# Methylplatinum(II) complexes containing <br> 2-(diphenylphosphino) pyridine ( $\mathbf{P h}_{2} \mathbf{P p y}$ ). <br> Crystal and molecular structure of $\left[\mathbf{P t M e}\left(\boldsymbol{\eta}^{2}-\mathbf{P h}_{\mathbf{2}} \mathbf{P p y}\right)\left(\mathbf{P h}_{\mathbf{2}} \mathbf{P p y}\right)\right]\left[\mathrm{BPh}_{4}\right]$ 

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#### Abstract

The reaction of [ $\mathrm{PtMeX}(\mathrm{COD})]$ with 2-(diphenylphosphino)pyridine $\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)$ in $1: 2$ stoichiometry yields [ $\mathrm{PtMeX}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}$ ] $(\mathrm{X}=\mathrm{Me}, \mathrm{Ia} ; \mathrm{Cl}, \mathrm{Ib}$; or I, Ic). Reaction of $[\mathrm{PtMeCl}(\mathrm{COD})]$ with one equivalent of $\mathrm{Ph}_{2} \mathrm{Ppy}$ gives the dinuclear complex $\left[\mathrm{PtMeCl}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]_{2}$ (II). Several reactions of Ib have been studied. Treatment of Ib with NaY gives the cationic complexes $\left[\mathrm{PtMe}\left(\eta^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right][\mathrm{Y}]\left(\mathrm{Y}=\mathrm{BPh}_{4}\right.$, Id or $\mathrm{BF}_{4}$, 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), $b 14.240(8), c 18.368(6) \AA, \alpha 80.93(4), \beta$ $74.60(3), \gamma 89.23(5)^{\circ}$. The platinum atom has square planar geometry. The phosphorus atom of the chelated phosphine is trans to the methyl group


## Introduction

2-(Diphenylphosphino)pyridine $\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)^{* *}$ 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

[^0]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 $\mathrm{Ph}_{2} \mathrm{Ppy}$ ligand has received little attention. In the present work, we have synthesized a number of methylplatinum(II) complexes containing $\mathrm{Ph}_{2} \mathrm{Ppy}$ and describe some of their reactions.

## Results and discussion

Reaction of [PtMeX(COD)] ( $\mathrm{X}=\mathrm{Me}, \mathrm{Cl}, \mathrm{I}$ ) with 2-(diphenylphosphino)pyridine ( $\mathrm{Ph}_{2} \mathrm{Ppy}$ ) in $1: 2$ stoichiometry in dichloromethane afforded the mononuclear complexes $\left[\mathrm{PtMeX}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right]\left(\mathrm{X}=\mathrm{Me}, \mathrm{Ia} ; \mathrm{Cl}, \mathrm{Ib}\right.$ or I, Ic). The ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ 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 ${ }^{1} \mathrm{H}$ NMR spectrum is complex in the $\mathrm{Pt}-\mathrm{Me}$ region owing to an $\mathrm{AA}^{\prime} \mathbf{M X}_{3} \mathrm{X}_{3}^{\prime}$ spin system, we have not calculated cis and trans ${ }^{3} J(\mathrm{Pt}-\mathrm{H})$ couplings. The ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ NMR spectra of Ia were similar to those reported for the symmetrical dimethyl platinum complexes, cis-[PtMe $\left.{ }_{2}\left(\mathrm{PR}_{3}\right)_{2}\right][8,9]$.

The platinum methyl resonance for Ib and Ic displayed a triplet pattern, because of coupling with the two equivalent ${ }^{31} \mathrm{P}$ nuclei, with platinum satellites. In the ${ }^{31} \mathrm{P}$ NMR spectra a single line with platinum satellites was observed with ${ }^{1} J(\mathrm{Pt}-\mathrm{P})$ similar to that observed for trans-[ $\mathrm{PtMeCl}\left(\mathrm{PR}_{3}\right)_{2}$ ] 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 $\left[\mathrm{PtX}_{2}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right](\mathrm{X}=\mathrm{C}$ or I$)$ [4].

