

Fig. 2. Difference synthesis in a section containing the O(1)—Cl—O(2) group, based on the reflections with  $\sin \theta/\lambda \leq 0.55 \text{ \AA}^{-1}$  and the atomic parameters from the high-order refinement. Contour interval  $0.1 \text{ e \AA}^{-3}$ ; zero contour omitted.

$106.4 (1)^\circ$  compares well with the  $106.8 (2)^\circ$  found in  $\text{NaClO}_3$  (Burke-Laing & Trueblood, 1977).

The librations of the  $\text{ClO}_3$  group cannot be derived uniquely from the thermal parameters; however, a TLX analysis (Pawley, 1963) resulted in an average Cl—O length of  $1.497 (2) \text{ \AA}$ , in agreement with the  $1.502 (3) \text{ \AA}$  in  $\text{NaClO}_3$ . Each O atom is involved in three K—O bonds, leading to a ninefold coordination of the K atom (Fig. 1). The position of the K atom in the conventional

refinement is identical with that in the high-order one. The Cl atom is shifted along its anticipated lone-pair direction by  $0.0034 (4) \text{ \AA}$  in the conventional refinement. The O atoms show displacements of  $0.0069 (22)$  and  $0.0099 (15) \text{ \AA}$  into the Cl—O bonds in the conventional refinement, compared with the high-order results. These shifts can be attributed to the aspherical distribution of the valence electrons, due to chemical bonding.

A final difference synthesis in a section through the chlorate group is shown in Fig. 2. Though some features are seen which may be related to bonding electrons, the figure is not very accurate. A study at low temperature would be required to give a clearer picture of the distribution of the bonding electrons.

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### Di- $\mu$ -chloro-bis[4,6- $\eta$ -(1-chlorocyclooctatrienyl)]dipalladium(II)

BY N. C. BAENZIGER, CAROL VALLEY GOEBEL, B. A. FOSTER AND J. R. DOYLE

*Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, USA*

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**Abstract.**  $(\text{ClC}_8\text{H}_8\text{PdCl})_2$ , monoclinic,  $P2_1/c$ ,  $a = 12.570 (1)$ ,  $b = 7.287 (4)$ ,  $c = 9.874 (5) \text{ \AA}$ ,  $\beta = 96.28 (5)^\circ$ ,  $Z = 2$ ,  $D_m = 2.00 (2)$ ,  $D_x = 2.08 \text{ g cm}^{-3}$ , FW 562.9,  $\sum \Delta|F|/\sum F_o = 0.030$  from 1492 reflections. The complex is a chlorine-bridged dimer with Pd forming allylic-type  $\pi$  bonds to a boat-shaped cyclooctatetraene molecule which has undergone addition of a Cl atom *trans* to the allylic-type bond. Pd—C =  $2.114 (4)$ ,  $2.104 (3)$ ,  $2.134 (3) \text{ \AA}$ ; C—C(allyl) =  $1.405 (5)$ ,  $1.421 (5) \text{ \AA}$ ; dihedral angle (allylic group/Pd coordination plane) =  $119.8^\circ$ .

**Introduction.** Intensity data (1492 observed present, 168 observed with intensity less than three standard deviations above the background) were collected using a four-circle diffractometer, a stepped  $\theta$ - $2\theta$  scan, and graphite-monochromatized Mo  $K\alpha$  radiation to  $2\theta = 52^\circ$ . Intensity was measured at a minimum of seven steps over the angular diffraction range of a peak; the actual peak position was determined from these steps and additional steps were measured so that three steps were measured on each side of the peak. The step size, adjusted to allow for  $\alpha_1$ - $\alpha_2$  separation, ranged from

0.07 to 0.11° (2 $\theta$ ). Backgrounds were measured at  $\pm 1.2^\circ$  from the peak center. The total net intensity was calculated by subtracting a linearly interpolated background from each step, summing the steps, multiplying by the step width, and adding corrections to the edges of the peak if the net step intensities at the limits of the scan were greater than zero. The correction was computed by fitting a Gaussian curve to the last two step values and using the Gauss error function to compute the additional area of the peak not covered by the step values. The data were corrected for Lorentz and polarization factors and for absorption [analytical method of de Meulenaer & Tompa (1965), as used in the program *ABSORB* described by Templeton & Templeton (1973) with local adaptation by F. J.

