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Synthesis, Crystal and Molecular Strucure of Bis(2-neopentyl-π-allyl palladium chloride)·$2CHCl_3$

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Bis(2-neopentyl-π-allyl palladium chloride)·2CHCl₃, $C_{18}H_{32}Pd_2Cl_8$, *MW 744.89, has been synthesized by a novel method involving a hexane/water/2-propanol detergentless microemulsion. The material has been characterized by IR, NMR, and single crystal X-ray diffractometry, (space group* $P\bar{1}$, $a = 5.686(9)$, $b = 12.591(7)$, $c = 10.56(3)$ Å, $\alpha = 86.4(1)$, $\beta = 82.9(2)$, $\gamma = 77.8(2)^\circ$, $Z = 1$, $D_{calc.} = 1.685$ g cm^{-1}, *final* R *factor 7.7% for 1993 observed data.)*

The two Pd atoms are bridged by two chlorides at 2.422(7) and 2.426(5) Å with Pd–Pd intramolecular distance of 3.487(5) Å. Each Pd atom is further coordinated to the π-allyl group of a 2,4,4-trimethyl-1-pentene molecule. The planer Pd_2Cl_2 *group forms a dihedral angle of 112° with the coordinated allyl group. The dimers are packed in linear arrays with Pd–Pd intermolecular distance of 4.075(5) Å. Crystal formation and integrity appear dependent upon the inclusion of two well ordered molecules of chloroform per dimer.*

TABLE I. Crystal Data.

Formula	$C_{16}H_{30}Cl_2Pd_2\cdot 2(CHCl_3)$
MW	744.89
Space Group	$P\bar{1}$
Systematic absences	none
a = 5.686(9) Å	
b = 12.591(7)	
c = 10.56(3)	
α = 86.4(1)°	
β = 82.9(2)	
γ = 77.8(2)	
V = 733(3) Å^3	
D_{calc} = 1.685 g cm^{-1}	
Z = 1	
$\mu(MoK_\alpha)$ = 48.85 cm^{-1}	
$F(000)$ = 846	

Introduction

As part of a study of the use of microemulsions [1] as a media for facilitating chemical reactions [2–6], we have undertaken a study of the conversion of long chain olefins to the corresponding methyl ketones using $PdCl_2$ as a catalyst. During the course of these investigations, we attempted to oxidize 2,4,4-trimethyl-1-pentene to ascertain whether an aldehyde would be produced at the number one carbon or oxidation at the number three carbon would produce a ketone function. The major product after reaction workup was found to be a crystalline yellow powder which showed no carbonyl absorption (IR) and the loss of a proton (NMR) and which contained palladium. The yellow-green needles formed on recrystallization of the material from chloroform were unstable if removed from a chloroform atmosphere for longer than one minute. Initial X-ray characterization of the material showed it to crystallize in triclinic space group $P\bar{1}$ in a cell of dimensions (Table I) inconsistent with those reported for bis(2-neopentyl-π-allyl palladium chloride) [7, 8]. We have determined the single crystal X-ray structure of the product of the oxidation to establish the identity of the material.

Experimental

Anhydrous $PdCl_2$ was converted to tetrachloropalladic acid on dissolving 0.203 g (1.14×10^{-3} mol) of $PdCl_2$ in 5 ml of concentrated HCl and evaporation to dryness. The H_2PdCl_4 was then dissolved in 25 ml of triply distilled water. Hexane

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TABLE II. Atomic Coordinates.

