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Crystal and Molecular Structure of the Chloropalladation Adduct ($Pd_2Cl_2(C_{10}H_{16}Cl)_2$) of a Vinylcyclopropane

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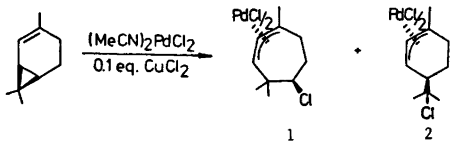
The compound $Pd_2Cl_2(C_{10}H_{16}Cl)_2$ crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19) with $a=10.556(6)$, $b=16.984(10)$, $c=13.229(4)$ Å and $z=4$. The X-ray investigation was based on 2423 independent reflections collected with an automatic computer controlled, Syntex $P2_1$ four-circle diffractometer. The structural parameters were refined by least-squares methods to a conventional R-value of 0.038.

The molecular structure is dimeric and contains a non-planar double palladium-chloro bridge, with a dihedral angle of 125.2°. A π-allyl group is coordinated to each of the palladium atoms, with the π-allyl groups arranged *cis* to one another. The Pd–Pd distance is 3.125 Å.

The palladium and the chlorine atoms on the ring are *trans* to one another showing that a *trans*-chloropalladation of the cyclopropane ring has occurred.

The present work is part of an investigation of the stereochemistry of the opening of cyclopropanes by palladium chloride complexes to give chloropalladation adducts. It has been reported that chloropalladation of a homoallylic cyclopropane occurs *cis*, but that the analogous chloropalladation of an allylic cyclopropane occurs *trans*.[2] Recently *cis*-chloropalladation of a methylene cyclopropane was established.[3] We have recently studied the mechanism of chloropalladation of vinylcyclopropanes [4] and we now report an X-ray crystal structure of one of the adducts (*1*) obtained from reaction of (+)-2-carene with bis(acetonitrile)palladium dichloride.

Reaction of (+)-2-carene with bis(acetonitrile)palladium dichloride gives two isomeric π-allylpalladium complexes *1* and *2* as products,



1 2

with a solvent dependent product ratio.[4] The stereochemistry of complex *2* was previously established by NMR spectroscopy.[4a] The X-ray analysis of complex *1*, reported in the present paper,* shows that the elements of Pd and Cl have added *trans* across the cyclopropane moiety in this case.

EXPERIMENTAL

Preparation of crystals. $(MeCN)_2PdCl_2$ and (+)-2-carene were stirred in benzene for 60 h. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel, using CCl_4–CH_2Cl_2 (3:2) as eluate. Recrystallization from hexane–chloroform gave the desired π-allylpalladium complex *1*, as yellow prismatic crystals, stable at room temperature.

X-Ray data. The intensity data were collected at ambient temperature by a computer-controlled four-circle diffractometer of type Syntex $P2_1$, using graphite-monochromatized Mo$K\alpha$-radiation ($\lambda=0.71069$ Å).

A crystal with maximum dimensions of about 0.3 mm was used. A preliminary determination of the symmetry and the unit cell was made from Weissenberg photographs. The lattice constants were refined by centering 20 selected reflections on the diffractometer. An orthorhombic unit cell was found with $a=10.556(6)$, $b=16.989(10)$,

* A preliminary report of this work has appeared.[4b]

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c=13.229(4) Å and V=2367.6 Å^3. The calculated density was 1.76 g/cm^3 for Z=4. Systematically absent reflections were $h00$ for $h=2n+1$; $0k0$ for $k=2n+1$, and $00l$ for $l=2n+1$ which are characteristic for the non-centrosymmetric space group $P2_12_12_1$ (No. 19).[5]

For the intensity data collection the ω-scan mode was used, with intensity dependent variable scan speeds from 0.49° min^{-1} up to 29.5 min^{-1}.

