## FOUR- AND FIVE-COORDINATE PALLADIUM(II) COMPLEXES CONTAINING 1,10-PHENANTHROLINE AND ITS 2,9-DIMETHYL DERIVATIVE

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(Received 2 January 1985; accepted after revision 22 May 1985)

Abstract—A series of potentially five-coordinate Pd(II) complexes,  $[Pd(PMe_2Ph)_3(2,9-R_2-phen)][BF_4]_2$  (R = H or Me; phen = 1,10-phenanthroline),  $[PdCl(PPh_3)_2(2,9-R_2-phen)]X$  (R = H or Me) and  $[PdCl(2,9-Me_2-phen)_2]PF_6$  have been obtained from reactions of  $[Pd(PMe_2Ph)_4][BF_4]_2$  and  $[PdCl(PPh_3)_3]X$  (X = BF<sub>4</sub> or PF<sub>6</sub>) with potentially bidentate phen and its 2,9-dimethyl derivative, respectively. By <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H}FT NMR and electronic spectroscopy, these Pd(II) complexes have been characterized. Formally a three-coordinate complex of Pd(II),  $[Pd(PR_2Ph)_3]BF_4$  (R = Et or Ph) has also been prepared by treating  $[PdCl(PPh_3)_3]BF_4$  and  $PdCl_2(PEt_2Ph)_3$  with AgBF<sub>4</sub>.

Many studies concerning ligand substitution and isomerization of  $d^8$  transition-metal complexes have been directed to monodentate phosphine ligands, especially to PMe<sub>3</sub> and P(OMe)<sub>3</sub>. In some of these studies five-coordinate intermediates have been isolated and their crystal structures have been determined.<sup>1-13</sup> The systematic kinetics for  $MX_{2}L_{1}$  $[M = Ni^{1,2}, X = CN, Cl \text{ or } Br, L = PMe_3 \text{ or}$  $P(OMe)_3$ ; M = Pd, Pt,<sup>10</sup> X = Cl, Br or I, L =  $PMe_3$ ; M = Pt,<sup>11</sup> L = 1-R-3,4-dimethylphosphole, X = Cl, Br or I] have been established by <sup>31</sup>P NMR spectroscopy. However, five-coordinate Pd(II) complexes stabilized only by neutral ligands, especially by bulky PPh<sub>3</sub>, are elusive. In addition, there have been only a few examples of fivecoordinate Pd(II) complexes<sup>5</sup> containing potentially bidentate 1,10-phenanthroline (phen) or its 2,9-dimethyl derivative (2,9-Me2-phen), and their solution behaviours have not been determined unambiguously compared with those of the corresponding Pt(II) complexes.9

The ligand substitution reactions of

## $[Pd(PPh_3)_4]X_2$

 $(X = BF_4 \text{ or } PF_6)$ ,<sup>14</sup> [PdCl(PPh<sub>3</sub>)<sub>3</sub>]X<sup>15</sup> and [Pd(PMe<sub>2</sub>Ph)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> may be expected to proceed comparatively readily due to the presence of bulky phosphines and the low coordination abilities of the anions. Several potentially five-coordinate Pd(II) complexes containing phen or 2,9-Me<sub>2</sub>-phen have been prepared from these precursors.

In the five-coordinate Pt(II) complexes of phen so

so MH

far isolated, it has been found that the crystal structures are mostly distorted square pyramid with elongation of the apical M—N bond length,<sup>5,9</sup> while no dissociation of the phen takes place in solution as evidenced by the observance of a <sup>195</sup>Pt satellite. Therefore, it seems that the apical M—N distance of the square-pyramid complex crystallographically determined is not the main factor in dominating its solution behaviour.

In this paper, the preparation and characterisation of potentially five-coordinate Pd(II) complexes are described. Some of the complexes that have been obtained have shown spectra sufficiently explicit to elucidate their dynamic structures. However, firm evidence by low-temperature NMR measurement, to freeze the dynamic motions of the complexes, has not been obtained on account of insufficient solubility. The preparation of the formally threecoordinate complexes of Pd(II),  $[Pd(PR_2Ph)_3]$  $[BF_4]_2$  (R = Et or Ph), is also described.

#### **EXPERIMENTAL**

All the solvents were purified before use by distillation over  $CaCl_2$  (CH<sub>2</sub>Cl<sub>2</sub> or acetone) or Na (benzene or diethyl ether). Elemental analyses were performed by the Microanalytical Centre, Department of Pharmaceutical Science, Kyoto University. Spectrometers used for NMR studies are;<sup>1</sup>H NMR, JEOL-100;<sup>13</sup>C NMR, Hitachi R-900 (22.6 MHz);<sup>31</sup>P{<sup>1</sup>H} NMR, JEOL FX-90Q (36.25 MHz) and FX-200 (100.14 MHz), whose measurements were performed by the Applied Research Centre of NM, JEOL Ltd (Akishima). Electroconductivities were measured by a Denki Kagaku Keiki AO-6 instrument in dried acetone. Electronic spectra were obtained in a Hitachi 200-20 spectrometer. All reactions were carried out in air except for the preparation of  $[Pd(PPh_3)_4]X_2$  (X = BF<sub>4</sub> or PF<sub>6</sub>)<sup>14</sup> which was carried out *in vacuo* or under nitrogen. PMe<sub>2</sub>Ph and PEt<sub>2</sub>Ph were prepared by the literature procedure.<sup>16</sup>

