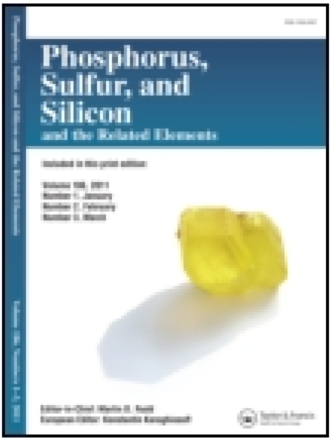

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Synthesis, Structure and Properties of New Pyridylaminophosphine Complexes

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SYNTHESIS, STRUCTURE AND PROPERTIES OF NEW PYRIDYLAMINOPHOSPHINE COMPLEXES

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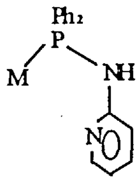
Reaction of diphenylphosphino-2-aminopyridine with a variety of late transition metal species eg Pt (II), Pd (II), Ru (II) and Rh (III) in most cases leads to five-membered metallocycles containing M-P-N(H)-C-N rings. Treatment of these species with base results in deprotonation of the amino group, formation of a neutral species and election delocalisation over the P-N bond.

Keywords: Phosphine, Metallocycle, Complex, X-Ray.

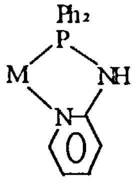
INTRODUCTION

Numerous mixed donor ligands incorporating both hard (eg O,N) and soft (eg P) donor atoms have been reported.[1-3] Here we describe the preparation of new late transition metal complexes with Ph_2PNHpy.[4]

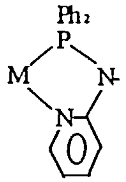
Diphenylphosphino-2-aminopyridine (Ph_2PNHpy), containing a P-N-C-N skeleton may exhibit a number of co-ordination modes.



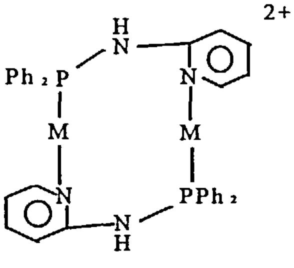
Soft donor



Chelating



Anionic chelating



Bridging

Results and discussion

Reaction of Ph_2PCl with 2-aminopyridine in THF proceeds in good yield to give LH (LH = Ph_2PNHpy). Two equivalents of Ph_2PNHpy react with $PtCl_2COD$ to give *cis*-[PtCl(Ph_2PNHpy-*P*, *N*)(Ph_2PNHpy-*P*)]Cl **1** (Figure 1). It is interesting to note that in the solid state one ligand forms a chelate five membered ring whilst the other is limited to monodentate P coordination.

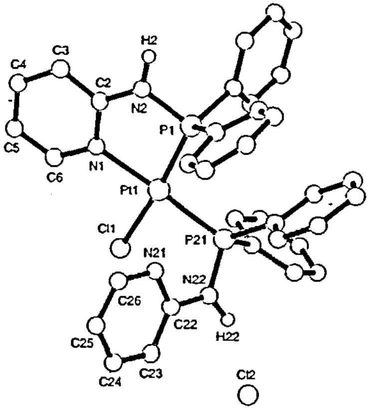


Figure 1
(X-Ray structure of *cis*-[PtCl(Ph_2PNHpy-*P*, *N*)(Ph_2PNHpy-*P*)]Cl)

A low temperature ^{31}P NMR study on this complex showed a singlet down to -80^{0}C, suggesting that a low energy fluxional process is taking place. In an attempt to halt the fluxional behaviour of bis-ligand complexes, two equivalents of ligand were reacted with PtMe(Cl)COD. ^{31}P NMR revealed two broad singlets with coupling constants consistent with the proposed structure **2** (Figure 2).

