement and other calculations were carried out on a HITAC-5020E computer at the University of Tokyo, with programs written by Dr. Tamaichi Ashida.

The final atomic positional parameters, along

Table 1. Final atomic coordinates with their estimated standard deviations ($\times10^2$Å) in parentheses

	x	*y*	*z*
Pd	0.2359(0.3)	0.1370(0.3)	0.1142(0.3)
Cl	−0.0120(1.2)	−0.0402(1.1)	0.1361(1.0)
C (1)	0.5072(4.6)	0.2942(4.6)	0.1377(5.1)
C (2)	0.4002(4.4)	0.3516(4.4)	0.2680(4.9)
C (3)	0.4780(3.9)	0.2554(3.9)	0.3216(4.4)
C (4)	0.3278(4.1)	0.2749(4.1)	0.4477(4.5)
C (5)	0.2472(4.5)	0.1693(4.5)	0.5994(4.9)
C (6)	0.4465(8.6)	0.2694(8.6)	0.7497(9.6)
O (1)	0.2262(2.5)	0.4717(2.5)	0.3145(2.8)
O (2)	0.1276(2.6)	0.3636(2.6)	0.4857(2.9)
O (3)	0.4186(3.0)	0.1748(3.0)	0.4976(3.3)

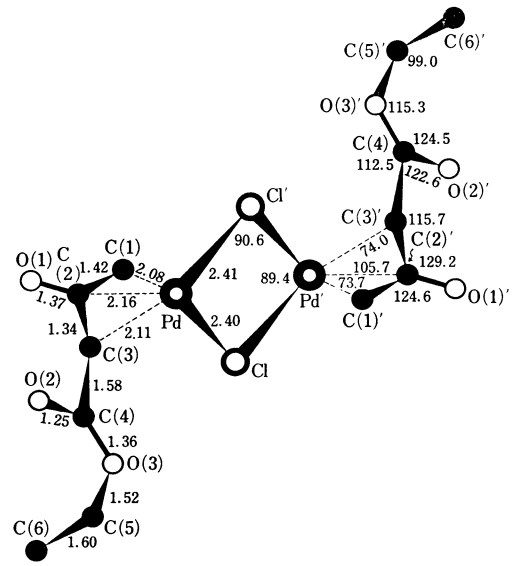

Fig. 1. Plan of the molecule with bond lengths (Å) and bond angles (°).

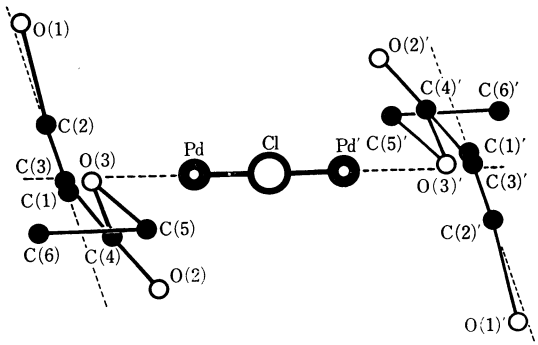

Fig. 2. The molecule viewed along the Cl-Cl′ vector.

Δ_I: Deviations from the plane of four atoms (Pd, Pd′, Cl & Cl′) (Å).

Δ_{II}: Deviations from the allyl plane (Å).

	Δ_I	Δ_{II}		Δ_I	Δ_{II}
C (1)	0.14	0.00	O (1)	2.05	0.13
C (2)	0.72	0.00	O (2)	2.07	0.69
C (3)	0.01	0.00	O (3)	0.01	0.29
C (4)	0.81	0.32			
C (5)	0.73	0.83			
C (6)	0.71	0.56			

4) H. P. Hanson, F. Herman, J. D. Lea and S. S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

TABLE 2.

(a) FINAL ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) WITH THEIR ESTIMATED STANDARD DEVIATIONS ($\times 10^4$) IN PARENTHESES

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
Pd	682(16)	78(3)	69(3)	9(11)	22(5)	60(11)
Cl	1003(76)	135(13)	76(11)	97(49)	81(19)	77(44)

(b) FINAL ISOTROPIC THERMAL PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS

	B		B		B
C(1)	6.54(0.97)	C(2)	6.08(0.91)	C(3)	5.16(0.78)
C(4)	5.43(0.82)	C(5)	6.17(0.92)	C(6)	14.04(2.42)
O(1)	5.15(0.51)	O(2)	5.50(0.54)	O(3)	6.56(0.63)