Chlorotris(triphenylphosphine)palladium(II) complexes, [PdCl(PPh<sub>3</sub>)<sub>3</sub>]X · (CH<sub>3</sub>)<sub>2</sub>CO (X =  $BF_4^{15}$  or  $PF_6$ )

 $[Pd(PPh_3)_4][PF_6]_2 \cdot (CH_3)_2CO (0.3 g)$  was suspended in 30 cm<sup>3</sup> of acetone, and 0.2 g of t-BuCl in 3 cm<sup>3</sup> CH<sub>2</sub>Cl<sub>2</sub> was added to the solution with vigorous stirring. The suspension dissolved in an hour, and a small amount of a canary yellow solid precipitated. After being stirred overnight, the solution was filtered and the filtrate was reduced in volume to about 10 cm<sup>3</sup> under reduced pressure. Addition of diethyl ether to the solution gave a yellow solid, which was recrystallized from acetone containing roughly an equimolar quantity of PPh<sub>3</sub> to give pale yellow needles of an acetone solvate (0.13 g, 57%). Found : C, 59.8; H, 4.5; Cl, 3.0. Calc. for the empirical formula: C, 60.48; H, 4.54; Cl, 3.14%. IR (Nujol mull): v(CO) (acetone of solvation), 1707 cm<sup>-1</sup> (vs). Conductance (in acetone): Λм 117  $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ . The BF<sub>4</sub> salt was prepared analogously as an acetone or  $CH_2Cl_2$  solvate (98%). Found: C, 60.8; H, 4.5. Calc. for the empirical formula : C, 60.12; H, 4.61%. IR (Nujol mull) : v(CO) (acetone of solvation),  $1709 \text{ cm}^{-1}$  (vs). <sup>1</sup>H NMR [in  $(CD_3)_2SO$ :  $\delta_{CH_2}(CH_2Cl_2 \text{ of solvation})$ , 5.75 ppm (s). Conductance (acetone):  $\Lambda_{\rm M}$  144  $\Omega^{-1} \cdot {\rm cm}^2 \cdot {\rm mol}^{-1}$ . The  ${}^{31}P{}^{1}H$  NMR spectra (CDCl<sub>3</sub>) show the AB<sub>2</sub> spin system at 32.52 (triplet, 1P) and 29.76 (doublet, 2P) ppm relative to 85%  $H_3PO_4$  at 0.00:  $J_{P,P} =$ 15.65 Hz.

# $Tetrakis (dimethyl phenyl phosphine) palladium (II) tetrafluoroborate, [Pd(PMe_2Ph)_4][BF_4]_2$

 $[Pd(PPh_3)_4][BF_4]_2 \cdot (CH_3)_2CO$  (2.0 g) was suspended in 30 cm<sup>3</sup> of acetone, and an acetone solution of PMe<sub>2</sub>Ph (1.1 g) was added to the solution. The yellow mixture gradually dissolved to a pale orange homogeneous solution. The solvent was then removed under reduced pressure, giving an orange oil, which was washed with diethyl ether several times to remove liberated PPh<sub>3</sub> and residual PMe<sub>2</sub>Ph. The oil was crystallized from methanol-diethyl ether to give pale yellow crystals (0.8 g,

65%). Found: C, 46.6; H, 5.1; P, 14.1. Calc. for the empirical formula: C, 46.16; H, 5.33; P, 14.88%. Conductance (acetone):  $\Lambda_M$  224 Ω<sup>-1</sup> · cm<sup>2</sup> · mol<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR [(CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta_P$  – 5.96 ppm (s).

Tris(dimethylphenylphosphine)(1,10 - phenanthroline)palladium(II) tetrafluoroborate, [Pd(PMe<sub>2</sub>Ph<sub>3</sub> (phen)][BF<sub>4</sub>]<sub>2</sub>

 $[Pd(PMe_2Ph)_4][BF_4]_2$  (0.27 g) was dissolved in acetone (25 cm<sup>3</sup>) (partial suspension), and 0.14 g of phen monohydrate (phen  $\cdot$  H<sub>2</sub>O) was added to the suspension. The yellow mixture gradually dissolved, turning pale yellow, and a small amount of white solid precipitated. After 30 min, the solution was filtered and the solvent was removed under reduced pressure to give a yellow oil. The oil product was washed with 25 ml of diethyl ether to remove liberated PMe<sub>2</sub>Ph and dissolved into 5 cm<sup>3</sup> of methanol. The solution was then dropped into 100 cm<sup>3</sup> of *n*-hexane with vigorous stirring, when a vellow crystalline solid was formed. The product was recrystallized from acetone-ethanol (0.13 g, 82%). Found : C, 49.2; H, 4.8; N, 3.1. Calc. for the empirical formula: C, 49.43; H, 4.73; N, 3.20%.

The corresponding  $2,9-Me_2$ -phen complex, [Pd(PMe\_2Ph)\_3(2,9-Me\_2-phen)][BF\_4]\_2 was prepared analogously (54%). Found : C, 50.0; H, 5.2; N, 3.1. Calc. for the empirical formula : C, 50.56; H, 5.03; N, 3.10%.

