STRUCTURAL STUDIES ON THE INTERACTIONS
OF A P₂N 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

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1995

ACKNOWLEDGEMENTS

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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, [Cu(SPNCPS)]ClO$_4$.

In Chapter Three the preparation of a series of copper(I) complexes of the general formula [Cu(PNCP)ClO$_4$] and [Cu(PNCP)L]ClO$_4$ (L- ligands containing S, N donor atoms) have been reported. The crystal structure of [Cu(PNCP)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 [Ag(PNCP)ClO$_4$] and the dinuclear complex [Ag(PNCP)(SCN)]$_2$ are presented. Both complexes were characterized by a variety of physicochemical techniques. The tridentate behaviour of PNCP in the complex [Ag(PNCP)ClO$_4$] was established but the Ag-N bond was long and weak. In the complex [Ag(PNCP)(SCN)]$_2$ the Ag-N bond not exist and PNCP acts as a bidentate ligand.

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ABBREVIATIONS

2-PCHO	o-(diphenylphosphino)benzaldehyde
2-PCHOS	o-(diphenylphosphinothioyl)benzaldehyde
2-PNH$_2$	o-(diphenylphosphino)aniline
2-PNH$_2$S	o-(diphenylphosphinothioyl)aniline
BDPE	α,α'-(dis(2-(diphenylphosphino)ethyl)amino)ethane
BDPX	α,α'-(dis(2-(diphenylphosphino)ethyl)amino)-m-xylene
diphos	2,11-(bis(diphenylphosphino)methyl)benzo[C]phenanthrene
dmpe	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-(diphenylphosphino-thioyl)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

2PCHO

2PNH₂

2-SPNH₂

2-SPCHO

PNCP

SPNCP

PNCPS

SPNCPS
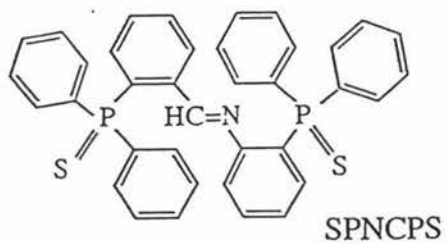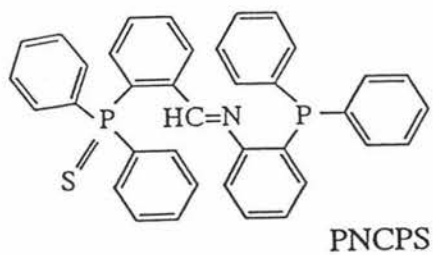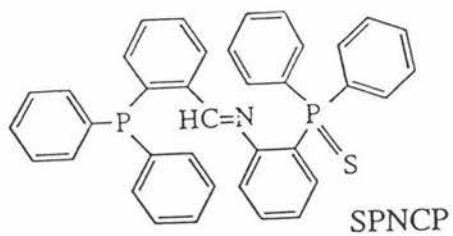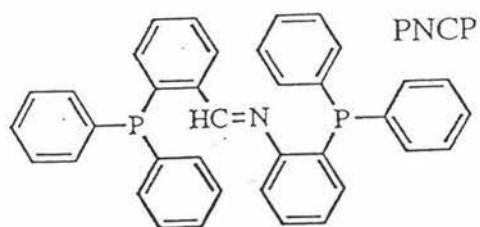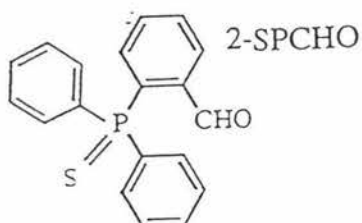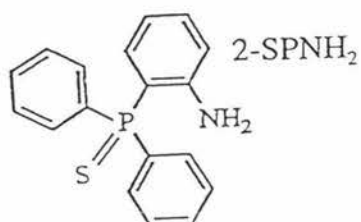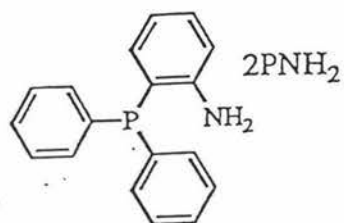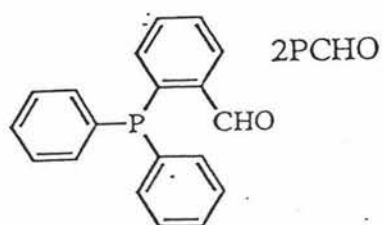
CHAPTER ONE
GENERAL INTRODUCTION

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 σ* 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 π-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 σ bonds with PR_3 ligands.

(2) Metals in oxidation state 0 or below form combined σ and π bonds to PF_3, PCl_3 and $P(OPh)_3$.

For other complexes the tendency for π-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 (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 PR_3, can be considered as derivatives of the phosphine molecule, PH_3, and these molecules can add oxygen and sulphur to give the tetrahedral phosphine oxides (R_3PO) and phosphine sulfides (R_3PS) 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 ß hydrogen atom are particularly stable; Me_3PO and Ph_3PO do not decompose below 700°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].

$$R_4POH \longrightarrow R_3PO + RH \qquad (1)$$
$$R_4POR' \longrightarrow R_3PO + RR' \qquad (2)$$

Nickel (II) halides form complexes $[NiX_2(Ph_2PCH_2PPh_2)]$ with diphosphines, which are stable in the solid state but decompose slowly when they are heated above 220°C, undergoing air oxidation to yield the diphosphine dioxides [10].

I-3-2 Tertiary Phosphine Sulfides

The tertiary phosphine sulfides, R_3PS, contain a P=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 $Me_2PCH_2PPh_2$ [13] as shown below.

$$Ph_3P=X \longrightarrow Ph_2P=XCH_2Li \longrightarrow Ph_2P=XCH_2PR^1R^2 \longrightarrow Ph_2PCH_2P=SR^1R^2$$
$$(R^1 \text{ and } R^2 \text{ are alkyl groups})$$
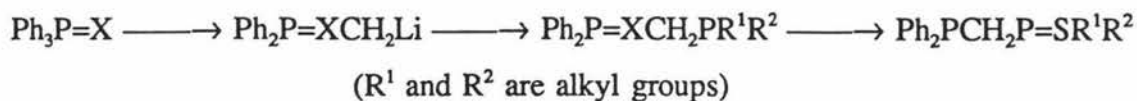
I-4 PHOSPHINE COMPLEXES OF TRANSITION METALS

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 $[Cu\{P(cyclohexyl)_3\}Cl]_2$ each copper(I) ion adopts a three fold coordination geometry, with two bridging chlorides and two terminal tricyclohexyl-phosphine molecules (Figure I-1) [15].
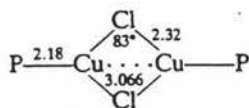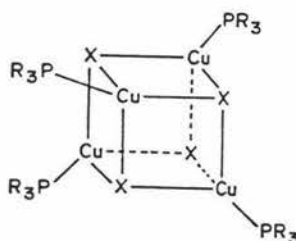
(Figure I-1)   (Figure I-2)
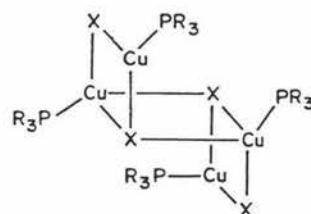
Copper(I) and silver(I) ions form the phosphine complexes $[M(PR_3)X]_4$ (X= Br, I; R= Et or Ph) which are known with both cubane and step structures. The metals adopt the tetrahedral geometry in cubane-like structures and trigonal geometry in step formation (Figure I-2) [16-19]. The halides are always 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. P-C$_n$-P where n=2 or 1 respectively. The chelating tendency increases as the chain length increases, so that for

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these two ligands, the tendency to chelate is greater for n=2 [20].
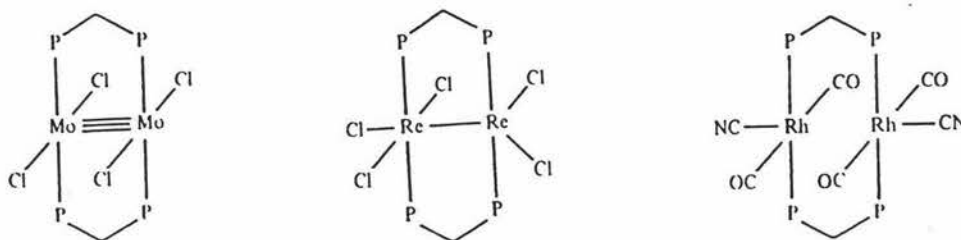
(Figure I-3)

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].
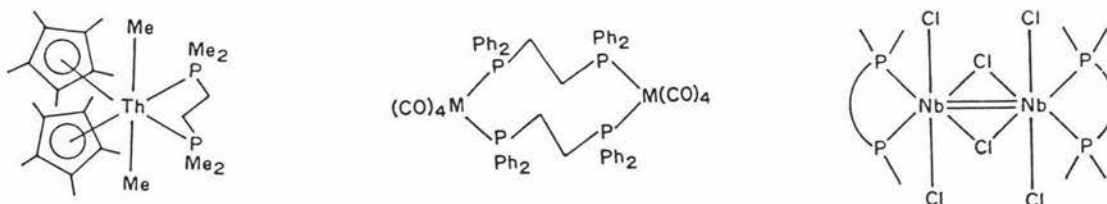
(Figure I-4)

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$_5$C$_5$)$_2$(dmpe)] [22] and [Nb$_2$Cl$_6$(R$_2$PCH$_2$CH$_2$PR$_2$)$_2$] (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].

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α-form

β-form
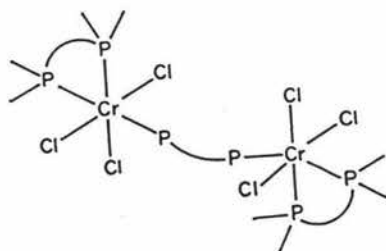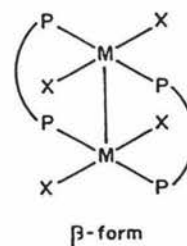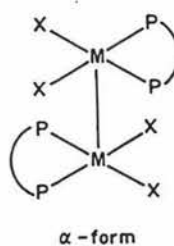
(Figure I-5)   (Figure I-6)

Similarly in [Mo$_2$Cl$_4$(dppe)$_2$] and [W$_2$Cl$_4$(dppe)$_2$], dppe displays bridging behaviour in the β-form and chelating behaviour in the α-form (Figure I-6) [26].

There are also many examples in the literature showing the capability of the bidentate ligand Ph$_2$P(CH$_2$)$_3$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].
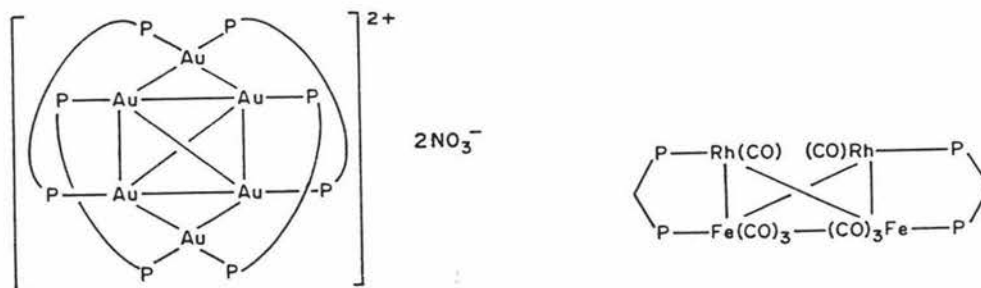
(Figure I-7)

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]:

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(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 $HC(PPh_2)_3$ [1,1,1-(trisdiphenylphosphino)-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 $Rh(tdpme)Cl_3$ [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 $[Rh_3Ag_3H_9(tdpme)_3]^{3+}$ (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 $RhH_3(tdpme)$ [34] which can be used to promote cluster growth on the addition of Ph_3PAuCl [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_3(tripod) (M= Rh or Ir; tripod= tdpme and triars) with different amounts of the cations $[Au(THF)L]^+$ (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
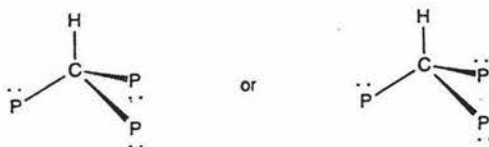
(Figure I-8)

(Figure I-9)

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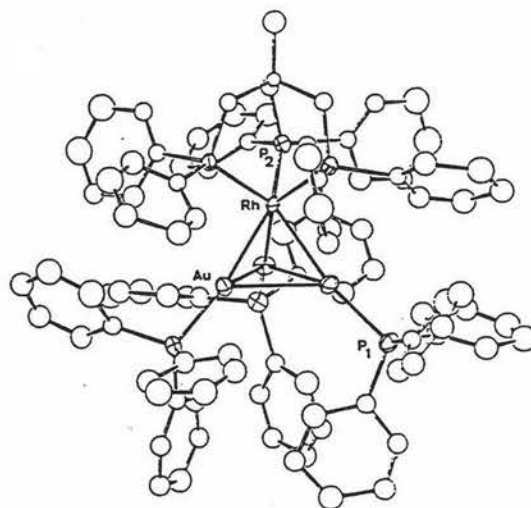
Their composition differs depending on the M:Au molar ratios. Type A has the 1:1 ratio [(tripod)MH$_3$(AuL)]$^+$, type B the 1:2 ratio [(tripod)MH$_3$(AuL)$_2$]$^{2+}$ and type C 1:3 [(tripod)MH$_2$(AuL)$_3$]$^{2+}$. As the M:Au ratio increases structural changes occur and this is clearly reflected in the ^{31}P and ^{1}H NMR spectra.

The results of the X-ray structure analysis of [(tdpme)Rh(μ-H)$_2$ (Au(PPh$_3$)$_3$)](CF$_3$SO$_3$)$_2$ the stoichiometry of which contains one less hydrogen than does type A above can best be described as a metallotetrahedrane cluster made up of a triangle of gold atoms capped by the rhodium tdpme fragment. In addition each gold is coordinated to one PPh$_3$ ligand. The cation lies on a crystallographic 3-fold axis which goes through the CH$_3$-C bond of tdpme, the rhodium atom and the centre of Au$_3$ 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^8 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^2-C$_8$H$_{13}$)] (1) and [(P$_2$N$_2$)Ir(σ,η^2-C$_8$H$_{13}$)] (2) (PNP= MePPh$_2$NPPh$_2$; P$_2$N$_2$= NEt$_2$PPh$_2$NPPh$_2$) are efficient catalyst precursors for the stereoselective hydrogen transfer reduction of α, β-unsaturated ketenes to allylic alcohols [equation, (1)].

$$\text{(1)}$$

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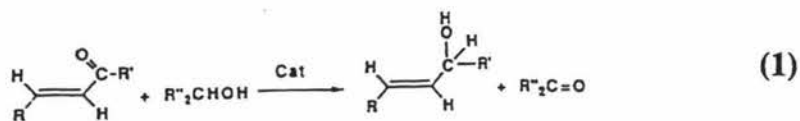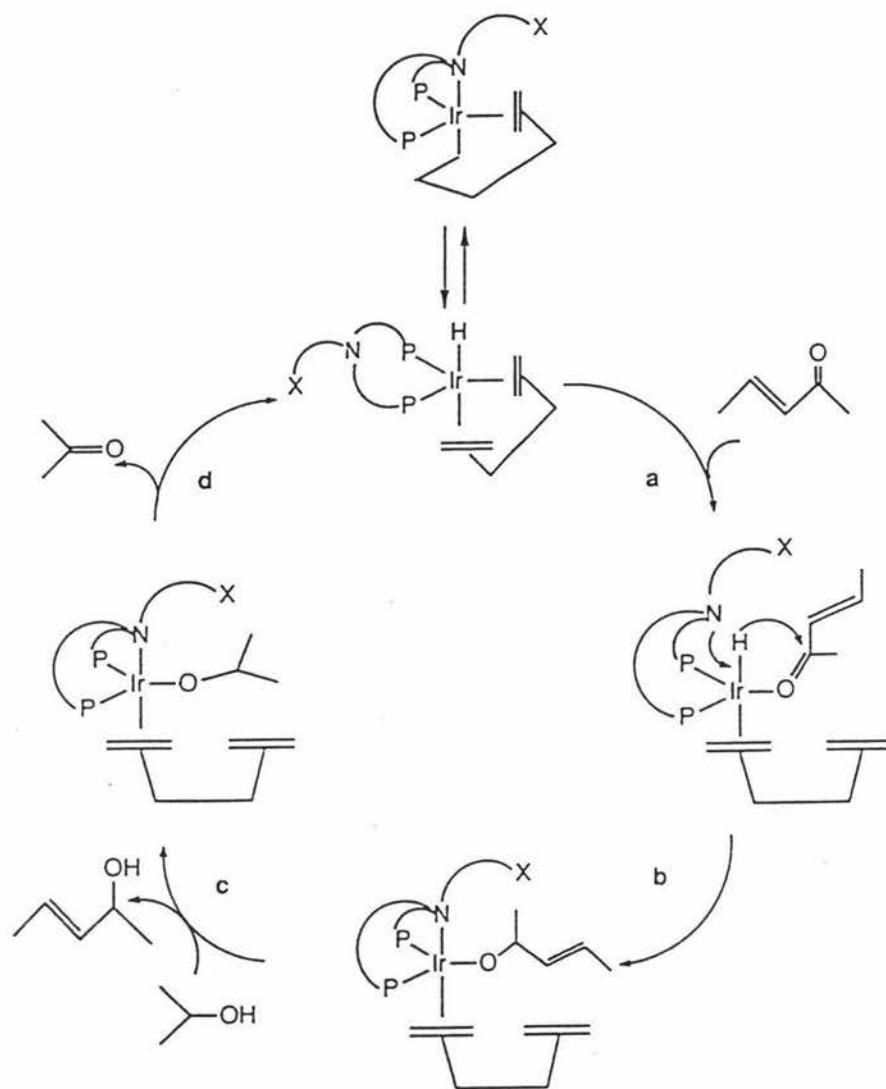
Scheme I

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 ß-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 σ,η^2- cyclooctenyl complex of tdpme generates a species, $[(tdpme)Ir(\sigma,\eta^2-C_8H_{13})]$, 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 $X_2P-NR-PX_2$ (X = 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].
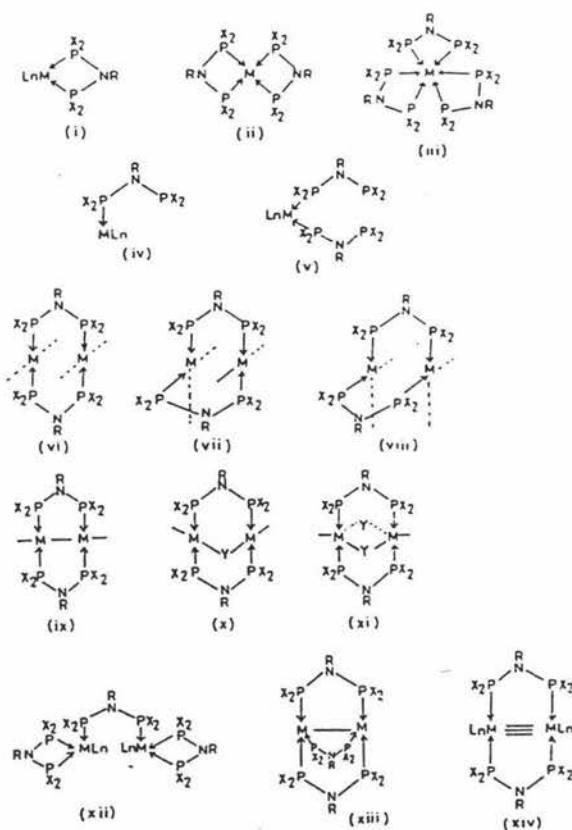
Possible coordinating modes of diphosphinoamines.

(Figure I-10)

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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 α,α'-bis(2-(diphenylphosphino)ethyl)amino) ethane (BDPE) and α, α'-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).

Scheme 3
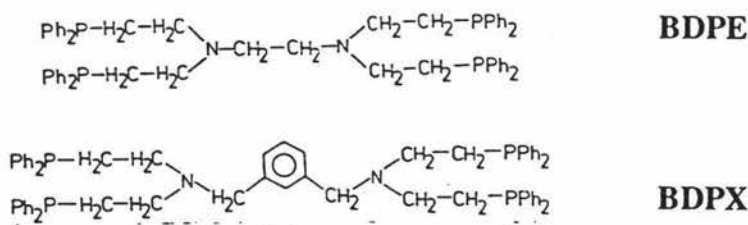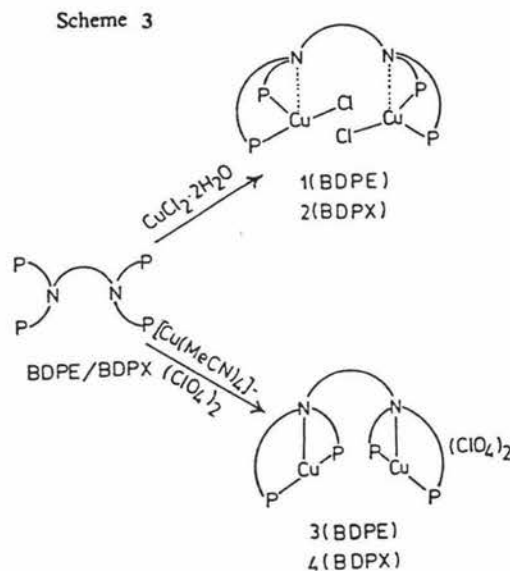
(Figure I-11)

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 $[Cu(PPh_3)_4]ClO_4$ [47] and $[Ag(PPh_3)_4]NO_3$ [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 $[Ag(PPh_3)Cl]_4$ and $[Ag(PPh_3)I]_4$.

X = I   X = Cl
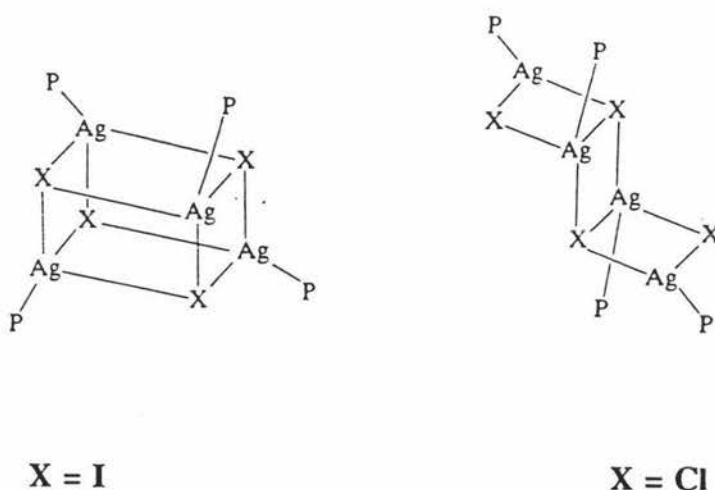
(Figure I-12)

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 $[Cu_3(dppm)_3OH](BF_4)_2$ (dppm=bis(diphenyl-phosphino)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

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[Ag(diphos)]$^+$ (diphos=2,11-bis(diphenylphosphino)methane)benzo[C]phenanthrene) [174, Figure IV-4]. The complex cation [(t-Bu)$_3$P-Ag-(P(t-Bu)$_3$]$^+$ 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$_3$)$_2$(terpy)]ClO$_4$ (terpy=2,2′:6′,2″-terpyridine) (Figure I-14) [186].

Thermal ellipsoid diagram for [Ag(PPh$_3$)$_2$(terpy)]ClO$_4$
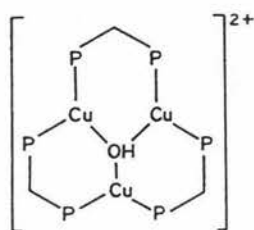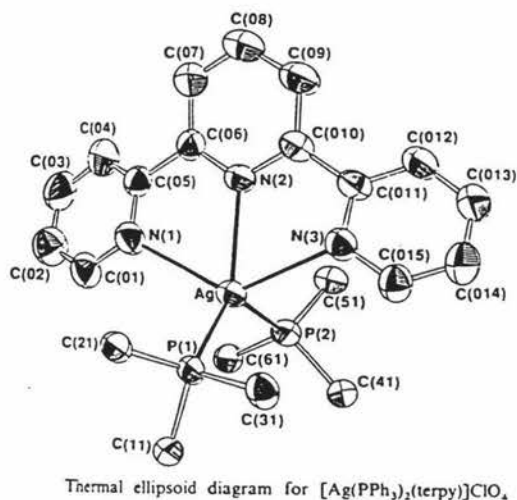
(Figure I-13)

(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)

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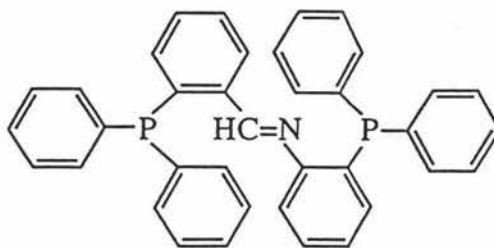
As well as containing two soft P atoms and one 'intermediate' hard N atom, the phosphorus atoms are inequivalent which is a rare feature in a ligand. In principle PNCP may bind to metal ions in a variety of coordination modes as shown in Figure I-16.
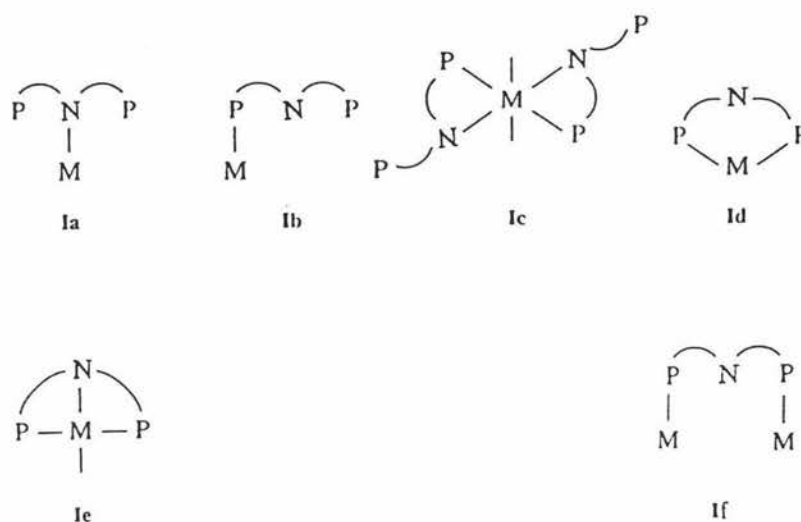
(Figure I-16)

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-(diphenylphosphinothioyl)-N-[2-(diphenylphosphino)-benzylidene]benzeneamine), PNCPS (2-(diphenylphosphino)-N-[2-(diphenylphosphino-thioyl)benzylidene]benzeneamine) and SPNCPS (2-(diphenylphosphinothioyl)-N-[2-(diphenylphosphinothioyl)benzylidene]benzeneamine) (Figure I-17).
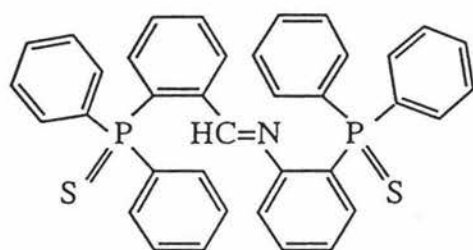
SPNCPS
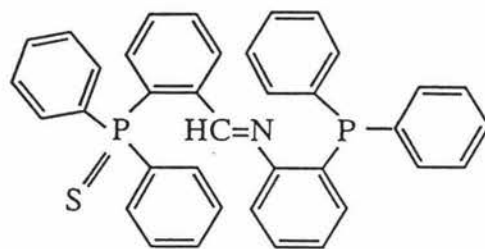
PNCPS
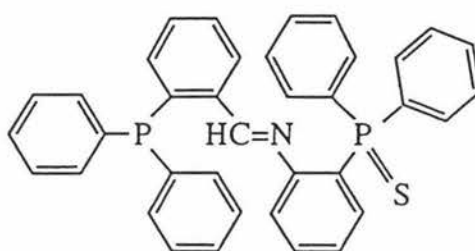
SPNCP

(Figure I-17)

CHAPTER TWO

SYNTHESIS OF SULFIDE LIGANDS OF 2-(DIPHENYLPHOSPHINO)-N-[2-DIPHENYLPHOSPHINO)BENZYLIDENE]BENZENEAMINE (PNCP)

II-1 INTRODUCTION

Since Bannister and Cotton reported the characterisation of the adducts $PbCl_2L_2$ (L= Ph_3PS, Ph_3PSe) and $SnCl_4L_2$ L= Ph_3PSe) in 1960 [63], tertiary phosphine sulfides have become an important class of ligands for transition metal ions. There are now many reports of complexes formed with phosphine oxides, sulfides and selenides but relatively few with tellurides due to the lower stability of the phosphorus-tellurium bond [64]. However, in contrast to the mono-tertiary phosphine chalcogenides R_3PE (E= O, S, Se), little attention has been paid to di- and poly- tertiary phosphine chalcogenides. Multidentate tertiary phosphine derivatives have been the subject of numerous studies with anionic ligands of the type $[R_2P(E)]_2CH^-$ [65-67], $[R_2P(E)]_3C^-$ [68-70] and $[R_2P(E)]_2N^-$ [71,72], and unsymmetrical phosphines such as $R_2P(CH_2)_nP(E)R_2$ [73-75] and $R_2P(S)(CH_2)_nPSeR_2$ (E= S,Se) [76,77], proving to be popular choices.

The selection of many tertiary phosphine chalcogenide ligands as complexing agents has been stimulated by the following factors:

1. The variety of coordination number and stereochemistries which have been discovered in their metal complexes.

2. The solvent extraction properties of the tertiary phosphine oxides towards some metals.

3. Their potential catalytic role when complexed with a metal.

II-1-1 The Nature of the Bonding in the Ligands

Phosphine chalcogenides with sulphur or selenium as donor atoms are typical 'soft' bases, forming complexes preferentially with 'soft' or 'class-B' acids [64,78]. The formation of bonds between R_3P and E (E= S or Se) atoms is believed to involve a σ component, $R_3P \rightarrow E$, and a π component from $E \rightarrow PR_3$ ($p\pi \rightarrow d\pi$ overlap) [78-80], leading to multiple bond formation. The two components are formally represented by the equations (A) and (B).

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$$R_3P + E \rightarrow R_3P^+ \rightarrow E^- \quad \text{(A)}$$

$$R_3P^+ + E^- \rightarrow R_3P = E \quad \text{(B)}$$

However a recent review suggests that the bonding may be more complicated than this simple description. It describes a model where d orbital participation is neglected in the π-bond formation of the P=O bond [81]. In phosphine chalcogenides, P-S and P-Se bond lengths lie in the range 1.94-1.95Å and 2.09-211Å respectively, which may be compared with a typical P-S single bond of about 2.085Å for the bridging bond in P_4S_{10} and a typical P-Se single bridged bond of 2.24Å in P_4Se_3. These shortened distances suggest the presence of some multiple character in P-S and P-Se bonds indicating that scheme B is a contributor to the overall bonding scheme.

