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**STRUCTURAL STUDIES ON THE INTERACTIONS  
OF A P<sub>2</sub>N TRIDENTATE LIGAND  
WITH COPPER(I) SILVER(I) AND S**

A Dissertation Presented in Partial Fulfilment of  
the Degree of Master of Philosophy at Massey University

**MASSEY UNIVERSITY  
NEW ZEALAND**

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## ABSTRACT

This thesis presents a study of the coordination chemistry, chemical reactivity, spectroscopy, structure and bonding of the hybrid polydentate ligand 2-(diphenylphosphino)-N-[2-(diphenylphosphino)benzylidene]benzeneamine (PNCP) with copper(I), silver(I) and sulfur. The hybrid polydentate (PNCP) ligand contains two inequivalent phosphorus (soft) and one nitrogen (hard) donor atoms,

Chapter One is a brief overview of tertiary phosphines used as monodentate, bidentate, tridentate and polydentate ligands with transition metals.

In Chapter Two, the preparation structure and characterisation of PNCP have been studied. Reactions of PNCP with sulphur have been investigated and a small site selectivity for one of the P atoms noted. Experiments have also included selective synthesis of the unsymmetrical mono-sulphide tertiary phosphine ligands SPNCP, PNCPS and of the di-sulfide SPNCPS ligand, as well as a study on the molecular structure of the 3-coordinate complex,  $[\text{Cu}(\text{SPNCPS})]\text{ClO}_4$ .

In Chapter Three the preparation of a series of copper(I) complexes of the general formula  $[\text{Cu}(\text{PNCP})\text{ClO}_4]$  and  $[\text{Cu}(\text{PNCP})\text{L}]\text{ClO}_4$  (L- ligands containing S, N donor atoms) have been reported. The crystal structure of  $[\text{Cu}(\text{PNCP})\text{ClO}_4]$  has been determined, and shows PNCP acts as a tridentate ligand coordinated to copper(I) *via* two phosphorus and one nitrogen donor atoms. The copper(I) atom has a distorted tetrahedral environment with two short Cu-P bonds and a slightly long Cu-N bond.

In Chapter Four, studies on the preparation of the mononuclear complex  $[\text{Ag}(\text{PNCP})\text{ClO}_4]$  and the dinuclear complex  $[\text{Ag}(\text{PNCP})(\text{SCN})]_2$  are presented. Both complexes were characterized by a variety of physicochemical techniques. The tridentate behaviour of PNCP in the complex  $[\text{Ag}(\text{PNCP})\text{ClO}_4]$  was established but the Ag-N bond was long and weak. In the complex  $[\text{Ag}(\text{PNCP})(\text{SCN})]_2$  the Ag-N bond not exist and PNCP acts as a bidentate ligand.

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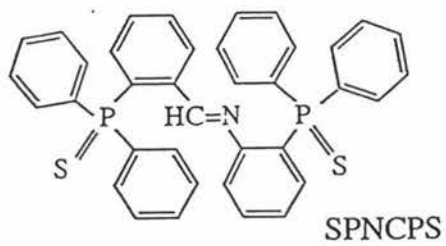
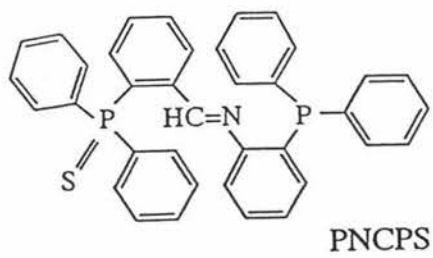
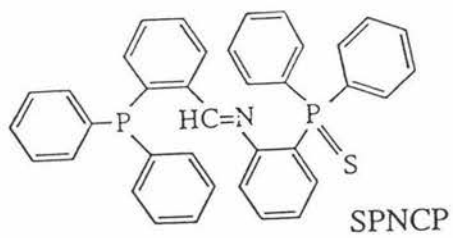
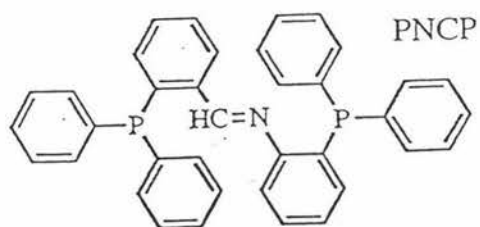
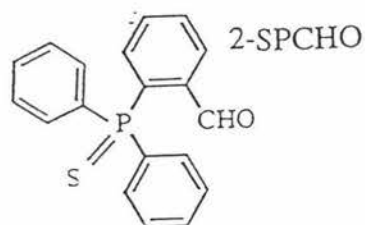
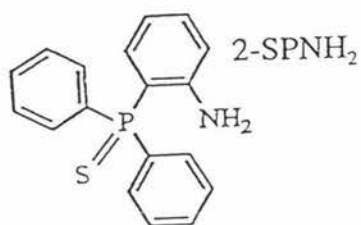
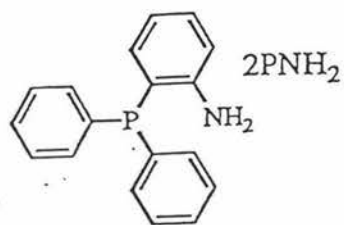
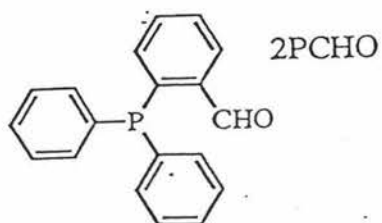
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## ABBREVIATIONS

