Metal Complexes of Heteroarenes, X [1]. η^1-Coordination of Phosphinine: Synthesis and Structure of *cis*-Dichloro-bis(2,6-dimethyl-4-phenyl-phosphinine)platinum

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Phosphinine Complex, Platinum, X-Ray Data, NMR Data, *trans*-Influence

Cis-Dichloro-bis(2,6-dimethyl-4-phenyl-η^1-phosphinine)platinum (**3**) has been prepared by ligand substitution from *cis* -dichloro(2,5-cyclooctadiene)platinum and characterized by spectroscopy (^{1}H, ^{13}C, ^{31}P NMR, IR, UV-Vis), CV and X-ray diffraction (space group $P2_1/c$, a = 14.998, b = 16.540, c = 11.506 Å, $\alpha = \gamma = 90°$, $\beta = 92.46°$, Z = 4). In line with findings for similar P hybridization states, the Pt-P bond length (221 pm) in **3** equals that in η^1-phosphaalkene Pt complexes and falls short of the respective parameters in Pt phosphane species. The stretching frequencies ν_{PtCl} and the bond length Pt-Cl indicate that phosphinines and phosphaalkenes, relative to phosphanes, adopt a lower position on the *trans*-influence scale. This gradation is also suggested by the coupling constants $^1J(^{195}\mathrm{Pt},^{31}\mathrm{P})$.

Introduction

Pyridine- and phosphane complexes of Pt(II), $(Py)_2PtX_2$ and $(R_3P)_2PtX_2$, respectively, are among the most extensively studied classes of coordination compounds; reference [2] provides access to the voluminous literature in this area. Our concern with the ligating properties of the heavier heteroarenes of group 15, C_5H_5E (E = P, As, Sb) in general [3] and their role in square planar M(d^8) complexes of the late transition metals in particular [4] initiated our preparation of the first fully characterized representative in the class [*cis*-(phosphinine)$_2$PtX$_2$] which forms the subject of this Note [5]. Obvious aims include the description of structural features and, connected with this, a placement of phosphinines on the *trans*-influence scale. The current state of phosphinine transition-metal chemistry has been delineated by Mathey *et al.* [6].

Results and Discussion

Following a well established general procedure [7], the complex **3** was prepared via substitution of 1,5-cyclooctadiene in **1** for the phosphinine **2** (eq. (1)). The choice of this phosphinine derivative was suggested by the higher stability and superior solubility of the complexes emerging from this synthesis.

cis-Dichloro-bis-(2,6-dimethyl-4-phenyl-η^1-phosphinine)platinum (**3**) is obtained as rod shaped yellow crystals which readily dissolve in halocarbon solvents. As opposed to the free ligand **2**, the complex **3** is only slightly air-sensitive in solution and air-stable in the solid state. **3** cannot be sublimed and fails to yield a molecular ion peak in the mass spectrum. As inferred from cyclic voltammetry, there are no accessible stable oxidation states of **3** apart from Pt(II): in the potential range -2.9 V < E < +1.6 V (DME / 0.1 M n-Bu$_4$NClO$_4$, -40°C), only one irreversible wave [E_{pc}(0/-) = -1.07 V] is observed.

The structure of **3** as determined by X-ray diffraction (Table I, [8]) is depicted in Fig. 1 where a stereoplot of the unit cell is also given; bond lengths and angles are collected in Table II with the parameters for the free ligand **2** [9] provided for comparison. The square-planar arrangement within the PtP_2Cl_2 frame is somewhat distorted in that angles P-Pt-Cl (*trans*) fall short of 180° . The angle Cl-Pt-Cl (*cis*) is smaller than 90°. The dihedral angle between the phosphinine- and the P_2PtCl_2 coordination planes amounts to 59.7 and 51.0°, respectively, placing the *ortho*-methyl groups of the ligands in positions where they can protect the complex against nucleo-

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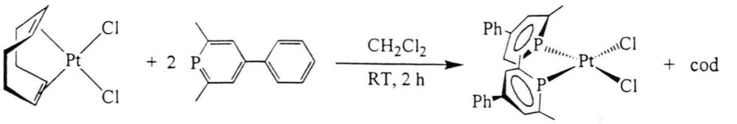

(1)

Table I. Crystal and refinement data for the structure determination of 3.

