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# PLATINUM(II) COMPLEXES CONTAINING 2-(ALKENYL)PYRIDINES

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## Summary

The ligands 2-(allyl)pyridine(APy), and 2-(1-methallyl)pyridine (1-MAPy) react with $[Pt_2X_4(PEt_3)_2]$ (X = Cl or Br), in acetone solution to give complexes of the type $[PtX(PEt_3)L][PtX_3(PEt_3)]$, (L = APy or 1-MAPy), which contain a bidentate 2-(alkenyl)pyridine, whereas the same reaction in benzene solution gives *trans*-$[PtBr_2(PEt_3)L]$, (L = APy or 1-MAPy), which contains a monodentate 2-(alkenyl)pyridine; $^1$H NMR spectra indicate that both types of product undergo olefin exchange in solution. The same reaction with 2-(3-methallyl)-pyridine [2-(2-butenyl)pyridine] (3-MAPy), 2-(3,3-dimethylallyl)pyridine [2-(3-methyl-2-butenyl)pyridine] (3,3-DMAPy), and 2-(3-butenyl)pyridine (BPy), in either acetone or benzene solution, gives only *trans*-$[PtBr_2(PEt_3)L]$. The reaction of *trans*-$[PtBr_2(PEt_3)L]$ (L = APy or 3-MAPy) with $AgClO_4$ gives $[PtBr(PEt_3)L]ClO_4$. Complexes of the type $[PtCl_2L]$, which contain bidentate 2-(alkenyl)pyridines, result on reaction of L = APy, 3-MAPy, 3,3-DMAPy, BPy, MBPy with $[Pt_2Cl_4(C_2H_4)_2]$.

## Introduction

Many palladium(II) and platinum(II) complexes with bidentate, or potentially bidentate, ligands, which contain a mono-olefin and a wide variety of functional groups, are now known [1]. Platinum(II) complexes containing *ortho*-styryldiphenylphosphine (SPP), (*ortho*-allylphenyl)diphenylphosphine (APP) and the analogous unsaturated dimethylarsine derivatives undergo interesting bromination reactions [2] and, in order to investigate the generality of these reactions with other less sterically constrained olefinic ligands, we required a series of 2-(alkenyl)pyridine platinum(II) complexes which are now described (see Fig. 1).

Previous work has shown that 2-allylpyridine (APy) forms a monomeric platinum(II) complex $[PtCl_2L]$ (L = APy) in which both the nitrogen and allyl groups are bonded to platinum [3]. However, this and related 2-(alkenyl)pyridine complexes, which can be obtained in much higher yield by addition of

TABLE 1

ANALYTICAL AND PHYSICAL PROPERTIES OF COMPLEXES OF THE TYPE *trans*-[$MX_2(PEt_3)L$]

| M | X | L | M.p. (°C) | Analysis found (calcd.)(%) | | | | $\Lambda$ [a] | Mol. wt.[b] found (calcd.) | IR bands ($cm^{-1}$) (Raman) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | X | | | $\nu$(C=C) | $\nu$(Pt—X) | Out-of-plane =CH deformation |
| Pt | Br | VPy | 131 | 26.9 (27.0) | 4.0 (3.8) | 2.3 (2.4) | 27.3 (27.65) | 0 | 600 (578) | 1638 | 235 | 980, 948 |
| Pt | Br | APy | 112 | 28.4 (28.35) | 4.0 (4.0) | 2.3 (2.4) | 26.7 (26.95) | 61.0 | 586 (592) | 1635 | 242 (211) | 1000, 921 |
| Pt | Br | 1-MAPy | 124-126 | 29.5 (29.7) | 4.3 (4.3) | 2.2 (2.3) | 25.8 (26.4) | 64.5 | 627 (606) | [c] | [c] | 995, 950 |
| Pt | Br | 3-MAPy | 92-95 | 30.0 (29.7) | 4.2 (4.3) | 2.3 (2.3) | 26.3 (26.4) | 20.1 | 634 (606) | [c] | 239 (215) | [c] |
| Pt | Br | 3,3-DMAPy | 105 | 30.7 (31.0) | 4.6 (4.4) | 2.2 (2.3) | | 0 | 601 (620) | 1650 | 235 (208) | |
| Pt | Br | BPy | 134-136 | 29.5 (29.7) | 4.6 (4.3) | 2.2 (2.4) | | 16.2 | 605 (607) | 1648 | 238 (208) | 1010, 911 |
| Pd | Cl | APy | 117 | 40.4 (40.6) | 5.9 (5.85) | 3.4 (3.4) | 17.2 (17.15) | 0 | 403 (414) | 1638 | 356 | 1005, 921 |
| Pd | Br | APy | 119 | 33.4 (33.4) | 4.9 (4.8) | 2.7 (2.8) | 31.7 (31.8) | 0 | 482 (503) | 1635 | [c] | 1000, 921 |

