STRUCTURE OF AND BONDING IN $[(C_3H_5)PdCl]_2$[*]

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INTRODUCTION

Although a large number of π-allyl complexes of transition metals recently have been prepared and characterized by chemical and spectroscopic methods[2], relatively little detailed X-ray information is available concerning the stereochemical nature of these complexes. Consequently, systematic structural investigations of a number of these complexes have been undertaken in this Laboratory, and this paper presents the results of a three-dimensional X-ray examination of $[(C_3H_5)PdCl]_2$. This stable yellow compound, the simplest member of a series of chloro-bridged allyl compounds of palladium, was first prepared independently by Smidt and Hafner[3] and by Moiseev *et al.*[4] from the reaction of palladium chloride with allyl alcohol[***] and shortly afterwards was synthesized by Hüttel and co-workers[6] from palladium chloride and allyl chloride. The first clear-cut suggestion that allylic transition metal complexes in general form sandwich-type "en-yl" structures was made for $[(C_3H_5)PdCl]_2$ by its synthesizers[3,4]. Primarily on the basis of the compound's NMR spectrum which showed the two terminal allylic carbons to be equivalent, Dehm and Chien[7] formulated a "non-classical" structure in which the allylic group is symmetrically bonded to the palladium in a delocalized fashion[§].

Similar conclusions on metal–allylic bonding have been reached by a number of

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[***] Moiseev *et al.*[4] also report the preparation below 10° of a second dark green form of $[(C_3H_5)PdCl]_2$; attempts by others[5] to synthesize this relatively unstable β-form complex have not been successful.

[§] Although accepted by others[8] it should be noted that Dehm's and Chien's NMR assignments[7] of the chemical shifts and coupling constants for the observed pair of doublets arising from the non-equivalent pairs of *syn*- and *anti*-hydrogens on the terminal carbons of the π-allyl group in $[(C_3H_5)PdCl]_2$ are reversed from those of Shaw and Sheppard[9,10] which like the NMR assignments[11] for the isomers of π-crotylcobalt carbonyl are based on the relative strength of the *cis*- and *trans*-coupling values in ethylenic systems. A reinterpretation of the 60 Mc spectral parameters of Dehm and Chien[7] for crotylpalladium chloride based on the presumably correct alternate assignment shows this compound to be the *syn*-isomer (as correctly determined by Dehm and Chien[7]) with the following chemical shifts (both the original values given in cps relative to an external benzene standard and the corresponding τ-values[8] in ppm are listed) and coupling constants (given in the notation of Dehm and Chien consistent with the Figure in their paper[7]): $\delta_A = 57.9$ ($\tau_A = 3.96$); $\delta_X = 143.1$ ($\tau_X = 5.38$); $\delta_{M'} = 146.1$ ($\tau_{M'} = 5.43$); $\delta_M = 209.7$ ($\tau_M = 6.50$); $\delta_{CH_3} = 299$ ($\tau_{CH_3} = 8.00$); $|J_{AX}| = 6.3$; $|J_{AM'}| = 12.0$; $|J_{AM}| = 11.5$. This alternate assignment for crotylpalladium chloride is strongly supported by the near-equality of the $J_{AM'}$ and J_{AM} values in contrast to the Dehm-Chien assignment.

investigators[2d,5,8–20] for other π-allyl metal complexes from their NMR spectra which in general show analogous patterns to those of $[(C_3H_5)PdCl]_2$[*]. The infrared spectra of a number of allylic metal complexes including $[(C_3H_5)PdCl]_2$ have been measured over a wide spectral range by Fritz[21,2a] who systematically examined them in connection with the infrared spectra of other hydrocarbon metal complexes. Fritz[21,2a] has given tentative vibrational assignments to the infrared bands of $[(C_3H_5)PdCl]_2$ to be expected for a C_3H_5 system with localized C_{2v} symmetry, but he was unable to reach any definite conclusions concerning the degree of planarity of the hydrogens with respect to the carbon atoms.

During the final stages of the X-ray refinement of $[(C_3H_5)PdCl]_2$ in this Laboratory, a communication by Rowe[1] appeared on the results of a two-dimensional X-ray determination of the same complex. Since our results stem from a three-dimensional least-squares isotropic-anisotropic refinement and thereby represent a much higher degree of accuracy, the present work offers the opportunity to compare the structural features of $[(C_3H_5)PdCl]_2$ with those of other compounds and to evaluate further the nature of bonding of this type complex.

EXPERIMENTAL PROCEDURE

Crystals of $[(C_3H_5)PdCl]_2$ were generously furnished to us by Dr. H. C. DEHM of the Hercules Powder Company. A crystal with an average radius of 0.015 cm was used for obtaining intensity data. The estimated absorption parameter, μR, of 0.66 is of sufficiently small value that absorption corrections could be neglected. The density of the crystal was measured by flotation in mixtures of bromoform and methyl iodide.

Measurements of a and c were made on a zero level Weissenberg photograph calibrated with NaCl powder patterns. The value of b was determined from $hk0$ and $0kl$ precession photographs which were internally calibrated with the other two axes.

Multiple-film equi-inclination photographs were obtained for nine reciprocal levels (*i.e.*, $h0l$ through $h8l$) with Zr-filtered MoKα radiation. The Weissenberg intensity data consisting of 535 independent reflections were visually estimated by comparison with calibrated standard intensities made with the same crystal. The intensities were corrected for the usual Lorentz polarization effects, and the derived structure factors [*i.e.*, $|F(hkl)|^2 \sim I(hkl)$] and weighting[**] were obtained from the Dacor program[22]. The final scaling of these observed structure factors for the different reciprocal layers is based on the least-squares refinement. For the calculation of structure factors the atomic scattering factors given by Thomas and Umeda[23], Dawson[24] and Berghuis *et al.*[25], were used for palladium, chlorine and carbon, respectively.