The P-C bond lengths in phosphine sulfides and selenides lie in the range 1.81-1.82Å [82-84] and 1.78-1.85Å [85,86] respectively, comparable with those observed in the tertiary phosphines, R_3P. However, the bond angles observed for the C-P-E and C-P-C angles in the sulfides and selenides are 111-115° (E= S or Se) and 104-108°, indicating the R_3PE structure is close to tetrahedral, as suggested by the formulation in equation (A) above.

X-ray data have suggested metal-donor atom bonds (M-S 2.19-2.77Å or M-Se 2.30-2.60Å) are simple single bonds implying the donation of a pair of electrons from the S or Se atom to the metal centre with no evidence of π back-bonding from filled metal orbitals to empty orbitals on sulphur. For example, the X-ray structure of the complex [Cu(Ph$_3$PS)(NS$_3$)] [91] shows trigonal planar geometry (Figure II-1,B). The Cu-S distance at 2.214Å is significantly longer than those in the analogous complex [CuL$_3$]BF$_4$ (L= ethylenethiourea) (2.072Å) [89], but shorter than those observed in [Cu(Me$_3$PS)$_3$]$^+$ (2.26Å) and [Cu(Me$_3$PS)Cl]$_3$ (2.265Å) [88,92]. The ^{31}P NMR data support metal-phosphorus π-bonding in the PR^{1}R^2 group of R$_2$P(S)CH$_2$PR^{1}R^2, but there is no evidence for metal-S π-bonding [75,77,89].

II-1-2 Types of Phosphine Sulfide Ligands

Recently, the tertiary phosphine sulfide ligand has been the subject of increasing scrutiny

[64,78]. The introduction of other donor atoms (*e.g.* N) into such polydentate ligands give potential for stereochemical variety.

Four types of tertiary phosphine sulfide ligands can be identified.

A. Monodentate tertiary phosphine sulfides such as $R_3P=S$

$(R_3= Ph_3, Me_3, Me_2Ph, n\text{-}Bu_3, Oct_3)$

B. Bidentate phosphine sulphides, a grouping which may be further subdivided into three categories:

   (i)   Symmetrical ligands *e.g.* $Ph_2P(S)(CH_2)_nP(S)Ph_2$

           $(n= 1, 2, 4$ and $6)$

   (ii)   Asymmetrical ligands e.g. $Ph_2P(S)CH_2PR^1R^2$ and $Ph_2P(S)CH_2P(S)Me_2$

           $(R^1, R^2=Ph_2; PhMe; i\text{-}Pr, Ph; Me_2; i\text{-}Pr_2; i\text{-}Bu_2).$

   (iii)   Anionic ligands *e.g.* $[Ph_2P(S)]_2CH^-$.

C. Iminotetramethyl or iminotetraphenyl-dithiophosphines, of which both neutral and anionic species are known. (*e.g.* $R_2P(S)NHP(S)R_2$ $(R= Me, Ph)$ and $[R_2P(S)]_2N^-)$

D. Tritertiary phosphine sulfides, exemplified by the following examples:

   (i) $[Ph_2P(S)]_3CH$

   (ii) $[Ph_2P(S)]CH[Me_2P(S)]_2$

   (iii) $MeC[CH_2P(S)Ph_2]_3$

   (iv) $Ph_2P(S)(CH_2)_2P(S)Ph(CH_2)_2P(S)Ph_2$

Type A ligands generally bind to a metal in a unidentate fashion, although in some instances bridging by sulphur atoms may occur. The former mode of binding has been identified in the complexes $[Cu(Me_3P)_3]ClO_4$, $[Cu(Ph_3P)(NS_3)]$, and $[Cu(Me_3PS)Cl]_3$ [88,91-93] (Figure II-1 A,B,C).

Type B(i) ligands usually act as chelating agents where n= 1, *e.g.* [CuClL] (L= $[Ph_2P(S)]_2CH_2$), and as bridging ligands when n≥2, *e.g.* [CuClL]$_2$ (L= $Ph_2P(S)$-$(CH_2)_2(S)PPh_2$) (Figure II-1 D, F,) [94,95]. However in one instance where n= 1, *i.e.* [CuClL]$_2$ (L= $[Ph_2P(S)]_2CH_2$), the ligand binds in both a unidentate fashion and as a bridging ligand (Figure II-1 E) [35]. B(ii) class ligands invariably form chelate complexes, *e.g.* $[M(CO)_4L]$ (L= $Ph_2P(S)CH_2PR_2$, M= Cr, Mo, W) (Figure II-1 U) [74,89], whereas type B(iii) ligands have been observed to bind in three different ways, as shown in complexes of gold, *e.g.* $[(C_6F_5)_2AuL]$ (L= $[Ph_2P(S)]CH^-)$ (Figure II-1 G-L) [65,66,97]. The ligands of type C in the free state exist with the two potential S donors in a *trans*

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Figure II-1 Types of phosphine sulfide ligands

A

B

C

D

E

F

G

H

I

J

K

L
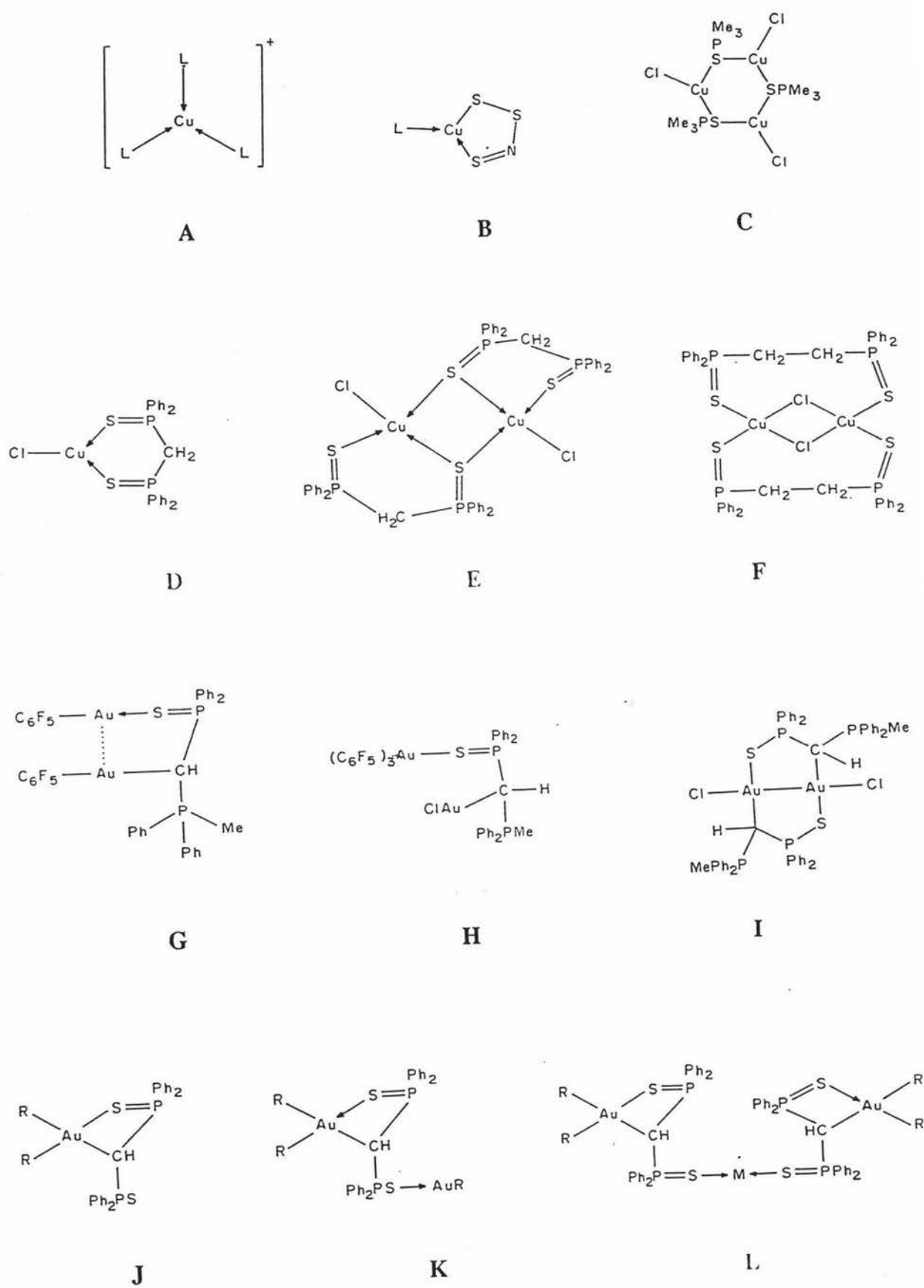
Figure II-1 Types of phosphine sulfide ligands

M

N

O

P

Q

R

S

T

U

21
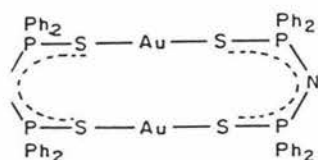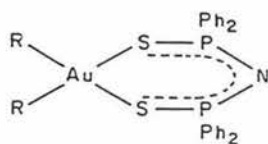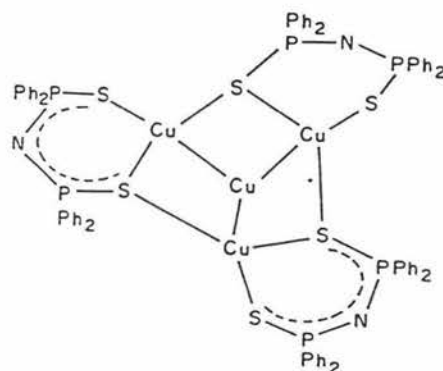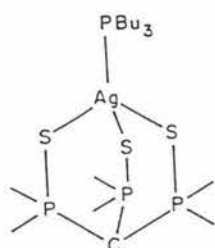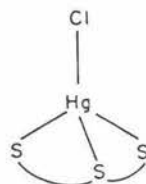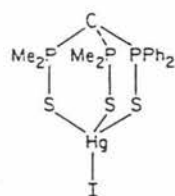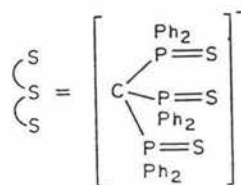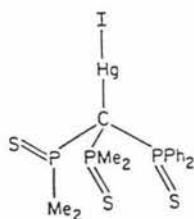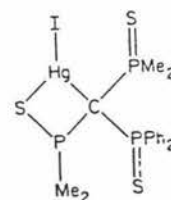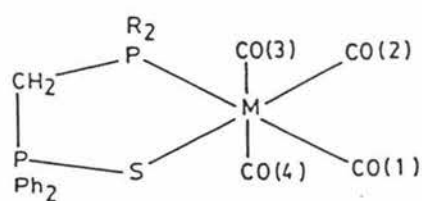
arrangement with respect to one another. Rotation about either the N-C or C-C bond is necessary for chelation and this arrangement is therefore preferred on complex formation. Type C ligands are usually deprotonated and bind to the metals in the anionic form *e.g.* copper and gold complexes $[Cu_4L_3]^+$, $[Au_2L_2]$ and $[R_2AuL]$ (L= $[Ph_2P(S)]_2N^-$) (Figure II-1 M,N,O) [66,71]. Type D ligands can have the *trans* conformation in complexes *e.g.* {HgI[Me_2P(S)]_2[Ph_2P(S)]} (Figure II-1 S) [69]. Type D(i, ii) ligands deprotonate and coordinate *via* two or three sulphur atoms, with the binding mode forming a cage-like structure *e.g.* [Ag(Bu_3P)L] and [HgLCl] (L= $[Ph_2P(S)]_3C^-$) (Figure II-1 P,Q,R) [68-70] Type D(iii) and D(iv) ligands are known to bind in both bidentate and tridentate fashions [68-70].

II-1-3 Coordination by Phosphine Sulfide Ligands

Many complexes have been synthesised with tertiary phosphine sulfide ligands and their coordination chemistry has been characterised by IR, NMR, and X-ray diffraction techniques. The IR spectra of these complexes show shifts to lower energies in the υ(P-S) stretching frequencies indicating coordination by a ligand to the metal ion. For example, the IR data for the Cu(I) complexes, (CuLCl) and (CuClL)_2 (Figure II-1 D, E) (where L= bis(diphenylphosphinothioyl)methane) (bdtm) [94,95] showed the υ(P-S) to have decreased by *ca.* 30-45 cm^{-1} on coordination. On removal of acetone from CuLCl a single υ(P-S) peak appears at 570 cm^{-1}, a decrease of *ca.* 28 cm^{-1} on coordination. Loss of acetone occurred on slow heating to 100°C and at a temperature above 140°C the monomer CuLCl changed into the dimer, (CuClL)_2. In this latter complex one sulphur atom of each ligand, acts as a bridge between two copper atoms (Figure II-1, E).

The X-ray structure of $[(CuClL)_2 \cdot 2(CuClL)]$ (L= bdtm) contains two molecules of a three-coordinate monomer and two molecules of a four-coordinate dimer [98]. The monomer, (CuClL) [94] has a trigonal planar geometry, whereas the dimer (CuClL)_2 has a distorted tetrahedral one. In the monomer, the distortion from the trigonal planar geometry is less than in [CuCl(bdtm)]·Me_2CO. The Cu-S bond lengths in the monomer are 2.259Å and 2.321Å. However, in the dimer Cu-S bonds (2.231-2.287Å) are shorter than those in the analogous dimer (CuClL')_2 (L'= Me_2P(S)P(S)Me_2 (2.317-2.486Å) [99].

Table 2-1 The ^{1}H and ^{31}P NMR of some Cu(I) complexes [78]

Compound	^{1}H NMR[a] (ppm)	^{31}P NMR[b] (ppm)	References
Me$_2$P(S)P(S)Me$_2$ (L′)	1.88(6.0)[c]		33, 34
[CuL′$_2$]BF$_4$	1.99(6.0)[c]		33, 34
[CuL′Cl]$_2$	2.14(6)[c]		33, 34
Ph$_2$P(S)CH$_2$P(S)Ph$_2$ (L″)[d,f]	3.91(13.4)[e] 7.22[g], 7.59[g]	35.5	33, 34, 37
[CuClL″]Me$_2$CO	4.04(12.5)[e] 2.15[h] 7.40[g], 7.78[g]	32.8	33, 34, 37
[CuL″$_2$](ClO$_4$)	4.06(12.5)[e] 7.33[g], 7.68[g]	33.1	33, 34, 37
[(CuClL″$_2$)·(CuClL″)]		32.8	37
Me$_2$PhPS (L‴)[f]		32.6	37
[CuL‴$_3$](ClO$_4$)		36.6	37

[a] in $(CD_3)_2CO$

[b] downfield from 85% H_3PO_4

[c] CH$_3$(quartet), $^2J_{(P+H)} + {}^3J_{(P+H)}$

[d] values of $J_{(P+H)}$ in parentheses

[e] CH$_2$(triplet)

[f] in CDCl$_3$

[g] C$_6$H$_5$(multiplet)

[h] CH$_3$ protons of Me$_2$CO

The coordination of S to a metal centre has also been established from the NMR data reported for a number of metal complexes. Chemical shift changes to low field and various coupling constants establish the metal-ligand interaction. The ^{1}H NMR data of some soluble Cu(I) complexes(e.g. CuLCl$_2$, L'= Me$_2$P(S)P(S)Me$_2$, [CuClL"]·Me$_2$CO, L"= Ph$_2$P(S)CH$_2$P(S)Ph$_2$) reveal deshielding of the CH$_3$, CH$_2$ and C$_6$H$_5$ protons of the ligand [94,95,98]. Similarly the ^{31}P NMR data for these species reveal shifts in the phosphorus chemical shift on coordination. However the magnitude of the shifts are small and thus reinforce the observation that the geometry around the phosphorus remains largely unaffected on complex formation.

II-1-4 Unsymmetrical Phosphine Sulfide Ligands

Tertiary phosphine sulfides have been extensively studied in the past three decades [64,78]. In contrast to the numerous studies on symmetrically substituted diphosphine molecules, those with unsymmetrically substituted phosphorus centres have received much less attention. However, they are now attracting more interest, particularly the diphosphine sulfide ligands such as: R$_2$P(S)CH$_2$PR$_2$, Ph$_2$PCH$_2$P(S)R^{1}R^2 [75,89] and R$_2$P(S)(CH$_2$)$_n$P(Se)Ph$_2$ (n= 1, 2) [77,100]. The resulting complexes have provided an interesting coordination chemistry as well as spectroscopic properties.

The unsymmetrical ligand, Ph$_2$P(S)CH$_2$PR^{1}R^2, [dialkyl(phosphinomethyl)diphenyl-phosphine sulfide], first reported by Seyferth [101], provides a novel unsymmetrical system in which the phosphorus nuclei are non-equivalent and P-P coupling is directly measurable from the ^{31}P NMR spectra. Grim and his coworkers [106] have now synthesized many unsymmetrical ligands of this type with different substituents on the phosphorus atoms which contain phosphorus in both the trivalent and pentavalent oxidation states.

The steps involved in the preparation of molecules such as Ph$_2$P(S)CH$_2$PR^{1}R^2 and Ph$_2$P(S)CH$_2$P(S)Ph$_2$ [75,89,102] are given below

$$Ph_3PS + CH_3Li \longrightarrow Ph_2P(S)CH_2Li + PhH \qquad (1)$$

$$Ph_2P(S)CH_2Li + R_2PCl \longrightarrow Ph_2P(S)CH_2PR_2 + LiCl \qquad (2)$$
$$R=Ph, Me, PhMe, i\text{-}Pr \qquad (10\text{-}50\%)$$

$$Ph_2P(S)CH_2PR_2 + S \longrightarrow Ph_2P(S)CH_2P(S)R_2 \qquad (3)$$
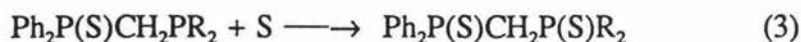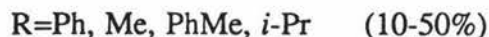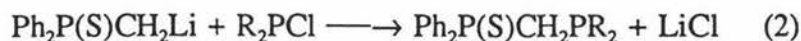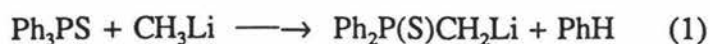
When dimethyl phosphine(diphenylthiophosphoryl)methane ($Ph_2P(S)CH_2PMe_2$) is heated at $ca.$ 160°C in an inert solvent such as diglyme, the transfer of sulphur from the less basic diphenyl phosphine group to the more basic dimethyl phosphine group occurs readily and $Ph_2PCH_2P(S)Me_2$ is formed in good yield (50%) [74].

Phosphorus-31 NMR [13] data are given in Table 2-2 for (phosphinomethyl)phosphine sulfides and phosphonium salts. The $Ph_2P(S)CH_2PR^1R^2$ compounds are characterized by two sets of doublets, one on the high-field side of H_3PO_4, assigned to the trivalent phosphorus (unoxidised) atom and the other on the down-field side of H_3PO_4, which is assigned to the phosphine sulfide phosphorus.

Table 2-2 Phosphorus-31 NMR data for (phosphinomethyl)phosphine sulfides and derivatives

Compound	δPPh_2,[a] ppm	δPR^1R^2,[a] ppm	$\|J_{PP}\|$, Hz
$Ph_2P(S)CH_2PMe_2$	39.0	-53.8	56
$Ph_2P(S)CH_2PPhMe$	39.1	-43.3	66
	(39.7)	(-42.8)	(67)
$Ph_2P(S)CH_2PPhEt$	39.6	-30.9	68
	(39.9)	(-30.6)	(68)
$Ph_2P(S)CH_2PPh(i\text{-}Pr)$	40.5	-19.3	71
	(40.9)	(-19.0)	(72)
$Ph_2P(S)CH_2PPh_2$	40.1	-28.0	76
	(40.5)	(-28.1)	(79)
$Ph_2P(S)CH_2P(i\text{-}Pr)_2$	41.6	-9.3	77
	(41.9)	(-9.4)	(77)
$Ph_2P(S)CH(CH_3)PPh_2$	51.8	-13.0	95
$Ph_2PCH_2P(S)Me_2$	-26.2	35.4	62
$Ph_2PCH_2P(S)PhMe$	-27.1	36.9	68
$Ph_2PCH_2P(S)Ph(i\text{-}Pr)$	-27.7	55.1	65
$Ph_2PCH_2P(S)(i\text{-}Pr)_2$	-27.8	65.6	52
$Ph_2P(S)CH_2P(S)Me_2$	32.4	35.3	17
	(32.8)	(35.9)	
$Ph_2P(S)CH_2P(S)Me$	33.3	34.6	16
$Ph_2P(S)CH_2P(S)Et$	33.3	44.4	15
$Ph_2P(S)CH_2P(S)Ph_2$	34.6		
	(36.8)		
$Ph_2P(S)CH_2P(S)Ph(i\text{-}Pr)$	33.1	53.3	18
$Ph_2P(S)CH_2P(S)Ph(i\text{-}Pr)_2$	31.9	69.5	16
$Ph_2P(S)CH(CH_3)P(S)Ph_2$	46.5		
$[Ph_2P(S)CH_2PMe_3]^+Br^-$	33.3	27.4	12
$[Ph_2P(S)CH_2PPhMe_2]^+Br^-$	33.7	22.9	12
$[Ph_2P(S)CH_2PPhEtMe]^+Br^-$	33.7	28.3	12
$[Ph_2P(S)CH_2PPh_2Me]^+Br^-$	33.7	21.2	9
$[Ph_2P(S)CH_2PPh(i\text{-}Pr)Me]^+Br^-$	33.7	32.1	13
$[Ph_2P(S)CH_2P(i\text{-}Pr)_2Me]^+Br^-$	33.4	44.2	14
$[Ph_2P(S)CH(CH_3)PPh_2Me]^+Br^-$	46.9	27.8	0
$[MePh_2PCH_2P(S)Me_2]^+Br^-$	20.4	34.5	12
$[MePh_2PCH_2P(S)PhMe]^+Br^-$	20.2	33.5	12
$[MePh_2PCH_2P(S)Ph(i\text{-}Pr)]^+Br^-$	20.7	50.7	15
$[MePh_2PCH_2P(S)(i\text{-}Pr)_2]^+Br^-$	22.9	64.4	14

[a] Positive values are ppm downfield from 85% H_3PO_4

Table 2-10 The ^{31}P NMR of M(CO)$_4$L complexes
[M = Cr, Mo, W; L = PhP(Y)CH$_2$PR$_1$R$_2$]

Compound	$\delta_{P(Y)}$[a] (ppm)	$\Delta P(Y)$[b] (ppm)	$\delta_{PR_1R_2}$[a] (ppm)	ΔPR_1R_2[b] (ppm)	$\lvert {}^2J_{(P\text{-}CH2\text{-}P)} \rvert$ (Hz)
Ph$_2$P(S)CH$_2$PPh$_2$	40.1		-28.0		76
Cr	57.5	17.4	63.9	91.9	83
Mo	55.5	15.1	37.9	65.9	78
W[c]	59.6	19.5	25.2	53.3	76
Ph$_2$P(Se)CH$_2$PPh$_2$	30.7		-27.2		85.1
Cr[d]	39.4	8.7	69.1	96.3	91.4
Mo	38.3	7.6	41.8	69.0	85.5
W[c]	41.8	11.1	27.5	54.7	83.7
Ph$_2$P(S)CH$_2$P(i-P)$_2$	41.6		-9.3		77
Cr[d]	57.9	16.3	82.3	91.6	70
Mo	55.5	13.9	60.5	69.8	64
W[c]	60.2	18.6	49.0	58.3	62
Ph$_2$P(S)CH$_2$PMe$_2$	39.0		-53.8		56
Cr	57.3	18.3	42.5	96.3	78
Mo	54.9	15.9	13.2	67.0	71
W[c]	59.1	20.1	-4.2	49.6	71
Ph$_2$P(S)CH$_2$P(t-Bu)$_2$	42.9		10.3		87
Cr	59.8	16.9	104.7	94.4	68.4
Mo	57.8	14.9	84.6	74.3	64.7
W[c]	62.2	19.3	76.2	65.9	61

[a] δ is positive if deshielded (downfield) from 85% H$_3$PO$_4$ as an external standard

[b] $\Delta = \delta_{complex} - \delta_{ligand}$

[c] ${}^1J_{(P\text{-}W)}$ values are 240, 227, 232, and 222 Hz, respectively

[d] The $J_{(P\text{-}Se)}$ value is 645 Hz

[c] ${}^1J_{(P\text{-}Se)}$ value is 627 Hz

Phosphorus-phosphorus coupling (56-77Hz) is directly observable in the ^{31}P spectra since the two phosphorus atoms are nonequivalent. An increase in the magnitude of ^2J(P-P) is observed as the bulkiness of the R^1 and R^2 groups increases.

The above unsymmetrical ligands react with $M(CO)_6$ (M= Cr, Mo, W) in diglyme at 120-140°C to give complexes of the type $M(CO)_4L$. Since coordination via the $Ph_2P(S)$ and PR^1R^2 groups increases the positive charge on the phosphorus atoms, increased deshielding of the $-CH_2-$ protons is expected. The low shifts in $\delta(CH_2)$, however, reveal π-bonding from the metal atom to the ligand via trivalent phosphorus [78]. The ^{31}P NMR data for $M(CO)_4L$ complexes are given in Table 2-10 [75,77,89]. From this table it can be seen that the shifts in $\delta(PR^1R^2)$ are higher than those in $\delta P(S)Ph_2$. The magnitude of $\Delta\delta(PR^1R^2)$ is typical of the five membered chelate rings [102-104]. The order of the relative shifts $\Delta\delta(PR^1R^2)$, is Cr>Mo>W, which can be interpreted in terms of M→PR^1R^2 π-bonding. The greater this π- bonding, the smaller the shift. The values of $\Delta\delta P(S)Ph_2$ vary as W>Cr>Mo although the magnitude of the change between any two consecutive metals is small. Furthermore, the substituents in PR^1R^2 do not appear to have a pronounced effect on $\Delta\delta(PR^1R^2)$. The values of ^2J(P-P) are high for Ph substituents on phosphorus atoms and these decrease with substituents such as i-Pr and t-Bu. For a given substituent on the PR^1R^2 group, the values of ^2J(P-P) have been observed to vary as Cr>Mo≥W. It is thus likely that the π-bonding between (a) M-PR_1R_2 and (b) P-Ph bonds, as well as the steric factors, all make contributions to the values of ^2J(P-P) [105, 106].

The ^{13}C nuclei of the CO groups in the $[M(CO)_4L]$ (Figure II-U) derivatives (L=$Ph_2P(S)CH_2PR^1R^2$) are less deshielded compared with those for L=$Ph_2PCH_2PPh_2$ due to the greater π-accepting property of the latter. In $Ph_2P(S)CH_2PR_2$ there is no evidence for π-bonding from the metal to the sulphur of the $P(S)Ph_2$ group. The chemical shifts of the CO(1) groups trans to R_2P groups (Cr(0) 16.1ppm, Mo(0) 15.2ppm) are at a lower frequency compared with CO(2) groups trans to the $Ph_2P(S)$ group (Cr(0) 17.9ppm, Mo(0) 17.8ppm) in Cr(O)-Mo(O) complexes. The ^2J values of the CO(1) group trans to R_2P are some 5 to 10Hz more positive than in the corresponding diphosphine complexes. This is attributed to a reduction in the strain in the five membered ring formed on binding to the metal by $Ph_2P(S)CH_2PR_2$ instead of the four membered chelate ring formed by $Ph_2PCH_2PPh_2$ [78,107].

II-1-5 The Present Study

Thio derivatives of PNCP have been synthesised, characterised and investigated to determine whether a specificity for either of the inequivalent phosphorus atoms towards sulphur is observed. The coordinating behaviour of SPNCPS towards Cu(I) was undertaken and its structure is compared with that of the un-coordinated SPNCPS ligand.

II-2 EXPERIMENTAL

II-2-1 Synthesis of PNCP

PNCP was prepared *via* a Schiff base condensation reaction of 2-PNH$_2$ (2-(diphenylphosphino)benzeneamine) and 2-PCHO (2-(diphenylphosphino)benzaldehyde) according to the following equation:

2-PCHO   +   2-PNH$_2$

PNCP
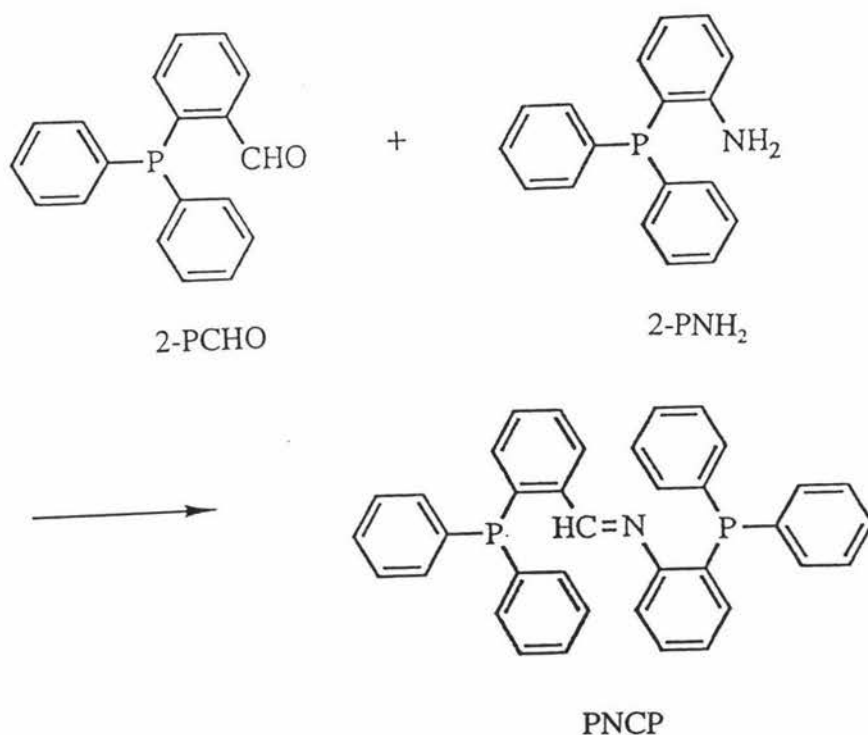
The choice of solvent is important since this reaction does not proceed in refluxing ethanol, but is successful in benzene according to the following procedure as outlined in [146]. To a three-necked flask was added 2-PCHO (1.160g, 4 mmol), 2-PNH$_2$ (1.108g, 4 mmol) and toluene-*p*-sulphonic acid (20mg, 0.10 mmol). Benzene (120 ml) was added and the solution flushed with argon for ten minutes. The system was fitted with a Dean-Stark trap and condenser and refluxed under argon for 7 hours. The solvent was removed from the resulting yellow solution by rotary evaporation to produce a yellow oil. This was dissolved in a small amount of dichloromethane, then methanol was added until crystallisation began. After standing for half an hour PNCP was filtered off as pale yellow crystals, washed well with methanol, and dried in *vacuo*. A second crop was obtained by concentration of the mother liquor by rotary evaporation and crystallisation from dichloromethane/methanol.