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$
Pd	0.2480(1)	0.0941(1)	0.4570(1)
Cl(1)	0.4697(4)	0.0582(2)	0.6418(2)
Cl(2)	0.5840(6)	0.1138(3)	0.0789(2)
Cl(3)	0.9329(6)	0.1406(4)	0.8653(6)
Cl(4)	0.4898(7)	0.2931(3)	0.8999(4)
C(1)	−0.002(2)	0.1406(9)	0.320(1)
C(2)	−0.031(2)	0.2257(9)	0.5191(9)
C(3)	0.017(2)	0.2345(7)	0.3850(7)
C(4)	0.134(1)	0.3238(7)	0.3235(8)
C(5)	−0.052(1)	0.4205(8)	0.2674(7)
C(6)	−0.175(2)	0.3808(9)	0.1625(9)
C(7)	0.092(2)	0.510(1)	0.217(1)
C(8)	−0.251(2)	0.467(1)	0.375(1)
C(9)	0.626(2)	0.158(1)	0.9155(8)
H(11)	−0.1248	0.0761	0.3711
H(12)	0.0342	0.1479	0.2336
H(21)	−0.2040	0.1845	0.5187
H(22)	−0.0322	0.2953	0.6197
H(41)	0.2127	0.3662	0.3795
H(42)	0.2804	0.3089	0.2321
H(61)	−0.2756	0.4357	0.1326
H(62)	−0.2538	0.3187	0.1636
H(63)	−0.0697	0.3530	0.1068
H(71)	0.2349	0.4757	0.1479
H(72)	0.1915	0.5424	0.3088
H(73)	0.0307	0.5842	0.1315
H(81)	−0.1666	0.4801	0.4705
H(82)	−0.3208	0.5545	0.3050
H(83)	−0.2201	0.5502	0.4105
H(91)	0.5301	0.1978	0.9881

(trace metal impurities removed by purification through silica gel), 2-propanol (treated with silica gel and twice distilled over molecular sieves), and the water solution were used to prepare a hexane/water/2-propanol water dispersed detergentless microemulsion by titrating the 25 ml of aqueous H_2PdCl_4 and 250 ml of hexane to clarity with 182 ml of 2-propanol. The resulting microemulsion was a translucent golden-brown and surface active. 2,4,4,-trimethyl-1-pentene (10 ml) was added to the reaction mixture which was then heated under reflux at 40 °C for 24 hours. The solution was then evaporated to near dryness and the product dissolved in a minimum amount of chloroform and eluted from a 3 × 25 cm silica gel column with chloroform. Bis(2-neopentyl-π-allyl palladium chloride) was recovered (52% yield).

Elemental analysis, Found: C, 35.25%; H, 5.97%; Pd, 42.49%; Cl, 14.48%. Calculated for $C_{16}H_{30}Pd_2Cl_2$: C, 37.97%; H, 5.98%; Pd, 47.04%; Cl, 14.01%.

Recrystallization of the above compound from chloroform gave the single crystal of bis(2-neopentyl-π-allyl palladium chloride)·$2CHCl_3$ used in the X-ray study.

A crystal (0.2 × 0.2 × 0.5 mm) was mounted in a 0.2 Lindman capillary which also contained a column of chloroform surrounding the crystal. Repeated attempts to stabilize a crystal in a chloroform atmosphere rather than in the liquid itself were unsuccessful. The crystal mounted in the liquid proved stable for the entire data collection period and no decays of intensity were noted. Data (1993 observed, $I > 3 \times \sigma(I)$, $\text{MoK}_\alpha = 0.71069$ Å) were collected on a Nonius-Enraf CAD-4 diffractometer at room temperature (25 °C) using a θ–2θ scan and a variable scan rate. Cell dimensions and their standard deviations were determined during usual alignment procedures. After correction for background, Lorentz, and polarization effects, the data were used for structure determination (heavy atom methods) [9] and full matrix least squares refinement (anisotropic thermal parameters (Table III), anomalous dispersion