[a] Conductivity ($\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$) of ca. $10^{-3}$ *M* nitromethane solution. [b] Measured in chloroform solution (ca. 1—10 × $10^{-3}$ *M*) at 36.6°. [c] Could not be identified.

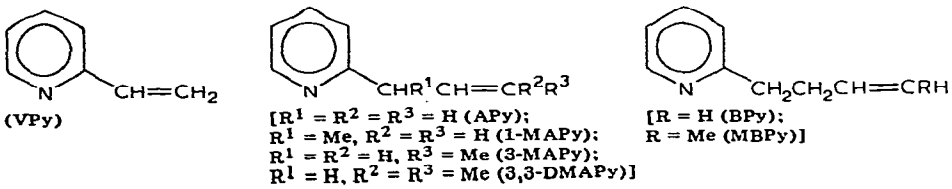



Fig. 1. Abbreviations for 2-(alkenyl)pyridines.

the appropriate 2-(alkenyl)pyridine to a toluene solution of $[Pt_2Cl_4(C_2H_4)_2]$, are rather insoluble and as a result products formed on cleavage of the halo-bridged complex, $[Pt_2X_4(PEt_3)_2]$ (X = Cl or Br) have also been investigated.

## Results and discussion

The halo-bridged complex $[Pt_2X_4(PEt_3)_2]$ (X = Cl or Br), which is readily available [4, 5], is known to react with a wide variety of ligands to give monomeric complexes of the type $[PtX_2(PEt_3)L]$. When the ligand is an amine [6] the product is invariably the *trans*-isomer whereas with carbon monoxide [7], olefins [7] or tertiary phosphines [8, 9] it is the *cis*-isomer. The nature of the products obtained from the above reaction using 2-(alkenyl)pyridines is found to depend on the following.

(*a*) Solvent, see eqn. (1).

$$[Pt_2X_4(PEt_3)_2] + 2L \;(L = APy \text{ or } 1\text{-}MAPy) \xrightarrow{\text{Benzene}} \textit{trans}\text{-}[PtX_2(PEt_3)L] \qquad (1)$$
$$\xrightarrow{\text{Acetone}} [PtX(PEt_3)L][PtX_3(PEt_3)]$$

It should be noted that identical products were obtained from acetone and benzene solutions on cleavage of the analogous halo-bridged palladium complex with APy. This product was shown to be *trans*-$[PdX_2(PEt_3)(APy)]$.

(*b*) The nature of the alkenyl group. Thus in acetone solution eqn. (2) applies.

$$[Pt_2Cl_4(PEt_3)_2] \xrightarrow{L = APy,\ 1\text{-}MAPy} [PtCl(PEt_3)L][PtCl_3(PEt_3)] \qquad (2)$$
$$\xrightarrow[3,3\text{-}DMAPy,\ BPy]{L = VPy,\ 3\text{-}MAPy} \textit{trans}\text{-}[PtCl_2(PEt_3)L]$$

Identical products were obtained when L = VPy, 3-MAPy, 3,3-DMAPy or BPy on carrying out this reaction in benzene solution.