Yield, 80% (1.825g). M.P. 176-178°C.

II-2-2 2-(diphenylphosphino)benzeneamine (2-PNH$_2$)

The ligand 2-(diphenylphosphino)benzeneamine was prepared according to a literature preparation [116]. The compound (2-aminophenyl)triphenylphosphonium chloride was synthesized first, then by its reduction to 2-PNH$_2$ with naphthalene and sodium as shown in Scheme I. The steps in the reaction are now given
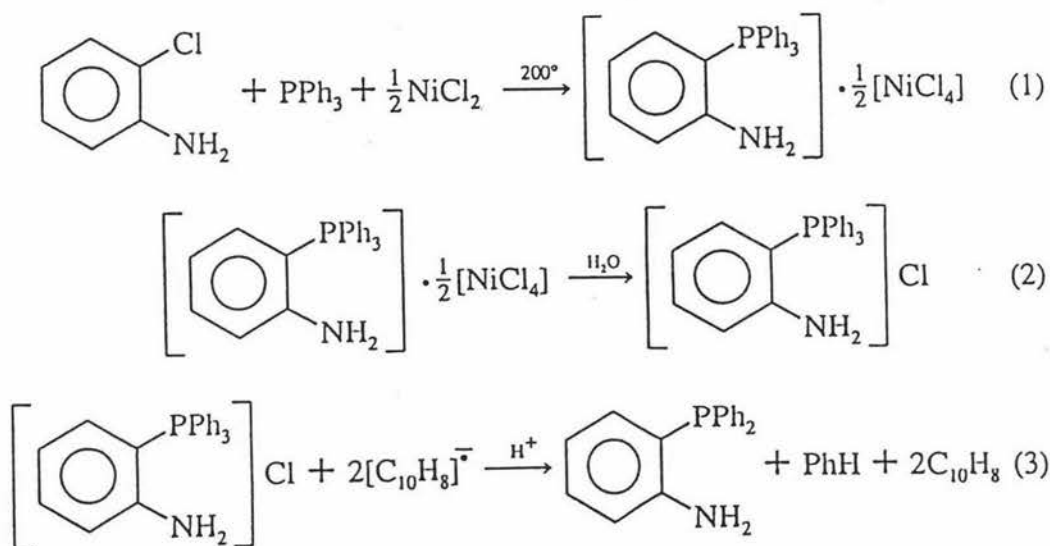
Scheme I

Step 1 and 2: Synthesis of (2-aminophenyl)triphenylphosphonium chloride

2-chlorobenzeneamine 64.0g (0.50 mol), triphenylphosphine 131g (0.50 mol) and NiCl₂ 32.5g (0.25 mol) were placed into a round-bottomed flask (500 ml). The mixture was heated to 200°C with stirring for 4 hours. The resulting dark blue melt was cooled to 180-160°C. then poured into 300 ml of hot (60°C) water previously acidified with a few drops of concentrated HCl. Boiling acidified water (200 ml) was added to the reaction vessel to extract any remaining material. The combined extracts were stirred while hot until the blue colour of the melt was completely discharged and then washed with diethyl ether (1×150, 2×100 ml), to remove unreacted starting materials, the aqueous phases were extracted with dichloromethane (3×150 ml). The dichloromethane extracts were dried over anhydrous Na₂SO₄ and evaporated to an orange oil. Tetrahydrofuran was added with vigorous stirring until white crystals began to form. The white crystalline product was collected by filtration, washed with THF then diethyl ether and dried (120°C, about 15 torr) overnight to remove solvent of crystallization. Yield 50% (95.6g), M.P. 299-300°C (Ref. 55, yield 57%, M.P. 293-295°C).

Step 3: Synthesis of (2-diphenylphosphino)benzeneamine (PNH₂)

A round-bottomed 1-L flask was charged with 500ml of anhydrous THF, 51g (0.39 mol) of naphthalene then a teflon-coated, magnetic stirring bar was inserted. Sodium wire, 8.3g (0.36 mol) was extruded into the vessel directly, which was then quickly fitted with a condenser and nitrogen inlet. The mixture was stirred until the sodium had completely dissolved. The resulting very dark solution was cooled in a solid CO₂-acetone bath until it was almost completely solid. (2-aminophenyl)triphenyl phosphonium chloride, 64.0g (0.164), was added and the mixture allowed to warm slowly to room temperature, then stirred for one hour. Acetic acid, 2g (0.03 mol) was added dropwise to discharge the last of the green colour. The orange-red mixture was treated slowly with 100 ml of a 20% ammonium chloride solution and sufficient water to dissolve any remaining solid.

The two resulting phases were separated and the aqueous layer was extracted with diethyl ether (1×100 ml). The combined organic phases were dried over anhydrous Na₂SO₄ and evaporated. The residue was taken up in 500ml of boiling 95% ethanol and treated with a solution of nickel nitrate hexahydrate, (26.0g, 0.09 mol) in 100 ml of boiling 95% ethanol. The resulting brown solution was treated with 2 ml of trifluoroacetic acid to

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ensure that deprotonation of the amino group did not occur. After storing overnight at 5°C the mixture of metal complex and crystallized naphthalene was filtered off and washed first with ethanol and then with diethyl ether to remove the naphthalene. A yield of 53.0g (86%) of orange crystals, $[Ni(H_2L)_2](NO_3)_2 \cdot H_2O$, was obtained.

The nickel complex was suspended in a mixture of benzene (300 ml) and water (300 ml) to which a few drops of concentrated HCl were added. The mixture was refluxed until the crystals dissolved. The two resulting phases were separated and the aqueous layer was extracted with benzene (50 ml). The combined organic extracts were washed with brine (100 ml), dried over anhydrous Na_2SO_4 then passed down a short alumina column (2.5×10 cm) eluting with benzene. The now colourless solution was evaporated to an oil, which was taken up in 180 ml of boiling 95% ethanol. Fluffy white crystals of the pure ligand were formed.

Yield 74% (29.9g), M.P. 83-84°C (Ref.55, yield 88%, M.P. 82-83°C).

II-2-3 Synthesis of 2-(diphenylphosphino)benzaldehyde (2-PCHO)

This was synthesized according to a literature procedure [115].

II-2-4 Reaction of PNCP with Sulphur in 1:1 Molar Ratio

PNCP (0.1375g, 0.25 mmol) and sulphur (0.0080g, 0.25 mmol) were dissolved in 10 ml CH_2Cl_2 and 2.5 ml ethanol. The solution was heated under a brisk flow of nitrogen gas for 10 minutes until the volume was reduced to approximately 5 ml. Yellow crystals appeared when this solution was left to stand at room temperature for about three days. The crystals were redissolved in $CDCl_3$ as solvent for NMR studies. In another preparation the whole of the reaction solution was taken to dryness by rotary evaporation and the solid formed redissolved in $CDCl_3$ and an identical NMR spectrum was obtained. The following products could be identified: PNCP, SPNCP, PNCPS, and SPNCPS. Their nature is discussed in Section II-3-4.

II-2-5 Preparation of 2-SPNH₂

2-PNH₂ (0.416g, 1.5 mmol) and sulphur (0.048g, 1.5 mmol) in a 50 ml flask were dissolved in 15 ml CH_2Cl_2 and 8 ml ethanol and the solution refluxed under nitrogen gas

for one hour and 20 minutes. After standing at room temperature for one day, white needle-like crystals of the product were filtered and washed with ethanol.

Yield: 85% (0.40g), M. P.: 184-185°C
Found: C, 69.90; H, 5.65; N, 4.64; S, 10.03 (%)
Calculated for $(PNC_{18}H_{16}S)$:
C, 69.90; H, 5.18; N, 4.53; S, 10.36 (%)

II-2-6 Preparation of 2-SPCHO

2-PCHO (0.290g, 1.0 mmol) and sulphur (0.032g, 1.0 mmol) were dissolved in 15 ml toluene in a 50 ml flask. The solution was flushed with nitrogen gas for two minutes, then heated with stirring under reflux in an atmosphere of nitrogen gas for 30 minutes. The solution was left to stand for one day in a fridge after which time the cream coloured product was filtered and washed with toluene. See Abbreviations (page ix) for the structural formula.

Yield: 65% (0.32g), M.P. 117-119°C
Found: C, 70.52; H, 4.92; S, 9.70; (%)
Calculated for $(POC_{19}H_{15}S)$:
C, 70.81; H, 4.66; S, 9.94; (%)

II-2-7 Preparation of SPNCP· ½CH₃OH

To a three-necked flask (500 ml) was added 2-PCHO (0.464g, 1.6 mmol), 2-SPNH₂ (0.469g, 1.6 mmol) and toluene-*p*-sulphonic acid(8mg) in benzene (200 ml). The solution was flushed with argon gas for ten minutes and then refluxed under argon for 7 hours using a Dean Stark trap. The solvent was removed by a rotary evaporator to produce a yellow oil, which was dissolved in a small amount of CH_2Cl_2. Methanol was then added until crystallisation began. After standing overnight at 4°C, the pale yellow crystals which formed were filtered off, washed with methanol and dried in *vacuo*. See Figure II-2 for its structure.

Yield: 83% (0.76g), M. P. 189-191°

Found: C, 75.79; H, 5.53; N, 2.66; S, 5.81 (%)

Calculated for $(P_2NC_{37.5}H_{31}SO_{0.5})$:

C, 75.38; H, 5.19; N, 2.35; S, 5.36 (%)

II-2-8 Preparation of PNCPS·½CH₃OH

The procedure for the preparation of PNCPS was the same as the above but the reagents were changed as follows: 2-SPCHO (0.2078g, 0.64 mmol) and 2-PNH₂ (0.1779g, 0.64 mmol). See Abbreviations (page ix) for its structural formula.

Yield: 52% (0.20g), M.P. 224-226°

Found: C, 75.28; H, 5.36; N, 2.55; (%)

Calculated for $(P_2NC_{37.5}H_{31}SO_{0.5})$:

C, 75.38; H, 5.19; N, 2.35; (%)

II-2-9 Preparation of SPNCPS

0.110g (0.20 mmol) of 2-(diphenylphosphino)-N-[2-(diphenylphosphino)-benzylidene]benzeneamine (PNCP) was dissolved in 15 ml CH_2Cl_2 and 4 ml ethanol to give an orange solution, and then 0.014g (0.40 mmol) of sulphur added. The solution was flushed with nitrogen gas for three minutes and then refluxed in a stream of nitrogen gas for a further 30 minutes. The solution colour changed from orange to yellow and on standing overnight at room temperature, a light yellow precipitate formed, which was recrystallised from a $CHCl_3$/toluene mixture. See Abbreviations (page ix) for its structural formula.

Yield: 88.4% (0.110g), M.P. 301-303°

Found: C, 72.14; H, 4.81; N, 2.34; S, 10.57 (%)

Calculated for $(P_2NC_{37}H_{29}S_2)$:

C, 72.43; H, 4.73; N, 2.28; S, 10.44 (%)

II-2-10 Preparation of a [Cu(SPNCPS)]ClO₄·H₂O

0.063g (0.13 mmol) of SPNCPS and 0.034g (0.13 mmol) of [Cu(CH₃CN)₄]ClO₄ were

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dissolved in 15 ml CH_2Cl_2 and 15 ml ethanol. The orange solution was refluxed for 25 minutes under a brisk flow of nitrogen gas. The solution volume was reduced to about 14 ml. On standing overnight at 5°C yellow crystals of [Cu(SPNCPS)]ClO$_4$·H$_2$O formed. These were filtered off and washed with ethanol, and dried in *vacuo*. See Figure II-5 for its structure.

Yield: 82% (0.07g)

Found: C, 55.93; H, 4.21; N, 1.77; (%)

Calculated for (CuP$_2$NC$_{37}$H$_{31}$S$_2$ClO$_5$):

C, 55.92; H, 3.90; N, 1.76; (%)

II-3 RESULTS AND DISCUSSIONS

II-3-1 Crystal structures

The results of four different single crystal X-ray diffraction analyses are presented here:

   i)   SPNCP

   ii) SPNCP + CH_2Cl_2

   iii) PNCP

   iv) [Cu(SPNCPS)]ClO$_4$

Selected bond distance and angle data for each of the above structures are give in Tables 2-3 to 2-9. Thermal ellipsoid diagrams which show the labelling systems used are given in Figures II-2 to II-5.

i) The crystal structure of 2-(diphenylphosphinothioyl)-N-[2-(diphenyl-phosphino)benzylidene]benzeneamine

In SPNCP one of the phosphorus atoms has been oxidised by the addition of a single sulphur atom. The two P atoms adopt a trans arrangement with respect to one another so as to minimise non-bonded steric interactions. The P-S bond length is 1.93(2)Å which is in good agreement with the range of distances found for other phosphine sulphide molecules (*e.g.* 1.94-1.95Å) [108] and indicates a bond with some multiple character. The range of P-C bond lengths determined is 1.814(5)-1.834(4)Å, these also being accord with those reported elsewhere (1.763-1.839Å [64,109,110]). The S-P-C angles are all greater than the C-P-C angles in line with the larger size of the S atom. However, the C-P-C

angles show some differences at the two P atoms, with those associated with P(1) being a little greater than their counterparts at P(2) (C-P(1)-C average 105.2°; C-P(2)-C average 101.9°). Thus the lone electron pair at P(2) must be responsible for a greater "crowding together" of the phenyl groups than is the S atom.

The -CH=N- "bridge" linking the two phenyl rings (*via.* C(11)-C(16) and C(41)-C(46)) shows some electron delocalisation across its length. The N-C(1) bond length of 1.263(5)Å is similar to that expected for a formal double bond (1.278Å [111]) and the N-C(12) and C(1)-C(42) distances of 1.416(5) and 1.478(6)Å respectively are comparable with lengths expected for similar bonds *exo* to phenyl rings (1.472Å and 1.53Å [112,113]). However, the -CH=N- bridge is not co-planar with its associated phenyl ring. Planes of "best fit" data show that this bridge is rotated by 38° with respect to the plane calculated through atoms C(11)-C(16) but by only 5° with respect to the plane containing atoms C(41)-C(46). Figure II-3 highlights this effect. These rotations are probably necessary to maintain appropriate non-bonded approaches between S, P(1) and P(2) with the atoms of the bridge N, C(1) and H(1) (see Table 2-4) There is thus a compromise between complete electron delocalisation and the need to minimise unacceptable steric pressures.

ii) The crystal and molecular structure of 2-(diphenylphosphinothioyl)-N-[2-(diphenylphosphino)benzylidene] benzeneamine with dichloromethane as solvent of crystallisation.

A second crystal structure determination of the SPNCP molecule was carried out when this compound was crystallised with CH_2Cl_2 as solvent of crystallisation. This second analysis provides a further comparison of the molecular geometry of the above molecule in the presence of different crystal packing effects. The data in Table 2-7 show the close correspondence between the two sets of distances and angles. The P-S and P-C distances are as expected. The S-P(1)-C angles (average 113.6°) are greater than the C-P(1)-C angles, with the slightly larger angles being associated with P(1), the P to which the S atom is attached (C-P(1)-C average, 102.4°). The most notable difference observed between the two structure determinations is associated with the planes of "best fit" data. The plane of the -CH=N- bridge lies at an angle of 31° to the plane containing atoms C(11)-C(16), a value which is 7° smaller than that observed for the non-solvated structure. However, the plane containing the atoms C(41)-C(46) is now rotated by only 23° relative to the bridge.

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This second rotation about the C(1)-C(42) bond may be compared with the 5° angle observed for the crystal structure where no solvent is present. This suggests that crystal packing forces must play at least some part in determining the rotation about this bond.

iii) The crystal and molecular structure of 2-(diphenylphosphino)-N-[2-(diphenylphosphino)benzylidene] benzeneamine

The pale yellow crystals (PNCP) were grown by the slow evaporation of anhydrous methanol solution.

This compound crystallises with two crystallographically distinct molecules in each asymmetric unit. The two phosphorus atoms of each molecule adopt the expected *trans* orientation with respect to one another, an arrangement which helps minimise unfavourable steric interactions. The range of the P-C bond lengths is 1.792(11)-1.864(8)Å, values which do not differ significantly from generally accepted values (*cf.* 1.87Å [113]). The C-P-C angles range from 100.6(4)-105.4(4)Å in agreement with those found in other tertiary phosphines [64, 78]. Each of the independent molecules has an approximate centre of symmetry at the mid-point of the C=N bond so that these two atoms were not able to be distinguished. Arbitrary C and N labels were assigned to them. It is unlikely that the difference in bond length observed for N(1)-C(3) and N(2)-C(4) is a real effect and probably arises from the pseudo-symmetry which is present. However, despite this inaccuracy, the multiple bond character of these two bond is clearly established. Calculation of planes of "best fit" through the phenyl rings and the -CH=N- bridge shows that some rotation has occurred about the C(phenyl)-N and C(phenyl)-C bonds but this differs in the two molecules with values of 36Å and 9Å being observed. Once again the ability to maintain acceptable non-bonded interactions and to satisfy packing forces allow such rotations, while still preserving a measure of electron delocalisation through the bridging atoms.

iv) The crystal and molecular structure of [Cu(SPNCPS)]ClO$_4$

The yellow crystals were grown by slowly evaporation of anhydrous chloroform solution.

The structure of the complex shows discrete [Cu(SPNCPS)]$^+$ cations and perchlorate anions. The ligand co-ordinates to the copper in a tridentate fashion *via* its two S and N donor atoms. The coordination geometry of the central copper is thus formally trigonal

planar although the Cu atom is displaced above the plane of the 3 donor atoms by 0.098Å. The two Cu-S bond distances are not identical, that to S(2), which is associated with the larger 7-membered chelate ring, being a little longer. However, both Cu-S bond lengths (Cu-S(1), 2.196(1); Cu-S(2), 2.207(2)Å) fall within the range expected for such distances (e.g. 2.19Å -2.321Å [91,94]). The Cu-N(1) distance of 2.005(4)Å is indicative of a predominantly σ-bond and may be compared with other Cu-N distances in trigonal copper complexes which cover the range 2.000-2.192Å [114]. The two P-S distances at 1.988(2) and 1.993(2)Å do not differ significantly from one another and are in accord with values observed for other P-S bond lengths. All six S-P-C bond angles are greater than their C-P-C counterparts with average values being 112.0 and 106.9° respectively. The average value for C-P-C(106.9°) in turn is a little greater than the C-P(1)-C average in SPNCP(105.2°), a result which probably arises from the formation of the chelate rings. Neither chelate ring is planar, the six membered ring taking up the boat configuration. The seven-membered chelate ring appears to be bent about a line joining the atoms S(2) and N(1). As a result atoms P(2), C(41), C(42) and C(1) all lie on the opposite side of the plane containing the three donor atoms to C(11) and C(12). This may be seen in the diagram (Figure II-5). In order to accommodate the extra C atom of the 7-membered ring the angles at both Cu and N (i.e. S(2)-Cu-N, 118.2(1); Cu-N-C(1), 128.3(4)°) have been widened in comparison with the angles at those atoms in the smaller chelate ring (S(1)-Cu-C, 110.8(1); Cu-N-C(1), 128.3(4)°). The angles at the P and S atoms within both chelate rings appear to be unaffected by the differences in ring size.

Table 2 - 3

Crystal data and structure refinement for PNCP

Empirical formula	$C_{37}H_{29}NP_2$
Formula weight	549.55
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	$P2_1$ (No. 4)
Unit cell dimensions	a = 15.026(3) A α = 90.0 deg.
	b = 11.600(2) A β = 98.51(3) deg.
	c = 17.261(3) A γ = 90.0 deg.
Volume	2975.5(9) A^3
Z	4
Density (calculated)	1.227 Mg/m^3
Crystal size	0.45 x 0.25 x 0.20 mm
Theta range for data collection	2.12 to 24.97 deg.
Reflections collected	5736
Independent reflections	5515 [R(int) = 0.0131]
Refinement method	Full-matrix least-squares on F^2
Data used in the refinement	5515
No. of parameters	721
Final R indices[I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1610
R indices (all data)	R1 = 0.0947, wR2 = 0.1851
Refinement program	SHELXL-93
Graphics program	ZORTEP

Table 2 - 4

Selected bond lengths [A] and angles [deg] for PNCP

P(1)-C(121)	1.792(11)	P(4)-C(421)	1.819(11)
P(1)-C(131)	1.825(10)	P(4)-C(431)	1.858(8)
P(1)-C(111)	1.828(8)	P(4)-C(411)	1.864(8)
P(2)-C(211)	1.815(8)	N(1)-C(3)	1.296(8)
P(2)-C(231)	1.821(12)	N(1)-C(112)	1.430(13)
P(2)-C(221)	1.861(9)	N(2)-C(4)	1.216(8)
P(3)-C(311)	1.834(9)	N(2)-C(212)	1.464(14)
P(3)-C(321)	1.840(9)	C(3)-C(312)	1.439(13)
P(3)-C(331)	1.858(9)	C(4)-C(412)	1.40(2)

P-C(average) 1.833

C(121)-P(1)-C(131)	101.5(4)	C(321)-P(3)-C(331)	102.7(4)
C(121)-P(1)-C(111)	105.4(4)	C(421)-P(4)-C(431)	102.3(4)
C(131)-P(1)-C(111)	101.8(4)	C(421)-P(4)-C(411)	100.6(4)
C(211)-P(2)-C(231)	103.1(4)	C(431)-P(4)-C(411)	101.0(4)
C(211)-P(2)-C(221)	103.4(4)	C(3)-N(1)-C(112)	123.1(6)
C(231)-P(2)-C(221)	101.9(5)	C(4)-N(2)-C(212)	123.3(7)
C(311)-P(3)-C(321)	103.9(4)	N(1)-C(3)-C(312)	118.3(7)
C(311)-P(3)-C(331)	103.3(4)	N(2)-C(4)-C(412)	125.9(8)

C-P-C(average) 102.6

Table 2 - 5

Crystal data and structure refinement for SPNCP

Empirical formula	$C_{37}H_{29}NP_2S$
Formula weight	581.61
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	$P2_1/a$ (No. 14 - $P2_1/c$)
Unit cell dimensions	a = 17.040(3) A α = 90.0 deg.
	b = 10.122(2) A β = 111.30(3) deg.
	c = 19.200(4) A γ = 90.0 deg.
Volume	3085.4(10) A^3
Z	4
Density (calculated)	1.252 Mg/m^3
Crystal size	0.40 x 0.30 x 0.2 mm
Theta range for data collection	1.0 to 25.0 deg.
Reflections collected	5606
Independent reflections	4251[R = 0.0493]
Refinement method	Full-matrix least-squares on F
Data used in the refinement	2315
No. of parameters refined	370
Final R indices [I>3sigma(I)]	R = 0.0547, Rw = 0.059
Refinement program	SHELX-76
Graphics program	ORTEP

Table 2 - 6

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Crystal data and structure refinement for SPNCP + solvent

Empirical formula	$C_{37}H_{29}NP_2S + CH_2Cl_2$
Formula weight	666.54
Temperature	273(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P1 (No.2)
Unit cell dimensions	a = 8.766(2) α = 101.71(2)
	b = 9.637(3) β = 94.69(2)
	c = 21.160(4) γ = 102.34(2)
Volume	1695.3(7) A^3
Z	2
Density (calculated)	1.304 Mg/m^3
Crystal size	0.35 x 0.18 x 0.09 mm
Theta range for data collection	2.5 to 25.0 deg.
Reflections collected	6370
Independent reflections	4558
Refinement method	Full-matrix least-squares on F
Data used in refinement	2172
No. of parameters	361
Final R indices[I>4sigma(I)]	R = 0.0772, Rw = 0.0850
Refinement program	SHELX-76
Graphics program	ORTEP

42

Table 2 - 7

Selected Distances (in Angstroms) and Angles (in degrees) for the SPNCP molecule

	SPNCP	SPNCP + solvent
P(1)-S	1.943(2)	1.939(2)
P(1)-C(11)	1.817(5)	1.841(2)
P(1)-C(21)	1.819(5)	1.820(5)
P(1)-C(31)	1.814(5)	1.807(2)
P(2)-C(41)	1.834(4)	1.840(2)
P(2)-C(51)	1.832(5)	1.830(3)
P(2)-C(61)	1.823(4)	1.822(2)
N-C(1)	1.263(5)	1.261(5)
N-C(12)	1.416(5)	1.406(4)
C(1)-C(42)	1.478(6)	1.455(5)
S...N	3.45	3.50
P(1)...N	2.96	2.96
P(2)...C(1)	3.10	3.08
P(2)...H(1)	2.67	2.68
S-P(1)-C(11)	115.0(2)	114.0(1)
S-P(1)-C(21)	111.1(2)	109.7(1)
S-P(1)-C(31)	114.4(2)	117.0(1)
C(11)-P(1)-C(21)	105.4(2)	104.8(1)
C(11)-P(1)-C(31)	104.6(2)	105.9(1)
C(21)-P(1)-C(31)	105.5(2)	104.4(1)
C(41)-P(2)-C(51)	101.2(2)	101.5(1)
C(41)-P(2)-C(61)	102.2(2)	103.2(1)
C(51)-P(2)-C(61)	102.4(2)	102.5(1)
P(1)-C(11)-C(12)	119.3(4)	119.2(1)
P(2)-C(41)-C(42)	119.1(4)	118.8(1)
N-C(12)-C(11)	117.4(4)	117.1(2)
C(1)-N-C(12)	122.9(4)	122.0(3)
N-C(1)-C(42)	122.0(5)	124.0(4)
C(1)-C(42)-C(41)	121.4(4)	122.2(2)
S-P(1)-C$_{average}$	113.5	113.6
C-P(1)-C$_{average}$	105.2	105.0
C-P(2)-C$_{average}$	101.9	102.4

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Table 2 - 8

Crystal data and structure refinement for [Cu(SPNCPS)]ClO4

Empirical formula	$C_{3?}H_{29}ClCuNO_4 P_2S_2$
Formula weight	776.66
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14 - $P2_1/c$)
Unit cell dimensions	a = 12.375(3) A α = 90.0 deg. b = 13.119(3) A β = 104.30(2) deg. c = 22.425(3) A γ = 90.0 deg.
Volume	3527.8(12) A^3
Z	4
Density (calculated)	1.462 Mg/m^3
Crystal size	0.55 x 0.45 x 0.15 mm
Theta range for data collection	2.13 to 24.98 deg.
Reflections collected	6353
Independent reflections	6186 [R(int) = 0.0333]
Refinement method	Full-matrix least-squares on F^2
Data used in the refinement	6150
No. of parameters	434
Final R indices [I>2sigma(I)]	R1 = 0.0474, wR2 = 0.1246
R indices (all data)	R1 = 0.0679, wR2 = 0.4656
Refinement program	SHELXL-93
Graphics program	ZORTEP

Table 2 - 9

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Selected bond lengths [A] and angles [deg] for [Cu(SPNCPS)]ClO4

Cu-S(1)	2.207(2)	Cu-S(2)	2.1958(14)
Cu-N(1)	2.005(4)	C(1)-N(1)	1.264(7)
P(1)-S(1)	1.988(2)	P(2)-S(2)	1.993(2)
P(1)-C(31)	1.805(5)	P(2)-C(41)	1.821(5)
P(1)-C(21)	1.810(5)	P(2)-C(51)	1.805(5)
P(1)-C(11)	1.804(5)	P(2)-C(61)	1.826(5)
N(1)-C(12)	1.451(6)	C(1)-C(42)	1.485(7)
P-C(average)	1.811		

