THE NATURE OF AMINOPHOSPHINES

by

ANDREW P. LANE

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This thesis is the original work of the author except in those portions where it is specifically stated to the contrary.

It has not been submitted in whole or part for a degree at any other University.

ANDREW P. LANE.

The Nature of Aminophosphines

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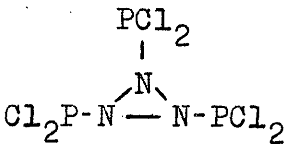
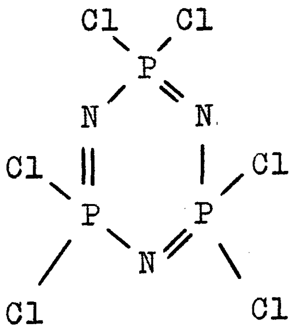
SURVEY.

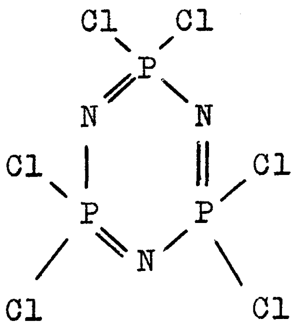
The general inorganic chemistry of phosphorous is comparatively old stretching back to the late 18th century. Somewhat surprisingly, compounds with phosphorous bound to nitrogen were amongst the first to be studied, perhaps due to the availability of phosphorus pentachloride which, in turn, was exceptionally reactive towards amines. This thesis is concerned with tervalent phosphorus - nitrogen compounds and therefore largely involves the reactions of phosphorus(III) chlorides or substituted phosphorus(III) chlorides with ammonia and primary or secondary amines. However, it is relavent to begin with a survey of the whole field of phosphorus-nitrogen chemistry as it has developed since those early days.

In 1834, Rose(1) described the reaction between ammonia and phosphorus pentachloride whilst in the same issue of the journal, Liebig and Wöhler(2) also published their results on this reaction. Although the main product was a polymeric material of formula $(PN_2H)_x$, a small amount of a stable crystalline solid was obtained containing phosphorus, chlorine and nitrogen, to which Wöhler assigned the formula $P_3N_2Cl_5$. However, Laurent and Gerhardt established the correct empirical formula as $PNCl_2$ and from vapour density measurements, Holmes and Glasstone(3) and Wichelhaus found the molecular formula was $P_3N_3Cl_6$, the latter postulating its structure as



Perhaps the greatest advance in this field was made by Stokes at the end of the 19th century, who established that $P_3N_3Cl_6$ was the start of an homologous series $(PNCl_2)_x$ by isolating compounds where x = 3,4,5,6,7. He also suggested that hexachlorocyclotriphosphazatriene* consisted of a planer ring of alternating phosphorus - nitrogen atoms and alternating double bonds giving rise to Kekulé structures, later to be described in resonance terms.



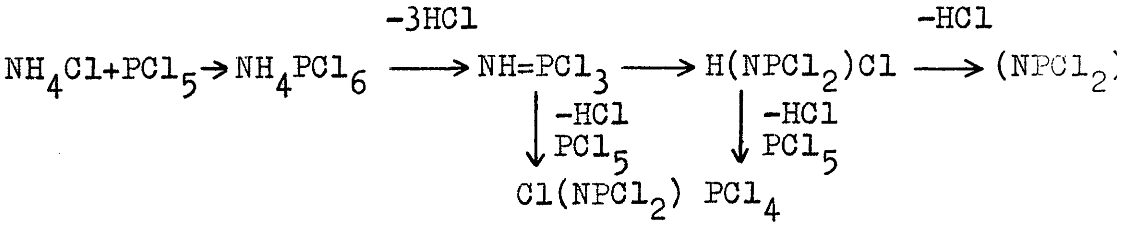


*The original name for these compounds of phosphontrilic chlorides was first suggested by Stokes and has since been used frequently. However, the nomenclature used in this thesis is that due to R.A.Shaw(30).

Stokes' ideas were largely substantiated by electron diffraction studies(4) which also established that the exocyclic substituents were normal to the plane of the ring. Further, it is now clear that the tetrameric chlorocyclophosphazene gives identical values for the P - N and P - Cl bond distances with the trimer, but the $N-\hat{P}-N$ and $P-\hat{N}-P$ bond angles indicate that the ring is puckered(5). In view of this, the trimeric systems were recently re-investigated and evidence of slight non-planarity was found(6).

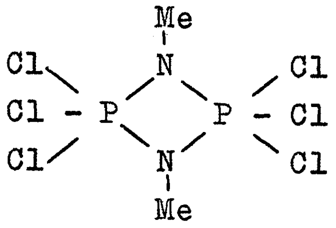
The synthetic route to chlorocyclophosphazenes used by Stokes involved heating sealed tubes containing phosphorus pentachloride and ammonium chloride to temperatures between 150 - 180°. This somewhat dangerous procedure was modified by Schenck and Römer(7) who refluxed the reactants in an inert solvent, e.g. sym. tetrachloroethane. After removal of the solvent, extraction of the higher cyclic compounds and open chain polymeric material with benzene leaves the crystalline tri - and tetrameric chlorocyclophosphazenes. Rather surprisingly this method, with only slight modifications, has since been used by all investigators in this field. However, modern techniques such as chromatography, fractional crystallisation and solvent extraction have led to the isolation and purification of $(PNCl_2)_7$ and $(PNCl_2)_8$ and there is indirect evidence of higher cyclic members $(PNCl_2)_x$ where $x = 9 - 17^{(8)}$.

The mechanism by which cyclophosphazenes are formed has recently come under study. The formation of these compounds involves partial ammonolysis of phosphorus pentachloride followed by elimination of hydrogen chloride resulting in cyclisation. Initial formation of ammonium hexachlorophosphate has been postulated$^{(9)}$ followed by elimination of hydrogen chloride to give $Cl_3P = NH$ which then loses more hydrogen chloride to form polymeric material or, reacts with phosphorus pentachloride.



$$\begin{tikzcd}
NH_4Cl+PCl_5 \arrow[r] & NH_4PCl_6 \arrow[r, "-3HCl"] & NH{=}PCl_3 \arrow[r] \arrow[d, "\begin{array}{l}-HCl\\ PCl_5\end{array}"] & H(NPCl_2)Cl \arrow[r, "-HCl"] \arrow[d, "\begin{array}{l}-HCl\\ PCl_5\end{array}"] & (NPCl_2 \\
 & & Cl(NPCl_2) & PCl_4 &
\end{tikzcd}$$

Ammonium hexachlorophosphate is unstable and has not been isolated but in the reaction of methyl ammonium chloride with phosphorus pentachloride, methylammonium hexachlorophosphate has been reported(10), although the product of this reaction, $(MeNPCl_3)_2$ was not a cyclophosphazene but a cyclophospha (V) azane



Direct synthesis of cyclophosphazenes from phosphorus halides has, until recently, been used only for the preparation of bromo-(11) and chloro-cyclophosphazenes; other derivatives being formed via substitution reactions. Extension of this method in recent years has given rise to cyclophosphazenes containing a carbon-phosphorus bond. Tri- and tetrameri methyl(12) and phenyl(13) cyclophosphazenes have been prepared by ammonolysis of the corresponding di-substitut trichlorophosphorane. Ammonolysis of trichlorobis-(trifluoromethyl)-phosphorane(14) caused rupture of the phosphorus-carbon bond. However, tri- and tetrameric trifluoromethylcyclophosphazenes are accessible by chlorination of aminobis-(trifluoromethyl) phosphine followed by removal of hydrogen chloride by a non-protonic base (triethylamine)

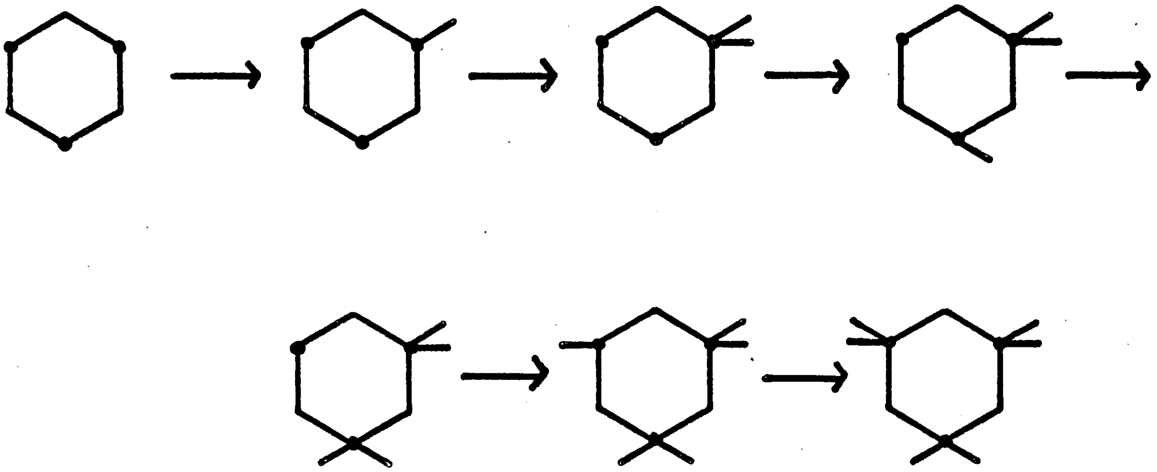
$$(CF_3)_2PNH_2 \xrightarrow{Cl_2} (CF_3)_2PNH_2(Cl_2) \xrightarrow{Et_3N} ((CF_3)_2PN)_x$$

$$(x = 3,4)$$

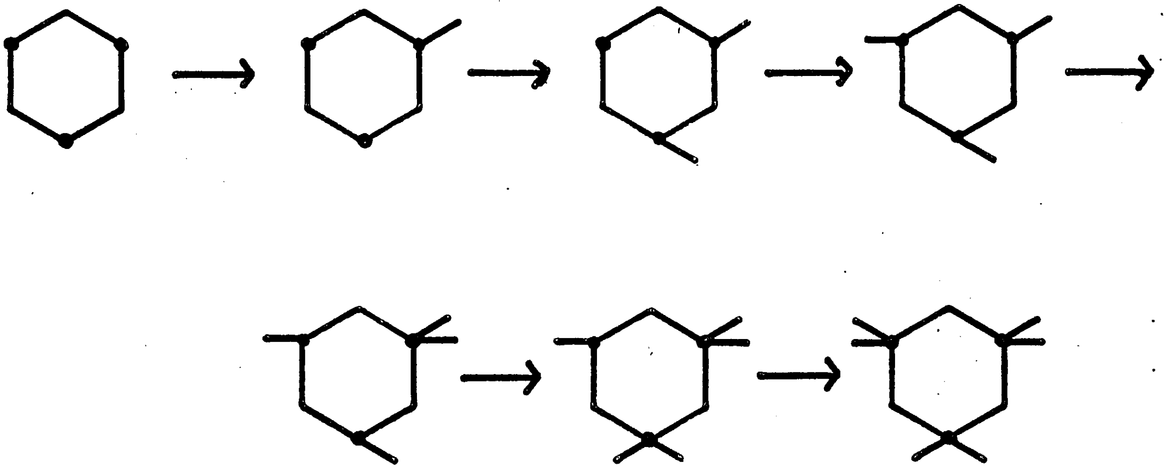
Replacement of the chlorine atoms in hexachlorocyclotriphosphazatriene is not the most commonly used route to substituted cyclotriphosphazenes. Two replacement patterns are possible (Fig.1) i. geminal, in which replacement occurs at phosphorus bonded to one chlorine atom and ii. non-geminal, replacement occuring at phosphorus bonded to two chlorine atoms. Both replacement patterns may be followed, but usually one predominates. Polar and steric effects are important$^{(15)}$ in deciding the type of replacement since, if the phosphorus atom is considered as a centre for nucleophilic attack, groups which increase the electron density on phosphorus will tend to inhibit further substitution at that centre and lead to non-geminal replacement. Similarly, a group causing a decrease in electron density on phosphorus will lead to geminal replacement. If polar effects could be neglected, steric requirements would be all important, the presence of a bulky group hinde ing further attack at that centre and causing a non-geminal

Figure 1:- Replacement Patterns in Cyclotriphosphazenes.