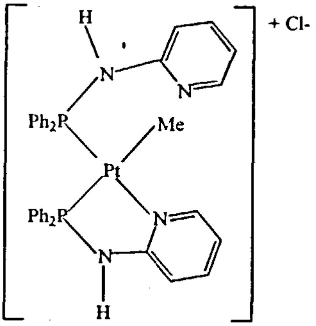


Figure 2

Treatment of **2** with one equivalent of base resulted in deprotonation of the chelated ligand. ^{31}P NMR data showed a narrowing of the peaks but resolution into doublets was not observed. VT NMR studies are currently underway on $[PtMe(Ph_2PNHpy\text{-}P)(Ph_2PNHpy\text{-}P, N)]Cl$ and $[PtMe(Ph_2PNHpy\text{-}P)(Ph_2PNpy\text{-}P, N)]$.

Treatment of **1** with ^{t}BuOK in methanol resulted in double deprotonation giving the neutral bis-chelate complex *cis*-$[Pt(Ph_2PNpy\text{-}P, N)_2]$ **3**. The reaction of **3** with tetrafluoroboric acid-diethylether complex ($HBF_4.OEt_2$) gave *cis*-$[Pt(Ph_2PNHpy\text{-}P, N)_2](BF_4)_2$. The structure of the palladium analogue was determined by X-Ray crystallography (Figure 3).

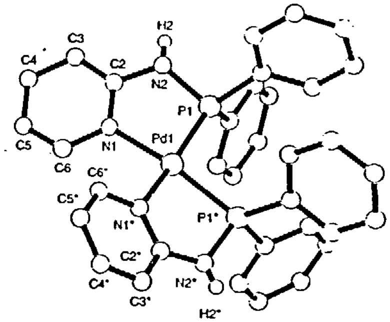


Figure 3

(Crystal structure of *cis*-$[Pd(Ph_2PNHpy\text{-}P, N)_2](BF_4)_2$, {anions not shown for clarity}).

The geometry of the metal centre shows considerable deviation from regular square planar. The P-Pd-N bond angles are 170^0 and 167^0.

Bis-phosphine dichloride complexes of platinum and palladium react with one equivalent of ligand which displaces one phosphine and one chloride ligand giving complexes of the type *cis*-$[MCl(PR_3)(Ph_2PNHpy\text{-}P, N)]Cl$ (Figure 4).

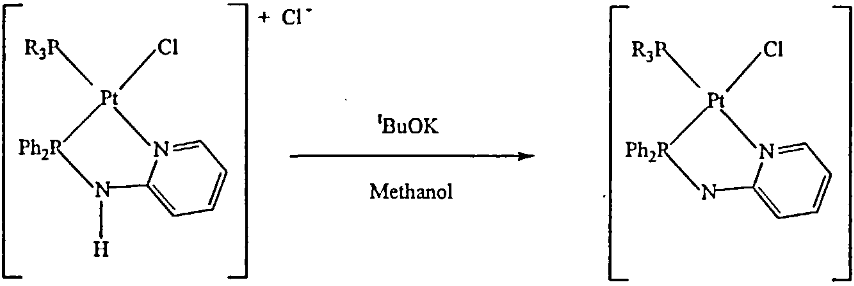


Figure 4

Other reactions of Ph_2PNHpy include:

$$[Me_5C_5RhCl_2]_2 + 2Ph_2PNHpy \longrightarrow [Me_5C_5RhCl(Ph_2PNHpy\text{-}P, N)]Cl$$

$$RuCl_2(PPh_3)_3 + 2Ph_2PNHpy \longrightarrow cis\text{-}RuCl_2(Ph_2PNHpy\text{-}P, N)_2$$

$$AuCl(tht) + Ph_2PNHpy \longrightarrow Ph_2P(AuCl)NHpy$$

$$Ph_2P(AuCl)NHpy + AgBF_4 \longrightarrow [\{Au(\mu\text{-}Ph_2PNHpy\text{-}P, N)\}_2][BF_4]_2$$

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