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Synthesis and structure of platinum(II)– and palladium(II)–phosphorin complexes in solid and solution state

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Abstract

The novel platinum and palladium complexes with phosphorin, [Pt(dmppn)$_2$X$_2$] (X = Cl (**1**), Br (**2**), I (**3**)) and [Pd(dmppn)$_2$X$_2$] (X = Cl (**4**), Br (**5**)), have been prepared using 4,5-dimethyl-2-phenylphosphorin (dmppn) with M(cod)X$_2$ or M(PhCN)$_2$X$_2$ (M = Pt, Pd). The crystal structure of **3** was determined by single crystal X-ray crystallography and shown a *cis* configuration in a square planar structure. The chemical shifts for these complexes were observed by ^{31}P{^{1}H} NMR spectroscopy in the solution and they showed significant upfield shifts over 30 ppm relative to that of the free ligand. These upfield shifts indicate that the phosphorin ligand undergoes strong π-back donation from the central metal compared with general phosphine ligands and the difference of these upfield shifts between Pt and Pd is clearly appeared the degree of π-back donation from the central metal. Molecular structure of platinum and palladium complexes in the solution was further estimated to have the *cis* configuration in the square planar with ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR data.

Keywords: Phosphorin; Platinum; Palladium; X-ray crystal structure; NMR spectroscopy

1. Introduction

The design and synthesis of platinum(II)– and palladium (II)–phosphine complexes have gained an importance in view of recent organic synthesis and stereochemistry. An attractive pursuit in this area is the design of functional supporting ligand by use of phosphorus ligand with tunable electronic and structural characteristics [1]. Furthermore, there are particularly successful experimental result [2] and theoretical interpretations [3] to find out that the stereochemical configuration around platinum atom on platinum(II) complexes PtL$_2$X$_2$ (L = phosphine, X = halide) is fairly dependent on the steric and electronic factor of the ligand. The reactivity of catalytic PtL$_2$X$_2$ complexes have been correlated to both σ donation and π back donation from a central metal. On the other hand, Phosphorin is classified into hetero benzene as pyridine and has a phosphorus atom in an aromatic ring. Recent research on the metal complexes with phosphorins and derivatives has been revealed a strong π-accepting ability of phosphorins [4] and developed by the use as the metal catalyst with a unique coordination mode of phosphorin derivatives in the field of catalytic chemistry [5]. However, only two examples of the isolated platinum(II)–phosphorin complexes have been reported. The first characterized compounds by NMR measurement have been reported in our previous communication for platinum(II) and palladium(II) complexes [M(dmppn)$_2$Cl$_2$] (M = Pt and Pd, dmppn = 4,5-dimethyl-2-phenylphosphorin) which presumed the square planar structure with a *cis* configuration in the solution [6]. On second report, the first X-ray crystal structure of platinum(II)–phosphorin complex [Pt(2,6-dimethyl-4-phenylphosphorin)$_2$Cl$_2$] has been revealed a *cis* configuration by Elschenbroich et al. [7]. This fact prompted us to attempt the synthesis and the structural influence of halogeno ligand in platinum(II) and palladium(II) complexes with phosphorin.

The present study describes the synthesis and structure of dihalogenobis(dmppn)platinum(II) complexes Pt(dmppn)$_2$X$_2$ (X = Cl (**1**), Br (**2**), I (**3**)) and dihalogenobis(dmppn) palladium(II) complexes Pd(dmppn)$_2$X$_2$ (X = Cl (**4**), Br(**5**)). Single crystal X-ray analysis on **3** has revealed the *cis* configuration in the square planar structure and estimated the steric and electronic factor of phosphorin in the solid state. A useful information on the configuration of halogeno series was

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obtained the coupling constants between platinum and phosphorus atom from $^{31}P\{^1H\}$ NMR spectroscopy.