Table 1. Position parameters (for Pd, Cl  $\times 10^5$ , for C  $\times 10^4$ , for H  $\times 10^3$ )

Standard deviations in the last significant digit are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
Pd	9422 (4)	44394 (3)	39122 (2)
Cl(1)	6624 (7)	69743 (11)	54312 (9)
Cl(2)	51012 (9)	9590 (17)	32706 (11)
C(1)	2418 (3)	5282 (5)	3280 (4)
C(2)	3237 (3)	4871 (5)	4395 (4)
C(3)	3902 (3)	3440 (6)	4474 (4)
C(4)	3816 (3)	1983 (5)	3415 (4)
C(5)	3008 (3)	613 (5)	3735 (4)
C(6)	1969 (3)	885 (5)	3402 (4)
C(7)	1469 (3)	2383 (5)	2599 (3)
C(8)	1880 (3)	4132 (5)	2288 (3)
H(1)	239 (3)	636 (5)	310 (3)
H(2)	332 (3)	580 (5)	515 (4)
H(3)	441 (3)	325 (5)	518 (4)
H(4)	365 (3)	245 (5)	251 (3)
H(5)	332 (4)	950 (5)	430 (4)
H(6)	154 (3)	5 (5)	364 (3)
H(7)	90 (3)	206 (4)	201 (3)
H(8)	147 (4)	472 (6)	137 (5)

Table 2. Interatomic distances (Å), bond angles (°) and least-squares planes in the yellow isomer

Standard deviations in the last significant digit are given in parentheses.

Pd—Cl(1)	2.429 (1)		
Pd—Cl(1)'	2.416 (1)		
Pd—C(1)	2.112 (4)		
Pd—C(8)	2.104 (3)		
Pd—C(7)	2.134 (3)		
Cl(1)—Pd—Cl(1)'	88.7 (3)		
Pd—Cl(1)—Pd	91.3 (2)		
C(1)—C(2)	1.454 (6)	C(1)—C(2)—C(3)	126.3 (4)
C(2)—C(3)	1.334 (5)	C(2)—C(3)—C(4)	121.4 (4)
C(3)—C(4)	1.486 (5)	C(3)—C(4)—C(5)	109.3 (3)
C(4)—C(5)	1.482 (5)	C(4)—C(5)—C(6)	121.7 (3)
C(5)—C(6)	1.327 (6)	C(5)—C(6)—C(7)	127.1 (4)
C(6)—C(7)	1.451 (5)	C(6)—C(7)—C(8)	130.3 (3)
C(7)—C(8)	1.421 (5)	C(7)—C(8)—C(1)	122.8 (3)
C(8)—C(1)	1.405 (5)	C(8)—C(1)—C(2)	130.7 (3)
C(4)—Cl(2)	1.800 (3)	C(3)—C(4)—Cl(2)	110.8 (3)
C(1)—Cl(2)'	3.725 (2)	C(5)—C(4)—Cl(2)	112.3 (3)
Cl(2)—Cl(2)''	3.946 (1)	H(4)—C(4)—Cl(2)	100.3 (15)
C(1)—H(1)	0.80 (4)	C(5)—H(5)	1.04 (4)
C(2)—H(2)	1.01 (4)	C(6)—H(6)	0.87 (4)
C(3)—H(3)	0.90 (4)	C(7)—H(7)	0.90 (4)
C(4)—H(4)	0.96 (4)	C(8)—H(8)	1.08 (4)
C(2)—C(1)—H(1)	112 (4)	C(8)—C(1)—H(1)	115 (4)
C(1)—C(2)—H(2)	116 (4)	C(3)—C(2)—H(2)	118 (4)
C(2)—C(3)—H(3)	124 (4)	C(4)—C(3)—H(3)	115 (4)
C(3)—C(4)—H(4)	113 (4)	C(5)—C(4)—H(4)	111 (4)
C(4)—C(5)—H(5)	114 (4)	C(6)—C(5)—H(5)	124 (4)
C(5)—C(6)—H(6)	117 (4)	C(6)—C(6)—H(6)	115 (4)
C(6)—C(7)—H(7)	115 (4)	C(8)—C(7)—H(7)	112 (4)
C(7)—C(8)—H(8)	113 (4)	C(1)—C(8)—H(8)	120 (4)
Sums of angles about C atoms			
C(1)	355.7	C(5)	359.7
C(2)	360.3	C(6)	359.1
C(3)	360.4	C(7)	357.3
C(4)	332.4 [C(3), C(5) and Cl(2) only]	C(8)	355.8
	656.7 (including H atoms)		

Table 2 (cont.)

