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SYNTHESIS AND STRUCTURE OF A σ-ALLYL CHELATE COMPLEX OF PALLADIUM(II)

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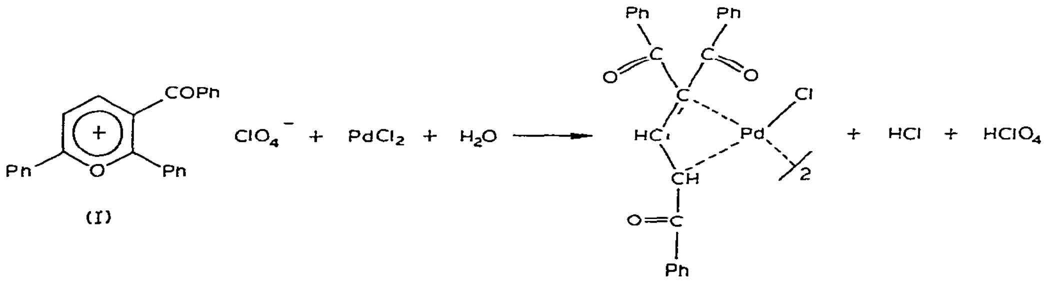
Summary

2,4,6-Triphenyl-3-benzoylpyrylium perchlorate is found to react with benzonitrilepalladium(II) to form *cis*-(1,3,3-tribenzoyl-2-phenyl-σ-allyl)palladium(II). The structure of the product is elucidated by X-ray analysis. Crystals are orthorhombic, *a* 9.720, *b* 21.295, *c* 22.312 Å, $Z = 4$, space group $P2_12_12_1$. The structure is refined with 2599 reflections to $R = 0.062$.

Earlier we reported on the synthesis of bis(acyl-π-allylpalladium) complexes from $PdCl_2$ and 2,6-disubstituted pyrylium salts [1]. The trisacyl-π-allyl ligand was also shown [2] to be formed from 2,6-diphenyl-3-benzoylpyrylium perchlorate (I) in similar conditions

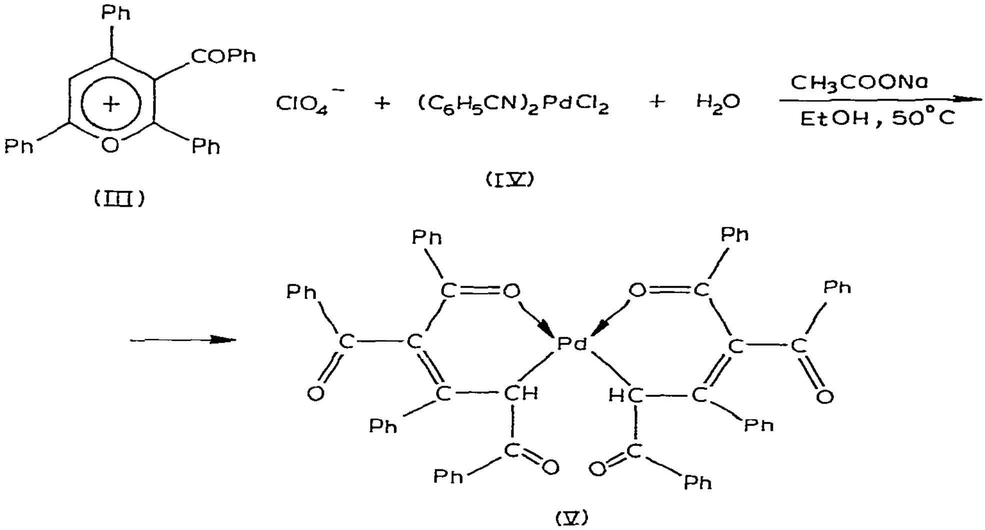


(I)

(II)

(1)

Further investigations showed that 2,4,6-triphenyl-3-benzoylpyrylium perchlorate (III) reacted with benzonitrilepalladium complex (IV) in ethanol in the presence of sodium acetate forming *cis*-(1,3,3-tribenzoyl-2-phenyl-σ-allyl)-palladium(II) (V).



