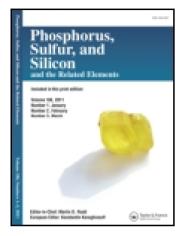
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Synthesis, Structure and Properties of New Pyridylaminophosphine Complexes

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SYNTHESIS, STRUCTURE AND PROPERTIES OF NEW PYRIDYLAMINOPHOSPHINE COMPLEXES

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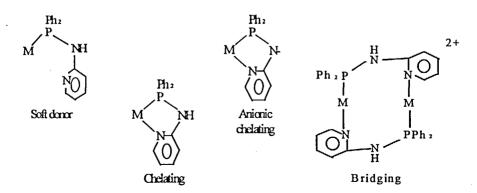
Reaction of diphenylphosphino-2-aminopyridine with a variety of late transition metal species eg Pt (II), Pd (II), Ru (II) and Rh (III) in most cases leads to five-membered metallocycles containing M-P-N(H)-C-N rings. Treatment of these species with base results in deprotonation of the amino group, formation 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 (Ph₂PNHpy), containing a P-N-C-N skeleton may exhibit a number of co-ordination modes.



Results and discussion

Reaction of Ph₂PCl with 2-aminopyridine in THF proceeds in good yield to give LH (LH = Ph₂PNHpy). Two equivalents of Ph₂PNHpy react with PtCl₂COD to give *cis*-[PtCl(Ph₂PNHpy-*P*, *N*)(Ph₂PNHpy-*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.

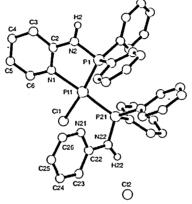


Figure 1 (X-Ray structure of *cis*-[PtCl(Ph₂PNHpy-*P*, *N*)(Ph₂PNHpy-*P*)]Cl)

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

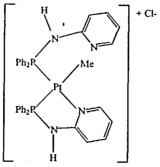


Figure 2

Treatment of **2** with one equivalent of base resulted in deprotonation of the chelated ligand. ³¹P NMR data showed a narrowing of the peaks but resolution into doublets was not observed. VT NMR studies are currently underway on [PtMe(Ph₂PNHpy-*P*)(Ph₂PNHpy-*P*, *N*)]Cl and [PtMe(Ph₂PNHpy-*P*)(Ph₂PNpy-*P*, *N*)].

Treatment of 1 with ^tBuOK in methanol resulted in double deprotonation giving the neutral bis-chelate complex *cis*-[Pt(Ph₂ PNpy-*P*, *N*)₂] **3.** The reaction of **3** with tetrafluoroboric acid-diethylether complex (HBF₄.OEt₂) gave *cis*-[Pt(Ph₂PNHpy-*P*, *N*)₂](BF₄)₂. The structure of the palladium

analogue was determined by X-Ray crystallography (Figure 3).

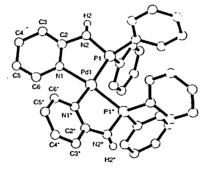
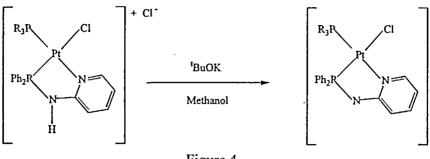


Figure 3

(Crystal structure of *cis*-[Pd(Ph₂PNHpy-P, N)₂](BF₄)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° and 167° .

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(PR₃)(Ph₂PNHpy-P, N)]Cl (Figure 4).





Other reactions of Ph₂PNHpy include:

[Me₅C₅RhCl₂]₂ + 2Ph₂PNHpy _____ [Me₅C₅RhCl(Ph₂PNHpy-P, N)]Cl

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

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

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

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