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FORMATION OF π-ALLYL LIGAND FROM PYRYLIUM SALTS. SYNTHESIS AND STRUCTURE OF NOVEL π-ALLYL COMPLEXES OF PALLADIUM(II)

L.Yu. UKHIN, V.I. IL'IN, Zh.I. ORLOVA,
Institute of Physical and Organic Chemistry, State University, Rostov-on-Don (U.S.S.R.)

N.G. BOKII * and Yu.T. STRUCHKOV
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

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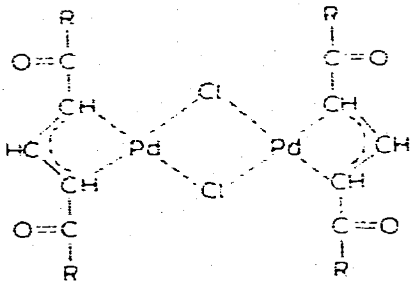
Summary

2,6-Disubstituted pyrylium salts are found to react with $PdCl_2$ in an unexpected manner with the ring opening and the formation of novel complexes of the π-allyl type. The structure of the complex with t-butyl substituents is elucidated by X-ray analysis. Crystals are monoclinic, a = 12.310, b = 10.932, c = 12.357 Å, γ = 112.71°, Z = 4, space group $P2_1/b$. The structure is refined with 2595 reflections to R = 0.034.

We have found that 2,6-disubstituted pyrylium salts  ClO_4^- react with $PdCl_2$ on heating in water-containing organic solvents (EtOH, MeOH, 50% $MeCO_2H$) with formation of π-allyl complex I:



(Ia) R = Ph
(Ib) R = t-Bu

The molecular structure of Ib was determined by an X-ray study. The main geometrical parameters of this molecule shown in Fig. 1 are very similar to those

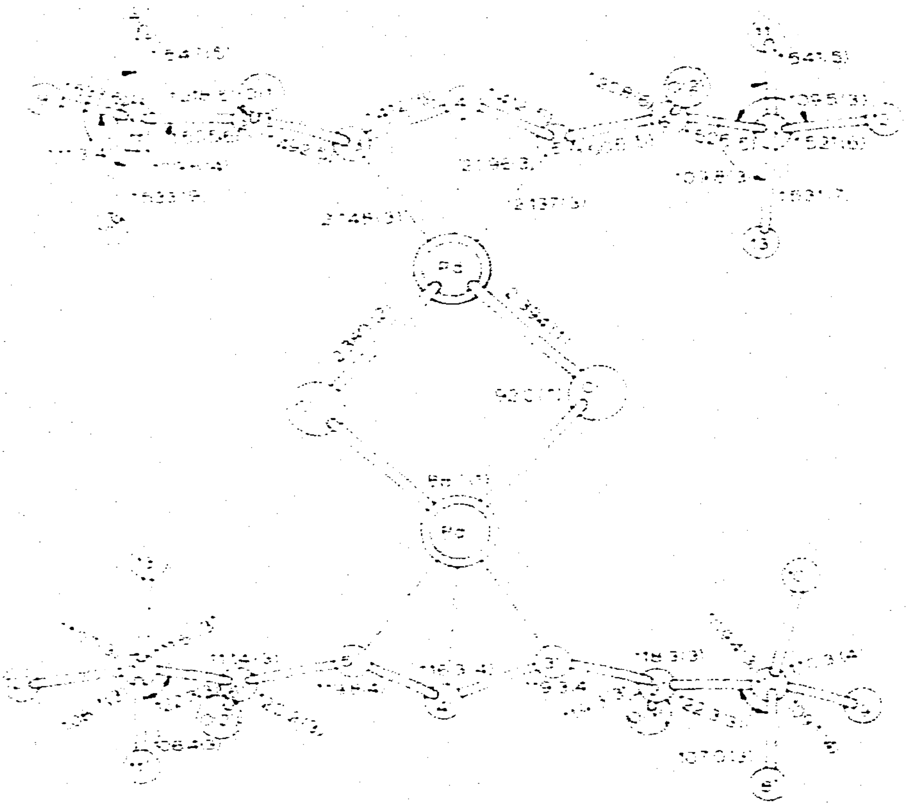
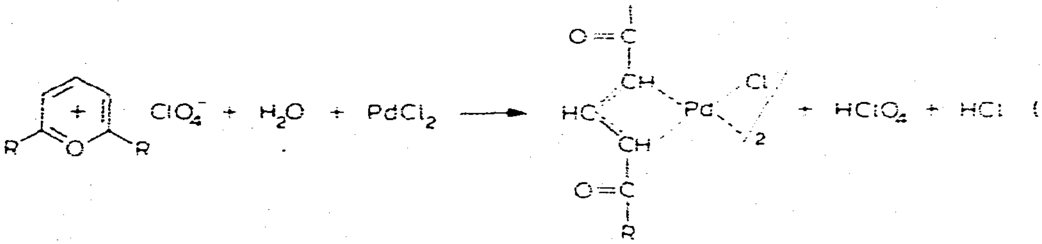