TABLE 3. THE OBSERVED AND CALCULATED STRUCTURE FACTORS

L FO FC	L FO FC	L FO FC	L FO FC	L FO FC	L FO FC	L FO FC	L FO FC
H,K= 0 0	H,K= 0 5	-3 21 22	7 14 -25	-9 22 -19	-5 20 18	8 0 8	3 8 6
-9 23 27	-11 14 -19	-2 8 13	8 9 -19	-8 20 -21	-4 0 0	9 11 12	4 23 -23
-8 35 37	-10 16 -22	-1 11 -4	H,K= 1 4	-7 14 -15	-3 29 -25	H,K= 1-10	5 30 -34
-7 24 24	-9 29 -31	0 11 -18	-11 29 -23	-6 7 7	-2 50 -45	0 6 7	6 24 -26
-6 0 -4	-8 8 6	H,K= 0 11	-10 18 -18	-5 27 26	-1 19 -18	1 13 18	H,K= 2 4
-5 86 -78	-7 35 32	-8 13 -13	-9 16 -13	-4 23 28	0 28 -28	2 11 12	-11 9 -1
-4 79 -68	-6 56 56	-7 0 -6	-8 25 21	-3 7 17	1 20 14	3 10 7	-10 10 8
-3 81 -71	-5 41 38	-6 0 7	-7 50 51	-2 0 1	2 38 38	4 10 -5	-9 24 18
-2 12 0	-4 23 18	-5 15 15	-6 55 52	-1 14 -20	3 31 32	5 14 -12	-8 26 22
H,K= 0 1	-3 47 -42	-4 25 21	-5 26 23	0 21 -27	4 29 26	6 14 -17	-7 17 15
-10 14 18	-2 68 -69	-3 17 10	-4 43 -31	1 16 -18	5 15 13	H,K= 1-11	-6 20 -16
-9 19 22	-1 65 -60	-2 0 -2	-3 63 -60	H,K= 1 10	6 23 -18	4 10 9	-5 28 -30
-8 0 12	0 22 -20	H,K= 1 0	-2 83 -89	-10 8 -10	7 25 -26	5 10 -3	-4 35 -36
-7 0 -3	1 21 18	-10 13 15	-1 43 -36	-9 13 -15	8 21 -22	6 0 -9	-3 32 -35
-6 58 -55	2 47 62	-9 12 7	0 24 16	-8 0 -11	9 0 -8	H,K= 2 0	-2 0 -4
-5 51 -45	3 40 38	-8 10 -10	1 71 58	-7 0 2	10 0 0	-10 11 -14	-1 42 44
-4 59 -51	4 17 19	-7 17 -20	2 74 62	-6 0 18	H,K= 1 -5	-9 14 -22	0 45 46
-3 3 -5	5 0 -5	-6 49 -48	3 41 34	-5 10 21	-5 23 23	-8 21 -18	1 31 35
-2 79 71	6 23 -23	-5 27 -23	4 0 -6	-4 7 17	-4 19 20	-7 0 -6	2 0 0
-1 93 125	7 20 -26	-4 6 -3	5 22 -27	-3 7 3	-3 20 16	-6 23 17	3 11 -12
0 74 63	H,K= 0 6	-3 36 32	6 19 -33	-2 0 -17	-2 15 -13	-5 34 24	4 34 -38
1 18 12	-11 16 -16	-2 67 74	H,K= 1 5	-1 23 -26	-1 34 -31	-4 40 40	5 21 -23
2 43 -35	-10 8 -15	-1 88 92	-11 12 -11	0 8 -15	0 39 -41	-3 17 14	H,K= 2 5
3 104 -94	-9 0 -3	1 37 -36	-10 0 -5	H,K= 1 11	1 21 -19	-2 0 -2	-11 11 11
4 91 -75	-8 25 23	2 53 -51	-9 16 11	-3 9 -12	2 21 -16	-1 24 -21	-10 17 14
5 17 -15	-7 34 31	3 75 -66	-8 41 37	H,K= 1 -1	3 31 29	0 27 -37	-9 15 12
6 35 27	-6 41 40	4 51 -43	-7 28 25	-10 15 18	4 36 38	1 23 -25	-8 9 -8
7 32 37	-5 14 12	5 14 11	-6 21 18	-9 22 26	5 41 39	2 17 -18	-7 13 -15