2-PCHO	o-(diphenylphosphino)benzaldehyde
2-PCHOS	o-(diphenylphosphinothioyl)benzaldehyde
2-PNH <sub>2</sub>	o-(diphenylphosphino)aniline
2-PNH <sub>2</sub> S	o-(diphenylphosphinothioyl)aniline
BDPE	$\alpha,\alpha'$ -(dis(2-(diphenylphosphino)ethyl)amino)ethane
BDPX	$\alpha,\alpha'$ -(dis(2-(diphenylphosphino)ethyl)amino)-m-xylene
diphos	2,11-(bis(diphenylphosphino)methyl)benzo[C]phenanthrene
dmpc	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diethylphosphino)ethane
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diethylphosphino)ethane
IR	infra-red
NMR	nuclear magnetic resonance
PNCP	2-(diphenylphosphino)-N-[2-(diphenylphosphinothioyl)-benzylidene]benzeneamine
PNCPS	2-(diphenylphosphino)-N-[2-(diphenylphosphinothioyl)benzylidene]benzeneamine
ppm	parts per million
SPNCP	2-(diphenylphosphinothioyl)-N-[2-(diphenylphosphino)-benzylidene]benzeneamine
tdpm	1,1,1-(tris(diphenylphosphino)methane
tdpme	(tris(diphenylphosphino)methyl)ethane (triphos)
terpy	2,2':6',2''-terpyridine



# CHAPTER ONE

## GENERAL INTRODUCTION

Tertiary phosphines are excellent ligating agents to metal ions and transition metals in a variety of oxidation states and are important constituents of compounds for application as catalysts (*e.g.* Wilkinson's catalyst), structure bonding relationships, spectroscopic studies, and chemical bonding with the chalcogenides and halogens. Since additional functional groups can enhance this coordination ability great scope exists for the development of metal extraction chemistry and catalysts [1].

### I-1 THE CHEMISTRY OF PHOSPHINES

A characteristic of all  $PR_3$  compounds is the presence of a lone pair of electrons on P. These compounds therefore can be both bases and nucleophiles. The P is of greater size and lower electronegativity than nitrogen, hence its higher polarizability and nucleophilic reactivity in comparison with analogous nitrogen containing compounds. In addition P has the ability to expand its valence shell to ten electrons and thus trivalent phosphorus compounds can also behave as electrophiles. However, electrophilic reactivity is generally found only for  $PR_3$  compounds containing electron-withdrawing substituents (*e.g.* Cl, F) [2].

The high nucleophilic reactivity of tertiary phosphines, which form strong bonds with C, N, O or S has led to their becoming a widely used class of reagents in organic synthesis (Table 1-1) [3].

### I-2 METAL PHOSPHINE COMPLEXES

Tertiary phosphines are the most commonly encountered ligands in transition metal complexes. The  $PR_3$  ligand forms complexes with nearly every transition metal [4].

The metal-phosphorus bond distance is reported to vary from 2.15Å to 2.55Å [5]. The bonding is thought to include back-donation of electron density from a metal d orbital to an unoccupied ligand orbital of appropriate symmetry [6]. However, it has been argued that, although there is little role for back-bonding in aliphatic or aromatic phosphine complexes, such bonding is important for complexes of  $PF_3$  and phosphites [6-8]. Orpen and Connelly [9] examined the metal-phosphorus and the phosphorus-substituent atom

bond lengths in the crystal structure of a series of transition metal complexes. They reasoned that if the back-bonding was occurring into  $\sigma^*$  orbitals, then the bonds to the phosphorus substituents would be weakened. They found that indeed there was a correlation between M-P bond strengthening and P-X bond weakening as measured by bond length. The issue of  $\pi$ -bonding is still not resolved but it has been suggested that bonding falls into two groups:

- (1) Metals in oxidation state II or higher form essentially pure  $\sigma$  bonds with  $\text{PR}_3$  ligands.
- (2) Metals in oxidation state 0 or below form combined  $\sigma$  and  $\pi$  bonds to  $\text{PF}_3$ ,  $\text{PCl}_3$  and  $\text{P(OPh)}_3$ .

For other complexes the tendency for  $\pi$ -bonding to occur will be greatest for metals in low oxidation states. The ability of phosphines to stabilise low oxidation states is an important feature of their chemistry [2].

**Table 1-1 Phosphorus bonds energies ( $\text{kJ mol}^{-1}$ )**

Bonding	E	Bonding	E
P-H	323	P-F	529
P-C	273	P-Cl	332
P-N	231	P-Br	265
P-O	361	P-I	185
P=O	546		
P=S	378		

### I-3 TERTIARY PHOSPHINE REACTIVITY WITH SULPHUR AND OXYGEN

Tertiary phosphines  $\text{PR}_3$ , can be considered as derivatives of the phosphine molecule,  $\text{PH}_3$ , and these molecules can add oxygen and sulphur to give the tetrahedral phosphine oxides ( $\text{R}_3\text{PO}$ ) and phosphine sulfides ( $\text{R}_3\text{PS}$ ) respectively. These phosphine sulfides and oxides have high P=S and P=O bond energies [Table 1-1].

### I-3-1 Tertiary Phosphine Oxides

The tertiary oxides form the most stable class of all organophosphorus compounds. Those oxides with no  $\beta$  hydrogen atom are particularly stable;  $\text{Me}_3\text{PO}$  and  $\text{Ph}_3\text{PO}$  do not decompose below  $700^\circ\text{C}$  [3]. In some instances the reactants interact to give the oxides directly, whereas in other instances the phosphine oxides may be prepared by the thermal decomposition of quaternary phosphonium hydroxides or alkoxides [equations (1), (2)] [3].

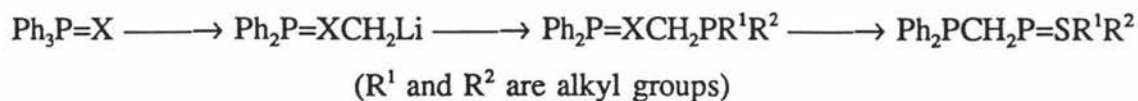


Nickel (II) halides form complexes  $[\text{NiX}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$  with diphosphines, which are stable in the solid state but decompose slowly when they are heated above  $220^\circ\text{C}$ , undergoing air oxidation to yield the diphosphine dioxides [10].