Fig. 1. Molecular structure of compound Ib with distances in Å and angles in degrees.

found in the π-allyl complexes of palladium(II) previously investigated [1]. The Pd_2Cl_2 fragment is planar as the molecule is situated in an inversion centre. The π-allyl group makes an angle of 107.5° with this fragment. As in other 1,3-disubstituted π-allyl complexes [1] substituents (C(2) and C(6) in Fig. 1) are displaced from the C(3)C(4)C(5) plane by 0.28 Å towards the Pd atom. Oxygen atoms are displaced even more (0.90 Å) and in the same direction. However central atoms C(1) and C(7) of t-butyl groups are pushed out in the opposite direction by 0.32 Å. Hydrogen atoms at C(3) and C(5) are displaced away from the Pd atom by 0.6 Å and the H atom at C(4) is displaced towards the metal by 0.2 Å.

An allyl ligand is formed as a result of pyrylium ring opening with participation of a water molecule:

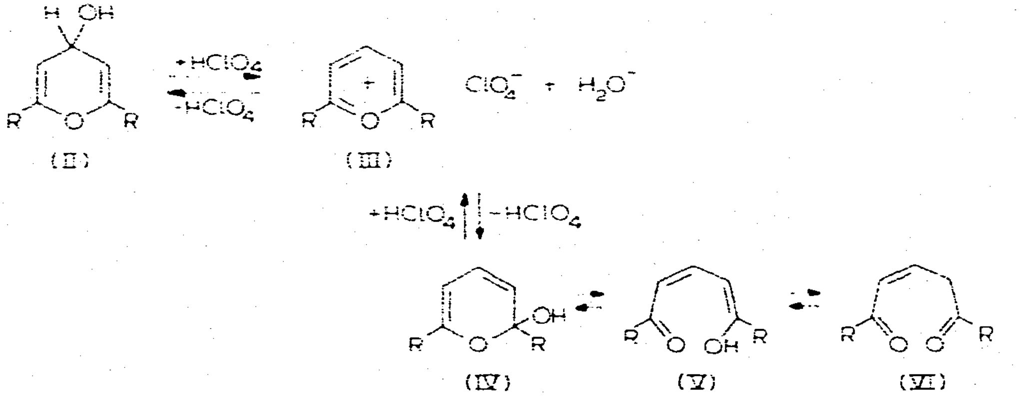


(1)

Intermediate formation of 1,5-endiones which are common products of pyrylium salt hydrolysis would clarify a subsequent reaction path. However according to refs. 2—4 pseudo-bases of pyrylium salts, i.e. 1,5-endiones, are formed from these salts in basic water solutions. Under the action of strong acids these pseudobases again convert into pyrylium salts [2]. However as is seen from eq. 1 the reaction is accompanied by acidity growth and this seems to exclude intermediate formation of 1,5-diones.

Moreover in the presence of a base, perchlorate of 2,6-diphenylpyrylium is hydrolyzed with formation of $\alpha,\alpha',\alpha'',\alpha'''$-tetraphenyl-$\gamma,\gamma'$-dipyranyl ether but not 1,5-endione [5]. Thus according to refs. 4 and 5 this salt behaves in a manner similar to perchlorates of diphenylcyclopropenylium [6] and tropylium [7].

The reason for this, at first sight unusual, reaction process between these pyrylium salts and $PdCl_2$ is readily explained by the following equilibrium system of pyrylium salt hydrolysis:



(2)

Interaction of $PdCl_2$ with an unsaturated δ-dicarbonyl compound (VI) will shift the equilibrium to the right. The extremely high tendency of palladium to form π-allyl complexes is well known and the final result will be determined by the stability of the π-allyl complex under the reaction conditions used (temperature, acidity of reaction media).