The reaction of [ $\mathrm{PtMeCl}(\mathrm{COD}$ )] 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 $\left[\mathrm{PtMeCl}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]$ which is possibly dimeric, like $\left.\left[\mathrm{Pt}_{2} \mathrm{Cl}_{2} \mathrm{Me}_{2}(\mu \text {-dppm })_{2}\right)\right]$ [12]. The IR spectrum of the complex II shows a band at $285 \mathrm{~cm}^{-1}$ attributable to $\nu(\mathrm{Pt}-\mathrm{Cl})$ [3]. A similar reaction between $[\mathrm{PtPhCl}(\mathrm{COD})]$ and bulky phosphine ligands such as tricyclohexylphosphine in a $1: 1$ stoichiometry gives exclusively the dinuclear complex $\left[\mathrm{Pt}_{2} \mathrm{Ph}_{2}(\mu-\mathrm{Cl})_{2}\left(\mathrm{PR}_{3}\right)_{2}\right]$ [13], for which two $\mathrm{Pt}-\mathrm{Cl}$ stretchings in the region $250-300 \mathrm{~cm}^{-1}$ have been reported [14].

The reaction of Ib with one equivalent of NaY in a methanol/dichloromethane mixture yielded the cationic complexes $\left[\mathrm{PtMe}\left(\eta^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right][\mathrm{Y}]\left(\mathrm{Y}=\mathrm{BPh}_{4}\right.$, $\mathrm{Id} ; \mathrm{BF}_{4}$, Ie). The ${ }^{1} \mathrm{H}$ NMR spectrum of Id shows a doublet for the $\mathrm{Pt}-\mathrm{Me}$ protons which is further split into a doublet of smaller couplings. The cis and trans ${ }^{3} J(\mathrm{P}-\mathrm{Pt}-\mathrm{C}-\mathrm{H})$ couplings have been clearly resolved; the cis couplings are smaller $(2.3 \mathrm{~Hz})$ than the trans $(7.9 \mathrm{~Hz})$. The ${ }^{31} \mathrm{P}$ NMR spectrum of the cation, Id or Ie, consists of two resonances each with platinum satellites (Table 1). The smaller coupling ${ }^{2} J(P-P t-P) 12 \mathrm{~Hz}$, indicates a cis disposition of phosphine ligands. The trans ${ }^{2} J(\mathbf{P}-\mathbf{P t}-\mathbf{P})$ coupling is usually large - a few hundred hertz - whereas the cis couplings are small [9]. ${ }^{2} J(\mathbf{P}-\mathrm{Pt}-\mathrm{P})$ coupling has not been observed for the complex $\left[\mathrm{PtCl}\left(\eta^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]^{+}[8]$. Of the two ${ }^{31} \mathrm{P}$ NMR resonances, the one at lower
Table 1
Physical, analytical, ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left({ }^{1} \mathrm{H}\right\}$ NMR spectra data for methylplatinum(II) complexes containing 2-(diphenylphosphino)pyridine