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[*] Of interest is that $[(C_3H_5)PdCl]_2$ and related complexes apparently undergo dissociation in strongly coordinating solvents such as dimethyl sulfoxide. Chien and Dehm[5] have shown via NMR that allyl- and substituted allylpalladium chloride complexes dissociate in dimethyl sulfoxide to give resulting σ-bonded allyl type structures. They postulated that this breakdown of the dimeric π-allylic palladium molecule into monomeric palladium species of presumed square planar configuration is accomplished by the coordination of two solvent dimethyl sulfoxide molecules to each palladium (with the other two sites occupied by the σ-bonded allyl group and the chlorine atom).

[**] A weight was assigned to each reflection as follows:

$$\sqrt{w} = 20/|F_0| \quad \text{if} \quad I_0 > \sqrt{20}\, I_{min}$$

$$\sqrt{w} = I_0^2/|F_0| I^2_{min} \quad \text{if} \quad I_0 \leq \sqrt{20}\, I_{min}$$

RESULTS

Unit cell and space group

Crystals of $[(C_3H_5)PdCl]_2$ (mol. wt. 366.4) are monoclinic with $a = 7.46 \pm 0.02$ Å, $b = 7.43 \pm 0.02$ Å, $c = 8.61 \pm 0.02$ Å, $\beta = 93.6 \pm 0.10°$; volume of unit cell, $V = 475.9$ Å^3; $\rho_{obsd.} = 2.51$ g·cm^{-3} *vs.* $\rho_{calcd.} = 2.56$ g·cm^{-3} for two dimeric units per unit cell. The total number of electrons per unit cell, $F(000) = 344$. The linear absorption coefficient for MoKα radiation ($\lambda = 0.7107$ Å), $\mu = 44$ cm^{-1}. The only systematic absences observed are $\{h0l\}$ for $h + l$ odd and $\{0k0\}$ for k odd. The indicated centrosymmetric space group, $P2_1/n(C^5_{2h})$, was verified by the structural determination. Since the unit cell contains only two dimeric molecules, each molecule must lie on a crystallographic center of symmetry, and the asymmetric unit of one-half molecule hence contains one palladium, one chlorine, and three carbons (and ideally the five hydrogens). These atoms all occupy the general 4-fold set of equivalent positions[26] (4e): x,y,z; $\bar{x},\bar{y},\bar{z}$; $x + 1/2,\ 1/2 - y,\ z + 1/2$; $1/2 - x,\ 1/2 + y,\ 1/2 - z$. The lattice parameters reported by Rowe[3] are based on an alternate unit cell with space group symmetry $P2_1/c$. By transformation of axes (*i.e.*, $a_n = a_c$, $b_n = b_c$, $c_n = a_c + c_c$) the values of Rowe based on our choice of axes are $a = 7.44 \pm 0.02$ Å, $b = 7.40 \pm 0.02$ Å, $c = 8.67 \pm 0.03$ Å, $\beta = 93.95°$, $V = 476.2$ Å^3 which are in reasonable agreement with our cell parameters.

Determination of the structure

Approximate coordinates for the palladium atoms were obtained from a three dimensional unsharpened Patterson function. The positional parameters of the chlorine and carbon atoms were revealed by a combination of three-dimensional Fourier and difference maps. These computations were made on the IBM 704 computer with the Sly-Shoemaker program[27]. The atomic parameters first were refined on the IBM 704 computer with the full-matrix Busing-Levy least-squares program[28]. The results obtained in the isotropic refinement with individual isotropic temperature factors and with separate reciprocal layer scale factors are listed in Table 1. At this point the reliability factors,

$$R_1 = \frac{\Sigma\,|F_0| - |F_c|}{\Sigma\,|F_0|} \times 100 \qquad \text{and} \qquad R_2 = \sqrt{\frac{\Sigma w\,|F_0| - |F_c|^2}{\Sigma w\,|F_0|^2}} \times 100$$

were 9.6 and 11.8% respectively. The parameter shifts for the last cycle all were less than 20% of their corresponding standard deviations. In order to obtain more meaningful positional parameters, the individual atomic isotropic thermal parameters were converted to anisotropic form given by the expression

$$\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}.$$

An attempt, however, to carry out a completely anisotropic least-squares refinement failed; the resulting thermal coefficients for a carbon atom refined to a non-positive definite value. The following procedure then was employed. An anisotropic least-squares refinement of the palladium and chlorine parameters was done with all carbon parameters held constant. The palladium and chlorine parameters thus obtained were used to calculate a fixed atom contribution which in turn was employed

TABLE 1

FINAL ATOMIC PARAMETERS AND STANDARD DEVIATIONS FOR ISOTROPIC LEAST-SQUARES REFINEMENT

Atom	x	y	z	$10^2\sigma_x$	$10^2\sigma_y$	$10^2\sigma_z$	B	σ_B
Pd	0.3735	0.1841	0.0497	0.030	0.029	0.026	2.65	0.084
Cl	0.6765	0.0808	0.1095	0.118	0.102	0.096	3.80	0.176
C_1	0.1115	0.2994	0.0208	0.403	0.405	0.378	3.10	0.525
C_2	0.2456	0.4256	0.0595	0.696	0.593	0.515	7.16	1.088
C_3	0.3615	0.4293	0.1877	0.508	0.488	0.403	4.68	0.705

in an isotropic least-squares refinement of only the carbon parameters. The isotropic temperature factors for the carbon atoms then were converted to anisotropic temperature factors, and a final anisotropic least-squares refinement was carried out in which all the palladium, chlorine and carbon parameters except the carbon temperature factors were varied. All parameter shifts for the last cycle were less than 5 % of their corresponding standard deviations. This refinement resulted in reliability factors of $R_1 = 6.9\,\%$ and $R_2 = 8.8\,\%$ for the 535 observed reflections. The final value of the function

$$\sqrt{\frac{w(|F_o|-|F_c|)^2}{m-n}}$$

was 1.389. The final positional parameters for the anisotropic refinement are listed in Table 2 and the thermal parameters in Table 3. Bond lengths, angles, and dihedral angles between planes for the dimeric unit are listed in Table 4. These calculations were done on the IBM 704 computer with the Busing-Levy Function and Error program[29].