2. Experimental

2.1. General procedure and materials

All reactions were performed using standard Schlenk techniques and filtration was carried out in the glove bag under nitrogen atmosphere. All solvents were purchased from Nacalai tesque and distilled with CaH_2 as drying reagent. Nitrogen gas was passed into all solvents prior to use. Dihalogeno(cyclooctadiene) platinum [Pt(cod)X_2] (X = Br, I) were purchased. Bis(benzonitrile)dichloro platinum(II) [Pt(PhCN)$_2$Cl$_2$] and bis(benzonitrile)dihalogeno palladium(II) [Pd(PhCN)$_2$X$_2$] (X = Cl, Br) were prepared by literature methods [8]. The ligand 4,5-dimethyl-2-phenylphosphorin (dmppn) was prepared by the method of Alcaraz et al. [9]. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL JNM-GX 400 FT-NMR spectrometer. Proton and carbon chemical shifts were recorded relative to internal $SiMe_4$, while the phosphorus chemical shifts were relative to external 85% H_3PO_4. Elemental analyses for C and H were carried out at Elemental Analysis Service Center, Kyushu University.

2.2. Preparation of Pt(dmppn)$_2$X$_2$

2.2.1. Pt(dmppn)$_2$Cl$_2$ (**1**)

The round-bottomed flask was charged with the solution of Pt(PhCN)$_2$Cl$_2$ (300 mg, 0.80 mmol) and dmppn (400 mg, 2.0 mmol) in benzene (20 cm^3). After stirred for 1 h, the mixture solution was added to 40 cm^3 of hexane and a pale yellow adduct was precipitated. The precipitate was filtered, washed with benzene–hexane (1:3) mixture solution, and dried at 45 °C under reduced pressure. Yield: 363 mg (68%). Anal. Calcd for C26H26Cl2P2Pt1 1.0 C_6H_6: C, 51.62; H, 4.34. Found: C, 51.12; H, 4.35. ^1H NMR ($CDCl_3$): δ (ppm) = 7.53 (d, J = 11 Hz, 1H, C3–H), 7.50 (d, J = 23 Hz, 1H, C6–H), 7.16–7.26 (m, 5H, phenyl–H), 2.30 (s, 3H, C4–methyl–H), 2.25 (d, J = 7 Hz, 3H, C5–methyl–H). ^{13}C NMR (CD_2Cl_2): δ (ppm) = 137.04 (six, C6), 138.00 (t, Ph–C1), 139.11 (t, C4), 139.84 (t, C3), 149.41 (t, C5), 151.07 (six, C2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) = 134.3 (J(Pt–P) = 4052 Hz).

2.2.2. Pt(dmppn)$_2$Br$_2$ (**2**)

The dmppn (400 mg, 2.0 mmol) in dichloromethane (20 cm^3) was added to the solution of Pt(cod)Br$_2$ (394 mg, 0.85 mmol) in benzene (10 cm^3). After stirred for 10 min, the dichloromethane was distilled off under reduced pressure and a yellow adduct was precipitated. The precipitate was filtered, washed with benzene–hexane (1:3) mixture solution, and dried under reduced pressure. Yield: 456 mg (71%). Anal. Calcd for C26H26Br2P2Pt1: C, 41.34; H, 3.47. Found: C, 41.79; H, 3.44. ^1H NMR ($CDCl_3$): δ (ppm) = 7.51 (d, J = 12 Hz, 1H, C3–H), 7.45 (d, J = 25 Hz, 1H, C6–H), 7.11–7.26 (m, 5H, phenyl–H), 2.27 (s, 3H, C4–methyl–H), 2.24 (d, J = 8 Hz, 3H, C5–methyl–H). ^{13}C NMR (CD_2Cl_2): δ (ppm) = 137.77 (six, C6), 137.82 (t, Ph–C1), 139.23 (t, C4), 139.63 (t, C3), 149.18 (t, C5), 150.66 (six, C2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) = 134.1 (J(Pt–P) = 3956 Hz).