| Complex | ${ }^{1} \mathrm{H}$ NMR (ppm) |  | ${ }^{31} \mathrm{P}$ NMR (ppm) | Recrystallisation solvent, yield (\%) | $\begin{aligned} & \text { m.p. } \\ & \left({ }^{\circ} \mathrm{C}\right) \end{aligned}$ | Analysis <br> Found (Calcd.) (\%)) |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\overline{\mathrm{Pt}}$-Me |  | Pt-P |  |  | C | H | N |
| $\mathrm{Ph}_{2} \mathrm{Ppy}$ |  |  | -3.95 |  |  |  |  |  |
| $c i s-\left[\mathrm{PtMe}_{2}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right]$ <br> (1a) | 0.44 | ${ }^{2} J(\mathrm{Pt}-\mathrm{H}) 69.5 \mathrm{~Hz}$ | $27.3{ }^{1} \mathrm{~J}(\mathrm{Pt}-\mathrm{P}) 1875 \mathrm{~Hz}$ | benzene/hexane 83 | 198-200 | $\begin{gathered} 57.85 \\ (57.52) \end{gathered}$ | $\begin{gathered} 4.54 \\ (4.56) \end{gathered}$ | $\begin{gathered} 3.71 \\ (3.73) \end{gathered}$ |
| trans-[ $\left.\mathrm{PtMeCl}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right]$ <br> (Ib) | -0.11 | $\begin{aligned} & { }^{2} J(\mathrm{Pt}-\mathrm{H}) 80 \mathrm{~Hz} ; \\ & { }^{3} J(\mathrm{P}-\mathrm{H}) 6.3 \mathrm{~Hz} \end{aligned}$ | $22.0{ }^{1} \mathrm{~J}(\mathrm{Pt}-\mathrm{P}) 3157 \mathrm{~Hz}$ | dichloromethane, 80 | 258-260 | $\begin{gathered} 55.01 \\ (54.44) \end{gathered}$ | $3.74$ (4.05) | $3.75$ |
| trans-[ $\left.\mathrm{PtMel}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right]$ <br> (Ic) | 0.06 | $\begin{aligned} & { }^{2} J(\mathrm{Pt}-\mathrm{H}) 77 \mathrm{~Hz} ; \\ & { }^{3} J(\mathrm{P}-\mathrm{H}) 7 \mathrm{~Hz} \end{aligned}$ | $25.9{ }^{1} \mathrm{~J}(\mathrm{Pt}-\mathrm{P}) 3091 \mathrm{~Hz}$ | Benzene/hexane 78 | 253-258 (dec. with melting) | $\begin{gathered} 47.94 \\ (48.68) \end{gathered}$ | $\begin{gathered} 3.82 \\ (3.62) \end{gathered}$ | $\begin{gathered} (.0 .3) \\ 3.63 \\ (3.24) \end{gathered}$ |
| $\left[\mathrm{PtMeCl}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]_{2}$ <br> (II) | insoluble |  |  | Dichloromethane 74 | 190-200 (dec.) | $\begin{gathered} 42.36 \\ (42.49) \end{gathered}$ | $\begin{gathered} 3.33 \\ (3.37) \end{gathered}$ | $\begin{gathered} 2.95 \\ (2.75) \end{gathered}$ |
| $\left[\mathrm{PtMe}\left(\eta^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}^{2}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}^{2}\left[\mathrm{BPh}_{4}\right]\right.\right.$ <br> (Id) | 0.90 | $\begin{aligned} & { }^{2} J(\mathrm{Pt}-\mathrm{H}) 61 \mathrm{~Hz} ; \\ & { }^{2} J(\mathrm{P}-\mathrm{H})_{\text {cis }} 2.3 \mathrm{~Hz} ; \\ & { }^{3} J(\mathrm{P}-\mathrm{H})_{\text {trans }} 7.9 \mathrm{~Hz} \end{aligned}$ |  | $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ /hexane, 66 | 184-186 | $\begin{gathered} 66.88 \\ (67.11) \end{gathered}$ | $\begin{gathered} 4.76 \\ (4.87) \end{gathered}$ | $\begin{gathered} 2.30 \\ (2.65) \end{gathered}$ |
| $\left[\mathrm{PtMe}\left(\eta^{2}-\mathrm{Ph}_{2} \mathrm{PPy}_{\mathrm{p}}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]\left[\mathrm{BF}_{4}\right]^{a}$ <br> (le) |  |  | $-17.6 \begin{gathered} { }^{1} J(\mathrm{Pt}-\mathrm{P}) 1396 \mathrm{~Hz} \\ { }^{J} J(\mathrm{P}-\mathrm{P}) 12 \mathrm{~Hz} \\ 19.0 \\ { }^{1} J(\mathrm{Pt}-\mathrm{P}) 4228 \mathrm{~Hz} \\ { }^{J} J(\mathrm{P}-\mathrm{P}) 12 \mathrm{~Hz} \end{gathered}$ | Acetone/hexane, 70 | 204-205 | $\begin{gathered} 50.85 \\ (51.05) \end{gathered}$ | $\begin{gathered} 3.96 \\ (3.79) \end{gathered}$ | $\begin{gathered} 3.21 \\ (3.40) \end{gathered}$ |
| $\text { trans- }\left[\mathrm{PtMe}\left(\mathrm{SnCl}_{3}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right]$ <br> (If) | 0.75 | $\begin{aligned} & { }^{2} J(\mathrm{Pt}-\mathrm{H}) 75 \mathrm{~Hz} ; \\ & { }^{3} \mathrm{~J}(\mathrm{P}-\mathrm{H}) 7 \mathrm{~Hz} \end{aligned}$ | $61.7 \begin{gathered} { }^{1} J(\mathrm{Pt}-\mathrm{P}) 3060 \mathrm{~Hz} \\ { }_{J}(\mathrm{Sn}-\mathrm{P}) 217 \mathrm{~Hz} \end{gathered}$ |  |  |  |  |  |