### I-3-2 Tertiary Phosphine Sulfides

The tertiary phosphine sulfides,  $\text{R}_3\text{PS}$ , contain a  $\text{P}=\text{S}$  linkage. Usually phosphine sulfides are produced more easily than their oxide analogues, and the reaction, normally exothermic, can be carried out in benzene or carbon disulphide with moderate warming. These phosphine sulfides are known to be oxidized to the corresponding oxides through the photo chemical transfer of oxygen heterocyclic N-oxides [11]. Tertiary phosphine sulfides are not easily oxidized by air to the oxides, but oxidation can be carried out with dilute nitric acid, hydrogen peroxide, alkali-bromine and other oxidising agents [3].

The formation of the monoxides and monosulfides [12] of tertiary diphosphines needs careful control of the reaction conditions, and selective monooxidation or monosulphurization of ditertiary phosphines are only possible if the two phosphorus atoms differ in their basicities as for example in  $\text{Me}_2\text{PCH}_2\text{PPh}_2$  [13] as shown below.

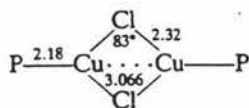


## I-4 PHOSPHINE COMPLEXES OF TRANSITION METALS

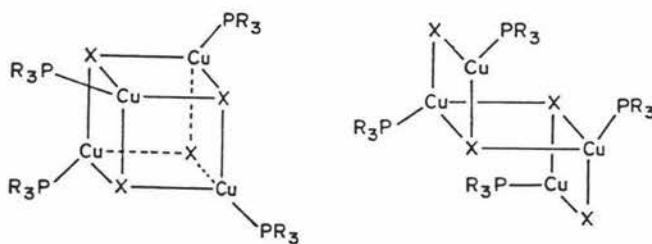
### I-4-1 Complexes with Monotertiary Phosphines

The most popular ligands remain triphenylphosphine and phenylalkylphosphines, but recently much interest has been shown in trimethylphosphine and in bulky ligands such as tricyclohexylphosphine and tri-tert-butylphosphine.

In general the monomeric phosphine ligands only coordinate as single ligand donors and do not involve any bridging role. In polynuclear structures the bridging ligands are generally halide ions with the phosphine in a terminal ligand capacity [14]. For example, in the complex  $[\text{Cu}\{\text{P}(\text{cyclohexyl})_3\}\text{Cl}]_2$  each copper(I) ion adopts a three fold coordination geometry, with two bridging chlorides and two terminal tricyclohexylphosphine molecules (Figure I-1) [15].



(Figure I-1)



(Figure I-2)

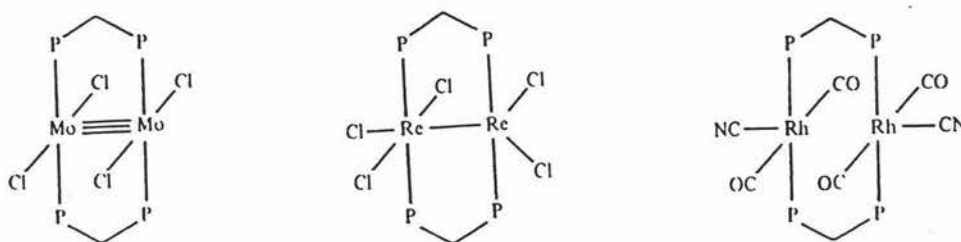
Copper(I) and silver(I) ions form the phosphine complexes  $[\text{M}(\text{PR}_3)\text{X}]_4$  ( $\text{X} = \text{Br}, \text{I}$ ;  $\text{R} = \text{Et}$  or  $\text{Ph}$ ) which are known with both cubane and step structures. The metals adopt the tetrahedral geometry in cubane-like structures and trigonal geometry in step formation (Figure I-2) [16-19]. The halides are always bridging with terminal sites characteristic for the phosphines.

### I-4-2 Complexes with Ditertiary Phosphines

The most widely used diphosphines are probably 1,2-bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)methane (dppm) *i.e.*  $\text{P}-\text{C}_n-\text{P}$  where  $n=2$  or  $1$  respectively. The chelating tendency increases as the chain length increases, so that for

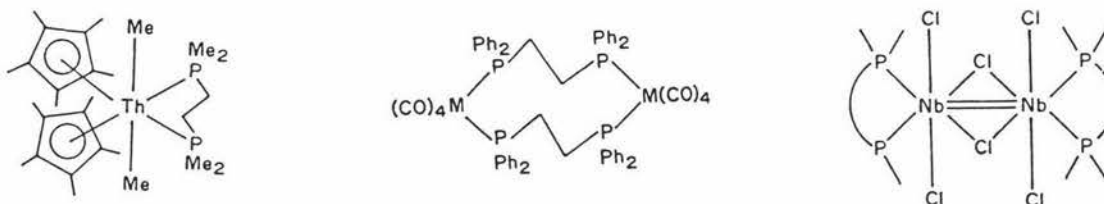


these two ligands, the tendency to chelate is greater for  $n=2$  [20].



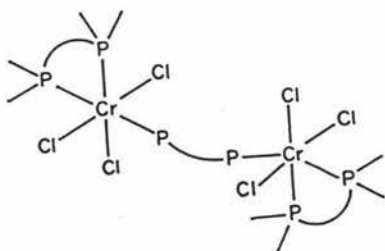
(Figure I-3)

The ligand properties of bidentate phosphines are strongly dependent on the nature of the  $C_n$  bridging units. The dppm ligand prefers to form bridged dinuclear complexes, rather than a strained four-membered chelate ring. When dppm forms dinuclear complexes, the metal phosphorus bonds are strong and the bridging diphosphine ligand can lock together two metal atoms in close proximity and hence promote organometallic reactions involving two metal centres (Figure I-3) [21].