2.2.3. Pt(dmppn)$_2$I$_2$ (**3**)

The dmppn (400 mg, 2.0 mmol) in benzene (5 cm^3) was added to the suspension of Pt(cod)I$_2$ (400 mg, 0.72 mmol) in benzene (20 cm^3) and stirred at room temperature. The suspension was temporarily dissolved and an orange-yellow precipitate appeared again. The precipitate was filtered, washed with benzene–hexane (1:3) mixture solution, and dried at 45 °C under reduced pressure. Recrystallization was performed with dichloromethane. Yield: 532 mg (87%). Anal. Calcd for C26H26I2P2Pt1: C, 36.77; H, 3.09. Found: C, 36.78; H, 3.09. ^1H NMR ($CDCl_3$): δ (ppm) = 7.45 (d, J = 15 Hz, 1H, C3–H), 7.43 (d, J = 26 Hz, 1H, C6–H), 7.11–7.26 (m, 5H, phenyl–H), 2.25 (d, J = 8 Hz, 3H, C5–methyl–H), 2.23 (s, 3H, C4–methyl–H). ^{13}C NMR (CD_2Cl_2): δ (ppm) = 137.41 (t, Ph–C1), 139.06 (six, C6), 139.19 (t, C4), 139.40 (t, C3), 148.55 (t, C5), 149.89 (six, C2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) = 135.4 (J(Pt–P) = 3712 Hz).

2.3. Preparation of Pd(dmppn)$_2$X$_2$

2.3.1. Pd(dmppn)$_2$Cl$_2$ (**4**)

Ligand dmppn (400 mg, 2.0 mmol) in benzene (5 cm^3) was added to solution of Pd(PhCN)$_2$Cl$_2$ (307 mg, 0.80 mmol) in benzene (20 cm^3) and stirred at room temperature. After 5 min, the solution was suspended and an orange-yellow precipitate appeared. The precipitate was filtered, washed with benzene–hexane (1:3) mixture solution, and dried at 45 °C under reduced pressure. Yield: 325 mg (70%). Anal. Calcd for C26H26Cl2P2Pd1 1.0 C_6H_6: C, 58.68; H, 4.96. Found: C, 58.60; H, 4.92. ^1H NMR ($CDCl_3$): δ (ppm) = 7.64 (d, J = 7 Hz, 1H, C6–H), 7.47 (d, J = 27 Hz, 1H, C3–H), 7.16–7.26 (m, 5H, phenyl–H), 2.28 (d, 3H, C5–methyl–H), 2.27 (s, 3H, C4–methyl–H). ^{13}C NMR (CD_2Cl_2): δ (ppm) = 139.3 (t, J = 5 Hz, C4), 139.4 (t, J = 6 Hz, C3), 139.4 (t, J = 16 Hz, Ph–C1), 141.4 (six, J = 34 Hz, C6), 149.1 (t, J = 11 Hz, C5), 155.7 (q, J = 42, 13 Hz, C2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) = 148.7.

2.3.2. Pd(dmppn)$_2$Br$_2$ (**5**)

This compound was prepared by similar procedures of complex **4**. Yield: 321 mg (60%). Anal. Calcd for C26H26Br2P2Pd1 2/3 C_6H_6: C, 50.13; H, 4.21. Found: C, 50.47; H, 4.27. ^1H NMR ($CDCl_3$): δ (ppm) = 7.546 (d, J = 18.1 Hz, 1H, C6–H), 7.498 (d, J = 20.8 Hz, 1H, C3–H), 7.12–7.33 (m, 5H, phenyl–H), 2.285 (d, J = 8.1 Hz, 3H, C5–methyl–H), 2.262 (d, J = 1.5 Hz, 3H, C4–methyl–H). ^{13}C NMR (CD_2Cl_2): δ (ppm) = 139.2 (d, J = 31 Hz, Ph–C1), 139.3 (d, J = 14 Hz, C3), 139.5 (d, J = 11 Hz, C4), 142.4 (d, J = 34 Hz, C6), 148.9 (d, J = 20 Hz, C5), 155.5 (dd, J = 34, 6 Hz, C2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) = 147.7.

