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Methylplatinum(II) complexes containing 2-(diphenylphosphino)pyridine (Ph₂Ppy). Crystal and molecular structure of [PtMe(η^2 -Ph₂Ppy)(Ph₂Ppy)][BPh₄]

Vimal K. Jain *

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)

V.S. Jakkal

Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)

and Rakesh Bohra

Department of Chemistry, University of Rajasthan, Jaipur 302004 (India) (Received August 8th, 1989; in revised form October 16th, 1989)

Abstract

The reaction of [PtMeX(COD)] with 2-(diphenylphosphino)pyridine (Ph₂Ppy) in 1:2 stoichiometry yields [PtMeX(Ph₂Ppy)₂] (X = Me, Ia; Cl, Ib; or I, Ic). Reaction of [PtMeCl(COD)] with one equivalent of Ph₂Ppy gives the dinuclear complex [PtMeCl(Ph₂Ppy)]₂ (II). Several reactions of Ib have been studied. Treatment of Ib with NaY gives the cationic complexes [PtMe(η^2 -Ph₂Ppy)(Ph₂Ppy)][Y] (Y = BPh₄, Id or BF₄, Ie). The crystals of Id are triclinic, space group $P\overline{1}$ with two molecules in a unit cell of dimensions a 10.006(6), b 14.240(8), c 18.368(6) Å, a 80.93(4), β 74.60(3), γ 89.23(5)°. The platinum atom has square planar geometry. The phosphorus atom of the chelated phosphine is *trans* to the methyl group

Introduction

2-(Diphenylphosphino)pyridine (Ph_2Ppy) ** has been used recently to synthesise a variety of homo- and hetero-binuclear complexes in which the phosphine acts as a bridging ligand [1-4]. The phosphine initially binds to the metal atom through

^{*} Author to whom all correspondence should be addressed

^{**} Abbreviations: Ph₂Ppy, 2-(diphenylphosphino)pyridine; COD, 1,5-cyclooctadiene; dppm, bis(diphenylphosphino)methanc; dba, dibenzylidencacetone.

the phosphorus atom to give a mononuclear complex, which on subsequent treatment with another metal complex, gives a binuclear product. Such complexes are usually rigid, unlike their often fluxional dppm analogues, and thus they show markedly different reactivity [5–7]. Recently the chemistry of organoplatinum(II) with the dppm ligand has received much attention [5,6]; however, the chemistry of complexes containing the Ph₂Ppy ligand has received little attention. In the present work, we have synthesized a number of methylplatinum(II) complexes containing Ph₂Ppy and describe some of their reactions.

Results and discussion

Reaction of [PtMeX(COD)] (X = Me, Cl, I) with 2-(diphenylphosphino)pyridine (Ph₂Ppy) in 1:2 stoichiometry in dichloromethane afforded the mononuclear complexes [PtMeX(Ph₂Ppy)₂] (X = Me, Ia; Cl, Ib or I, Ic). The ¹H and ³¹P{¹H} NMR spectral data for Ia are consistent with a *cis* configuration. The Pt-Me protons appeared as a quartet with platinum satellites on either side. Since the ¹H NMR spectrum is complex in the Pt-Me region owing to an AA'MX₃X'₃ spin system, we have not calculated *cis* and *trans* ³J(Pt-H) couplings. The ¹H and ³¹P NMR spectra of Ia were similar to those reported for the symmetrical dimethyl platinum complexes, *cis*-[PtMe₂(PR₁)₂] [8,9].

The platinum methyl resonance for Ib and Ic displayed a triplet pattern, because of coupling with the two equivalent ³¹P nuclei, with platinum satellites. In the ³¹P NMR spectra a single line with platinum satellites was observed with ¹J(Pt-P) similar to that observed for *trans*-[PtMeCl(PR₃)₂] complexes [9-11]. Thus we assigned the *trans* configuration to Ib and Ic. At room temperature we could not detect the formation of any cationic species such as those observed for [PtX₂(Ph₂Ppy)₂] (X = C or I) [4].