(2)

The structure of V (Fig. 1) was established by an X-ray study. The Pd atom of V is σ-bonded with two carbon atoms and coordinated by two keto-oxygen atoms, thus having a square planar *cis* coordination with some tetrahedral distortion Indeed, O(1)PdC(4) and O(2)PdC(8) planes (Fig 1) make a dihedral

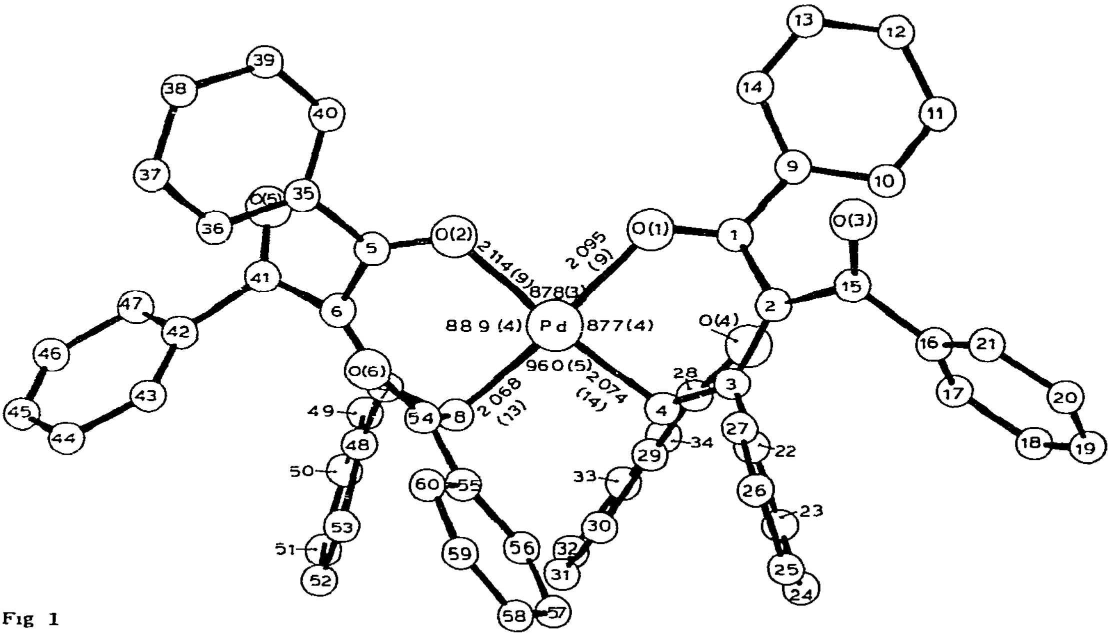
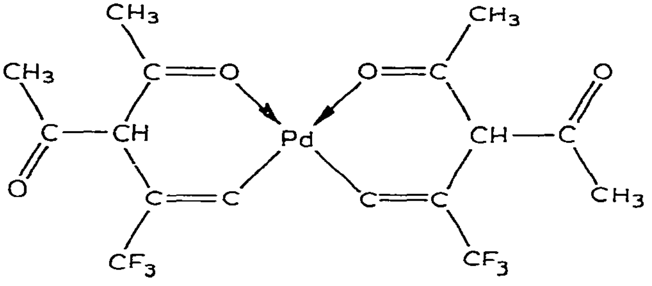


Fig 1

angle of 6.1° and displacements from the mean coordination plane of the Pd atom are equal to ±0 05 and ±0 11 Å for O and C atoms, respectively

A similar coordination of palladium was also found in the adduct of hexafluorobut-2-yne to bis(acetylacetonato)palladium (VI) [3]



(VI)

Pd—O bond lengths in V (av 2.104 Å) and VI (av 2 114 Å) as well as C=O distances (1 230 Å in V and VI) are essentially equal, but Pd—C bond lengths are somewhat different As can be expected, the Pd—C(sp^3) bond in V (2 071 Å) is longer than the Pd—C(sp^2) bond in VI (1.998 Å) but very similar to Pd—C(sp^3) bond lengths in *cis*-chloro(benzylacetoacetato)dipyridinepalladium (2 051(8) Å [4]) and acetylacetonato(acetylacetonyl)triphenylphosphinepalladium (2 11(1) Å [5])