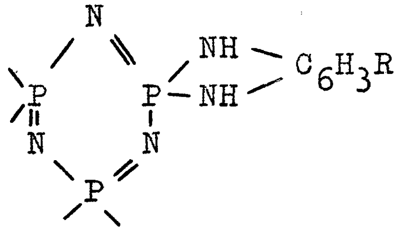
Scheme i. Geminal Replacement.



Scheme ii. Non-Geminal Replacement.



replacement. In practice, however, steric, polar effects and the nature of the reaction medium must be considered together. Friedal-Crafts phenylation of hexachlorocyclotriphosphazatriene gives a geminal replacement(16) whereas with ammonia and amines, non-geminal replacement occurs. Exceptions to the latter case are reported with aromatic o-diamines which, due to steric requirements, give spiro compounds(17).



R = Me,H.

Similar reaction patterns occur in octachlorocyclotetraphosphazatetraene, non-geminal replacement by amines being established by P^{31} N.M.R.(18,19). Both geminal and non-geminal phenylation has been reported.

Reactions of ammonium fluoride with phosphorus pentachloride and fluorination of cyclophosphazenes with hydrogen fluoride have failed to produce fluorocyclophosphazenes but, fluorination of tri- and tetrameric chlorocyclophosphazenes with potassium fluorosulphite gave the required products(20). A modification of this technique, using sulphur dioxide and potassium floride, enabled Chapman et.all(8) to isolate the cyclic compounds $(PNF_2)_x$ where $x = 3 - 17$; tri-heptameric fluorides were obtained from the corresponding chlorides while the remaining compounds were isolated from a mixture of higher cyclic chlorides by gas phase chromatography. A similar reaction involving sulphur dioxide and sodium iodide failed to produce iodocyclophosphazenes and, to date, no cyclophosphazenes with an iodine-phosphorus bond have been isolated(9). Fluorination of chlorocyclophosphazenes proceeds by geminal replacement; the highly electronegative fluorine atom reducing the electron density on phosphorus sufficiently to permit a second nucleophilic attack. One interesting facet of this work occurs on fluorination of hexachlorocyclotriphosphazatriene with lead fluoride which brings about a change in ring size to produce chlorofluorocyclotetraphosphazenes. The tetramers undergo polymerisation at 300° to a rubber which then depolymerises at 400° to form the chlorofluorocyclotriphosphazenes.

Aryl cyclophosphazenes are conveniently prepared by means of the Friedal-Crafts reaction catalysed by aluminium trichloride. Bode and Bach(21) isolated 22.44 tetrachloro 66.diphenyl cyclotriphosphazatriene but with more vigorous conditions, the tetra- and hexaphenyl derivatives were obtained(16,22). The geminal structure of the di- and tetraphenyl compounds was established by hydrolytic degradation involving the isolation of diphenylphosphinic acid. Extensions of the Friedal-Crafts method to aromatic compounds having an electron releasing substituent was limited in success but electron withdrawing substituents gave the required aryl cyclophosphazenes. No alkyl cyclophosphazenes or aryl derivatives of octachlorocyclotetraphosphazatetraene have been isolated by the Friedal-Crafts reaction. Grignard reagents react with chlorocyclophosphazenes but their preparative usefulness is limited. However, using phenyl magnesium bromide, the hexaphenyl trimer(23), an octaphenyl and two diphenyl derivatives of the tetrameric chloride have been isolated. It was suggested that the presence of a geminal - PCl_2 group would cause substantial ring cleavage by organo-metallic reagents so Tesi and Slota(24), using the compound 2.4.6. trichloro 2.4.6.

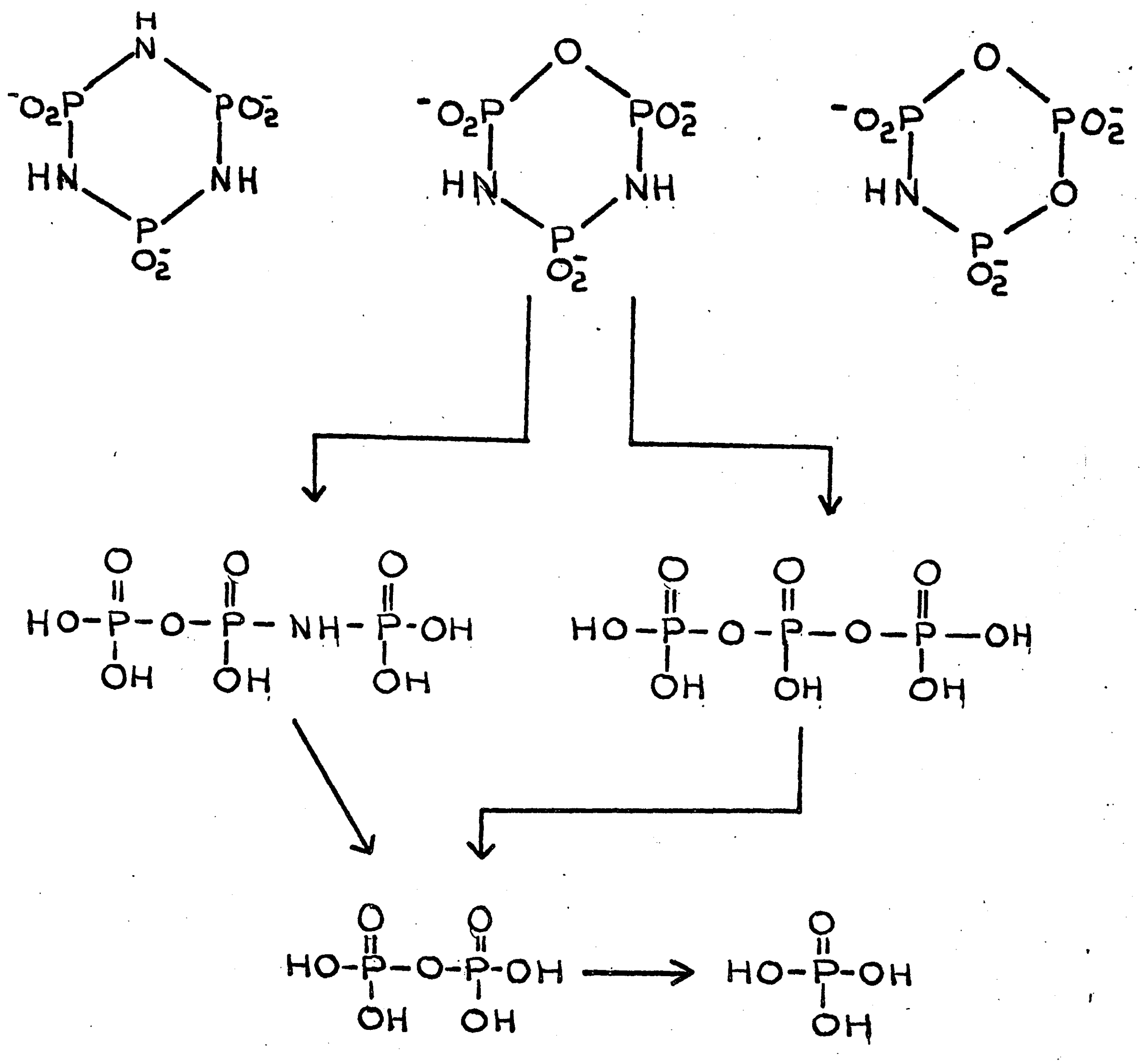
tridimethylaminocyclotriphosphazatriene (in which there are no geminal - PCl_2 groups) isolated 2.4.6. trichloro 2.4.6. trimethylcyclotriphosphazatriene from reaction with methyl magnesium iodide followed by deamination with hydrogen chloride. Analogous reactions with phenyl and vinyl magnesium bromide were also reported indicating the potential of this procedure for the formation of alkyl and aryl cyclophosphazenes.

Ammonolysis and aminolysis reactions proceed readily but, with some amines, to obtain complete substitution forcing conditions are necessary. Complete substitution of hexachlorocyclotriphosphazatriene occurs with primary unbranched alkylamines(15) (Me-Bu^n) at room temperature but with branched primary amines, temperatures up to 120° are required and with Bu^tNH_2, only the tetra-substituted compound was isolated. Of the secondary alkylamines, only dimethylamine, diethylamine and piperidine gave complete substitution and with the first two amines, products of formula $P_3N_3Cl_{6-n}(NR_2)_n$ (N = 1-4, 6) were isolated; the non-geminal replacement again being established by N.M.R.

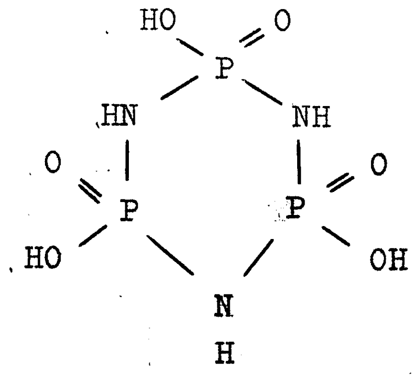
Despite the ever increasing interest in cyclophosphazene chemistry, very few kinetic studies have been carried out. However, Capon et.al(25) found the reaction between piperidine and hexachlorocyclophosphazatriene to have mixed second and third order kinetics. $P_3N_3Cl_5(C_5H_{11}N)$ was found to react 50 times slower and $P_3N_3Cl_4(C_5H_{11}N)_2$ 500 times slower than $P_3N_3Cl_6$ with piperidine thus indicating why complete aminolysis is, in some cases, quite difficult to achieve. Kinetic studies have also shown that complete substitution in octachlorocyclotetraphosphazatetraene occurs under less vigorous conditions and 10^2-10^3 times faster than the corresponding reaction with hexachlorocyclotriphosphazatriene(27).
Only one reaction with tertiary amines has been reported(28). Trimethylamine and hexachlorocyclotriphosphazatriene react to produce tetramethylammonium chloride and a mixture of chlorodimethylamine derivatives, $P_3N_3Cl_{6-n}(NMe_2)_n$.

Hydrolysis of halogenocyclophosphazenes under acidic, neutral or alkaline conditions gives

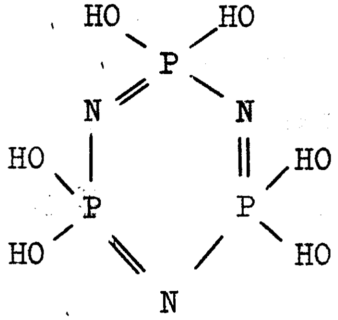
FIGURE 2:- SCHEME FOR HYDROLYSIS OF HEXACHLOROCYCLOPHOSPHAZATRIENE.



hydroxyoxocyclophosphazanes,



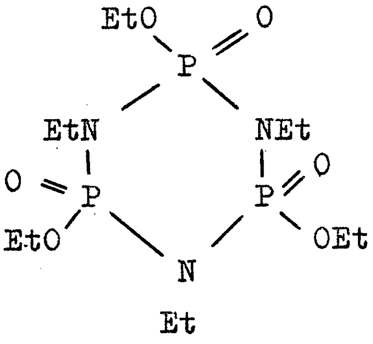
and not hydroxycyclophosphazenes

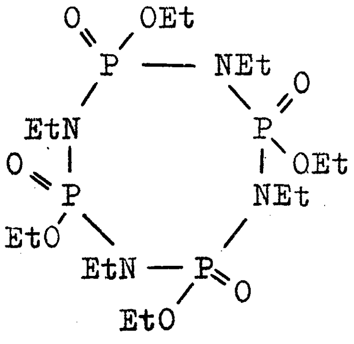


This is confirmed by I.R. data on the sodium salt $Na_3(PO_2NH)_3$ in which a peak (3200-2900cm^{-1}) corresponding to ν N-H was found whilst ν P=N was absent. Further acid hydrolysis of the hydroxyoxocyclophosphazenes leads to phosphoric acid by way of cyclic intermediates$^{(29)}$. It is believed that water can add to hydroxyoxocyclophosphazanes forming a P - O - P linkage without ring cleavage and the reaction scheme in Fig.2. is suggested $^{(30)}$.