Chlorobis(2,9 - dimethyl - 1,10 - phenanthroline)palla dium(II) hexafluorophosphate, [PdCl(2,9-Me<sub>2</sub>Ph)<sub>2</sub>] PF<sub>6</sub>

[PdCl(PPh<sub>3</sub>)<sub>3</sub>]PF<sub>6</sub> · (CH<sub>3</sub>)<sub>2</sub>CO (0.3 g) was dissolved in 3-pentanone (30 cm<sup>3</sup>), and 0.085 g of 2,9-Me<sub>2</sub>-phen ·  $\frac{1}{2}$ H<sub>2</sub>O was added to the solution. The yellow mixture slowly became homogeneous and turned orange, giving a small amount of yellow solid. The solution was then filtered, and the filtrate was warmed at 100°C for a few minutes to give brown crystals in insoluble in 3-pentanone (0.06 g, 26%). Found: C, 48.6; H, 3.8; N, 7.5. Calc. for [PdCl(2,9-Me<sub>2</sub>-phen)<sub>2</sub>]PF<sub>6</sub> ·  $\frac{1}{3}$ (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>CO: C, 48.67; H, 3.76; N, 7.65%. IR (Nujol mull): v(CO) (3-pentanone of solvation), 1710 cm<sup>-1</sup> (s). <sup>1</sup>H NMR [in (CD<sub>3</sub>)<sub>2</sub>SO]:  $\delta_{Me}$ (3-pentanone) 0.93 ppm (t);  $\delta_{CH_2}$ (3-pentanone) 2.40 ppm (q);  $J_{H,H'} = 7$  Hz.

 $\begin{array}{ll} Bis(1,10 - phenanthroline)(triphenylphosphine)palla - \\ dium(II) & tetrafluoroborate, & [Pd(PPh_3)(phen)_2] \\ [BF_4]_2 \cdot (CH_3)_2CO \end{array}$ 

The preparation of this complex and the  $PF_6^-$  salt have been described previously.<sup>14</sup>

[PdCl(PPh<sub>3</sub>)<sub>3</sub>]BF<sub>4</sub> · (CH<sub>3</sub>)<sub>2</sub>CO (0.2 g) was suspended in acetone (20 cm<sup>3</sup>), and 0.05 g of phen · H<sub>2</sub>O was added to the mixture. The suspension gradually dissolved, turning orange. After 30 min, the solution was reduced in volume to about 5 cm<sup>3</sup> under reduced pressure, and addition of diethylether to the solution gave orange crystals of an acetone solvate (91%). Found : C, 61.5; H, 4.2; H, 2.6; Cl, 3.6. Calc. for the empirical formula : C, 61.77; H, 4.47; N, 2.82; Cl, 3.58%. IR (Nujol mull):  $\nu$ (CO) (acetone of solvation), 1706 cm<sup>-1</sup> (s). The PF<sub>6</sub><sup>-</sup> salt was prepared analogously as orange crystals (96%). Found : C, 58.4; H, 3.8; N, 2.7; Cl, 3.3. Calc. for the empirical formula : C, 58.13; H, 3.86; N, 2.82; Cl, 3.58%.

## Chloro(triphenylphosphine)(trimethylphosphite)(1,10phenanthroline)palladium(II) tetrafluoroborate, [Pd $Cl(P(OMe)_3)(PPh_3)(phen)]BF_4$

[PdCl(PPh<sub>3</sub>)<sub>2</sub>(phen)]BF<sub>4</sub> · (CH<sub>3</sub>)<sub>2</sub>CO (0.19 g) was dissolved in 20 cm<sup>3</sup> of acetone, and 0.036 g of P(OMe)<sub>3</sub> was added to the solution. The orange solution turned pale yellow in a few minutes. The solution was then reduced in volume to  $10 \text{ cm}^3$  under reduced pressure, and addition of diethyl ether to the solution gave yellow crystals (0.13 g, 84%). Found : C, 49.6; H, 3.9; N, 3.7. Calc. for the empirical formula : C, 49.84; H, 4.06; N, 3.52%.

## Chlorobis(trimethylphosphite)(1,10 - phenanthroline) palladium(II) tetrafluoroborate, $[PdCl(P(OMe)_3)_2$ (phen)]BF<sub>4</sub>

[PdCl(PPh<sub>3</sub>)<sub>2</sub>(phen)]BF<sub>4</sub> · (CH<sub>3</sub>)<sub>2</sub>CO was suspended in 20 cm<sup>3</sup> of acetone containing 0.06 g of PPh<sub>3</sub>, and to the solution 0.1 g of P(OMe)<sub>3</sub> was added with vigorous stirring, when the orange solution turned off white via pale yellow. The solution was then reduced in volume to about 5 cm<sup>3</sup> under reduced pressure. Addition of diethyl ether to the solution gave a white solid. Recrystallization from ethanol and ether gave off white crystals (0.8 g, 38%). Found: C, 33.6; H, 3.9; N, 4.5. Calc. for the empirical formula: C, 32.90; H, 3.99; N, 4.26%.

Chloro(1,10 - phenanthroline)(triphenylphosphine) palladium(II) hexafluorophosphate, [PdCl(PPh<sub>3</sub>) (phen)]PF<sub>6</sub>

0.3 g of  $[PdCl(PPh_3)_3]PF_6 \cdot (CH_3)_2$  CO was suspended in 20 cm<sup>3</sup> of 3-pentanone and an acetone

solution of phen  $\cdot$  H<sub>2</sub>O (0.08 g) was added to the suspension. The mixture slowly dissolved and a yellow solid gradually precipitated. The yellow powder obtained was then filtered and washed with acetone and diethyl ether (0.13 g, 66%). Found : C, 49.1; H, 3.3; N, 3.8. Calc. for the empirical formula : C, 49.40; H, 3.18; N, 3.84%.