Although an opening of the pyrylium ring occurs through breakage of the O—C bond the α-carbon atom cannot be considered as a site for the primary attack by nucleophilic species. This is because a salt with both α-positions shielded by t-butyl groups reacts just as easily and smoothly as perchlorate of 2,6-diphenylpyrylium.

Experimental

Perchlorates of 2,6-diphenyl- and 2,6-di-t-butyl pyrylium were prepared according to the literature [8].

$[(\pi\text{-}C_{17}H_{13}O_2)PdCl]_2$ *(Ia)*

A suspension of 2,6-diphenylpyrylium perchlorate (1.3 g) and finely-powdered $PdCl_2$ (0.6 g) in ethyl alcohol (100 ml) was boiled with intense stirring. The greenish yellow precipitate formed was collected by filtration, washed with alcohol and dried on the filter. This raw product (0.95 g) was extracted by a boiling mixture of acetonitrile (20 ml) and dimethyl formamide (40 ml) and filter-

TABLE 1. ATOMIC COORDINATES AND TEMPERATURE FACTORS [a]

Atom	x	y	z	B_{11} or B_j	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	0.36985(2)	0.38135(2)	0.45419(2)	481(2)	771(2)	494(2)	278(3)	−74(3)	−34(3)
Cl(1)	0.44944(7)	0.47557(9)	0.62587(7)	617(6)	1263(10)	519(5)	−27(13)	227(9)	−141(12)
O(1)	0.2482(3)	0.4520(3)	0.2185(2)	146(3)	124(3)	77(2)	162(6)	10(4)	16(4)
O(2)	0.1103(3)	0.3374(3)	0.6033(2)	134(3)	135(3)	88(2)	166(6)	44(4)	29(5)
C(1)	0.3112(4)	0.3074(4)	0.1126(3)	103(4)	116(4)	56(2)	100(7)	3(5)	18(5)
C(2)	0.2755(3)	0.3553(3)	0.2158(3)	62(3)	77(3)	64(2)	33(4)	−20(4)	−5(4)
C(3)	0.2687(3)	0.2773(3)	0.3169(3)	64(2)	77(3)	55(2)	34(4)	−16(4)	−14(4)
C(4)	0.1952(3)	0.2848(3)	0.4022(3)	52(2)	72(3)	61(2)	16(4)	−27(4)	−22(4)
C(5)	0.2072(3)	0.2266(3)	0.5014(3)	54(2)	67(3)	62(2)	14(4)	4(4)	1(4)
C(6)	0.1473(3)	0.2491(3)	0.6013(3)	58(2)	86(3)	61(2)	35(5)	−4(4)	−6(4)
C(7)	0.1306(3)	0.1526(3)	0.6957(3)	67(3)	89(3)	58(2)	44(5)	2(4)	−1(5)
C(8)	0.2133(5)	0.1701(4)	0.0855(4)	198(7)	107(4)	64(3)	78(9)	−45(7)	−20(6)
C(9)	0.3195(5)	0.4959(5)	0.0209(3)	173(6)	139(6)	57(3)	130(10)	34(6)	44(6)
C(10)	0.4303(5)	0.2957(6)	0.1290(4)	147(5)	267(9)	82(3)	268(12)	66(7)	61(9)
C(11)	0.0366(4)	0.0174(4)	0.6595(4)	90(3)	100(4)	92(3)	22(6)	2(5)	16(6)
C(12)	0.0843(4)	0.2023(5)	0.7935(3)	142(5)	157(6)	62(3)	124(9)	55(6)	3(6)
C(13)	0.2453(4)	0.1356(4)	0.7234(4)	84(3)	140(5)	82(3)	85(7)	−10(5)	33(6)
H(3) [b]	0.287(3)	0.193(4)	0.307(3)	2.1(7)					
H(4)	0.152(3)	0.344(4)	0.395(3)	1.7(8)					
H(5)	0.232(4)	0.145(4)	0.500(3)	1.7(8)					
H(8-1)	0.220(5)	0.133(6)	0.015(5)	5.0(1.3)					
H(8-2)	0.138(5)	0.178(6)	0.063(4)	6.6(1.4)					
H(8-3)	0.201(5)	0.107(5)	0.135(5)	6.1(1.4)					
H(9-1)	0.372(5)	0.496(5)	0.040(4)	4.1(1.2)					
H(9-2)	0.342(5)	0.374(5)	−0.049(4)	3.9(1.1)					
H(9-3)	0.235(5)	0.415(6)	0.013(5)	5.2(1.2)					
H(10-1)	0.460(5)	0.286(6)	0.076(5)	3.8(1.4)					
H(10-2)	0.423(4)	0.243(5)	0.186(4)	3.4(1.1)					
H(11-1)	0.062(4)	−0.020(5)	0.589(4)	2.5(9)					
H(11-2)	−0.044(4)	0.024(4)	0.641(4)	3.1(9)					
H(11-3)	0.018(3)	−0.049(4)	0.733(3)	2.7(8)					
H(12-1)	0.066(5)	0.140(5)	0.850(4)	4.9(1.2)					
H(12-2)	0.132(5)	0.286(6)	0.813(5)	5.3(1.3)					
H(13-1)	0.234(4)	0.085(4)	0.788(4)	3.0(1.0)					
H(13-2)	0.301(4)	0.218(4)	0.748(3)	1.2(8)					
H(13-3)	0.279(4)	0.101(5)	0.666(4)	2.7(1.0)					