Halogenocyclotetraphosphazenes are hydrolysed more readily than the trimers but follow a similar mechanism.

Replacement of the chlorine atoms in chlorocyclophosphazenes by - OR or - SR groups gives the esters or thio-esters of the hypothetical hydroxycyclophospazene acids. This is conveniently achieved by using an alcohol or thiol in the presence of a nitrogenous base (pyridine)(31,32), or with a metal alkoxide or thio-alkoxide(30). Re-arrangement occurs on heating the ethyl esters of $(PNCl_2)_x$, ($x = 3,4$), to 200° giving the corresponding esters of the cyclophosphazane acids(33).





Attack of a ring nitrogen on the α carbon of the alkoxy group is suggested as the mechanism for this re-arrangement since the phenyl esters are recovered unchanged after heating to 300°.

Apart from chlorocyclophosphazenes, the reaction of ammonium chloride with phosphorus pentachloride produces open chain compounds of formula $(PNCl_2)_xPCl_5$ having molecular weights similar to the chlorocyclophosphazanes. They are differentiated from the cyclic compounds by their insolubility in light petroleum, reactivity with water and U.V. spectrum(34). Although no individual members have been isolated from the reaction, compounds where x = 1 - 3 have been prepared by other methods. The monomer, isolated from the reaction of tetrasulphur tetranitride with phosphorus trichloride and from phosphorus pentachloride with hexachlorocyclotriphosphazene(35), has been assigned an ionic structure $(PNCl_3)^- \; PCl_4^+$. The dimer, isolated as the anilide(36) and the trimer(37) have not been fully investigated.

A further related group of linear phosphazenes encompasses the phosphinimines or monophosphazenes, $R_3P{=}NR'$, isolated by Staudinger and Meyer(38). These compounds, which are isoteric with the tertiary phosphine methylenes and oxides, are isolated from the reaction of a tertiary phosphine with an alkyl, aryl or acyl azide. The initial product is an unstable azide

$$R_3P = N - N = NR'$$

which decomposes at room temperature, losing nitrogen, to form the monophosphazene. By using this method, Staudinger(38,39) prepared compounds where R = Ph, Et, $Am^{\underline{i}}$, R_3=Ph(Et)$_2$ and R=Ph, Me, Et, PhCO, H and also isolated two azides,

$Ph_3P = N - N = N$ (α naphthyl); $Ph(Et)_2P=N-N=NPh$

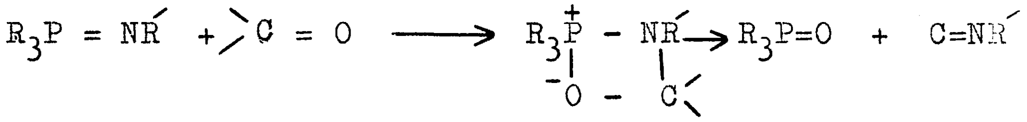
and, in addition, a monoarsazene $Ph_3As = NPh$.

An alternative preparation involves reaction of a primary amine with a dihalogenophosphorane in the presence of a hydrogen halide acceptor(40).

$$R'NH_2 + R_3PX_2 \xrightarrow[2Et_3N]{-2HX} R'N=PR_3 + Et_3NH^+ \quad X^-$$

The monophosphazenes closely resemble the phosphine methylenes in their reactions(48). Hydrolysis gives a tertiary phosphine oxide and a primary amine while reaction with carbonyl compounds involves addition followed by elimination of the phosphine oxide, (probably from an intermediate betaine) to give the imine.

$$R_3P = NR' + H_2O \longrightarrow R_3P = O + R'NH_2$$



$$R_3P = NR' + {>}C = O \longrightarrow \begin{array}{c}R_3\overset{+}{P} - NR' \\ | \qquad\;\; | \\ {}^{-}O \;-\; C{<}\end{array} \longrightarrow R_3P{=}O + C{=}NR'$$

With carbon disulphide, the tertiary phosphine sulphide and an isothiocyanate are formed.

$$R_3P = NR' + CS_2 \longrightarrow R_3P = S + R'N = C = S$$

Alkyl halides give rise to phosphonium salts, by addition to the nitrogen centre, which then hydrolyse to a secondary amine and a phosphine oxide.

$$R_3P{=}NR' + R''Br \longrightarrow (R_3P{-}NR'R'')^{+}\ Br^{-} \xrightarrow{-H_2O} R_3P{=}O + R'R''NH + H$$

The salts of monophosphazenes are also obtained from chloramine or methyl chloramine and tertiary phosphines(41). Of interest are the ligand properties of 2,2,2 triphenylphosphazene, $PH_3P = NH$, which, like triphenylphosphine oxide, forms complexes with Ni(II), Co(II) and Zn(II)(42).

Finally, products comprising larger P^V-N polymers have been referred to by Shaw(43) in terms of addition and condensation polymers. The latter class are insoluble grey-white solids known as phosphams and having the formula $(NPNH)_x$(1,2). They are formed from phosphorus pentachloride and ammonia, by reaction of molten hexachlorocyclophosphazatriene with ammonia or ammonium chloride and by thermal decomposition of aminocyclophosphazenes(44). The structure of phosphams is still unknown but on heating to 450° they lost ammonia to form a nitride, P_3N_5, which loses nitrogen at 700° to form a red polymer $(P\ N)_x$. Moureu and Wétroff(45) have proposed the following reaction scheme.

$$PCl_5 + NH_3 \rightarrow P(NH_2)_5 \xrightarrow[-30^\circ]{-2NH_3} PN_3H_4 \xrightarrow{-NH_3} PN_2H \xrightarrow[400^\circ]{-NH_3} P_3N_5 \xrightarrow[700^\circ]{-N_2} (PN)$$

The compound $(P\ N)_x$ is also obtained from the action of ammonia on phosphorus trichloride followed by thermal decomposition and will be discussed later.

Addition polymers are formed by thermal or catalytic polymerisation of halogeno-cyclophosphazenes and have molecular weights of 120,000 - 300,000(30). Hexachlorocyclotriphosphazatriene can be polymerised in a sealed tube at 260° - 350° to an insoluble elastomer which, because of its resemblance to unvulcanised rubber, was called "inorganic rubber" but at higher temperatures depolymerisation to lower cyclic compounds occurs. In the case of the tetramer, polymerisation takes place but at a slower rate. Catalytic polymerisation is effected by a wide variety of reagents ranging from metals to organic materials which cause a lowering of the temperature required for polymerisation to about 200°(46). At present, the mechanism by which halogenocyclophosphazenes polymerise is unknown.

The nature of the bonding in the cyclophosphazene is of considerable interest. The equality and shortness of the P - N bonds in hexachlorocyclotriphosphazene (1.58Å as compared to 1.78Å for a single bond) lend further support to the Kekulé type resonance structures suggested by Stokes. This evidence, the stability of these compounds and the reactions in which they take part led to the belief that the cyclophosphazenes possessed "Aromaticity" involving overlap and delocalisation of atomic orbitals as found in benzene. In cyclophosphazenes, four of the five electrons on nitrogen are accommodated in sp^2 hybridised orbitals; Two forming σ bonds with phosphorus and the lone pair taking up the remaining orbital. The fifth electron is contained in a p_z orbital and is available for π bonding as in nitrogen containing aromatic systems such as pyridine and 1.3.5. triazine. Phosphorus has five electrons for four bonds which are formed from sp^3 hybridised orbitals thus leaving only the d orbitals for π bonding(9). Existence of this d_π — p_π bonding in cyclophosphazenes leading to "aromaticity" is now confirmed but where there are two schools of thought as to its exact nature. Paddock and Craig(47) state that the maximum overlap with the p_z orbital on nitrogen will occur with the d_{xz} orbital in preference to the d_{yz}.

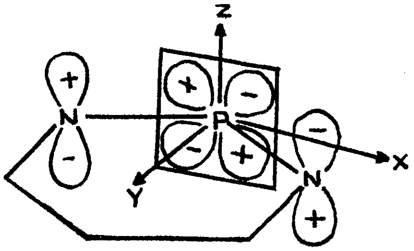
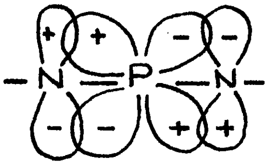


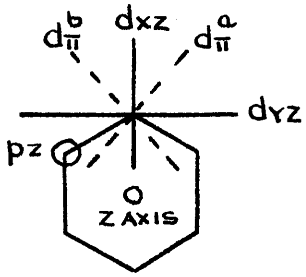
Figure 3.

However, due to the symmetry of the p_z and d_{xz} orbitals, maximum overlap is only permitted provided the orbitals are alternate in sign. e.g.

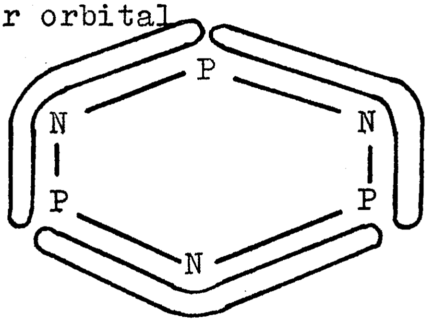


The repeating unit is therefore two P - N units thus leading to mismatching in the trimer but not in the tetramer. Using the axes given in Figure 3, the d_{xz} and $d_{x^2 - y^2}$ orbitals are thought to cause delocalisation in the lone pair on nitrogen forming π' bonds in the plane of the ring while the d_{z^2} and d_{xz} orbitals are involved in exocyclic π bonding.

Dewar et.al.(49), place equal importance on the d_{xz} and d_{yz} orbitals replacing them by a pair of linear combinations d_{π}^{a} and d_{π}^{b}



each capable of combining with one adjacent p_z orbital giving rise to a three centred molecular orbital



Weak interaction exists between these three centred orbitals. The planarity required to form π molecular orbitals in systems involving $p_\pi - p_\pi$ interactions is far less important in the cyclophosphazenes since the d orbitals are more diffuse; hence, the stability of the tetramer as compared to cyclooctatetraene.

Cyclophosphazenes have received a great deal of attention in the last fifty years and the chemistry of these compounds is a highly ordered discipline within the general chemistry of phosphorus. Such statements, cannot, unfortunately, be made concerning the chemistry of tervalent phosphorus-nitrogen compounds. Although they have been known since the end of the 19th century most research workers have tended to use the oxides and sulphides of tervalent phosphorus halides in reactions with amines due to the stability of the products obtained. Thus, the pioneering work of Michaelis at the turn of the century lay dormant till 1946 and only recently has interest been revived due mainly to the work of

Holmes and Forstner, Sisler and Smith, Nöth and Vetter, and Ewart. Tervalent phosphorus-nitrogen chemistry is still in its infancy and, on the whole, only simple systems have been synthesised consisting of no more than two $\mathrm{P}^{\overline{\mathrm{III}}}$ -N units.

The name phospha(III)azane, suggested by Shaw as a basis for the nomenclature of these compounds, has not been widely adopted. Instead, they are more usually regarded as either phosphine or amine derivatives. For example -

Me_2PNMe_2 $Ph_2P\text{-}N(Et)\text{-}PPh_2$

Dimethylaminodimethylphosphine; ethylamino bis diphenylphosphin

or

Dimethylphosphinodimethylamine; bis(diphenylphosphino)ethylamin

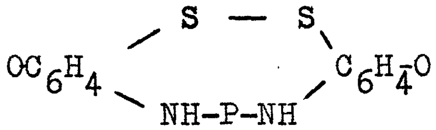
$PhP(NEt_2)(NMe_2)$

Ndiethyl N$'$ dimethylaminophenylphosphine.