S(2)-Cu-S(1)	130.32(6)		
N(1)-Cu-S(1)	110.83(12)	N(1)-Cu-S(2)	118.22(12)
P(1)-S(1)-Cu	94.22(7)	P(2)-S(2)-Cu	94.84(6)
C(11)-P(1)-S(1)	113.9(2)	C(41)-P(2)-S(2)	112.4(2)
C(21)-P(1)-S(1)	109.2(2)	C(51)-P(2)-S(2)	115.2(2)
C(31)-P(1)-S(1)	113.1(2)	C(61)-P(2)-S(2)	108.0(2)
C(21)-P(1)-C(11)	107.3(2)	C(51)-P(2)-C(41)	107.1(2)
C(31)-P(1)-C(11)	106.5(2)	C(41)-P(2)-C(61)	108.5(2)
C(31)-P(1)-C(21)	106.4(2)	C(51)-P(2)-C(61)	105.3(2)
C(12)-N(1)-Cu	114.1(3)	C(1)-N(1)-Cu	128.3(4)
C(1)-N(1)-C(12	117.5(4)	N(1)-C(1)-C(42)	121.9(5)
C(16)-C(11)-P(1)	119.2(4)	C(46)-C(41)-P	117.3(4)
C(12)-C(11)-P(1)	121.9(4)	C(42)-C(41)-P(2)	123.8(4)
C(13)-C(12)-N(1)	121.2(4)	C(43)-C(42)-C(1)	115.2(5)
C(11)-C(12)-N(1)	118.6(4)	C(41)-C(42)-C(1)	126.7(4)
S-P-C(average)	112.0	C-P-C(average)	106.9
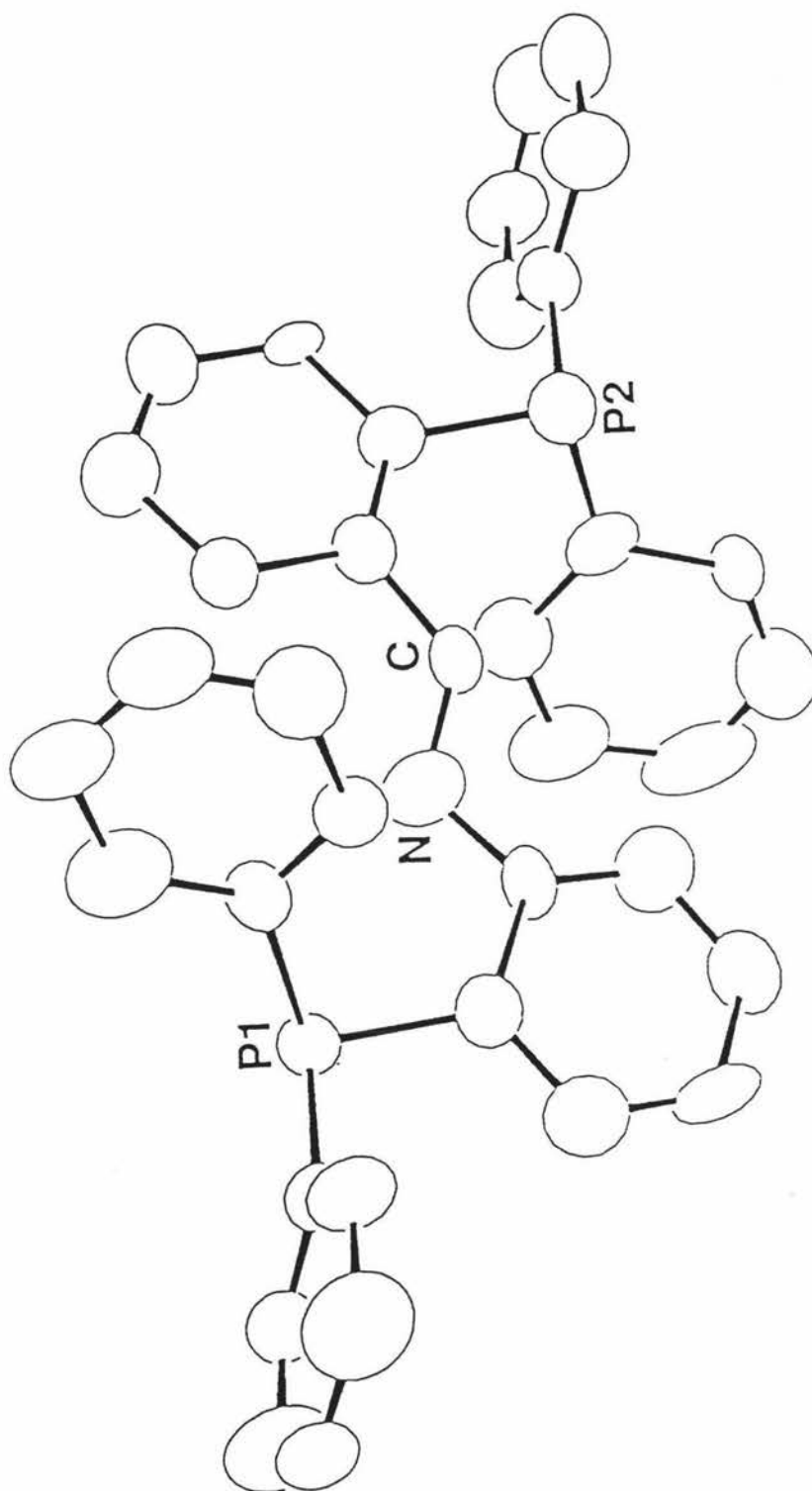
Figure II-2 Thermal ellipsoid diagram for PNCP drawn at the
50% probability level
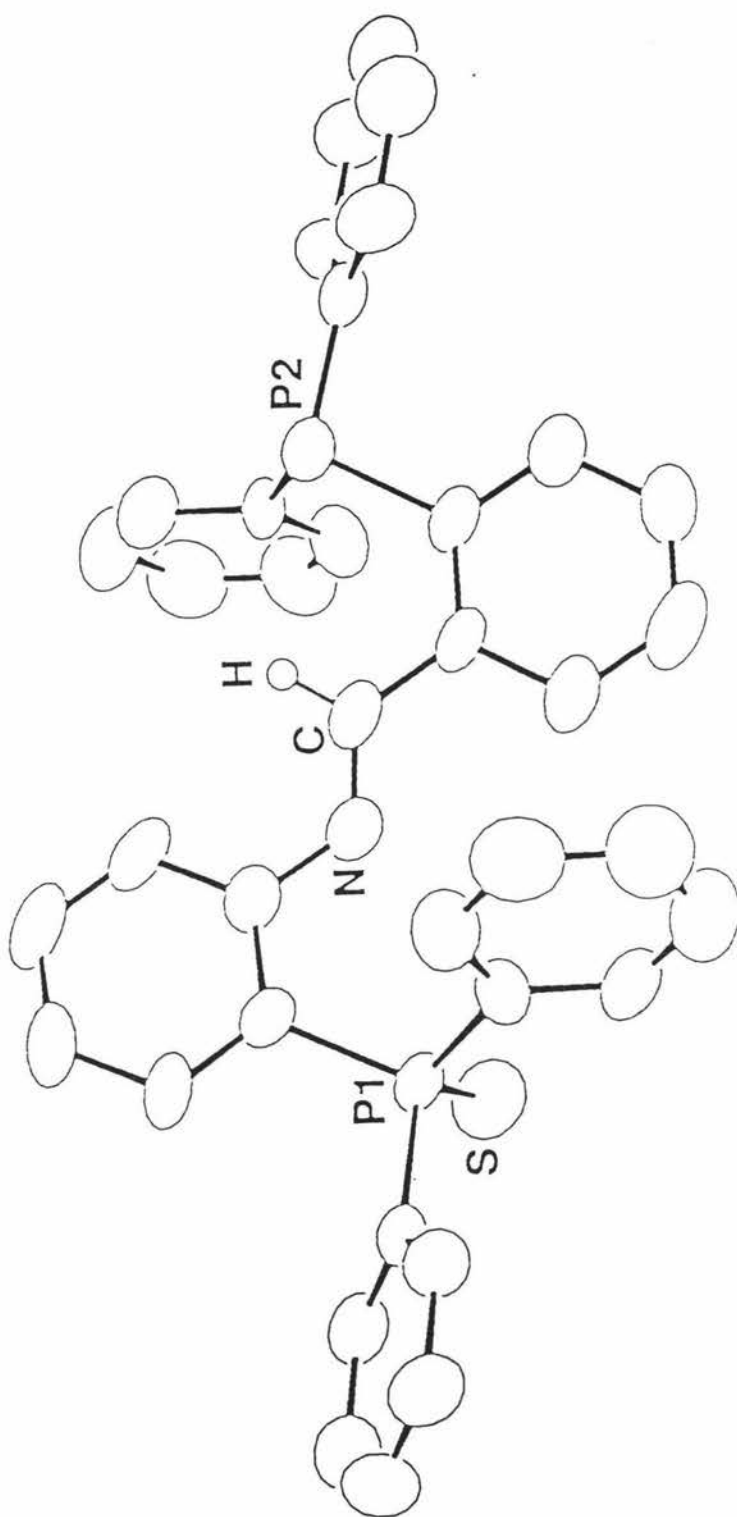
Figure II-3 Thermal ellipsoid diagram for SPNCP drawn at the
50% probability level
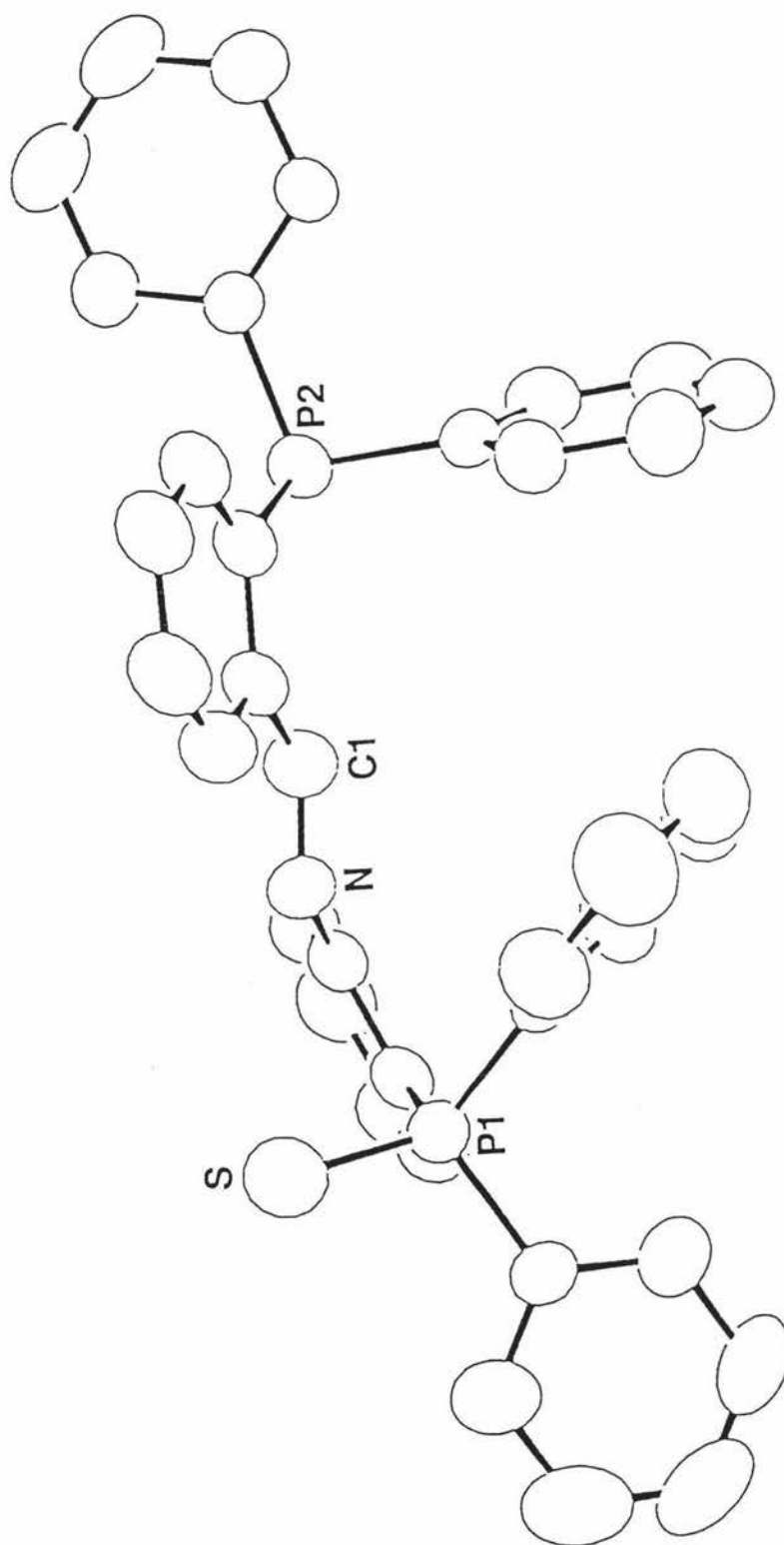
Figure II-4 Thermal ellipsoid diagram for SPNCP + solvent
drawn at the 50% probability level
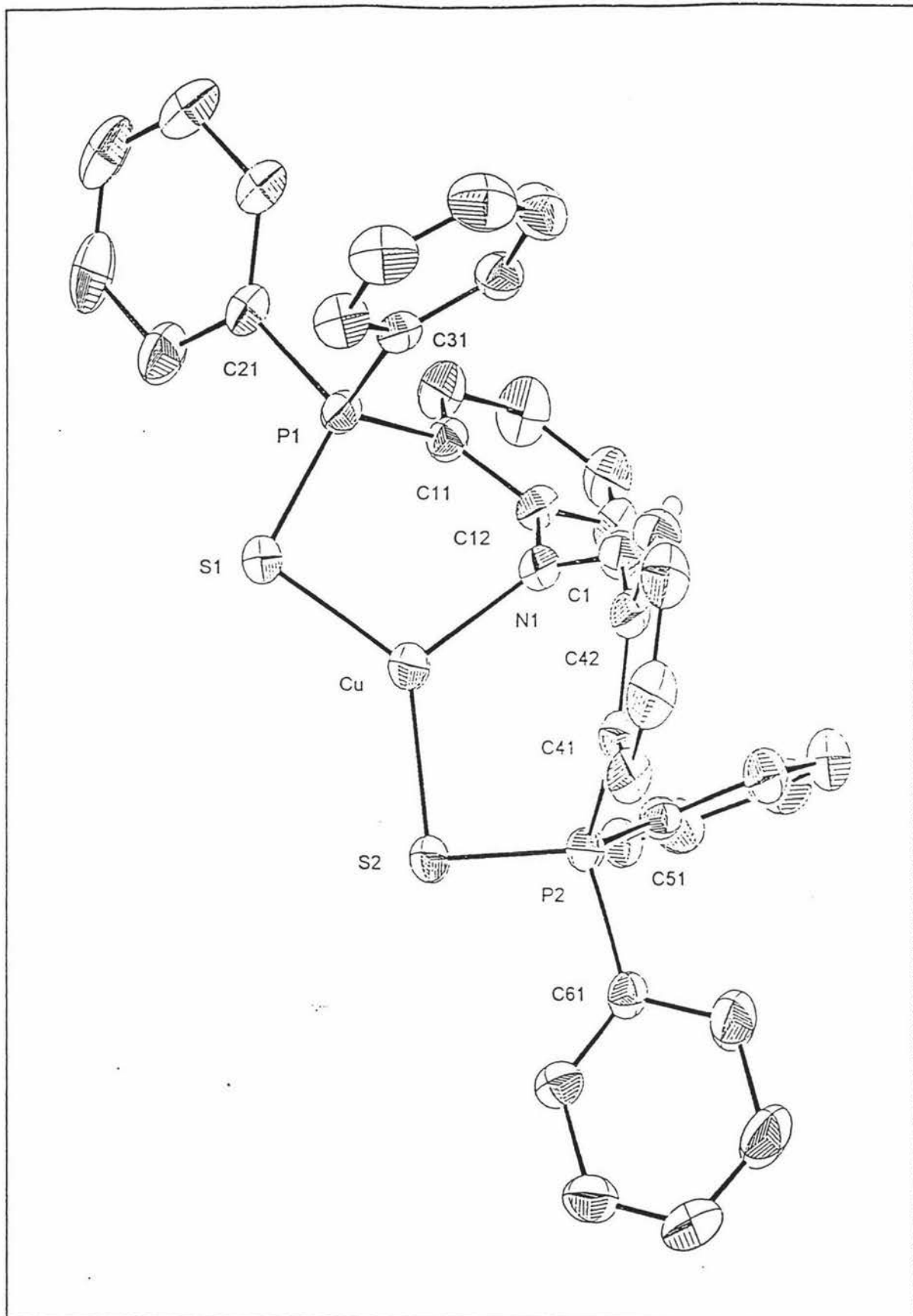
Figure II-5 Thermal ellipsoid diagram for [Cu(SPNCPS)]ClO$_4$

drawn at the 50% probability level

II-3-2 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy has proved to be valuable for characterizing the phosphines, their sulphides and complexed disulfides. Selected ^{1}H and ^{31}P{^{1}H} NMR data for the ligands 2-SPCHO, 2-SPNH$_2$, SPNCP, PNCPS and SPNCPS are given in Table 2-11 as well as for their un-oxidised precursors.

In the ^{1}H NMR spectrum for 2-PCHO a doublet resonance peak was observed at 10.50 ppm for the aldehyde proton and for PNCP and PNCPS the imine proton resonance near 8.90 ppm was a doublet. For 2-PCHO, PNCP and SPNCP the doublet splitting of the signal arises from ^{31}P-^{1}H coupling, the phosphorus atom nearest the imine proton giving rise to the coupling. This was confirmed by a decoupling experiment for PNCP which showed that the imine proton was not coupled to the phenyl protons.

Furthermore a 2D ^{1}H COSY experiment showed only a very minor coupling from the aromatic proton to the imine proton. However when the phosphorus atom nearest to the imine proton (or aldehyde proton) was oxidised with sulphur to form the products PNCPS and 2-SPCHO the imine and aldehyde protons appeared as singlets, the ^{31}P-^{1}H coupling now being reduced. The exact reason for this is not clear but could be attributed to an angle change about the phosphorus upon oxidation. In contrast, when the phosphorus atom nearest the imine N of PNCP is oxidised to give SPNCP, the imine proton resonance remains as a doublet, thus allowing the two isomers PNCPS and SPNCP to be distinguished. The imine proton remained as a singlet resonance in the fully oxidised compound SPNCPS. For 2-PNH$_2$ and 2-SPNH$_2$ the amine proton resonances were not split by the phosphorus.

The ^{1}H NMR spectrum of [Cu(SPNCPS)]ClO$_4$ showed a singlet at 8.57 ppm for the imine hydrogen compared with 8.91 ppm for the free ligand SPNCPS. This up field shift was indicative of ligand SPNCPS being coordinated.

In the ^{31}P{^{1}H} NMR data the chemical shifts for the phosphorus (III) atoms occurred in the range -11.6 to -20.2 ppm whereas that for the phosphorus(V) atoms lies in the range 40-42 ppm (Table 2-11). The isomers PNCPS and SPNCP could also be clearly distinguished from one another since the chemical shift for each type of phosphorus atom was different in both compounds. Upon coordination to copper(I) the chemical shifts for the two phosphorus atoms of SPNCPS moved from 41.9 and 41.1 ppm (free ligand) to 35.8 and 33.6 ppm (coordinated ligand) respectively. Thus ^{31}P{^{1}H} NMR can also be used to

distinguish between the free and coordinated SPNCPS ligand.

Table 2-11 ^{1}H and ^{31}P{^{1}H} NMR data for the compounds[a]

Compound	^{1}H(δ/ppm)	^{31}P(δ/ppm)[b]
2-PNH$_2$	4.14	-20.2
	[s, 2H(NH$_2$)]	
2-PCHO	10.50	-11.6
	[d, 5.5Hz, 1H(CHO)]	
PNCP	8.92	-14.2, -14.8
	[d, 5.5Hz,(-CH=N-)]	
2-SPNH$_2$	5.16	39.8
	[s, broad, 2H(NH$_2$)]	
2-SPCHO	10.71	40.3
	[s, 1H(CHO)]	
SPNCPS	8.91	-41.9, -41.1
	[s, 1H(-CH=N-)]	
SPNCP	8.87	42.2, -15.3
	[d, 6.2Hz,1H(-CH=N-)]	
PNCPS	9.02	-13.9, 40.9
	[s, 1H(-CH=N-)]	
[Cu(SPNCPS)]ClO$_4$	8.57	35.8, 33.6
	[s, 1H(-CH=N-)]	

[a] in CDCl$_3$

[b] with reference to external 85% H$_3$PO$_4$ set at zero ppm

d= doublet

s= singlet

II-3-3 Infra-red Spectra and Mass Spectral Data

Selected infra-red spectral data have been tabulated for the compounds, 2-SPNH$_2$, 2-SPCHO, PNCP, SPNCPS, PNCPS and SPNCP and are given in Table 2-12. Upon oxidation of the ligands a new band appeared in the range 628-635 cm^{-1} which compared well with that for other copper phosphine sulfide complexes [78,95] and was assigned to a υ(P=S) stretch 536-639 cm^{-1}. Other bands below 600 cm^{-1} also appeared but their position and assignment was less certain because of overlap with ligand bands. Upon coordination of SPNCPS to Cu(I) the υ(P=S) stretch moved from 635 cm^{-1} to 604 cm^{-1} consistent with the binding of S to copper. Simultaneously the υ(C=N) absorption moved from 1614 cm^{-1} to 1603 cm^{-1} consistent with the imine N binding to the copper [94]. X-ray structural studies confirmed these findings (see section II-3-1). A single band at 1096 cm^{-1} in the IR of [Cu(SPNCPS)]ClO$_4$ is assigned to a υ(Cl-O) stretching frequency and is consistent for an ionic ClO$_4^-$ [154] and this has been verified by a single crystal X-ray structural determination (see Chapter III-3-3)

Table 2-12 Infra-red data for the phosphine sulfides

Compound	υ(P-C) (cm^{-1})	υ(P=S) (cm^{-1})	υ(C=N) (cm^{-1})	υ(Cl-O) (cm^{-1})
PNCP	1091		1620	
2-SPNH$_2$	1098	628		
2-SPCHO	1096	639		
PNCPS	1098	634	1620	
SPNCP	1097	632	1613	
SPNCPS	1095	635	1614	
[Cu(SPNCPS)ClO$_4$	1096	604	1603	1096, 622

Mass spectra (Table 2-13) were obtained by the LSMS technique. The highest molecular mass peak for all the compounds corresponded with the protonated parent ion, MH$^+$, except for the [Cu(SPNCPS)]$^+$ ion.

Table 2-13 Mass spectral data for the compounds[a] (m/z)

Compound	Found	Calculated	Relative Intensity(%)
[2-PCHOSH]$^+$	323	323	100
[2-PNH$_2$SH]$^+$	310	310	100
[PNCPSH]$^+$	582	582	100
[SPNCPH]$^+$	582	582	100
[SPNCPSH]$^+$	614	614	55[b]
[Cu(SPNCPS)]$^+$	676[c]	676	100

[a] in NBA/CH$_2$Cl$_2$

[b] formed cesium complex [SPNCPSCs]$^+$ (m/z 746,)

[c] ^{63}Cu

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II-3-4 A Study of the Interaction of PNCP with Sulphur: Is There Any Evidence for Site Selectivity?

The inequivalent phosphorus atoms in PNCP provide an opportunity to investigate if there is any preference for one site or the other when PNCP is oxidised by one mole equivalent of sulphur. This reaction was studied by $^{31}P\{^1H\}$ NMR spectroscopy. Possible products, such as PNCP, PNCPS and SPNCP have been isolated by independent syntheses as described in the experimental section and have been characterised by methods already discussed including $^{31}P\{^1H\}$ NMR studies. These compounds provide useful "standards" to assign the spectra.

PNCP was reacted with sulphur in a 1:1 ratio in toluene, the solvent removed by evaporation, and the product completely redissolved in $CDCl_3$ and then a ^{31}P NMR spectrum recorded (see experimental for full details). The spectrum (Figure II-6) was complex but could be completely assigned. The major product was the mono sulphide SPNCP (50%) with a minor amount of its isomer PNCPS (7%), as well as the disulphide SPNCPS (27%) and unreacted PNCP (16%). Although there are a number of products these results indicate that the phosphorus atom nearest the imine N is more reactive than
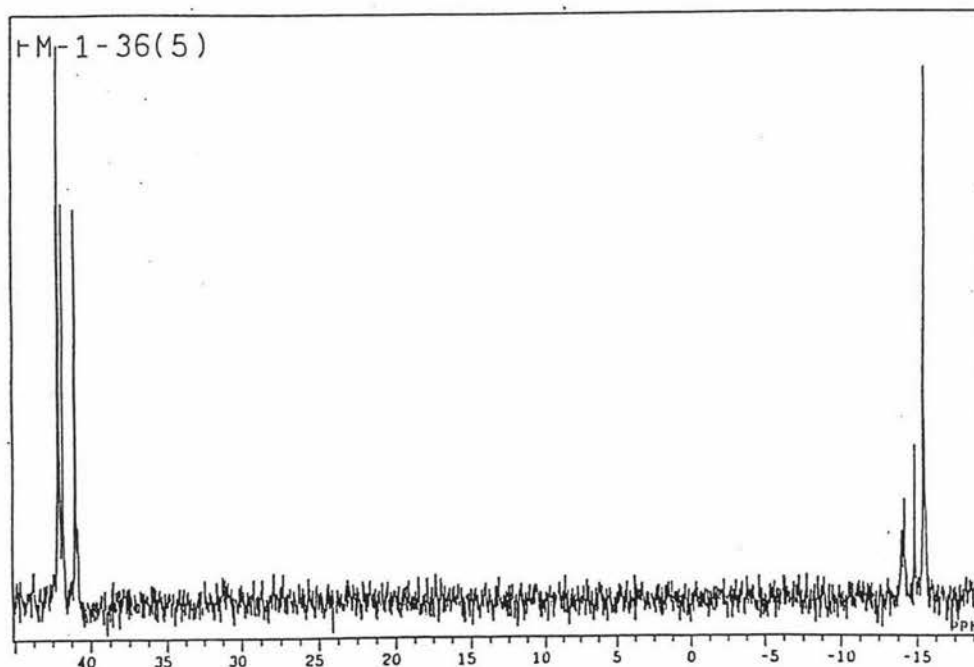
(Figure II-6)

the other as illustrated in the PNCPS: SPNCP ratio which was observed at 7:1. This was supported by the resonance structures below (Figure II-7) which show enhanced basicity of the phosphorus atom nearest the imine N.

The results of this reaction indicated a certain amount of site selectivity and this was even more specific when O_2 was used as oxidant (see Appendix 1). Preliminary studies suggest that there was close to 100% preference for oxidation to occur (under the conditions given) at the same phosphorus atom as in SPNCP *i.e.* nearest the imine N to give OPNCP. The dioxide OPNCPO was not detected. Further studies are required on these interesting reactions which up to now could not be easily investigated because of a lack of suitable diphosphines containing inequivalent phosphorus atoms.

(Figure II-7)

II-4 SUMMARY

Independent syntheses of the compounds PNCP, PNCPS, SPNCP, and SPNCPS have been achieved and crystal structures of PNCP, SPNCP and [Cu(SPNCPS)]ClO$_4$ have been performed. The SPNCPS ligand coordinates to the copper in a tridentate fashion *via* its two S and N donor atoms, giving the Cu atom a trigonal planar geometry.

In its reaction with S the PNCP ligand shows a small preference for oxidation to occur on the P atom nearest the imine N, which is the most basic P atom.

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CHAPTER THREE

STUDIES ON COORDINATION COMPLEXES OF COPPER(I) WITH MIXED PHOSPHORUS AND NITROGEN DONOR LIGANDS

III-1 INTRODUCTION

Phosphines have been used extensively as ligands in transition metal coordination complexes and organometallic compounds. This interest is, in part, due to the ability of the empty 3d orbitals of phosphine to receive electron density from filled t_{2g} d-orbitals of a metal to form π-bonds. Of the multitude of tertiary phosphines synthesised for use as ligands, undoubtedly the most widely used are triphenylphosphine derivatives.

Diphosphines containing a P-C-P framework have been the subject of numerous investigations during the past three decades [131,132]. Interest in analogous diphosphinoamine ligands (e.g. PR_2-NX-PR_2) has been growing rapidly. Such ligands have proved very versatile [133] because substituents on both phosphorus and nitrogen atoms can be varied with attendant changes in the P-N-P bond angle and the conformation around the phosphorus centres [134,135].

Two widely studied functionalised triphenylphosphines are phenyl-2-carbaldehyde-diphenylphosphine [117-119] (Figure III-1) and phenyl-2-aminodiphenylphosphine [120-122] (Figure III-2) The coordination chemistry of the these ligands is summarised briefly below.
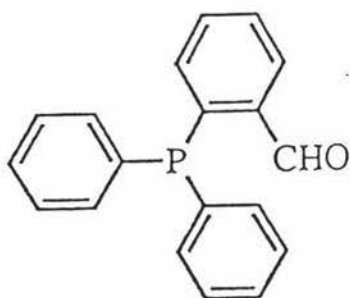
(Figure III-1)
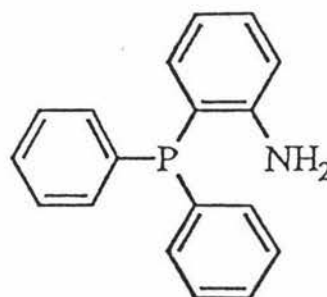
(Figure III-2)

III-1-1 Phenyl-2-carbaldehydediphenylphosphine

Hydridoacyl metal complexes provide insight into several important homogenous catalytic processes such as the decarbonylation of aldehydes, the hydroformylation of olefins, and, in general, all those processes that require C-H bond activation of the CHO functionality at a some stage of the catalytic cycle [125-127]. Hence much of the interest shown in forming coordination complexes with the ligand phenyl-2-carbaldehydediphenyl phosphine(2-PCHO) has been with the aim of developing a greater understanding of the interactions between aldehydes and metal centres in catalytic processes. The strong donor capability of the phosphine and the chelate effect of the ligand promotes the attack of the CHO group on the metal centre and this stabilises the coordination complex thus formed. The ligand 2-PCHO reacts rapidly with [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] in benzene to form the acyl hydride [Pt(2-PCO)H(PPh$_3$)] (Figure III-3) [128] which decomposes in the presence of ethanol and PPh$_3$ to form [Pt(PPh$_3$)$_3$]. Thus an oxidative addition of the aldehyde occurs to form [Pt(2-PCO)H(PPh$_3$)], which then undergoes a reductive elimination of the acyl group to form [Pt(PPh$_3$)$_3$]. Similar oxidative addition products have been isolated for rhodium (Figure III-4) [124] and iridium (Figure III-5) [123].
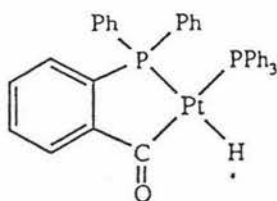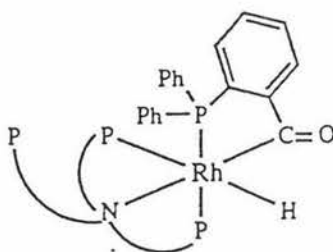
(Figure III-3)   (Figure III-4)   (Figure III-5)
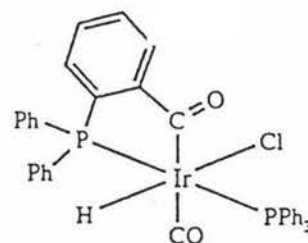
The phosphine aldehyde, 2-PCHO, is a potentially valuable ligand precursor *via* elaboration of the carbonyl group by condensation and/or reduction reactions. The tetradentate ligand N,N'-bis-[-0-(diphenylphosphino)benzylidene]ethylenediamine (en=P$_2$) (Figure III-6) is readily prepared by the condensation of two equivalents of phenyl-2-carbaldehydediphenylphosphine with ethylenediamine in boiling ethanol. This chelating

agent is soluble in common organic solvents and is conveniently crystallized from alcohols [129].

The en=P_2 ligand forms the complexes [Cu(en=P_2)]ClO$_4$ (Figure III-7), [Cu(en=P_2)- (*t*-BuNC)]ClO$_4$ (Figure III-8), [Ag(en=P_2)]BF$_4$, [Ag(en=P_2)(*t*-BuNC)]BF$_4$, [Ni(en=P_2)]BF$_4$ and Mo(CO)$_3$(en=P_2). X-ray crystallographic studies have shown that the ligand is capable of providing tetrahedral, trigonal and trigonal bipyramidal geometries for copper(I) and silver(I) complexes, a square-planar geometry for the nickel(II) complex and an octahedral geometry for the molybdenum(0) complex where it binds facially.