8 37 41	-4 28 -24	6 45 46	-5 10 -10	-8 22 20	6 11 13	3 6 1	-6 21 -19
9 14 14	-3 67 -64	7 32 34	-4 48 -47	-7 0 -1	7 11 -10	4 30 27	-5 28 -26
H,K= 0 2	-2 48 -46	8 22 25	-3 76 -77	-6 41 -38	8 27 -29	5 26 27	-4 8 -7
-10 6 10	-1 36 -32	H,K= 1 1	-2 24 -19	-5 64 -62	9 20 -22	6 19 19	-3 11 8
-9 0 -3	0 36 27	-10 10 -6	-1 11 3	-4 56 -52	10 17 -14	7 0 0	-2 31 35
-8 22 -21	1 64 46	-9 12 -14	0 65 52	-3 13 -8	11 12 3	8 0 -8	-1 20 20
-7 30 -30	2 49 48	-8 34 -29	1 72 58	-2 61 60	H,K= 1 -6	H,K= 2 1	0 24 23
-6 26 -22	3 24 21	-7 30 -25	2 38 32	-1 58 76	-5 12 10	-10 16 -24	1 0 0
-5 21 -17	4 11 -5	-6 0 -4	3 0 -1	0 72 122	-4 31 29	-9 18 -21	2 15 -14
-4 8 8	5 28 -29	-5 31 31	4 12 -27	1 19 18	-3 29 27	-8 9 -4	3 26 -26
-3 53 55	6 25 -29	-4 14 13	H,K= 1 6	2 57 -54	-2 28 23	-7 23 19	4 20 -19
-2 63 63	H,K= 0 7	-3 50 57	-10 10 11	3 85 -84	-1 7 -4	-6 52 45	5 0 -8
-1 46 45	-9 8 15	-2 29 26	-9 25 25	4 71 -64	0 37 -34	-5 34 28	H,K= 2 6
0 30 -26	-8 15 18	-1 20 15	-8 0 1	5 30 -23	1 54 -49	-4 35 28	-11 14 17
1 7 -2	-7 20 20	0 71 -71	-7 11 10	6 15 12	2 36 -35	-3 15 -13	-10 6 6
2 88 -80	-6 0 -1	1 24 10	-6 25 -20	7 38 42	3 0 3	-2 40 -54	-9 14 -12
3 41 -41	-5 15 -14	2 100 -83	-5 32 -31	8 32 35	4 23 21	-1 58 -53	-8 25 -22
4 27 -26	-4 32 -36	3 11 -12	-4 39 -36	9 14 15	5 41 43	0 9 -12	-7 19 -19
5 24 19	-3 43 -39	4 12 7	-3 7 -5	H,K= 1 -2	6 35 34	1 11 -10	-6 19 -19
6 31 35	-2 13 -11	5 43 36	-2 0 5	-9 24 24	7 0 8	2 24 23	-5 8 4
7 34 37	-1 21 17	6 32 27	-1 41 34	-8 31 33	8 12 -13	3 40 37	-4 24 24
8 13 17	0 37 34	7 31 26	0 46 41	-7 25 26	9 25 -25	4 26 27	-3 26 27
H,K= 0 3	1 41 37	H,K= 1 2	1 20 24	-6 9 -4	10 18 -20	5 9 6	-2 14 15
-10 15 -15	2 19 18	-10 25 -23	2 0 -4	-5 52 -48	H,K= 1 -7	6 12 -6	-1 13 13
-9 21 -26	3 0 -3	-9 32 -34	3 11 -17	-4 71 -66	-3 31 33	7 12 -12	0 15 -13
-8 29 -29	4 28 -26	-8 20 -20	4 28 -32	-3 58 -54	-2 29 34	8 16 -17	1 19 -18
-7 22 -19	5 19 -25	-7 0 1	H,K= 1 7	-2 15 -10	-1 20 19	H,K= 2 2	2 15 -18
-6 0 4	H,K= 0 8	-6 46 42	-11 10 18	-1 53 58	0 7 -6	-11 15 -20	3 14 -13
-5 46 40	-9 8 14	-5 33 27	-10 7 14	0 80 114	1 33 -30	-10 15 -20	4 0 0
-4 60 61	-8 0 0	-4 74 73	-9 10 2	1 55 62	2 44 -52	-9 12 -13	H,K= 2 7