The refined structure was verified by the calculation of three-dimensional electron density and difference Fourier maps which revealed no spurious peaks or holes in the electron density distributions. These maps did not clearly show the presence of the hydrogen atoms, and hence no further attempt was made to locate them. A comparison of the scaled observed structure factors and the calculated structure factors based on the anisotropic refinement is given in Table 5.

TABLE 2

FINAL POSITIONAL PARAMETERS AND STANDARD DEVIATIONS FOR ANISOTROPIC LEAST-SQUARES REFINEMENT

Atom	x	y	z	$10^2\sigma_x$	$10^2\sigma_y$	$10^2\sigma_z$
Pd	0.3736	0.1841	0.0496	0.022	0.021	0.020
Cl	0.6752	0.0796	0.1079	0.081	0.083	0.079
C_1	0.1134	0.3040	0.0204	0.319	0.350	0.300
C_2	0.2460	0.4233	0.0570	0.572	0.483	0.423
C_3	0.3609	0.4289	0.1870	0.388	0.380	0.310

TABLE 3

FINAL ANISOTROPIC TEMPERATURE COEFFICIENTS IN $Å^2 \times 10^4$

Those for carbon atoms were transformed from isotropic values and were not varied in the anisotropic least-squares refinement.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	111 ± 4	124 ± 3	106 ± 3	41 ± 3	8 ± 2	−9 ± 3
Cl	106 ± 12	204 ± 12	201 ± 13	40 ± 10	−19 ± 10	−100 ± 11
C_1	166	166	123	0	8	0
C_2	354	354	263	0	18	0
C_3	225	225	167	0	11	0

TABLE 4

INTERATOMIC DISTANCES, BOND ANGLES, AND DIHEDRAL ANGLES IN $[(C_3H_5)PdCl]_2$

Bond lengths (Å) *with standard deviations*

Bond	*Length (Present work)*	*Length (Rowe*[1]*)*
Pd...Pd′	3.460 ± 0.007	
Pd–Cl	2.403 ± 0.009	2.39
Pd–Cl′	2.398 ± 0.008	2.39
Cl...Cl′	3.328 ± 0.015	
Pd–C_1	2.14 ± 0.024	2.1$_1$ ± 0.05
Pd–C_2	2.02 ± 0.037	2.1$_1$ ± 0.05
Pd–C_3	2.17 ± 0.028	2.1$_1$ ± 0.05
C_1–C_2	1.35 ± 0.045	1.3 ± 0.1
C_2–C_3	1.37 ± 0.040	1.3 ± 0.1

Bond angles with standard deviations

Angle	*Angle (Present work)*	*Angle (Rowe*[1]*)*
Cl′–Pd–Cl	87.8 ± 0.3°	
Pd′–Cl–Pd	92.2 ± 0.3°	
Cl–Pd–C_1	172.4 ± 0.7°	
Cl′–Pd–C_3	168.7 ± 0.8°	
Cl′–Pd–C_1	99.8 ± 0.7°	
Cl–Pd–C_3	103.2 ± 0.8°	
Pd–C_1–C_2	66.4 ± 1.9°	
Pd–C_3–C_2	64.9 ± 1.9°	
C_1–Pd–C_3	69.2 ± 1.0°	66°
C_1–C_2–C_3	128.6 ± 3.3°	123°

Dihedral angles between planes each defined by three atoms

Planes	*Angle (Present work)*	*Angle (Rowe*[1]*)*
(Cl′–Pd–Cl) (C_1–C_2–C_3)	108.2 ± 4.2°	~90°
(C_1–Pd–C_3) (C_1–C_2–C_3)	106.2 ± 4.2°	
(Pd–C_1–C_2) (Pd–C_3–C_2)	135.8 ± 3.0°	

