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The Crystal Structure of the Dimeric Complex $(C_8H_{11}PdCl)_2$

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The structure of the dimeric complex $(C_8H_{11}PdCl)_2$ has been determined by X-ray analysis. The crystals are rhombohedral, space group $R\bar{3}$, with $a=27{\cdot}155$, $c=6{\cdot}669$ Å, $Z=9$ (hexagonal axes). The intensities were collected on a four-circle diffractometer with Mo $K\alpha$ radiation. The structure was solved by the heavy-atom method and refined by full-matrix least squares to a final R of 0·048 for 731 non-zero reflexions. This complex obtained from cycloocta-1,5-diene is shown to have a σ-allyl structure.

Introduction

Crystal structures of diene–palladium compounds have been reported to be generally π-allylic complexes (Maitlis, 1971; Heck, 1974). Crystals of the allyl palladium complex obtained from 1,5-cyclooctadiene (Agami, Levisalles & Rose-Munch, 1972) were supplied for X-ray analysis. They were found to have a σ-allyl structure. Some results have already been published (Dahan, Agami, Levisalles & Rose-Munch, 1974).

Experimental

A single crystal, $0{\cdot}10\times0{\cdot}10\times0{\cdot}25$ mm, was selected for the X-ray investigation. The density was determined by flotation in a mixture of carbon tetrachloride and bromoform and was in good agreement with the calculated value.

The lattice constants were obtained from a least-squares analysis of the setting of 25 reflexions measured on a four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å).

The intensities were collected in the Philips Research Laboratories on a Philips PW 1100 computer-controlled four-circle diffractometer in the ω-scan mode (scan width $=1{\cdot}40°$, scan speed $=0{\cdot}058°\ s^{-1}$).

With Zr-filtered Mo $K\alpha$ radiation, 967 reflexions up to $2\theta=40°$ were measured. Throughout the data collection, three reference reflexions were recorded after each sequence of 116 measured reflexions. The intensities of the standard reflexions remained constant to within $\pm1{\cdot}5$%.

With $I\leq2\sigma(I)$, 160 reflexions were omitted as unobserved. Standard deviations $\sigma(I)$ were calculated from

$$\sigma(I)=(I_1+I+I_2)^{1/2},$$

where I_1 and I_2 are the background counts and I the peak count.

76 other reflexions were redundant owing to space group equivalence. The remaining 731 reflexions were used in the structure determination. The crystal data are given in Table 1.

Table 1. *Crystal data*

Formula	$C_{16}H_{22}Pd_2Cl_2$
M.W.	497·60
Density	$D_m=1{\cdot}730$, $D_x=1{\cdot}747$ g cm^{-3}
Space group	$R\bar{3}$
Hexagonal cell	$a=27{\cdot}155$ (7), $c=6{\cdot}669$ (6) Å, $Z=9$, $V=4259$ Å^3, $F(000)=2196$
Systematic absences	$hkil$ when $-h+k+l\neq3n$
Linear absorption coefficient	$\mu=21$ cm^{-1} ($\lambda=0{\cdot}7107$ Å)

The data were corrected for Lorentz and polarization effects but not for absorption.

Structure determination

The structure was solved by the heavy-atom method. The Pd atom was located from a Patterson function. A structure factor calculation based on the coordinates of this atom gave an R of 0·30 ($R=\sum||F_o|-|F_c||/\sum|F_o|$). From the subsequent Fourier synthesis the Cl atom was revealed. Then a difference synthesis resulted in the location of all the C atoms. All calculations were performed on an IBM 370–165 computer.

The scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for Pd, Cl and C and from Stewart, Davidson & Simpson (1965) for H. Corrections for anomalous dispersion were carried out for the Pd ($\Delta f'=-1{\cdot}0$) and Cl ($\Delta f'=0{\cdot}1$) atoms.

A full-matrix least-squares calculation with the local version *SIRIUS* of the program *ORFLS* (Busing, Martin & Levy, 1962) was used to refine the atomic coordinates and isotropic temperature factors of all non-hydrogen atoms. R fell to 0·10 and was then reduced to 0·051 by anisotropic refinement.

All H atoms were located from another difference synthesis. Their isotropic temperature factors were those of the atoms to which they were bonded. The H atom parameters were not refined.

During the last cycles of refinement, the weighting scheme was

$$\sigma=0{\cdot}013|F_o|+0{\cdot}30 \text{ for } |F_o|\leq11{\cdot}6$$
$$\sigma=0{\cdot}81 \text{ for } |F_o|>11{\cdot}6\,.$$

The final R was 0·048 $\{R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0{\cdot}058\}$.