The reaction of [PtMeCl(COD)] with one equivalent of 2-(diphenylphosphino)pyridine afforded an off-white complex II. This compound is insoluble in common organic solvents, and so no NMR data are available. However, microanalytical data established the formation of [PtMeCl(Ph₂Ppy)] which is possibly dimeric, like [Pt₂Cl₂Me₂(μ -dppm)₂)] [12]. The IR spectrum of the complex II shows a band at 285 cm⁻¹ attributable to ν (Pt-Cl) [3]. A similar reaction between [PtPhCl(COD)] and bulky phosphine ligands such as tricyclohexylphosphine in a 1:1 stoichiometry gives exclusively the dinuclear complex [Pt₂Ph₂(μ -Cl)₂(PR₃)₂] [13], for which two Pt-Cl stretchings in the region 250-300 cm⁻¹ have been reported [14].

The reaction of Ib with one equivalent of NaY in a methanol/dichloromethane mixture yielded the cationic complexes $[PtMe(\eta^2-Ph_2Ppy)(Ph_2Ppy)][Y]$ (Y = BPh₄, Id; BF₄, Ie). The ¹H NMR spectrum of Id shows a doublet for the Pt-Me protons which is further split into a doublet of smaller couplings. The *cis* and *trans* ³*J*(P-Pt-C-H) couplings have been clearly resolved; the *cis* couplings are smaller (2.3 Hz) than the *trans* (7.9 Hz). The ³¹P NMR spectrum of the cation, Id or Ie, consists of two resonances each with platinum satellites (Table 1). The smaller coupling ²*J*(P-Pt-P) 12 Hz, indicates a *cis* disposition of phosphine ligands. The *trans* ²*J*(P-Pt-P) coupling is usually large – a few hundred hertz – whereas the *cis* couplings are small [9]. ²*J*(P-Pt-P) coupling has not been observed for the complex [PtCl(η^2 -Ph_2Ppy)(Ph_2Ppy)]⁺ [8]. Of the two ³¹P NMR resonances, the one at lower

rnysical, analytical, H and $P\{H_{j}$	} NMK spe	ctra data for methylpla	ttinum(II) complexes contair	iing 2-(diphenylphosl	ohino)pyridine			
Complex	¹ H NMR	(mdg)	³¹ P NMR (ppm)	Recrystallisation solvent, yield (%)	ш.р. (°С)	Analysis Found (C	Calcd.) (%	
	Pt-Me		Pt-P			ပ ပ	H	z
Ph ₂ Ppy			- 3.95					
cis-[PtMe ₂ (Ph ₂ Ppy) ₂]	0.44	² J(Pt-H) 69.5 Hz	27.3 ¹ J(Pt-P) 1875 Hz	benzene/hexane	198-200	57.85	4.54	3.71
(1 a)				83		(57.52)	(4.56)	(3.73)
trans-[PtMeCl(Ph ₂ Ppy) ₂]	-0.11	² J(Pt-H) 80 Hz;	22.0 ¹ J(Pt-P) 3157 Hz	dichloromethane,	258-260	55.01	3.74	3.75
(P)		J(P-H) 6.3 Hz		80		(54.44)	(4.05)	(3.63)
trans-[PtMeI(Ph2 Ppy)2]	0.06	2 <i>J</i> (Pt-H) 77 Hz;	25.9 ¹ J(Pt-P) 3091 Hz	Benzene/hexane	253-258 (dec.	47.94	3.82	3.63
(I c)		J(P-H) 7 Hz		78	with melting)	(48.68)	(3.62)	(3.24)
[PtMeCl(Ph2Ppy)]2	insoluble			Dichloromethane,	190-200 (dec.)	42.36	3.33	2.95
(II)				74		(42.49)	(3.37)	(2.75)
[PtMe(n ² -Ph ₂ Ppy)(Ph ₂ Ppy][BPh ₄]	0.00	² J(Pt-H) 61 Hz;	-17.6 ¹ $J(Pt-P)$ 1391 Hz	CH ₂ Cl ₂ /hexane,	184–186	66.88	4.76	2.30
(PI)		2 J(P-H) _{cis} 2.3 Hz;	² J(P–P) 12 Hz	66		(67.11)	(4.87)	(2.65)
		³ J(P-H) _{trans} 7.9 Hz	19.2 ¹ J(Pt-P) 4226 Hz					
			² J(P-P) 12 Hz					
$[PtMe(\pi^{2}-Ph_{2}Ppy)(Ph_{2}Ppy)][BF_{4}]^{a}$			-17.6 J(Pt-P) 1396 Hz	Acetone/hexane,	204-205	50.85	3.96	3.21
(I e)			² J(P-P) 12 Hz	70		(51.05)	(3.79)	(3.40)
			19.0 ¹ J(Pt-P) 4228 Hz					,
			² J(P-P) 12 Hz					
trans-[PtMe(SnCl ₃)(Ph ₂ Ppy) ₂]	0.75	² J(Pt-H) 75 Hz;	61.7 ¹ J(Pt-P) 3060 Hz					
(JI)		J(P-H) 7 Hz	J(Sn-P) 217 Hz					
^a Contains small impurities of [PtCl((η ² -Ph ₂ Ppy)	(Ph ₂ Ppy)] ⁺				ł		