2.4. Crystallography of Pt(dmppn)$_2$I$_2$ (**3**)

An orange prismatic crystals suitable for X-ray diffraction study of Pt(dmppn)$_2$I$_2$ (**3**) were isolated from CH_2Cl_2

Table 1
Crystallographic data for complex **3**

Formula	$C_{26}H_{26}PtI_2P_2$
F_w	849.34
Crystal system	Orthorhombic
Space group	*Pbcn*
a (Å)	19.10(1)
b (Å)	9.423(7)
c (Å)	14.797(6)
V (Å^3)	2667(2)
Z	4
D_{calc} (mg m^{-3})	1.584
Crystal size (mm^3)	0.20×0.10×0.20
Radiation Mo Kα (λ)	0.71069
μ (Mo Kα) (cm^{-1})	76.98
T (K)	293
Total reflections	2692
R^a	0.048
$R_w{}^{b,c}$	0.060

[a] $R=\Sigma[|F_0|-|F_c|]/\Sigma|F_0|$.

[b] $R_w=[\Sigma w(|F_0|-|F_c|)^2/\Sigma w|F_0|^2]^{1/2}$.

[c] $w=1/\sigma^2(F_0)$.

solution. The crystal was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation ($\lambda=$ 0.71069 Å) and a 12 kW rotating anode generator. Cell constants and an orientation matrix were obtained from a least-squares refinement using 23 reflections in the range $27.79° < 2\theta < 29.99°$. For the intensity data collection, the $\omega-2\theta$ scan mode was used at the scan rate 16 min^{-1} and scan width was $(1.00+0.30\tan\theta)°$. The intensities of three standard reflections were monitored after every 150 reflections. Over the course of data collection, the standards increased by 1.2% and, therefore, a linear correction factor was applied to the data to account for this phenomenon. An empirical absorption and Lorentz-polarization absorption correction were applied. Crystallographic data are given in Table 1.

All the calculations were performed by using teXsan crystallographic software package of the Molecular Structure Corporation. The structure was solved by heavy atom Patterson methods and expanded using Fourier techniques [10]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions (d(C–H)=0.95 Å) but not refined. The final cycle of full-matrix least-squares refinement with scattering factors was based on 1866 observed reflections ($I>3.00\sigma(I)$) and 142 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber [11] and anomalous dispersion effects were included in F_{calc} [12]; the values of $\Delta f'$ and $\Delta f''$ were those of Cregh and McAuley [13].

3. Results and discussion

3.1. Synthesis

Dihalogenobis(dmppn)platinum(II) complexes Pt(dmppn)$_2$X$_2$ (X=Cl (**1**), Br (**2**), I (**3**)) and dihalogenobis(dmppn)palladium(II) complexes Pd(dmppn)$_2$X$_2$ (X=Cl (**4**), Br(**5**)) were prepared using 4,5-dimethyl-2-phenylphosphorin (dmppn) with M(cod)X$_2$ or M(PhCN)$_2$X$_2$ (M=Pt, Pd) by the ligand exchange reaction. The elemental analysis of present five complexes was identified as the composition of M(dmppn)$_2$X$_2$, respectively. These isolated complexes were stable against air and moisture in a dichloromethane solution although free dmppn ligand in the solution was gradually received the oxidation by the air or moisture. Attempts to obtain the palladium(II) and platinum(II) complexes through direct reactions of MCl$_2$ (M=Pd, Pt) with dmppn in methanol were unsuccessful because of the decomposition of π system of phosphorin; the decomposition of π system in phosphorin ring was presumed the disappearance of the signals assignable to the aromatic protons in phosphorin ring by ^{1}H NMR spectroscopy and the appearance of the characteristic ν(P=O) stretching band by IR spectroscopy.

3.2. Crystallography of Pt(dmppn)$_2$I$_2$ (3)

The single crystal of Pt(dmppn)$_2$I$_2$ (**3**) appropriate for X-ray crystallography was obtained as orange prismatic crystals by recrystallization from CH$_2$Cl$_2$ solution. The crystal structure of **3** is shown in Fig. 1 and this complex crystallizes as a monomeric square planar structure. This is the first example of diiodobis(phosphorin)platinum(II) complex that has been established the molecular structure by X-ray crystallography although only one example for the crystal structure of dichloro complex [Pt(2,6-dimethyl-4-phenylphosphorin)$_2$Cl$_2$] (**6**) has been reported by Elschenbroich et al. [7]. Selected bond lengths and angles are listed in Table 2 and the atom numbering is shown in Fig. 1. The coordination geometry of two phosphorus and two iodine atoms bound to platinum atom is a *cis* configuration and the angles of P–Pt–I (88.8°) and P–Pt–P* (91.7°) are slightly distorted from the angle of ideal square planar geometry.