The molecular weight and analytical data for all the neutral complexes of the type *trans*-$[MX_2(PEt_3)L]$ [M = Pd or Pt; X = Cl or Br; L = 2-(alkenyl)pyridine] are given in Table 1, and both IR and Raman spectra are consistent with the presence of an uncoordinated olefinic group and a *trans*-$PtX_2$ configuration. The $^1$H NMR spectra usually consist of sharp lines and are generally complicated. Nevertheless, it is evident from the integration and position of the resonances that none of the above ligands has undergone isomerisation. However, of particular interest is the $^1$H NMR spectra of *trans*-$[PtBr_2(PEt_3)L]$ (L = APy or 1-MAPy). In chloroform solution all the resonances are sharp and in the ex-

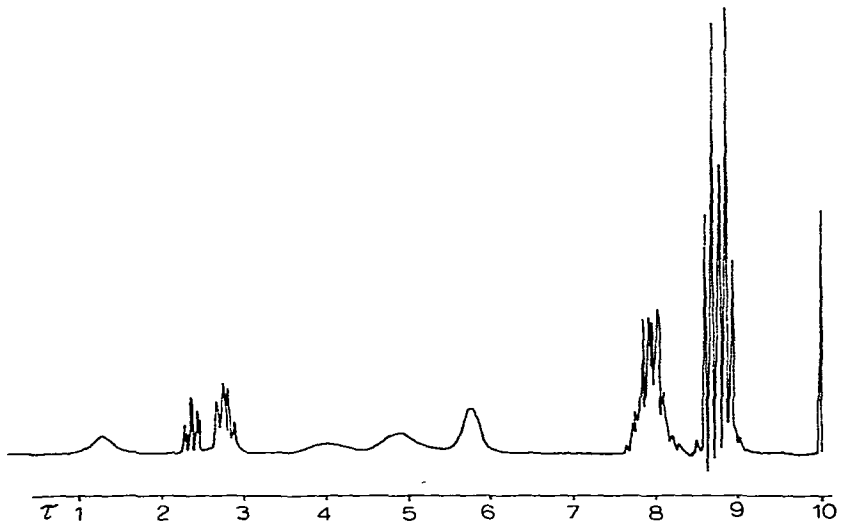
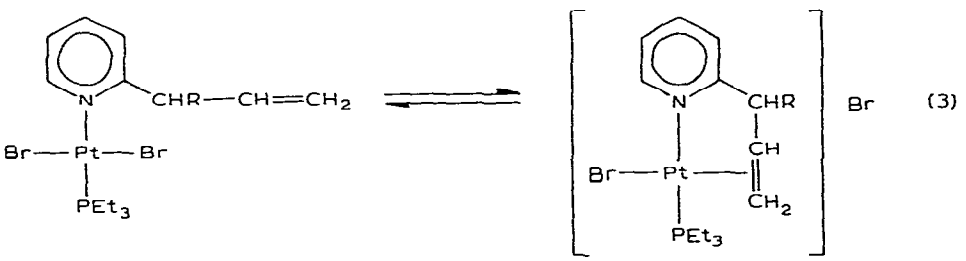



Fig. 2. 100 MHz $^1$H NMR spectrum of *trans*-[$PtBr_2(PEt_3)(APy)$] in deuterochloroform solution at 25°.

pected positions except those attributable to the 2-pyridine proton and alkenyl protons which are very broad and symmetrical (see Fig. 2); in benzene solution these resonances are somewhat sharper but still quite broad. Since, of all the pyridine ring protons, only the 2-proton resonance is broad, this suggests that dissociation of pyridine does not occur and that equilibrium (3) is responsible for these broad resonances. Support for this comes from conductivity measurements in nitromethane solution, which gives values typical for 1/1 electrolytes and suggests that complete dissociation of bromide occurs in this solvent. How-




(3)

(R = H or Me)

ever, in the much less polar solvents, chloroform and benzene, equilibrium (3) although facile, must still be in favour of the non-electrolyte because molecular weight determinations in chloroform solution are not significantly different from those expected: much lower values would have resulted if there had been a significant concentration of the ionic species. It is significant that the $^1$H NMR spectrum of *trans*-[$PdX_2(PEt_3)(APy)$] (X = Cl or Br) in chloroform solution (see Fig. 3) consists entirely of sharp resonances, which suggests that equilibrium (3) is not possible for palladium due to the reduced strength of the palladium—olefin bond.