To enable the chemistry of aminophosphines to be reviewed it is necessary to select a system of classification. A convenient basis for classification is, as has been adopted in the phosphazenes, a division into linear and cyclic compounds with a further breakdown of the linear group into "skeletal families". This is adequate for present day requirements, but in

TABLE 1

SKELETAL STRUCTURES OF KNOWN LINEAR P^{III}-N COMPOUNDS

CLASS	SKELETON		EXAMPLE	REFERENCES
			$Cl_2P(NHBu^t)_2$	50
			Cl_2PNEt_2	50
			$PhP(Cl)NEt_2$	
I	P - N		$(CF_3)_2PNH_2$	52
			Ph_2PNHEt	54
			Me_2PNMe_2	55
				60
II	N - P - N		$Et_2N\text{-}PPh\text{-}NEt_2$	54
			$(Me_2N)_2PCl$	57
III	$P\text{-}N(P\text{-}N)_x\text{-}P$	x=o	$(Ph_2P)_2NEt$	54
			$(Ph_2P)_2NH$	63
		$x \geq 1$	UNKNOWN	
IV	P-NN		$(Ph_2P)_2N\text{-}NMePPh_2$	65
			$PhP(NHNMe_2)_2$	65
			$Ph_2PNH\text{-}NMe_2$	65
V	$P\text{-}X\text{-}P{<}^{N}_{N}$	X=O	$(Me_2N_2)P\text{-}P(NMe_2)_2$	59
			$Ph_2P\text{-}P(NMe_2)_2$	66
		$X=C_6H_4p$	$p(Me_2N)_2PC_6H_4P(NMe_2)_2$	57
VI	$N\text{-}P{<}^{N}_{N}$		$P(NMe_2)_3$	50

the future, synthesis of more complicated $\overset{\text{III}}{\text{P}}$-N systems may render this classification too cumbersome for convenience. The skeletal structures of known $\overset{\text{III}}{\text{P}}$-N compounds are given in Table 1. and will be discussed below with particular reference to those cases where conversion of one group into another occurs.

The main synthetic route to $\overset{\text{III}}{\text{P}}$-N systems consists of ammonolysis or aminolysis of phosphorus(III) chloride, mono- or disubstituted chlorophosphines resulting in the elimination of hydrogen chloride by employing a hydrogen chloride acceptor in the reaction. The amine can itself be employed as the hydrogen chloride acceptor so that a stoichiometric ratio of 1:4 in the reaction of $RPCl_2$ and RNH_2 is all that is required; alternatively another base, such as a tertiary amine, may be added.

$$RPCl_2 + 4R_2NH \longrightarrow RP(NR_2)_2 + 2R_2NH_2^+Cl^-$$

$$RPCl_2 + 2R_2NH \xrightarrow{2Et_3N} RP(NR_2)_2 + 2Et_3NH^+Cl^-$$

Hydrogen chloride is thus conveniently removed as the solid amine hydrochloride. Other alternative methods of synthesis have been exploited and will be dealt with where applicable to a particular compound.

CLASS I P - N

This group comprises by far the largest number and variety of all the known aminophosphines since synthesis is achieved by elimination of one molecule of hydrogen chloride between phosphorus(III)chloride, mono- or disubstituted chlorophosphines and ammonia, primary or secondary amines.

e.g.

$$PCl_3 \quad + \quad Et_2NH \xrightarrow{B} Cl_2PNEt_2 \quad + \quad BHCl$$

The fully substituted compounds R_2PNR_2 are easily handled but those containing a -P-Cl or an N-H group are prone to undergo changes due to aerial oxidation or hydrolysis and extreme care is needed in their preparation and handling to avoid such effects.

The phosphorus(III)chloride-ammonia reaction has already been mentioned(45) and is of interest since the final product of thermal decomposition is identical with that from the same reaction with phosphorus pentachloride. With primary amines, the proposed reaction scheme

$$2RNH_2 \quad + \quad PCl_3 \longrightarrow RHN\text{-}PCl_2 \quad + \quad RNH_3^+ \ Cl^-$$

is not followed due to the instability of the -P(Cl)-NH- grouping which readily undergoes transformations which will be dealt with later in discussion of Class Vl. However, Michaelis(50) has reported the preparation of four alkylaminodichlorophosphines which were high boiling liquids but, apart from attaining analytical figures, were not further characterised. Similar transformations are not observed with secondary amines and the reaction

$$PCl_3 + 2R_2NH \longrightarrow Cl_2P\text{-}NR_2 + R_2NH_2^+ Cl^-$$

proceeds without difficulty. Aromatic and aliphatic dichlorophosphines undergo fluorination and oxidation on treatment with antimony(III)fluoride according to the equation

$$3RPCl_2 + 4SbF_3 \longrightarrow 3RPF_4 + 2Sb + 2SbCl_3$$

however, in the presence of a dialkylamino (or alkoxy) group attached to phosphorus oxidation does not occur, instead simple replacement takes place with antimony(III) fluoride, or even with sodium fluoride, to give the corresponding dialkylaminodifluorophosphines(51).

$$3R_2PCl_2 + 2SbF_3 \longrightarrow 3R_2NPF_2 + 2SbCl_3$$

$(R{=}Me_2N\ ;\ R_2{=}\ C_5H_{10}N)$

Preparation of chloroamino compounds $RP(Cl)NH_2$ and $RP(Cl)\text{-}NHR$, have been unsuccessful due to the instability of the -NH-PCl group and to further reaction of the chlorine atom leading to the N-P-N structures. One stage aminolysis has been achieved with secondary amines to give $RP(Cl)NR_2$(57).

The reaction of monochlorophosphines with ammonia and primary amines gives rise to the compounds R_2PNH_2 and R_2PNHR suggesting that it is easier to control replacement of the hydrogen atoms of the $-NH_2$ group than the chlorine atoms in the $-PCl_2$ group. When strongly electron withdrawing substituents are attached to phosphorus, the reactivity of hydrogen atoms on nitrogen is greatly reduced so that the reaction of bis(trifluoromethyl)chlorophosphine and ammonia gave a 96% yield of bis(trifluoromethyl)aminophosphine;(52)

$$(CF_3)_2PCl \quad + \quad 2NH_3 \longrightarrow (CF_3)_2PNH_2 \quad + \quad NH_4Cl$$

similar results were obtained with methylamine and aniline. In the absence of the electron withdrawing group on phosphorus the reactivity of -NHR increases and on heating ethyl aminodiphenylphosphine to 200° under reduced pressure self condensation occurs with elimination of ethylamine(53).

$$2Ph_2P\text{-}NHEt \xrightarrow[10^{-2}\ \text{mm.}]{200^{\circ}} (Ph_2P)_2NEt \quad + \quad EtNH_2$$

Preparations of fully substituted aminophosphines (54-56) of Class I proceed readily according to the equation

$$R_2PCl \quad + \quad 2R_2NH \longrightarrow R_2P\text{-}NR_2 \quad + \quad R_2NH_2^+Cl^-$$

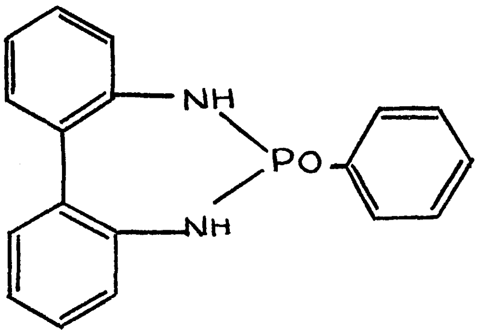
There are three alternative routes for preparing these compounds and are of interest since two of them do not require the use of an alkyl or aryl substituted chlorophosphine as starting material. Dimethylaminodimethylphosphine is conveniently prepared by the action of methylmagnesium iodide on dimethylaminodichlorophosphine (55).

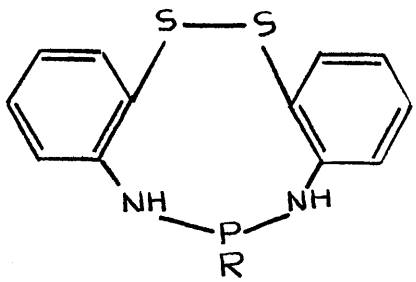
$$2MeMgI \quad + \quad Me_2N\text{-}PCl_2 \longrightarrow Me_2N\text{-}PMe_2 \quad + \quad 2IMgCl$$

Evleth et.al. (57) have preferred to use organolithium reagents for this and similar reactions finding that the product yields were superior than with the Grignard reagent. A rather different method was employed in the synthesis of diphenylaminodiphenylphosphine (56); on addition of diphenylamine to a suspension of sodium hydride in diglyme, hydrogen is liberated and the sodium salt formed, Ph_2NNa, eliminates sodium chloride on refluxing with chlorodiphenylphosphine to give the required product. Conversion to the sodium salt is more directly applicable to reactions involving secondary amines since the primary amine analogues $RN(Na)_2$ are unknown.

CLASS II:- N - P - N

Elimination of two molecules of hydrogen chloride between phosphorus(III)chloride or a mono-substituted chlorophosphine and ammonia, primary or secondary amines produces compounds with the N-P-N structure. Only one compound has been reported having a phosphorus-chlorine bond(59), $(Me_2N)_2PCl$, and the only evidence for simple molecules of the type $RP(NHR)_2$ is a methyl iodide adduct isolated by Ewart(54), of formula $C_{11}H_2IN_2P$ corresponding to $\left[Ph(Me)P(NHEt)_2\right]^+I^-$, from the product of the reaction of dichlorophenylphosphine and ethylamine. The NH-P-NH structure has, however, been encountered in heterocyclic molecules(60). i.e.





Secondary alkylamines with dichlorophenylphosphine give bis(dialkylamino)phenylphosphines, $PhP(NR_2)_2$ (54,57,61). Compounds containing different amine groups are prepared by isolation of the intermediate dialkylaminochlorophenylphosphine followed by further reaction with a different amine.

CLASS III:- $P - N - (P - N)_x - P$

A compound of this class, where x = 0, has been mentioned previously as resulting from the self condensation of ethylaminodiphenylphosphine to give ethylaminobis(diphenylphosphine) $(Ph_2P)_2NEt$. A more obvious synthetic route to P-N-P compounds consists of complete replacement of hydrogen in a primary amine group by a monochlorophosphine.

$$2R_2PCl \quad + \quad 3RNH_2 \longrightarrow (R_2P)_2NR \quad + \quad 2RNH_3^+Cl^-$$

However, this equation is not strictly followed for in the reaction of ethylamine with chlorodiphenylphosphine only 60% yields of the product, $(PH_2P)_2NEt$, could be obtained and the intermediate Ph_2PNHEt was always isolated. The low yields are probably due to preferential formation of the intermediate, Ph_2PNHEt, which then undergoes partial self condensation on heating.

$$Ph_2PCl+2EtNH_2 \longrightarrow Ph_2PNHEt+EtNH_3^+Cl^- \longrightarrow \tfrac{1}{2}(Ph_2P)_2NEt+EtNH_2$$

If the above equation represents this reaction, and it is feasible since excess amine was always employed, then it points to the fact that amine elimination of this type is less effective than the elimination of HCl and lends further support to the lack of reactivity of hydrogen in the RNH-group. It is therefore expected that use of a non-protonic base, such as pyridine or methylamine, as a hydrogen chloride acceptor in this reaction, would increase the yield of $(Ph_2P)_2NEt$.

Two compounds have been reported having the P-NH-P skeleton. The sodium salt of dimethylphosphine in liquid ammonia has the formula $Na^+[Me_2PNH]^- xNH_3$ or $Na^+[Me_2PNPMe_2]^- xNH_3$ which on heating with ammonium bromide leads, through an intermediate of uncertain composition (thought to be Me_2PNH_2), to $(Me_2P)_2NH$(62). Aminobis(diphenylphosphine), $(Ph_2P)_2NH$, was prepared directly from chlorodiphenylphosphine and ammonia (63).