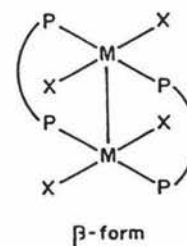
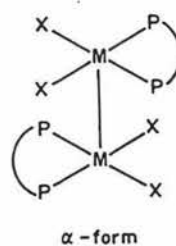


(Figure I-4)

The diphosphine ligands  $P-C_n-P$  ( $n=2, 3$ ) such as dppe, dmpe (1,2-bis(dimethylphosphino)ethane) and dppp (1,3-bis(diphenylphosphino)propane) are excellent chelate ligands which form five-membered ring complexes, as found in  $[ThMe_2(Me_5C_5)_2(dmpe)]$  [22] and  $[Nb_2Cl_6(R_2PCH_2CH_2PR_2)_2]$  ( $R=Me, Et, Ph$ ) [23,24] (Figure I-4). In the dinuclear complex  $[Cr(dmpe)_{1,5}Cl_3]$ , dmpe acts both as a chelating and a bridging ligand (Figure I-5) [25].



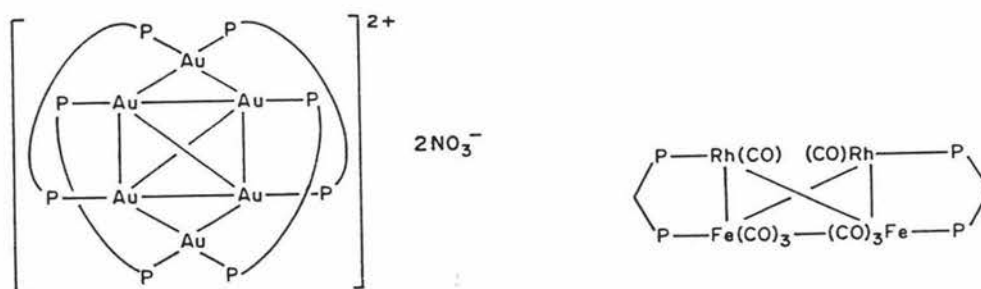
(Figure I-5)



(Figure I-6)

Similarly in  $[\text{Mo}_2\text{Cl}_4(\text{dppe})_2]$  and  $[\text{W}_2\text{Cl}_4(\text{dppe})_2]$ , dppe displays bridging behaviour in the  $\beta$ -form and chelating behaviour in the  $\alpha$ -form (Figure I-6) [26].

There are also many examples in the literature showing the capability of the bidentate ligand  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n=2, 3$ ) for stabilizing cluster compounds by the formation of bridges between adjacent transition metal atoms. Two examples are shown in (Figure I-7) [27-29].



(Figure I-7)

### I-4-3 Complexes with Polytertiary Phosphines

The polyphosphine-metal complexes are thermodynamically more stable than their comparable monophosphine analogues. The former exhibit several advantages over the latter including [1, 30]:

- (1) Excellent bonding ability to metal
- (2) Strong '*trans* influence' (*i.e.* lone pair orientation)
- (3) Increasing basicity (or nucleophilicity) at metal
- (4) Control on the stereochemistry and stoichiometry

1) Excellent bonding ability to metal

The bonding ability of these ligands arises from their thermodynamic stability.

2) Strong '*trans* influence' (*i.e.* lone pair orientation)

The major types of polydentate phosphine ligands are shown in Table 1-2 [31]. The most common tripodal polyphosphine ligand HC(PPh<sub>2</sub>)<sub>3</sub> [1,1,1-(tris(diphenylphosphino)-methane)] (tdpm) shows that the free molecule has the phosphorus atom lone pairs in a *trans* orientation (Figure I-8) [30, 32, 33]. This means that two of the lone pairs are *cis* to each other but the third one is *trans* to each of the others. This influence favours the ligand to bind through two of the *cis* P atoms to a single metal but leaves the third P atom unbound or bound to another metal.

3) Increasing basicity at the metal

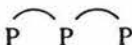


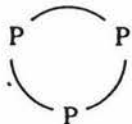

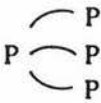
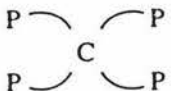
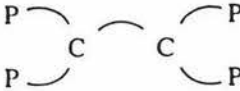


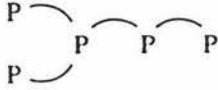
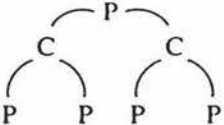
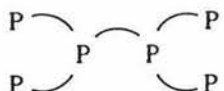
In the complex Rh(tdpme)Cl<sub>3</sub> [34] the tdpme [tdpme= (tris(diphenylphosphino)methyl)-ethane] ligand promotes the concentration of electron density on the metal atom since its reaction with the silver(I) ion and dihydrogen facilitates cluster and H bridge formation in the complex ion [Rh<sub>3</sub>Ag<sub>3</sub>H<sub>9</sub>(tdpme)<sub>3</sub>]<sup>3+</sup> (Figure I-9) cluster which are worthy of note [34].

4) Control on the stereochemistry and stoichiometry

The above tripodal ligand can stereochemically control the isolation of the *fac* isomer of the complex RhH<sub>3</sub>(tdpme) [34] which can be used to promote cluster growth on the addition of Ph<sub>3</sub>PAuCl [35].

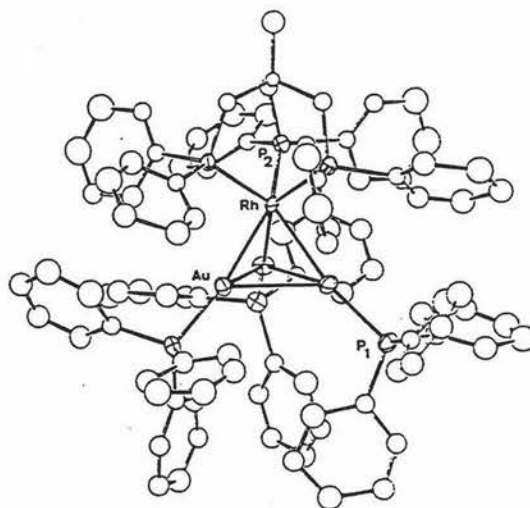
The stoichiometric incorporation of certain metal fragments into a cluster may not only change the size of the cluster but also influence its subsequent physical and chemical properties. Three distinct sets of compounds can be formed by treatment of MH<sub>3</sub>(tripod) (M= Rh or Ir; tripod= tdpme and triars) with different amounts of the cations [Au(THF)L]<sup>+</sup> (L= tertiary phosphine or arsine; THF= tetrahydrofuran).