All hkl reflections up to 2θ=50° and part of the $hk\bar{l}$ reflections ($1k\bar{l}$ and $2k\bar{l}$) were measured. Of 2791 reflections, 2423 had intensities larger than $1.96\sigma(I)$ and were considered observed. Averaging the Friedel pairs gave 2390 independent reflections, 2072 with $I>1.96\ \sigma(I)$. The intensities were corrected for Lorentz and polarization effects and converted to scaled $|F_o|$ values. After every 50th reflection, three check reflections were measured. No systematic variation in their intensities was observed during the data collection.

The absorption coefficient μ(Mo$K\alpha$) is 19.3 cm^{-1}. A semiempirical absorption correction was used,[6] based on a rotation around the diffraction vector for a few selected reflections. The measured relative variation in transmission ratio was from 1 to 0.74.

The program system supplied by Syntex (XTL version 2) [7] for a NOVA 1200 computer with a disk memory unit, was used for all calculations. In addition, the thermal-ellipsoid plot program for crystal structure illustration, ORTEP 2,[8] was used.

The scattering factors used for all nonhydrogen atoms were calculated from analytical expressions for the neutral atoms.[5] For the hydrogen atoms the spherical form factors proposed by Stewart *et al.* were used.[9] Anomalous dispersion corrections were included for palladium and chlorine.[5]

STRUCTURE DETERMINATION AND REFINEMENT

The positions of the palladium atoms were found from the three dimensional Patterson map,

Table 1. Final fractional atomic positional parameters and the isotropic temperature factors. The estimated standard deviations are given in parentheses.

Atom	x	y	z	B_{iso}
Pd1	0.06795(6)	0.19699(4)	0.10210(5)	3.04(3)
Pd2	−0.22982(6)	0.21068(3)	0.10782(5)	2.69(3)
Cl1	0.0525(3)	0.1359(2)	0.4703(2)	4.8(1)
Cl2	−0.2016(3)	−0.0257(2)	0.3185(2)	4.4(1)
Cl3	−0.0651(2)	0.3130(1)	0.1205(2)	3.5(1)
Cl4	−0.0935(2)	0.1471(2)	−0.0143(2)	3.2(1)
C1	0.2530(9)	0.1593(7)	0.1333(6)	3.6(4)
C2	0.1804(9)	0.0899(6)	0.1167(7)	3.2(4)
C3	0.1194(11)	0.0409(6)	0.1943(7)	3.4(4)
C4	0.1430(11)	0.0611(6)	0.3040(7)	4.1(5)
C5	0.0941(10)	0.1398(6)	0.3353(6)	3.3(4)
C6	0.1838(10)	0.2102(6)	0.3170(7)	3.3(4)
C7	0.2191(9)	0.2163(6)	0.2056(7)	3.8(4)
C8	0.1206(12)	0.2895(6)	0.3486(8)	4.5(5)
C9	0.3098(11)	0.2011(9)	0.3753(8)	5.6(6)
C10	0.2018(11)	0.0486(8)	0.0164(8)	4.9(5)
C11	−0.4118(8)	0.2038(6)	0.1645(7)	3.2(4)
C12	−0.3427(10)	0.2461(6)	0.2372(7)	2.9(4)
C13	−0.2781(10)	0.2081(5)	0.3301(7)	3.2(4)
C14	−0.2962(11)	0.1206(6)	0.3488(7)	3.8(5)
C15	−0.2531(9)	0.0677(5)	0.2628(7)	3.0(4)
C16	−0.3485(9)	0.0527(5)	0.1815(7)	2.6(3)
C17	−0.3833(10)	0.1299(6)	0.1265(7)	2.9(4)
C18	−0.2941(12)	−0.0031(6)	0.1000(8)	4.4(5)
C19	−0.4734(12)	0.0180(7)	0.2176(9)	5.6(6)
C20	−0.3626(13)	0.3321(6)	0.2487(8)	5.0(6)