Higher homologues of this class where $x > 1$ have not been prepared containing tervalent phosphorus. However, Gutmann et.al.(64) have prepared the corresponding phosphoryl compounds by elimination of potassium chloride between a phenyl phosphoryl chloride and the potassium salt of an aminophosphine oxide e.g. $Ph_2P(O)N(K)Ph$.

$$2PH_2P(O)N(K)Ph+PhPOCl_2 \rightarrow Ph_2P(O)-N(Ph)-P(O)(Ph)-N(Ph)-P(O)Ph_2 + 2KCl$$

This is an extremely versatile method for the formation of linear P(O)-N chains as is illustrated by the following reaction.

$$PhP(O)(NHPh)(NKPh)+Ph_2POCl \longrightarrow Ph_2P(O)-NPh-P(O)Ph-NHPh$$

This product on gentle heating condenses with the loss of aniline to form

$$Ph_2P(O)-NPh- P(O)Ph-NPh\ _2P(O)Ph_2$$

Application of this method to tervalent systems will require the formation of similar potassium derivatives but so far no attempt has been made to prepare these compounds.

CLASS IV:- P - N - N

This class of compound is formed from hydrazines and phosphorus(III)chlorides and can therefore give rise to P-N, P-N-P and N-P-N type structures. The use of excess reactant base as a hydrogen chloride acceptor, as noted above in reactions involving amines, cannot be applied to the formation of this class of compound since the hydrazonium chlorides were soluble in the solvent used and instead,

TABLE 2 :- CLASS IV COMPOUNDS. HYDRAZINOPHOSPHINES.

$Ph_2P\text{-}NH\text{-}NMe_2$

$(Ph_2P)_2N\text{-}NMe_2$

$Ph_2P\text{-}N(Et)\text{-}NMe_2$

$Ph_2P\text{-}NH\text{-}NH\text{-}PPh_2$

$(Ph_2P)_2N\text{-}N(Me)PPh_2$

$PhP(CI)\text{-}NH\text{-}NMe_2$

$PhP(NH\text{-}NMe_2)_2$

triethylamine was added to the reactions. The products of the reactions between phosphorus(III)chloride, mono- and diphenylchlorophosphine and hydrazine and substituted hydrazines are shown opposite(65). Hydrazinophenylphosphines do not differ from the corresponding amine derivatives in their reactions with alkyl halides, oxygen and sulphur. However, the nitrogen protons in the phosphorus substituted hydrazines were found to be less labile than the parent hydrazine; whilst the first hydrogen could be substituted at 35° temperatures of up to 110° were necessary for a second substitution. The effect of the bulky phenyl group causing steric shielding has been given as a possible explanation of this and further comment will be made later in light of the current concepts of bonding in these compounds.

CLASS V: $- P - X - P{<}^{N}_{N}$

Compounds of Class V, where x=0, are amino substituted biphosphines and symmetrical molecules are prepared by a Wurtz reaction (59).

$$2(Me_2N)_2PCl+2Na \longrightarrow (Me_2N)_2P-P(NMe2)_2+2NaCl$$

By using a sodium derivative of one of the phosphines the unsymmetrical aminobiphosphines are prepared (66).

$Ph_2PNa + ClP(NMe_2)_2 \longrightarrow Ph_2P\text{-}P(NMe_2)_2 + NaCl$

An attempt to prepare P.P.diphenyl P.P.bis(dimethylamino) biphosphine by elimination of mercuric iodide between two molecules of dimethylaminophenyliodophosphine

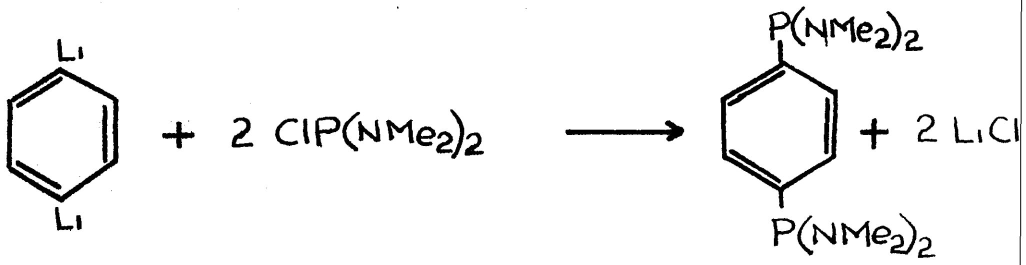
$2Ph(Me_2N)PI + Hg \longrightarrow Ph(Me_2N)P\text{-}P(NMe_2)Ph + HgI_2$

resulted in an interesting rearrangement. The above equation was not followed and instead the products obtained were phenylcyclophosphine and the mercuric iodide adduct of bisdimethylaminophenylphosphine (66).

$2Ph(Me_2N)PI + Hg \longrightarrow 1/N(PhP)_n + PhP(NMe_2)_2.HgI_2$

The mechanism for this reaction will be discussed in Chapter 1.

One compound has been reported where $X{=}C_6H_4$ (57), and is prepared thus:



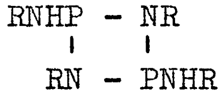
CLASS VI:- $N - P{<}^{N}_{N}$ AND CYCLIC SYSTEMS

$N-P{<}^{N}_{N}$ and cyclic structures are discussed jointly because the former compounds provide the only known link between linear and cyclic systems. Complete substitution of phosphorus(III)chloride with primary and secondary amines giving compounds with the $N-P{<}^{N}_{N}$ skeleton, was first studied by Michaelis (50,61) and since then other investigators have extended the known compounds. Products from secondary amines are far more easily characterized and purified than those from primary amines, (primary amine derivatives have never been isolated free of chlorine), since the latter compounds undergo secondary reactions involving amine elimination. The products of this amine elimination have been studied by Holmes and Forstner (67) who, from the reaction of phosphorus(III) chloride and methylamine obtained a compound of molecular formula $P_4(NMe)_6$ presumably from amine elimination of $P(NHMe)_3$ (which was not isolated).

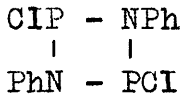
$$PCl_3 + 6MeNH_2 \longrightarrow P(MHMe)_3 \xrightarrow{-NH3} P_4(NMe)_6$$

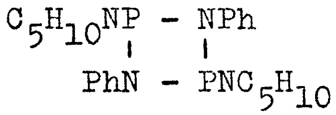
N.M.R. studies on phosphorus tri-Nmethylimide, $P_4(NMe)_6$, strongly indicate that it has the cage like structure of P_4O_6 consisting of interlocking six membered P-O rings in which oxygen is replaced by -NMe. This structure is even more attractive when it is realized that -NMe is isoelectronic with oxygen. The corresponding arsenic compound, $As_4(NMe)_6$, has also been prepared and assigned the same structure since it gives an identical cracking pattern with $P_4(NMe)_6$ (68,69).

Similar reactions with other primary (70) amines (ethyl, isopropyl, isobutyl, tert.butyl) failed to form phosphorus tri-Nmethylimides giving instead amide-imide compounds, which were dimeric where R=Et and Bu^t probably involving a four membered ring.

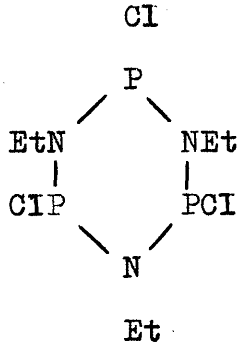


Dimeric amide-imide compounds were first reported by Michaelis (71) but their cyclic structure was not realised till 1946 when due to their usefulness in preparing Nmono-substituted amides a more thorough investigation was carried out (72) and it was suggested that Michaelis' original compounds, which he formulated as PhN=PCl and PhN=P(piperidyl) were in fact four membered cyclic systems.





Cyclic tervalent phosphorus-nitrogen systems have the same empirical formula as cyclophosphazenes, $(R_2PN)_x$, but the substituent groups are attached to both phosphorus and nitrogen atoms whereas in the cyclophosphazenes, both groups are on phosphorus. Only two trimers are known in this series, one originating from a study of aminosilanes in which phosphorus(III)chloride reacted with ethylaminobistrimethylsilane to give a compound having the empirical formula of $(ClPNEt)_x$ (73). This was found to be trimeric and has the structure

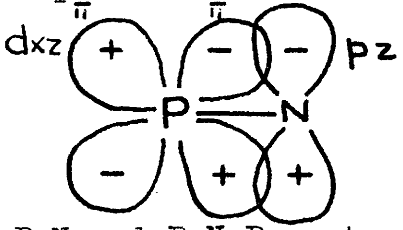


Also dichlorophenylphosphine and aniline in the presence of triethylamine give the cyclic compound $P_3N_3Ph_6$ (74). Apart from the preparation of these trimers, the chemistry of cyclic $\overset{\text{III}}{P}$ - N systems has not been investigated.

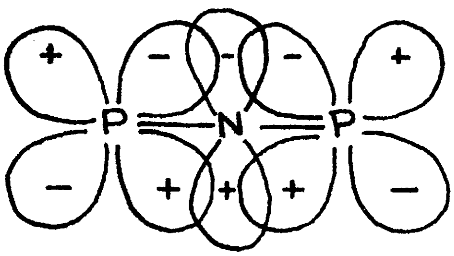
BONDING IN TERVALENT PHOSPHORUS-NITROGEN SYSTEMS.

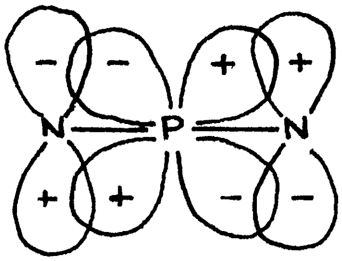
The detailed nature of the bonding in tervalent phosphorus-nitrogen systems has not until recently, received any attention. Practical and theoretical considerations have now been correlated and from which, the basis of a theory has emerged but until these systems receive a more sophisticated treatment, this theory will remain, on the whole, mere conjecture.

The electronic configuration of phosphorus, $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^3$, leads to either p^3 or sp^3 symmetry and thus triply bonded phosphorus compounds have bond angles ranging from 90° to $109^\circ\ 28'$, the exact value of this angle being dependent upon steric requirements, bond pair - bond pair repulsion and the electronegativity of the substituent groups. The formation of σ bonds with nitrogen, which is considered to be sp^2 hybridised, and two σ bonds with the remaining substituents gives rise to a situation where both phosphorus and nitrogen possess a lone pair of electrons. This leads to the problem as to which atom would be more capable of donating its lone pair or, in other words, which atom has the greater base strength. On electronegativity considerations alone nitrogen with a Pauling electronegativity of 3.0 might be expected to be more basic than phosphorus (2.1) but Burg (55) found that in the preparation of a 1:1 methyl iodide adduct of dimethylaminodimethylphosphine the methyl group was attached to phosphorus indicating that the greater electron donor bonding power resides on phosphorus; this has been confirmed by later workers. The explanation is similar to that used for the delocalisation of the nitrogen lone pair in hexachlorocyclotriphosphazatriene. It is assumed that the p_z orbital containing the lone pair on nitrogen is suitably positioned to overlap with the diffuse vacant set of 3d orbitals on phosphorus resulting in p_{π} ——— d_{π} back bonding.



With the N-P-N and P-N-P systems, the lone pair is considered to be completely delocalised over the whole system via the 3d orbitals, i.e.





This theory is adequate for most aminophosphines and the reactions in which they take part but it fails to explain the lack of reactivity of the $-NH_2$ group in $(CF_3)_2PNH_2$ and the -NHNHMe group in $Ph_2PNHNHMe$. If the lone pair on nitrogen is delocalised by means of the 3d orbitals, according to the theory, then these groups should show enhanced reactivity especially in the case of $(CF_3)_2PNH_2$ because of the highly electron withdrawing trifluoromethyl group. However, no logical explanation has been forwarded to account for this anomaly.