**Table 1-2 Major types of polydentate phosphine ligands**

Tridentate:	Linear 	Tripodal 	Branched 	Macrocyclic 
Tetradentate:		Linear (or facultative) 		Tripodal 
	Spirocyclic 	Branched 		Macrocyclic 
Pentadentate:		Linear 		Branched 
		Nonlinear 		
Hexadentate:				Branched 



**(Figure I-8)**



**(Figure I-9)**

Their composition differs depending on the M: Au molar ratios. Type A has the 1:1 ratio [(tripod)MH<sub>3</sub>(AuL)]<sup>+</sup>, type B the 1:2 ratio [(tripod)MH<sub>3</sub>(AuL)<sub>2</sub>]<sup>2+</sup> and type C 1:3 [(tripod)MH<sub>2</sub>(AuL)<sub>3</sub>]<sup>2+</sup>. As the M: Au ratio increases structural changes occur and this is clearly reflected in the <sup>31</sup>P and <sup>1</sup>H NMR spectra.

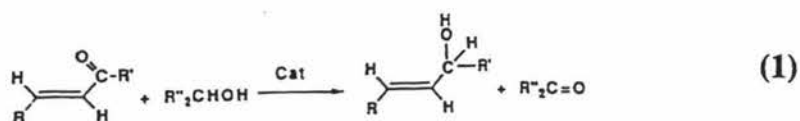
The results of the X-ray structure analysis of [(tdpme)Rh(μ-H)<sub>2</sub>(Au(PPh<sub>3</sub>)<sub>3</sub>)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> the stoichiometry of which contains one less hydrogen than does type A above can best be described as a metallocubane cluster made up of a triangle of gold atoms capped by the rhodium tdpme fragment. In addition each gold is coordinated to one PPh<sub>3</sub> ligand. The cation lies on a crystallographic 3-fold axis which goes through the CH<sub>3</sub>-C bond of tdpme, the rhodium atom and the centre of Au<sub>3</sub> triangle face. The triphosphine ligand is thus excellent for stereochemical control.

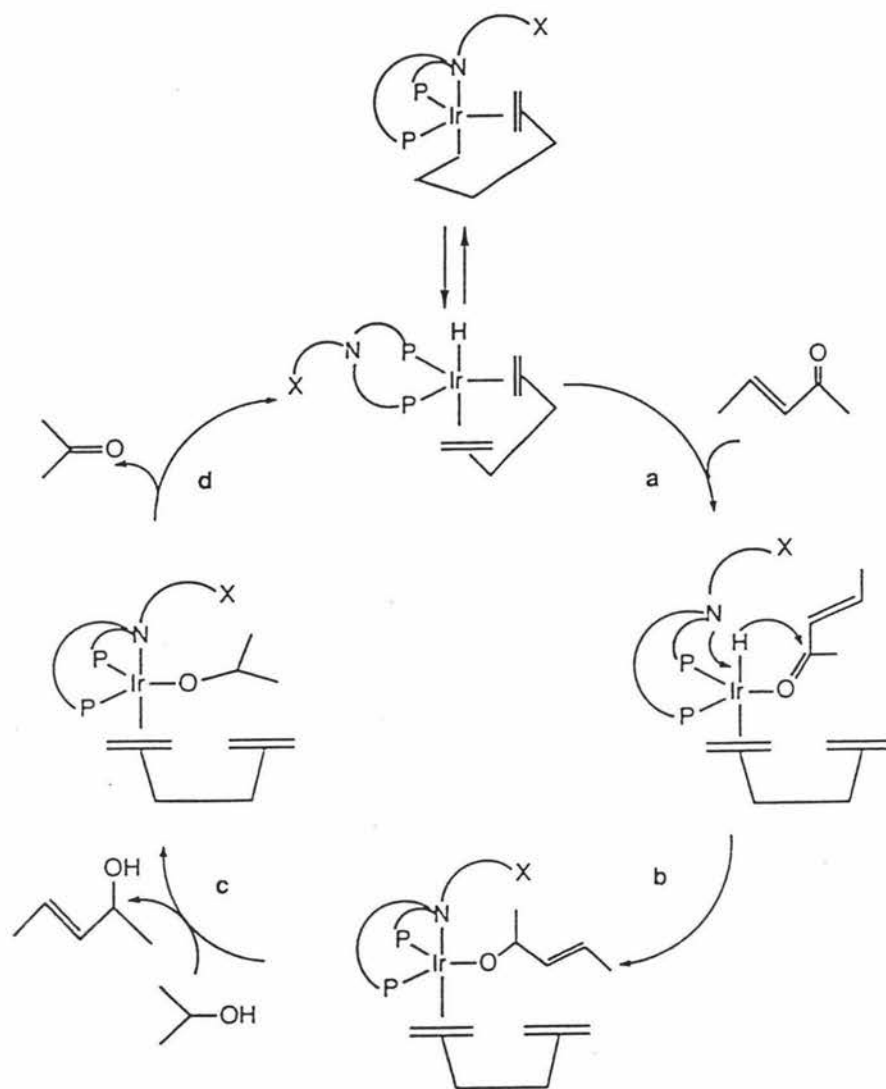
The ligand tdpme as a polydentate ligand forms complexes with almost all transition metals, especially those with the d<sup>8</sup> configuration. The [M(tdpme)] fragment (M= Rh, Ir) is able to coordinate other important reactive ligands such as acyl groups, alkyls, aryls, carbon monoxide, hydrides and olefins in a stable way and in a large variety of different arrangements and bonding modes. Excellent reviews of polyphosphine ligands currently exist [1,14,31].