A related type of interaction of an allyl group with a metal has been ob-

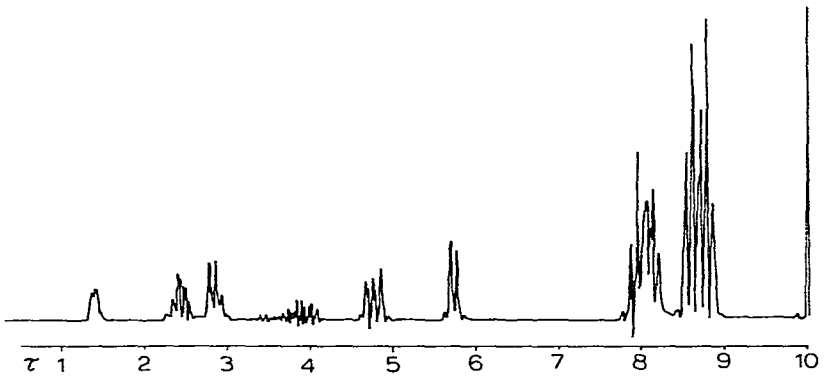



Fig. 3. 100 MHz $^1$H NMR spectrum of *trans*-[$PdBr_2(PEt_3)(APy)$] in deuterochloroform solution at 25°.

served in σ-bonded *ortho*-allylphenylnickel(II) complexes of the type *trans*-[$NiCl(PEt_3)_2L$] [L = *o*-($CH_2$=$CHCH_2$)Ph] [10]. In this case, it was suggested that there was a weak interaction of the allyl group with the metal and a related 5-coordinate complex must presumably be involved as an intermediate in the formation of [$PtBr(PEt_3)L$]Br (L = APy or 1-MAPy).

It is possible to displace equilibrium (3) to the right hand side by replacement of bromide with a non-coordinating anion, e.g. eqn. (4).

$$\textit{trans}\text{-}[PtBr_2(PEt_3)(APy)] + AgClO_4 \xrightarrow{\text{acetone}} [PtBr(PEt_3)(APy)]ClO_4 + AgBr \quad (4)$$

The IR spectrum of the resulting white crystalline complex lacks the bands at ca. 1650, 1000 and 921 $cm^{-1}$, which are attributable to an uncoordinated allyl group, and analytical and physical data are consistent with the formulation [$PtBr(PEt_3)(APy)$]$ClO_4$ which contains a bidentate APy ligand (see Table 2). Attempts to obtain similar complexes for 3-MAPy, 3,3-DMAPy and BPy gave intractable oils except for 3-MAPy. In this case a good yield of [$PtBr(PEt_3)$-(3-MAPy)]$ClO_4$ could be obtained from *trans*-[$PtBr_2(PEt_3)$(3-MAPy)], which contained an equal mixture of *cis*- and *trans*-3-MAPy. Although it is well known that transition metal complexes containing *cis*-olefins are more stable than the analogous *trans*-olefin complexes [11], there appears to be no distinction between the coordinative ability of *cis*- and *trans*-3-MAPy towards platinum(II). However, this ability to coordinate in a bidentate manner is obviously less favourable for 3-MAPy than for either APy or 1-MAPy since the $^1$H NMR spectrum of *trans*-[$PtBr_2(PEt_3)$(3-MAPy)] in chloroform solution consists only of sharp lines and the conductivity of a nitromethane solution of the 3-MAPy derivative is considerably less than that required for a 1/1 electrolyte (see Table 1). This reduced tendency of olefins to coordinate to transition metals on increasing alkylation of the olefinic double bond is well known [12, 13], and can be used to explain our inability to isolate [$PtBr(PEt_3)$(3,3-DMAPy)]$ClO_4$. Similarly, it proved impossible to isolate an analogous complex with BPy, which would require BPy to form the sterically less favourable 6-membered ring.