C=O bond lengths in chelate rings of V are close to the standard values of a C=O distance in aldehydes and ketones (1 215 Å [6]) and to the average value of C=O bond lengths in benzoyl groups of V (1 217 Å) In cycles, C—C bonds are clearly alternating, viz , formally double and ordinary bonds have average lengths of 1.380 and 1.469 Å, respectively (see Table 1) The average length of exocyclic C—C bonds is 1.497 Å, that of benzene ring bonds is 1 402 Å The sp^3-hybridization of C(4) and C(8) is confirmed by bond angle values PdC(4)-

TABLE 1

THE MAIN BOND LENGHTS *d* AND BOND ANGLES *ω*

Atoms	*d* (Å)	Atoms	*ω* (deg)
Pd—O(1)	2 095(9)	O(1)—Pd—O(2)	87 8(3)
Pd—O(2)	2 114(9)	O(1)—Pd—C(4)	87 7(4)
Pd—C(4)	2 074(14)	O(2)—Pd—C(8)	88 9(4)
Pd—C(8)	2 068(13)	C(4)—Pd—C(8)	96 0(5)
O(1)—C(1)	1 245(15)	Pd—O(1)—C(1)	124 7(8)
O(2)—C(5)	1 215(15)	O(1)—C(1)—C(2)	121 4(1 1)
C(1)—C(2)	1 455(18)	C(1)—C(2)—C(3)	122 1(1 1)
C(2)—C(3)	1 381(18)	C(2)—C(3)—C(4)	122 9(1 1)
C(3)—C(4)	1 466(17)	C(3)—C(4)—Pd	104 5(9)
C(5)—C(6)	1 478(17)	Pd—O(2)—C(5)	123 0(8)
C(6)—C(7)	1 378(17)	O(2)—C(5)—C(6)	121 9(1 1)
C(7)—C(8)	1 478(17)	C(5)—C(6)—C(7)	121 0(1 1)
		C(6)—C(7)—C(8)	123 4(1 1)
		C(7)—C(8)—Pd	104 0(8)

TABLE 2

TORSIONAL ANGLES φ OF THE CHELATE CYCLES

Bond	φ (deg)	Bond	φ (deg)
Pd—O(1)	−22 7	Pd—O(2)	−18 7
O(1)—C(1)	−17 1	O(2)—C(5)	−23 7
C(1)—C(2)	31 0	C(5)—C(6)	36 7
C(2)—C(3)	16 2	C(6)—C(7)	14 5
C(3)—C(4)	−61 4	C(7)—C(8)	−60 4
C(4)—Pd	53 5	C(8)—Pd	52 4

C(3) 104 5°, PdC(4)C(28) 104.8°, C(3)C(4)C(28) 116.2°, PdC(8)C(7) 104.0°, PdC(8)C(54) 102.8°, C(7)C(8)C(54) 115 8°.

Both chelate cycles in V have the same configuration They are nonplanar (displacements of atoms from mean planes reach 0 5 Å) and their geometry does not correspond to any standard conformation [7]. However, best of all the cycles conformation can be described as a distorted twist boat Displacements of C(2) and C(4) from the PdO(1)C(1)C(3) plane (with its atomic deviations of 0 00, 0 02, −0 03 and 0 01 Å) are equal to 0 27 and −0 89 Å Similarly for displacements of C(6) and C(8) from the PdO(2)C(5)C(7) plane (0 00, −0.04, 0.07, −0 02 Å) the values are −0.29 and 0.88 Å. Torsional angles of these cycles are listed in Table 2.

Formation of a σ-allyl metallocycle occurs only with combination of an aryl substituent in position 4 and an acyl group in position 3 of a pyrylium cation

As was already mentioned (eq. 1) a cation with one acyl group and an unsubstituted γ-position gives rise to a ligand of the π-allyl type 2,4,6-Triphenylpyrylium perchlorate, i e. the salt with aryl in position 4 but without acyl in position 3 does not interact with $PdCl_2$ at all [2] $PdCl_2$ can be used in reaction instead of the benzonitrile complex (IV) but in this case the yield of the final product is decreased.

