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Molecular Structure of *trans*-Chloro(η^1-phenyl)-bis(triphenylphosphine)platinum(II)

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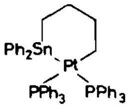
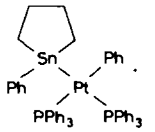
trans-*[PtCl(η^1-C_6H_5)(PPh_3)$_2$] crystallizes in the orthorhombic space group* Pbca *with the lattice constants* a = *1180.0(4),* b = *2370.5(2),* c = *2554.9(5) pm (Z = 8). The structure was solved by Patterson and Fourier methods and refined to a final value of R = 0.073 (R_w = 0.073). The crystal contains discrete molecules with square-planar arrangement of the ligands around the Pt atom. The P–Pt–P angle is slightly distorted due to steric repulsion. Important bond lengths and angles are: Pt–Cl = 240.8(5), Pt–P1 = 230.3(6), Pt–P2 = 229.7(6), Pt–C1 = 200(2) pm; P1–Pt–P2 = 176.0(2), Cl–Pt–C1 = 179.9(1)°.*

Introduction

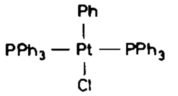
In the course of our studies on novel metallacycles with endocyclic tin–transition metal bonds we reported the attempted synthesis of the stannaplatinacyclohexane **I** from 1,1-diphenyl-1-stannacyclopentane and ethylene-bis(triphenylphosphine)platinum(0) [1]. In fact, the platinum moiety is inserted into the more polar tin–phenyl bond [2] to give the *cis*-bis(phosphine) complex **II** which slowly dissociates in solution reforming the parent stannacyclopentane. An additional decomposition product, the tin-free platinum compound **III**, was isolated and recrystallized from chloroform.



I



II



$$\mathrm{PPh_3 - \overset{\overset{\large Ph}{|}}{\underset{\underset{\large Cl}{|}}{Pt}} - PPh_3}$$

III

TABLE I. Crystal Data of *trans*-[Pt(Ph)Cl(PPh_3)$_2$] (**1**).

Formula	$C_{42}H_{35}ClP_2Pt$
Molecular weight	832.24
Space group	*P*bca, orthorhombic
Lattice constants	a = 1180.0(4) pm
	b = 2370.5(2) pm
	c = 2554.9(5) pm
	V = 7146.5 × 10^6 pm^3
	Z = 8
	ρ_x = 1.547 g/cm^3

III turned out to be identical with the known *trans*-[PtCl(Ph)(PPh_3)$_2$] (**1**) [3]. Evidence has been given that **1** can result from the acidic cleavage of *cis*-[PtPh(PPh_3)$_2$(Ph_2SnCl)] by impurities of hydrogen chloride present in solution. Controlled addition of HCl gives a mixture of **III** (30%) and its *cis*-isomer (55%) and some *cis*-[$PtCl_2$(PPh_3)$_2$] (15%) indicating a non-stereospecific reaction. However, no removal of the stannyl group was observed by thermal reaction of *trans*-[PtCl(PPh_3)$_2$($SnPh_3$)] or *cis*-[PtPh(PPh_3)$_2$($SnPh_3$)] [3], and different mechanisms may be involved in destannylation [4]. For definite proof and elucidation of the molecular structure of **1**, an X-ray analysis has been carried out which is described in this paper.

Experimental

A single crystal of size 0.06 × 0.16 × 0.42 mm^3 obtained from chloroform was used for the X-ray analysis. Precession photographs led to the orthorhombic space group *P*bca.

The cell dimensions were determined from 25 reflections at high diffraction angles and refined by least-squares methods (Table I). With the four-circle diffractometer CAD4 [5] and CuK_α-radiation (graphite monochromator) 8691 intensities in the range of θ = 5–56° were collected. 2575 unique reflections with $F \geqslant 2\sigma(F)$ have been used for subsequent calculations performed with SHELX-76 [6]. The structure was solved from Patterson and Fourier syntheses and refined using anisotropic temperature parameters for Pt, P and Cl. The phenyl rings were treated as

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TABLE II. Positional and Thermal Parameters $B_{eq} \times 10^4$ [pm^2]. $B_{eq} = 8/3\ \pi^2\ (U_{11} + U_{22} + U_{33})$. Estimated standard deviations in parentheses.