Since the base strength on nitrogen has been reduced addition reactions to aminophosphines are concerned wholly with the phosphorus atom and as a result, the properties of aminophosphines are not significantly different from those of simple phosphines. There is thus no tendency to form ammonium salts with alkyl halides as in the monophosphazenes,

$$R_3P{=}NR' + R''Br \longrightarrow (R_3P{-}NR'R'')^+ Br^-$$

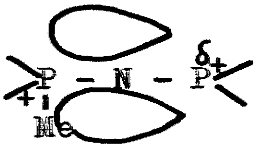
but instead, quaternisation of phosphorus takes place.

$$Me_2P{-}NMe_2 + MeI \longrightarrow (Me_3P{-}NMe_2)^+ I^- \quad (55)$$

In systems containing more than one phosphorus atom as in $(Ph_2P)_2NEt$ and including phosphorus tri-Nmethylimide, quaternisation occurs at only one centre forming salts of the type.

$$\left[(Ph)_2MeP\text{-}NEt\text{-}PPh_2\right]^+ \quad I^-$$

This is not to be expected since bis(diphenylphosphino) methane and 1.1.1.tris(diphenylphosphinomethyl) ethane form di- and tri-methiodides respectively (75). Replacement of -NEt by $-CH_2$ must cause the phosphorus atoms to act independently of each other whereas the p_z orbital on nitrogen provides an 'electronic bridge' between the two centres and formation of a positive centre by an alkyl group will inhibit further reaction at the other centre. This may be represented diagramatically as



In the case of the biphosphines, where the phosphorus atoms are joined, quaternisation also occurs at only one phosphorus centre; but with tetraphenyl- and tetracyclohexylbiphosphine alkyl iodides split the P-N bond (76).

$$R_2P\text{-}PR_2 \quad + \quad R'I \longrightarrow R_2R'P \quad + \quad R_2PI$$

Splitting of the P-N bonds in P-N-P systems has not been reported but the low yield obtained with n-propyl iodide could be accounted for on this basis. The alkyl iodide adducts of aminophosphines are water soluble and conductance values correspond to 1:1 electrolytes. Further ion association takes place with mercuriciodide (as with other Group V^B 'onium iodides) and results have shown a significant concentration of the tri-iodomercurate ion(77).

$$[Me_3PNMe_2]^+X^- \quad + \quad HgI_2 \longrightarrow [Me_3PNMe_2]^+ \; HgI_3^-$$

Experimentally, the position of the alkyl group on phosphorus, in the case of $[Me_3P\text{-}NMe_2]^+I^-$ was established by alkaline hydrolysis of the P-N bond from which dimethylamine was distilled and converted quantitatively into its hydrochloride.

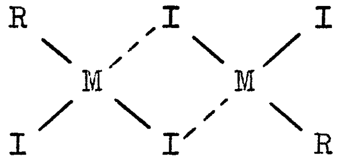
$$(Me_3P\text{-}NMe_2)^+I^- \quad + \quad NaOH \longrightarrow (Me_3P\text{-}NMe_2)^+OH^- + NaI \longrightarrow$$
$$Me_3P{=}O + Me_2NH$$

Scission of the P-N bond can also be effected with hydrogen chloride. With concentrated aqueous hydrochloric acid, ethylaminobisdiphenylphosphine forms salts of indefinite composition containing up to two molecules of hydrogen chloride (53).

Oxides of aminophosphines are formed either by direct oxidation or by using the phosphoryl compound as starting material. Direct oxidation is achieved by refluxing with manganese dioxide, treatment with hydrogen peroxide and nitric acid or simply by bubbling a stream of oxygen through material in an inert solvent. Normally oxidation occurs without formation of polymeric material but with phosphorus tri-Nmethylimide the cage structure is broken to yield a polymeric compound $P_2O_2(NMe)_3$ (78). In the reaction with sulphur, the cage structure remains intact (68) and, in fact, all aminophosphines are easily converted into sulphides by refluxing with elemental sulphur in an inert solvent. The diselenide of ethylaminobisdiphenylphosphine has been prepared (79), $[Ph_2P(Se)]_2NEt$, but no tellurides have been reported.

Since the beginning of the century, tervalent phosphorus compounds have been known to act as good ligands with transition metals of class B . The high stability of these complexes is probably due to appreciable double bond character in the metal-phosphorus bond; a σ bond is formed by donation of the lone pair on phosphorus and any excess negative charge on the central metal atom is dispersed by d_{π} — d_{π} back bonding between the filled or partially filled d orbitals on the metal and the vacant 3d orbitals on phosphorus. In aminophosphine complexes, the extent to which the 3d orbitals are being used in p_{π} —— d_{π} bonding with nitrogen is an important factor and in some cases competition for the d orbitals on phosphorus between nitrogen and the metal is to be expected.

The aminophosphine complexes so far studied are limited to those with cadmium(11)iodide, mercury(11)iodide and molybdenum or nickel carbonyls. Both 1:1 and 2:1 complexes are formed with HgI_2 and CdI_2 using $Ph(NMe_2)_2$ and $P(NMe_2)_3$ as ligands(80). The 1:1 complexes are dimeric e.g.



Nickel carbonyl complexes in which two carbonyls have been replaced are reported with $(Me_2N)_3P$, $(Me_2N)_2PCl$ and $(Me_2N)_2PCN$ and complete substitution occurs with Me_2NPF_2 and $C_5H_{10}NPF_2$(51), which also replace two or three carbonyl groups from molybdenum hexacarbonyl. In P-NR-P systems, complex formation with mercury(11)iodid and molybdenum hexacarbonyl leads to compounds of formula

$(PNP)HgI_2$(54) $(PNP)Me(CO)_4$(81)

suggesting that P-N-P is acting as a bidentate ligand. Aminophosphine complexes and the nature of the bonding involved will be discussed in Chapter IV.

This survey of tervalent phosphorus-nitrogen compounds has shown the lack of a systematic approach to this subject and also, those sections where further knowledge would be desirable. The author feels that an approved nomenclature and classification would facilitate a greater understanding of aminophosphines.

The subject is essentially one of academic interest but recently sulphides of the type $RP(S)(NHR)_2$ have come into prominence because bis(phenylamino)phenylphosphinesulphide showed border line activity against the tumour adenocarcinoma 755^82). This led to the screening of various analogues of the compound but they did not show activity against this tumour, sacoma 180 or leukemia I.120. Despite this failure it is conceivable that derivatives of aminophosphines could be of therapeutic value and thus benefit mankind. The anhydride of bis(dimethylamino)phosphinic acid, "Schradan", has been used as an insecticide(83) and in view of their similarity to this compound, aminophosphines might have some potential in this field.

Future development of tervalent phosphorus-nitrogen chemistry will undoubtedly lie in the preparation and systematic investigation of cyclic systems along the lines of the cyclophosphazenes and also in the formation of linear $\overset{\overline{III}}{P}$-N polymers of Class III. The work described in this thesis extends from studies of simple molecules having the NH-P-NH structure to transition metal complexes of P-N-P and N-P-N compounds thus giving a broad understanding of "the Nature of Aminophosphines".

Chapter I.

Effect of Heat on Bis(alkylamino)phenylphosphines.

INTRODUCTION.

Thermally induced self-condensation of molecules giving rise to simple or polymeric compounds is well known especially in compounds derived from the elements in Groups IIIB-VIB. In particular, given the compound Y-NHR it is possible, under certain reaction conditions, to cause self condensation with the elimination of amine to form a product Y-NR-Y. As the number of -NHR groups attached to Y increase, so the products of condensation become more complex. Therefore, with $Y(NHR)_2$ it would be expected that cyclic compounds $(Y\text{-}NR)_x$ and linear polymers $RNH\text{-}(Y\text{-}NR)_x\text{-}Y\text{-}NHR$ will be produced and from $Y(NHR)_3$, the products would be 3-dimensional polymers.

Examples of this type of condensation are found in the chemistry of silicon-nitrogen compounds. In the reaction of trimethylsilylchloride and ammonia (84), hexamethyldisilazane is the sole organo-silicon product and is presumably formed from condensation of trimethylsilylamine. As the size of the organic group attached to silicon increases, the tendency for this condensation decreases so that tri-n-propylsilyl chloride and ammonia (85) gives the tri-n-propylsilylamine exclusively. Apart from methylamine, reactions of primary amines with triorganosilyl chlorides do not give disilazane derivatives. However, condensation to give disilazanes is possible (86), e.g.

$$2Me_3SiNHCR_2CH{=}CH_2 \xrightarrow[(NH_4)_2SO_4]{Boil} (Me_3Si)_2NCH_2CH{=}CH_2 + CH_2{=}CHCH_2NH_2$$

Reactions of dialkylsilyl chlorides with ammonia do not give the simple compounds $R_2Si(NH_2)_2$, unless the alkyl group is bulky, but instead cyclic compounds, $(R_2SiNH)_x(x=3,4)$(87) are formed. Diphenylsilyl chloride also gives the trimer, $(Ph_2SiNH)_3$(88) when treated with ammonia in toluene. Substitutions at the nitrogen atom limits polysilazane formation so that in the reaction of methylamine and dimthylsilyl chloride (89), $Me_2Si(NHMe)_2$ is the main product along with small amounts of $(Me_2SiNMe)_x(x=3,4)$ and a linear polymer $MeNH{-}SiMe_2{-}NMe{-}SiMe{-}NHMe$. As the size of the alkyl group on nitrogen increases, these compounds become more stable to condensation. Thus, $Me_2Si(NHEt)_2$ is stable to distillation whereas $Me_2Si(NHMe)_2$ rapidly decomposes on boiling to give the tri and tetrameric cyclic compounds(89).

Products derived from thermal condensation of some pentavalent phosphorus compounds have been dealt with in the general survey and more examples could be cited. On the other hand, condensation reactions involving tervalent phosphorus-nitrogen systems are little known being limited to the reaction of Ph_2PNHEt giving $(Ph_2P)_2NEt$ on heating to 200° under reduced pressure and the condensation of $P(NHMe)_3$ to give $P_4(NMe)_6$. Ewart(54) studied the reaction of dichlorophenylphosphine and ethylamine in an attempt to isolate cyclic systems of the type $(PhP\text{-}NEt)_x$ from condensation of the intermediate $PhP(NHEt)_2$. This intermediate was never isolated, but on heating the crude reaction product at 220° in an evacuated sealed tube for ten days a viscous brown oil was isolated, the analytical figures of which indicated a formula of $(PhP\text{-}NEt)_3$ although no further confirmation was obtained.

Since bis(alkylamino)phenylphosphines had become available in a pure form, it was of interest to see whether these compounds would undergo thermal condensation to give products analogous to those formed with the corresponding silicon-nitrogen compounds, i.e. linear polymers,

$RNH(PhP\text{-}NR)_x\text{-}PPh\text{-}NHR$ (x=1,2,3---)

or cyclic systems,

$(PhP\text{-}NR)_x$ (x=2,3,4---).

In view of the reactivity of these compounds to atmospheric oxidation and hydrolysis, it was decided to heat them in an evacuated sealed tube in preference to refluxing them in a high boiling solvent such as nitrobenzene sym.tetrachloroethane or naphthalene.

RESULTS AND DISCUSSION.

The first attempt to effect thermal condensation of a bis(alkylamino)phenylphosphine was carried out using bis(isopropylamino)phenylphosphine, $PhP(NHPr^i)_2$, contained in an evacuated sealed tube. This tube was heated at 180° for 24 hours after which time it was found that the original clear liquid had turned a pale yellow but on cooling, this yellow colour appeared to be discharged and when at room temperature, a white crystalline solid (needles) crystallised from the liquid. On opening the tube, a distinct smell of amine was noticed. The solid product was filtered off under a stream of dry nitrogen and then sublimed at 115° (oil bath)/10^{-3}mm.to give white crystals (prisms) which were identified by their i.r. spectrum and melting point as bis(isopropylamino)phenylphosphine oxide. Isolation of the oxide was very surprising since the aminophosphine had been freshly distilled into the tube which was then sealed immediately while still under vacuum. The ingress of oxygen must therefore have occurred due to a fault in the distillation process or during filtration and so rigorous precautions were taken to exclude oxygen from all subsequent reactions.