Plane normals [ $pX + qY + rZ = d$  (Å)]; *X*, *Y* and *Z* are coordinates in Å relative to the orthogonal unit vector set parallel to **a**, **b** and **c\***

Plane	<i>p</i>	<i>q</i>	<i>r</i>	<i>d</i>	Deviations from planes (Å)					
					Pd	Cl(1)	Cl(1)'	C(1)	C(8)	C(7)
A Pd, Cl(1), Cl(1)'	0.4647	-0.4739	0.7480	1.693	0	0	0	0.14	-0.46	0.12
B C(1), C(8), C(7)	-0.8923	0.4231	0.1574	-0.261						
C C(3), C(4), C(5)	0.6593	-0.5240	0.5392	3.970						
D C(1), C(2), C(6), C(7)	-0.7242	0.1542	0.6721	0.830	C(1)	C(2)	C(6)	C(7)		
					0.02	-0.01	0.01	-0.02		
E C(2), C(3), C(5), C(6)	-0.2856	-0.1757	0.9421	2.422	C(2)	C(3)	C(5)	C(6)		
					0.01	-0.01	0.01	-0.01		

Angles between normals to planes (°)

A/B	119.8	B/D	35.2	E/C	65.7
B/C	136.5	D/E	35.6		

Hollander]. The linear absorption coefficient  $\mu = 25.4 \text{ cm}^{-1}$ ; crystal bounding-planes separations were (100) 0.0016, (011) 0.0074, (01 $\bar{1}$ ) 0.0097 cm; corrections ranged from 0.63 to 0.92. The yellow crystals were one of two isomeric crystalline products from the addition of cyclooctatetraene to a benzene solution of bis(benzonitrile)palladium chloride.

The cell dimensions were determined by two different methods: back-reflection Weissenberg photographs gave  $a = 12.570$  (1),  $b = 7.289$  (5),  $c = 9.878$  (4) Å,  $\beta = 96.24$  (4) $^\circ$  at 295 (1) K, and  $a = 12.531$  (12),  $b = 7.210$  (3),  $c = 9.758$  (6) Å,  $\beta = 96.59$  (2) $^\circ$  at 100 (5) K. From twelve well centered reflections ( $2\theta > 33^\circ$ ) on the diffractometer,  $a = 12.567$  (7),  $b = 7.285$  (4),  $c = 9.869$  (5) Å,  $\beta = 96.32$  (5) $^\circ$  at 295 (1) K. Interatomic distances were calculated on the basis of the weighted average  $a = 12.570$ ,  $b = 7.287$ ,  $c = 9.874$  Å,  $\beta = 96.28^\circ$ . Systematic absences,  $h0l$  for  $l$  odd and  $0k0$  for  $k$  odd, indicated the unique space group  $P2_1/c$ . The density of the crystals was obtained pycnometrically.

The structure was solved by Patterson and electron density methods. H atoms were located by difference electron density maps and were included in the full-matrix least-squares refinement. The function minimized was  $RS = \sum w(|F_o| - |F_c|)^2$ ;  $(RS/\sum wF_o^2)^{1/2} = 0.026$ . Scattering factors for Pd, C and Cl were from *International Tables for X-ray Crystallography* (1962), those for H from Stewart, Davidson & Simpson (1965). Positional parameters are given in Table 1, bond distances and angles in Table 2.\* A plan view of half the molecule is given in Fig. 1 with an elevation view in Fig. 2. The other half of the molecule is generated by a center of symmetry.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33232 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

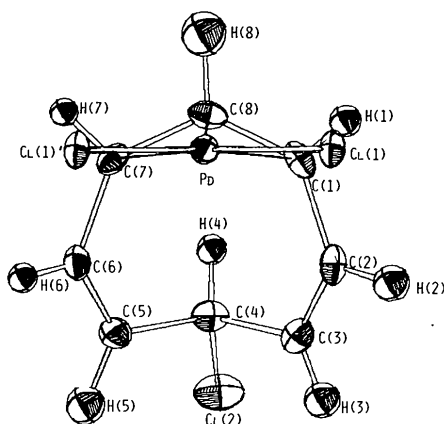


Fig. 1. An ORTEP plot (Johnson, 1965) of the title compound. The thermal ellipsoids are plotted at the 50% probability level. This view shows the molecule projected along the Pd-Pd interatomic vector of the dimer with only one of the  $\text{C}_8\text{H}_8\text{Cl}$  ligands shown.

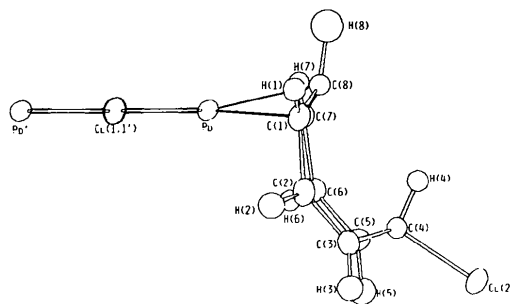


Fig. 2. An elevation view of the complex showing half of the dimer, the orientation of the Pd coordination plane to the  $\text{C}_8\text{H}_8\text{Cl}$  ligand, and the boat shape of the ligand.