Complex V is quite stable under ambient conditions both in crystalline form and in solution ($CHCl_3$). The IR spectrum of V has strong bands in vibrational regions of carbonyl groups, aromatic rings and olefinic bonds 1650, 1620, 1596, 1590, 1580 and 1565 cm^{-1} (UR-20 apparatus, $CHCl_3$ solution)

An excess of triphenylphosphine in acetonitrile leads to a reductive substitution of chelate σ-allyl ligands with formation of tetrakis(triphenylphosphine)palladium(0).

Experimental

The starting pyrylium salt was synthesized according to the known technique [8]

(1) cis-(1,3,3-Tribenzoyl-2-phenyl-σ-allyl)palladium(II) (V)

A solution of 0 2 g (2 4 mmol) of sodium acetate in 2 ml of water was added under stirring to the suspension of 0 54 g (1 04 mmol) of 2,4,6-triphenyl-3-benzoylpyrylium perchlorate and 0 2 g (0 52 mmol) of palladium benzonitrile

TABLE 3

ATOMIC COORDINATES $(\times 10^4)$ AND TEMPERATURE FACTORS

Atom	x	y	z	B_{iso} (Å^2)	Atom	x	y	z	B_{iso} (Å^2)
Pd	4596(1)	4076(1)	3772(1)		C(28)	3203(14)	4097(7)	4902(6)	3 0(3)
O(1)	6099(9)	4440(4)	4348(4)		C(29)	2239(14)	3550(6)	4966(6)	2 8(3)
O(2)	6212(9)	3762(4)	3213(4)		C(30)	1100(16)	3439(7)	4586(6)	4 0(3)
O(3)	6200(10)	6237(4)	4589(4)		C(31)	288(18)	2912(6)	4667(6)	4 3(3)
O(4)	3984(10)	4231(4)	5294(4)		C(32)	577(20)	2492(7)	5124(7)	5 2(4)
O(5)	6725(10)	2076(4)	3054(4)		C(33)	1649(18)	2601(7)	5512(7)	4 9(4)
O(6)	4193(9)	3942(4)	2260(4)		C(34)	2462(16)	3148(6)	5431(7)	3 9(3)
C(1)	5924(13)	4895(6)	4690(6)	2 5(3)	C(35)	7060(14)	3280(6)	2341(6)	2 5(3)
C(2)	4780(14)	5228(5)	4610(5)	2 1(2)	C(36)	6651(16)	3022(6)	1791(6)	4 0(4)
C(3)	3535(13)	5138(5)	4373(6)	2 0(2)	C(37)	7615(16)	2992(7)	1306(8)	5 0(4)
C(4)	3129(14)	4476(6)	4329(6)	2 4(3)	C(38)	8981(16)	3194(6)	1418(6)	4 1(4)
C(5)	6084(13)	3332(6)	2860(6)	2 4(3)	C(39)	9339(17)	3462(7)	1956(7)	4 6(4)
C(6)	5024(12)	2841(5)	2937(5)	1 9(3)	C(40)	8400(17)	3500(7)	2422(7)	4 4(4)
C(7)	3741(14)	2985(6)	3161(6)	2 4(3)	C(41)	5597(17)	2185(6)	2869(5)	2 5(3)
C(8)	3211(14)	3634(6)	3208(6)	2 0(3)	C(42)	4759(15)	1683(5)	2549(5)	2 7(3)
C(9)	6972(14)	4978(6)	5163(6)	2 6(3)	C(43)	3782(15)	1824(6)	2103(6)	3 2(3)
C(10)	6634(15)	5267(6)	5708(6)	3 4(3)	C(44)	3142(16)	1331(7)	1787(7)	3 8(4)
C(11)	7635(16)	5294(6)	6157(8)	4 8(4)	C(45)	3504(18)	700(7)	1957(7)	4 9(4)
C(12)	8984(16)	5070(7)	6035(7)	4 6(4)	C(46)	4407(19)	549(7)	2368(7)	5 4(4)
C(13)	9286(18)	4768(7)	5522(7)	5 1(7)	C(47)	5120(15)	1051(6)	2705(6)	4 0(3)
C(14)	8281(16)	4720(6)	5082(7)	3 8(3)	C(48)	2718(13)	2490(5)	3347(5)	2 0(3)
C(15)	5074(12)	6010(6)	4741(5)	2 6(3)	C(49)	3156(14)	2039(6)	3785(7)	3 5(3)
C(16)	4035(14)	6385(6)	5098(6)	2 8(3)	C(50)	2158(18)	1582(7)	3954(7)	4 7(4)
C(17)	3156(14)	6096(6)	5490(6)	3 2(3)	C(51)	878(16)	1599(7)	3723(8)	5 3(4)
C(18)	2238(17)	6490(7)	5817(7)	4 4(4)	C(52)	460(19)	2039(7)	3294(6)	4 8(3)
C(19)	2240(17)	7128(7)	5725(7)	4 7(4)	C(53)	1385(16)	2516(7)	3118(7)	4 0(3)
C(20)	3121(17)	7416(7)	5334(7)	4 4(4)	C(54)	3294(13)	4022(6)	2646(6)	2 4(3)
C(21)	4051(15)	7054(6)	4992(6)	3 6(3)	C(55)	2187(14)	4508(6)	2532(6)	2 6(3)
C(22)	2548(14)	5593(6)	4144(6)	2 2(3)	C(56)	1093(15)	4608(6)	2932(6)	3 5(3)
C(23)	1198(16)	5590(6)	4341(6)	3 3(3)	C(57)	55(16)	5049(7)	2796(7)	4 6(4)
C(24)	239(16)	6029(6)	4133(6)	3 7(3)	C(58)	108(18)	5351(7)	2223(7)	5 8(4)
C(25)	599(18)	6445(6)	3679(7)	4 7(3)	C(59)	1204(20)	5273(8)	1835(8)	6 0(4)
C(26)	1968(16)	6448(7)	3452(7)	3 9(3)	C(60)	2295(18)	4842(8)	1967(8)	5 3(4)
C(27)	2925(13)	6021(6)	3688(6)	3 2(3)					