Effect of heat on Bis(ethylamino)phenylphosphine. PhP(NHEt

As mentioned previously, bis(ethylamino) dimethylsilane does not condense to form ring compounds as readily as bis(methylamino)dimethylsilane due to the size of the aliphatic group attached to nitrogen. Therefore, further attempts at thermal condensation of bis(isopropylamino)phenylphosphine were temporarily halted in favour of the ethyl analogue since it was thought that the less bulky -NHEt group would be more easily condensed than the $-\mathrm{NHPr}^{i}$ group.

The procedure adopted, before heating, was to distil a pure sample of $\mathrm{PhP(NHEt)_2}$ under reduced pressure into a weighed tube containing a sintered glass plate and then seal the tube while still under vacuum. This method ensured the exclusion of oxygen and water vapour, provided an exact weight of the sample used and enabled any solid formed during heating to be separated from the liquid present.

A tube containing the aminophosphine, which had been prepared in the above manner, was heated for 24 hours at 160° and centrifuged to ensure that all the liquid was at one side of the sintered plate. As before, the originally clear liquid had turned a pale yellow colour which appeared to discharge on cooling accompanied by the crystallisation of a white solid. When completely cool, the tube was upended and centrifuged, thus separating the solid from the liquid (which had a very pale yellow colour), and transferred to a dry box filled with nitrogen in which all subsequent operations were performed. The solid on removal from the tube appeared to be waxy, probably due to slight adherence of the liquid, melted over the range 92-127^{o} and had an i.r. spectrum similar to the starting material apart from a new broad peak centred at 1181cm^{-1}. Attempts to recrystallise the solid from organic solvents failed since it was soluble in cold benzene, pyridine, dimethylformamide, tetrahydrofuran, chloroform and alcohols and other solvents, such as cyclohexane and diethylether, caused transformation of the material into a viscous white oil. With cold water,the solid dissolved slowly giving an alkaline solution (pH.10) which on heating gave off an alkaline vapour with an odour characteristic of amine leaving a neutral solution. Evaporation of this solution to dryness left a white solid which was recrystallised from petroleum ether 60-80 to give white crystals which were identified as bis(ethylamino)phenylphosphine oxide. The oxide was also obtained from the solid by treating it with 2M sodium hydroxide to yield crystals of the oxide on standing.

From the above evidence, oxide formation with water accompanied by amine elimination, the white solid appeared to be a phosphazene of formula

$HN{=}P(Ph)(NHEt)_2$ or $EtN{=}P(Ph)(NHEt)_2$

Since a molecular weight determination failed to distinguish between these two compounds, the volatile component from the reaction with water was steam distilled onto concentrated hydrochloric acid which on evaporation to dryness left a white solid. This was identified as ethylammonium chloride showing the compound to be, 2,2 bis-(ethylamino)2phenyl lethylphosphazene, $EtN{=}P(Ph)(NHEt)_2$. A quantitative yield of the oxide was obtained on hydrolysis of the phosphazene according to the following equation

$$EtN{=}PPh(NHEt)_2 + H_2O \longrightarrow EtNH_2 + O{=}PPh(NHEt)_2$$

which gives further confirmation of the structure.

Purification of the phosphazene was effected by repeated sublimation at 90° (oil bath)/10^{-3}mm. but the material obtained still melted over the range 110-122° (sealed tube) and analytical figures were disappointing, falling between the phosphazene and the oxide probably due to hydrolysis during the analytical procedure.

Identification of the white solid as a phosphazene enables explanations to be given for earlier observations. Thus, the peak at 1181cm.$^{-1}$ can now be ascribed to the P=N stretching frequency(30) and isolation of the oxide from heating bis(isopropylamin phenylphosphine must be due to hydrolysis of the phosphazene of this compound during the filtration stage, despite attention to this point in the experimental procedure.

The formation of 2,2 bis(ethylamino)2phenyl lethyl phosphazene as a product of heating bis(ethylamino)-phenylphosphine was surprising in the light of earlier discussion and seemed indicative of a rearrangement reaction. Therefore the filtered liquid from which the phosphazene had been removed was investigated in order to find further products of this rearrangement.

On standing, a pale yellow crystalline solid precipitated from the filtered liquid and was identified as the tetramer of cyclophenylphosphine, $(PhP)_4$, (See Appendix 3). Several experiments were carried out in which the phosphazene formed from heating $PhP(NHEt)_2$ was isolated and the remaining liquid treated with alcohol in order to precipitate all the cyclophenylphosphine. It was found that a 1:1 relationship existed between the molar quantaties of the phosphazene and cyclophenylphosphine. (The results shown in Table 6 show a slightly greater preponderance of the phosphazene but this is attributed to incomplete separation of the attendant liquid). The equation for the rearrangement of $PhP(NHEt)_2$ on heating may now be written as

$$2PhP(NHEt)_2 \longrightarrow \tfrac{1}{4}(PhP)_4 + EtN{=}P(Ph)(NHEt)_2$$

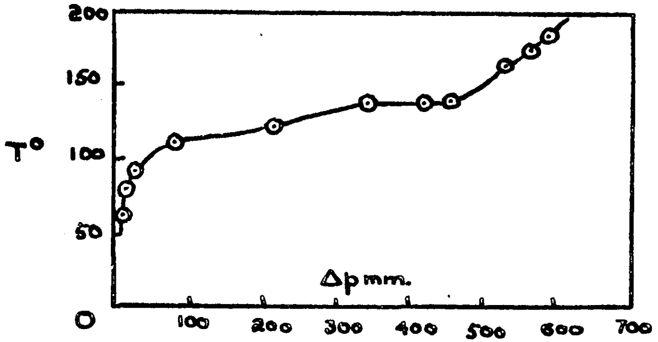
which, for completion, requires that one molecule of ethylamine be liberated in the reaction. By attaching a side arm with a break seal to the reaction tubes it was possible to quantitatively isolate the volatile component which was identified as ethylamine. The molar ratio of ethylamine to cyclophenylphosphine and the phosphazene was always greater than one indicating that along with the rearrangement of $PhP(NHEt)_2$, which proceeds according to the equation

$$2PhP(NHEt)_2 \longrightarrow \tfrac{1}{4}(PhP)_4 + EtN{=}P(Ph)(NHEt)_2 + EtNH_2$$

another reaction was also taking place.

The conditions and limits of formation of 2.2 bis(ethylamino)2phenyl lethylphosphazene

Three tubes containing $PhP(NHEt)_2$ were heated at 80°, 110° and 142° respectively. Solid appeared in the tube at 142° after 19¼ hours and the amount continued to increase during frequent observations made up to 51¾ hours but the other tubes showed no signs of depositing solid even on cooling to -78°. Heating at these temperatures was continued for a further 72 hours after which time the tube at 110° deposited a small amount of solid while the solid in the tube at 142° had decreased slightly. The most suitable temperature for phosphazene formation must occur when ethylamine liberation is at a maximum. By attaching a manometer to the tube and measuring the amount of ethylamine lost at varying temperatures the following graph was obtained,



indicating that ethylamine is lost most readily at temperatures between 125° and 145°. Thus, the aminophosphazene does not form to any great extent below 110° but between 125° and 145° formation is very rapid. At temperatures above 145° ethylamine liberation falls off and heating for longer than 24 hours above 170° produced red liquids from which only small amounts of solid precipitate.

The effect of near constant temperatures and varying time factors on the quantity of phosphazene producedis summarised in Table 3.

TABLE 3.

Tube No.	Temp. °C.	Time Hrs.	Molar Ratio $EtN{=}P(Ph)(NHEt)_2 : PhP(NHEt)_2$	Colour of Liquid.
1	142-148	48	1 : 7.23	Very Pale Yellow
2	142-148	96½	1 : 5.56	Pale Yellow
3	142	122¼	1 : 5.45	Pale Yellow
4	159-161	24		Pale Yellow
5	157-166	48	1 : 5.3	Yellow
6	158-163	72	1 : 5.77	Orange

Comparing tubes 1,2 and 3, it is seen that the amount of phosphazene increases on heating up to 96½ hours but thereafter, additional phosphazene formation is small. The amount of phosphazene produced in tube 4 was not measured but was observed to be less than in 5 and 6. In these last two tubes, phosphazene formation was more rapid than in the tubes 1, 2 and 3, which had been heated at about 10° lower, but the molar quantity was nearly the same. Therefore, in the temperature ranges studied, the ratio of aminophosphine to phosphazene reaches a limiting value of 5.3 : 1 which is not reduced on heating for further periods of time.

In tubes 4, 5 and 6, the intensity of the colour increased with increased times of heating and in particular, the amount of phosphazene in tube 6 was proportionally less than in tube 5 whilst the colour was more intense. It would therefore seem that the phosphazene itself takes part in further reaction probably involving amine elimination and the formation of a P-N skeleton containing a red chromophore. (It has already been stated that the amine liberated was greater than that required for the rearrangement equation).

The extent to which ethylamine is liberated and hence the amount of phosphazene formed was found to be dependent not only upon temperature and time but also on the volume of the reaction vessel. In most cases, the capacity of the tubes was between 10ml. and 30ml. but one reaction was carried out in an apparatus of volume, 240ml., which was gradually heated up to 160°. The ratio of ethylamine produced in this reaction to the amount of phosphazene was 1:1.74 which is far lower than was found with the tubes of smaller capacity. There is a slight possibility of experimental error (ca.10%)

in the quantity of the amine due to the method of calculation (all the apparatus was not at the same temperature) but despite this, the result shows that in previous reactions an equilibrium pressure was set up which limited phosphazene formation.

An amine-aminophosphine ratio of 1:2 is equivalent to complete rearrangement of the starting material to give the phosphazene and cyclophenylphosphine. The product from the reaction in the 240ml.vessel was yellow and some liquid still remained and therefore, condensation reactions other than the rearrangement had taken place. Results have shown that complete rearrangement is impossible and will be discussed later.

The effect of heat on bis(isopropylamino)phenylphosphine. $PhP(NHPr^{i})_2$

The white solid obtained on heating bis(isopropylamino)phenylphosphine at 138°-144° for 90 hours was identified as 2,2bis(isopropylamino) 2phenyl 1 isopropylphosphazene by hydrolysing it to isopropylamine and bis(isopropylamino)phenylphosphine oxide. As before, the phosphazene was purified by sublimation giving white crystals at 110°-115° (oil bath)/10^{-3}mm. which analysed correctly for

$Pr^{i}N{=}P(Ph)(NHPr^{i})_{2}$.

It was established that formation of the phosphazene followed the same reaction scheme as the ethyl analogue, i.e.

$$2PhP(NHPr^{i})_{2} \xrightarrow{140^{\circ}} \tfrac{1}{4}(PhP)_{4} + Pr^{i}N = P(Ph)(NHPr^{i})_{2} + Pr^{i}NH$$

but again, the amount of isopropylamine was greater than that required for the above equation.

Comparative quantities of the phosphazene produced to the aminophosphine after heating over a temperature range of 137°-148° is given in Table 4.

Table 4.

Tube No.	Temp. °C.	Time Hrs.	Molar Ratio $PhP(NHPr^{i})_{2}$ = $Pr^{i}N{=}PPh(NHPr^{i})_{2}$
1	138-144	90	9.79 : 1
2	140-147	116½	9.06 : 1
3	140-145	163	8.1 : 1

The quantity of phosphazene increases steadily with the duration of heating indicating that the temperatures used were below those required for maximum phosphazene formation. The molar ratios of phosphazene to aminophospine are far greater than those in the ethyl analogue at similar temperatures and this could therefore be attributed to the size of the isopropyl group inhibiting the mechanism by which these P=N compounds are formed.