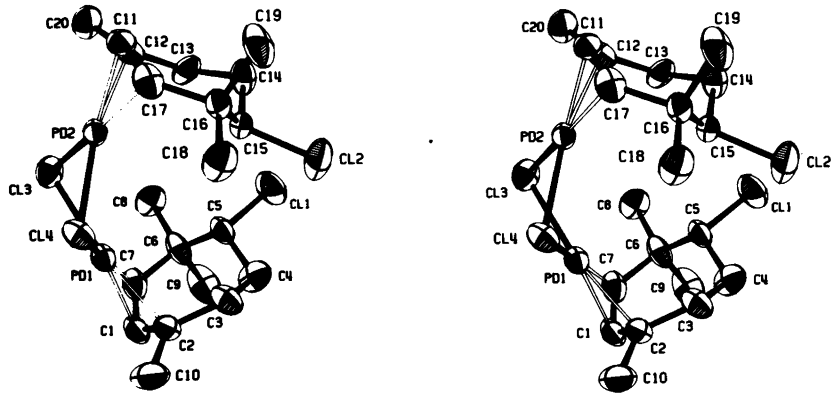


Fig. 1. A stereoscopic view of the molecular structure of $Pd_2Cl_2(C_{10}H_{16}Cl)_2$.

assuming the space group $P2_12_12_1$, and used as the starting point for a full-matrix least-squares refinement. The function minimized was $\Sigma w||F_o|-|F_c||^2$ including reflections with $F_o>3.92\ \sigma(F_o)$. The weighting scheme used was $w=1/[\sigma^2(F_o)+(0.04\ F_o)^2]$ which, according to a weight analysis, gave a satisfactory error distribution.

The chlorine and the carbon atoms were found from a subsequent Fourier difference synthesis. Full matrix least-squares refinements with all atoms isotropic and with mean values of the Friedel pairs gave $R=0.068$.* New refinements with anisotropic temperature coefficients gave $R=0.047$. The present limited set of data do not allow the determination of the absolute configuration of the molecule. Thus, the R_w values without averaging over the Friedel pairs were 0.073(0.074)* for isotropic atoms and 0.052(0.053)* for anisotropic atoms *i.e.* no significant differences.

From another Fourier difference synthesis 12 of the 32 hydrogen atoms could be located and refined ($R=0.040$). The final refinement with an additional 17 hydrogen atoms, geometrically inserted with fixed parameters ($B=5$ Å^2), gave $R=0.038$ ($R_w=0.055$). Three hydrogen atoms belonging to a methyl group, C20, were not included.

Positional and thermal parameters are given in Table 1. Listings of structure factors, anisotropic temperature factors and hydrogen positions are available from the authors on request.

The highest remaining peak in a final difference electron density map was 0.6 e/Å^3 close to Pd1.

* The conventional R-value is defined as $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, and the weighted as $R_w=(\Sigma w||F_o|-|F_c||^2/wF_o^2)^{1/2}$. The values in parentheses are for the enantiomorphous structure.

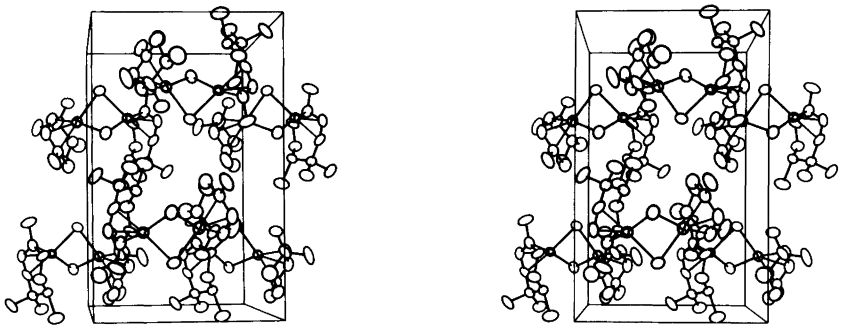


Fig. 2. A stereoscopic view of the unit cell. The *a* axis is horizontal, the *b* axis is vertical and origo is the lower, left rear corner.