Chlorobis(triphenylphosphine)(2,9 - dimethyl - 1,10 phenanthroline)palladium(II) tetrafluoroborate, [Pd Cl(PPh<sub>3</sub>)<sub>2</sub>(2,9-Me<sub>2</sub>-phen)]**BF<sub>4</sub>** · (CH<sub>3</sub>)<sub>2</sub>CO

This complex was prepared by an analogous procedure to the corresponding 1,10-phen complex. Recrystallization from warm ethanol-acetone gave an orange crystal of an acetone solvate. Found: C, 62.5; H, 4.8; N, 2.8. Calc. for the empirical formula: C, 62.43; H, 4.75; N, 2.75%. IR (Nujol mol):  $\nu$ (CO) (acetone of solvation), 1713 cm<sup>-1</sup> (s). Yield 94%. The PF<sub>6</sub> salt was prepared analogously (64%). Found: C, 59.3; H, 4.8; N, 2.4. Calc. for the empirical formula: C, 59.06; H, 4.49; N, 2.60%. IR (acetone of solvation):  $\nu$ (CO) (acetone of solvation), 1709 cm<sup>-1</sup>.

Tris(triphenylphosphine)palladium(II) tetrafluoroborate, [Pd(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub>

[PdCl(PPh<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>] · (CH<sub>3</sub>)<sub>2</sub>CO was dissolved in 30 cm<sup>3</sup> of  $CH_2Cl_2$ , and an acetone solution of  $AgBF_4(0.14 g)$  was added to the solution. The yellow solution on addition of AgBF<sub>4</sub> turned canary yellow and AgCl precipitated. The solution was filtered after an hour and the filtrate was reduced in volume to about 10 cm<sup>3</sup> under reduced pressure. Addition of diethyl ether to the solution gave a canary yellow powder, which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>diethyl ether giving canary yellow crystals (0.4 g, 56%). Found: C, 55.9; H, 4.0. Calc. for  $[Pd(PPh_3)_3][BF_4]_2 \cdot \frac{3}{2}(CH_2Cl_2): C,$ 55.81; H. 4.05%. Conductance (acetone):  $\Lambda_{M}$ 234  $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ . <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  38.94 (1P) and 37.86 (2P) ppm. The structure of this complex is uncertain, but may resemble  $[Rh(PPh_3)_3]BF_4.$ 

#### Tris(diethylphenylphosphine)palladium(II) tetrafluoroborate, [Pd(PEt<sub>2</sub>Ph)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub>

 $PdCl_2(PEt_2Ph)_2$  (2 g) was suspended in 50 cm<sup>3</sup> of acetone, and 0.66 g of  $PEt_2Ph$  was added to the suspension as the yellow mixture dissolved to the deep orange of  $PdCl_2(PEt_2Ph)_3$ .<sup>8</sup> An acetone solution of AgBF<sub>4</sub> (1.57 g) was then added to the solution, when AgCl precipitated. After 10 min, a white precipitate AgCl was filtered, and the solvent was removed under reduced pressure to give a dark yellow oil. The oil was dissolved in methanol (15 cm<sup>3</sup>), and the solution was dropped into diethyl ether (150 cm<sup>3</sup>) with vigorous stirring, giving a yellow solid. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether to give deep yellow crystals (1.51 g, 43%). Found: C, 41.8; H, 5.4; P, 10.5. Calc. for [Pd(PEt<sub>2</sub>Ph)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub>  $\cdot \frac{3}{2}$ (CH<sub>2</sub>Cl<sub>2</sub>): C, 41.75; H, 5.34; P, 10.26%. Conductance (acetone):  $\Lambda_{\rm M}$  186  $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ .  ${}^{31}\text{P}{}^{1}\text{H}$  NMR [(CD<sub>3</sub>)<sub>2</sub>CO)] of this complex shows three resonances at 36.30 (1P, broad singlet), 32.41 (1P, doublet) and 27.78 (1P, doublet) ppm with a formal  $J_{\rm P,P}$  of the latter two of 13.7 Hz <sup>19</sup>F NMR [(CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$  -149.4 ppm (relative to CFCl<sub>3</sub> at 0.00). Further details about this complex are now under investigation.

Bis(diethylphenylphosphine)(1,10 - phenanthroline) palladium(II) tetrafluoroborate,  $[Pd(PEt_2Ph)_2 (phen)][BF_4]_2$ 

The deep yellow solution of

$$[Pd(PEt_2Ph)_3][BF_4]_2$$

[amount of the precursor, PdCl<sub>2</sub>(PEt<sub>2</sub>Ph)<sub>2</sub>, 1.58 g], in acetone was bubbled through with CO for 30 min, while it turned orange. The solution was then added to phen  $\cdot$  H<sub>2</sub>O (0.62 g) to give grey crystals of [Pd(phen)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>. The solution was filtered and the solvent of the filtrate was removed under reduced pressure to give a deep green oil. The oil product was dissolved in ethanol, partially giving black Pd metal. After separation of the solid, addition of ethyl ether to the solution gave deep yellow prisms. Found : C, 48.4; H, 5.1; N, 3.3. Calc. for the empirical formula : C, 48.49; H, 4.83; N, 3.53%. Conductivity (acetone):  $\Lambda_{\rm M}$  294  $\Omega^{-1} \cdot {\rm cm}^2 \cdot {\rm mol}^{-1}$ . <sup>31</sup>P{<sup>1</sup>H} NMR [(CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$  33.00 ppm (s).