**Discussion.** A comparison of the bond distances and angles of the Pd-allyl moiety with similar values reported for 20 other compounds (Lippard & Morehouse, 1969, a summary; Benedetti, Maglio, Palumbo & Pedone, 1973; Churchill & Mason, 1964; Dahl & Oberhänsli, 1965; Kilbourn, Mais & Owston, 1968; Kulizade, Kukina & Porai-Koshits, 1969; Levdič & Porai-Koshits, 1962; Minasyants & Struchkov, 1968; Oberhänsli & Dahl, 1965; Oda, Yasuoka, Ueki, Kasai & Kakudo, 1970; Smith, 1969) containing the Pd-allyl group discloses that the results for this complex fall within the wide range of values reported for this group. In the twenty structures the C-C bond lengths of the allylic group are not significantly different ( $\Delta\text{C-C}$  bond length less than  $3\sigma$ ) from each other. Our results lie just barely outside those limits: 1.405 (5) and 1.421 (5) Å,  $\Delta\text{C-C}/\sigma = 3.2$ ; weighted average of literature values = 1.392, 1.421 Å. The weights used were the squared reciprocals of the standard deviations reported for the values. Many of the instances of asymmetry in the allylic C-C distances reported may easily be an artifact of the data. We have collected two earlier data sets on this crystal. Data set 1, visually estimated from Weissenberg and precession films,  $R = 0.078$ , gave the allylic bond distances as 1.38 (3) and 1.56 (3) Å. Data set 2, densitometer integrated Weissenberg and precession films,  $R = 0.087$ , gave the distances as 1.38 (4) and 1.48 (4) Å. The present data set,  $R = 0.03$ , gives these distances as 1.405 (5) and 1.421 (5) Å. The three Pd-C distances are nearly identical [our values: 2.112 (4), 2.104 (3), 2.134 (3) Å; literature weighted averages: 2.124, 2.117, 2.149 Å]. The dihedral angle between the allylic group and the square-planar coordination plane of Pd is  $119.8^\circ$ ; the literature weighted average is  $115.8^\circ$ .

The chlorocyclooctatrienyl anion is symmetrically disposed toward the Pd atom, and it adopts a configuration which is unique for cyclooctatetraene derivatives. Cyclooctatetraene has been found in the tub, chair, planar, and multicyclic forms, but it has not been reported in the boat form displayed in this complex (Schröder, 1965; Paquette, 1975), nor has this

form been suggested as an intermediate in cyclooctatetraene reactions. [A very similar cyclooctadienyl form has been found in acetylacetonato(cycloocta-2,4-dienyl)palladium (Churchill, 1966).] This new conformation has an approximate mirror plane with the equivalent bond-distance pairs: allylic, 1.405, 1.421 Å; adjacent single bonds, 1.451, 1.454 Å; double bonds, 1.327, 1.334 Å; and terminal single bonds, 1.486, 1.482 Å. The C—Cl bond [1.800 (3) Å] is significantly longer than the single-bond distance (1.76 Å), though it is very nearly identical with the distance found in pentamethylbenzyl trichloride [1.796 (11) Å] (Baenziger & Schultz, 1973). Chemical reactions of this complex indicate that this Cl atom is quite labile, in keeping with the longer distance, as is also observed for the pentamethylbenzyl trichloride molecule.

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### Structure of Tri- $\mu$ -iodo-diiodotetrakis(methyldiphenylphosphine)diiridium Triiodide Formed from Oxidative Additions of I<sub>2</sub> to the Cation {Ir[PCH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>}<sup>+</sup>

BY MAGRIET J. NOLTE,\* ERIC SINGLETON AND ERWIN VAN DER STOK

National Chemical Research Laboratory, Council for Scientific and Industrial Research, PO Box 395, Pretoria 0001, South Africa

(Received 26 August 1977; accepted 12 December 1977)

**Abstract.** {Ir<sub>2</sub>I<sub>5</sub>[PCH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>}I<sub>3</sub>,  $M_r = 2200.6$ , monoclinic,  $P2_1/c$ ,  $a = 12.45$  (2),  $b = 28.98$  (2),  $c = 17.38$  (2) Å,  $\beta = 107.7$  (1)°,  $V = 5976$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 2.46$ ,  $D_c = 2.45$  g cm<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 90.6$  cm<sup>-1</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å. Anisotropic least-squares refinement converged to  $R = 0.09$  for 3993 observed reflections. Coordination around Ir is approximately

octahedral and the binuclear compound has a triple I bridge. Ir—I lengths average 2.75 (P *trans*) and 2.68 Å (I *trans*). Ir—P lengths average 2.33 Å.

**Introduction.** During studies on oxidative addition reactions of the cations [IrL<sub>4</sub>]<sup>+</sup> ( $L =$  neutral donor ligand) with the halogens  $X_2$  ( $X = \text{Cl, Br and I}$ ) we found (Singleton & van der Stok, unpublished) that when  $L = \text{P}(\text{OCH}_3)(\text{C}_6\text{H}_5)_2$  and  $\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$ , addition reactions were usually accompanied by loss of

\* To whom correspondence should be addressed.