Table 2. Selected interatomic distances, Å.[a]

(i) The chloro-palladium bridge			
Pd1–Cl3	2.431(2)	Pd2–Cl3	2.463(2)
Pd1–Cl4	2.448(2)	Pd2–Cl4	2.418(2)
Pd1–Pd2	3.153(1)		
Cl3–Cl4	3.347(3)		
(ii) The π-allyl groups			
Pd1–C1	2.10(1)	Pd2–C11	2.07(1)
Pd1–C2	2.18(1)	Pd2–C12	2.17(1)
Pd1–C7	2.13(1)	Pd2–C17	2.14(1)
C1–C2	1.42(1)	C11–C12	1.41(1)
C1–C7	1.41(1)	C11–C17	1.39(1)
(iii) The carbon–carbon and carbon–chloro σ-bonds			
C2–C3	1.48(1)	C12–C13	1.55(1)
C3–C4	1.51(1)	C13–C14	1.52(1)
C4–C5	1.49(2)	C14–C15	1.52(1)
C5–C6	1.55(2)	C15–C16	1.50(1)
C6–C7	1.53(1)	C16–C17	1.54(1)
C6–C8	1.56(1)	C16–C18	1.57(1)
C6–C9	1.54(2)	C16–C19	1.52(2)
C2–C10	1.51(2)	C12–C20	1.48(1)
C5–Cl1	1.84(1)	C15–Cl2	1.83(2)
(iiii) Intermolecular distance			
Pd1–Pd2[b]	3.838(1)		

[a] Estimated standard deviations in parentheses. [b] Symmetry code 1/2+x, 1/2−y, z̄.

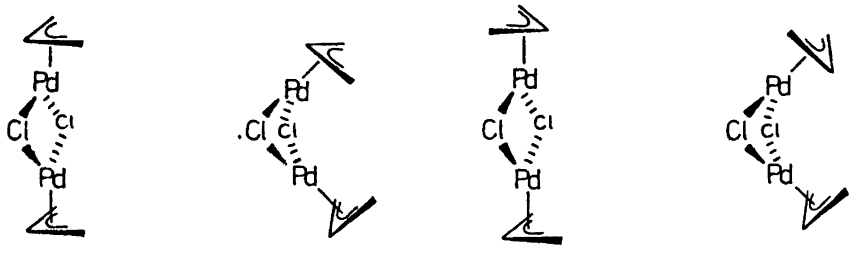
DISCUSSION

The molecular structure and the packing of the unit cell are shown in Figs. 1 and 2. Selected interatomic distances are given in Table 2, selected angles in Table 3.

The molecule is a dimeric complex, with the palladium atoms linked together by a double chloro bridge. Each palladium atom further coordinates a π-allyl group as an organic ligand. From the ORTEP drawing of the molecular structure, Fig. 1, it can be seen that the chloro bridge is bent, with an angle of 125.2°, *cf.* Table 3. Fig. 1 also shows that the allyl groups are arranged *cis* to one another. The conformation usually observed [10–17] in dimeric π-allylpalladium chloride complexes is one with a planar bridge, with a *trans* arrangement of the allyl groups and with a center of symmetry. However, two reported structures, $[\eta^3$-cycloheptenyl-PdBr$]_2$[18] and $[\eta^3$-(2,3,4)-pentenyl-PdCl$]_2$[19] resemble the complex *1*. They have a non-planar bridge and a *cis* arrangement of the π-allyl groups. To our knowledge, no structure with a *cis* arrangement of the allyl groups and a planar chloropalladium bridge has been reported.