TABLE 5

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	FO	FC
0	0	2	140.2	139.8
		6	30.1	-28.4
		8	36.0	-37.5
		10	27.4	-26.0
1	0	3	88.5	-83.5
		5	70.5	-68.5
		7	28.3	-25.0
		-3	23.5	24.8
		-5	89.2	90.3
		-7	78.5	82.4
		-9	31.8	35.4
2	0	0	59.8	-51.2
		2	43.0	38.9
		4	100.5	92.7
		6	83.8	86.2
		8	27.0	29.4
		-2	69.3	-66.3
		-4	73.0	-67.2
		-6	76.3	-74.7
		-8	30.9	-32.0
3	0	1	93.2	83.2
		3	42.9	-39.0
		5	78.5	-69.0
		7	45.4	-53.6
		9	22.1	-25.2
		-1	148.7	153.6
		-3	93.3	85.2
		-5	42.2	40.7
4	0	0	130.7	-132.5
		2	59.3	-57.7
		-2	112.8	-108.7
		-4	32.7	-32.4
		-6	27.9	27.4
		-8	35.0	37.6
5	0	1	52.3	49.5
		3	57.4	59.9
		5	51.6	52.3
		-1	32.0	26.9
		-5	38.2	-39.7
		-7	49.6	-53.7
		-9	25.2	-25.7
6	0	0	25.9	22.4
		2	45.9	-43.5
		4	59.3	-54.4
		6	34.0	-40.6
		-2	49.5	50.7
		-4	41.7	42.8
		-6	36.8	35.9
7	0	-1	62.9	-67.2
		-3	55.4	-62.1
		-5	30.2	-28.3
8	0	0	33.4	37.1
		-2	37.1	39.0
9	0	3	29.4	-35.5
0	1	2	174.2	-119.9
		3	22.0	16.2
		4	137.3	-122.0
		5	27.0	-24.9
		6	55.9	-73.0
		8	24.3	-25.8
1	1	-2	74.2	-75.3
		2	21.9	-18.2
		-3	137.3	-134.1
		3	15.2	8.5
		-4	23.5	22.8
		4	23.6	-21.0
		-5	87.3	-72.7
		5	42.2	40.3
		-6	38.2	38.1
		6	15.9	-15.3
		-7	17.1	-7.9
		7	49.5	49.6
		-8	19.9	19.2
		-9	20.1	20.2
		9	31.6	30.7
2	1	0	96.6	108.9
		1	37.4	-26.2
		-2	83.7	84.3
		2	91.9	95.3
		-3	14.9	-14.9
		3	32.5	33.2
		-4	31.2	25.9
		4	42.6	39.0
		-5	34.4	-34.7
		5	33.1	32.4
		-6	18.1	-16.4
		6	21.5	-18.0
		-7	29.4	-27.3
		7	26.9	23.9
		-8	38.4	-39.9
		8	34.9	-38.6
		-10	27.3	-27.7
3	1	0	71.3	69.6
		-1	51.3	-46.4
		1	117.4	-123.6
		-2	64.8	67.1
		2	20.1	18.4
		-3	24.3	24.0
		3	102.5	-107.2
		-4	24.5	22.7
		4	41.6	-39.3
		-5	49.1	47.3
		5	49.3	-50.7
		6	30.5	-28.4
		-7	43.3	44.2
		-9	27.2	25.4
4	1	0	13.6	10.2
		-1	64.1	-64.9
		1	35.1	-29.4
		-2	60.4	-58.9
		2	62.1	59.1
		-3	39.0	-36.8
		-4	79.2	-82.9
		4	57.7	58.0
		-6	54.5	-60.5
		6	42.0	44.1
		-7	22.5	20.7
		-8	22.8	-22.2
5	1	-1	63.5	67.8
		1	37.4	38.4
		-2	20.4	15.3
		-3	63.8	64.6
		4	36.0	35.8
		-5	43.4	44.9
		5	26.0	-25.4
		-6	25.5	-21.4
		6	24.6	20.4
		7	32.1	-35.1
6	1	0	64.2	-67.7
		-1	38.4	29.4
		-2	39.6	-39.9
		2	51.5	-55.1
		-3	25.0	24.3
		3	27.5	-27.2
		5	30.8	-29.3
7	1	-1	31.7	30.9
		1	49.5	55.1
		-2	35.1	-36.2
		3	41.0	42.5
		-5	29.0	-30.2
		5	21.3	20.5
		-7	27.9	-27.9
8	1	-4	32.4	34.2
		-6	31.0	29.8
9	1	-1	29.1	-29.5
1	2	-2	92.7	-95.9
		-3	21.2	-20.0
		3	90.4	95.5
		-4	87.1	-92.8
		4	28.2	30.0
		-5	35.4	-37.0
		5	39.4	37.4
		-6	25.3	-25.5
		6	35.2	35.4
		-7	36.6	-36.2
		8	31.7	33.4
		-9	27.5	-27.3
2	2	0	26.1	-23.9
		-1	72.0	66.0
		1	83.7	84.5
		-2	47.7	52.4
		2	69.7	-64.5
		-3	55.5	55.0
		3	81.5	79.7
		-4	72.0	72.9
		4	57.9	-58.1
		-5	17.4	11.9
		-6	40.7	37.0
		-7	19.3	-17.7
		7	29.2	-29.4
		-9	32.2	-27.2
		9	28.5	-26.3
3	2	0	62.2	-60.7
		-1	51.3	-48.6
		1	17.6	-15.9
		-2	18.8	12.1
		2	100.5	-102.9
		-3	79.2	-82.3
		-4	51.2	54.2
		4	63.5	-65.0
		-5	49.0	-46.2
		5	32.3	33.7
		-6	41.4	41.5
		7	38.3	37.1
		-8	23.8	27.0
4	2	0	58.3	56.4
		-1	13.1	-10.0
		1	38.8	35.4
		-2	50.1	50.3
		2	69.7	70.2
		-3	65.9	-71.0
		3	47.8	45.9
		-4	23.9	23.7
		4	27.0	25.3
		-5	61.4	-61.7
		5	31.0	34.9
		6	21.8	-15.9
		-7	24.9	-23.2
		7	23.2	21.9
		-8	25.2	-19.0
5	2	0	29.0	33.0
		-1	24.3	-24.7
		1	59.3	-57.1
		-2	43.3	45.5
		2	25.3	28.0
		-3	21.2	20.1
		3	49.9	-49.0
		-4	44.4	45.0
		-5	34.5	31.8
		-6	22.3	19.3
		6	28.9	-30.1
		-7	29.4	24.6
		8	26.0	-27.1
6	2	-1	45.4	-42.5
		1	60.7	-63.0
		-2	24.7	-19.4
		2	26.2	23.5
		3	42.1	-43.9
		-4	42.4	-41.6
		4	28.1	25.6
		-6	30.7	-27.8
7	2	0	35.7	34.1
		-1	24.7	22.8
		1	18.4	16.9
		2	34.3	34.3
		-3	28.7	30.5
		-4	27.3	-30.9
		-5	24.6	24.6
		-6	29.3	-28.9
8	2	0	30.5	-34.1
		-2	24.6	-21.7
		2	26.4	-26.9
		-3	23.6	20.8
		-5	24.7	25.8
1	3	-2	21.0	19.4
		2	102.0	117.6
		-3	19.0	18.2
		-4	36.6	-29.4
		4	76.6	77.5
		5	40.0	-35.5
		-6	49.7	-51.4
		6	25.2	25.6
		7	18.3	-16.2
		-8	40.1	-41.6
2	3	0	52.5	-52.0
		-1	48.9	46.3
		1	37.0	-33.0
		-2	66.1	-61.4
		-3	86.0	84.2
		3	59.9	-71.1
		4	21.6	19.4
		-5	56.6	70.3
		5	67.0	-66.5
		-6	19.1	15.5
		-7	37.2	39.0
		7	40.9	-42.6
3	3	0	75.4	-76.4
		-1	49.4	48.1
		1	13.1	12.2
		-2	93.8	-90.2
		2	24.7	-23.2
		-3	30.4	29.8
		-4	69.0	-70.2
		4	22.9	22.7
		-5	17.7	-13.6
		5	19.0	19.5
		-6	23.2	-20.2
		6	43.5	44.2
		-7	24.3	-20.8
		8	31.7	34.0
4	3	0	20.5	15.9
		-1	57.0	70.4
		1	73.6	75.9