#### **RESULTS AND DISCUSSION**

<sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR and conductivity data of [Pd(PMe<sub>2</sub>Ph)<sub>3</sub>(2,9-R<sub>2</sub>-phen)][BF<sub>4</sub>]<sub>2</sub> (R = H or Me) are shown in Fig. 1 and Table 1. The <sup>31</sup>P NMR spectrum of the phen complex explicitly shows the typical AB<sub>2</sub> spin system : the <sup>31</sup>P doublet appears at a higher field than the <sup>31</sup>P triplet with  $J_{P,P} = 22.79$  Hz. In contrast, for the 2,9-Me<sub>2</sub>-phen complex the relative positions are reversed and its <sup>31</sup>P-<sup>31</sup>P coupling constant (20.34 Hz) is close to that of the phen complex.

In the five-coordinate Pd(II) and Pt(II) complexes so far studied,  $PdX_2(PMe_3)_3$  (X = Br or I),<sup>10</sup>  $[M(P(OMe)_3)_5]^{2+}$  (M = Pd or Pt)<sup>1</sup> and  $PtX_2L_3$  (X = Cl, Br and I; L = 1-R-3,4-dimethylphosphole),<sup>11</sup>



Fig. 1. <sup>31</sup>P NMR of: (A)  $[Pd(PMe_2Ph)_3(phen)][BF_4]_2$ , and (B)  $[Pd[PMe_2Ph)_3(2,9-Me_2-phen)][BF_4]_2$  in  $(CD_3)_2CO$ .

axial phosphines or phosphites always appear at a higher field than equatorial ones, whereas, in the corresponding Ni(II) complexes, NiX<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub> (X = CN or Br)<sup>2</sup> and [Ni{P(OMe)<sub>3</sub>}<sub>5</sub>]<sup>2+,1</sup> the relative shifts are reversed. On the other hand, in the tetragonal pyramidal PdCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub><sup>10</sup> with one chloride atom in the axial position, the <sup>31</sup>P doublet appears at a higher field than the <sup>31</sup>P triplet with a larger  $J_{P,P}$  than those of the corresponding bromide and iodide complexes.

These estimations for the previous works may be referred to the present case. The NMR spectrum of  $[Pd(PMe_2Ph)_3(2,9-R_2-phen)][BF_4]_2$  (R = H or Me) accordingly fits two idealized structures with one trigonal bipyramid (A or C) and one tetragonal pyramid (B or D) as shown in Fig. 2.

<sup>1</sup>H NMR of  $[Pd(PMe_2Ph)_3(2,9-Me_2-phen)]$  $[BF_4]_2$  shows an equivalency of the two nitrogen atoms of the N-heterocyclic ligand, which corresponds to either fluxional motion of the ligand or a symmetrical environment around its halves. In addition, relatively large <sup>1</sup>H NMR downfield shifts for 2,9- and 3,8-protons of the N-heterocyclic ligand upon coordination have been observed: 0.84 and 0.45 ppm for the phen complex and 0.95 and 0.47 ppm for the 2,9-Me<sub>2</sub>-phen complex, respectively. The coupling pattern of 3,4(7,8)-protons in the 2,9-Me<sub>2</sub>phen complex turns out to be an AB quartet  $[J_{A,B}/(\delta_A - \delta_B) = 0.2]$ . These downfield shifts for the corresponding protons of the N-heterocyclic ligand upon coordination are due to paramagnetic anisotropy of the metal.<sup>17</sup> It should also be noticed that in a seldom ion pair complex, [Pd(PEt<sub>2</sub>Ph)<sub>2</sub>(phen)][BF<sub>4</sub>]<sub>2</sub>, such a coordination shift of the phen has not been obtained but, rather, a higher field shift, particularly for its 2,9-protons.

|   |   |                          |                   |             |                                     |                 |               |               | *                  |                        | 4                   |           |
|---|---|--------------------------|-------------------|-------------|-------------------------------------|-----------------|---------------|---------------|--------------------|------------------------|---------------------|-----------|
|   |   | N                        | -heterocy         | clic ring ( | ð) <sup>e</sup>                     |                 | $J_{\rm H,H}$ |               | PR <sub>2</sub> Ph | $(\delta)^{cd}$ (R = M | le or Et)           |           |
| Complex   | awv   | 2,9-R                    | 4,7-H             | 3,8-H       | 5,6-H                               | $J_{2,3}^{2,3}$ | J2.4<br>(7.9) | J3,4<br>(7,8) | Ring<br>proton     | Methyl<br>proton       | Methylene<br>proton | [1] (H,H) |
| Phen <sup>e</sup>   |   | 9.12                     | 8.48              | 7.76        | 8.00                                | 4.5             | 1.5           | 8.0           |                    |                        |                     |           |
| 2,9-Me <sub>2</sub> -phen   |   | 2.80                     | 8.33              | 7.58        | 7.83                                |                 |               | 7.5           |                    |                        |                     |           |
| [Pd(PMe <sub>2</sub> Ph) <sub>3</sub> (phen)][BF <sub>4</sub> ] <sub>2</sub>  | 300   | 96.6                     | 8.78              | 8.21        | 8.08                                | 5.5             | 2.0           | 8.0           | 7.75 (m)           | 2.18 (bd)              |                     |           |
|   |   |                          |                   |             |                                     |                 |               |               | 7.03 (m)           | 1.38 (bs)              |                     |           |
| [Pd(PMe <sub>2</sub> Ph) <sub>3</sub> (2,9-Me <sub>2</sub> -phen)][BF <sub>4</sub> ] <sub>2</sub>   | 278   | 3.75                     | 8.45              | 8.05        | 7.68                                |                 |               | 8.0           | 7.80 (m)           | 2.47 (d)               |                     | 9.0       |
|   |   |                          |                   |             |                                     |                 |               |               | 6.46 (m)           | 1.63 (t)               |                     | 5.0       |
| [Pd(PEt2Ph)2(phen)][BF4]2   | 294   | 8.94                     | 8.94              | ł           | 8.29                                |                 |               |               | 8.04 (m)<br>7.56   | 1.24 (m)               | 2.54 (m)            |           |
| <sup>a</sup> Satisfactory relative intensities for each ${}^{b}$ Conductivity ( $\Omega^{-1} \cdot \operatorname{cm}^{2} \cdot \operatorname{mol}^{-1}$ ) of ca 1 ${}^{c}$ Chemical shifts are relative to Me.Si at | complexes cc<br>[0 <sup>-3</sup> M aceto<br>0.00. | ould be ob<br>me solutio | tained : m<br>ns. | casured i   | n (CD <sub>3</sub> ) <sub>2</sub> C | <u>o</u>        |               |               |                    |                        |                     |           |
| <sup>d</sup> m, multiplet; d, doublet; t, triplet due to<br>* Measured in $(CD_{3})_{2}SO$ .  | 0  J <sub>P,H</sub> +J <sub>P,H</sub>             | ; s, singlet             | ; bd, bros        | ad double   | t; bs, broa                         | ıd singlet.     |               |               |                    |                        |                     |           |