-3 15 15	-7 0 -8	-3 0 -1	-8 12 -12	2 25 19	3 24 -23	-8 23 20	-11 9 5
-2 7 5	-6 16 -17	-2 48 -45	-7 21 -19	3 40 -39	4 9 3	-7 40 37	-10 6 -7
-1 5 -10	-5 24 -25	-1 44 -49	-6 32 -30	4 73 -74	5 23 24	-6 52 45	-9 20 -22
0 43 -45	-4 20 -16	0 13 -14	-5 15 -11	5 44 -44	6 31 31	-5 30 29	-8 21 -18
1 40 -40	-3 8 5	1 64 -51	-4 10 4	6 19 -16	7 25 26	-4 16 -14	-7 27 -27
2 37 -31	-2 22 17	2 6 -1	-3 28 22	7 15 11	8 0 2	-3 65 -71	-6 0 13
3 0 -3	-1 18 20	3 47 30	-2 25 24	8 27 27	9 14 -14	-2 37 -50	-5 25 23
4 24 22	0 30 24	4 41 33	-1 23 27	9 20 24	10 16 -15	-1 33 -41	-4 33 32
5 28 30	1 8 10	5 24 22	0 0 2	H,K= 1 -3	H,K= 1 -8	0 3 2	-3 22 19
6 21 24	3 19 -19	6 19 14	1 10 -3	-8 32 30	-3 10 8	1 32 30	-2 11 6
7 10 13	H,K= 0 9	7 0 -4	2 24 -20	-7 20 26	-2 25 28	2 74 77	-1 20 -19
H,K= 0 4	-10 0 11	8 14 -18	3 22 -22	-6 29 28	-1 29 29	3 21 17	0 28 -25
-11 5 -9	-9 0 0	H,K= 1 3	4 6 -13	-5 13 -9	0 14 16	4 6 5	1 22 -20
-10 26 -29	-8 17 -15	-11 20 -19	H,K= 1 8	-4 42 -43	1 14 -10	5 16 -18	2 6 -8
-9 23 -26	-7 15 -18	-10 33 -32	-11 11 14	-3 57 -61	2 17 -16	6 20 -24	3 0 5
-8 30 -28	-6 18 -23	-9 29 -26	-10 0 4	-2 27 -27	3 41 -41	7 21 -21	H,K= 2 8
-7 13 11	-5 0 -5	-8 0 0	-9 14 -14	-1 18 -14	4 12 -17	H,K= 2 3	-11 8 -7
-6 44 44	-4 10 12	-7 32 28	-8 25 -22	0 47 46	5 10 2	-11 13 -15	-10 9 -12
-5 61 63	-3 25 22	-6 61 60	-7 30 -30	1 50 53	6 16 17	-10 10 -9	-9 20 -20
-4 26 22	-2 14 16	-5 54 57	-6 0 -5	2 57 62	7 14 16	-9 14 12	-8 14 -18
-3 30 26	-1 23 19	-4 10 10	-5 0 6	3 0 3	8 20 18	-8 28 26	-7 0 0
-2 57 -62	0 11 -3	-3 39 -39	-4 36 31	4 0 1	H,K= 1 -9	-7 45 41	-6 20 20
-1 60 -56	1 8 -13	-2 59 -58	-3 27 26	5 54 -54	-1 11 16	-6 27 23	-5 27 26
0 43 -47	2 9 -17	-1 71 -80	-2 14 17	6 24 -26	0 27 24	-5 4 1	-4 27 26
1 16 -13	H,K= 0 10	0 40 -28	-1 7 0	7 17 -15	1 12 9	-4 67 -71	-3 13 5
2 11 10	-9 7 -10	1 11 6	0 14 -15	8 0 0	2 17 1	-3 42 -43	-2 17 -17
3 44 41	-8 16 -18	2 84 69	1 25 -24	9 0 7	3 10 -12	-2 43 -52	-1 31 -29
4 33 34	-7 21 -21	3 40 31	2 14 -17	10 20 19	4 14 -19	-1 0 1	0 24 -21
5 16 17	-6 0 -4	4 41 33	3 7 -6	H,K= 1 -4	5 12 -18	0 42 44	1 11 -10
6 0 0	-5 6 11	5 10 -2	H,K= 1 9	-7 25 23	6 0 -4	1 63 71	2 14 10
7 0 -11	-4 19 20	6 7 -16	-10 11 -8	-6 18 23	7 0 6	2 30 26	