		-2	14.0	10.2
		-3	38.0	38.6
		3	43.1	41.6
		-4	17.1	10.9
		4	41.1	-39.6
		-6	17.7	15.0
		6	22.5	-24.1
		-7	31.7	-28.6
		7	21.5	-22.4
		-9	27.2	-25.5
5	3	0	48.5	-49.4
		-1	40.1	-38.7
		2	63.9	-67.7
		-3	32.0	-32.7
		3	21.8	20.4
		-4	25.7	26.2
		4	45.7	-48.0
		-6	34.7	34.9
		6	16.4	-21.0
		-8	27.5	27.6
6	3	-1	23.0	-25.8
		1	18.2	13.5
		-2	34.3	37.9
		-3	51.6	-52.2
		3	35.6	35.5
		-5	44.1	-46.1
		5	35.6	38.0
		-7	23.1	-22.0
7	3	0	33.7	35.7
		-2	47.4	44.6
		3	18.9	-17.9
		-4	36.2	34.2
8	3	-1	30.6	-33.0
		1	30.8	-35.3
9	3	0	23.5	19.5
		2	24.0	25.7
0	4	3	56.0	55.1
		5	73.8	73.0
		7	45.7	47.6
1	4	-2	95.1	89.4
		2	22.8	21.2
		-4	49.9	51.1
		4	49.1	-48.2
		-6	27.5	29.3
		6	62.0	-62.1
		8	32.4	-37.4
		-10	20.2	-14.5
2	4	0	20.3	16.5
		-1	115.3	-121.9
		1	100.9	-109.6
		-3	46.6	-48.4
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		-7	27.1	29.7
		-9	19.1	23.8
3	4	0	54.3	53.5
		-1	17.7	-21.8
		1	14.7	-17.7
		-2	17.7	18.9
		2	58.2	56.5
		-4	31.0	-27.8
		4	52.4	52.0
		-6	51.6	-57.4
		6	36.2	34.2
		-8	38.0	-40.2
4	4	-1	35.7	36.8
		-3	38.2	37.9
		3	50.0	-52.7
		-5	42.1	43.4
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		-7	33.6	34.3
		7	24.2	-29.2
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		-4	40.3	-41.4
		4	37.5	32.9
		6	33.5	30.0
6	4	-1	60.7	64.4
		1	41.6	44.4
		-3	42.2	41.2
		3	20.0	20.8
7	4	2	32.6	-35.2
		4	29.6	-33.5
8	4	3	23.5	31.2
0	5	3	36.6	37.6
		4	30.1	33.2
		5	17.7	10.8
		6	30.6	27.9
		7	19.9	-19.1
1	5	2	73.1	-84.6
		-3	25.0	26.2
		-4	23.6	23.5
		4	61.3	-63.8
		-5	19.0	13.6
		5	29.0	-28.4
		-6	29.3	27.8
		6	22.0	-21.4
		-8	25.8	23.5
2	5	0	40.9	-45.2
		-1	24.0	-24.3
		1	39.3	37.8
		-2	33.7	-34.4
		2	28.5	-26.3
		-3	57.6	-62.8
		3	56.9	53.7
		-5	54.8	-57.7
		5	42.3	41.9
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		7	22.4	22.8
3	5	0	34.0	34.5
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		-2	50.5	52.6
		3	26.3	27.3
		-4	51.7	52.9
		-5	29.9	-33.0
		5	25.8	24.6
		-6	25.8	28.2
		6	23.2	-23.4
		-7	22.7	-22.2
		9	24.1	-24.4
4	5	-1	40.2	-41.9
		1	54.0	-53.9
		-2	18.8	21.5
		-3	18.4	-19.2
		3	34.0	-32.8
		-4	22.7	22.3
		4	30.5	-29.1
		-6	19.7	17.7
		6	23.0	-20.0
5	5	0	50.1	49.9
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		-3	27.1	-22.0
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		4	34.2	30.6
		-5	25.9	-27.0
6	5	0	18.1	20.5
		1	23.9	-20.0
		-3	29.2	27.5
		-5	40.5	38.9
		-7	22.2	25.2
7	5	0	22.7	-23.6
		-2	26.2	-25.0
8	5	-1	30.7	29.5
0	6	2	36.6	40.5
		3	25.0	-27.3
		4	24.6	23.6
		5	23.2	-21.9
1	6	0	19.0	-22.2
		1	39.3	-44.8
		-2	37.0	-41.0
		-3	20.0	18.2
		3	56.8	-59.2
		-4	35.3	-32.6
		-5	25.8	24.6
		5	29.3	-27.4
		6	25.6	23.8
		-7	25.7	20.1
2	6	-1	37.8	40.3
		1	37.4	38.3
		-2	39.5	-38.2
		2	33.2	35.2
		-3	35.7	34.0
		3	39.9	24.8
		-4	57.6	-51.8
		4	36.1	36.7
		-6	28.7	-25.2
3	6	0	25.8	-25.8
		-1	28.5	31.4
		2	34.5	-34.1
		-3	52.8	46.3
		4	23.8	-20.5
		-5	35.7	28.9
		-6	24.4	14.7
4	6	0	39.4	-39.4
		1	17.7	17.7
		-2	24.1	-20.0
		2	46.7	-47.7
		-3	26.2	-23.6
		3	23.2	23.4
		4	20.7	-22.7
		-5	22.8	-20.8
		5	22.0	20.3
5	6	1	36.6	36.2
		-2	33.6	27.5
		-3	23.6	-23.7
		3	34.3	35.0
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6	6	-1	21.2	-23.5
		1	16.8	-21.8
		-3	21.1	-20.6
		-4	33.3	32.5
0	7	2	23.6	-26.6
		4	34.8	-35.0
		6	29.2	-29.7
1	7	-1	43.9	-50.4
		1	26.6	-29.2
		-2	19.4	19.4
		-3	47.8	-45.0
		-5	19.9	-20.0
		5	29.4	24.8
		7	32.4	27.7
2	7	0	48.2	49.7
		-2	43.1	40.0
		2	35.3	36.3
		5	16.0	-15.4
		-8	25.7	-21.1
3	7	-1	22.6	-19.0
		1	35.5	-37.4
		3	37.3	-36.5
		-5	25.7	19.5
		5	25.9	-21.6
		-7	28.6	24.7
4	7	-1	22.5	19.5
		-2	30.7	-30.7
		2	16.4	17.8
		-4	34.9	-32.6
		4	31.9	29.7
		-6	27.4	-20.8
		6	27.0	26.1
5	7	-1	40.0	36.9
		1	26.7	19.5
		-3	40.4	37.0
		-5	23.5	17.3
6	7	0	27.6	-27.2
		-2	21.4	-21.4
0	8	2	28.5	-32.1
1	8	0	11.1	-13.7
		-1	18.1	20.9
		1	28.1	33.9
		3	29.5	28.9
		-5	28.5	-25.6
		5	24.2	22.1
		-7	26.1	-23.3
2	8	-2	23.3	16.8
		2	18.2	-17.9
		-4	29.5	25.9
		4	29.3	-29.9
		-6	28.8	26.0
		6	25.5	-24.5
		-8	18.4	11.8
3	8	-1	35.1	-34.9
		1	19.5	-17.8
		-3	29.1	-26.9
		5	20.8	19.4
4	8	0	37.4	37.2
		-1	15.4	-14.9
		-2	31.3	30.2
		2	23.4	22.0
5	8	-1	16.3	-13.5
		1	21.6	-21.6
		3	23.6	-22.8
		-5	18.1	16.6
		-7	22.9	20.6
6	8	2	17.3	14.6
		-4	19.3	-15.6
		4	19.2	20.2
7	8	-1	23.6	22.5
		-3	23.7	20.8
8	8	-2	20.0	-17.3