#### I-4-4 Complexes with Hybrid Polyphosphine Ligand Containing N and P

##### Donor Atoms

Studies on polyphosphine-stabilized metal complexes as catalysts have been performed for many years. However, the non-dissociative character of the chelating polyphosphines may be a disadvantage in some catalytic processes. The hybrid polydentate ligands containing phosphorus and nitrogen donor atoms offer the possibility of supplying vacant coordination sites at the metal by dissociation of either P or N donors. For example, the cyclooctenyl iridium complexes [(PNP)Ir-(σ,η<sup>2</sup>-C<sub>8</sub>H<sub>13</sub>)] (1) and [(P<sub>2</sub>N<sub>2</sub>)Ir(σ,η<sup>2</sup>-C<sub>8</sub>H<sub>13</sub>)] (2) (PNP= MePPh<sub>2</sub>NPPh<sub>2</sub>; P<sub>2</sub>N<sub>2</sub>= NEt<sub>2</sub>PPh<sub>2</sub>NPPh<sub>2</sub>) are efficient catalyst precursors for the stereoselective hydrogen transfer reduction of α, β-unsaturated ketenes to allylic alcohols [equation, (1)].





**Scheme I**

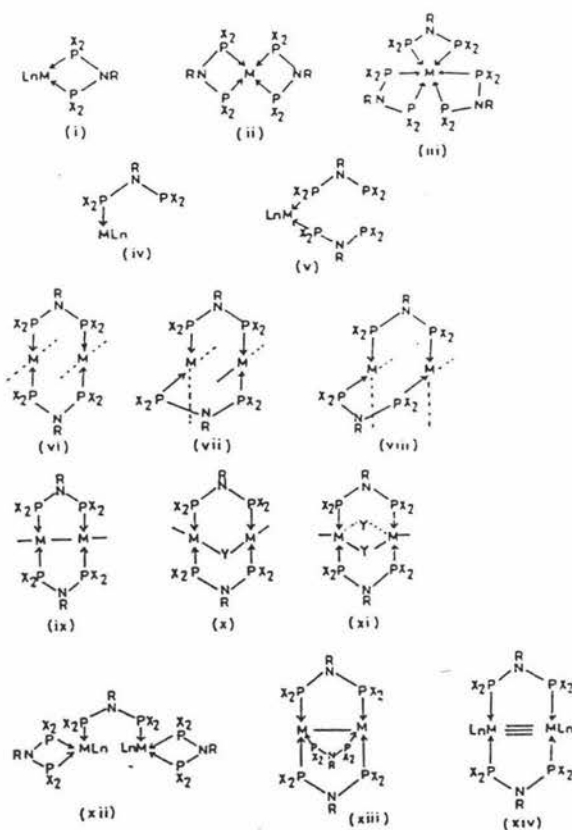
The proposed catalysis cycle is illustrated in scheme I [36].

- (a) The ketone approaches the metal and displaces one olefinic end of cod (cod=cycloocta-1,5-diene).
- (b) The selective transfer of hydride to the carbonyl group occurs to give an alkoxy complex, a path that may be promoted by intramolecular coordination of the nitrogen donor to metal.
- (c) A new alkoxy complex and allylic alcohol is formed with the secondary alcohol in excess.

(d) Finally, the hydrido catalyst is restored *via* a  $\beta$ -H elimination process.

A crucial point to explain the effectiveness of (1) and (2) in the catalytic reaction is believed to be the ability of the hybrid polydentate PNP and  $P_2N_2$  ligands to readily fasten/unfasten a nitrogen donor to and from the metal at different steps of the catalytic cycle. Indeed the substitution of phosphorus for nitrogen as it occurs in the reacted  $\sigma, \eta^2$ -cyclooctenyl complex of tdpme generates a species,  $[(\text{tdpme})\text{Ir}(\sigma, \eta^2\text{-C}_8\text{H}_{13})]$ , which is totally inactive for the stereoselective reduction of benzylideneacetone [1,36].

The hybrid polydentate ligand containing P-N-P donor atoms has exhibited [53-55] better flexibility of its back-bone compared with P-O-P donors and better thermal stability than the P-C-P donor framework ligands. When the diphosphineamine ligands  $X_2\text{P-NR-PX}_2$  ( $X = \text{F, Cl, Me, Ph; R = Me,}$ ) coordinate to transition metals they show the 'best fit' geometry in *e.g.* Cr(0) octahedral [56,57], Fe(0) trigonal bipyramidal [58,59], Ni(0) tetrahedral complexes [60, 61]. The possible modes of coordination of a diphosphineamine ligand are varied and these are shown in (Figure I-10) [50-52].

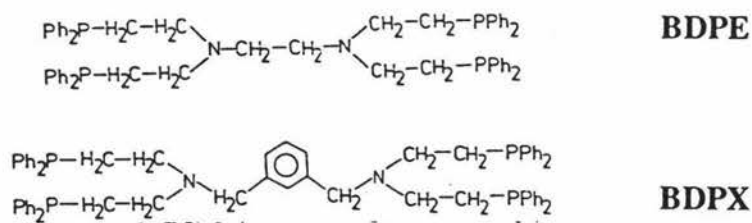
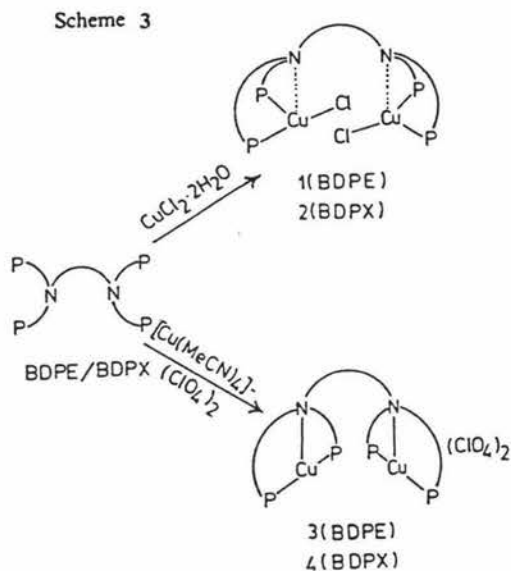


Possible coordinating modes of diphosphinoamines.