[^1]


Fig. 1. PLUTO drawing of the molecule $\left[\mathrm{PtMe}\left(\eta^{2}-\mathrm{Ph}_{2} \mathbf{P p y}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}^{2}\right)\right]\left[\mathrm{BPh}_{4}\right]$.
frequency ( $\delta-17.6 \mathrm{ppm}$ ) with a smaller ${ }^{1} J(\mathrm{Pt}-\mathrm{P})$ is assigned to the phosphorus trans to the methyl group. The other resonance at higher frequency ( $\delta 19.2 \mathrm{ppm}$ ) with ${ }^{1} J(\mathrm{Pt}-\mathrm{P}) 4226 \mathrm{~Hz}$ is assigned to the phosphine ligand trans to the chelated nitrogen of the pyridine ring. The ${ }^{1} J(\mathrm{Pt}-\mathrm{P})(1391 \mathrm{~Hz})$ for the phosphorus trans to the methyl group is much smaller than the values reported for platinum(II) complexes of the type cis- $\left[\operatorname{PtMe} e_{2}\left(\mathrm{PR}_{3}\right)_{2}\right]$ and cis- $\left[\operatorname{PtMeX}\left(\mathrm{PR}_{3}\right)_{2}\right]$ in which the phosphine ligand is trans to methyl group. The lower value of ${ }^{1} J(\mathbf{P t}-\mathrm{P})$ indicates a longer $\mathrm{Pt}-\mathrm{P}$ 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 $\mathrm{Pt}-\mathrm{P}$ bonds in $\left[\mathrm{PtCl}\left(\eta^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]^{+}$, however, have the same length [3].

Complex Id crystallized as a single cation [ $\left.\mathrm{PtMe}\left(\eta^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]^{+}$and a single anion $\left[\mathrm{BPh}_{4}\right]^{-}$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 [ $\left.\mathrm{PtMe}\left(\eta^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]^{+}$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 $(\AA)$ and angles ( ${ }^{\circ}$ ) with e.s.d.'s for [ $\left.\mathrm{PtMe}\left(\eta^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]\left[\mathrm{BPh}_{4}\right]$