TABLE 3. THE OBSERVED AND CALCULATED STRUCTURE FACTORS (Continued)

L	FO	FC
H,K= 2 9		
-10	14	-13
-9	11	-9
-8	9	-3
-7	15	15
-6	17	16
-5	21	22
-4	10	2
-3	7	-8
-2	26	-25
-1	22	-20
0	7	-8
H,K= 2 10		
-8	11	9
-7	13	12
-6	13	8
-5	8	1
-4	10	-8
-3	17	-17
-2	16	-14
-1	8	-3
H,K= 2 -1		
-9	9	-5
-8	12	-18
-7	25	-25
-6	14	-11
-5	0	0
-4	21	18
-3	39	37
-2	48	44
-1	11	14
0	14	-18
1	34	-34
2	45	-50
3	30	-22
4	0	0
5	21	18
6	38	37
7	21	22
8	12	3
9	11	-11
H,K= 2 -2		
-7	10	-13
-6	47	-44
-5	24	-20
-4	20	-15
-3	28	24
-2	44	49
-1	62	67
0	13	7
1	5	-5
2	54	-54
3	54	-49
4	37	-36
5	17	15
6	23	19
7	31	34
8	28	19
9	9	1
H,K= 2 -3		
-8	9	15
-7	9	4
-6	24	-21
-5	47	-45
-4	40	-37
-3	9	-6
-2	28	23
-1	49	49
0	63	71
1	16	13
2	24	-22
3	47	-44
4	54	-48
5	22	-18
6	9	8
7	22	21
8	24	23
9	9	13
H,K= 2 -4		
-6	10	3
-5	21	-22
-4	41	-38
-3	41	-37
-2	0	-4
-1	21	22
0	44	44
1	39	39
2	25	22
3	20	-16
4	33	-29
5	36	-31
6	13	-15
7	0	2
8	10	12
9	11	13
H,K= 2 -5		
-5	9	1
-4	18	-17
-3	25	-23
-2	37	-31
-1	10	-7
0	13	11
1	27	23
2	30	28
3	18	18
4	10	6
5	19	-20
6	16	-17
7	15	-15
8	6	-7
9	9	2
H,K= 2 -6		
-5	11	14
-4	9	7
-3	12	-10
-2	15	-13
-1	30	-27
0	19	-18
1	0	0
2	19	20
3	15	13
4	32	29
5	11	10
6	9	-6
7	15	-19
8	12	-15
9	9	-11
H,K= 2 -7		
-3	9	11
-2	10	-3
-1	12	-13
0	29	-26
1	27	-22
2	13	-9
3	23	21
4	17	15
5	28	26
6	14	11
7	10	-5
8	13	-18
9	10	-13
H,K= 2 -8		
-3	20	22
-2	13	13
-1	6	0
0	22	-18
1	26	-21
2	28	-26
3	10	-1
4	12	13
5	24	21
6	18	16
7	11	8
8	9	-5
H,K= 2 -9		
-1	16	12
0	6	0
1	17	-16
2	19	-17
3	20	-18
4	9	-2
5	9	9
6	16	16
7	11	10
H,K= 2-10		
2	12	-8
3	19	-14
4	12	-11
5	0	-3
H,K= 3 0		
-7	24	22
-6	26	23
-5	23	25
-4	7	-9
-3	24	-26
-2	25	-36
-1	24	-23
0	5	-9
1	18	20
2	31	30
3	22	19
4	10	9
5	11	-5
6	14	-16
7	12	-10
H,K= 3 1		
-8	21	19
-7	34	29
-6	22	19
-5	0	2
-4	30	-38
-3	30	-36
-2	37	-36
-1	0	0
0	18	23
1	38	38
2	33	30
3	0	8
4	17	-15
5	21	-20
6	15	-17
7	10	-6
H,K= 3 2		
-10	0	3
-9	18	14
-8	24	22
-7	18	14
-6	0	-2
-5	23	-21
-4	37	-41
-3	20	-26
-2	0	-3
-1	16	19
0	37	40
1	33	35
2	0	3
3	14	-13
4	24	-23
5	22	-21
6	8	-9
H,K= 3 3		
-10	12	11
-9	14	13
-8	9	1
-7	0	-1
-6	21	-20
-5	26	-27
-4	13	-10
-3	5	0
-2	9	12
-1	29	33
0	25	25
1	0	5
2	16	-13
3	14	-14
4	24	-25
5	9	-8
H,K= 3 4		
-11	14	11
-10	11	7
-9	9	-4
-8	14	-9
-7	22	-21
-6	13	-11
-5	8	-5
-4	12	13
-3	11	6
-2	28	33
-1	8	7
0	5	-11
1	11	-11
2	12	-11
3	18	-20
4	9	-4
5	8	4
H,K= 3 5		
-11	8	7
-10	9	-4
-9	17	-15
-8	20	-20
-7	13	-14
-6	8	3
-5	15	12
-4	24	23
-3	22	23
-2	5	3
-1	11	-8
0	17	-13
1	22	-18
2	11	-11
3	12	-1
4	9	10
H,K= 3 6		
-10	14	-13
-9	18	-18
-8	13	-13
-7	0	-5
-6	14	14
-5	33	29
-4	23	19
-3	8	9
-2	13	-14
-1	23	-17
0	27	-25
1	9	-8
2	0	2
3	19	14