(Figure I-10)

However the ligand  $X_2P-NR-PX_2$  coordinates only in a monodentate or bridging bidentate fashion as chelation produces an unstable four-membered ring.

The longer chain polydentate ligands  $\alpha, \alpha'$ -bis(2-(diphenylphosphino)ethyl)amino) ethane (BDPE) and  $\alpha, \alpha'$ -bis(2-(diphenylphosphino)ethyl)amino)-m-xylene (BDPX) (Figure I-11) [62] formed the copper(I) complexes  $[Cu_2(BDPE)Cl_2]$ ,  $[Cu_2(BDPX)Cl_2]$ ,  $[Cu_2(BDPE)](ClO_4)_2$  and  $[Cu_2(BDPX)](ClO_4)_2$  (Scheme 3). The ligands are dinucleating and two phosphorus atoms and a nitrogen atom bind to each metal with a different geometry for the chloro and perchlorate complexes (Figure I-11).



(Figure I-11)

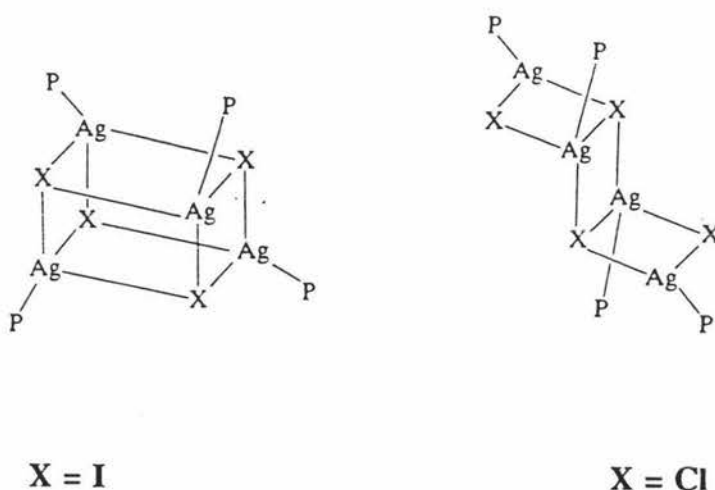
### I-5 TWO, THREE AND FOUR COORDINATE COMPLEXES OF COPPER(I) AND SILVER(I) WITH TERTIARY PHOSPHINE LIGANDS

The electronic configuration of copper(I) and silver(I) involves a filled 3d shell and hence the  $Cu^+$  and  $Ag^+$  ions are diamagnetic and of spherical symmetry. A extensive range



of coordination complexes has been observed for both copper(I) and silver(I), with bi- [37], tri- [38], tetra- [39,40], penta- [41], hexa- [42] and octa- [43] nuclear species as well as infinite chain and ribbon structures. In the solid state the stereochemistry of copper(I) complexes with phosphine ligands is dominated by four coordination but significant numbers of three coordinate species [44] are also known. However for silver(I) complexes with phosphine ligands, four coordination number is dominant, but two [45,46] and five [see Chapter Four] coordination modes are also observed. Both copper(I) and silver(I) complexes with six coordination are unknown.

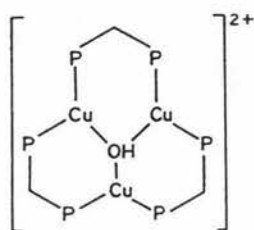
The four coordinate complexes of copper(I) and silver(I) are generally tetrahedral, especially, when four equivalent ligands are involved as in  $[\text{Cu}(\text{PPh}_3)_4]\text{ClO}_4$  [47] and  $[\text{Ag}(\text{PPh}_3)_4]\text{NO}_3$  [47,48]. But many complexes show distorted tetrahedral geometry, which may be attributed to steric and electronic effects; two are given in Figure I-12 for the species  $[\text{Ag}(\text{PPh}_3)\text{Cl}]_4$  and  $[\text{Ag}(\text{PPh}_3)\text{I}]_4$ .



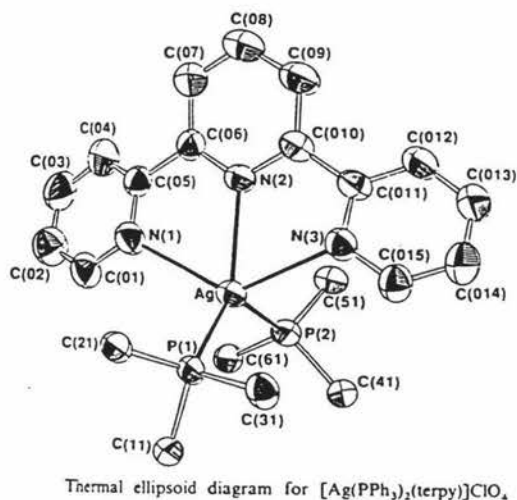
(Figure I-12)

Three coordinate copper(I) and silver(I) complexes are unusual and these occur where polydentate, macrocyclic or acyclic ligands impose geometrical constraints on the metal centre [44]. For example in the complex  $[\text{Cu}_3(\text{dppm})_3\text{OH}](\text{BF}_4)_2$  (dppm=bis(diphenylphosphino)methane) the coppers are arranged in a triangle capped by an OH ligand. Each dppm bridges two copper atoms to give each copper a trigonal planar geometry (Figure I-13) [44]. Silver(I) displays a trigonal planar structure in the complex ion

[Ag(diphos)]<sup>+</sup> (diphos=2,11-bis(diphenylphosphino)methane)benzo[C]phenanthrene) [174, Figure IV-4]. The complex cation [(t-Bu)<sub>3</sub>P-Ag-(P(t-Bu)<sub>3</sub>)]<sup>+</sup> contains a linear arrangement of the phosphorus atoms about the silver(I) ion [45]. A distorted trigonal-bipyramidal geometry about silver has been observed in the complex [Ag(PPh<sub>3</sub>)<sub>2</sub>(terpy)]ClO<sub>4</sub> (terpy=2,2':6',2''-terpyridine) (Figure I-14) [186].