The coordination geometry of complexes is favorable for *trans* isomer according to more hindered ligand and the iodo ligand acts as a sterically more hindered ligand than chloro and bromo on the current stereochemical study with

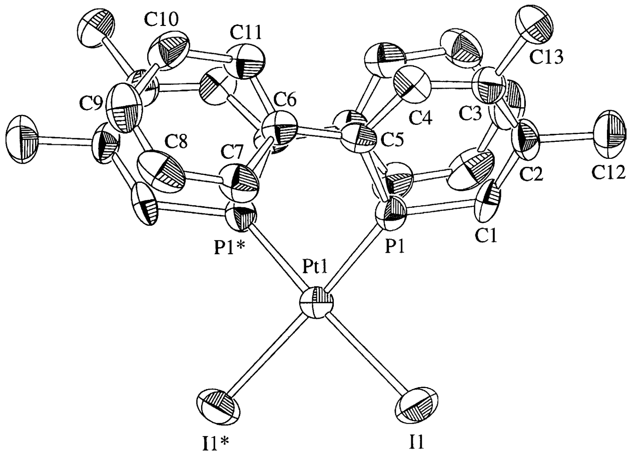

Fig. 1. A view of Pt(dmppn)$_2$I$_2$ (**3**), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted.

Table 2
Selected bond lengths and angles on complex **3**

Bond length (Å)			
Pt–I	2.631(2)	C6–C7	1.35(2)
Pt–P	2.236(4)	C7–C8	1.40(3)
P–C1	1.72(2)	C8–C9	1.37(2)
C1–C2	1.38(2)	C9–C10	1.40(2)
C2–C3	1.41(2)	C10–C11	1.37(2)
C3–C4	1.36(2)	C11–C6	1.38(2)
C4–C5	1.41(2)	C12–C2	1.51(2)
C5–P	1.75(2)	C13–C3	1.49(2)
C5–C6	1.43(2)		
Bond angles (°)			
I–Pt–P	88.8(1)	C2–C3–C13	119(1)
I–Pt–I*	92.00(7)	C3–C2–C12	121(1)
P–Pt–P*	91.7(2)	C3–C4–C5	127(1)
P–Pt–I*	171.2(1)	C4–C3–C13	116(1)
Pt–P–C1	129.6(6)	C4–C5–C6	122(1)
Pt–P–C5	123.9(6)	C5–C6–C7	120(1)
P–C1–C2	122(1)	C5–C6–C11	120(1)
P–C5–C4	116(1)	C6–C7–C8	118(1)
P–C5–C6	120(1)	C6–C11–C10	122(1)
C1–P–C5	106.5(8)	C7–C6–C11	118(1)
C1–C2–C3	122(1)	C7–C8–C9	123(1)
C1–C2–C12	116(1)	C8–C9–C10	116(1)
C2–C3–C4	124(1)	C9–C10–C11	119(1)

dihalogenobis(PR_3)platinum(II) complexes (PR_3 = tertiary phosphines). Indeed, the crystal structure of *cis*-diiodobis(PR_3)platinum(II) complexes were few reported as compared with the *cis*-dichrolobis(PR_3)platinum(II) complexes [14]. These results demonstrate that phosphorin acts as a less hindered ligand than many kinds of phosphines because **3** isolates as a *cis* isomer.