Anisotropic temperature factors in the form $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	2 32(4)	2 69(4)	2 96(4)	−0 09(5)	0 00(5)	−0 61(4)
O(1)	2 6(5)	2 2(4)	4 3(5)	0 5(4)	−0 5(4)	−1 9(4)
O(2)	3 4(5)	2 3(4)	2 9(4)	−0 6(4)	0 5(4)	−2 1(4)
O(3)	3 0(5)	3 0(4)	4 7(6)	−1 4(4)	0 2(4)	0 4(4)
O(4)	3 8(5)	3 7(5)	3 2(5)	−1 0(4)	−1 3(4)	−0 2(4)
O(5)	2 4(5)	4 0(5)	4 8(6)	1 2(4)	−0 4(4)	1 0(4)
O(6)	3 7(6)	4 0(5)	2 5(4)	0 6(4)	0 4(4)	1 1(4)

complex in 20 ml of ethanol Stirring was continued for 5 min at room temperature and then for 5 min at 50°C. The precipitate formed was filtered off, dried on filter, washed several times with $CHCl_3$ An orange filtrate was precipitated with ether. A bright-red precipitate was filtered off, washed with diethyl ether and dried. The yield of combined precipitate is 0 2 g (40%), darkens above 140° C, m p. 202—208° C (dec).

(2) X-ray structure determination

Crystals of V are orthorhombic, a 9 720(2), b 21.295(4), c 22.312(3) Å, V 4618(1) Å^3, D_c 1 42 g cm^{-3} for Z 4, space group $P2_12_12_1$. Intensities of 2599 independent reflections with $F^2 > 2\sigma$ were measured with a four-circle automated diffractometer Syntex $P2_1$ using Mo radiation with a graphite monochromator and $\theta/2\theta$ scanning in the region $2 \leqslant 2\theta \leqslant 44°$.

The structure is solved by a heavy atom method and refined by a full-matrix least squares technique taking into account an anisotropy of Pd and O atom thermal vibrations The final R value is 0 062 Positional and temperature factors are given in Table 3. Main bond lengths and angles are listed in Table 1. The molecular structure is shown in Fig 1

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