: í. Physical analytical ¹U and ³¹D(¹U) MMD

Table 1

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Fig. 1. PLUTO drawing of the molecule [PtMe(η^2 -Ph₂Ppy)(Ph₂Ppy)][BPh₄].

frequency (δ -17.6 ppm) with a smaller ¹J(Pt-P) is assigned to the phosphorus *trans* to the methyl group. The other resonance at higher frequency (δ 19.2 ppm) with ¹J(Pt-P) 4226 Hz is assigned to the phosphine ligand *trans* to the chelated nitrogen of the pyridine ring. The ¹J(Pt-P) (1391 Hz) for the phosphorus *trans* to the methyl group is much smaller than the values reported for platinum(II) complexes of the type *cis*-[PtMe₂(PR₃)₂] and *cis*-[PtMeX(PR₃)₂] in which the phosphine ligand is *trans* to methyl group. The lower value of ¹J(Pt-P) indicates a longer Pt-P distance (see later) probably because of the strong *trans* influence of the methyl group and strain in the four-membered chelate ring. The two different Pt-P bonds in [PtCl(η^2 -Ph₂Ppy)(Ph₂Ppy)]⁺, however, have the same length [3].

Complex Id crystallized as a single cation $[PtMe(\eta^2-Ph_2Ppy)(Ph_2Ppy)]^+$ and a single anion $[BPh_4]^-$ in the asymmetric unit. The crystal of the complex contains discrete molecular units separated by normal Van der Waals distances. A PLUTO drawing [15] of the molecule with the numbering scheme is shown in Fig. 1. The cation $[PtMe(\eta^2-Ph_2Ppy)(Ph_2Ppy)]^+$ consists of discrete monomeric molecules in a square-planar geometry around the central platinum atom. One phosphine ligand forms a four-membered chelate ring through the phosphorus and the pyridyl nitrogen, the other bonds through the phosphorus atom only. The two phosphines are mutually *cis* and the methyl group is *trans* to the phosphorus of the chelating phosphine ligand. The atoms in the coordination sphere around the platinum form a

Table 2

Selected bond distances (Å) and angles (°) with e.s.d.'s for $[PtMe(\eta^2-Ph_2Ppy)(Ph_2Ppy)][BPh_4]$