It is significant that only with APy and 1-MAPy, which have both been shown (see above) to readily behave as bidentate ligands towards platinum(II),

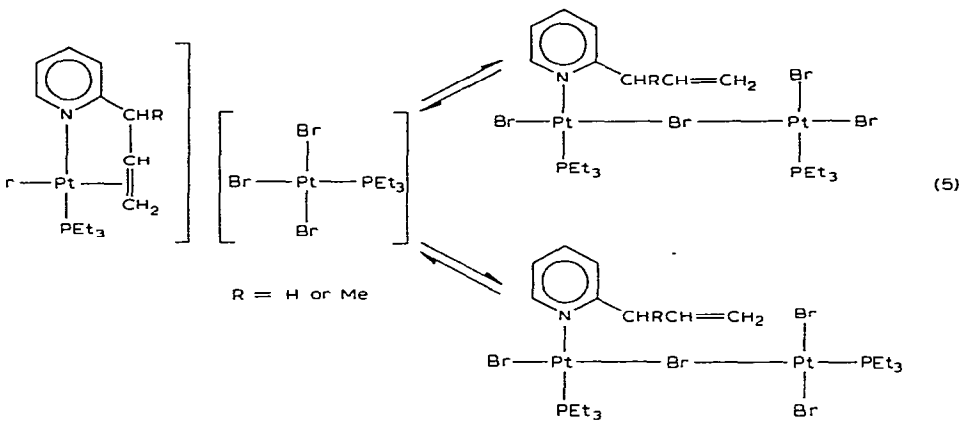
TABLE 2

ANALYTICAL AND PHYSICAL PROPERTIES OF COMPLEXES OF THE TYPE [PtX(PEt$_3$)L]Y

| X | L | Y | Colour | M.p. (°C) | Analysis found (calcd.) (%) | | | | $\Lambda^a$ | Mol. wt.[b] found (calcd.) | Concn.[c] ($\times 10^{-3}$ M) | IR bands (cm$^{-1}$) (Raman) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | X | | | | $\nu$(C=C) | $\nu$(Pt–X) | | |
| Cl | APy | $PtX_3(PEt_3)$ | Yellow | 142-144 | 27.2 (27.0) | 4.6 (4.4) | 1.5 (1.6) | 15.7 (16.0) | 66.5 | 638 (888) | 2.7 | 1505 | 334 s (332 s) | 328 (sh) (291 m) | 275 s (270 m) |
| Br | APy | $PtX_3(PEt_3)$ | Orange | 122-124 | 22.6 (22.5) | 3.8 (3.7) | 1.3 (1.3) | 29.6 (30.0) | 65.7 | 777 (1065) | 1.8 | 1505 | 240 m (232 m) | 211 m (210 vs) | 188 s, 182 s (185 s) |
| Cl | 1-MAPy | $PtX_3(PEt_3)$ | Yellow | 156 | 28.3 (28.0) | 4.7 (4.6) | 1.6 (1.55) | 15.9 (15.7) | 67.7 | 910<br>874<br>852<br>(902) | 18.1<br>8.45<br>3.8 | *d* | 344 m | 326 m | 282 m[e] |
| Br | 1-MAPy | $PtX_3(PEt_3)$ | Orange | 124-125 | 23.2 (23.3) | 3.9 (3.8) | 1.2 (1.3) | 29.3 (29.6) | 64.5 | 1075<br>930<br>819<br>(1080) | 10.43<br>7.9<br>2.7 | *d* | 236 s (234 m) | 206 m (207 vs) | 186 s (186 m) |
| Br | APy | $ClO_4$[f] | White | 192-195 | 31.6 (31.4) | 4.0 (4.2) | 2.2 (2.15) | | 65.0 | | | 1500 | | 230 s (230 s) | |
| Br | 3-MAPy | $ClO_4$[g] | White | 100-105 | 30.6 (30.7) | 4.5 (4.5) | 2.1 (2.1) | | 79.6 | | | 1500 | | 225 s (225 s) | |

[a] Conductivity ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$) of ca. $10^{-3}$ *M* nitromethane solution. [b] Measured in chloroform solution at 36.6°. [c] Concentration of solution used for mol. wt. determination. [d] Could not be identified. [e] Raman spectrum could not be obtained due to fluorescence. [f] Contains benzene of crystallisation (0.5 mol) as shown by analysis and $^1$H NMR. [g] Contains acetone of crystallisation (0.66 mol) as shown by analysis and $^1$H NMR.