The bond lengths of Pt–I and Pt–P are showed about *cis*-diiodobis(PR_3)platinum(II) and *trans*-platinum(II) complexes revealed that phosphorus atom was situated in *trans* position of iodine atom by X-ray crystallography in Table 3 [14–16]. The Pt–P length (2.236(4) Å) on **3** is included in the range of the lengths on the collated *cis*-complexes (2.219(3)–2.271(4) Å) and shorter than that on *trans*-complexes (2.292(6)–2.371(2) Å). On the other hand, The Pt–I length (2.631(2) Å) on **3** is rather closed to the region of the lengths on *trans*-complexes (2.599(2)–2.626(2) Å) and appreciably shorter than that on *cis*-complexes (2.629(1)–2.672(2) Å) in spite of the *cis* configuration. Trans influence is employed to interpret the difference of bond length between *cis* and *trans* isomer and almost all phosphines have been classified as the ligand contributed strongly *trans* influence relative to iodo ligand. The shortness of Pt–I length on **3** can be explained that phosphorin is classified as the ligand of weaker *trans* influence than phosphines. Trans influence mainly results from σ effect in a recent theory [17]. In fact, Pt–I lengths on *cis*-platinum complexes with phosphine ligands came longer than those on *trans*-complexes, while Pt–P lengths were contrary shorter. This observation reveals that tertiary phosphines are highly σ donor and π acceptor ligand relative to iodo ligand. However, the bond lengths of both Pt–P and Pt–I on **3** are short as mentioned above and, therefore, phosphorin can be regarded lower σ donor ligand but higher π acceptor ligand than tertiary phosphines. This interpretation is in fair agreement with current reports of phosphorin research [4].

Table 3
Bond lengths of Pt–I and Pt–P in the complexes of $Pt(PR_3)_2I_2$

Complexes	Pt–I (Å)	Pt–P (Å)	Refs.
3	2.631(2)	2.236(4)	
cis-$Pt\{P(CH_3)_3\}_2I_2$	2.665(2)	2.244(4)	[7a]
	2.672(2)	2.271(4)	
cis-Pt(biphosphole)I_2	2.658(2)	2.219(3)	[7b]
	2.662(2)	2.247(3)	
cis-$Pt(PPh_2C{\equiv}CPh)_2I_2$	2.629(1)	2.257(2)	[8]
	2.648(1)	2.266(2)	
trans-$Pt\{P(CH_3C_6H_5)_3\}_2I_2$	2.622(1)	2.348(2)	[9a]
trans-$Pt\{P(C_6H_{11})_3\}_2I_2$	2.612(1)	2.371(2)	[9b]
trans-$Pt\{P(C_6F_5)_3\}_2I_2$	2.626(2)	2.292(6)	[9c]
trans-$Pt\{P(CH_3)_3\}_2I_2$	2.599(2)	2.315(4)	[9d]

The P–C bond lengths (1.72(2) and 1.75(2) Å) on **3** were almost same as those (1.712(4) and 1.719(4) Å) on **6**. The most of P–C lengths on $Pt(PR_3)_2X_2$ (X = halides) are situated in the range of 1.80–1.89 Å and those on *cis*-$Pt(PEt_3)((C_6H_2Me_3)\text{-}P{=}CPh_2)Cl_2$ (**7**) were reported 1.66(1) Å (P=C bond) and 1.79(1) Å (P–C bond) by Kroto et al. [18]. These differences of bond lengths obviously show that phosphorus atom of dmppn are included in an aromatic π system because P–C lengths of **3** are intermediate between those of tertiary phosphines (sp^3 hybridization) and phospha–alkene (sp^2 hybridization).

The phosphorin ring of one ligand in **3** appeared to be piled up the phenyl ring of another ligand as shown in Fig. 2. The intramolecular distances between atoms of phosphorin ring and ones of phenyl ring between two ligands were calculated and it was turned out that the distances between most neighboring atoms were in the range of 3.58–4.05 Å (P1–C7* 3.58(2) Å, C1–C8* 3.63(2) Å, C2–C9* 3.75(3) Å, C3–C9* 3.99(2) Å, C4–C10* 4.05(2) Å, C5–C6* 3.95(2) Å). These distances are sufficiently considered that π–π interaction exist between π system of phosphorin and phenyl ring on two dmppn ligands in **3**. Additionally, the six atoms in the phosphorin ring are approximately located on the least square plane and the C–C lengths in phosphorin ring are reasonable as the bond distances on