DISCUSSION

The crystal structure of $[(C_3H_5)PdCl]_2$ consists of individual molecules of *idealized* point group symmetry C_{2h}–$2/m$; the required crystallographic molecular symmetry is C_i–$\bar{1}$. The overall molecular configuration (shown in Fig. 1) with each palladium symmetrically linked to an allylic group is in agreement with the proposed configuration based on the NMR measurements[7]. In general the overall crystallographic results of Rowe[1] are confirmed (see Table 4 for a comparison of molecular parameters) except that our more precisely determined atomic coordinates (besides providing more refined molecular parameters) reveal that the plane of the three allylic carbons is not perpendicular to the plane of the $(PdCl)_2$ bridge system but intersects it at a dihedral angle of 108 ± 4° with the central carbon tipped away from the palladium.

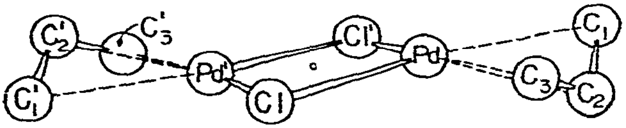

Fig. 1. The molecular configuration of $[(C_3H_5)PdCl]_2$.

The dimeric molecule (see Fig. 2 for intramolecular bond lengths and angles) is linked together by the two bridged chlorine atoms such that the palladium and chlorine atoms form a planar rhombus. The two independent Pd–Cl bond lengths are 2.40 Å (individu ale.s.d. ± 0.008 Å); which value on comparison with the two unsymmetrical bridge Pd–Cl bond lengths[30,31] in $[(styrene)PdCl_2]_2$ compares favorably with the bridge Pd–Cl distance (2.394 ± 0.015 Å) *trans* to the olefin–Pd bond but is significantly longer than the bridge Pd–Cl distance (2.324 ± 0.010 Å) *cis* to the olefin–Pd bond*.

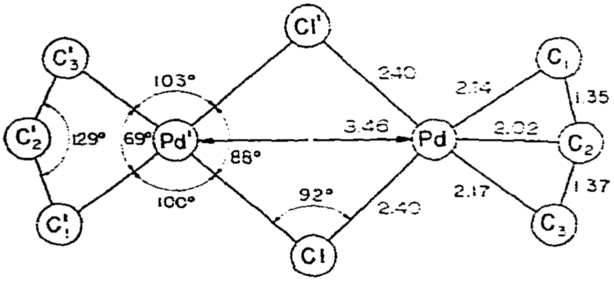

Fig. 2. Intramolecular distances and angles.