| $\mathrm{Pt}(1)-\mathrm{P}(1)$ | 2.325(5) | $\mathrm{P}(2)-\mathrm{C}(31)$ | 1.78(2) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Pt}(1)-\mathrm{P}(2)$ | 2.207(5) | $\mathrm{N}(1)-\mathrm{C}(2)$ | 1.32(2) |
| $\mathrm{Pt}(1)-\mathrm{N}(1)$ | 2.07(2) | N(1)-C(6) | 1.39(3) |
| $\mathrm{Pt}(1)-\mathrm{C}(1)$ | 2.05(2) | $\mathrm{N}(2)-\mathrm{C}(31)$ | 1.45(3) |
| $\mathrm{P}(1)-\mathrm{C}(6)$ | 1.81(2) | $\mathrm{N}(2)-\mathrm{C}(32)$ | 1.33(3) |
| $P(1)-C(7)$ | 1.82(2) | $\mathrm{B}(1)-\mathrm{C}(36)$ | 1.64(2) |
| $\mathrm{P}(1)-\mathrm{C}(13)$ | 1.78 (2) | $B(1)-C(42)$ | 1.65(3) |
| $\mathrm{P}(2)-\mathrm{C}(19)$ | 1.84(2) | $\mathrm{B}(1)-\mathrm{C}(48)$ | 1.63(3) |
| P(2)-C(25) | 1.85(2) | $\mathrm{B}(1)-\mathrm{C}(54)$ | 1.69(3) |
| $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{P}(2)$ | 106.3(2) | $\mathrm{P}(1)-\mathrm{C}(13)-\mathrm{C}(14)$ | 122(1) |
| $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{N}(1)$ | 70.4(5) | $\mathrm{P}(1)-\mathrm{C}(13)-\mathrm{C}(18)$ | 120(1) |
| $\mathrm{P}(1)-\mathrm{Pt}(1)-\mathrm{C}(1)$ | 161.096 | C(6)-P(1)-C(13) | 104(1) |
| $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{N}(1)$ | 176.5(4) | $\mathrm{Pt}(1)-\mathrm{N}(1)-\mathrm{C}(2)$ | 138(2) |
| $\mathrm{P}(2)-\mathrm{Pt}(1)-\mathrm{C}(1)$ | 92.6(6) | $\mathrm{Pt}(1)-\mathrm{N}(1)-\mathrm{C}(6)$ | 103(1) |
| $\mathrm{N}(1)-\mathrm{Pt}(1)-\mathrm{C}(1)$ | 90.6(8) | $\mathrm{C}(2)-\mathrm{N}(1)-\mathrm{C}(6)$ | 119(2) |
| $\mathrm{Pt}(1)-\mathrm{P}(1)-\mathrm{C}(6)$ | 82.1(6) | $\mathrm{N}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 122(2) |
| $\mathrm{Pt}(1)-\mathrm{P}(1)-\mathrm{C}(7)$ | 122.4(7) | N(1)-C(6)-C(5) | 121(2) |
| $\mathrm{Pt}(1)-\mathrm{P}(1)-\mathrm{C}(13)$ | 125.8(6) | $\mathrm{P}(2)-\mathrm{C}(25)-\mathrm{C}(26)$ | 117(2) |
| C(6)-P(1)-C(7) | 105.4(8) | $\mathrm{P}(2)-\mathrm{C}(25)-\mathrm{C}(30)$ | 121(2) |
| $\mathrm{C}(7)-\mathrm{P}(1)-\mathrm{C}(13)$ | 108.1(8) | $\mathrm{P}(2)-\mathrm{C}(31)-\mathrm{N}(2)$ | 119(2) |
| $\mathrm{Pt}(1)-\mathrm{P}(2)-\mathbf{C}(19)$ | 114.8(6) | $\mathrm{P}(2)-\mathrm{C}(31)-\mathrm{C}(35)$ | 125(1) |
| $\mathrm{Pt}(1)-\mathrm{P}(2)-\mathrm{C}(25)$ | 112.7(6) | $\mathrm{C}(31)-\mathrm{N}(2)-\mathrm{C}(32)$ | 120(2) |
| $\mathrm{Pt}(1)-\mathrm{P}(2)-\mathrm{C}(31)$ | 114.2(7) | $\mathrm{N}(2)-\mathrm{C}(31)-\mathrm{C}(35)$ | 116(2) |
| $\mathbf{C}(19)-\mathbf{P}(2)-\mathrm{C}(25)$ | 103.6(9) | $\mathrm{N}(2)-\mathrm{C}(32)-\mathrm{C}(33)$ | 124(2) |
| $\mathbf{C}(19)-\mathrm{P}(2)-\mathrm{C}(31)$ | 102.5(8) | C(36)-B(1)-C(42) | 108(2) |
| $\mathrm{C}(25)-\mathrm{P}(2)-\mathrm{C}(31)$ | 107.9(9) | $C(36)-B(1)-C(48)$ | 113(2) |
| $\mathrm{P}(1)-\mathrm{C}(6)-\mathrm{N}(1)$ | 104(1) | $\mathrm{C}(36)-\mathrm{B}(1)-\mathrm{C}(54)$ | 107(2) |
| $P(1)-C(6)-C(5)$ | 135(2) | $\mathrm{C}(42)-\mathrm{B}(1)-\mathrm{C}(48)$ | 111(2) |
| $\mathrm{P}(1)-\mathrm{C}(7)-\mathrm{C}(8)$ | 121(1) | $\mathrm{C}(42)-\mathrm{B}(1)-\mathrm{C}(54)$ | 108(2) |
| $\mathrm{P}(1)-\mathrm{C}(7)-\mathrm{C}(12)$ | 120(2) | $\mathrm{C}(48)-\mathrm{B}(1)-\mathrm{C}(54)$ | 109(2) |