H,K= 3 7		
-10	14	-11
-9	14	-13
-8	0	-6
-7	13	11
-6	24	23
-5	19	18
-4	11	9
-3	9	-7
-2	25	-22
-1	29	-25
0	6	-8
1	0	2
2	21	15
H,K= 3 8		
-10	10	-8
-9	11	-2
-8	9	6
-7	14	17
-6	6	7
-5	11	10
-4	0	-7
-3	20	-17
-2	20	-18
-1	8	-8
0	7	2
H,K= 3 9		
-9	10	8
-8	0	8
-7	9	4
-6	6	1
-5	0	-6
-4	13	-12
-3	11	-10
-2	0	-3
-1	9	3
H,K= 3 10		
-5	15	-12
-4	10	-3
H,K= 3 -1		
-9	11	-16
-8	0	-5
-7	0	6
-6	25	23
-5	14	10
-4	24	24
-3	6	-5
-2	17	-18
-1	20	-27
0	10	-12
1	15	-19
2	13	11
3	18	14
4	19	20
5	11	10
6	6	4
7	11	-10
H,K= 3 -2		
-8	8	-13
-7	13	-12
-6	6	5
-5	13	12
-4	17	16
-3	22	19
-2	11	12
-1	11	-9
0	23	-23
1	19	-17
2	20	-22
3	0	0
4	14	14
5	19	16
6	18	17
7	6	5
8	0	-5
H,K= 3 -3		
-7	6	-13
-6	21	-19
-5	0	-2
-4	10	9
-3	24	21
-2	28	25
-1	20	18
0	8	-5
1	25	-25
2	29	-27
3	22	-18
4	0	-2
5	15	12
6	22	21
7	14	14
8	11	5
H,K= 3 -4		
-6	14	-18
-5	24	-21
-4	9	-9
-3	9	9
-2	33	30
-1	29	23
0	22	19
1	8	-3
2	28	-25
3	33	-29
4	21	-16
5	0	3
6	11	9
7	19	18
8	11	11
H,K= 3 -5		
-5	12	-18
-4	22	-20
-3	9	-7
-2	11	4
-1	33	30
0	24	21
1	17	14
2	10	-4
3	16	-13
4	30	-29
5	9	-7
6	9	-1
7	9	8
8	10	10
H,K= 3 -6		
-4	13	-17
-3	12	-14
-2	11	-10
-1	0	3
0	20	19
1	20	18
2	12	10
3	6	0
4	0	-4
5	18	-19
6	9	-8
7	0	-2
H,K= 3 -7		
-3	11	-13
-2	8	-11
-1	14	-11
0	9	8
1	9	7
2	20	17
3	7	7
4	11	8
5	9	-3
6	11	-9
7	11	-11
H,K= 3 -8		
-1	14	-12
0	12	-12
1	10	-3
2	9	4
3	14	13
4	8	11
5	8	7
6	10	-1
H,K= 4 0		
-4	23	-28
-3	15	-9
-2	0	-8
-1	0	10
0	17	20
1	22	21
2	0	3
3	0	-2
4	15	-13
H,K= 4 1		
-4	12	-7
-3	11	-8
-2	0	10
-1	19	18
0	17	20
1	0	5
2	9	-4
3	12	-12
4	15	-14
H,K= 4 2		
-4	5	3
-3	11	4
-2	19	19
-1	14	9
0	0	6
1	9	-5
2	11	-10
3	14	-12
4	8	-6
H,K= 4 3		
-4	10	10
-3	15	12
-2	0	8
-1	0	1
0	7	-10
1	0	-9
2	0	-8
3	8	-5
H,K= 4 4		
-4	15	12
-3	11	11
-2	9	-5
-1	14	-13
0	12	-11
1	0	-8
2	8	-2
3	7	5
H,K= 4 5		
-4	9	8
-3	11	-2
-2	18	-18
-1	14	-11
0	9	-11
1	7	0
2	10	9
H,K= 4 6		
-2	15	-13
-1	8	-11
0	0	0
1	7	10
H,K= 4 7		
-4	5	-7
-3	12	-12
-2	10	-5
H,K= 4 8		
-4	8	-8
H,K= 4 -1		
-4	12	-13
-3	24	-21
-2	19	-15
-1	0	-3
0	6	7
1	15	15
2	23	19
3	9	4
H,K= 4 -2		
-4	7	3
-3	12	-7
-2	16	-16
-1	12	-14
0	0	-5
1	0	4
2	0	9
3	13	12
H,K= 4 -3		
-3	9	4
-2	0	-4
-1	0	-6
0	12	-17
1	0	-6
2	0	0
3	0	6
4	12	9
H,K= 4 -4		
-3	10	11
-2	0	8
-1	0	-3
0	0	-4
1	15	-16
2	11	-10
3	0	-2
4	10	7
H,K= 4 -5		
-2	14	16
-1	0	6
0	0	0
1	8	-7
2	15	-13
3	12	-11
4	10	-1
H,K= 4 -6		
-1	0	14
0	7	7
1	0	0
2	11	-8
3	10	-9
4	14	-10
H,K= 5 0		
-4	4	0
-3	0	2
-2	0	6
-1	8	8
0	6	4
1	9	-1
H,K= 5 1		
-4	10	5
-3	0	3
-2	8	10
H,K= 5 2		
-4	7	4
-3	0	9
-2	8	-2
-1	0	-3
0	5	-6
H,K= 5 3		
0	6	-7
H,K= 5 -1		
-4	8	-9
-3	0	-2
-2	0	4
-1	8	7
0	6	9
H,K= 5 -2		
-3	0	-8
-2	0	-3
-1	0	2
0	8	10
1	7	5