Habitus, colour	Block, yellow
Crystal size	0.30 × 0.25 × 0.20 mm
Crystal system	Monoclinic
Space group	$P2_1/c$, Z= 4
Unit cell dimensions	a = 14.9985(10) Å b = 16.5396(7) Å c = 11.5064(7) Å β= 92.466(6)°
Volume	2851.7(3) Å^3
Cell refinement	5000 selected reflections
Chemical formula	$C_{27}H_{28}Cl_4P_2Pt$
Formula weight	751.32
F(000)	1464
Density (calculated)	1.750 Mg/m^3
Absorption coefficient	5.423 mm^{-1}
Diffraktometer type	Stoe IPDS
Wavelength	MoKα(71.073 pm)
Temperature	193(2) K
θ-Range for data coll.	2.16 - 25.92°
Index ranges	h : -18/18 k: -20/20 l : -14/14
Data collection software	Stoe Expose
Cell refinement software	Stoe Cell
Data reduction software	Stoe Integrate
Reflections collected	24543
Independent reflections	5531 [R(int) = 0.0717]
Observed reflections	4353 [$I > 2\sigma(I)$]
Refl. used for refinement	5531
Absorption correction	Numerical (SHELXTL)
Max. and min. Transmiss.	0.4102, 0.2930
Solution	Direct methods
Refinement	Full-matrix refinement at F^2
Treatm. of hydrogen atoms	Calculated positions, fixed isotr. U's
Largest diff. peak and hole	1.083 and -0.854 $*10^{30}$ e/m^3
Programs used	SHELXS-97 (Sheldrick, 1997), SHELXL-97 (Sheldrick, 1997), SHELXTL
Data / parameters	5531 / 311
Weighting scheme	$1/[\sigma^2(F_o^2)+(0.0293P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Goodness-of-fit on F^2	0.917
R index (all data, F^2)	wR_2 = 0.0584
R index conventional [$I > 2\sigma(I)$]	R = 0.0276

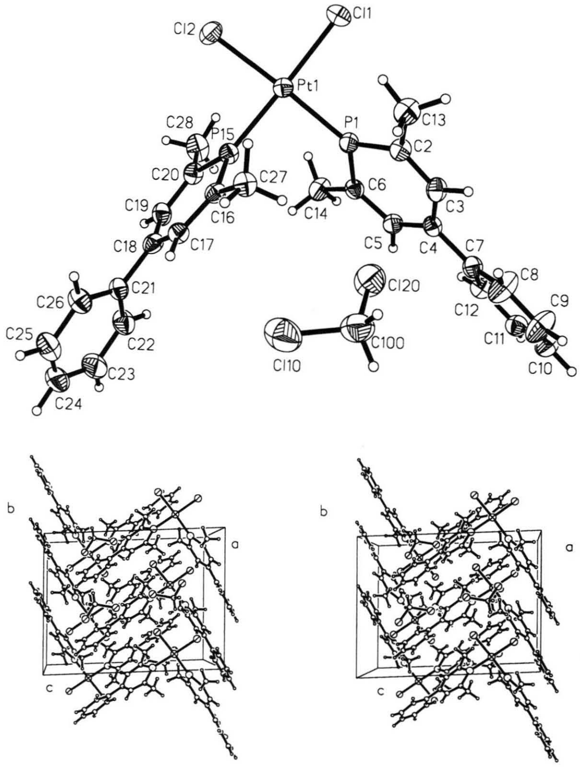

Fig. 1. Structure of **3** in the crystal; top: SHELXTL plot, the ellipsoids are drawn at the 50 % level; bottom: stereoview of the unit cell.

philic attack from an axial direction. A discussion of the Pt-P and Pt-Cl bond lengths benefits from a comparison with the respective parameters in **4** [10], **5** [11] and **6** [12] (Fig. 2).

The Pt-P distances in **3** lie between those for **4** and **5** whereas the Pt-Cl distances in **3** are shorter than in **4** and **5**. The inference of a π-acceptor strength of phosphinine approaching that of the trisorganophosphite ligand $(MeO)_3P$ from the Pt-P bond lengths data alone is flawed, however, since differing hybridization states of phosphorus in phosphanes ($\approx$ sp^3) and phosphinines ($\approx$ sp^2) must be taken into account, the latter leading to Pt-P bond shortening,

Table II. Selected bond lengths (pm) and bond angles (°) of the ligand **2** and the complex **3**.