(Figure III-6)

ORTEP drawing and numbering scheme for cation [Cu(en=P_2)]$^+$

(Figure III-7)

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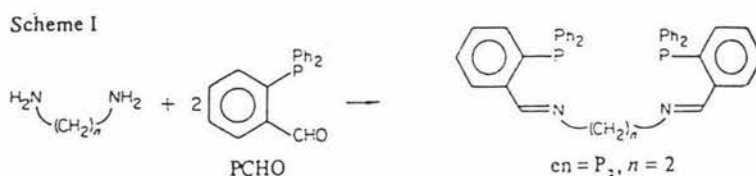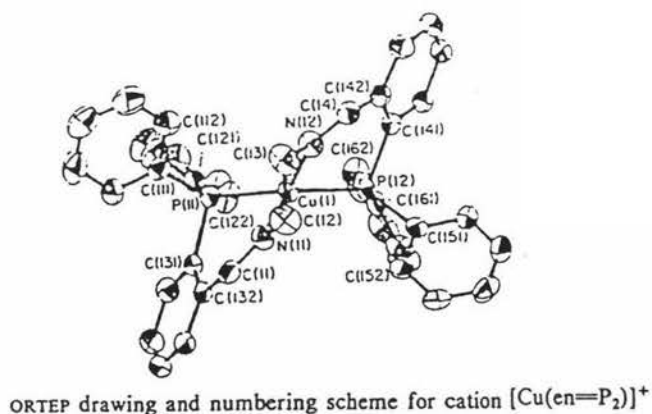
The reaction of equimolar quantities of the ligand with $[Cu(CH_3CN)_4]ClO_4$ affords the complex $[Cu(en=P_2)]ClO_4$ which is four-coordinate and reacts readily with an additional ligand (tert-butylisocyanide, t-BuNC) to form the adduct $[Cu(en=P_2)(t\text{-BuNC})]ClO_4$. The crystal structure reveals that the t-BuNC has displaced one of the imine donors of the en=P_2 ligand. The detailed mechanism (Figure III-9) by which $[Cu(en=P_2)(t\text{-BuNC})]ClO_4$ undergoes imine site exchange could involve either a three-coordinate [147] intermediate, where the ligand binds through the two phosphorus atoms, or a five-coordinate PNNP intermediate where the ligand binds all four donor atoms.

In this example the en=P_2 ligand acts in a tridentate PNP fashion instead of its more normal tetradentate PNNP mode [129]. The chiral tetradentate ligand, 2,2'-bis[o-(diphenyl-phosphino)benzyldeneamino]-6,6'-dimethylbiphenyl, PPNN is formed from the condensation reaction of phenyl-2-carbaldehydediphenylphosphine with (R)- or (S)-2,2'-dimethyl-6,6'-diamino-diphenyl as shown in Figure III-10.

The rhodium(I) and iridium(I) complexes, $[Rh(PPNN)]BPh_4$ and $[Ir(PPNN)]BPh_4$ have been synthesized and characterized. Both complexes have approximately square-planar P_2N_2 coordination core geometries (Figure III-11) [130].
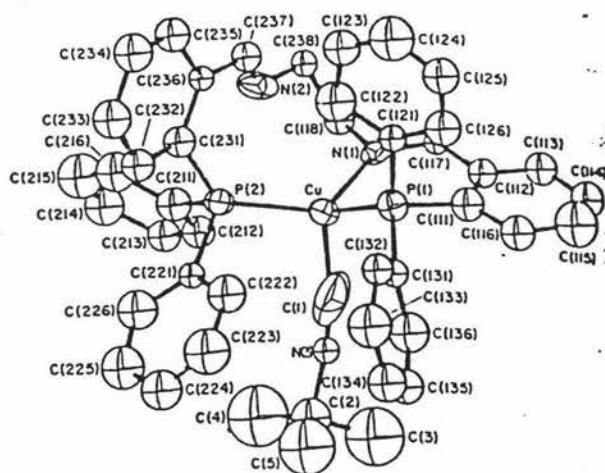
ORTEP drawing and numbering scheme for $[Cu(en=P_2)(t\text{-BuNC})]^+$
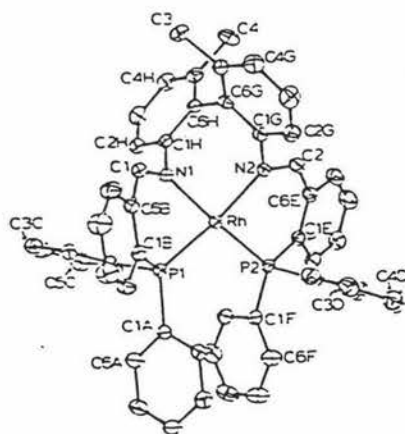
ORTEP drawing of the cation $[Rh(PPNN)]^+$

(Figure III-8)   (Figure III-11)

59
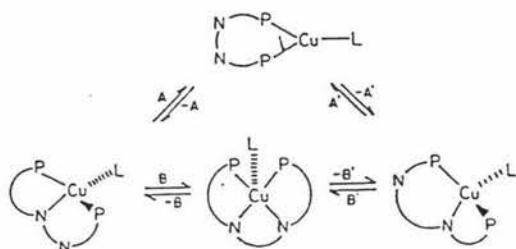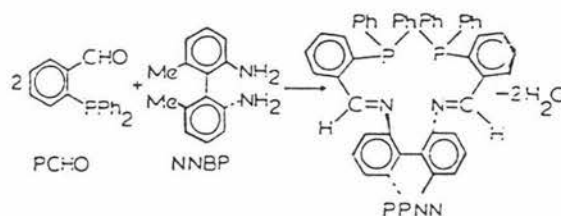
(Figure III-9)

(Figure III-10)

III-1-2 2-aminophenyldiphenylphosphine

2-PNH$_2$ (2-aminophenyldiphenylphosphine) is a hybrid bidentate ligand containing a 'soft' phosphorus and 'hard' primary aromatic amine donor set, and has the additional feature that a chelate ring can be formed upon coordination [120,136,137].

A series of bis-chelate amino and amido complexes (obtained from deprotonation of the 2-PNH$_2$ complexes) have been characterised with Ni(II) [20] and Pt(II) [120,137-139], with the ligand coordinating through both the phosphorus and nitrogen donor atoms.

Bidentate coordination and facile deprotonation were also observed on reaction of two mole equivalents of 2-PNH$_2$ with [Rh(cod)Cl]$_2$ (cod=cyclo-octa-1,5-diene). A variety of products, including those obtained by insertion of the low-valent Rh(I) centre into an N-H bond resulted. Thus the rhodium-amido-complex (Figure III-12) and rhodium-amino-complex (Figure III-13) [144] where isolated. The unusual reaction of oxygen with rhodium(I) carbonyl complexes of 2-aminophenyldiphenylphosphine yielded the rhodium(II) amido-bridged dimer (Figure III-14). This species was also prepared by oxidative addition of halogen to a rhodium(I) amido-bridge dimer.

60
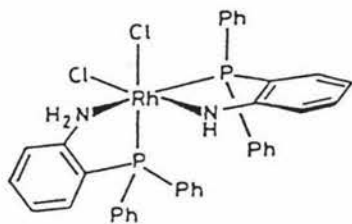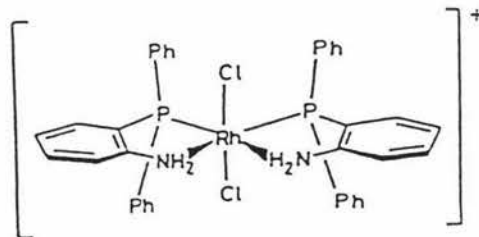
(Figure III-12)

(Figure III-13)

The deprotonation reaction has also provided a convenient route to prepare multidentate ligands [141] and macrocyclic [121,142] ligands. The new P_2N_2 multidentate ligand N,N'-bis[2-(diphenylphosphino)-phenyl]propane-1,3-diamine (Figure III-15) was prepared by linking the nitrogen atoms of two molecules of the parent bidentate ligand 2-PNH$_2$. This was achieved by the reaction of 1,3-bis(toluene-p-sulphonyloxy)propane, tsO(CH$_2$)$_3$Ots, with cis-[Ni(2-PNH$_2$)$_2$] in refluxing toluene over anhydrous potassium carbonate (Figure III-16).
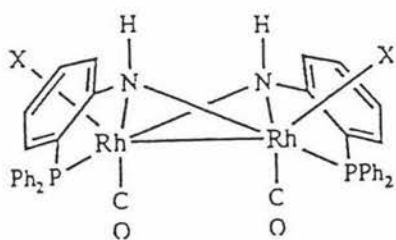
(Figure III-14)
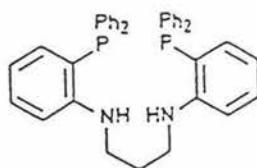
(Figure III-15)
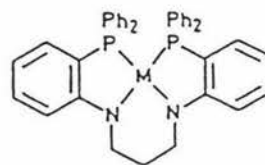
(Figure III-16)

Coordination complexes formed with Ni(II), Rh(I), Pd(II) and Pt(II) have been characterised by X-ray crystallography [121,142] and show the planar tetradentate nature of the ligand (Figure III-16). It also behaves as a trans-spanning P_2 ligand [121,143] in the rhodium complex (Figure III-17).
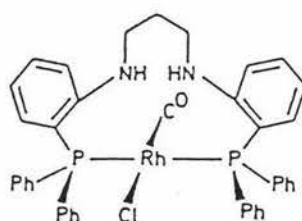
(Figure III-17)

A series of multidentate ligands have been synthesized by the condensation reaction of PNH$_2$ with ligands containing aldehyde groups. The tetradentate iminophosphine ligand has been prepared and its copper(I) complexes crystallographically characterised [section, II-1-2].

The tridentate ligand MePNN {(2-pyridyl)-N-[2-(diphenylphosphino)benzy-lidene]methylamine} (Figure III-18) was prepared by Rauchfuss *et al.* [145] and its molybdenum chemistry investigated.

The new unsymmetrical tridentate ligand PNCP (Figure III-19) has been synthesised [146] in our laboratory by the condensation of 2-PNH$_2$ with 2-PCHO (see Chapter Two) and its nickel complex [Ni(PNCP)Cl]ClO$_4$ has been characterised. The structure consists of a nickel atom in an approximately square-planar coordination geometry (Figure III-20) bound to the two phosphorus atoms, and the nitrogen atom of the PNCP ligand. The inequivalent phosphorus atoms are *trans* to each other, and the fourth position in the coordination sphere is occupied by a chlorine atom.

MePNN
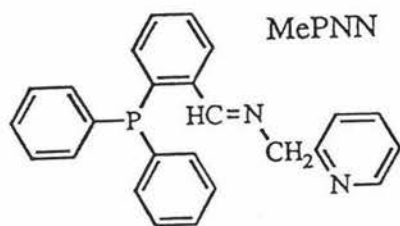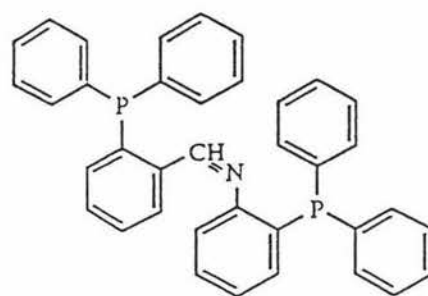
(Figure III-18)

(Figure III-19)

(Figure III-20)

63
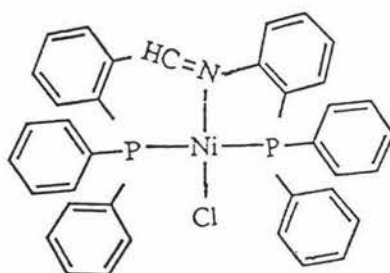
III-1-3 The Present Study

PNCP is a new tridentate ligand containing inequivalent phosphorus atoms which should have a distinctive ability to stabilise metal ions in low oxidation states with interesting geometries. The coordination characteristics of PNCP towards copper(I) have been studied by spectroscopic and X-ray diffraction techniques. In acting as a tridentate ligand interest was in whether PNCP provides a T-shape or pyramidal coordination geometry. In addition, when the PNCP:Cu ratio in the complexes is greater than 1:1, other modes of coordination of PNCP are potentially possible. Both of these aspects have been studied and the results are reported in this chapter.

III-2 SYNTHESIS OF COPPER COMPLEXES

III-2-1 Preparation of [Cu(PNCP)Cl]

To a refluxing suspension of CuCl (0.015g, 0.15 mmol) in ethanol (10 ml) was added PNCP (0.083g, 0.15 mmol) in dichloromethane (8 ml). A red orange solution formed immediately and refluxing was continued under a flow of nitrogen gas for 30 minutes. The solution was filtered while hot and on standing at 4°C overnight, the red orange crystalline product was filtered off and washed with ethanol.

Yield: 85% (0.083g) M.P. 222-225°C.

Found: C, 68.21; H, 4.53; N, 2.10; P, 9.60

Calculated for ($CuC_{37}H_{29}ClNP_2$):

C, 68.52; H, 4.48; N, 2.16; P, 9.56

III-2-2 Preparation of [Cu(PNCP)Br]

To a refluxing suspension of CuBr(0.022g, 0.15 mmol) in ethanol (10 ml) was added PNCP (0.083g, 0.15 mmol) dissolved in dichloromethane (8 ml). The red orange solution was refluxed under a flow of nitrogen gas for 20 minutes. The resulting precipitate was filtrated off, washed with ethanol and recrystallised from dichloromethane (5 ml) at room temperature.

Yield:	81% (0.085g) M.P. 219-221°C.
Found:	C, 63.95; H, 4.21; N, 1.92; P, 8.80
Calculated for (CuC$_{37}$H$_{29}$BrP$_2$):	
	C, 64.12; H, 4.18; N, 2.02; P, 8.94

III-2-3 Preparation of [Cu(PNCP)(CH$_3$CN)]ClO$_4$

[Cu(CH$_3$CN)$_4$]ClO$_4$ [163] (0.098g, 0.3 mmol) and PNCP (0.166g, 0.3 mmol) were dissolved in dichloromethane (15 ml). To this red orange solution, ethanol (15 ml) was slowly added and the solution was refluxed under a brisk flow of nitrogen gas for 45 minutes. When the volume was approximately 15 ml, the solution was transferred to a beaker. After standing overnight at 4°C, the resulting red orange product was filtered off and washed with ethanol. The product was dissolved in acetonitrile (4 ml) and orange crystals appeared on standing overnight at 4°C.

Yield:	76% (0.201g) M.P. 260-262°C.
Found:	C, 61.33; H, 4.75; N, 3,42; Cl, 4.84; P, 7.96
Calculated for (CuC$_{39}$H$_{32}$ClN$_2$P$_2$O$_4$):	
	C, 61.58; H, 4.76; N, 3.50; Cl, 4.45; P, 7.75

III-2-4 Preparation of [Cu(PNCP)ClO$_4$]·CH$_3$CH$_2$OH

The method of preparation was similar to that of [Cu(PNCP)(CH$_3$CN)]ClO$_4$ described in (II-2-3) above but in the recrystallisation step the solvent used was a mixture of dichloromethane and ethanol (4 ml/2 ml).

Yield:	73% (0.193g) M.P. 255-256°C.
Found:	C, 61.56; H, 4.18; N, 1.75
Calculated for (CuC$_{39}$H$_{35}$ClNP$_2$O$_5$):	
	C, 61.78; H, 4.62; N, 1.85

III-2-5 Preparation of [Cu(PNCP)(PPh₃)]ClO₄·CH₃CH₂OH

To [Cu(PPh₃)₂(CH₃CN)₂]ClO₄ (0.154g, 0.2 mmol) dissolved in hot ethanol (30 ml) was added PNCP (0.110g, 0.2 mmol) dissolved in hot ethanol (10 ml). The orange solution was refluxed under a brisk flow of nitrogen gas for three hours. The yellow crystalline product appeared on standing the solution at 4°C overnight. The product was filtered, washed with ethanol and recrystallised from an ethanol/dichloromethane mixture (3 ml/5 ml).

Yield:	85% (0.224g) M.P. 242-245°C.
Found:	C, 67.17; H, 4.99; N, 1.25; P, 9.17
Calculated for (CuC₅₇H₅₀ClNP₃O₅):	
	C, 67.06; H, 4.94; N, 1.37; P, 9.10

III-2-6 Preparation of [Cu(PNCP)(TU)]ClO₄ (TU=thiourea)

[Cu(PNCP)ClO₄]·EtOH (0.125g, 0.3 mmol) was dissolved in dichloromethane (5 ml). To this red orange solution, thiourea (TU) (0.023g, 0.3 mmol) dissolved in ethanol (15 ml) was slowly added and the mixture refluxed under a brisk flow of nitrogen gas for three hours. Upon filtration of the hot solution a red-orange precipitate was collected after one hour, washed with ethanol and vacuumed dried. On standing overnight the mother liquor yielded a second crop of crystalline product. This was filtered, dried and combined with the first crop.

Yield:	69% (0.102g) M.P. 206-209°C
Found:	C, 57.44; H, 4.61; N, 5.78; P, 7.47
Calculated for (CuC₃₈H₃₃ClN₃P₂SO₄):	
	C, 57.82; H, 4.22; N, 5.33; P, 7.86

III-2-7 Preparation of [Cu₂(PNCP)₂(SCN)]ClO₄·H₂O

To [Cu(PNCP)(CH₃CN)]ClO₄ (0.104g, 0.14 mmol) dissolved in dichloromethane (5 ml), sodium thiocyanate (0.006g, 0.07 mmol) dissolved in ethanol (15 ml) was added slowly (in 5 minutes) with stirring under a nitrogen gas flow. The red orange solution was

refluxed with a flow of nitrogen gas for 30 minutes, after which time an orange precipitate formed and this was collected by vacuum filtration and washed with ethanol. The product was recrystallized from ethanol/CH_2Cl_2 (3ml/5ml).

Yield: 75% (0.083g) M.P. 253-256°C.

Found: C, 63.54; H, 4.24; N, 3.06; P, 9.45

Calculated for ($Cu_2C_{75}H_{60}ClN_3P_4SO_4$):

C, 64.23; H, 4.28; N, 3.00; P, 8.85

III-2-8 Preparation of [Cu(PNCP)(Me$_2$NPC)]

[Me$_2$NPC=4-dimethylaminophenylcyanamide anion]

To [Cu(PNCP)(CH$_3$CN)]ClO$_4$ (0.091g, 0.12 mmol) dissolved in dichloromethane (5 ml) was added slowly (in five minutes) with stirring under a nitrogen gas flow, Me$_2$NPC (0.019g, 0.12 mmol) dissolved in a solution containing ethanol (10 ml) and sodium (0.003g, 0.12 mmol). The dark red solution was refluxed under a nitrogen atmosphere for 20 minutes whereupon red brown crystals of the product formed, These were collected by vacuum filtration and washed with ethanol.

Yield: 83% (0.091g) M.P. 228-230°C.

Found: C, 71.12; H, 5.06; N, 7.43

Calculated for ($CuC_{44}H_{39}N_4P_2$):

C, 71.37; H, 5.04; N, 7.24

III-2-9 Preparation of [Cu$_2$(PNCP)$_2$(Me$_2$NPC)]ClO$_4$·2H$_2$O

A similar procedure to that reported in II-2-8 above was followed, but with the following amounts:

[Cu(PNCP)]ClO$_4$ (0.127g, 0.18 mmol), Me$_2$NPC (0.015g, 0.09 mmol) and sodium (0.002g, 0.09 mmol). The product was brown in colour.

Yield: 73% (0.105g) M.P. 217-220°C.

Found: C, 64.30; H, 4.64; N, 4.23; P, 7.90

Calculated for ($Cu_2C_{81}H_{72}ClN_7P_2O_6$):

                       C, 65.43; H, 4.80; N, 4.60; P, 8.15

III-2-10 Preparation of [Cu(PNCP)$_2$]ClO$_4$·2H$_2$O

[Cu(CH$_3$CN)$_4$]ClO$_4$ (0.049g, 0.15 mmol) and PNCP (0.167g, 0.304 mmol) were dissolved in dichloromethane (15 ml) and ethanol (15 ml). This orange solution was refluxed under a brisk flow of dry nitrogen gas for 45 minutes until the solution was approximately 13ml in volume whereupon a yellow crystalline product precipitated. This was filtered off and the mother liquor was left standing overnight at 4°C. A second crop of the product was collected and vacuumed dried. The two crops were combined and recrystallised from a dichloromethane/ethanol mixture.

Yield: 72% (0.156g) M.P. 195-197°C.

Found: C, 68.57; H, 5.16; N, 2.14

Calculated for ($Cu_2C_{74}H_{62}ClN_3P_4O_6$):

                       C, 68.47; H, 4.78; N, 2.15

III-2-11 Preparation of [Cu$_2$(PNCP)$_3$](ClO$_4$)$_2$·H$_2$O

To [Cu(PNCP)]ClO$_4$ (0.086g, 0.12 mmol) dissolved in dichloromethane (5 ml) was added slowly [Cu(PNCP)$_2$]ClO$_4$ (0.138g, 0.12 mmol) dissolved in dichloromethane (5 ml). Another 15ml of ethanol was added and the solution refluxed under a brisk flow of nitrogen gas for 30 minutes. When the volume of the solution was approximately 13ml, the precipitated orange product was collected by vacuum filtration and recrystallized from ethanol and dichloromethane (3 ml/5 ml).

Yield: 71% (0.159g) M.P. 274-276°C.

Found: C, 66.20; H, 4,50; N, 1.83; P, 9.59

Calculated for ($Cu_2C_{111}H_{89}Cl_2N_3P_6O_9$):

                    C, 66.93; H, 4.47; N, 2.11; P, 9.33

III-2-12 Preparation of $[Cu_2(PNCP)_2(SNC_5H_5)](ClO_4)\cdot 2H_2O$

To 2-mercaptopyridine (0.0045g, 0.049 mmol) dissolved in a solution containing ethanol (10 ml) and sodium (0.0012g, 0.049 mmol) was added slowly under a flow of nitrogen gas [Cu(PNCP)]ClO$_4$ (0.070g, 0.098 mmol) dissolved in dichloromethane (5 ml). The reaction mixture was refluxed under nitrogen gas for 25 minutes. The resulting red product was isolated by filtration, washed with ethanol and re-precipitated from a dichloromethane and ethanol solution (5 ml/3 ml).

Yield:	74% (0.056g)
Found:	C, 63.49; H, 4.32; N, 2.96; P, 7.94
Calculated for (Cu$_2$C$_{79}$H$_{67}$ClN$_3$P$_4$O$_6$):	
	C, 64.40; H, 4.55; N, 2.85; P, 8.42

III-3 RESULTS AND DISCUSSION

III-3-1 Synthese of Copper Complexes Containing of PNCP

Complexes of the type [Cu(PNCP)X] (X= Cl$^-$, Br$^-$, ClO$_4{}^-$) were prepared by reaction of the appropriate copper salt with PNCP in a 1:1 mole ratio. Complexes of the type [Cu(PNCP)L]ClO$_4$ (L= P(C$_6$H$_5$)$_3$, CH$_3$CN, thiourea, 4-dimethylaminophenylcyanamide) have also been reported. The addition of two mole equivalents of PNCP to one mole of [Cu(CH$_3$CN)$_4$]ClO$_4$ resulted in the formation of [Cu(PNCP)$_2$]ClO$_4$ whereas the interaction of the compound with [Cu(PNCP)ClO$_4$] produced [Cu$_2$(PNCP)$_3$](ClO$_4$)$_2$. Species of the type [Cu$_2$(PNCP)$_2$X]ClO$_4$·yH$_2$O (X= SCN$^-$ or 4-dimethylaminophenylcyanamide anion; y= 0 or 1) have also been obtained.

The reactions are fully discussed in the Experimental and Section III-2-1 including analytical data. The spectroscopy of these compounds and the structure of [Cu(PNCP)ClO$_4$] will be discussed in the following section.

III-3-2 Crystal Structure of [Cu(PNCP)ClO$_4$]

The crystal structure of [Cu(PNCP)ClO$_4$] is shown in Figure III-14 and bond distance and angle data are given in Table 3-2.

The coordination geometry of the central copper is tetrahedral with the ligand coordinating to the copper in a tridentate fashion *via* its two phosphorus and nitrogen

donor atoms. The perchlorate anion occupies two disordered sites each of which is bound to the copper *via* a single oxygen atom. The two Cu-P bond distances of 2.203(1)Å and 2.208(1)Å are shorter than the range of values 2.24-2.29Å typically observed for distorted tetrahedral Cu(I) complexes [129,156,157]. The Cu-N bond distance of 2.159(5)Å is a little longer than that found in other distorted tetrahedral complexes such as Cu(I) diphosphine diamine complexes (2.081Å) [129] and the square pyramidal Cu(I) complex [Cu(cyclops)(CO)] 2.100Å [158]. The Cu-O bond distance of 2.164(1)Å is comparable with those found in other distorted tetrahedral CuO_2P_2 complexes (Cu-O range, 2.162-2.257Å) [160-162]. These bonds lengths suggest that in [Cu(PNCP)]ClO$_4$ the Cu-P bonds are a little stronger than their countparts in other complexes whereas the Cu-N is a little weaker. The Cu-O coordination appears normal for the perchlorate anion. The C(1)-N bond distance at 1.168Å shows considerable multiple bond character but it is shorter than the C(1)-N bond (1.263Å) in SPNCP and the expected value of 1.287Å [111]. The C(12)-N bond distance of 1.510Å is longer than the similar bond 1.416(5)Å in SPNCP and also longer than the expected value of 1.472(5)Å [164]. The C(1)-C(42) bond length of 1.475(7)Å is similar to the comparable bond 1.478(6)Å in compound SPNCP and somewhat shorter than the expected bond length 1.53Å [113]. This fact may be attributed to the nitrogen donor atom of the PNCP ligand being one of donor atoms bound to the tetrahedral copper(I).

The ideal angle for tetrahedral geometry is 109° [129]. For the complex under study the angles observed are O(1)-Cu-P(1) 108.4(2)°, O(1)-Cu-P(2) 108.8(2)°, P(1)-Cu-N 86.18(1)°, P(2)-Cu-N 94.21(1)° and P(1)-Cu-P(2) 142.75(5)°. Two of the angles are very close to the ideal angle but the remaining three are not. Of particular note is the angle P(1)-Cu-P(2) [142.75(5)°]. This larger angle is a result of the constraints imposed on the complex by the tridentate ligand which forms five and six membered chelate rings. Other bonds and angles within the complex do not differ significantly from comparable Cu(I) complexes.

Table 3 - 1

Crystal data for [Cu(PNCP)(ClO$_4$)].

Empirical formula	C$_{37}$H$_{29}$ClCu O$_4$P$_2$
Formula weight	712.54
Temperature	293(2) K
Wavelength	0.71069 A
Crystal system	Monoclinic
Space group	P2$_1$/c (No. 14)
Unit cell dimensions	a = 17.4070(10) A α = 90.000(10) deg. b = 9.6630(10) A β = 107.330(10) deg. c = 20.3440(10) A γ = 90.000(10) deg.
Volume	3266.6(4) A^3
Z	4
Density (calculated)	1.449 Mg/m^3
Crystal size	0.53 x 0.30 x 0.28 mm
Theta range for data collection	2.35 to 24.97 deg.
Reflections collected	6228
Independent reflections	5724 [R(int) = 0.0229]
Refinement method	Full-matrix least-squares on F^2
Data used in refinement	5721
No. of parameters refined	455
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1123
R indices (all data)	R1 = 0.0838, wR2 = 0.1532
Refinement program	SHELXL-93
Graphics program	ZORTEP

Table 3 - 2

Selected bond lengths [A] and angles [deg] for [Cu(PNCP)(ClO4)].

Cu-N	2.159(5)	P(1)-C(31)	1.827(4)
Cu-O(21)	2.164(11)	P(2)-C(61)	1.824(5)
Cu-O(11)	2.193(6)	P(2)-C(51)	1.832(5)
Cu-P(1)	2.2032(12)	P(2)-C(41)	1.835(5)
Cu-P(2)	2.2081(13)	N-C(1)	1.168(7)
P(1)-C(21)	1.822(5)	N-C(12)	1.510(6)
P(1)-C(11)	1.825(4)	C(1)-C(42)	1.475(7)

N-Cu-O(21)	123.2(5)	C(61)-P(2)-C(41)	103.1(2)
N-Cu-O(11)	87.9(2)	C(51)-P(2)-C(41)	105.4(2)
N-Cu-P(1)	86.18(14)	C(61)-P(2)-Cu	115.3(2)
O(21)-Cu-P(1)	103.5(3)	C(51)-P(2)-Cu	123.5(2)
O(11)-Cu-P(1)	108.4(2)	C(41)-P(2)-Cu	103.0(2)
N-Cu-P(2)	94.21(13)	C(1)-N-C(12)	119.6(6)
O(21)-Cu-P(2)	107.2(4)	C(1)-N-Cu	124.4(5)
O(11)-Cu-P(2)	108.8(2)	C(12)-N-Cu	115.2(3)
P(1)-Cu-P(2)	142.75(5)	N-C(1)-C(42)	126.9(7)
C(21)-P(1)-C(11)	102.7(2)	C(13)-C(12)-N	126.3(4)
C(21)-P(1)-C(31)	105.1(2)	C(11)-C(12)-N	115.8(4)
C(11)-P(1)-C(31)	106.0(2)	C(43)-C(42)-C(1	110.0(5)
C(21)-P(1)-Cu	123.1(2)	C(41)-C(42)-C(1)	131.2(5)
C(11)-P(1)-Cu	101.35(14)	Cl-O(11)-Cu	130.5(4)
C(31)-P(1)-Cu	116.4(2)	Cl-O(21)-Cu	131.0(8)
C(61)-P(2)-C(51)	104.3(2)		
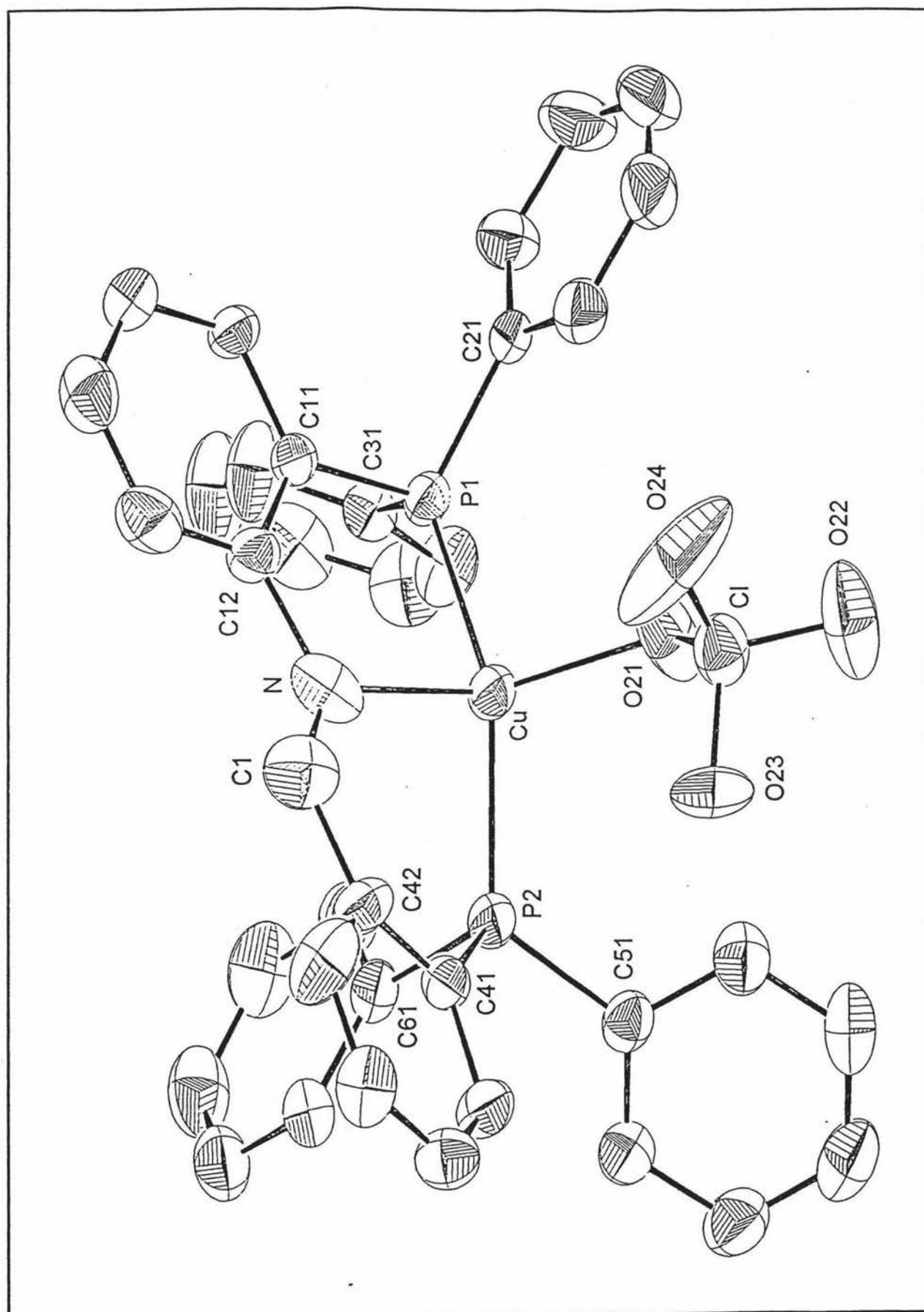
Figure III-14 Thermal ellipsoid diagram for [Cu(PNCP)ClO₄]

drawn at the 50% probability level

III-3-3 Nuclear Magnetic Resonance (NMR)

Selected ^{1}H and ^{31}P NMR data obtained for the copper(I) complexes with PNCP are listed in Table 3-3

^{1}H NMR spectra

Small changes in the chemical shifts of the imine protons are observed on coordination of PNCP to copper. In comparison with free PNCP where the phosphorus atoms are *trans* to each other, the coordinated ligand binds in a *cis*-configuration (see Chapter Two). Two factors could influence this shift: (a) the strength of the imine nitrogen to copper bond, and (b) the shielding effect of the copper. For [Cu(PNCP)ClO$_4$] the Cu-N bond is considered to be only slightly longer than expected (see Section III-3-1), and most of the shifts were similar to that in PNCP. However in [Cu(PNCP)(PPh$_3$)]ClO$_4$ a signal was observed at 9.46 ppm. The reason for this lower field shift will require further structural studies and may imply a difference in the Cu-N interaction. Also for [Cu$_2$(PNCP)$_2$-(Me$_2$NPC)]ClO$_4$ two separate imine proton signals were observed at 8.70 ppm and 9.25 ppm. The origin of this chemical inequivalence may be attributed to the fact that one copper atom may have the negatively charged amido nitrogen bound (see Figure III-21), whereas the other has the neutral imine nitrogen atom bound. Such coordination modes have been established in other copper(I) compounds [151-153], and may explain this chemical inequivalence.