Pt(1)-P(1)	2.325(5)	P(2)-C(31)	1.78(2)
Pt(1)-P(2)	2.207(5)	N(1)-C(2)	1.32(2)
Pt(1)-N(1)	2.07(2)	N(1)-C(6)	1.39(3)
Pt(1)C(1)	2.05(2)	N(2)-C(31)	1.45(3)
P(1)-C(6)	1.81(2)	N(2)-C(32)	1.33(3)
P(1)-C(7)	1.82(2)	B(1)-C(36)	1.64(2)
P(1)C(13)	1.78(2)	B(1)-C(42)	1.65(3)
P(2)-C(19)	1.84(2)	B(1)-C(48)	1.63(3)
P(2)-C(25)	1.85(2)	B(1)-C(54)	1.69(3)
P(1)-Pt(1)-P(2)	106.3(2)	P(1)-C(13)-C(14)	122(1)
P(1)-Pt(1)-N(1)	70.4(5)	P(1)-C(13)-C(18)	120(1)
P(1)-Pt(1)-C(1)	161.0(6)	C(6) - P(1) - C(13)	104(1)
P(2)-Pt(1)-N(1)	176.5(4)	Pt(1)-N(1)-C(2)	138(2)
P(2)-Pt(1)-C(1)	92.6(6)	Pt(1) - N(1) - C(6)	103(1)
N(1)-Pt(1)-C(1)	90.6(8)	C(2)-N(1)-C(6)	119(2)
Pt(1) - P(1) - C(6)	82.1(6)	N(1)-C(2)-C(3)	122(2)
Pt(1)-P(1)-C(7)	122.4(7)	N(1)-C(6)-C(5)	121(2)
Pt(1)-P(1)-C(13)	125.8(6)	P(2)-C(25)-C(26)	117(2)
C(6) - P(1) - C(7)	105.4(8)	P(2)-C(25)-C(30)	121(2)
C(7) - P(1) - C(13)	108.1(8)	P(2)-C(31)-N(2)	119(2)
Pt(1)-P(2)-C(19)	114.8(6)	P(2)-C(31)-C(35)	125(1)
Pt(1) - P(2) - C(25)	112.7(6)	C(31)-N(2)-C(32)	120(2)
Pt(1)-P(2)-C(31)	114.2(7)	N(2)-C(31)-C(35)	116(2)
C(19)-P(2)-C(25)	103.6(9)	N(2)-C(32)-C(33)	124(2)
C(19)-P(2)-C(31)	102.5(8)	C(36)-B(1)-C(42)	108(2)
C(25)-P(2)-C(31)	107.9(9)	C(36)-B(1)-C(48)	113(2)
P(1)-C(6)-N(1)	104(1)	C(36)-B(1)-C(54)	107(2)
P(1)-C(6)-C(5)	135(2)	C(42)-B(1)-C(48)	111(2)
P(1)-C(7)-C(8)	121(1)	C(42)-B(1)-C(54)	108(2)
P(1)-C(7)-C(12)	120(2)	C(48)-B(1)-C(54)	109(2)

(C-C) _{av}	for	aromatic	rings	on	phosphine	ligand	=1.38(4)	
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least-squares plane, with the deviations P(1) 0.008(6), P(2) -0.006(7), N(1) -0.01(2), C(1) 0.01(3) Å. The platinum atom is 0.017 Å away from this mean plane. The anion $[BPh_4]^-$ has the usual tetrahedral geometry. The bond lengths and bond angles are similar to those reported previously for this anion [16]. The average B-C bond length is 1.65 Å and the angles at the boron atom lie in the range of 108 and 113° (average 109.9°) consistent with a tetrahedral environment around boron. The average C-C distance of the phenyl group in $[BPh_4]^-$ is 1.41 Å with the individual values ranging from 1.31 to 1.47 Å [16]. The four phenyl rings are planar with a maximum deviation of 0.04(4) Å.

The bond lengths and bond angles for the molecule are listed in Table 2. The various bond lengths are normal within experimental error. The Pt-P(1) distance *trans* to the methyl group is much longer (2.325(5) Å) than that of Pt-P(2) (2.207(5) Å). The longer bond is expected because of the *trans* influence of the methyl group. It may be noted that the Pt-P distances for the cation $[Pt_2Cl(\eta^2-Ph_2Ppy)(Ph_2Ppy)]^+$ for both chelating and monodentate phosphines are of the same order (viz. Pt-P(1) 2.223 and Pt-P(2) 2.232 Å, respectively) [3]. The two chemically nonequivalent Pt-P bond lengths in *cis*-chloro-*p*-tolyl-bis(triethylphosphine)platinum(II) (a) and *cis*-

chloro-perfluorophenyl-bis(triethylphosphine)platinum(II) (b) [17] differ significantly: 2.320(9) against 2.247(6) Å for a, and 2.326(7) against 2.226(7) for b; the

longer Pt-P bond is *trans* to the R group. If no *trans* influence is present, the Pt-P bond lengths fall in the range 2.22-2.28 Å; in our structure this value is 2.207(5)Å.

Because of the four-membered chelate ring various angles around platinum deviate from the normal value of 90°. Thus the P(1)-Pt-N(1) angle has been compressed to 70.4(5)°, while the adjacent angle P(1)-Pt-P(2) has opened to 106.3(2)°. The other angles C(1)-Pt-N(1) and C(1)-Pt-P(2) show little deviation – 90.6(8) and 92.6(6)°, respectively. However, in the cation $[PtCl(Ph_2Ppy)_2]^+$ the Cl-Pt-N(1) angle is (96.0) [3]. This may be ascribed to the steric demands of the groups attached to the platinum atom. The other angles of the chelating phosphine ligand are similar to those observed for $[PtCl(Ph_2Ppy)_2]^+$ [3] and $[RuCl_2(CO)_2(Ph_2Ppy)]$ [18].