Holden and Baenziger[30] point out that a similar lengthening of the metal chlorine bond *trans* to an olefin linkage is also observed in Zeise's salt[33], $K[(C_2H_4)PtCl_3]\cdot H_2O$. The symmetrical Pd–Cl bridging bonds in $PdCl_2$ were found[34] to be 2.31 Å which is similar to the Pd–Cl bridging distance[30,31] (2.324 ± 0.010 Å) *cis* to the Pd–olefin bond (and *trans* to a terminal Pd–Cl bond) in $[(styrene)PdCl_2]_2$.

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* The corresponding unsymmetrical Pd–Cl distances follow the same trend in one of the two crystallographically different dimers[32] in $[(C_2H_4)PdCl_2]_2$, but in the other dimer the trend is in the opposite direction. The relatively large uncertainties in positional parameters and the seemingly "unrealistic" Pd–Cl distances obtained by X-ray diffraction for this latter complex do not make these differences meaningful.

The distance from the palladium to the two terminal allylic carbons of 2.14 ± 0.02_4 and 2.17 ± 0.02_8 Å are equivalent within experimental error; the average Pd–C distance of 2.15 ± 0.02 Å is somewhat longer than the distance of 2.02 ± 0.04 Å from the palladium to the central allylic carbon atom.

The symmetrical orientation of the allyl group with respect to the $(PdCl)_2$ bridge system is further shown by the fact that the *idealized* molecular mirror plane, which intersects the two palladium atoms and which is perpendicular to the *quasi* two-fold axis passing through the two chlorine atoms, encompasses the central allylic carbon within 0.04 Å; the mirror-related terminal carbons are separated by an average distance of 1.21 Å (the mean of 1.24 and 1.18 Å) from this plane. These results verify that within experimental error the dimeric molecule has *idealized* C_{2h} symmetry. For the allyl group the mean value of 1.36 ± 0.03 Å for the two carbon–carbon bond lengths made equivalent by this point group symmetry lies well within one standard deviation of their individual values (1.35 ± 0.045 and 1.37 ± 0.040 Å).

Considerable speculation has been made concerning the nature of bonding of allylic metal systems. Although the π-allylic–palladium bonding has been considered to be of a non-classical nature[10], it also has been conceptually viewed from a valence bond picture as involving the usual overlap of two dsp^2 σ-type hybrid orbitals of each palladium with the delocalized π-orbitals of the allylic group.

The X-ray work on $[(C_3H_5)PdCl]_2$, which confirms the equivalence of the terminal methylene carbons, supports the premise that this allylic–palladium complex can be considered formally to arise from the interaction of a palladium (II) with an allylic anion (with four π-electrons available for bonding) which functions as a chelating group by occupying two square planar coordination sites.

The geometry and stereochemical disposition of the palladium-bonded allylic group are completely compatible with this structural formulation. Although the structures of the two ethylene-metal complexes, $[ClRh(C_2H_4)_2]_2$ (ref. 35) and $[(C_2H_4)PdCl_2]_2$ (ref. 32), show the C–C axis of each ethylene to be symmetrically bonded to the metal and perpendicular to the four-coordinated metal plane, it is noteworthy for the substituted olefinic complex, $[(styrene)PdCl_2]_2$, that the $(PdCl)_2$ plane cuts the double bond of the styrene molecule off center (closer to the terminal olefinic carbon)[30,31]. In addition the double bond is not perpendicular to the $(PdCl)_2$ plane but intersects it along the palladium bond at an angle of 106°. Since the plane of the olefinic carbons and the palladium is essentially perpendicular to the $(PdCl)_2$ plane, the dihedral angle[30] between the $(PdCl)_2$ plane and the plane of the ethylene group as defined by the olefinic carbons and the attached phenyl carbon also is 106°. Hence, the orientation of the π-type orbital of the terminal olefinic carbon of the styrene molecule with respect to the $(PdCl)_2$ plane presumably is not unlike that for each of the π-type orbitals of the terminal allylic carbons in $[(C_3H_5)PdCl]_2$.

The spatial arrangement of the allylic carbons which possess a large bond angle of 128.6 ± 3.3°, is such that the plane of the $(PdCl)_2$ bridge system cuts the carbon–carbon bonds very close to the terminal carbons; the central carbon (C_2) is 0.50 Å above and the terminal carbons 0.04 and 0.09 Å below the $(PdCl)_2$ plane. The resulting *cis* Cl–Pd–C(terminal) and *trans* Cl–Pd–C(terminal) bond angles are 101° (av.) and 171° (av.), respectively. The Cl–Pd–Cl angle of 87.8 ± 0.3° in $[(C_3H_5)PdCl]_2$ compares well with the corresponding angle found in $[(styrene)PdCl_2]_2$ (86°)[30,31], $[(C_2H_4)PdCl_2]_2$ [86° (av.)][32], and $PdCl_2$ (87°)[34] which is characteristic of palladium chloride bridged compounds. Moreover, the allylic bidentate group produces a bond lengthening of the bridge Pd–Cl distance similar to that for a bridge Pd–Cl distance *trans* to an olefin linkage.

Since the hydrogen coordinates were not determined for $[(C_3H_5)PdCl]_2$, no direct conclusions can be reached concerning the effect of this organopalladium interaction on distortion of the otherwise planar π-C_3H_5 moiety. Any displacement of the hydrogens from the plane of the three carbons presumably would be away from the palladium due to the unsymmetrical perturbation of the allylic π-electron density in bonding to the palladium. Structural work[36] on three cyclobutenyl metal complexes, each containing an allylic group substituted with carbon substituents whose positions were accurately determined, suggests that any bending of the hydrogens from the allylic carbon plane should not exceed 0.15 Å.