Figure III-21

74
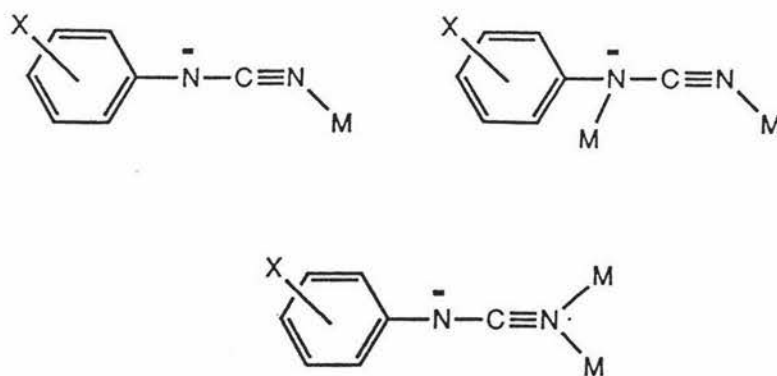
Furthermore, whereas the imine proton signal appears as a doublet in PNCP with $^4J(P-H)$ 5.5Hz, in its complexes (except for [Cu(PNCP)Br]) it appears as a singlet. As was outlined in Chapter 2, the reduction in this coupling was associated with the nearest phosphorus atom binding to sulphur or a metal. For [Cu(PNCP)Br] the imine proton signal appeared to be split but with a reduced $^4J(P-H)$ coupling of about 1.1Hz.

^{31}P NMR spectra

As already discussed in Chapter Two, the inequivalent phosphorus atoms in PNCP gave rise to two distinct $^{31}P\{H\}$ signals. Such is also the case when PNCP is coordinated to Cu(I). In general, the spectra are consistent with PNCP remaining bound to the copper in solution. However, the signals at room temperature were quite broad probably due to fast exchange processes, and unfortunately since the variable temperature accessory on the NMR instrument was not operational, spectra were not able to be run in the temperature range -55° to -80°C where such processes are known to be slowed down [129, 150]. The $^{31}P\{H\}$ spectra could be arranged into two groups:

(a) where the signals were about -12 ppm and -22 ppm.

(b) where the signals were about -5 ppm and -12 ppm.

The reasons for the groupings are not certain but factors such as coordination number, geometry, charge on the complex ion and types of ligands presumably contribute.

A third chemical shift in [Cu(PNCP)(PPh$_3$)]ClO$_4$ at -0.89 ppm was assigned to coordinated triphenylphosphine.

III-3-4 Infra-red Spectroscopy and Mass Spectra

Selected infra-red spectra are listed for the complexes in Table 3-4. The $\upsilon(C=N)$ frequencies for the complexes (1606-1616 cm^{-1}) are less than those observed for the free ligand PNCP (1620 cm^{-1}) and are consistent with the imine nitrogen bound to the metal. This was confirmed by an X-ray diffraction study as discussed in section III-3-1.

The infra-red spectrum of [Cu(PNCP)(CH$_3$CN)]ClO$_4$ exhibits a weak band at 2272 cm^{-1} assignable to a $\upsilon(C\equiv N)$ frequency which is consistent with CH$_3$CN being bound to the metal (see Section III-2-2). For the compounds [Cu(PNCP)(Me$_2$NPC)] and [Cu$_2$(PNCP)$_2$-Me$_2$NPC)]ClO$_4$ the $\upsilon(C\equiv N)$ frequencies do not clearly distinguish between terminal or bridging phenylcyanamide [151-153]. Similarly for the thiocyanate ion in [Cu$_2$(PNCP)$_2$(SCN)]ClO$_4$, with $\upsilon(C\equiv N)$ at 2111 cm^{-1}, it is not possible to distinguish its

coordination mode.

The υ(P-C) stretching frequencies for the complexes (1093-1097 cm^{-1}) are a little greater than that observed for PNCP at 1091 cm^{-1}.

The infra-red spectra of the perchlorate compounds show intense bands assignable to υ(Cl-O) frequencies in the range 1025-1130 cm^{-1} and about 622 cm^{-1}. Most of the complexes displayed a single strong absorption in the range 1035-1060 cm^{-1} (and a weaker one at about 622 cm^{-1}) consistent with the anionic nature of the ClO_4^- group (Figure III-3). However for [Cu(PNCP)ClO$_4$] the υ_3 band is split(1130 and 1036 cm^{-1}) which suggests coordinated character for the perchlorate group and consistent with unidentate binding (Figure III-4) [154]. Indeed this was confirmed from X-ray crystallography (see Section III-3-2). This result shows that in order for copper(I) to obtain four coordination the ClO_4^- ion has to bind. The infra-red spectra of [Cu(PNCP)$_2$]ClO$_4$ and [Cu$_2$(PNCP)$_3$](ClO$_4$)$_2$ show the presence of ionic perchlorate, as for the other compounds.

The mass spectral data reported in Table 3-6 were obtained by the method of liquid secondary ion mass spectrometry using m-nitrobenzylalcohol as the matrix. Good correlations were observed between theoretical spectra obtained from isotope abundance calculations (giving the number and relative intensities of the lines) and the experimental spectra for the parent ions M$^+$, or the protonated parent ions, MH$^+$, for all the compounds. Figure III-5 shows the experimental mass spectrum for the M$^+$ ion of [Cu(PNCP)$_2$]ClO$_4$ and it is compared with a theoretical spectrum obtained by an isotope abundance calculation. The agreement is good thus confirming the species. Complexes that contain a PNCP:Cu ratio greater than 1:1 all form daughter ions by loss of PNCP from the parent ion.

Table 3-3 NMR data of Cu(I) complexes with PNCP[a]

Complex	^{31}P (ppm)	$^1H^i$ (ppm)
PNCP	-13.7, -14.3	8.92^b(d)
[Cu(PNCP)Cl]	e	e
[Cu(PNCP)Br]	-13.4, -22.4	8.83^c(d)
[Cu(PNCP)ClO$_4$]^j	-6.03^h, -12.0^h	8.99(s)
[Cu(PNCP)(CH$_3$CN)]ClO$_4$	-12.4, -17.2	8.99(s)
[Cu(PNCP)(PPh$_3$)]ClO$_4$	-0.89, -7.63, -11.4,	9.46(s)
[Cu(PNCP)(TU)]ClO$_4$	e	8.86(s)
[Cu(PNCP)(Me$_2$NPC)]	-12.9, -20.7	8.80(s)
[Cu$_2$(PNCP)$_2$(Me$_2$NPC)]ClO$_4$	g	$8.70(s)^f$
		$9.25(s)^f$
[Cu$_2$(PNCP)$_2$(SCN)]ClO$_4$	g	8.77(s)
[Cu(PNCP)$_2$]ClO$_4$	g	8.89(s)
[Cu$_2$(PNCP)$_3$](ClO$_4$)$_2$	e	e
[Cu$_2$(PNCP)$_2$(SNC$_5$H$_5$)]ClO$_4$	e	e

[a] in CDCl$_3$ at room temperature

[b] doublet, 1H, 5.5Hz. ^{4}J(P-H) coupling

[c] doublet, 1H, 1.1Hz. Possible ^{4}J(P-H) coupling

d =doublet

e spectrum not recorded

[f] two separate singlet signals

g spectrum not resolved

[h] split band

[i] imine proton

[j] ethanol protons also observed

s =singlet

Table 3-4 Infra-red data of complexes with PNCP[a]

Complexes	υ(C=N) (cm^{-1})	υ(P-C) (cm^{-1})	υ(Cl-O) (cm^{-1})	υ(C≡N) (cm^{-1})
PNCP	1621(m)	1091(s)		
[Cu(PNCP)Cl]	1610(m)	1095(s)		
[Cu(PNCP)Br]	1610(m)			
[Cu(PNCP)ClO$_4$]	1611(m)		1130(s) 1036(s) 622(s)	
[Cu(PNCP)(CH$_3$CN)]ClO$_4$	1610(m)		1093(s) 622(s)	272(w)
[Cu(PNCP)(PPh$_3$)]ClO$_4$	1611(m)		1091(s) 625(s)	
[Cu(PNCP)(TU)]ClO$_4$	1616(m)		1094(s) 622(s)	
[Cu$_2$(PNCP)$_2$(SCN)]ClO$_4$	1616(m)		1097(S) 623(s)	2111(s)
[Cu(PNCP)(Me$_2$NPC)]	1606(m)	1095(s)		2140(s) 2095(m)
[Cu$_2$(PNCP)$_2$(Me$_2$NPC)]ClO$_4$	1614(m)		1093(s) 621(s)	2169(s)
[Cu(PNCP)$_2$]ClO$_4$	1610(m)		1093(s) 629(s)	
[Cu$_2$(PNCP)$_3$](ClO$_4$)$_2$	1612(m)		1094(s) 625(s)	
[Cu$_2$(PNCP)$_2$(SNC$_5$H$_5$]ClO$_4$	1619(m)		1093(s) 624(s)	

a. nujol mull

III-4 CONCLUSION AND COMMENTS

Copper(I) reacts readily with PNCP to form complexes with Cu:PNCP ratios of 1:1, 1:1.5 and 1:2. The reaction of Cu and PNCP in a 1:3 ratio merely produces $[Cu(PNCP)_2]ClO_4$. PNCP acts as tridentate chelating agent forming stable complexes with copper(I).

The four-coordinated complex $[Cu(PNCP)ClO_4]$ contains a unidentate perchlorate group which can be displaced by ligands containing N, S and P donor atoms to form adducts of the type $[Cu(PNCP)L]ClO_4$ (L= ligands containing N, S and P donor atoms).

More interesting is the geometry and coordination behaviour of PNCP in the complexes $[Cu(PNCP)_2]ClO_4$ and $[Cu_2(PNCP)_3](ClO_4)_2$. Does PNCP bind in a bidentate or monodentate fashion? In the later case does the complex contain two tridentate and one bridging PNCP ligands while in the former does it contain two bidentate forms? These complexes need further investigation by low temperature ^{31}P NMR and X-ray diffraction study to resolve these issues.

Table 3-5 Mass data of complexes with PNCP

Mass Spectral Data For [Cu(PNCP)Cl]
Cu=^{63}Cu
m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Cu(PNCP)]$^+$	621	612(100%)
[Cu(PNCP)ClH]$^+$	647	647(19%)

Mass spectral data for [Cu(PNCP)(CH$_3$CN)]ClO$_4$
Cu=^{63}Cu
m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Cu(PNCP)]$^+$	621	612(100%)
[Cu(PNCP)(CH$_3$CN)]$^+$	654	654(1%)

Mass spectral data for [Cu(PNCP)ClO$_4$]·EtOH
Cu=^{63}Cu
m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Cu(PNCP)]$^+$	621	612(100%)
[Cu(PNCP)ClO$_4$H]$^+$	712	712(2.5%)

Mass spectral data for [Cu(PNCP)(PPh$_3$)ClO$_4$

Cu=^{63}Cu

m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Cu(PNCP)]$^+$	621	612(100%)
[Cu(PNCP)(PPh$_3$)]$^+$	847	847(3%)

Mass spectral data for [Cu(PNCP)(TU)]ClO$_4$

Cu=^{63}Cu

m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Cu(PNCP)]$^+$	621	612(100%)
[Cu(PNCP)(TU)]$^+$	688	688(7.5%)
[Cu(PNCP)(TU)H(ClO$_4$)]$^+$	789	789(1.5%)

Mass spectral data for [Cu$_2$(PNCP)$_2$(SCN)]ClO$_4$

Cu=^{63}Cu

m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Cu(PNCP)]$^+$	612	612(100%)
[Cu(PNCP)$_2$]$^+$	1161	1161(1%)
[Cu$_2$(PNCP)$_2$(SCN)]$^+$	1283	1283(7%)

Mass spectral data for [Cu(PNCP)(Me$_2$NPC)]
Cu=^{63}Cu
m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Cu(PNCP)]$^+$	612	612(100%)
[Cu(PNCP)(Me$_2$NPC)]	733	733(2%)
[Cu(PNCP)$_2$]$^+$	1161	1161(1%)

Mass spectral data for [Cu$_2$(PNCP)$_2$(Me$_2$NPC)]ClO$_4$
Cu=^{63}Cu
m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Cu(PNCP)]$^+$	612	612 (100%)
[Cu(PNCP)$_2$]$^+$	1161	1161 (1%)
[Cu$_2$(PNCP)$_2$]$^{2+}$	1226	1226 (1%)

Mass spectral data for [Cu(PNCP)$_2$]ClO$_4$
Cu=^{63}Cu
m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Cu(PNCP)]$^+$	612	612 (100%)
[Cu(PNCP)$_2$]$^+$	1161	1161 (5%)
[Cu(PNCP)$_2$ClO$_4$H]$^+$	1226	1262 (2.5%)

Mass spectral data for $[Cu_2(PNCP)_3](ClO_4)_2$

$Cu={}^{63}Cu$

m/z

Observed Ions	Calculated	Found (Relative Intensity)
$[Cu(PNCP)]^+$	612	612 (100%)
$[Cu(PNCP)_2]^+$	1161	1161 (5%)
$[Cu_2(PNCP)_2ClO_4H]^{2+}$	1325	1325 (1%)

Mass spectral data for $[Cu_2(PNCP)_2(SNC_5H_5)]ClO_4$

$Cu={}^{63}Cu$

m/z

Observed Ions	Calculated	Found (Relative Intensity)
$[Cu(PNCP)]^+$	612	612 (100%)
$[Cu(PNCP)(SNC_5H_5)]^+$	723	723 (1.5%)
$[Cu_2(PNCP)_2(SNC_5H_5)H]^{2+}$	1336	1335 (8%)
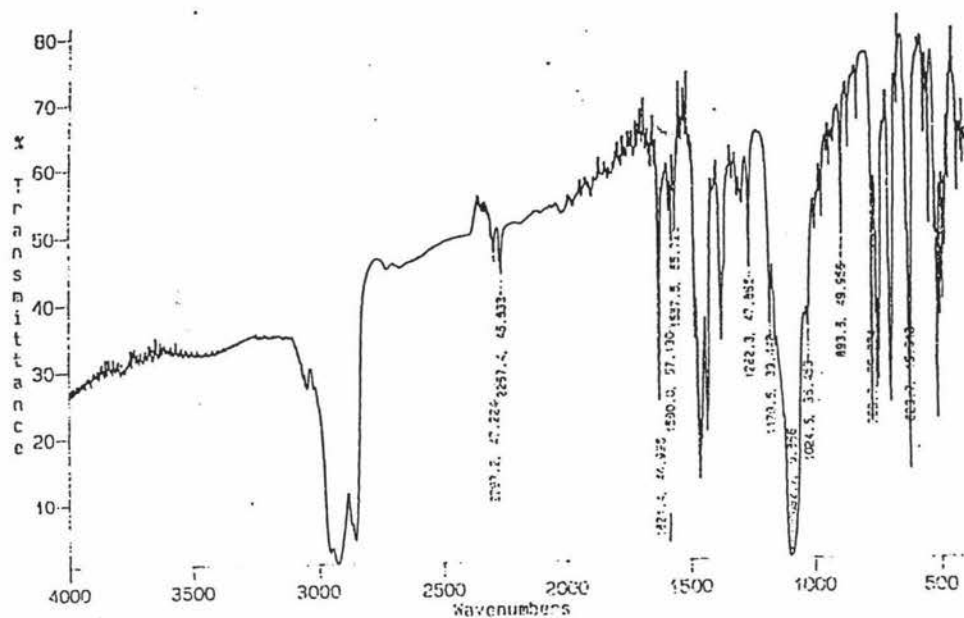
(Figure III-22)
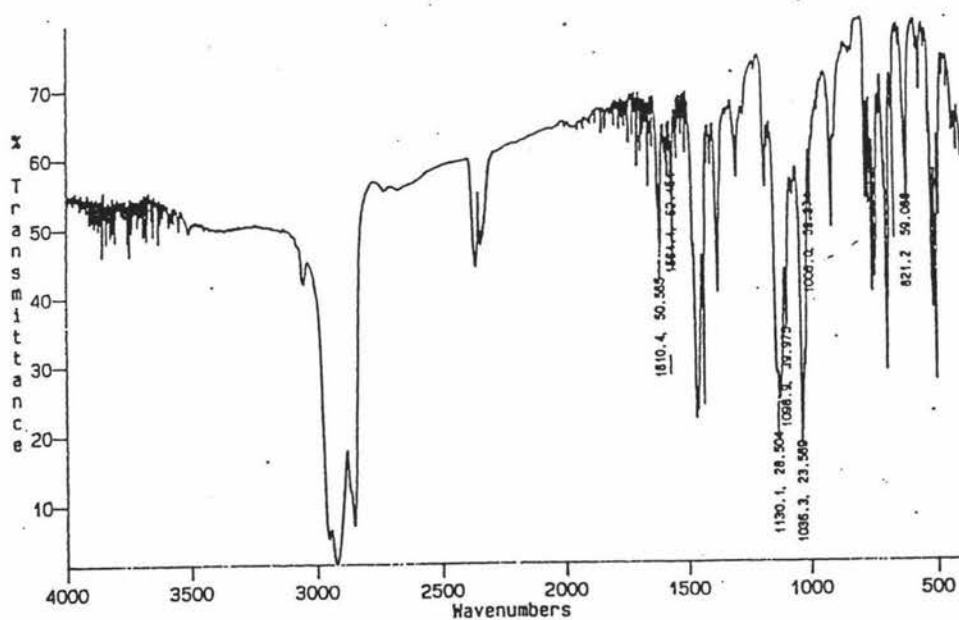
(Figure III-23)

Infra-red spectrum of complexes [Cu(PNCP)(CH₃CN)]ClO₄ (Figure III-22) and [Cu(PNCP)ClO₄] (Figure III-23)

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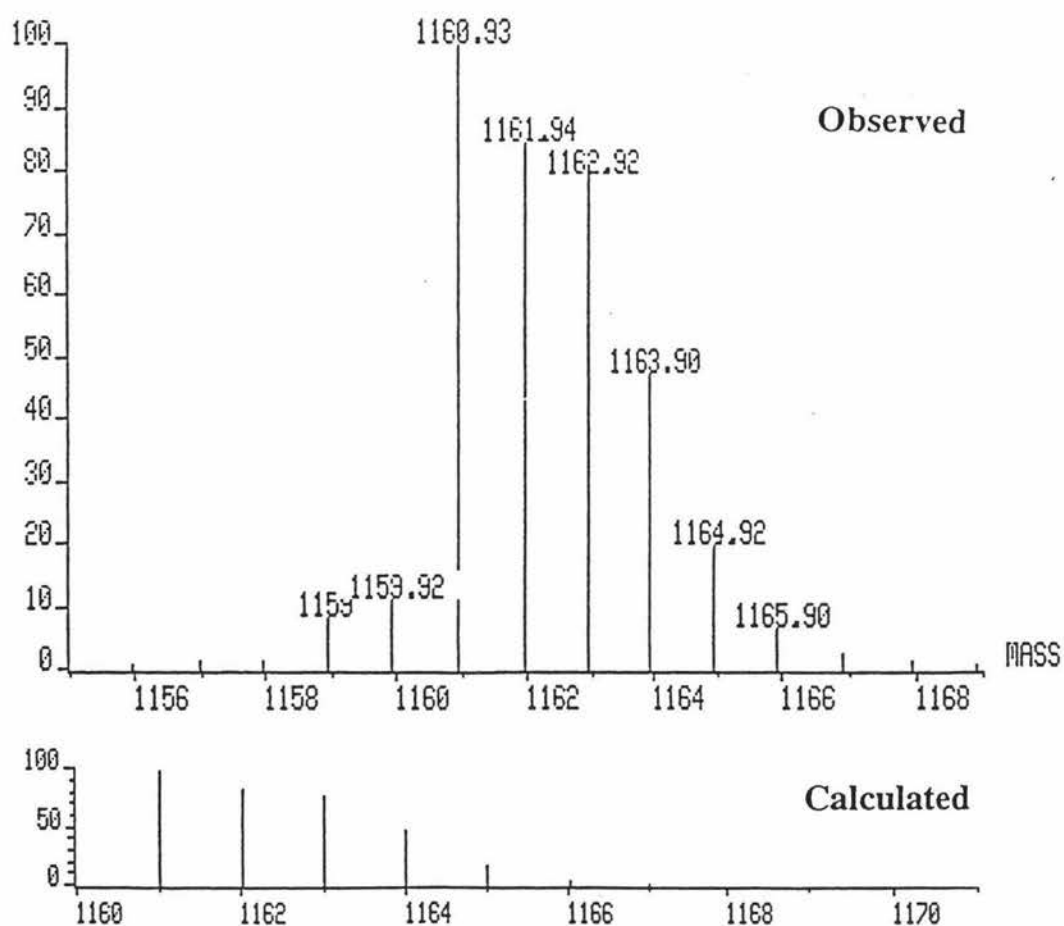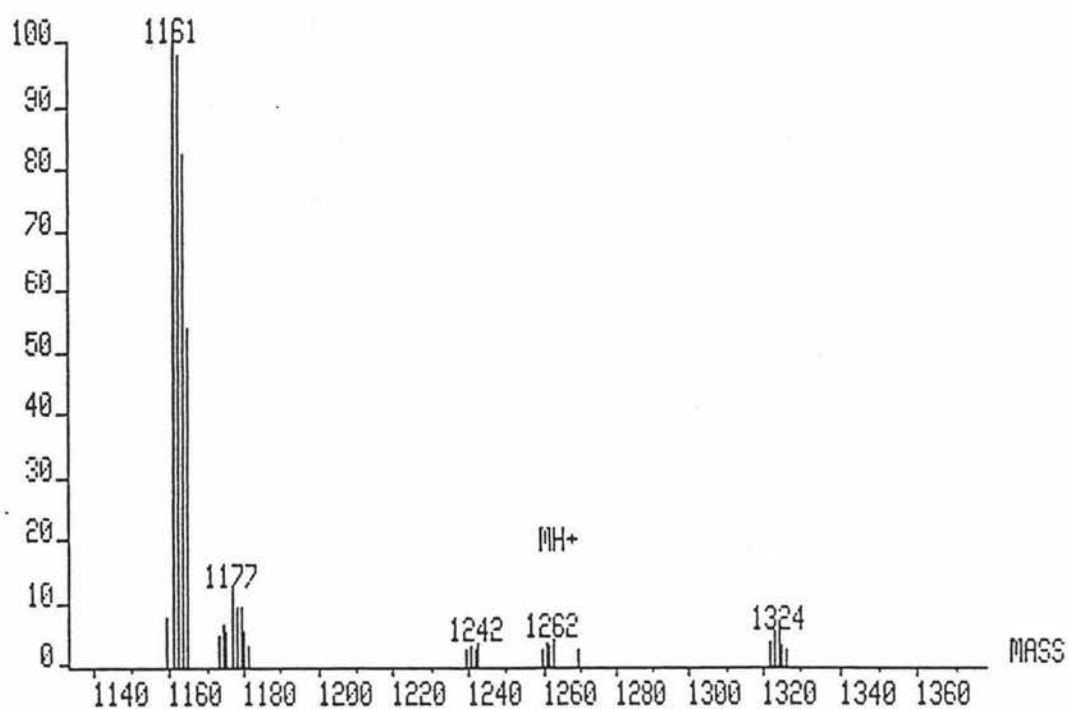
Figure III-24

Mass spectrum, observed and calculated parent ion cluster for [Cu(PNCP)$_2$]ClO$_4$

CHAPTER FOUR

STUDIES ON COORDINATION COMPLEXES OF SILVER(I) WITH PNCP

IV-1 INTRODUCTION

The preparation of stable complexes of transition metals in low oxidation states depends to a large extent upon the use of strong π-acceptors ligands such as carbon monoxide or tertiary phosphines [165].

Many silver complexes containing N-donor ligands and halides have been reported and there also exists an extensive chemistry for P- and S-donor ligands. The silver(I) ion has been characterized as a class-B or 'soft' acid, for which the following metal-ligand stability order is observed: N<<P>As>Sb; O<<S ~Se~Te; F<Cl<Br<I. Comparative studies between ligands with these donor atoms allowed the relative stability of silver bonds to be determined as P>S>N>O [166-168].

Silver complexes with tertiary phosphines have been much studied in the last two-three decades and an extensive range of coordination complexes has been observed for silver(I), in mono-, di-, tri- or tetra-nuclear complexes with bidentate phosphine ligands [169-172].

IV-1-1 Silver Complexes Containing Ditertiary Phosphine Ligands

Thermodynamic and spectroscopic studies on silver(I) complexes formed with multidentate phosphine ligands in dimethyl sulfoxide [168] indicate that (Table IV-1) the complex formation between silver(I) and all the phosphines is enthalpy controlled; both the enthalpy and the entropy changes are in fact negative. The stability constants of ML complexes with the diphosphines are all much larger than those for the silver(I) complexes with the unidentate ligand, triphenylphosphine. Also, the enthalpy and entropy changes are respectively more exothermic and negative for the silver(I)-diphosphine systems indicating that the ligands act as chelating agents.

Silver(I) complexes with dppm [bis(diphenylphosphino)methane] of the type $[Ag_2(dppm)_2(NO_3)_2]$ and $[Ag_4(dppm)_4(NO_3)_2]$ $[PF_6]_2$ have been synthesized [equation (I), (II)] and characterized by IR, ^1H NMR spectroscopy and X-ray diffraction [171] (Figure IV-1, Figure IV-2). The molecules are found to contain $[Ag_2(dppm)_2]^{2+}$ core structures with the two silver atoms bridged by the dppm ligands to give eight-membered $Ag_2P_4C_2$ rings. The tetranuclear complex consists of two $[Ag_2(dppm)_2]^{2+}$ subunits linked by two
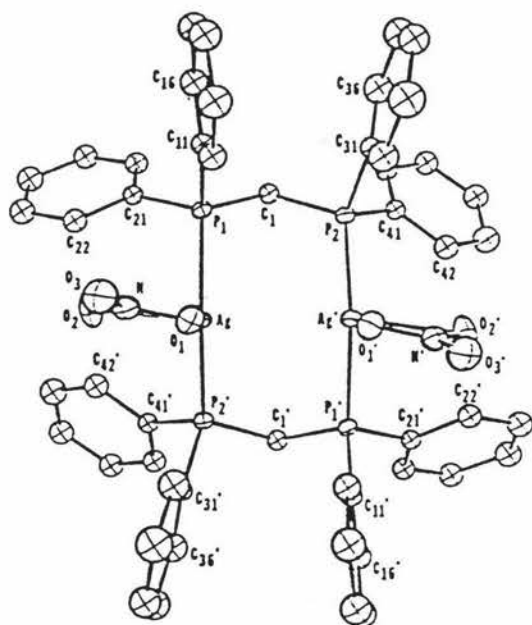
Molecular structure and atom labeling for $[Ag_2(dpm)_2(NO_3)_2]$.