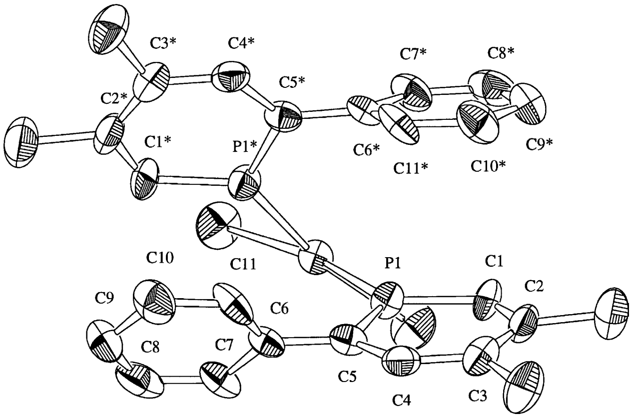

Fig. 2. Another view of complex **3**, with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted.

aromatic compounds as shown in Table 2. The least square plane of both the phosphorin and phenyl ring is pitched at a dihedral angle of 56.15°. This angle is larger than those of Iodocopper(I) complex with dmppn [19] and possessed to the effects of not only a steric repulsion between the hydrogen atoms, the one is bound to C4 in the phosphorin ring and another one to C11 in the phenyl ring, but also π–π stacking between phosphorin and phenyl ring of each dmppn ligands.

3.3. NMR studies

The $^{31}P\{^{1}H\}$ NMR spectra on platinum complexes **1–3** showed signals near 135 ppm while those on palladium complexes **4** and **5** did near 148 ppm as shown in Table 4. These observations are typical for the η^1 coordination of metal complexes with phosphorin; phosphorus resonances of phosphorin in the case of η^6 coordination have been observed upper field than 50 ppm [20]. It is noticeable that both platinum and palladium complexes showed significant upfield shifts of the phosphorus resonance by over 48 and 35 ppm relative to that of the free dmppn, respectively. The degrees of the upfield shifts in platinum complexes were greater than those of palladium complexes. Such coordination shifts were reported in previous studies [21] and this difference has been considered to attribute to different dsp^2 hybrid orbitals of each complexes as treated in VB theory; platinum complex is expressed as 5d6s6p^2 while palladium as 4d5s5p^2.

Furthermore, chemical shifts of adjacent carbon atoms to phosphorus (C2 and C6) also showed upfield shifts in the range of 13–18 ppm and those of C3 and C5 observed downfield shifts in the range of 3–7 ppm in present complexes as shown in Table 4. These assignments were performed by ^{13}C-DEPT and ^{13}C–^{1}H COSY measurement for present complexes. These changes in the direction of the shifts indicate the alteration of π-system of the phosphorin due to π-back donation because these changes of carbon resonance in phosphorin are consistent with the changes on an aromatic compound introduced to an electron donor group. Therefore, the main factor of these upfield shifts in the phosphorin is plausibly attributed to π-back donation from the central metal to stabilize the metal–phosphorus bonding.

The $^{31}P\{^{1}H\}$ NMR spectra on present platinum complexes were observed only three signals in both $CDCl_3$ and CD_2Cl_2, respectively. Then, these three complexes are speculated to exist one isomer without the *cis–trans* isomerization in the solution. The coupling constant $^{1}J(^{31}P–^{195}Pt)$ is determined with the separated width of two outside signals in pseudo triplet. The $^{1}J(^{31}P–^{195}Pt)$ for complexes **1**, **2**, and **3** were respectively determined to be 4052, 3976, and 3712 Hz. The $^{1}J(^{31}P–^{195}Pt)$ is most informative for the determination between the *cis* and *trans* configurations in the solution. The $^{1}J(^{31}P–^{195}Pt)$ for platinum(II) complexes $Pt(PR_3)_2X_2$ are typically greater than 3000 Hz on the *cis* configuration of two phosphorus atoms and smaller than 3000 Hz on the *trans* configuration according to previous studies [22]. Indeed, it was reported that the *cis*-complexes **6** and **7** were observed the $^{1}J(^{31}P–^{195}Pt)$ of 3907 and 4294 Hz; two phosphorus atoms occupied mutually a *cis* position as determined by X-ray crystallography. While *trans*-complex **7** was measured the $^{1}J(^{31}P–^{195}Pt)$ of 2590 Hz; this complex was observed in the solution and not isolated [6,18]. These observations support that these platinum complexes have the *cis* configuration in the solution and this interpretation is consistent with result that **3** revealed the *cis* configuration in the solid state by X-ray crystallography.