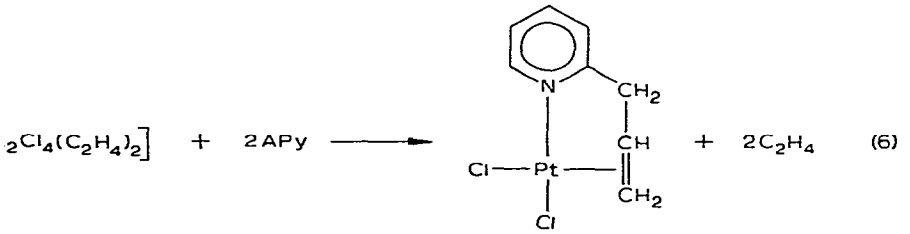
e complexes of the type $[PtX(PEt_3)L][PtX_3(PEt_3)]$ (X = Cl or Br; L = APy 1-MAPy) obtained on cleavage of the halogen-bridged complex, $[Pt_2X_4(PEt_3)_2]$, in acetone solution. These complexes were characterised in the normal ay and analytical and physical data are shown in Table 2. As expected for this rmulation, the molecular weight in chloroform solution is low and decreases th increasing dilution (see Table 2). The $^1$H NMR spectra of these complexes tegrate correctly and have sharp resonances except for those which are attri- itable to the *ortho*-pyridine proton and alkenyl protons: in these cases, the sonances are broad and asymmetrical, which is perhaps due to the type of uilibria shown in eqn. (5).




(5)

On passing an acetone solution of $[PtBr(PEt_3)L][PtBr_3(PEt_3)]$ (L = APy 1-MAPy) down a bromide anion-exchange column, it was possible to isolate *trans*-$[PtBr_2(PEt_3)L]$, which must have resulted from $[PtBr(PEt_3)L]Br$.

As mentioned earlier, APy has been shown to react with $K_2[PtCl_4]$ to give e monomeric complex $[PtCl_2APy]$ in which both the nitrogen and allyl oup are bonded to platinum [3]. The same complex has now been prepared, t in much higher yield, by reaction (6).




(6)

Using this reaction, the related ligands, 3-M APy, 3,3-DMAPy, BPy and MBPy e similar complexes (see Table 3). Analytical and molecular weight data sup- rt a monomeric formulation and the IR spectra all show the absence of a band ca. 1650 $cm^{-1}$ due to $\nu$(C=C) in the free olefin and the presence of a peak at 1500 $cm^{-1}$ which is mainly due to $\nu$(C=C) of the coordinated olefin. The far spectra of all these complexes have two intense bands in the region 310—350 $^{-1}$ which can be assigned to $\nu$(Pt—Cl) and are thus consistent with a *cis* confi- ation.

TABLE 3

ANALYTICAL AND PHYSICAL PROPERTIES OF COMPLEXES OF THE TYPE $[PtCl_2L]$.

| L | M.p. (°C) | Analysis found (calcd.) (%) | | | | Mol. wt.,[a] found (calcd.) | IR bands ($cm^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | | C | H | N | Cl | | ν(C=C) | ν(Pt—Cl) |
| APy | 216-218 | 25.0 (24.95) | 2.3 (2.4) | 4.0 (3.6) | 18.0 (18.4) | 409 (385) | 1503 | 345, 325 |
| 3-MAPy[b] | 90-98, 130-135[c] | 27.8 (27.1) | 2.9 (2.8) | 3.0 (3.5) | 18.5 (17.8) | 386 (399) | 1494 | 340, 328 |
| 3,3-DMAPy[b] | 180 (dec.) | 30.3 (29.0) | 3.4 (3.15) | 2.9 (3.4) | 16.9 (17.2) | 371 (413) | 1493 | 342, 317 |
| BPy | 215-220 (dec.) | 27.1 (27.1) | 2.9 (2.8) | 3.6 (3.5) | 17.8 (17.8) | 405 (399) | 1501 | 344, 326 |
| MBPy | 193 (dec.) | 29.3 (29.0) | 3.3 (3.15) | 3.3 (3.4) | 17.2 (17.2) | 404 (413) | 1495 | 340, 319 |

[a] Measured in chloroform solution (ca. $1 \times 10^{-3}$ *M*) at ca. 35°. [b] Could not be recrystallised. [c] These two m.p.'s are probably due to complexes containing *cis*- and *trans*-3-MAPy.