[a] Anisotropic temperature factors are in the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$ ($\times 10^5$ for Pd and Cl, $\times 10^4$ for O and C). For hydrogen atoms temperature factors are isotropic (B_j). [b] Numbers of hydrogens are the same as corresponding carbon atoms.

ed. To the filtrate cooled to room temperature 50 ml of ethyl ether and 140 ml of ethyl alcohol were added and the mixture was cooled by liquid nitrogen. The precipitate formed was filtered and dried (0.26 g). The filtrate was diluted with water and after 24 h an additional amount of the complex (0.19 g) was isolated. The total yield of pure product was 0.45 g (34%), m.p. 225—235°C (dec.).

Ia is a yellow crystalline solid almost insoluble in the majority of organic solvents. It dissolves only by heating in acetonitrile, dimethyl formamide and nitrobenzene, but is decomposed by dimethyl sulfoxide and amines. Found: C, 52.54; H, 3.31; Cl, 9.29; Pd, 27.22. $C_{34}H_{26}O_4Cl_2Pd_2$ calcd.: C, 52.20; H, 3.35; Cl, 9.06; Pd, 27.25%. IR spectrum: strong ν(CO) 1660 cm^{-1} (vaseline oil).

$[(\pi\text{-}C_{13}H_{21}O_2)PdCl]_2$ (Ib)

2.0 g of 2,6-di-t-butylpyrylium perchlorate and 1.4 g of finely-powdered $PdCl_2$ were boiled for 10 min in 120 ml ethyl alcohol with intense stirring. The dark brown solution was filtered while hot and the filtrate was cooled in the refrigerator. After 7 h the precipitate formed was filtered, washed with alcohol and ether and dried on the filter. The raw product (1.7 g) containing a mixture of pyrylium salt was dissolved in 30 ml of boiling nitromethane, cooled, filtered, washed and dried on the filter and then in vacuo.

Ib is a yellow crystalline powder, rapidly darkening above 185°C; m.p. 206°C (dec.). Yield 0.5 g (24%). Found: C, 44.63; H, 6.03; Cl, 10.45; Pd, 29.85. $C_{26}H_{42}O_4Cl_2Pd_2$ calcd.: C, 44.46; H, 6.03; Cl, 10.10; Pd, 30.30%. Molecular weight (by measurement of thermal effect of condensation in $CHCl_3$ at 30°C): found 685 ± 12, calcd. 702. IR spectrum: strong ν(CO) 1690 cm^{-1} (vaseline oil).

X-ray structural analysis of Ib. Monocrystals grown from ethyl alcohol are monoclinic, $a = 12.310(2)$, $b = 10.932(2)$, $c = 12.357(1)$ Å, $\gamma = 112.71(1)^\circ$, $D_m = 1.528$, $D_c = 1.543$ g cm^{-3}, $Z = 2$, space group $P2_1/b$. Intensities were measured with the automatic Hilger & Watts diffractometer (Mo radiation, graphite monochromator). ω-Scanning gave 2595 reflections with $F^2 > 3\sigma$ and $2\theta \leqslant 53^\circ$. The structure was solved by a heavy-atom method and refined by an anisotropic least squares technique; $R = 0.034$ with inclusion of hydrogen atoms (19 of 21 were located by difference synthesis). For data collection and structure solution we used the same experimental procedures and programmes as described in [9]; anisotropic refinement was performed with the programme described in [10]. Atomic coordinates and temperature factors are given in Table 1.

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