The reason for the bending of the halide bridge in *cis*-complexes is not clear. The Pd–Pd intramolecular distance, 3.152 Å, (Table 2), is shorter than in corresponding dimeric complexes having a planar Pd–Cl bridge. This indicates some non-bonding interactions between the metal centers. [20] (The Pd–Pd distance in elemental palladium is 2.75 Å[21] and in $Pd(NH_3)_4PdCl_4$ 3.25 Å.[22]) Packing forces could be one reason why bending occurs in the *cis*-complexes. From Fig. 3, which shows the possible *cis* and *trans* conformations, it can be seen that the *trans* conformation (*4*) loses its center of symmetry on bending, whereas the bending of the *cis* conformation (*3*) occurs within the C_{2v}-symmetry. In Table 4 we have summarized the π-allyl groups that lead to dimeric *cis*- and *trans*-complexes, respectively.

For each of the two allyl groups in compound



3 4

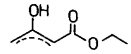
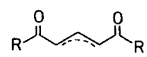
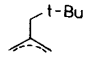
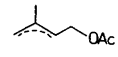
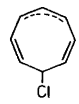
Fig. 3. Possible *cis* (3) and *trans* (4) conformations for a dimeric chlorobridged π-allylpalladium complex.

Table 3. Selected angles, in degrees. [a]

(i) The chloro-palladium bridge			
Pd1–Cl3–Pd2	80.19(8)		
Pd1–Cl4–Pd2	80.77(8)		
Cl3–Pd1–Cl4	86.62(8)		
Cl3–Pd2–Cl4	86.58(8)		
(ii) The π-allyl groups			
C2–C1–C7	122.5(9)	C12–C11–C17	126.8(9)
C1–C2–C3	126.7(9)	C11–C12–C13	124.0(8)
C6–C7–C1	132.3(9)	C16–C17–C11	130.5(8)
(iii) The σ-bond angles of the organic ligand			
C2–C3–C4	118.0(9)	C12–C13–C14	118.8(8)
C3–C4–C5	114.4(9)	C13–C14–C15	114.6(8)
C4–C5–C6	116.1(8)	C14–C15–C16	115.4(8)
C5–C6–C7	110.7(8)	C15–C16–C17	110.9(8)
C3–C2–C10	114.1(9)	C13–C12–C20	113.0(8)
C5–C6–C8	111.2(8)	C15–C16–C18	110.6(8)
C5–C6–C9	111.9(9)	C15–C16–C19	115.6(8)
C8–C6–C9	108.5(9)	C18–C16–C19	106.6(8)
C4–C5–Cl1	108.6(7)	C14–C15–Cl2	107.3(6)
(iiii) Dihedral angles			
Cl3–Pd1–Cl4/Cl3–Pd2–Cl4	125.2	Cl3–Pd1–Cl4/C7–C1–C2	118.6
Cl3–Pd2–Cl4/C17–C11–C12	120.7		

[a] Estimated standard deviations in parentheses.

Table 4. Conformation of bis (π-allylpalladium) complexes, (*cf.* Fig. 3).

cis conformation	Ref.	*trans* conformation	Ref.
	18		10
	19		11
			12
	This work		13
			14
			15
			16
			17

1, the three Pd–C distances (Table 2) are found to be different, but with similar variations. The shortest Pd–C distance is the one to the central carbon atom, with an average distance of 2.08 Å. To the terminal carbon atoms the average distances are 2.18 Å and 2.13 Å, with the longest distance to the most substituted carbon. A similar variation is reported for [η^3-(2,3,4)-pentenyl-PdCl]$_2$[19] *5* and π-allylpalladium complexes *6* with nonidentical ligands.[23] This asymmetry may have

5

6

different origins. In the latter case it may be due to *trans* effects from the ligands, but in complex *1*, reported in this paper, it is probably a steric effect.

The remainder of the molecule is in accordance with previous reports. For example, the dihedral angles between the plane through the allyl group and the palladium-chloro plane (Cl–Pd–Cl) are 118.6 and 120.7°, which are only slightly larger than the corresponding angle in [η^3-(1,2,3)-propenyl-PdCl]$_2$,[10] 111.5°.

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