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

The bond lengths and bond angles for the molecule are listed in Table 2. The various bond lengths are normal within experimental error. The $\mathrm{Pt}-\mathrm{P}(1)$ distance trans to the methyl group is much longer (2.325(5) $\AA$ ) than that of $\mathrm{Pt}-\mathrm{P}(2)(2.207(5)$ $\AA$ ). The longer bond is expected because of the trans influence of the methyl group. It may be noted that the $\mathrm{Pt}-\mathrm{P}$ distances for the cation $\left[\mathrm{Pt}_{2} \mathrm{Cl}\left(\boldsymbol{\eta}^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]^{+}$ for both chelating and monodentate phosphines are of the same order (viz. $\mathrm{Pt}-\mathrm{P}(1)$ 2.223 and $\mathrm{Pt}-\mathrm{P}(2) 2.232 \AA$, respectively) [3]. The two chemically nonequivalent $\mathrm{Pt}-\mathrm{P}$ 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 $2.247(6) \AA$ for $a$, and $2.326(7)$ against $2.226(7)$ for $b$; the longer $\mathrm{Pt}-\mathrm{P}$ bond is trans to the R group. If no trans influence is present, the $\mathrm{Pt}-\mathrm{P}$ bond lengths fall in the range $2.22-2.28 \AA$; in our structure this value is $2.207(5) \AA$.

Because of the four-membered chelate ring various angles around platinum deviate from the normal value of $90^{\circ}$. Thus the $\mathbf{P}(1)-\mathbf{P t}-\mathrm{N}(1)$ angle has been compressed to $70.4(5)^{\circ}$, while the adjacent angle $\mathrm{P}(1)-\mathrm{Pt}-\mathrm{P}(2)$ has opened to 106.3(2) ${ }^{\circ}$. The other angles $\mathrm{C}(1)-\mathrm{Pt}-\mathrm{N}(1)$ and $\mathrm{C}(1)-\mathrm{Pt}-\mathrm{P}(2)$ show little deviation $90.6(8)$ and $92.6(6)^{\circ}$, respectively. However, in the cation $\left[\mathrm{PtCl}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right]^{+}$the $\mathrm{Cl}-\mathrm{Pt}-\mathrm{N}(1)$ 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 $\left.\left[\mathrm{PtCl}^{( } \mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right]^{+} \quad[3]$ and $\left[\mathrm{RuCl}_{2}(\mathrm{CO})_{2}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]$ [18].

The phenyl and pyridyl rings in $\left[\mathrm{PtMe}\left(\boldsymbol{\eta}^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]^{+}$(Id) are planar to within 0.03(2) $\AA$. 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 $\mathrm{SnCl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ in dichloromethane or $\mathrm{CDCl}_{3}$ yielded the corresponding trichlorostannate complex, $\left[\mathrm{PtMe}\left(\mathrm{SnCl}_{3}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right]$, If, whose ${ }^{1} \mathrm{H}$ NMR spectrum showed a triplet pattern for the $\mathrm{Pt}-\mathrm{Me}$ protons. The ${ }^{31} \mathrm{P}$ NMR spectrum exhibited a single line with platinum-195 and tin-117/119 sateilites. The spectra are consistent with the expected trans configuration of the complex. It is note worthy that the ${ }^{31} \mathrm{P}$ chemical shift is deshielded and ${ }^{1} J(\mathrm{Pt}-\mathrm{P})$ is reduced by 97 Hz with respect to Ib , although ${ }^{2} J(\mathrm{Sn}-\mathrm{P})$ lies in the range typical of ${ }^{2} J(\mathbf{S n}-\mathbf{P})$, cis $[19,20]$. In organoplatinum(II) trichlorostannate complexes, trans- $\left[\mathrm{PtR}\left(\mathrm{SnCl}_{3}\right)\right.$ $\left.\left(\mathrm{PR}_{3}\right)_{2}\right] \quad(\mathrm{R}=\mathrm{Ph}$ or COPh$)$, shielding of the ${ }^{31} \mathrm{P}$ nucleus and the much larger reduction in ${ }^{1} J(\mathrm{Pt}-\mathrm{P})(\sim 350 \mathrm{~Hz})$ than that of the corresponding chloro-complexes are observed [21]. Recently several new modes of bonding of the $\mathrm{SnCl}_{2}$ ligand other than the normal $\mathrm{M}-\mathrm{SnCl}_{3}$ fashion have been reported [22-24]. For example, in [ $\left.\mathrm{Rh}_{2} \mathrm{Sn}_{2}(\mathrm{CO})_{2} \mathrm{Cl}_{6}\left\{\mu-\left(\mathrm{Ph}_{2} \mathrm{P}\right)_{2} \mathrm{py}\right\}_{2}\right]$, the pyridiyl nitrogens are coordinated to one of the tin centres.