The $^{31}P\{^{1}H\}$ NMR spectra for palladium complexes **4** and **5** were observed as a slightly broad singlet (half-line width 49 Hz), respectively. The *trans* isomers of palladium(II) complexes $Pd(PR_3)_2Cl_2$ generally have greater coupling constants $^{2}J(^{31}P–^{31}P)$ than 150 Hz while the *cis* isomers have smaller ones than 20 Hz [23]. Additionally, the ^{13}C signal patterns of adjacent carbon atoms to phosphorus (C2 and C6) in **4** were observed as multiplets while those in **5** as doublet of doublets and doublet. These signal patterns of **4** and **5** suggests to possesses the *cis* configuration in the solution. Because the signal patterns of the carbon atoms bonded to phosphorus between the *cis* and *trans* isomers showed distinct multiplicities on the previous ^{13}C NMR studies of $Pd(PR_3)_2Cl_2$. The patterns on the *cis* isomers have been observed as multiplets or doublet of doublets or doublet, while those on the *trans* isomers have appeared as 1:2:1 triplet [23].

Table 4
^{31}P- and ^{13}C-NMR data for free ligand, $Pt(dmppn)_2X_2$ (X = Cl (**1**), Br (**2**), I (**3**)), and $Pd(dmppn)_2X_2$ (X = Cl (**4**), Br(**5**)) in CD_2Cl_2

Sample	$\delta^{31}P^{a}$ $(\Delta\delta)^{c}$	$\delta^{13}C^{b}$ $(\Delta\delta)^{c}$				
		C2	C6	C3	C5	C4
dmppn	183.8	168.5	154.8	136.1	142.0	139.5
1	134.3 (49.5)	151.1 (17.4)	137.0 (17.8)	139.8 (−3.7)	149.4 (−7.4)	139.1 (0.4)
2	134.1 (49.7)	150.7 (17.8)	137.8 (17.0)	139.6 (−3.5)	149.2 (−7.2)	139.2 (0.3)
3	135.4 (48.4)	149.9 (18.6)	139.1 (15.7)	139.4 (−3.3)	148.6 (−6.6)	139.2 (0.3)
4	148.7 (35.1)	155.7 (12.8)	141.4 (13.4)	139.4 (−3.3)	149.1 (−7.1)	139.3 (0.2)
5	147.7 (36.1)	155.5 (13.0)	142.4 (12.4)	139.3 (−3.2)	148.9 (−6.9)	139.5 (0.0)

[a] Chemical shifts in ppm relative to H_3PO_4 (85% aqueous solution).

[b] Chemical shifts in ppm relative to TMS.

[c] $\Delta\delta = \delta(\text{dmppn}) - \delta(\text{complex})$.

4. Conclusions

Platinum complexes with phosphorin exhibit a great useful information of both donor and acceptor character as the ligand by means of comparison of phosphines. Complex **3** is the first example of diiodo platinum complex with phosphorin that was established the molecular structure by X-ray crystallography. The crystal structure of **3** shows that this complex crystallized as a monomeric distorted square planar structure and the coordination geometry situates in a *cis* configuration. Further, the coordination geometry of present platinum and palladium complexes can be presumed a square planar structure with the *cis* configuration by multinuclear NMR study.

Three ideas can be borne out by the result of X-ray crystallography and NMR measurement: (i) phosphorin acts as a less hindered ligand than PR_3 (PR_3 = tertiary phosphines and phosphites), (ii) phosphorin is classified in a lower σ donor ligand but higher π acceptor ligand than PR_3, (iii) phosphorus atom of phosphorin is included in an aromatic π system. Study on novel platinum and palladium complexes with phosphorin revealed that phosphorin had a quite different donor and acceptor character as ligand compared with phosphines and phosphites for general use in the supporting ligand of complexes with catalytic reaction. Especially, the electronic factor of phosphorin contributes the different effect relative to phosphines and causes to reduce the electron density on the donated metal center.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2006.02.010. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 231727 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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