Table 1. <sup>1</sup>H NMR<sup>*a*</sup> and conductivity data of [Pd(PMe<sub>2</sub>Ph)<sub>3</sub>(2,9-R<sub>2</sub>-phen)][BF<sub>4</sub>]<sub>2</sub> (R = H or Me) and [Pd(PEt<sub>2</sub>Ph)<sub>2</sub>(phen)][BF<sub>4</sub>]<sub>2</sub>

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Fig. 2. Possible structures of  $[Pd(PMe_2Ph)_3(2,9-R_2-phen)][BF_4]_2$ .

Some physical properties of  $[PdCl(PPh_3)_2(2,9-R_2-phen)]X$  (R = H or Me; X = BF<sub>4</sub> or PF<sub>6</sub>) are given in Table 2.

The conductivity data of the complexes evidently indicate that dissociation of Cl or association of the anion does not occur in acetone solution.

<sup>31</sup>P NMR spectral data of the complexes show a single resonance, which is consistent with an equivalency of the two PPh<sub>3</sub> ligands. <sup>1</sup>H NMR spectra of them also show an equivalency of the two nitrogen atoms of the N-heterocyclic ligand. These NMR data indicate either symmetrical environments around both the phosphines and the halves of the N-heterocyclic ligand or a rapid dynamic motion which may average the respective nuclei equivalently. Low-temperature NMR data could not be obtained on account of the insufficient solubility of the complexes. Any fluxional motion of  $[PdCl(PPh_3)_2(2,9-Me_2-phen)]X (X = BF_4 \text{ or } PF_6),$ however it might occur, will be expected to be considerably restricted because of the steric crowdedness of the ligand compared to the corresponding phen complex.

The visible spectrum of  $[PdCl(PPh_3)_2(phen)]PF_6$ is shown in Fig. 3, together with those of squareplanar complexes,  $[PdCl(PPh_3)(phen)]PF_6$  and  $[Pd(PEt_2Ph)_2(phen)][BF_4]_2$ . The spectrum of  $[PdCl(PPh_3)_2(phen)]PF_6$  (quite analogous to that of the  $BF_4^-$  salt) with two electronic transitions at 355 and 338 nm unexpectedly shows a marked resemblance to those of the square-planar complexes, the absorptions of which may be concerned with charge-transfer bands  $(M \rightarrow L \text{ or } L \rightarrow M)^8$ possibly combined with a  $d \rightarrow d$  transition.<sup>18</sup> Any characteristic absorption bands previously found for five-coordinate Pt(II) and Pd(II)<sup>19</sup> complexes have not been observed in the longer-wavelength region for the present case, and the  $d \rightarrow d$  transition has not been resolved.

Direct evidence of the solution structure of  $[PdCl(PPh_3)_2(phen)]PF_6$  has been minor. However, the electronic spectral data of the complex seem indicative that the geometry in solution is likely close to a square-planar conformation in which one nitrogen atom of the phen might be approaching to the coordination sphere from the fifth or sixth apical site of the coordination plane. The fluxional motion of the complex is accordingly explained as a rapid oscillation of the phen as observed in Pd(dmp)(2,9-Me\_2-phen)(NO\_3) (dmp = N,N-dimethylbenzyl-amine).<sup>20</sup>

On the other hand, the visible spectrum of  $[PdCl(PPh_3)_2(2,9-Me_2-phen)]PF_6$  is, as expected, different from that of the corresponding phen complex and it shows a broad and intensive electronic transition at 360 nm which is most probably caused by five coordination.

 $[PdCl(PPh_3)_2(phen)]PF_6$  did not convert to  $[PdCl(PPh_3)(phen)]PF_6$  but was recovered whether it had been warmed in acetone or in ethanol solution. The reaction of  $[PdCl(PPh_3)_2(phen)]BF_4$  with  $P(OMe)_3$  proceeds via a successive displacement of  $PPh_3$  by  $P(OMe)_3$  to give

[PdCl{P(OMe)<sub>3</sub>}(PPh<sub>3</sub>)(phen)]BF<sub>4</sub>

and

$$[PdCl{P(OMe)_3}_2(phen)]BF_4$$

The <sup>1</sup>H NMR spectra of both phosphite complexes similarly show an equivalency between the two nitrogen atoms of the phen. The <sup>1</sup>H NMR of the bisphosphite complex shows two doublets due to Meprotons of the  $P(OMe)_3$  ligand, which is consistent with two mutually *cis*- $P(OMe)_3$ . The <sup>1</sup>H NMR coordination shifts for 2,9-protons of the phen have been obtained in these cases; 0.60 ppm for the bisphosphite complex and 0.53 ppm for the monophosphite complex.