with their estimated standard deviations, are given in Table 1, while the thermal parameters are shown in Table 2. The observed and calculated structure factors are given in Table 3.

Results and Discussion

A plan of the molecule is shown in Fig. 1. The bond distances and angles, along with their estimated standard deviations are listed in Table 4. Figure 2 shows the molecule viewed parallel to the plane containing the chlorine bridge along the Cl-Cl′ line. The refinement is not enough to make a detailed discussion of the bond distances and angles, which may be due to a strong thermal vibration or disorder in the ligand group. Nevertheless, some conclusions can be drawn.

The most important conclusion drawn from the present structure determination is that the π-allyl coordination of the ethyl acetoacetate group to the palladium atom is established for this complex. The coordination configuration resembles those found in the dimeric π-allylpalladium chloride.[5]

Four heavier atoms, palladium and chlorine and their centrosymmetric equivalents, lie on the same plane. This plane of the four atoms fits the equation:

$$-0.765X + 0.595Y + 0.247Z = 0\,.$$

where the orthogonal axes, X, Y, and Z, refer to the triclinic axes by the following transformation:

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

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

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

5) A. E. Smith, *Acta Crystallogr.*, **18**, 331 (1965).

TABLE 4. BOND DISTANCES (Å) AND BOND ANGLES (°) WITH THEIR RESPECTIVE ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Pd-Cl	2.40(0.01)	Cl-Pd-Cl′	89.4(0.4)
Pd-Cl′	2.41(0.01)	Cl-Pd-C (3)	104.3(1.2)
Pd-C (1)	2.08(0.05)	C (1)-Pd-Cl′	102.7(1.5)
Pp-C (2)	2.16(0.05)	Pd-C (1)-C (2)	73.7(2.9)
Pd-C (3)	2.11(0.04)	Pd-C (3)-C (2)	74.0(2.8)
C (1)-C (2)	1.42(0.07)	Pd-C (2)-O (1)	122.1(3.2)
C (2)-C (3)	1.34(0.07)	C (1)-C (2)-C (3)	105.7(4.3)
C (3)-C (4)	1.58(0.06)	C (1)-C (2)-O (1)	124.6(4.3)
C (5)-C (6)	1.60(0.10)	C (3)-C (2)-O (1)	129.2(4.3)
C (2)-O (1)	1.37(0.06)	C (2)-C (3)-C (4)	115.7(4.0)
C (4)-O (2)	1.25(0.05)	C (3)-C (4)-O (2)	122.6(3.9)
C (4)-O (3)	1.36(0.06)	C (3)-C (4)-O (3)	112.5(3.6)
C (5)-O (3)	1.52(0.06)	O (2)-C (4)-O (3)	124.5(4.0)
		C (4)-O (3)-C (5)	115.3(3.5)
		O (3)-C (5)-C (6)	99.0(4.6)