All the complexes of the type $[PtCl_2 L]$ [L = 2-(alkenyl)pyridine] are sparingly soluble in solvents with which they do not react. This made it difficult to obtain $^1$H NMR spectra. However, it was possible to obtain NMR spectra in DMSO-$d_6$ but it seems probable that replacement of the olefin and/or the pyridine by the solvent occurs. Nevertheless it was possible to show that the positions and intensities of the alkenyl resonances in DMSO-$d_6$ solutions of $[PtCl_2 L]$ (L = APy, 3-MAPy, 3,3-DMAPy, BPy or MBPy) were very similar to the spectrum of the analogous free ligand in the same solvent. Thus no isomerisation of 2-(alkenyl)pyridine occurs on coordination to platinum(II) and is thus similar to APP [14], (4-pentenyl)diphenylphosphine [15] and (4-pentenyl)phenyl sulphide [16] which have all been shown to coordinate in a bidentate manner to platinum(II) without isomerisation. This should be compared with the reaction of APP [14, 17] and 2-(alkenyl)pyridines [18] with Group VIA metals and also mesityl oxide with $Na_2[PtCl_4]$ [19]. In all these cases, the metal induces isomerisation in the olefinic side-chain to produce a ligand which can form a stable 5-membered ring by coordination to the metal.

## Experimental

Analytical and spectroscopic measurements were made as described previously [20]. $^1$H NMR spectra at 100 MHz were recorded on a JEOL PS 100 spectrometer at 25.0°.

The preparation of 2-(alkenyl)pyridines is described elsewhere [18].

*Preparation of complexes of the type trans-$[PtBr_2(PEt_3)L]$, [L = 2-(alkenyl)-pyridine]*

On shaking a benzene solution of any of the ligands shown in Fig. 1 (2 mol) with $Pt_2Cl_4(PEt_3)_2$ (1 mol) at room temperature for 18 h, complexes of the type *trans*-$[PtBr_2(PEt_3)L]$, were obtained as yellow crystals on concentration and recrystallisation from benzene/petroleum ether (60/80).

In the case of L = 3-MAPy, 3,3-DMAPy and BPy, the same complexes, as obtained above, were obtained on addition of L (2 mol) to an acetone solution of $Pt_2Cl_4(PEt_3)_2$ at either room temperature or ca. 70°.

In both acetone and benzene solution a ca. 90—95% yield of product was obtained.

*Preparation of complexes of the type $[PtBr(PEt_3)L]ClO_4$ (L = APy or 3-MAPy)*

Addition of an acetone solution of silver perchlorate (1 mol) to an acetone solution of the complex, *trans*-$[PtBr_2(PEt_3)L]$ resulted in an immediate precipitate of silver bromide which was filtered off. Concentration of the filtrate gave white crystals which were recrystallised from either acetone/petroleum ether (60/80) or benzene/petroleum ether (60/80) to give the product in ca. 70% yield.

*Preparation of complexes of the type $[PtX(PEt_3)L]$ $[PtX_3(PEt_3)]$ (X = Cl or Br; L = 1-MAPy or APy)*

Addition of APy or 1-MAPy (2 mol) to a boiling acetone solution of $Pt_2X_4(PEt_3)_2$ resulted in an immediate colour change. After boiling for ca.

1 min, the solution was cooled and concentration gave the product which was recrystallised from acetone/petroleum ether (60/80), (70% yield).

*Preparation of complexes of the type [$PtCl_2$ L], (L = APy, 3-MAPy, 3,3-DMAPy, BPy or MBPy)*

Boiling a solution of [$Pt_2Cl_4(C_2H_4)_2$] (1 mol) in acetone/toluene (50/50) for ca. 30 min. with the 2-(alkenyl)pyridine (2 mol) gave a yellow precipitate of the product. This was filtered off and (when L = APy, BPy or MBPy) recrystallised from chloroform solution to give the product in ca. 80—90% yield. When L = 3-MAPy (50/50, *cis/trans*) or 3,3-DMAPy, the resulting product was sparingly soluble in all solvents with which it did not react and this made recrystallisation impossible.

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