(Figure IV-1)
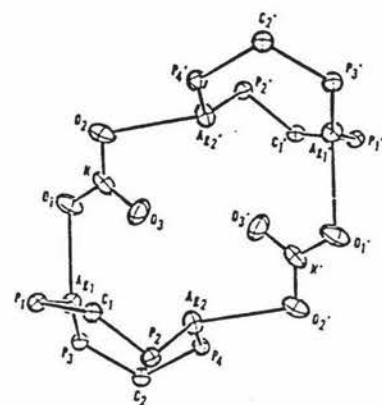
Core structure of the $[Ag_4(dpm)_4(NO_3)_2]^{2+}$ dication showing the anti–anti bridge-bonding mode of the nitrate ligand.
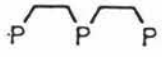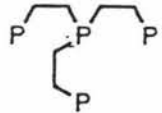
(Figure IV-2)
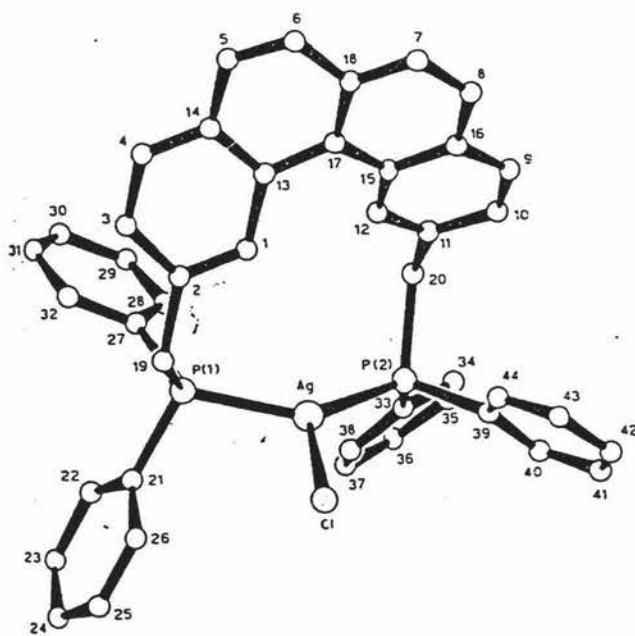
Perspective view of the complex $[Ag(Ph_2P(CH_2)_5PPh_2)Cl]$.

(Figure IV-4)

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Table IV-1 Overall stability constants and thermodynamic functions for Ag(I)-phosphine system[a] in DMSO (at 25°C and $I = 0.1$ mol dm^{-3})

		log ß	-ΔG°	-ΔH°	-ΔS°
PPh$_3$	ML	6.85	37.6	51.8	48
	ML$_2$	10.73	61.3	89.9	96
	ML$_3$	13.17	75.2	126.2	171
dppm P⌒P	M$_2$L	12.46 (5)	71.1 (3)	107 (6)	120 (21)
	M$_2$L$_2$	22.75 (6)	129.8 (4)	188 (4)	195 (15)
	M$_2$L$_3$	25.57 (21)	146 (1)	261 (6)	386 (23)
dppe P⌒P	ML	7.73 (5)	41.1 (3)	87 (6)	144 (21)
	ML$_2$	13.91 (5)	79.4 (3)	149 (2)	233 (8)
	M$_2$L	11.91 (5)	68.0 (3)	110 (2)	141 (7)
	M$_2$L$_2$	18.28 (9)	104.3 (6)	186 (10)	269 (25)
dppp P⌒P	ML	8.65 (5)	49.4 (3)	95 (5)	153 (18)
	ML$_2$	14.39 (7)	82.1 (4)	162 (2)	268 (8)
	M$_2$L	12.37 (4)	70.6 (2)	115 (2)	149 (7)
	M$_2$L$_3$	20.13 (9)	114.9 (5)	195 (7)	269 (25)
etp P⌒P⌒P	ML	11.69 (7)	66.7 (4)	109 (2)	142 (8)
	ML$_2$	16.69 (14)	95.3 (8)	159 (2)	214 (9)
	M$_2$L	15.45 (16)	88.2 (9)	135 (3)	157 (13)
	M$_2$L$_3$	32.01 (17)	182.7 (9)	291 (6)	368 (23)
PP$_3$	ML	13.29 (6)	75.9 (3)	140 (4)	215 (14)
	ML$_2$	16.25 (28)	93 (1)	173 (9)	268 (34)
	M$_2$L	17.88 (9)	102.0 (5)	166 (3)	215 (11)

[a]ΔG° and ΔH° in kJ mol^{-1}; ΔS° in J K^{-1} mol^{-1}. The substituents at trivalent phosphorus are phenyl groups.

bridging nitrate anions.

$$2AgNO_3 + 2dppm \longrightarrow [Ag_2(dppm)_2)(NO_3)_2] \qquad (1)$$

$$2[Ag_2(dppm)_2(NO_3)_2] \longrightarrow [Ag_4(dppm)_4(NO_3)_2][PF_6]_2 \quad (2)$$

The dppm is potentially a chelate ligand but the two donor atoms are separated by a single methine group, and therefore the formation of a mononuclear species gives rise to a highly strained four-membered chelate ring. It is not surprising therefore that there is no evidence for formation of mononuclear species of silver(I) with dppm, rather it acts as a bridging ligand [170].

The silver(I) complexes of the type, $[Ag(dppp)X]_2$ (where dppp= 1,3-bis-(diphenylphosphino)propane) are more stable than the complex [Ag(dppe)X] (where dppe= 1,2-bis(diphenylphosphino)ethane) because of the greater stability of the six-membered chelate ring relative to the five-membered one [168,173]. However they generally adopt dimeric structures in the solid state where X is a halide and P_2 is a diphosphine, with the exception of the monomeric silver chloride complex of PC_8P, $[Ag(PC_8P)X]$, (where PC_8P= [2,11-[bis(diphenylphosphino)methyl]benzo[C]phenanthrene] and X= ClO_4^-, NO_3^-, $SnCl_3^-$, Cl^-) [167,174].

The dinuclear coordination of silver is also exemplified in $[Ag(PC_5P)Cl]_2$ [PC_5P=bis (diphenylphosphino)pentane] (Figure IV-3). In the complex $[Ag(PC_8P)Cl]$ the silver adopts a distorted trigonal coordination geometry with two P atoms and one Cl atom acting as donor atoms.

$$X = -CH_2CH_2CH_2CH_2CH_2-$$

(Figure IV-3)

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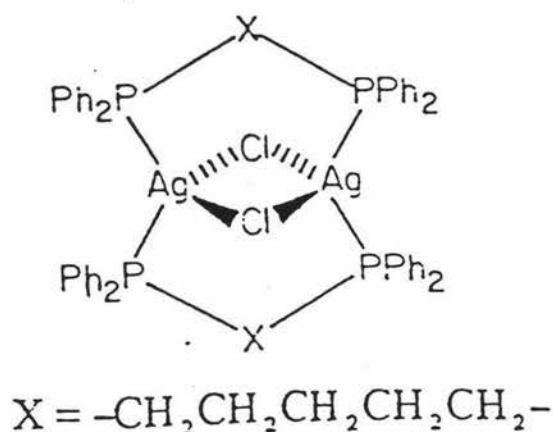
However in [Ag(PC$_8$P)ClO$_4$] the silver atom is bonded to two P atoms and to two oxygen atoms of the perchlorate in a distorted tetrahedral arrangement (Figure IV-4, Figure IV-5).
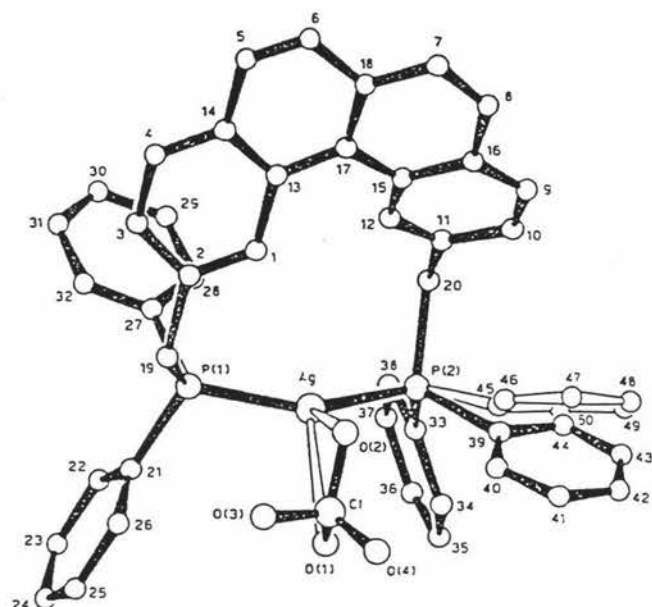
Perspective view of the complex [Ag(Ph$_2$P(CH$_2$)$_5$PPh$_2$)(ClO$_4$)].

(Figure IV-5)
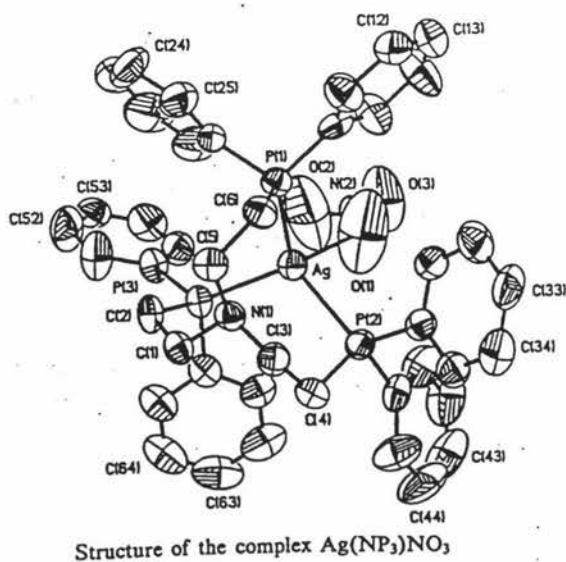
Structure of the complex Ag(NP$_3$)NO$_3$

(Figure IV-7)

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IV-1-2 Silver(I) Complexes Containing Tritertiary Phosphine Ligands

For etp [(bis(2-(diphenylphosphino)ethyl)phenylphosphine] and PP_3 [tris(2-(diphenylphosphino)ethylphosphine], the thermodynamic functions suggest that these ligands act in both a ter- and tetra-dentate fashion, giving rise to two and three fused five-membered chelate rings, respectively, with a tetrahedral configuration around the metal ion. The thermodynamic data for the complex ion $[Ag(etp)_2]^+$ indicates that both ligands act as bidentate groups whereas in the complex $[Ag(PP_3)_2]^+$ one ligand probably binds in a ter- and the other in a uni-dentate fashion [168]. The X-ray structural data for the complex [Ag(triphos)I] [triphos= 1,1,1-tris(diphenyl phosphino)methyl)ethane] [176] showed that the silver atom is formally four-coordinate with three Ag-P bonds, one Ag-I bond and three six-membered rings (Figure IV-6) whereas in the $[Ag(NP_3)NO_3]$ $[NP_3=$ tris(2-(diphenylphosphino)ethyl)amine] [175], the silver atom is bound in a tridentate fashion forming a distorted tetrahedral complex, $[Ag(NP_3)NO_3]$, where there are three Ag-P bonds and one Ag-O bond (Figure IV-7).

A view of Ag(triphos)I with H atoms and phenyl groups omitted.
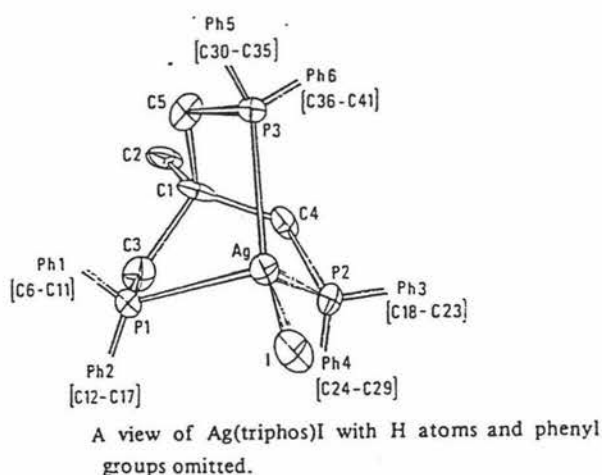
(Figure IV-6)

IV-1-3 Tridentate Ligands Containing Phosphorus and Nitrogen Donor Atoms

In contrast to the numerous studies on silver complexes with diphosphine ligands, diphosphineamine hybrid ligands have received much less attention. For example the reaction of silver(I) halides with dppa [bis-(diphenylphosphino)amine] in ethanol yields the

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trinuclear complex $[Ag_3(\mu_3-X_2)(\mu-dppa)_3]X$ (X= Cl, Br, I) (Figure IV-8) [177] in which the silver atoms are formally four-coordinate with two Ag-P bonds and two Ag-X bonds. The halide bridges the two silver atoms. There are thus three six-membered rings but no Ag-N bond.

Another novel ligand, (en=P$_2$), [N,N´-bis[o-(diphenylphosphino)benzylidene]-ethylenediamine], forms complexes with nickel, copper and silver to give a rich coordination chemistry. The four-coordinate complexes $[M(en=P_2)]^{+1}$ (M= Cu, Ag) react with an additional ligand L (L= tert-butylisocyanide, t-BuNC) to form [M(en=P$_2$)(t-BuNC)]$^+$ (M= Ag, Cu). In the case of silver(I) a five-coordinate adduct was obtained [Chapter III-1-2].

$(M=Cu, Ag ; X=Cl, Br, I)$
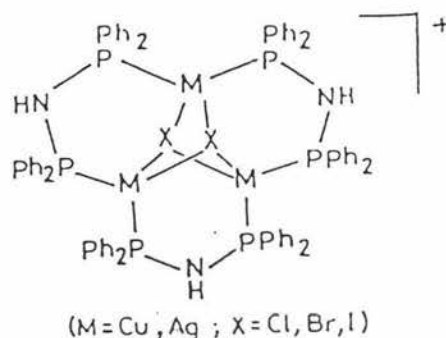
(Figure IV-8)

IV-1-4 The Thiocyanate Ion as a Ligand in Silver Complexes

In the growing literature on thiocyanate complexes of transition metal ions very little has appeared to date on complexes with silver(I). Those known include several silver thiocyanate triakylphosphines [178-180] and thiosemicarbazide [181] species. An X-ray crystallographic study by Panattoni and Frasson on the structure of Ag(SCN)·P(^{n}Pr)$_3$ was found to contain zigzag polymeric -Ag-SCN-Ag-SCN- chains cross-linked in pairs by Ag-S bonds to form double chains having a stair-step configuration (Figure IV-9). The silver-sulfur bond distances of 2.83(2)Å and 2.88(2)Å are substantially longer than the calculated single-bond covalent value of 2.56Å [180].

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R = Pr
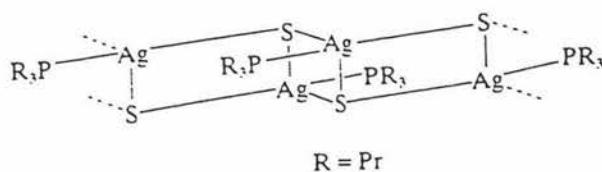
(Figure IV-9)

The triakylphosphine adducts of silver(I) thiocyanate AgSCN·PR$_3$ [where PR$_3$= PMe$_3$, PEt$_3$, P(^{n}Bu)$_3$] are found to have the indicated stoichiometry even when their preparations were carried out with a AgSCN:PR$_3$ molar ratio in excess of 1:2 [182]. With PPh$_3$ only 1:2 adducts were isolated irrespective of the mole ratio used in their preparation.

The investigation of the complexes of silver(I) thiocyanate with the mixed tertiary phosphines, such as PPh$_2$Et was undertaken with the expectation that both the 1:1 and 1:2 adducts might be isolated. The stoichiometries apparently cannot be entirely attributed to steric effects since the bulky mixed tertiary phosphine ligand, PPh$_2$Et surprisingly gives AgSCN·3PPh$_2$Et. However with the exception of PPh$_2$Et, the relative σ-donor (PPh$_3$<PEt$_3$<P(^{n}Pr)$_3$<P(^{n}Bu)$_3$) and π-acceptor (PR$_3$<PR$_2$Ph<PRPh$_2$<PPh$_3$) properties of the tertiary phosphines, are in accord with the series studied since π-bonding can relieve excessive negative charge on the metal allowing another group to coordinate [183].

IV-1-5 The Present Study

Since little attention has been paid to silver complexes of diphosphineamine ligands, we were interested in synthesising silver(I) complexes with PNCP [2-(diphenylphosphino)-N-[2-(diphenylphosphino)benzylidene] benzeneamine] (see Chapter Two) and to study their coordination chemistry with the anions NO$_3^-$, ClO$_4^-$ and SCN$^-$. Of particular interest was the coordination geometry in preparations involving Ag:PNCP ratios of 1:1 and 1:2.

IV-2 SYNTHESIS OF SILVER(I) COMPLEXES

IV-2-1 Preparation of [Ag(PNCP)NO$_3$]·CH$_3$CH$_2$OH

To a refluxing suspension of AgNO$_3$ (0.058g, 0.30 mmol) in ethanol (10 ml) was added PNCP (0.166g, 0.30 mmol) in ethanol (10 ml). A yellow solution formed on refluxing

under a flow of nitrogen gas for 30 minutes. The solution was filtered while hot and on standing at room temperature overnight, a dark yellow crystalline product appeared. This was filtered and washed with ethanol.

Yield:　　　　　　　84.8% (0.190g), M.P. 269-272°C

Found:　　　　　　　C, 60.11; H, 4.66; N, 3.74; P, 7.96

Calculated for $(AgC_{39}H_{35}P_2N_2O_4)$:

C, 59.70; H, 4.46; N, 3.59; P, 7.90

IV-2-2 Preparation [Ag(PNCP)ClO$_4$]

To AgClO$_4$ (0.0415g, 0.20 mmol) dissolved in hot ethanol (10 ml) was added PNCP (0.1100g, 0.20 mmol) in dichloromethane (5 ml). The light yellow solution was refluxed under a flow of nitrogen gas for 20 minutes. The solution was filtered while hot and left to stand at room temperature overnight. The yellow crystals which appeared were filtered, washed with ethanol and recrystallized from ethanol/dichloromethane (2 ml/3 ml).

Yield:　　　　　　　73% (0.111g), M.P. 308-310°C.

Found:　　　　　　　C, 58.76; H, 3.98; N, 2.29

Calculated for $(AgC_{37}H_{29}P_2NClO_4)$:

C, 57.30; H, 3.74; N, 1.85

IV-2-3 Preparation of [Ag(PNCP)(SCN)]

To [Ag(PNCP)NO$_3$] (0.0717g, 0.094 mmol) dissolved in dichloromethane (5 ml) was added, slowly (five minutes) with stirring, sodium thiocyanate (0.033g, 0.282 mmol) dissolved in ethanol (15 ml). The yellow solution was then refluxed under nitrogen gas for 30 minutes. The solution was filtered and on standing at room temperature overnight, a yellow crystalline product appeared. This was filtered, washed with ethanol and recrystallized from methanol.

Yield: 67% (0.070g), M.P. 241-243°C.

Found: C, 62.82; H, 4.05; N, 3.96

Calculated for $(AgC_{38}H_{29}P_2N_2S)$:

                                    C, 62.20; H, 3.95; N, 3.81

IV-2-4 Preparation of [Ag(PNCP)(PPh₃)]NO₃

To [Ag(PNCP)NO₃] (0.180g, 0.25 mmol) dissolved in hot ethanol (15 ml) was added slowly PPh₃ (0.130g, 0.50 mmol) dissolved in ethanol (5 ml). The yellow solution was refluxed under nitrogen gas for 30 minutes. The light yellow precipitate was filtered, washed with ethanol and re-precipitated from ethanol/dichloromethane (3 ml/5 ml).

Yield: 77.4% (0.240g)

Found: C, 66.80; H, 4.63; N, 2.69

Calculated for $(AgC_{55}H_{44}P_3N_2O_3)$:

                                      C, 66.00; H, 4.40; N, 2,80

IV-2-5 Preparation of [Ag(PNCP)₂]NO₃·CH₂Cl₂

To [Ag(PNCP)NO₃] (0.170g, 0.24 mmol) dissolved in hot ethanol (15 ml) was added slowly PNCP (0.132g, 0.24 mmol) dissolved in dichloromethane (10 ml). The yellow solution was refluxed under nitrogen gas for 30 minutes and the solution was filtered while hot and left to stand at room temperature overnight. The light yellow product was filtered off and washed with ethanol and then re-precipitated from ethanol/dichloromethane (3 ml/5 ml).

Yield: 75% (0.240g)

Found: C, 65.40; H, 4.63; N, 3.25

Calculated for $(AgC_{76}H_{60}P_4N_3Cl_2O_3)$:

                                      C, 65.37; H, 4.37; N, 3.06

IV-3 RESULTS AND DISCUSSION

IV-3-1 Syntheses of Silver Complexes Containing PNCP

Complexes of the type [Ag(PNCP)X] (X= SCN⁻, ClO₄⁻, NO₃⁻) are prepared by the

reaction of the appropriate silver salt with PNCP in a 1:1 mole ratio. The complex [Ag(PNCP)₂]NO₃ is prepared in a similar way to the above but with the reactants in a 1:2 mole ratio. These reactions are fully discussed in the Experimental Section IV-2 including analytical data. The structures and spectroscopy of these complexes will be discussed in the following section.

IV-3-2 Crystal structure of [Ag(PNCP)ClO₄]

A thermal ellipsoid diagram for the complex [Ag(PNCP)ClO₄] showing the numbering scheme used is depicted in Figure IV-10. Bond length and angle data are given in Table 4-3.

The complex [Ag(PNCP)ClO₄] crystallized as a discrete monomer. The 2-(diphenyl-phosphino)-N-[2-(diphenylphosphino)benzylidene]benzeneamine) ligand (PNCP) coordinates as a neutral, bidentate moiety *via* the P(1) and P(2) atoms. The third coordination site is occupied by an oxygen from the perchlorate anion. Although the N of the PNCP ligand is bent towards the Ag atom, any interaction is very weak as indicated by the long Ag-N distance.

The bond lengths of the two Ag-P bonds, at 2.438(3)Å and 2.447(3)Å, are considered to be normal for this neutral ligand since they are similar to those found (2.361Å-2.616Å) [175,176,184] in other distorted tetrahedral silver(I) complexes. The bond length of Ag-O of 2.62(5)Å is comparable with the values of 2.416Å and 2.682Å found in the distorted tetrahedral Ag-O bonds in the complex [Ag(PC₈P)ClO₄] [174].

The Ag-N distance of 2.93(1)Å is a longer bond than normal for Ag-N bonds as found for example in [Ag(qpy)PF₆] [qpy=2,2':6',2":6",2""-quinquepyridine] and [Ag(PPh₃)₂ (terpy)ClO₄] [terpy=2,2':6',2"-terpyridine] (2.479Å and 2.614(2)Å respectively) [185, 186]. It is also significantly longer than the axial silver-nitrogen interaction of 2.7408Å reported for the dinuclear six-coordinate silver(I) complex [Ag(2,3,2-N₅)]₂(ClO₄)₂ [187].

The bond angles (Table 4-3) for the P(1)-Ag-P(2), P(1)-Ag-O(11), P(2)-Ag-O(11), P(1)-Ag-N and P(2)-Ag-N are 129.28(9), 93.1(12), 124.3(12), 64.0(2) and 65.3(2)° respectively, values which are greater than comparable angles in the copper(I) complex [Cu(PNCP)ClO₄].

IV-3-3 Crystal Structure of [Ag(PNCP)(SCN)]$_2$·CHCl$_3$

Yellow crystals of the complex [Ag(PNCP)(SCN)]$_2$·CHCl$_3$ were obtained by the slow evaporation of a chloroform solution.

The molecule structure consists of a centrosymmetric dimer, with discrete tetrahedral silver coordination geometry for each metal atom. The dimersation occurs *via* the " end-to-end" SCN bridging of two thiocyanate anions to the two silver atoms (see Figure IV-11, Table 4-5). This structure is a new steric configuration for dimeric silver(I) complexes with diphosphine and thiocyanate.

The silver atom is bound to the two phosphorus atoms of PNCP, a sulphur atom from one of two thiocyanate anions and the nitrogen from another in a distorted tetrahedral geometry. As was observed with the [Ag(PNCP)ClO$_4$] complex the N of the PNCP is bent towards the Ag atom but the approach of these two atoms is a long one (3.204(6)Å) which represents only a very weak interaction, if any interaction at all. The Ag-P distances of 2.466(2)Å and 2.500(2)Å are comparable with those found (2.361Å and 2.616Å) [175,176, 184,188] in other distorted tetrahedral complexes, but they are longer than the Ag-P bonds found in the complex [Ag(PNCP)ClO$_4$]. This difference can by attributed to the formation of a nine-membered ring and the reluctance of Ag to interact with the N. The Ag-N bond length of 2.312(6)Å to the NCS anion is not significantly different from the Ag-N distance (2.35Å) in [Ag(PPh$_3$)$_2$(SCN)]$_2$ [189], but it is shorter than the range of Ag-N bond distances observed (2.439-2.614Å) in silver(I) five-coordinate complexes [Ag(qpy)PF$_6$] and [Ag(PPh$_3$)$_2$(terpy)ClO$_4$] [185, 186].

The Ag-S distance of 2.677(2)Å is significant longer than the Ag-S bond lengths observed in [Ag(PPh$_3$)$_2$(SCN)]$_2$ [189] and in [AgLClO$_4$] (2.555Å and 2.600Å respectively) L= [2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo-(20),2,14,16,18-pentane], both of which exhibit five-fold coordination involving N$_3$S$_2$ donor atoms.

The N(1)-C(1) and N(2)-C(2) bond lengths of 1.219(9)Å and 1.139(8)Å are shorter than expected for a formal double bond length of 1.287Å [111] and the N-C(1) double bond of 1.263Å in SPNCP. The distances of N(1)-C(12) (1.446Å) and C(1)-C(42) (1.437(10)Å) are comparable with lengths expected for similar bonds *exo* to phenyl rings 1.472(5)Å and 1.53Å [67, 113] and 1.416(5)Å, 1.478(6)Å in SPNCP. Other bond lengths are not significantly different from those of the free ligand and SPNCP.

The bond angles P(1)-Ag-P(2), N'(2)-Ag-P(1), N'(2)-Ag-P(2), N'(2)-Ag-S, P(1)-Ag-S and

P(2)-Ag-S are 123.97(6), 106.2(2), 106.5(2), 101.7(2), 112.23(7), and 104.02(7)° respectively. They are very similar to the ideal tetrahedral angle of 109°28′ [see Chapter Two]. Because of the constraints imposed by the geometry of the free ligand it is not surprising that the angle P(1)-Ag-P(2) at 123.97(6)° is greater than the ideal tetrahedral angle. The angles, C(1)-N(1)-C(12) and N(1)-C(1)-C(42), are 120.4(6)° and 125.6(7)° respectively. They are different from the similar angles in PNCP and SPNCP, which shows the flexible nature and folding of the nine-membered ring complex. Rotation about the bonds at either end of the -CH=N- bridge (*i.e.* C(1)-C(42)) can occur to change these angles as the geometry requires. Within the eight-membered ring, (arising from the centre of symmetry) angles of 178.1(7) and 95.2(2)° are observed for C(2)-S-Ag and N(2)-C(2)-S respectively. Thus the linear geometry of the SCN anion is retained in the complex.

Table 4 - 2

Crystal data for [Ag(PNCP)(ClO$_4$)].

Empirical formula	C$_{37}$ H$_{29}$ Ag Cl N O$_4$ P$_2$
Formula weight	756.87
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Orthorhombic
Space group	P2$_1$2$_1$2$_1$ (No. 19)
Unit cell dimensions	a = 9.7080(10) A α = 90 deg. b = 16.895(3) A β = 90 deg. c = 20.408(5) A γ = 90 deg.
Unit cell volume	3347.3(11) A^3
Z	4
Density (calculated)	1.502 Mg/m^3
Crystal size	0.33 x 0.27 x 0.26 mm
Theta range for data collection	1.56 to 24.98 deg.
Reflections collected	6230
Independent reflections	5858 [R(int) = 0.0987]
Refinement method	Full-matrix least-squares on F^2
Data used in refinement	5839
No. of parameters refined	423
Final R [I>2sigma(I)]	R1 = 0.0598, wR2 = 0.1593
R indices (all data)	R1 = 0.1197, wR2 = 0.2423
Refinement program	SHELXL-93
Graphics program	ZORTEP

99

Table 4 - 3

Selected bond lengths [Angsroms] and angles [deg] for [Ag(PNCP)(ClO$_4$)].

Ag-P(2)	2.438(3)	P(1)-C(11)	1.820(12)
Ag-P(1)	2.447(3)	P(1)-C(21)	1.829(12)
Ag-O(31)	2.54(3)	C(1)-N	1.09(2)
Ag-O(21)	2.49(2)	C(1)-C(12)	1.46(2)
Ag-O(11)	2.62(5)	C(1)-H(1)	0.93
Ag-N	2.926(10)	N-C(42)	1.57(2)
P(2)-C(51)	1.810(11)		
P(2)-C(61)	1.819(10)		
P(2)-C(41)	1.796(11)		
P(1)-C(31)	1.816(10)		

P(2)-Ag-P(1)	129.28(9)	C(61)-P(2)-Ag	115.0(3)
P(2)-Ag-O(31)	125.8(6)	C(41)-P(2)-Ag	105.3(3)
P(1)-Ag-O(31)	104.9(6)	C(31)-P(1)-C(11)	104.1(5)
P(2)-Ag-O(21)	104.8(5)	C(31)-P(1)-C(21)	103.7(5)
P(1)-Ag-O(21)	120.6(6)	C(11)-P(1)-C(21)	105.7(5)
P(2)-Ag-O(11)	124.3(12)	C(31)-P(1)-Ag	107.2(3)
P(1)-Ag-O(11)	93.1(12)	C(11)-P(1)-Ag	113.0(4)
P(2)-Ag-N	65.3(2)	C(21)-P(1)-Ag	121.4(4)
P(1)-Ag-N	64.0(2)	N-C(1)-C(12)	121(2)
O(31)-Ag-N	168.7(7)	C(1)-N-C(42)	120.9(12)
O(21)-Ag-N	153.3(6)	C(1)-N-Ag	134.6(12)
O(11)-Ag-N	135.9(11)	C(42)-N-Ag	103.7(7)
C(51)-P(2)-C(61)	102.1(5)	Cl-O(11)-Ag	119(3)
C(51)-P(2)-C(41)	106.2(5)	Cl-O(21)-Ag	130.4(14)
C(61)-P(2)-C(41)	105.3(5)	Cl-O(31)-Ag	115.6(14)
C(51)-P(2)-Ag	121.8(4)		

Table 4 - 4

Crystal data for [Ag(PNCP)(SCN)]$_2$.CHCl$_3$

Empirical formula	C$_{39}$H$_{30}$AgCl$_3$N$_2$P$_2$S
Formula weight	834.87
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2$_1$/c (No. 14)
Unit cell dimensions	a = 15.032(3) A α = 90 deg.
	b = 15.595(3) A β = 115.38(3) deg.
	c = 17.498(3) A γ = 90 deg.
Volume	3706.1(12) A^3
Z	4
Density (calculated)	1.496 Mg/m^3
Crystal size	0.40 x 0.30 x 0.07 mm
Theta range for data collection	1.50 to 22.48 deg.
Reflections collected	5157
Independent reflections	4819 [R(int) = 0.0343]
Refinement method	Full-matrix least-squares on F^2
Data used in refinement	4818
No. of parameters refined	439
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.1362
R indices (all data)	R1 = 0.0677, wR2 = 0.1614
Refinement program	SHELXL-93
Graphics program	ZORTEP

Table 4 - 5

Selected bond lengths [A] and angles [deg] for [Ag(PNCP)(SCN)]₂.CHCl₃.