INTERMOLECULAR HYDROGEN-BOND DISTANCE (Å)

O (1)-O (2)″	2.81(0.04)

DIHEDRAL ANGLES (°)

Pd, Pd′, Cl, Cl′/C (1), C (2), C (3)	108.4
Pd, C (1), C (3)/C (1), C (2), C (3)	106.1

Fig. 3(a)

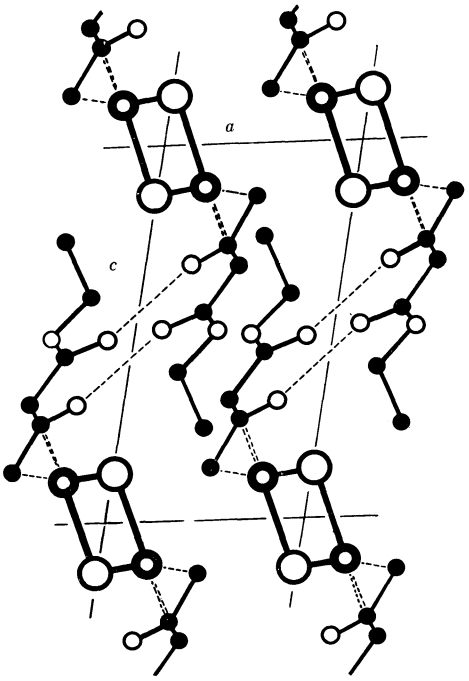

Fig. 3(b)

Fig. 3. Crystal structure.
(a) Projected down along the *a* axis, and (b) Projected down along the *b* axis.

The π-allyl fragment, which must be planar, makes an angle of 108° with this plane of four atoms (Fig. 2) and an angle of 106° with the plane containing the palladium and two carbon atoms, C(1) and C(3). These two values are very similar to those found in other allyl complexes.[6-8] The two carbon atoms of the π-allyl fragment, C(1) and C(3) are 0.13 and 0.10 Å respectively below the plane of the four atoms, while the C(2) atom is 0.72 Å above the plane.

The distance of Pd-Pd′ is 3.418±0.006 Å, which with the values which have previously appeared in the literature;[5,6] this Pd-Pd distance indicates that there is no metal-metal interaction. The average palladium-chlorine distance of 2.41±0.01 Å is identical, within the range of experimental error, with that in dimeric π-allylpalladium chloride, 2.413±0.002 Å.[5] The angle of Cl-Pd-Cl′ is 89.4±0.4°, which is very close to the expected square planar value of 90°. The three palladium-carbon distances are also equal, with a mean of 2.12±0.05 Å, which corresponds to that of 2.117±0.008 Å found in dimeric π-allylpalladium chloride.[5] Recently, it was pointed out that the bonding of the metal to the allyl group is not always symmetrical.[6] A typical example of the symmetrical bonding is π-allylpalladium chloride, while a representative unsymemtrical one is triphenylphosphine-2-methylallylpalladium chloride.[9] In the present complex, however, the symmetrical bonding is again observed.

The C(4) atom bonded to C(3) is 0.32 Å out of the plane of the π-allyl fragment, bent towards the palladium, as can be seen in Fig. 2. The hydroxyl group, a part of the ligand which is attached to the central carbon atom of the π-allyl fragment, does not lie on the π-allyl plane; O(1) is 0.13 Å out of the plane, bent towards the palladium. This value is smaller than that in the triphenylphosphine-2-methylallylpalladium chloride[9] and other π-allylpalladium complexes.[6,7] The shift from the plane may result from the interaction of hydrogen bonds discussed below and from the σ-π electron mixing in the ligand with the metal atom in a way which has been discussed for metal-cyclic ligand bonds by Kettle.[10]

The crystal structure is shown in Fig. 3. The intermolecular atomic contacts less than 4.5 Å were calculated for this complex. None of them, however, is short enough to suggest any significant deviations from normal van der Waals interactions except for the hydrogen bonds.

The hydrogen bonding, between the enolic hydroxyl group of one molecule and the carbonyl group of the other molecules related by the center of symmetry, forms endless sheets of molecules extended along the c axis. This hydrogen bond distance is 2.81±0.04 Å.

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10) S. F. A. Kettle, *Inorg. Chim. Acta*, **1**, 303 (1967).