Positional and thermal parameters are listed in Tables 2 and 3.*

Description and discussion of the structure

Fig. 1 shows the structure viewed along **c**. All geometrical calculations were made with the NRC programs (Ahmed, Hall, Pippy & Huber, 1966). The bond lengths and angles are represented on Fig. 2. The average standard deviations are 0·001 Å on Pd–Cl, 0·006 Å on Pd–C, 0·009 Å on C–C distances; 0·04° on Cl–Pd–Cl and Pd–Cl–Pd, 0·2° on Cl–Pd–C and C–Pd–C, 0·6° on C–C–C angles.

The distances and angles involving H atoms are given in Table 4.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31585 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Fractional coordinates* ($\times 10^3$) *and isotropic B values* (Å^2) *of the hydrogen atoms*

	x	y	z	B
H(C1)	395	531	−153	5·44
H(C2)	300	459	−197	6·65
H(C3)	256	389	−45	6·51
H1(C4)	314	350	94	6·17
H2(C4)	279	370	280	6·17
H(C5)	387	395	317	5·08
H(C6)	421	481	459	5·70
H1(C7)	366	531	484	6·99
H2(C7)	313	472	353	6·99
H1(C8)	409	567	202	8·12
H2(C8)	333	548	140	8·12

Table 2. *Fractional atomic coordinates* ($\times 10^5$) *and thermal parameters* ($\times 10^5$) *in the form*:
$T=exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$

Estimated standard deviations ($\times 10^5$) are in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	43273 (1)	48744 (1)	7885 (5)	130 (1)	179 (1)	1918 (9)	59 (1)	22 (2)	70 (2)
Cl	50927 (4)	46811 (5)	20416 (16)	147 (2)	204 (2)	1974 (29)	70 (2)	34 (6)	149 (7)
C(1)	37621 (22)	50971 (25)	−1246 (94)	172 (12)	269 (14)	3950 (184)	122 (12)	−93 (36)	−42 (43)
C(2)	32037 (26)	45899 (32)	−8254 (92)	245 (15)	387 (18)	3194 (177)	150 (14)	169 (40)	286 (47)
C(3)	29386 (26)	40990 (25)	1195 (93)	277 (16)	329 (19)	3858 (217)	182 (15)	−267 (46)	−172 (53)
C(4)	31141 (26)	38543 (29)	16368 (96)	161 (12)	264 (15)	4664 (224)	108 (12)	124 (41)	173 (44)
C(5)	36759 (20)	42033 (25)	26323 (84)	177 (12)	291 (15)	3583 (165)	122 (11)	174 (36)	214 (42)
C(6)	38528 (25)	47093 (28)	35483 (70)	245 (13)	377 (19)	1305 (127)	117 (13)	21 (33)	−143 (38)
C(7)	35170 (27)	50269 (24)	35556 (88)	259 (16)	330 (18)	4007 (220)	133 (14)	156 (48)	−196 (54)
C(8)	36629 (24)	53870 (25)	17103 (91)	118 (12)	174 (12)	8987 (396)	27 (10)	370 (32)	398 (58)

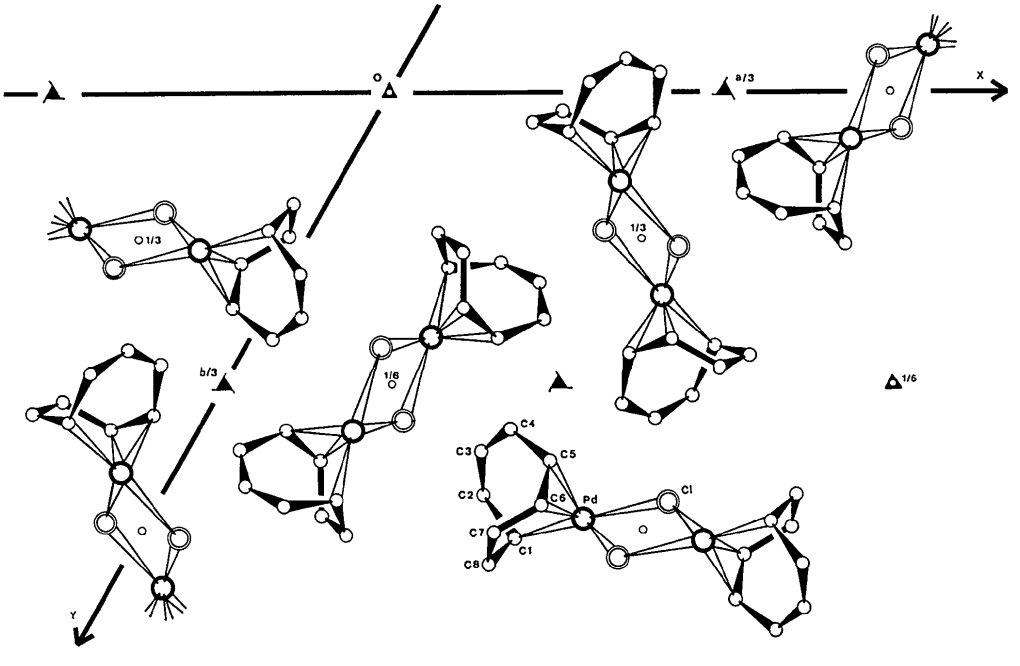

Fig. 1. The structure viewed along **c**.