The visible spectral data for the phosphite complexes are shown in Table 3, together with the other complexes that I have obtained. The spectra of the phosphite complexes, analogously to the bisphosphine complex, resemble considerably those of the square-planar complexes. Consequently, the solution structure of the bis-phosphite complex, is likely tetragonal pyramid, possibly approaching a square-planar conformation in which the two  $P(OMe)_3$  are *cis.* The solution structure of the mono-phosphite complex (pale yellow) may be analogous to the bisphosphite complex, while an enantiomer of this complex is uncertain.

|  |                     | \$(N-1     | <sup>1</sup> H N<br>neterocycl | MR <sup>b</sup><br>ic ring pr | oton) |                  |                  |                  | P(OI            | Me) <sub>3</sub> | {H1}d16              | NMR€                     | NN H <sup>91</sup>    | ١R  |
|--|---------------------|------------|--------------------------------|-------------------------------|-------|------------------|------------------|------------------|-----------------|------------------|----------------------|--------------------------|-----------------------|---|
| Complex  | $\Lambda_{M}{}^{a}$ | 2,9-R      | 4,7-H                          | 5,6-H                         | 3,8-H | J <sub>2,3</sub> | J <sub>2,4</sub> | J <sub>3,4</sub> | б <sub>Ме</sub> | J <sub>P,H</sub> | $\delta_{\rm PPh_3}$ | $\delta_{\mathrm{PF}_6}$ | $\delta_{\mathbf{F}}$ | J <sub>P.F</sub>  |
| PdCl(PPh <sub>3</sub> ),(phen)]BF <sub>4</sub>   | 167                 | 9.20       | 8.73                           | 8.12                          | 7.84  | 4.8              | 1.3              | 8.4              |                 |                  | 16.56                |                          | -218.76               |   |
| PdCl(PPh <sub>a</sub> ) <sub>2</sub> (phen)]PF,  | 152                 | 9.41       | 8.60                           | 7.99                          | 7.80  | 5.3              | 2.0              | 8.8              |                 |                  | 17.63                | - 145                    | -67.69                | 708   |
| PdCl(P(OMe) <sub>3</sub> )(PPh <sub>3</sub> )(phen)]BF <sub>4</sub>                                  | 152                 | 9.65       | 8.65                           | 8.05                          | 7.94  | 6.0              | 2.0              | 8.8              | 3.78            | 10.0             |                      |                          |                       |   |
| [PdCl(P(OMe) <sub>3</sub> ) <sub>2</sub> (phen)]BF <sub>4</sub>                                      |                     | 9.72       | 8.96                           | 8.25                          | 8.05  | 5.0              |                  | 9.0              | (4.08<br>3.74   | 11.0             |                      |                          |                       |   |
| PdCl(PPh <sub>3</sub> ) <sub>2</sub> (2,9-Me <sub>2</sub> -phen)]BF <sub>4</sub>                     | 159                 | 2.95       | 8.25                           | 7.78                          | •     |                  |                  | 6.7              | ,               |                  | 14.40                |                          |                       |   |
| PdCl(PPh <sub>3</sub> ) <sub>2</sub> (2,9-Me <sub>2</sub> -phen)]PF <sub>6</sub>                     | 153                 | 2.94       | 8.23                           | 7.78                          | °     |                  |                  | 7.0              |                 |                  | 11.04                |                          |                       |   |
| $PdCl(2,9-Me_2-phen)_2]PF_6$   |                     | 2.79       | 8.78                           | 8.20                          | 7.90  |                  |                  | 8.0              |                 |                  |                      |                          |                       |   |
| <sup>a</sup> Conductivity ( $\Omega^{-1} \cdot \mathrm{cm}^2 \cdot \mathrm{mol}^{-1}$ ) of <i>ca</i> | $10^{-3}$ M aceto   | ne solutio |                                |                               |       |                  |                  |                  |                 |                  |                      |                          |                       | and a local second s |

Table 2. NMR and conductivity data

<sup>a</sup> Conductivity  $(\Omega^{-1} \cdot \mathrm{cm}^2 \cdot \mathrm{mol}^{-1})$  of ca  $10^{-3}$  M acetone solution. <sup>b</sup> Measured in  $(\mathrm{CD}_3)_2\mathrm{CO}$ . Chemical shifts are relative to  $\mathrm{Me}_4\mathrm{Si}$  at 0.00. <sup>c</sup> Measured in  $(\mathrm{CD}_3)_2\mathrm{SO}$ . Chemical shifts are relative to  $\mathrm{H}_3\mathrm{PO}_4$  at 0.00. <sup>d</sup> Measured in  $(\mathrm{CD}_3)_2\mathrm{SO}$ . Chemical shifts are relative to  $\mathrm{CFCl}_3$  at 0.00. <sup>e</sup> Obscured owing to overlapping with the resonances of PPh<sub>3</sub>. <sup>f</sup> Measured in  $(\mathrm{CD}_3)_2\mathrm{SO}$ .



Fig. 3. Visible spectra of : (A)  $[PdCl(PPh_3)(phen)]PF_6$ , (B)  $[PdCl(PPh_3)_2(phen)]PF_6$ , and (C)  $[Pd(PEt_2Ph)_2$  $(phen)][BF_4]_2$ .