	2	**3**		**2**	**3**
Pt1 - Cl1		234.62(11)	Cl1 - Pt1 - Cl2		91.88(4)
Pt1 - Cl2		233.84(10)	Cl1 - Pt1 - P1		91.04(4)
Pt1 - P1		222.00(10)	Cl2 - Pt1 -P15		86.37(4)
Pt1 - P15		220.91(11)	P1 - Pt1 - P15		90.80(4)
P1 - C2	174.8(5)	171.9(4)	P1 - Pt1 - Cl2		176.51(4)
P1 - C6	173.6(5)	171.2(4)	P15 - Pt1 - Cl1		176.87(4)
C2 - C3	138.7(7)	138.2(6)	C6 - P1 - C2	102.4(2)	107.71(19)
C3 - C4	139.4(7)	140.0(6)	P1 - C2 - C3	122.9(4)	118.7(3)
C4 - C5	138.7(7)	139.0(5)	C2 - C3 - C4	124.7(5)	126.9(4)
C5 - C6	138.2(7)	138.7(5)	C3 - C4 - C5	121.7(4)	120.7(4)
C2 - C13	150.7(8)	150.7(5)	C4 - C5 - C6	125.4(5)	126.7(4)
C6 - C14	151.1(8)	150.1(5)	C5 - C6 - P1	122.9(4)	119.1(3)
C4 - C7	149.3(7)	148.7(5)	P1 - C2 - C13	116.7(4)	120.1(3)
			P1 - C6 - C14	117.5(4)	119.8(3)

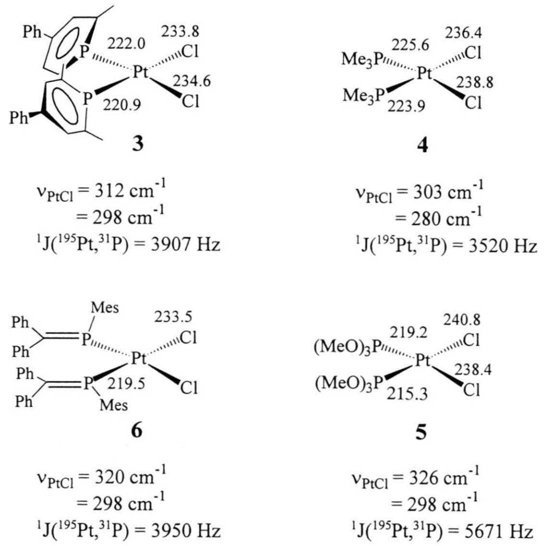

Fig. 2. Structural and spectroscopic parameters for **3** and the related molecules **4** - **6** relevant to the *trans*-influence gradation.

Tab. III. ^{1}H, ^{13}C, and ^{31}P NMR data for the ligand **2** and the complex **3**, solvent: CD_2Cl_2, δ (ppm), J (Hz).

	2	**3**
δH-3,5($\Delta\delta$)[a]	7,75	7.94(0.19)
$^3J(^{31}P,^1H)$	6.9	27.5[b]
δH-7,8($\Delta\delta$)	2.74	2.74(0.0)
$^3J(^{31}P,^1H)$	15.0	22.6[b]
δH-10,14($\Delta\delta$)	7.60	7.53(-0.7)
$^3J(^1H,^1H)$	7.5	7.2
δH-11,13($\Delta\delta$)	7.47	7.47(0.0)
$^3J(^1H,^1H)$	7.4	7.7
δH-12($\Delta\delta$)	7.39	7.41(0.02)
δP($\Delta\delta$)	194.1	128.4(-65.7)
$^1J(^{195}Pt,^{31}P)$		3907.4
δC-2,6($\Delta\delta$)	168.5	150.4(-18.1)
$^1J(^{31}P,^{13}C)$	49.9	27.8
$^3J(^{31}P,^{13}C)$		20.1
δC-3,5($\Delta\delta$)	132.1	137.5(5.4)
$^1J(^{13}C,^1H)$	154.3	n.r.
$^2J(^{31}P,^{13}C)$	13.3	6.3
δC-4($\Delta\delta$)	143.3	141.3(-2.0)
$^3J(^{31}P,^{13}C)$	15.6	15.1
δC-7,8($\Delta\delta$)	24.6	21.6(-3.0)
$^3J(^{31}P,^{13}C)$	6.8	7.0
δC-9($\Delta\delta$)	142.2	139.9(-2.3)
δC-10,14($\Delta\delta$)	128.8	128.5(-0.3)
δC-11,13($\Delta\delta$)	127.6	126.8(-0.8)
δC-12($\Delta\delta$)	127.6	127.8(0.2)

[a] $\Delta\delta = \delta$(complex) - δ(ligand); [b] filled-in doublet.