Recently Balch et al. [4] reported the reaction:
$\operatorname{PtX}_{2}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}+\mathrm{Ptdba}_{2} \rightarrow\left[\mathrm{Pt}_{2} \mathrm{X}_{2}\left(\mu-\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right]+2 \mathrm{dba}$
and observed that the reaction was facile when the trans- $\mathrm{Pt}(\mathrm{II})$ complex was used. Thus it was expected that the use of trans- $\left[\mathrm{PtMeCl}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right]$ in the above reaction might yield the corresponding methylplatinum(I) complex, $\left[\mathrm{Pt}_{2} \mathrm{MeX}\left(\mu-\mathrm{Ph}_{2} \mathrm{Ppy}_{2}\right]\right.$. So the reaction of Ib with $\mathrm{Ptdba}_{2}$ was carried out in refluxing dichloromethane to give $\left[\mathrm{Pt}_{2} \mathrm{Cl}_{2}\left(\mu-\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right.$ ], identified from its ${ }^{31} \mathrm{P}$ NMR data [4].

## Experimental

[ $\mathrm{PtMe}_{2}(\mathrm{COD})$ ], [PtMeX(COD)] $(\mathrm{X}=\mathrm{Cl}, \mathrm{I})$ [25] and $\mathrm{Ph}_{2} \mathrm{Ppy}$ [2] were prepared by previously published procedures. All reactions were carried out in spectrograde solvents under nitrogen.
${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ 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 ${ }^{31} \mathrm{P}$ respectively. Some ${ }^{1} \mathrm{H}$ NMR spectra were recorded on a Bruker AM-500 or Varian VXR-300s instrument. Chemical shifts are relative to an internal solvent
peak ( $7.26 \mathrm{ppm} \mathrm{CHCl}_{3}$ ) for ${ }^{1} \mathrm{H}$, and to external $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ for ${ }^{31} \mathbf{P}$. Microanalyses were performed by Bio-organic and Analytical Chemistry Divisions, BARC, Bombay. Melting points were determined in a capillary and are uncorrected.

## Preparation of $\left[\mathrm{PtMeX}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right](X=\mathrm{Me}, \mathrm{Cl}$ or I)

To a benzene solution of $\left[\mathrm{PtMe}_{2}(\mathrm{COD})\right](161 \mathrm{mg}, 0.48 \mathrm{mmol})$ was added a benzene solution of $\mathrm{Ph}_{2} \mathrm{Ppy}$ ( $238 \mathrm{mg}, 0.91 \mathrm{mmol}$ ) 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 ( $300 \mathrm{mg}, 83 \%$ ).

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

## Reaction of [PtMeCl(COD)] with Ph Ppy in 1:1 stoichiometry

To a dichloromethane solution of $[\mathrm{PtMeCl}(\mathrm{COD})]$ ( $155 \mathrm{mg}, 0.44 \mathrm{mmole}$ ) was added a solution of $\mathrm{Ph}_{2} \mathrm{Ppy}$ ( $116 \mathrm{mg}, 0.44 \mathrm{mmole}$ ) dropwise to give a pale yellow solution. The solvent was removed under vacuum and the residue was washed with hexane and dried (yield $164 \mathrm{mg}, 73 \%$ ).

Reaction of Ib with $\mathrm{NaY}\left(Y=B P h_{4}\right.$ or $\left.B F_{4}\right)$
To a dichloromethane solution of $\operatorname{trans}-\left[\mathrm{PtMeCl}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}\right](150 \mathrm{mg}, 0.19 \mathrm{mmole})$, was added a methanolic solution of $\mathrm{NaBPh}_{4}$ ( $77 \mathrm{mg}, 0.24 \mathrm{mmol}$ ) 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ to give a pale yellow crystalline solid. This was recrystallised several times from $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ /hexane to give a colourless crystalline product (yield, $135 \mathrm{mg}, 65 \%$ ).