Atom	x	y	z	B_{eq}
Pt	0.4025(1)	0.3333(0)	0.3571(0)	2.81(4)
P1	0.3731(5)	0.4293(2)	0.3603(3)	3.9(3)
P2	0.4271(5)	0.2372(2)	0.3559(3)	3.9(3)
Cl	0.4097(6)	0.3343(3)	0.4513(2)	3.5(3)
C1	0.397(1)	0.3324(7)	0.2789(7)	1.6(7)
C2	0.488(1)	0.3534(7)	0.2503(7)	1.8(8)
C3	0.486(1)	0.3512(7)	0.1957(7)	2.0(9)
C4	0.392(1)	0.3298(7)	0.1698(7)	2.2(9)
C5	0.300(1)	0.3088(7)	0.1984(7)	2.0(9)
C6	0.303(1)	0.3101(7)	0.2530(7)	1.6(7)
C11	0.487(1)	0.4635(6)	0.3968(6)	1.1(6)
C12	0.472(1)	0.5141(6)	0.4239(6)	1.8(8)
C13	0.563(1)	0.5383(6)	0.4507(6)	1.8(8)
C14	0.668(1)	0.5120(6)	0.4505(6)	2.1(9)
C15	0.683(1)	0.4614(6)	0.4235(6)	2.1(9)
C16	0.593(1)	0.4372(6)	0.3967(6)	1.3(6)
C21	0.371(1)	0.4661(7)	0.2976(5)	1.1(6)
C22	0.460(1)	0.4999(7)	0.2804(5)	1.6(7)
C23	0.460(1)	0.5208(7)	0.2294(5)	1.7(8)
C24	0.371(1)	0.5079(7)	0.1955(5)	2.1(9)
C25	0.282(1)	0.4741(7)	0.2126(5)	1.6(7)
C26	0.282(1)	0.4532(7)	0.2636(5)	1.4(7)
C31	0.239(1)	0.4498(7)	0.3892(6)	1.2(6)
C32	0.195(1)	0.5039(7)	0.3818(6)	1.9(8)
C33	0.092(1)	0.5188(7)	0.4048(6)	2.1(8)
C34	0.033(1)	0.4797(7)	0.4351(6)	2.4(9)
C35	0.077(1)	0.4256(7)	0.4424(6)	1.9(6)
C36	0.180(1)	0.4107(7)	0.4195(6)	1.8(8)
C41	0.561(1)	0.2118(6)	0.3851(6)	1.1(6)
C42	0.596(1)	0.1569(6)	0.3739(6)	1.4(6)
C43	0.694(1)	0.1356(6)	0.3964(6)	1.8(8)
C44	0.759(1)	0.1691(6)	0.4302(6)	2.3(9)
C45	0.724(1)	0.2240(6)	0.4414(6)	2(1)
C46	0.625(1)	0.2454(6)	0.4189(6)	1.7(8)
C51	0.413(1)	0.1973(6)	0.2992(5)	1.2(6)
C52	0.496(1)	0.2965(6)	0.2612(5)	1.4(7)
C53	0.489(1)	0.1787(6)	0.2132(5)	2.1(8)
C54	0.400(1)	0.1419(6)	0.2031(5)	2.1(7)
C55	0.317(1)	0.1327(6)	0.2411(5)	2.1(9)
C56	0.323(1)	0.1604(6)	0.2892(5)	1.9(8)
C61	0.321(1)	0.2981(8)	0.4031(7)	1.5(7)
C62	0.219(1)	0.2276(8)	0.3978(7)	2.1(8)
C63	0.124(1)	0.2048(8)	0.4287(7)	3(1)
C64	0.149(1)	0.1625(8)	0.4648(7)	3(1)
C65	0.260(1)	0.1430(8)	0.4702(7)	3(1)
C66	0.346(1)	0.1659(8)	0.4393(7)	2.1(8)

rigid groups and restricted to their ideal geometry (C–C–C angle 120°, d(C–C) = 139.5 pm). The calculation led to a final R value of 0.073 ($R_w = 0.073$) when taking the calculated positions of the hydrogen atoms into account.