reflecting the inherently smaller covalent radius for P(sp^2). Not surprisingly, the distance Pt-P in **3** matches that for Pt-P (phosphaalkene) in **6** where the ligand, as in **3**, possesses two-coordinate phosphorus. Yet, the significantly shortened Pt-Cl distances in **3** attest to a pronounced π-acceptor character of η^1-phosphinine [13] which favors multiple bonding between Pt and Cl, effected by Pt $\leftarrow$ Cl π-donation. The most notable change which the ligand **2** experiences upon coordination in **3** is the increase of the C6-P-C2 bond angle by 5.3° with attendant decrease of the P-C2-C3 angle by 4°. These changes are in the direction toward the ideal benzene structure. They include partial rehybridization which provides the P lone pair with higher 3p content, resulting in enhanced M-P bonding. The small but significant shortening of the P-C2 resp. P-C6 bond lengths is probably an outcome of two countervailing effects:

P-C bond shortening caused by the build up of positive partial charge on P as a result of the P → M σ-donor contribution and the population of the intraligand antibonding MO $b_1(\pi^*)$ effected by P ← M π-backbonding.

Spectral features which have served to place a specific ligand L on the *trans*-influence scale [14] include the stretching frequency ν_{PtX}, observed in complexes of the type *cis*-L_2PtX_2, and the scalar coupling $^1J(^{195}Pt,^{31}P)$. In Fig. 2, the relevant data for complex **3** are compared with those of related compounds. Based on the IR and NMR criteria, the *trans*-influence of the phosphinine in **3** mimicks that of phosphaalkene in **6** and is smaller than in **4** and **5;** the agreement of the Pt-Cl bond lengths in **3** and **6** further illustrates this kinship. Close resemblance is also exhibited by the values of $^1J(^{195}Pt,^{31}P)$ for **3** and **6** (Table III). According to ref. [15], this would imply similar s-orbital contributions to the Pt-P bonds in **3** and **6**. Somewhat disturbingly, however, $^1J(^{195}Pt,^{31}P)$ for complex **5**, in which the s-character of the P lone pair at the ligand $P(OMe)_3$ should be lower than in a phosphaalkene or phosphinine, is particularly large. Apparently, the electronegativity of the substituents at a phosphorus ligand and the positive partial charge they generate on the ligating atom also exert an influence on $^1J(^{195}Pt, P)$ [12]. In view of these uncertainties, the dubious exercise of apportioning the overall *trans*-influence of phosphinine into σ- and π-components will not be attempted here.

Experimental Section

All manipulations were carried out under nitrogen protection, solvents were dried and saturated with nitrogen by standard procedures. Instrumental analysis was performed with equipment listed previously [1]. 2,6-Dimethyl-4-phenyl-phosphinine (**2**) was prepared via the Märkl route [16], *cis*-dichloro-(2,5-cyclooctadiene)platinum (**1**) is a commercial product.

cis-Dichloro-bis(2,6-dimethyl-4-phenyl-η^1-phosphinine)platinum (**3**)

To a solution of 202 mg (0.54 mmol) of *cis*-dichloro-(2,5-cyclooctadiene)platinum (**1**) in 30 ml of methylene chloride are added during 15 min at r.t. 16 mg (1.08 mmol) of 2,6-dimethyl-4-phenyl-phosphinine (**2**), dissolved in 20 ml of methylene chloride. After stirring for 2 h and reduction to a volume of 3 ml the pale yellow solution is filtered and layered with 15 ml of benzene. Within one week at room temperature**3** · CH_2Cl_2 is obtained as light yellow cubes. Yield: 284 mg (71%).

$C_{26}H_{26}Cl_2P_2Pt \cdot CH_2Cl_2$ (751.36)
Calcd C 46.86 H 4.93 %,
Found C 45.93 H 4.70 %.

IR (4000-500 cm^{-1} KBr pellet, 500-100 cm^{-1} Nujol): 3044 s, 2974 s, 2914 s, 1960 m, 1811 w, 1600 w, 1576 w, 1490 m, 1437 m, 1373 m, 1283 w, 1266 m, 1171 w, 1131 vw, 1078 w, 1027 vw, 971 vw, 887 w, 847 vw, 765 s, 739 vs, 731 vs, 700 vs, 646 w, 529 vw, 448 w, 251 vw, 312 vw, 298 vw.

UV-vis (CH_2Cl_2): λ_{max} = 304 nm, E = 36800 [$lmol^{-1}cm$]. MS (EI, 70 eV): *m/z* = 200 (100, $\mathbf{2}^+$), 185 (33, $\mathbf{2}^+$-CH_3). NMR data: see Table III.

Acknowledgements

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