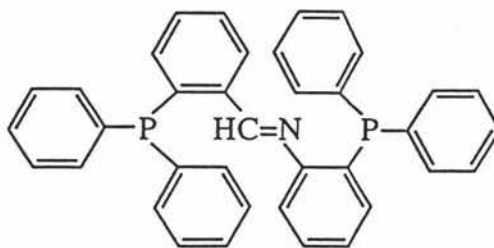
(Figure I-13)



(Figure I-14)

## I-6 THE PRESENT STUDY

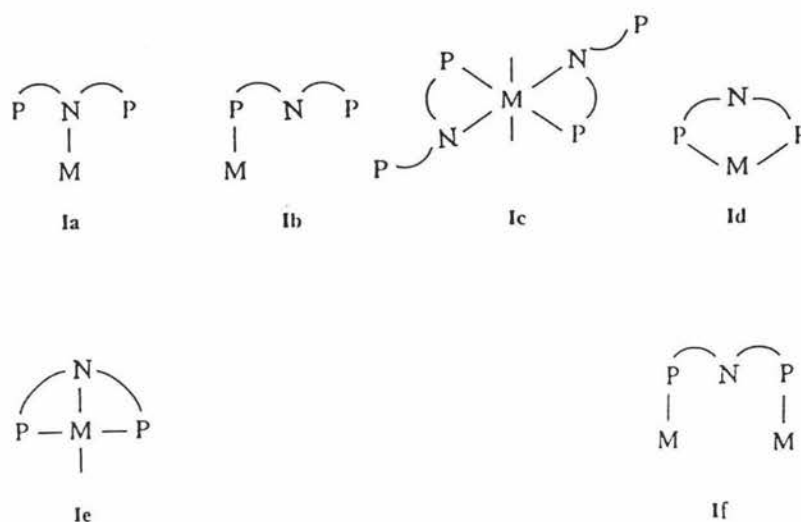
The ligand 2-(diphenylphosphono)-N-[2-(diphenylphosphino)benzylidene] benzeneamine (PNCP) (Figure I-15) was first synthesized in our laboratory a few years ago.



PNCP

(Figure I-15)

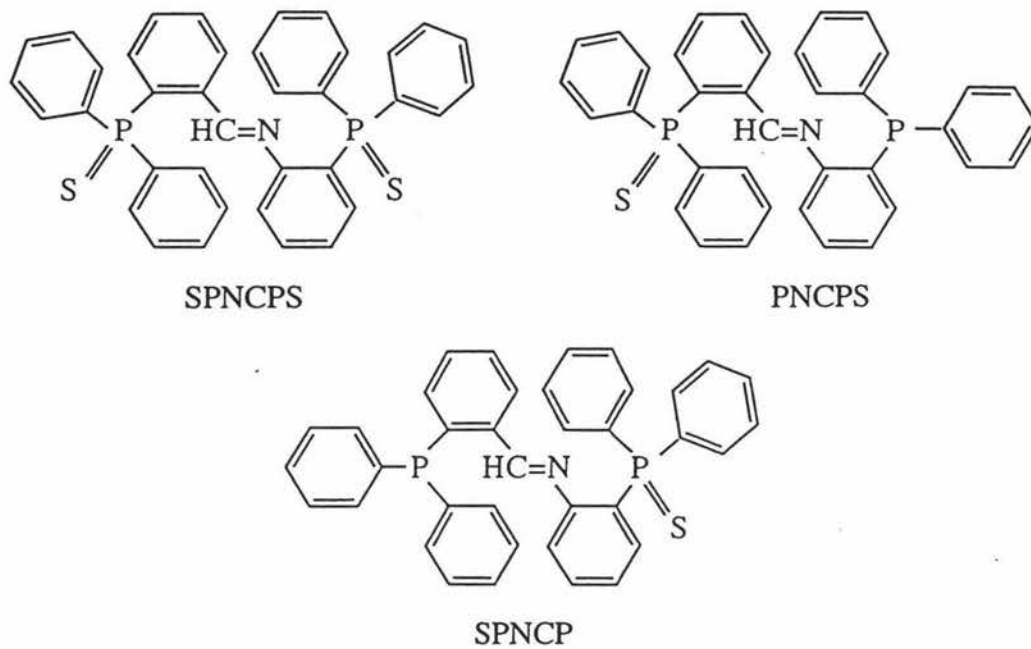
As well as containing two soft P atoms and one 'intermediate' hard N atom, the phosphorus atoms are inequivalent which is a rare feature in a ligand. In principle PNCP may bind to metal ions in a variety of coordination modes as shown in Figure I-16.



(Figure I-16)

The present work was undertaken to investigate the steric configuration of the PNCP ligand and to establish its mode(s) of coordination when bound to silver(I) and copper(I) salts and to determine whether PNCP binds in an equivalent way. This will be determined by X-ray crystallography. The ability of PNCP to form mono- and bi-metallic complexes will be studied.

The relative reactivity of the two phosphorus donor atoms towards oxidation with sulphur will be undertaken as well as the selected syntheses of the unsymmetrical monosulfide isomers SPNCP (2-(diphenylphosphinothiyl)-N-[2-(diphenylphosphino)benzylidene]benzeneamine), PNCPS (2-(diphenylphosphino)-N-[2-(diphenylphosphinothiyl)benzylidene]benzeneamine) and SPNCPS (2-(diphenylphosphinothiyl)-N-[2-(diphenylphosphinothiyl)benzylidene]benzeneamine) (Figure I-17).



(Figure I-17)