TABLE III. Thermal Parameters in the Form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)] \times 10^4$ for Pd and $\times 10^3$ for all other Atoms.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	373(4)	571(5)	329(4)	−127(3)	−77(2)	67(3)
Cl(1)	53(1)	66(2)	35(1)	−9(1)	−14(1)	−2(1)
Cl(2)	93(2)	100(2)	41(1)	−32(2)	−4(1)	−1(1)
Cl(3)	46(2)	210(5)	89(2)	6(2)	14(2)	13(3)
Cl(4)	86(2)	95(3)	121(3)	7(2)	−22(2)	19(2)
C(1)	66(7)	73(8)	56(6)	−21(6)	−25(5)	9(5)
C(2)	72(8)	74(8)	41(6)	−2(6)	−14(5)	12(5)
C(3)	35(5)	61(6)	31(5)	−9(4)	−6(3)	9(4)
C(4)	14(4)	59(6)	40(5)	−5(3)	3(3)	−2(4)
C(5)	32(5)	60(6)	29(4)	−7(4)	−5(3)	6(4)
C(6)	64(6)	84(8)	45(6)	−5(5)	−27(4)	−1(5)
C(7)	30(5)	86(8)	64(7)	−9(5)	10(4)	14(6)
C(8)	30(5)	98(9)	56(6)	10(5)	6(4)	−25(6)
C(9)	57(6)	96(8)	19(5)	−17(5)	−0(4)	0(4)

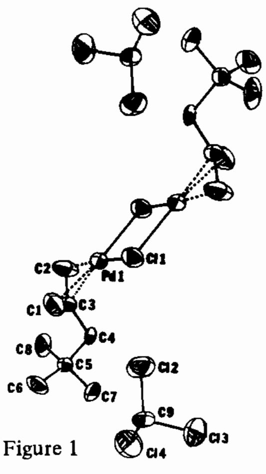

Figure 1

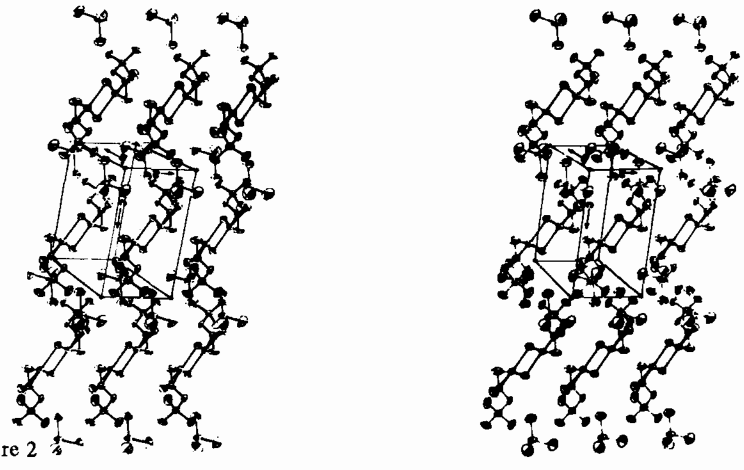

Figure 2

Fig. 1. Projection of $C_{16}H_{30}Pd_2Cl_2 \cdot 2CHCl_3$.
Fig. 2. Packing of $C_{16}H_{30}Pd_2Cl_2 \cdot 2CHCl_3$ in the cell.

TABLE IV. Bond Distances (A) and Angles (°).

Pd–Cl(1)	2.422(7)	Cl(1)–Pd–Cl(1)′	88.0(2)
Pd–Cl(1)′	2.426(5)	Pd–Cl(1)–Pd′	92.0(2)
Pd–Pd′	3.487(5)	C(1)–Pd–C(2)	68.8(4)
Pd–C(1)	2.122(12)	C(1)–Pd–C(3)	39.4(4)
Pd–C(2)	2.114(10)	C(2)–Pd–C(3)	38.9(4)
Pd–C(3)	2.129(9)	C(1)–C(3)–C(2)	114.5(9)
C(1)–C(3)	1.43(2)	C(1)–C(3)–C(4)	123.8(7)
C(2)–C(3)	1.41(1)	C(2)–C(3)–C(4)	120.2(9)
C(3)–C(4)	1.50(1)	C(3)–C(4)–C(5)	112.9(7)
C(4)–C(5)	1.57(1)	C(4)–C(5)–C(6)	110.5(8)
C(5)–C(6)	1.54(1)	C(4)–C(5)–C(7)	106.8(7)
C(5)–C(7)	1.55(2)	C(4)–C(5)–C(8)	119.5(7)
C(5)–C(8)	1.55(1)	C(6)–C(5)–C(7)	112.7(8)
C(9)–Cl(2)	1.78(1)	C(6)–C(5)–C(8)	108.2(8)
C(9)–Cl(3)	1.73(1)	C(7)–C(5)–C(8)	109.2(8)
C(9)–Cl(4)	1.73(1)	Cl(2)–C(9)–Cl(3)	109.4(5)
		Cl(2)–C(9)–Cl(4)	109.0(5)
		Cl(3)–C(9)–Cl(4)	109.7(7)