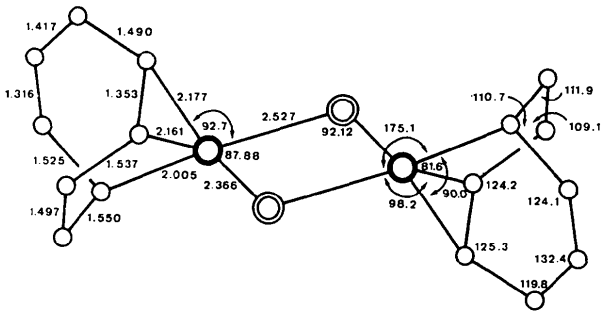

Fig. 2. Bond lengths (Å) and angles (°).

Table 4. *Distances* (Å) *and angles* (°) *involving hydrogen atoms*

Average standard deviations are 0·04 Å and 3°.

C(1)–H(C1)	1·08	Pd——C(1)–H(C1)	101
		C(2)——C(1)–H(C1)	102
		C(8)——C(1)–H(C1)	124
C(2)–H(C2)	0·94	C(1)——C(2)–H(C2)	124
		C(3)——C(2)–H(C2)	111
C(3)–H(C3)	0·97	C(2)——C(3)–H(C3)	107
		C(4)——C(3)–H(C3)	121
C(4)–H1(C4)	1·10	C(3)——C(4)–H1(C4)	107
C(4)–H2(C4)	1·09	C(3)——C(4)–H2(C4)	107
		C(5)——C(4)–H1(C4)	105
		C(5)——C(4)–H2(C4)	108
		H1(C4)–C(4)–H2(C4)	111
C(5)–H(C5)	1·11	Pd——C(5)–H(C5)	105
		C(4)——C(5)–H(C5)	114
		C(6)——C(5)–H(C5)	116
C(6)–H(C6)	1·11	Pd——C(6)–H(C6)	97
		C(5)——C(6)–H(C6)	111
		C(7)——C(6)–H(C6)	123
C(7)–H1(C7)	1·08	C(6)——C(7)–H1(C7)	107
C(7)–H2(C7)	0·96	C(6)——C(7)–H2(C7)	102
		C(8)——C(7)–H1(C7)	108
		C(8)——C(7)–H2(C7)	112
		H1(C7)–C(7)–H2(C7)	118
C(8)–H1(C8)	1·04	C(7)——C(8)–H1(C8)	99
C(8)–H2(C8)	1·07	C(7)——C(8)–H2(C8)	109
		C(1)——C(8)–H1(C8)	97
		C(1)——C(8)–H2(C8)	110
		H1(C8)–C(8)–H2(C8)	128

The only intermolecular interactions are of the van der Waals type. The two Pd atoms are joined by Cl bridges in an approximate square planar arrangement, as generally in this kind of complex: $(C_3H_5PdCl)_2$ (Smith, 1965), $(MeC_4H_3PdCl)_2$ (Mason & Wheeler, 1968) and $PdCl(C_6H_8Cl)_2$ (Broadbent & Pringle, 1971).

The cyclooctadiene ligand has a skewed conformation as observed when coordinated to other metals: 1,5-cyclooctadiene–duroquinonenickel (Glick & Dahl, 1965) and 1,5-cyclooctadiene–acetylacetonatorhodium(I) (Tucker, Scutcher & Russell, 1975). The distance between C(1) and the midpoint of C(5)–C(6) is 2·77 Å. The skewing of the diene makes the C(3)···C(7) and C(4)···C(8) distances non-equivalent at 3·18 and 3·67 Å respectively. The difference between these two values decreases as the ligand becomes more strongly bonded to a metal, the difference being 0·58 Å in the duroquinonenickel complex, 0·43 Å in the acetylacetonatorhodium(I) complex and 0·49 Å in the present study.

The C–C–C angles within the ring are greater than the respective ideal values for sp^2 or sp^3 hybridization. The C–C–H angles are correspondingly smaller as often happens when seven or eight-membered carbocyclic rings have a multiple attachment to a single metal atom (Cotton, LaPrade, Johnson & Lewis, 1971).

The angle between the planes (Pd, Cl, Pd′) and [C(1), C(5), C(6)] is 97·7°. It is significantly different from the value found with the π-allylic group, 111·5 ± 0·9° (Maitlis, 1971).

The Pd–Cl length (2·527) is larger than Pd–Cl′ (2·366 Å) which shows the larger *trans*-influence of the σ C–Pd bond [Pd–C(1) = 2·005] compared with the π C–Pd bond [Pd–C(5) = 2·177, Pd–C(6) = 2·161 Å].

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