The phenyl and pyridyl rings in $[PtMe(\eta^2-Ph_2Ppy)(Ph_2Ppy)]^+$ (Id) are planar to within 0.03(2) Å. The molecular dimensions of these rings are in accord with accepted values. The four-membered chelate ring, PtNCP, has a planar structure.

The reaction of Ib with an excess of $SnCl_2 \cdot 2H_2O$ in dichloromethane or $CDCl_3$ yielded the corresponding trichlorostannate complex, $[PtMe(SnCl_3)(Ph_2Ppy)_2]$, If, whose ¹H NMR spectrum showed a triplet pattern for the Pt-Me protons. The ³¹P NMR spectrum exhibited a single line with platinum-195 and tin-117/119 satellites. The spectra are consistent with the expected *trans* configuration of the complex. It is note worthy that the ³¹P chemical shift is deshielded and ¹J(Pt-P) is reduced by 97 Hz with respect to Ib, although ²J(Sn-P) lies in the range typical of ²J(Sn-P), *cis* [19,20]. In organoplatinum(II) trichlorostannate complexes, *trans*-[PtR(SnCl_3) (PR_3)_2] (R = Ph or COPh), shielding of the ³¹P nucleus and the much larger reduction in ¹J(Pt-P) (~ 350 Hz) than that of the corresponding chloro-complexes are observed [21]. Recently several new modes of bonding of the SnCl_2 ligand other than the normal M-SnCl_3 fashion have been reported [22-24]. For example, in [Rh_2Sn_2(CO)_2Cl_6 { μ -(Ph_2P)_2py}_2], the pyridiyl nitrogens are coordinated to one of the tin centres.

Recently Balch et al. [4] reported the reaction:

$$PtX_{2}(Ph_{2}Ppy)_{2} + Ptdba_{2} \rightarrow \left[Pt_{2}X_{2}(\mu - Ph_{2}Ppy)_{2}\right] + 2dba$$

and observed that the reaction was facile when the *trans*-Pt(II) complex was used. Thus it was expected that the use of *trans*-[PtMeCl(Ph₂Ppy)₂] in the above reaction might yield the corresponding methylplatinum(I) complex, $[Pt_2MeX(\mu-Ph_2Ppy)_2]$. So the reaction of Ib with Ptdba₂ was carried out in refluxing dichloromethane to give $[Pt_2Cl_2(\mu-Ph_2Ppy)_2]$, identified from its ³¹P NMR data [4].

Experimental

 $[PtMe_2(COD)]$, [PtMeX(COD)] (X = Cl, I) [25] and Ph₂Ppy [2] were prepared by previously published procedures. All reactions were carried out in spectrograde solvents under nitrogen.

¹H and ³¹P NMR spectra were recorded on a Varian FT-80A spectrometer operating in Fourier transform mode at 80 MHz for proton and at 32.203 MHz for ³¹P respectively. Some ¹H NMR spectra were recorded on a Bruker AM-500 or Varian VXR-300s instrument. Chemical shifts are relative to an internal solvent peak (7.26 ppm CHCl₃) for ¹H, and to external 85% H_3PO_4 for ³¹P. Microanalyses were performed by Bio-organic and Analytical Chemistry Divisions, BARC, Bombay. Melting points were determined in a capillary and are uncorrected.

Preparation of $[PtMeX(Ph_2Ppy)_2]$ (X = Me, Cl or I)

To a benzene solution of $[PtMe_2(COD)]$ (161 mg, 0.48 mmol) was added a benzene solution of Ph₂Ppy (238 mg, 0.91 mmol) dropwise with stirring. After the addition was complete, the mixture was stirred at room temperature for 30 min. Then the solvent was evaporated under vacuum, to leave an off-white solid which was washed with hexane and recrystallized from benzene-hexane as a white crystalline solid (300 mg, 83%).

Ib and Ic were prepared similarly; the relevant data are listed in Table 1.

Reaction of [PtMeCl(COD)] with Ph₂Ppy in 1:1 stoichiometry

To a dichloromethane solution of [PtMeCl(COD)] (155 mg, 0.44 mmole) was added a solution of Ph_2Ppy (116 mg, 0.44 mmole) dropwise to give a pale yellow solution. The solvent was removed under vacuum and the residue was washed with hexane and dried (yield 164 mg, 73%).