The positional and thermal parameters are given in Table II, bond lengths and angles in Table III.

TABLE III. Selected Bond Distances (pm) and Angles (°) of 1. Estimated standard deviations in parentheses.

Distances		Angles	
Pt–P1	230.3(6)	P1–Pt–P2	176.0(2)
Pt–P2	229.7(6)	Cl–Pt–C1	179.9(1)
Pt–Cl	240.8(5)	P1–Pt–C1	92.3(5)
Pt–C1	200(2)	P2–Pt–C1	91.4(5)
P1–C11	183(2)	Cl–Pt–P1	87.8(2)
P1–C21	182(2)	Cl–Pt–P2	88.5(2)
P1–C31	181(2)	C11–P1–C21	104.5(7)
P2–C41	181(2)	C11–P1–C31	108.3(7)
P2–C51	182(2)	C21–P1–C31	102.4(7)
P2–C61	181(2)	C41–P2–C51	102.1(7)
		C41–P2–C61	105.3(8)
		C51–P2–C61	104.9(8)

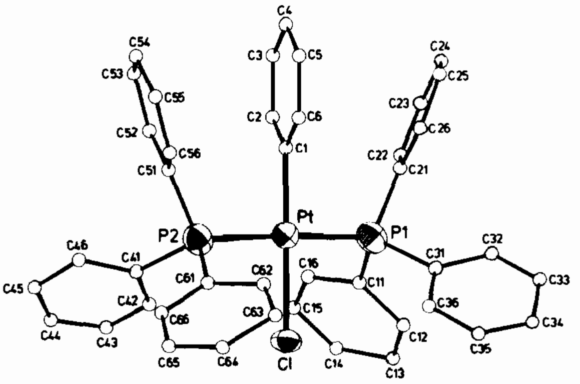

Fig. 1. Molecular structure of *trans*-[Pt(Ph)Cl(PPh$_3$)$_2$] (1).

Description of the Structure

The molecular geometry and atom numbering of the complex *trans*-[Pt(Ph)Cl(PPh$_3$)$_2$] are shown in Fig. 1.

The crystal structure of **1** is composed of discrete molecules which exhibit a square-planar coordination for the central Pt atom, the tertiary phosphine ligands occupying *trans* positions. The P–C bonds of the two phosphine ligands are approximately in an eclipsed arrangement (dihedral angles: P1–C21/Pt–C1 = 5.6°, Pt–C1/P2–C51 = 9.4°, P1–C21/P2–C51 = 14.9°). As a consequence of this conformation, the three phenyl rings C1–C6 (A), C21–C26 (B) and C51–C56 (C) adopt the minimal van der Waals distance to each other (central distances A–B 346 pm, A–C 353 pm). The repulsion of their π-systems results in a slight distortion of the P1–Pt–P2 angle to 176°.

The Pt–P bond lengths (Table II) are equal within experimental errors and consistent with the values found in *trans*-[Pt(CH$_3$)Cl(PPh$_2$CH$_3$)$_2$] [7] and *trans*-[Pt(CH$_3$)Cl(PPh$_3$)$_2$] [8]. In other complexes of this type, Pt–P distances range from 227 to 237 pm [7, 9–11]. The Pt–Cl bond length is in the range of the expected value [7, 8], while the Pt–C bond is significantly shortened in comparison to σ-alkyl–Pt complexes [7, 8] due to the sp^2 hybridized phenyl carbon. A short Pt–C distance of the same order is also reported for *trans*-[$Pt(C_2F_5)Cl(PPh_2CH_3)_2$] [7]; in this case, an influence of the electronegativity of the C_2F_5 ligand is proposed. The P–C bond lengths and angles at the P atoms do not show any irregularities, the values are close to those observed in other Pt(II) complexes with tertiary phosphine ligands [10].

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