The $\mathrm{BF}_{4}$ salt was prepared similarly and the product was three times recrystallized from acetone/ hexane mixture.

Reaction of [PtMeCl( $\left.\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}$ ] with $\mathrm{SnCl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$
To a solution of trans $-\mathrm{PtMeCl}\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)_{2}(146 \mathrm{mg})$ in $\mathrm{CDCl}_{3}(3 \mathrm{ml})$ was added an excess of $\mathrm{SnCl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}(220 \mathrm{mg})$ and the reaction mixture was stirred for 30 min to give a wine-red solution. This was filtered and studied by ${ }^{1} \mathbf{H}$ and ${ }^{31} \mathbf{P}\left\{{ }^{1} \mathbf{H}\right\}$ NMR spectroscopy.

Crystal structure study of $\left[P t M e\left(\eta^{2}-P h_{2} P p y\right)\left(P h_{2} P p y\right)\right]\left[B P h_{4}\right]$
Crystal data. $\mathrm{C}_{59} \mathrm{H}_{51} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{BPt}, \mathrm{M}_{\mathrm{r}}=1055.9$, triclinic, a 10.006 (6), b 14.240(8), c $18.368(6) \AA, \alpha 80.93(4), \beta 74.60(3), \gamma 89.23(5)^{\circ}, V 2490.65 \AA^{3}, Z=2, D_{C} 1.40 \mathrm{gm}$ $\mathrm{cm}^{-3}, F(000) 1064$, Mo- $K_{\alpha}$ radiation, $\lambda 0.71069 \AA, \mu\left(\mathrm{Mo}-K_{\alpha}\right) 27.8 \mathrm{~cm}^{-1}$. 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 $2 \leqslant \theta \leqslant 22^{\circ}$ with $0 \leqslant h \leqslant 10,-14 \leqslant k \leqslant 14$ and $-18 \leqslant l \leqslant 18$ on an Enraf Nonius CAD-4 diffractometer by $\omega / 2 \theta$ scan technique with a graphite monochromator and $\mathrm{Mo}-K_{a}$ 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 ( $\times 10^{4}$ for Pt and P ; $\times 10^{3}$ for remaining atoms) and equivalent isotropic temperature factors ( $\AA^{2} \times 10^{3}$ for Pt and $\mathrm{P} ; \AA^{2} \times 10^{2}$ for remaining atoms) with e.s.d.'s in parenthesis for $\left[\mathrm{PtMe}\left(\eta^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}^{2}\right)\right]\left[\mathrm{BPh}_{4}\right]$.

| Atom | $x$ | $y$ | $z$ | $U_{\text {eq }}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\overline{\mathrm{Pt}}$ (1) | 2008(1) | 2306(1) | 2172(1) | 48(1) |
| $\mathbf{P}(1)$ | 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) | S(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) |
| C(45) | 267(5) | 141(3) | 919(2) | 17(1) |

Table 3 (continued)

| Atom | $\boldsymbol{x}$ | $y$ | $z$ | $U_{\text {eq }}$ |
| :---: | :---: | :---: | :---: | :---: |
| C(46) | 178(5) | 63(3) | 916(2) | 16(1) |
| C(47) | 155(3) | 60(2) | 841(1) | 10(1) |
| $\mathrm{C}(48)$ | -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) |

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 $\left[\mathrm{PtMe}\left(\eta^{2}-\mathrm{Ph}_{2} \mathrm{Ppy}\right)\left(\mathrm{Ph}_{2} \mathrm{Ppy}\right)\right]^{+}$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 leastsquares refinement and the calculation of the bond lengths angles on a NORSKDATA ND-560 computer system.

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    ** Abbreviations: $\mathrm{Ph}_{2} \mathrm{Ppy}$, 2-(diphenylphosphino)pyridine; COD, 1,5-cyclooctadiene; dppm, bis(diphenylphosphino)methanc; dba, dibenzylidencacetonc.

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