Reaction of Ib with $NaY (Y = BPh_4 \text{ or } BF_4)$

To a dichloromethane solution of trans-[PtMeCl(Ph₂Ppy)₂] (150 mg, 0.19 mmole), was added a methanolic solution of NaBPh₄ (77 mg, 0.24 mmol) with stirring. The mixture was stirred at room temperature for one hour and the solvent was removed under vacuum to leave an oily residue. This was dissolved in dichloromethane, and passed through a Florisil column eluting with CH₂Cl₂ to give a pale yellow crystalline solid. This was recrystallised several times from CH₂Cl₂/hexane to give a colourless crystalline product (yield, 135 mg, 65%).

The BF_4 salt was prepared similarly and the product was three times recrystallized from acetone/hexane mixture.

Reaction of $[PtMeCl(Ph_2Ppy)_2]$ with $SnCl_2 \cdot 2H_2O$

To a solution of *trans*-PtMeCl(Ph₂Ppy)₂ (146 mg) in CDCl₃ (3 ml) was added an excess of $SnCl_2 \cdot 2H_2O$ (220 mg) and the reaction mixture was stirred for 30 min to give a wine-red solution. This was filtered and studied by ¹H and ³¹P{¹H} NMR spectroscopy.

Crystal structure study of $[PtMe(\eta^2 - Ph_2Ppy)(Ph_2Ppy)][BPh_4]$

Crystal data. $C_{59}H_{51}N_2P_2BPt$, $M_r = 1055.9$, triclinic, a 10.006(6), b 14.240(8), c 18.368(6) Å, a 80.93(4), β 74.60(3), γ 89.23(5)°, V 2490.65 Å³, Z = 2, D_C 1.40 gm cm⁻³, F(000) 1064, Mo- K_{α} radiation, λ 0.71069 Å, $\mu(Mo-K_{\alpha})$ 27.8 cm⁻¹. Space group $P\overline{1}$ with equivalent positions $\pm [x, y, z]$.

Data collection, solution and refinement of structure. Data were collected in the range of $2 \le \theta \le 22^{\circ}$ with $0 \le h \le 10$, $-14 \le k \le 14$ and $-18 \le l \le 18$ on an Enraf Nonius CAD-4 diffractometer by $\omega/2\theta$ scan technique with a graphite monochromator and Mo- K_{α} radiation. Accurate cell constants and the orientation matrix were obtained by least-squares refinement of 25 reflections. A total of 6154 reflections were collected, of which 5409 were unique and of these 4757 with $I > 2.5\sigma(I)$ were used in the structure solution and refinement. The intensities of

Table 3

Fractional coordinates (×10⁴ for Pt and P; ×10³ for remaining atoms) and equivalent isotropic temperature factors (Å²×10³ for Pt and P; Å²×10² for remaining atoms) with e.s.d.'s in parenthesis for [PtMe(η^2 -Ph₂Ppy)[Ph₂Ppy)][BPh₄].