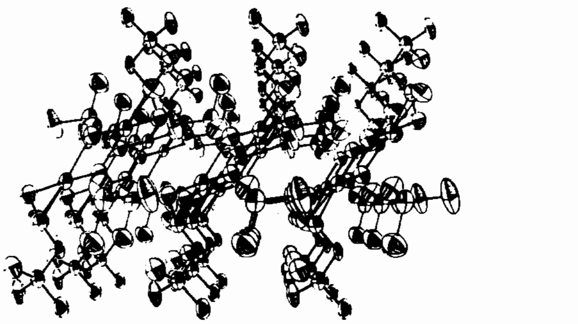

Fig. 3. Projection view of $C_{16}H_{30}Pd_2Cl_2 \cdot 2CHCl_3$ showing chloroform packing.

corrections [10]). Hydrogen atomic coordinates were included but not refined during the final cycles. Bond angles and distances (Table IV) are based on the final atomic coordinates (Table II). A list of calculated and observed structure factors is available on request.

Discussion

The two palladium atoms of the dimeric structure (Fig. 1) are bridged by two chlorine atoms and the Pd_2Cl_2 group is centered about the 0.5, 0.0, 0.5 inversion center of the $P\bar{1}$ cell. Pd–Cl distances, 2.422(7) and 2.426(5) Å, are comparable to those observed in other Pd_2Cl_2 clusters: 2.41 Å in bis(allyl)Pd_2Cl_2 at –140 °C [11] and 2.403(9), 2.398(8) Å in the same material at room temperature [12]; 2.41 Å [7], and 2.40, 2.42 Å [8] in two determinations of the structure of bis(2-neopentyl-π-allyl palladium chloride). Angles within the Pd_2Cl_2 group are in agreement with other literature values.

Each palladium atom is coordinated to the allyl group of a 2-neopentyl allyl molecule as evidenced by the nearly equal Pd–C distances of 2.122(12), 2.114(10), and 2.129(9) Å. The allyl group forms a dihedral angle of 112.7° with the plane of the Pd_2Cl_2 group which is in agreement with the dihedral angles reported for the allylic clusters [11, 12] but is substantially more acute than the 128° reported for the structure of bis(2-neopentyl-π-allyl palladium chloride) [8].

Two determinations of the structure of dimeric 2-neopentyl-π-allyl palladium chloride (*1*: orthorhombic space group $C222_1$, $a = 5.67$, $b = 45.7$, and $c = 8.05$ Å and *2*: monoclinic space group $P2_1/m$, $a = 22.875(13)$, $b = 8.051(5)$, $c = 5.667(4)$ Å, and $\beta = 97.5°$) mention no problems of crystal instability.

We were unable to stabilize the material other than in a chloroform atmosphere. The dimeric palladium groups are packed in planes roughly parallel to the 011 plane of the cell (Fig. 2), however no Pd–Pd intermolecular contact distance is less than 4.037(5) Å. The chloroform molecules fill channels in the cell between parallel allylic groups as can be seen in Fig. 3 viewed down the *a* axis. There are, however, no significant short contact distances Cl2–Cl1 = 3.75(1) Å and Cl3–C2 = 3.74(2) Å). This lack of strong interaction between the chloroform and the dimeric palladium molecule is reflected in the ease with which the chloroform leaves the crystal lattice leading to the collapse of the crystalline structure.

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