The <sup>1</sup>H NMR of  $[Pd(PPh_3)(phen)_2][PF_6]_2$  and  $[PdCl(2,9-Me_2-phen)_2]PF_6$  show that all four nitrogen atoms of the two *N*-heterocyclic ligands are equivalent, which corresponds to fluxional motion.

For  $[Pd(PPh_3)(phen)_2][PF_6]_2$ , there are <sup>1</sup>H NMR signals broadening below - 50°C and even at -100°C no sharp limiting spectrum could be obtained, while, on addition of free phen to  $[Pd(PPh_3)(phen)_2][PF_6]_2$  at room temperature, signal broadening is observed with a pattern similar to that obtained at lower temperatures and no separate signals could be obtained. These <sup>1</sup>H NMR spectral data of  $[Pd(PPh_3)(phen)_2][PF_6]_2$  may suggest that inter- or intramolecular exchange of phen readily occurs.

An intramolecular ligand rearrangement system of this type of five-coordinate complexes has so far been proposed in which the fluxional motion of  $[Pt(CN)(phen)_2]NO_3$  has been explained by pseudorotation with a trigonal-bipyramid trans-



 $L_1 = L_3 = P(OMe)_3; L_1 = Cl$  $L_2 = PPh_3; L_3 = P(OMe)_3; L_1 = Ct$ 

ition state, while that of

 $[M(hfac)_{2}{P(o-tolyl)_{3}}] (M = Pd \text{ or } Pt;$ hfac = 1,1,1,5,5,5-hexafluoroacetylacetone)<sup>21</sup>

has been best rationalized by two rapid equilibria of twist motion and concurrent oscillation. For both cases, the mechanism of the fluxional motions has noticeably been proposed not to be dissociative, since the <sup>195</sup>Pt satellite has been observed.

The fluxional motion of the present complexes is sufficiently explained by two synchronous rearrangement systems as proposed for [Pd(hfac)<sub>2</sub>{P(o $tolyl_{3}$ : one is a rapid oscillation of the apical phen which may result to average its two nitrogen atoms and the other is a twist motion of the square pyramid which may average the environments between the two N-heterocyclic ligands equivalently as shown in Scheme 1. The visible spectral data of  $[Pd(PPh_3)(phen)_2][PF_6]_2$  and  $[PdCl(2,9-Me_2-Me_3)(phen)_2][PF_6]_2$ phen)<sub>2</sub>]PF<sub>6</sub> similarly show three absorption maxima, two of which are at 338-360 nm, with a resemblance to those of square-planar complexes, and the latter at 400-430 nm is now comparable with the characteristic absorptions of PdX<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>  $(X = Cl \text{ or } Br)^8$  at 410-444 nm. It is roughly indicated from these spectral data that the solution structure of  $[PdY(2,9-R_2-phen)_2][PF_6]_{1 \text{ or } 2}$  (Y =  $PPh_3$  or Cl; R = H or Me) is tetragonal pyramid with one nitrogen atom of the phen possibly at the

| Table  | 3  | Flectronic  | enectral | data in | visible | region |
|--------|----|-------------|----------|---------|---------|--------|
| 1 4010 | 5. | Clock offic | spoona   | uata m  | 131010  | region |

| Complex  |                     | $\lambda_{\max}\left(arepsilon ight)$ |            |
|--|---------------------|---------------------------------------|------------|
| $[PdCl(PPh_3)_2(phen)]X (X = BF_4 \text{ or } PF_6)$                 | 338 (4840)          | 355 (4560)                            |            |
| [PdCl(P(OMe) <sub>3</sub> )(PPh <sub>3</sub> )(phen)]BF <sub>4</sub> | 338 (3750)          | 355 (2500)                            |            |
| $[PdCl(P(OMe)_3)_2(phen)]BF_4$                                       | 338 (2210)          | 355 (1080)                            |            |
| $[PdCl(PPh_3)_2(2,9-Me_2-phen)]X (X = BF_4 \text{ or } PF_6$         | 5)                  | 360 (19,500, br)                      |            |
| [PdCl(PPh <sub>3</sub> )(phen)]PF <sub>6</sub>                       | 338 (8200)          | 355 (7290)                            |            |
| $[Pd(PEt_2Ph)_2(phen)][BF_4]_2$                                      | 338 (3290)          | 355 (2840)                            |            |
| $[Pd(PMe_2Ph)_3(phen)][BF_4]_2$                                      | 347 (3195, sh)      | 385 (841)                             |            |
| $[Pd(PMe_2Ph)_3(2,9-Me_2-phen)][BF_4]_2$                             | 325 (23,800, br sh) | , ,                                   | 412 (1060) |
| [PdCl(2,9-Me <sub>2</sub> -phen) <sub>2</sub> ]PF <sub>6</sub>       | 340 (3195, sh)      | 360 (2330)                            | 400 (940)  |
| $[Pd(PPh_3)(phen)_2]X_2 (X = BF_4 \text{ or } PF_6)$                 | 338 (5000, sh)      | 355 (3690)                            | 430 (540)  |



apical position. Thus, the proposed fluxional behaviour of these complexes is based on the crystal structure of  $[Pt(CN)(phen)_2]NO_3^9$  with a distorted square pyramid.

Acknowledgement—I am grateful to Dr K Hata (JEOL Ltd) for obtaining  ${}^{31}P{}^{1}H{}FT$ ,  ${}^{19}F$  and  ${}^{1}HFT$  NMR spectra.

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