The large allylic carbon bond angle of 128.6 ± 3.3° in $[(C_3H_5)PdCl]_2$ may be a stereochemical consequence of its function as a bidentate group. Of prime interest is the effect of other transition metals with different valences on the geometry of the allylic group, and toward this end structural investigations of other open allylic species of the form $(C_3H_5)MX_3$ are underway. It is tempting to suggest for these latter complexes of possible octahedral metal valency (with the π-C_3H_5 fragment then occupying three coordination sites) that the allylic carbon angle may significantly decrease below 120° to obtain maximum overlap of the appropriate orbitals.

If not isomorphous, the corresponding palladium bromide[37,2a] and iodide[9,2b] complexes as well as the recently prepared nickel analogues[2a] of formula $[(C_3H_5)NiX]_2$ $[X = Br$ (ref. 38), I (ref. 39)] are presumed to possess in the solid state a molecular configuration (of *idealized* C_{2h} symmetry) similar to that found for $[(C_3H_5)PdCl]_2$. With regard to the high resolution NMR studies of these and related compounds (including higher homologues) carried out in solution, it should be noted that an apparent conformational change of these diamagnetic dimeric compounds occurs on dissolution in non-polar organic solvents as indicated by the relatively high observed dipole moments determined in benzene for $[(C_3H_5)PdCl]_2$ (2.08 D)[3] and (2.23 D)[4], $[(C_3H_5)PdBr]_2$ (2.18 D)[37], $[(C_3H_5)NiBr]_2$ (1.31 D)[38], and $[(C_3H_5)NiI]_2$ (1.62 D)[39] and in cyclohexane for $[(C_3H_5)NiI]_2$ (1.48 D)[39]. These measurements certainly indicate that, in solution, $[(C_3H_5)PdCl]_2$ and the other presumably isostructural molecular compounds mentioned above have undergone considerable deformation from the centrosymmetric configuration in the solid state.

Although Moiseev *et al.*[4] rationalized the dipole moment of $[(C_3H_5)PdCl]_2$ in benzene as resulting from partial dissociation into monomers, Fischer and Bürger[38,39] instead suggested that the dipole moment of these dimeric complexes arises from an angular distortion in the halogen bridging atoms, whereby each of the metal(II) centers retains a four-coordinated planar configuration. Fischer and Bürger[39] assumed that the large observed dipole moments cannot be explained by solvent effects only. We also support their postulation of a non-planar $(MX)_2$ fragment in solution in that this type of angular distortion, although as yet not found in the solid state for Ni(II) and Pd(II) compounds, has been observed in the solid state for two isoelectronic Rh(I) compounds, $[(ClRh(CO)_2]_2$ (ref. 40) and $[ClRh(C_2H_4)_2]_2$ (ref. 35). Of significance is that the dipole moments of $[ClRh(CO)_2]_2$ (1.62 D in benzene)[41] and the presumably isomorphous $[BrRh(CO)_2]_2$ (2.23 D in isooctane)[41] are similar with those of the dimeric allylic Ni(II) and Pd(II) halogen-bridged complexes. A possible reorientation of the two allylic groups from a *trans* to a *cis* conformation in the process of dissolving also would contribute to the dipole moment.

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NOTE ADDED IN PROOF

Since acceptance of our paper, we have received a manuscript from Dr. A. E. SMITH (*Acta Cryst.*, in the press) on a three-dimensional anisotropic structural determination of $[(C_3H_5)PdCl]_2$ at −140°. We are indebted to Dr. SMITH of Shell Development Company for forwarding to us his results prior to publication in order to allow a detailed comparison of the structure at the two different temperatures. Although SMITH's X-ray analysis at −140° yields, as expected, considerably more accurate molecular parameters primarily due to the greater contribution to the intensities at the lower temperature of the scattering powers of the light atoms relative to those of palladium and chlorine atoms, it is gratifying that a comparison of the molecular parameters shows no significant differences in configuration other than that the three allylic carbons now are essentially equidistant from the palladium as contrasted to our results which indicate (on the borderline of significance) that the central carbon is 0.1 Å nearer to the palladium. Of special interest is that our bond lengths and angles agree within three standard deviations with those found by Dr. SMITH. Noteworthy is that the five hydrogens approximately located by the low temperature study are coplanar with the allylic carbons within experimental error. *Our interpretations of the X-ray results at room temperature and resulting conclusions remain unchanged.*

SUMMARY

The molecular configuration of $[(C_3H_5)PdCl]_2$ has been elucidated from a three-dimensional X-ray analysis. The yellow molecular crystals are monoclinic with $a = 7.46 \pm 0.02$ Å, $b = 7.43 \pm 0.02$ Å, $c = 8.61 \pm 0.02$ Å, and $\beta = 93.6 \pm 0.01°$; the unit cell of symmetry $P2_1/n(C^5_{2h})$ contains two dimeric molecules. The structure has been refined to R_1 and R_2 values of 6.9 and 8.8 % respectively, by the application of an anisotropic–isotropic least-squares method. The dimeric molecule of *idealized* point symmetry C_{2h}–$2/m$ (*i.e.*, the required crystallographic molecular symmetry is C_i–$\bar{1}$) consists of a $(PdCl)_2$ rhombus with each palladium symmetrically bonded to an allylic group. The overall crystallographic results of Rowe[1] based on two-dimensional data are substantiated with the notable exception that our more precisely determined atomic coordinates (which provide more refined molecular parameters) reveal that the plane of the three allylic carbons is not perpendicular to the plane of the $(PdCl)_2$ bridge system; the dihedral angle between these two planes is 108° (e.s.d. ± 4°) with

the central allylic carbon tipped away from the palladium; the palladium, however, is closer to this central carbon (Pd–C = 2.02 ± 0.04 Å) than to the two terminal carbons (mean Pd–C = 2.15 ± 0.02 Å). The allylic carbons possess a bond angle of 128.6 ± 3.3° and an average C–C distance of 1.36 ± 0.03 Å. The structure and bonding of $[(C_3H_5)PdCl]_2$ are discussed with respect to other related organometallic complexes.

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