Atom	x	У	Z	$U_{ m eq}$	
Pt(1)	2008(1)	2306(1)	2172(1)	48(1)	
P(1)	2171(5)	3164(3)	3125(3)	40(5)	
P(2)	1416(6)	3327(3)	1283(3)	45(6)	
N(1)	251(2)	140(1)	305(1)	6(6)	
N(2)	270(2)	458(1)	-4(1)	9(1)	
C(1)	202(3)	120(1)	159(1)	8(1)	
C(2)	272(2)	49 (1)	323(1)	6(1)	
C(3)	298(3)	11(1)	392(2)	9 (1)	
C(4)	305(3)	70(2)	445(1)	7(1)	
C(5)	282(2)	164(1)	429(1)	7(1)	
C(6)	260(2)	201(1)	357(1)	5(1)	
C(7)	65(2)	352(1)	381(1)	4(1)	
C(8)	- 59(2)	368(1)	362(1)	5(1)	
C(9)	-180(2)	385(2)	416(1)	7(1)	
C(10)	- 169(2)	396(2)	488(1)	6(1)	
C(11)	- 49(3)	385(1)	506(1)	6(1)	
C(12)	73(2)	365(2)	454(1)	6(1)	
C(13)	359(2)	392(1)	310(1)	4 (1)	
C(14)	341(2)	485(1)	329(1)	5(1)	
C(15)	454(3)	537(2)	324(1)	7(1)	
C(16)	589(3)	512(2)	297(1)	7(1)	
C(17)	609(2)	419(2)	274(1)	7(1)	
C(18)	495(2)	364(1)	279(1)	6(1)	
C(19)	78(2)	446(1)	158(1)	5(1)	
C(20)	- 43(2)	484(1)	145(1)	6(1)	
C(21)	- 83(2)	573(1)	165(1)	6(1)	
C(22)	1(3)	615(1)	199(1)	8(1)	
C(23)	120(3)	574(1)	212(1)	7(1)	
C(24)	157(2)	489(1)	191(1)	5(1)	
C(25)	-2(2)	287(1)	97(1)	5(1)	
C(26)	- 111(3)	241(2)	153(1)	8(1)	
C(27)	- 225(3)	205(2)	132(2)	11(1)	
C(28)	- 221(4)	217(2)	55(2)	12(1)	
C(29)	- 109(4)	261(2)	3(2)	14(2)	
C(30)	3(3)	296(2)	20(1)	9(1)	
C(31)	280(2)	370(1)	46(1)	6(1)	
C(32)	373(3)	488(2)	-66(1)	8(1)	
C(33)	495(3)	438(2)	-87(1)	8(1)	
C(34)	506(3)	351(2)	- 41(2)	9(1)	
C(35)	401(2)	321(2)	24(1)	7(1)	
B(1)	155(2)	133(1)	702(1)	5(1)	
C(36)	259(2)	206(1)	633(1)	5(1)	
C(37)	395(2)	183(1)	593(1)	6(7)	
C(38)	487(3)	248(2)	539(1)	7(1)	
C(39)	447(3)	343(2)	522(1)	8(1)	
C(40)	318(3)	371(2)	562(1)	7(1)	
C(41)	229(2)	304(1)	616(1)	6(1)	
C(42)	202(3)	135(1)	781(1)	7(1)	
C(43)	279(3)	210(2)	789(1)	9(1)	
C(44)	320(4)	215(2)	857(2)	12(1)	
(45)	207(5)	141(3)	91 9(2)	17(1)	

Table 3 (continued)

Atom	x	у	Z	U _{eq}
C(46)	178(5)	63(3)	916(2)	16(1)
C(47)	155(3)	60(2)	841(1)	10(1)
C(48)	-9(3)	158(1)	714(1)	7(1)
C(49)	- 109(3)	146(2)	784(2)	9(1)
C(50)	- 246(4)	163(2)	797(3)	12(1)
C(51)	- 295(4)	193(2)	729(3)	13(1)
C(52)	- 208(4)	208(2)	661(3)	12(1)
C(53)	-62(3)	189(2)	647(2)	9(1)
C(54)	179(3)	23(1)	678(1)	7(1)
C(55)	96(3)	-18(2)	640(1)	9(1)
C(56)	125(4)	-111(3)	617(2)	13(1)
C(57)	242(6)	-149(3)	625(2)	16(2)
C(58)	332(4)	-118(2)	663(2)	14(2)
C(59)	301(3)	-27(2)	690(2)	11(2)

 $\overline{U_{\rm eq}} = (U_{11} + U_{22} + U_{33})^{1/2}$

two standard reflections measured at regular intervals did not change significantly over the period of data collection. The data were corrected for Lorentz and polarization factors. No absorption correction was applied.

The structure was solved by the heavy atom method. The Patterson synthesis was used for fixing the position of platinum atom. The Pt atom coordinates (Table 3) were determined first, and these coordinates together with successive Fourier syntheses were used to locate all the other atoms. The non-hydrogen atoms were given anisotropic temperature factors. Final fractional coordinates with estimated standard deviations are listed Table 3. Only 30 hydrogen atoms were located for the cation [PtMe(η^2 -Ph₂Ppy)(Ph₂Ppy)]⁺ and these were given isotropic thermal parameters. The final *R*-factor for this structure without weighting scheme is 7.96%. The SHELX-76 program [26] was used for Patterson and Fourier syntheses, the least-squares refinement and the calculation of the bond lengths angles on a NORSK-DATA ND-560 computer system.

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