Ag-N(2)#1	2.312(6)	P(2)-C(61)	1.834(6)
Ag-P(1)	2.466(2)	P(2)-C(51	1.832(6)
Ag-P(2)	2.500(2)	P(2)-C(41)	1.844(6)
Ag-S	2.677(2)	N(1)-C(1)	1.219(9)
Ag-N(1)	3.204(6)	N(1)-C(12)	1.446(8)
S-C(2)	1.647(8)	C(1)-C(42)	1.437(10)
P(1)-C(31)	1.820(6)	C(2)-N(2)	1.139(8)
P(1)-C(21)	1.829(6)	N(2)-Ag#1	2.312(6)
P(1)-C(11)	1.838(6)		

N(2)#1-Ag-P(1)	106.2(2)	C(61)-P(2)-C(51)	103.8(3)
N(2)#1-Ag-P(2)	106.5(2)	C(61)-P(2)-C(41)	103.2(3)
P(1)-Ag-P(2)	123.97(6)	C(51)-P(2)-C(41)	101.4(3)
N(2)#1-Ag-S	101.7(2)	C(61)-P(2)-Ag	111.7(2)
P(1)-Ag-S	112.23(7)	C(51)-P(2)-Ag	114.7(2)
P(2)-Ag-S	104.02(7)	C(41)-P(2)-Ag	120.1(2)
N(2)#1-Ag-N(1)	124.1(2)	C(1)-N(1)-C(12)	120.4(6)
P(1)-Ag-N(1)	62.89(11)	C(1)-N(1)-Ag	119.8(5)
P(2)-Ag-N(1)	61.14(11)	C(12)-N(1)-Ag	109.2(4)
S-Ag-N(1)	133.92(12)	N(1)-C(1)-C(42)	125.6(7)
C(2)-S-Ag	95.2(2)	N(2)-C(2)-S	178.1(7)
C(31)-P(1)-C(21)	103.9(3)	C(2)-N(2)-Ag#1	160.3(5)
C(31)-P(1)-C(11)	102.0(3)	(13)-C(12)-N(1)	121.6(6)
C(21)-P(1)-C(11)	103.7(3)	C(11)-C(12)-N(1)	118.8(6)
C(31)-P(1)-Ag	117.2(2)	C(43)-C(42)-C(1)	115.5(7)
C(21)-P(1)-Ag	110.3(2)	C(41)-C(42)-C(1)	125.5(6)
C(11)-P(1)-Ag	118.0(2)		

Symmetry transformations used to generate equivalent atoms:
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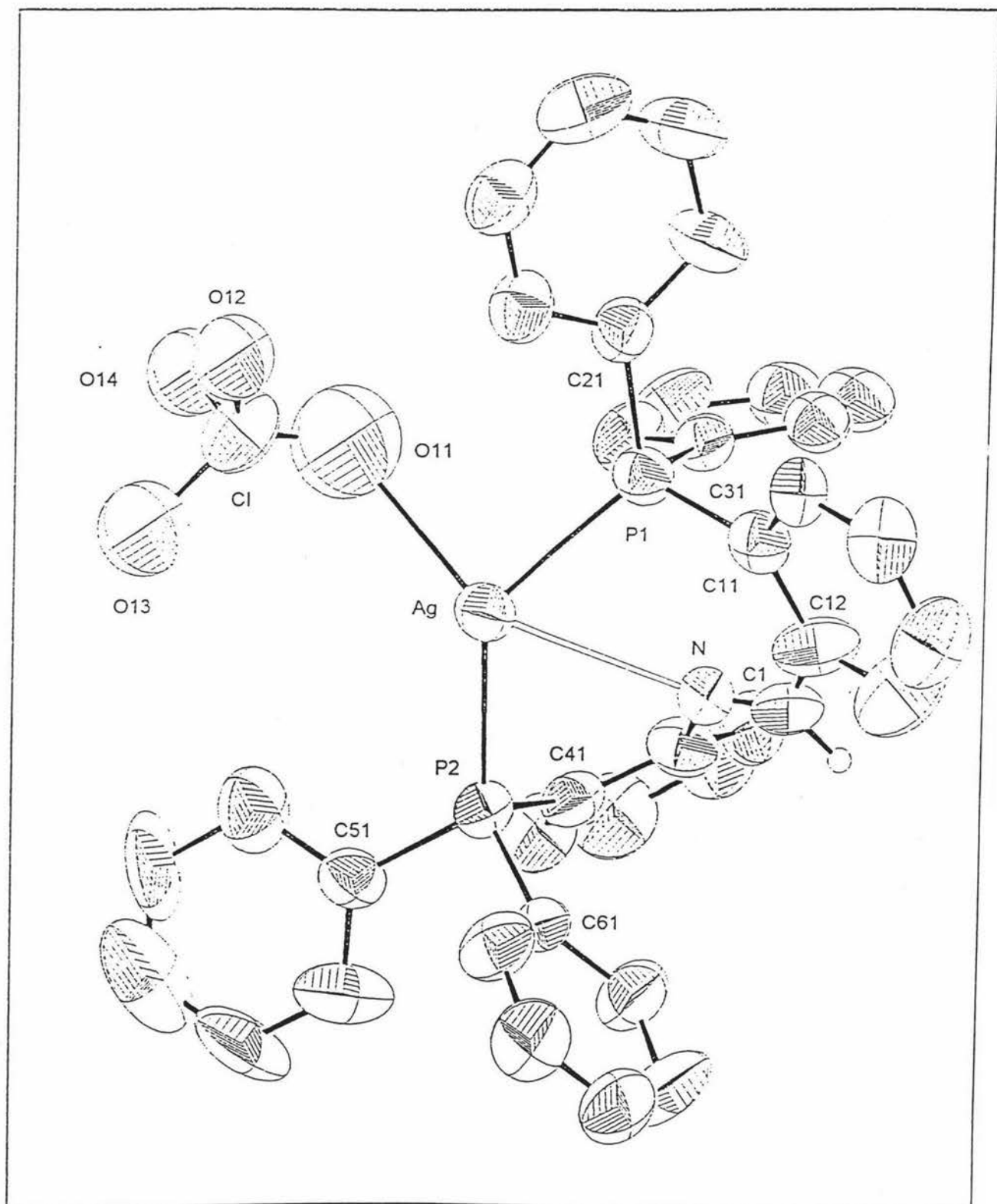
Figure IV-10 Thermal ellipsoid diagram for [Ag(PNCP)ClO$_4$] drawn at the 50% probability level
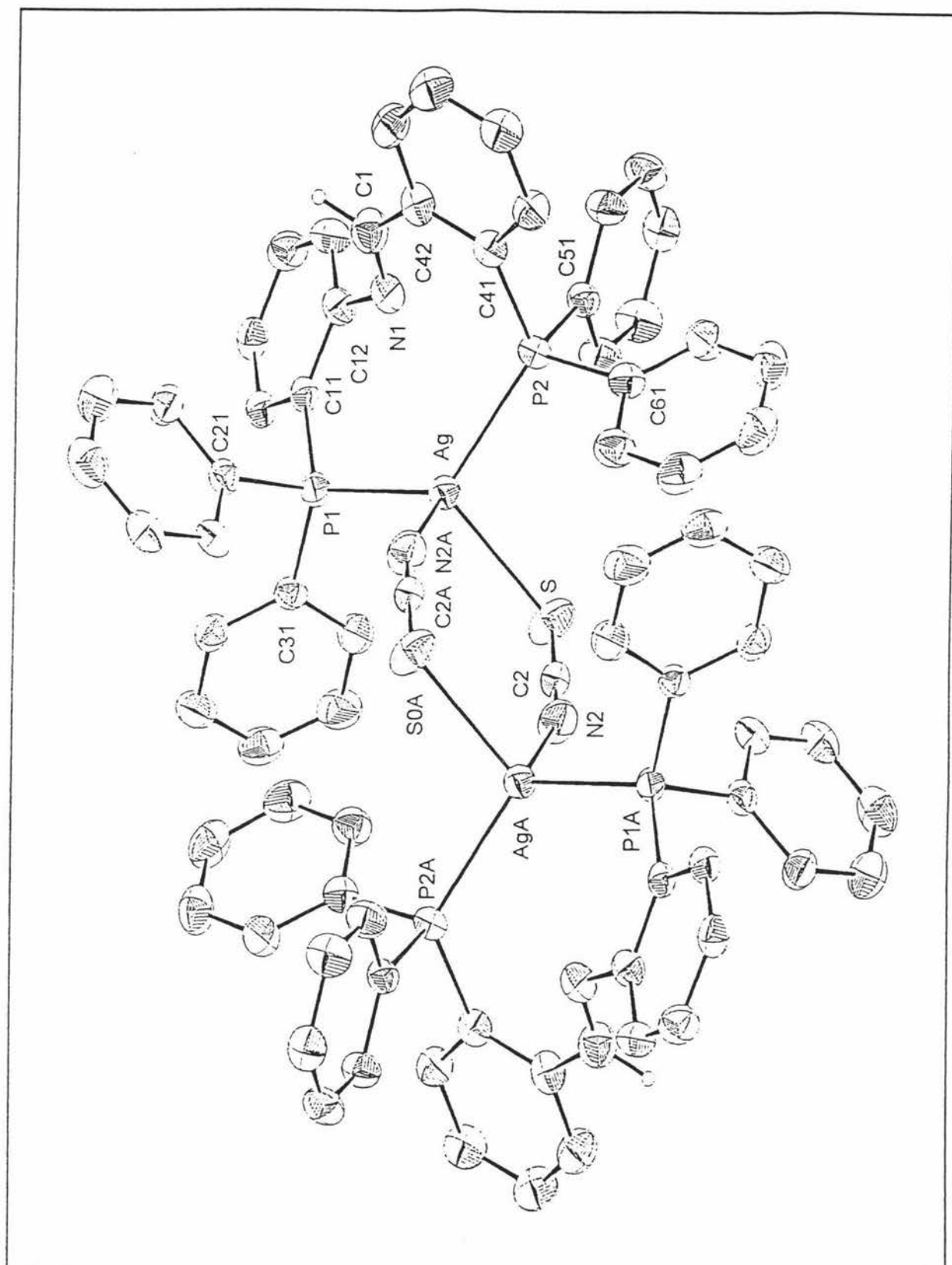
Figure IV-11 Thermal ellipsoid diagram for [Ag(PNCP)(SCN)]₂ drawn at the 50% probability level

IV-3-3 Nuclear Magnetic Resonance Spectroscopy

The ^{1}H NMR spectral data are shown in Table 4-6 for the imine proton in the silver(I) complexes with the PNCP ligand. The resonances shift to lower frequencies relative to the free ligand on coordination. This may be contrasted with the spectra of copper(I) complexes with PNCP in which the imine proton chemical shift is similar or shifted to higher frequencies relative to the free ligand. This chemical shift difference may be attributed to the stronger binding of PNCP to the copper(I) ion via the imine nitrogen relative to that with silver.

The ^{1}H NMR spectra of the imine proton shows a doublet for the free ligand but a singlet in the silver complexes. This difference can be attributed to the reduction of ^{4}J(P-H) coupling (see Chapter One) and the changed geometry of the complexed ligand, PNCP, relative to the free ligand. In the complexes the two phosphorus atoms are in *cis* positions with respect to each other but in the free ligand they take up the *trans* arrangement.

The ^{31}P NMR spectrum for the complex [Ag(PNCP)NO$_3$] shows two broad singlet peaks which indicate that two phosphorus atoms are in inequivalent environments but this spectrum can not distinguish the ^{1}J(Ag-P) coupling because of the fast exchange which occurs at room temperature.

Table 4-6 NMR data of silver(I) complexes with PNCP[a]

Compounds	^{1}H (ppm)	^{31}P (ppm)
PNCP	8.92(d)	-14.1, -14.8
[Ag(PNCP)NO$_3$]	7.91(s)	4.58, -11.8
[Ag(PNCP)ClO$_4$]	8.03(s)	b
[Ag(PNCP)(PPh$_3$)NO$_3$]	8.03(s)	b
[Ag(PNCP)(SCN)]$_2$	7.99(s)	b

[a] in CDCl$_3$ at room temperature

b spectrum not recorded

d =doublet

s =singlet

IV-3-4 Infra-red Spectroscopy and Mass Spectra

Selected infra-red spectral data for the silver complexes are given in Table 4-7.

The IR spectra for silver(I) complexes in this chapter show that the υ(C=N) stretching frequencies lie in the range 1636-1649 cm^{-1} compared with the free ligand value of 1620 cm^{-1}. These stretching frequencies differ from those of copper(I) complexes (1606-1616 cm^{-1}), the difference being attributed to the stronger bonding of copper to the imine nitrogen atom. X-ray data shows that for [Ag(PNCP)(SCN)]$_2$·CHCl$_3$ the imine nitrogen-silver bond length represents only a very weak interaction and this complex shows the greatest υ(C=N) stretching frequency.

The IR data together with the imine proton NMR data, suggest that the imine nitrogen binds weakly to the metal in all the silver complexes.

The υ(P-C) stretching frequencies at 1091-1099 cm^{-1} are similar to those shown by the analogous copper complexes and the free ligand.

In the IR spectrum the perchlorate anion in [Ag(PNCP)ClO$_4$] gives rise to three bands at 1115 cm^{-1}, 1039 cm^{-1} and 620 cm^{-1} which are comparable with the υ(Cl-O) stretching frequencies found for the complex [Cu(PNCP)ClO$_4$] (1130, 1030 and 622 cm^{-1}). For reasons already outlined in (Section III-3-4 of Chapter Three), these bands are consistent with the coordination of the perchlorate anion to the metal (Cu, Ag) via a single oxygen atom. This result is confirmed from the crystal structure determination of both complexes.

The coordinated υ(N-O) stretching frequencies in the complex [Re(CO)$_5$NO$_3$] are observed at 1497 (υ_5), 1271(υ_1) and 992 cm^{-1}(υ_2) [191,192]. There are three υ(N-O) stretching bands in complex [Ag(PNCP)NO$_3$] at 1407, 1296 and 891 cm^{-1} but there are only two in the complex [Ag(PNCP)$_2$]NO$_3$ at 1342 and 890 cm^{-1}. This difference may be attributed to the coordination of the NO$_3^-$ anion in the complex [Ag(PNCP)NO$_3$]. In [Ag(PNCP)$_2$]NO$_3$ and [Ag(PNCP)(PPh$_3$)]NO$_3$ the NO$_3^-$ group is ionic.

The mass spectral data (Table IV-4 to IV-8) were obtained by the method of Liquid Secondary Ion Mass Spectrometry using m-nitrobenzyl alcohol as the matrix. Isotope abundance cluster calculations were performed to distinguish the parent ion (M$^+$) and the protonated parent ion (MH$^+$). For the complexes [Ag(PNCP)(SCN)]$_2$ and [Ag(PNCP)$_2$]X (X= NO$_3^-$, ClO$_4^-$), daughter ions were observed by loss of the PNCP ligand. For all complexes, the peaks corresponding to the parent ions are relatively weak ($\geq$10%), the most intense peak being attributed to the daughter ion [Ag(PNCP)]$^+$. For all mass spectra

the ion $[Ag(PNCP)_2]^+$, is observed even though some of the parent complexes had 1:1 PNCP:silver ratios. This result suggested that complexes of the type $[Ag(PNCP)_2]X$ could be synthesized, which was subsequently proved to be correct.

IV-4 CONCLUSIONS

PNCP forms the following compounds with silver(I) salts:

(i) $[Ag(PNCP)X]$ $(X= NO_3^-, ClO_4^- SCN^-)$

(ii) $[Ag(PNCP)(PPh_3)]NO_3$

(iii) $[Ag(PNCP)_2]NO_3$

The nitrogen donor atom of PNCP coordinates to silver in a very weak bond; the Ag-P bond lengths are normal in the complex $[Ag(PNCP)ClO_4]$. In $[Ag(PNCP)(SCN)]_2$, the phosphorus atoms, but not the N, of PNCP bind. Both ends of the bridging SCN^- ligand bind, the N to one metal, the S to another. The N of this latter ligand is preferred to the N of PNCP because of its greater basicity. Thus PNCP is able to coordinate to the soft silver(I) ion in a bidentate manner in a distorted tetrahedral coordination geometry. This situation seems favoured the better the anion covalently binds to the silver. The mass spectra of all the compounds contain the ion $[Ag(PNCP)_2]^+$ which motivated its successful synthesis in the laboratory.

Table 4-7 Infra-red data of silver(I) complexes with PNCP[a]

Complex	$\upsilon(C=N)$ (cm^{-1})	$\upsilon(P-C)$ (cm^{-1})	$\upsilon(Cl-O)$ (cm^{-1})	$\upsilon(N-O)$ (cm^{-1})
PNCP	1620(m)	1091(m)		
[Ag(PNCP)ClO$_4$]	1636(m)	1095(m)	1115(s) 1039(s) 620(s)	
[Ag(PNCP)$_2$]ClO$_4$[b]	1036(m)		1094(s) 625(s)	
[Ag(PNCP)NO$_3$]·CH$_3$CH$_2$OH	1627(m)	1098(m)		1047(s) 1296(s) 891(m)
[Ag(PNCP)$_2$]NO$_3$	1636(m)	1089(m)		1342(s) 890(m)
[Ag(PNCP)(PPh$_3$)]NO$_3$	1639(m)	1099(m)		1342(s) 892(m)
[Ag(PNCP)(SCN)]$_2$	1646(s)	1099(m)	2101(s) [(C≡N)]	

[a] in nujol mulls on KBr discs

[b] see Appendix II for its preparation

s =strong

m =medium

Table 4-8 Mass spectral data for silver complexes

[Ag(PNCP)]NO$_3$
Ag=^{107}Ag
m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Ag(PNCP)]$^+$	658	658(100%)
[Ag(PNCP)$_2$]$^+$	1207	1207(1%)

[Ag(PNCP)(SCN)]$_2$
Ag=^{107}Ag
m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Ag(PNCP)]$^+$	658	658(100%)
[Ag(PNCP)$_2$]$^+$	1207	1207(5%)
[Ag$_2$(PNCP)$_2$(SCN)]$^+$	1372	1372(10%)

[Ag(PNCP)(PPh$_3$)]NO$_3$
Ag=^{107}Ag
m/z

Observed Ions	Calculated	Found (Relative Intensity)
[Ag(PNCP)]$^+$	658	658(100%)
[Ag(PNCP)(PPh$_3$)]$^+$	920	920(10%)
[Ag(PNCP)$_2$]$^+$	1207	1207(4%)
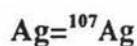
$$[Ag(PNCP)_2]NO_3$$
$$Ag={}^{107}Ag$$
$$m/z$$

Observed Ions	Calculated	Found (Relative Intensity)
$[Ag(PNCP)]^+$	658	658(100%)
$[Ag(PNCP)_2]^+$	1207	1207(21%)

$$[Ag(PNCP)ClO_4]$$
$$Ag={}^{107}Ag$$
$$m/z$$
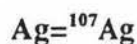
Observed Ions	Calculated	Found (Relative Intensity)
$[Ag(PNCP)]^+$	658	658(100%)
$[Ag(PNCP)HClO_4]^+$	757	757(<1%)
$[Ag(PNCP)_2]^+$	1207	1207(8%)

IV-5 OVERALL SUMMARY

The molecule PNCP is a new hybrid polydentate ligand containing two phosphorus (soft) and one nitrogen (hard) donor atoms. The two phosphorus atoms are inequivalent. Reaction with sulfur indicates that the phosphorus nearest the imine N is the more reactive one on oxidation. Upon coordination the PNCP configuration changes from one in which the two phosphorus atoms are in a *trans* arrangement to one where they adopt a *cis* geometry. Metal complexes of PNCP have been prepared where the molar ratio M:PNCP varies from 1:1, 1:1.5, 1:2 for M = Cu and 1:1 and 1:2 for M = Ag.

PNCP coordinates in a tridentate fashion in the complexes [Cu(PNCP)ClO$_4$] and [Ag(PNCP)ClO$_4$], but in a bidentate fashion in [Ag(PNCP)(SCN)]$_2$. When the nitrogen

donor atom of PNCP binds to copper(I) and silver(I) in the complexes [M(PNCP)ClO$_4$] the M-N bond distance is shorter for the copper complex [2.159(5)Å] than for the silver analogue [2.926(1)Å] indicating a much weaker bond for the latter. Both complexes exhibit distorted tetrahedral coordination geometry. These differences in bond length are accompanied by differences in the P(1)-M-P(2) bond angles which are related to the geometric constraints arising from the N coordination (P(1)-Cu-P(2), 142.75(5)°; P(1)-Ag-P(2), 129.28(9)°). At the same time the P-Ag-N angles of 64.0(2)° and 65.3(2)° are smaller than the corresponding copper analogues of 94.21(1)° and 86.18(1)° indicating that as N binds more strongly to the metal the P-M-N angles increase. In the dinuclear complex, [Ag(PNCP)(SCN)]$_2$, no coordination of N from PNCP occurs.

The potential of the hybrid polydentate ligand PNCP to exhibit different coordination modes suggests a range of stereochemistries, and stoichiometries may be possible with other first row transition metals such as Fe, Co, Ni, and Zn where it may bind in a tridentate fashion, but to second row transition metals with about the same size as Ag, such as Cd and Hg, it may adopt a bidentate mode in a tetrahedral configuration. Further studies with Rh, Ir, Pt, and Pd seem warranted.

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APPENDIX I

PREPARATION OF OPNCP

50mg of PNCP was dissolved in 15ml $CHCl_3$, and oxygen gas bubbled through the solution for a total of 7 hours and the solution maintained at a constant volume of 15 ml. The $CHCl_3$ was removed by rotary evaporator and the residue was redissolved in $CDCl_3$ for determination by NMR spectra (See Figure AI-1).

Table A1 ^1H and ^{31}P NMR data for OPNCP

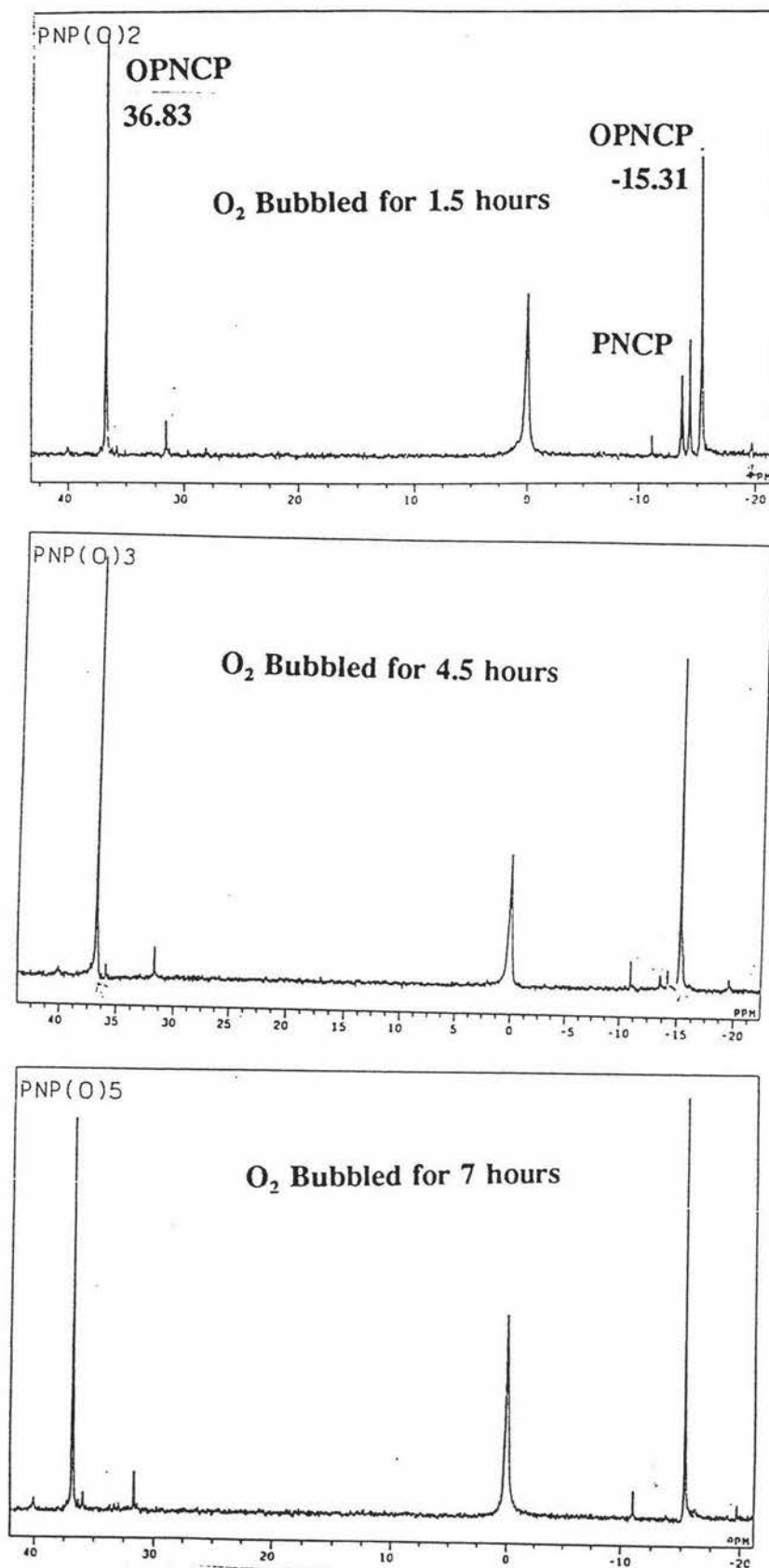| Compound	$^1H(\delta/ppm)$	$^{31}P(\delta/ppm)$
OPNCP	8.9	-15.7 36.3
	[d, 6.2Hz, -CH=N-]	

Figure A1 ^3P {^1H} NMR spectra of PNCP after bubbling oxygen though for the stated lengths of time (85% is used as an internal reference at zero ppm)

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APPENDIX II

MISCELLANEOUS REACTIONS FOR CHAPTER THREE AND CHAPTER FOUR

Attempted Preparation of [Cu₃(PNCP)₃(S₃C₃N₃)]

To $[Cu(PNCP)(CH_3CN)]ClO_4$ (0.22g, 0.29 mmol) dissolved in dichloromethane (5 ml) with stirring was added sodium trithiocyanuric acid (0.017g, 0.096 mmol) dissolved in ethanol (10 ml). The light yellow solution was then refluxed under nitrogen gas for 25 minutes. After filtration the solution was left to stand at room temperature overnight. A light orange crystalline product was formed and this was filtered and washed with dichloromethane/ethanol (3 ml/2 ml).

Yield:	68% (0.160g), M.P. 195-197°C
Found:	C, 68.39; H, 5.27; N, 2.36

Calculated for $(CuC_{74}H_{62}N_2P_4ClO_5)$:

C, 68.47; H, 4.62; N, 2.16

IR spectra data (cm⁻¹)

	$\upsilon(C=N)$	$\upsilon(Cl-O)$
$[Cu(PNCP)_2]ClO_4$	1610(m)	1095(s), 621(s)

Mass spectral data

$Cu={}^{63}Cu$

m/z

Observed Ion	Calculated	Found (Relative Intensity)
$[Cu(PNCP)]^+$	612	612 (100%)
$[Cu(PNCP)_2]^+$	1161	1161 (12%)
$[Cu(PNCP)_2ClO_4H]^+$	1262	1262 (1%)

CONCLUSION

The attempt to synthesize the complex $[Cu_3(PNCP)_3(S_3C_3N_3)]$ failed, spectroscopic and other evidence suggests the formation of $([Cu(PNCP)_2]ClO_4 \cdot 2H_2O)$. Further studies are required on this reaction.

Preparation of [Ag(PNCP)₂]ClO₄

[Ag(PNCP)ClO$_4$] (0.0955g, 0.133 mmol) in dichloromethane (5 ml) was slowly added slowly to a solution of PNCP (0.0730g, 0.133 mmol) in dichloromethane (5 ml) and ethanol (10 ml). The solution was refluxed under a flow of nitrogen gas for 20 minutes and the precipitate was filtered and washed with ethanol. It was recrystalised from dichloromethane/ethanol (5 ml/3 ml).

Yield: 95% (0.16g)

IR Spectral data (cm⁻¹)

	υ(C=N)	υ(Cl-O)
[Ag(PNCP)₂]ClO₄	1036(m)	1094(s)*, 625(s)

APPENDIX III
GENERAL EXPERIMENTAL TECHNIQUE AND INSTRUMENTATION

AIII-1 GENERAL EXPERIMENTAL TECHNIQUE

Most compounds synthesized in this thesis were air-stable except for PNCP when dissolved in $CHCl_3$. All synthetic reactions were performed under an atmosphere of purified nitrogen gas.

AIII-2 PURIFICATION OF SOLVENTS

The solvents, such as dichloromethane and acetonitrile, were distilled from CaH_2. Methanol and ethanol were distilled from their respective magnesium alkoxides. Tetrahydrofuran was pre-dried over KOH pellets, and then distilled from sodium benzophenone under an atmosphere of purified nitrogen gas. These solvents were stored over type 4A molecular sieves (excluding tetrahydrofuran). The deuterated NMR solvent $CDCl_3$ was used as supplied commercially (Aldrich Chemical Co.)

AIII-3 INSTRUMENTATION

Nuclear Magnetic Resonance Spectroscopy was performed at 6.34 Tesla on a JEOL GX270W Spectrometer operating in the Fourier transform mode at 270.0 and 109.4 MHz for ^1H and ^{31}P nuclei, respectively. Chemical shift data (δ) were expressed in parts per million (ppm) to high-frequency (downfield) shift from tetramethylsilane as an internal reference for the ^1H nuclei, and ^{31}P chemical shift data were referenced with respect to 85% H_3PO_4 as an external standard.

Infra-red Spectra were recorded on a BIO-RAD FTS-40 Spectrophotometer as a thin film of nujol mull between KBr discs.

Mass Spectra were recorded by using a Varian VG70-250S double focussing magnetic sector Mass Spectrometer with the method of the liquid secondary ion mass spectrometer (LSIMS) at AgResearch Ltd., Palmerston North. The samples were dissolved in a suitable solvent (usually CH_2Cl_2) and m-nitrobenzylalcohol was used as a matrix.

Elemental analysis were carried out using standard technique at the Microanalytical Laboratory of the University of Otago, Dunedin.

Measurement of melting points employed a Reichert hot-stage melting point apparatus and are uncorrected.