Effect of heat on Bis(tert.butylamino)phenylphosphine.PhP(NHBu^t)

Only a preliminary investigation was carried out as to the effect of heat on this aminophosphine and, unfortunately, very few quantitative details are available. Despite this, sufficient evidence was collected to show that this compound behaves differently from those discussed above.

The white cyrstalline solid isolated from heating bis(tert.butylamino)phenylphosphine for 307 hours at 142°-144° had a melting point of 299° and the i.r. spectrum showed the presence of P=N (1204cm.$^{-1}$) and bonded NH(3150cm.$^{-1}$) groups. The solid was insoluble in cold water but on heating to 60° it dissolved to give a solution of pH8. Refluxing this solution for two hours failed to change its pH and no solid was formed but on adding 5M sodium hydroxide, followed by a further hour's refluxing, a white solid precipitated and this was identified as bis(tert.butylamino)phenylphosphineoxide. However, under these conditions the compound appeared to have decomposed since a black amorphous material was isolated along with the oxide and a more convenient method of hydrolysis was to dissolve the solid in alcohol and reflux with very dilute sodium hydroxide from which a pure sample of the oxide was obtained. Insufficient material was available to isolate the remaining hydrolysis product but from the i.r. evidence and the production of the oxide on hydrolysis, the compound was assumed to be 2,2bis(tert.butylamino) 2phenyl 1 tert.butylphosphazene, $Bu^tN=P(Ph)(NHBu^t)_2$.

The formation of tertiary butylamine as one of the reaction products on heating this aminophosphine was established but addition of alcohol to the filtered liquid failed to produce cyclophenylphosphine and therefore it is impossible to represent this reaction by an equation.

This phosphazene, unlike the others which were isolated, appeared during the heating process and cooling of the solution failed to give a further precipitate. However, after standing for three months, more solid could be seen in the liquid but even then, the total amount produced was far less than in the other two aminophosphines studied. This was quantitatively confirmed since the ratio of amine to aminophosphine was 1:22, about three times greater than with $PhP(NHPr^i)_2$ and six times greater than $PhP(NHEt)_2$. The colour of the filtered liquid was a deep orange and is interesting in view of the extent to which rearrangement has taken place and the temperature involved. Since 73% of the starting material was recovered unchanged this colour must represent a small proportion of the products from the heating process.

Properties of 2.2bis(alkylamino)2phenyl 1 alkylphosphazene

The phosphazenes isolated were all white crystallin solids of formula $RN{=}P(Ph)(NHR)_2$ where $R{=}Et, Pr^i, Bu^t$. The ethylphosphazene was found to be monomeric and, since dimerisation requires the substituents of phosphorus to be electron withdrawing, as in $Cl_3P{=}NMe$(90), the other phosphazenes were also assumed to be monomers. Apart from the butylphosphazene, these compounds could be hydrolys by water to give the corresponding aminophosphine oxides and the amine. The difficulty experienced in hydrolysing the tertiary butylphosphazene could be due to steric shielding of the phosphorus centre or to the formation of a salt $\left[PhP(NHBu^t)_3\right]^+OH^-$ and this latter suggestion might account for the decomposition on refluxing with sodium hydrozide since there would be three equivalent P-N bonds capable of being broken. In general, the ease with which these compounds hydrolyse is $Et > Pr^i \gg Bu^t$.

The strength of the P=N bond in these phosphazenes will increase with the amount of p_π ——d_π bonding from nitrogen to phosphorus which is facilitated by increasing the positive charge on phosphorus. Therefore, in the phosphazenes $EtN{=}PPh_3$ and $EtN{=}PMe_3$, E(P=N) is 98.4kcal. and 69.7kcal. respectively(91), the latter value being low on account of the inductive effect of the methyl groups. With -NHR groups attached to phosphorus, the inductive effect of R, which will be transmitted, to the phosphorus atom via nitrogen decreases in the order $Et > Pr^i \gg Bu^t$ so that the positive charge on phosphorus where $R{=}Bu^t$ will be greater than with $R{=}Pr^i$ or Et. Thus, the P=N bond in the butylphosphazene will be stronger than in the other two compounds and this is reflected by the high P=N stretching frequency at 1204cm^{-1}.as compared to 1170cm.$^{-1}$ and 1180cm.$^{-1}$ for the isopropyl and ethylphosphazenes respectively.

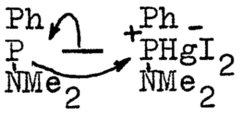
Mechanisms for the formation of 2.2bis(alkylamino) 2phenyl 1 alkylphosphazenes.

Explanation of the rearrangement of bis(alkylamino) phenylphosphines on heating to give cyclophenylphosphine and a phosphazene is difficult since no kinetic studies have been carried out on tervalent phosphorus-nitrogen systems. However, three possible mechanisms are proposed; a free radical reaction and two ionic reactions involving migrations.

The formation of cyclophenylphosphine from the reaction of phenyl(dimethylamino)iodophosphine and mercury.

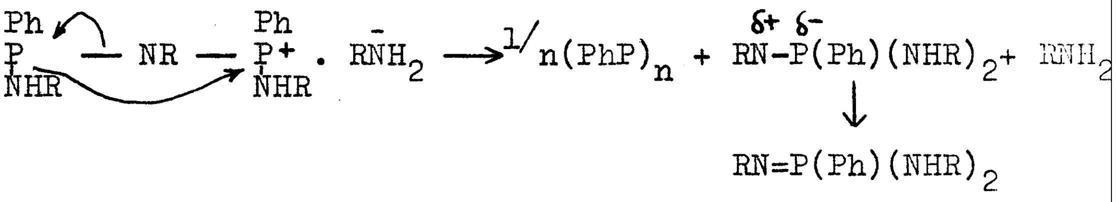
$$2Ph(NMe_2)PI + Hg \longrightarrow {}^{1}/n(PhP)n + PhP(NMe_2)_2HgI_2$$

has already been mentioned. The mechanism given by Nöth and Vetter for this reaction involves initial formation of the diphosphine, in the form of a mercury(II)iodide complex, which then undergoes rearrangement.



$$\overset{Ph}{\underset{NMe_2}{P}}\;\overset{+Ph\,-}{\underset{NMe_2}{PHgI_2}} \longrightarrow {}^{1}/n(PhP)n + PhP(NMe_2)_2HgI_2.$$

For a similar reaction to take place with the bis(alkylami phenylphosphines it would be necessary for one molecule of amine to be eliminated between two molecules of the aminophosphine to form a complex of the type $\text{Ph(NHR)P-NR-P(Ph)(NHR)}.\text{RNH}_2$ which would then rearrange to give the required products



$$\underset{\text{NHR}}{\overset{\text{Ph}}{\text{P}}} - \text{NR} - \underset{\text{NHR}}{\overset{\text{Ph}}{\text{P}^{+}}} \cdot \overset{-}{\text{R}}\text{NH}_2 \longrightarrow {}^{1}/n(\text{PhP})_n + \overset{\delta+}{\text{R}}\overset{\delta-}{\text{N}}\text{-P(Ph)(NHR)}_2 + \text{RNH}_2$$

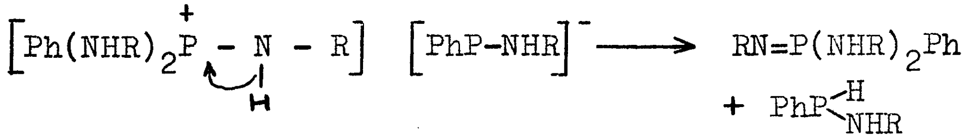
$$\downarrow$$

$$\text{RN=P(Ph)(NHR)}_2$$

A mechanism of this type would involve a negative charge on nitrogen and is therefore unlikely. A more attractive ionic scheme is one where the phosphorus atom of one molecule attacks the nitrogen atom of another to form an ionic complex

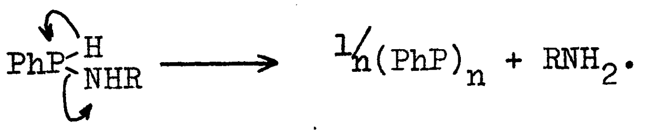
$$(\text{RNH})_2\text{PhP}{:}\ \text{RNH-P(Ph)(NHR)} \longrightarrow \left[\text{PhP(NHR)}_3\right]^{+}\left[\text{PhPNHR}\right]^{-}$$

which rearranges to give the phosphazene



$$\left[\text{Ph(NHR)}_2\overset{+}{\text{P}} - \underset{\underset{\text{H}}{|}}{\text{N}} - \text{R}\right]\ \left[\text{PhP-NHR}\right]^{-} \longrightarrow \text{RN=P(NHR)}_2\text{Ph} + \text{PhP}{<}\begin{array}{l}\text{H}\\ \text{NHR}\end{array}$$

The remaining rearrangement products are obtained due to the instability of the phosphine, PhP(H)(NHR), which disproportionates to give cyclophenylphosphine and amine,



$$\text{PhP}{<}\begin{array}{l}\text{H}\\ \text{NHR}\end{array} \longrightarrow {}^{1}/n(\text{PhP})_n + \text{RNH}_2.$$

This mechanism is in accordance with the present theory of bonding in these aminophosphines since it involves electron donation from phosphorus to a nitrogen atom on which the electron density has been reduced by p_{π} ——— d_{π} back bonding. Also, it explains why the amount of phosphazene produced should decrease in the order $Et > Pr^{i} \gg Bu^{t}$ for as R become more bulky, both the phosphorus and nitrogen atoms will be sterically shielded thus inhibiting the reaction. In the case of the tert.butylphosphine, where no cyclophenylphosphine was isolated it was thought that the size of the alkyl group might stabilise the phosphine $PhP(H)(NHBu^{t})$ but an i.r. spectrum of the alcohol solution of the filtered liquid failed to show the presence of a P-H group and this problem still remains unanswered.

In considering a free radical mechanism, it is difficult to predict the initial bond fission since reliable data on bond dissociation energies in aminophosphine systems was not found in the literature. However, since the products of the rearrangement showed no signs of phenyl migration, the initiation step was presumed to be the homolytic fission of a P-N bond.

$$\mathrm{PhP(NHR)_2} \longrightarrow \mathrm{Ph\dot{P}\text{-}NHR} + \mathrm{\dot{N}HR}$$

Formation of a di-radical is not expected since the species $\mathrm{Ph\dot{P}\text{-}NHR}$ would be resonance stabilised due to the phenyl group. Combination of four $\mathrm{Ph\dot{P}\ NHR}$ radicals leads to the formation of the tetrameric cyclophenylphosphine according to the scheme in Figure 4. The eight $\mathrm{\dot{N}HR}$ radicals produced in the reaction,

$$\begin{tikzcd}
\mathrm{4PhP(NHR)_2} \arrow[r] & \mathrm{4Ph\dot{P}\ \ NHR} \arrow[d] & + \ \mathrm{4\dot{N}HR} \\
& \mathrm{(PhP)_4} & + \ \mathrm{4\dot{N}HR}
\end{tikzcd}$$

now combine with four molecules of the aminophosphine to give ethylamine and the phosphazene

$$\begin{tikzcd}
\mathrm{PhP(NHR)_2} + \mathrm{\dot{N}HR} \arrow[r] & \mathrm{(Ph)(NHR)\ddot{P}} \overset{\curvearrowright}{-} \mathrm{\dot{N}R} + \mathrm{RNH_2} \arrow[d] \\
\mathrm{(Ph)(NHR)_2P{=}NR} & \mathrm{(Ph)(NHR)\dot{P}{=}NR} \arrow[l, "\mathrm{\dot{N}HR}"']
\end{tikzcd}$$

The oxidation step is explained as a radical stabilisation and the overall equation may be written as,

$$\mathrm{8PhP(NHR)_2} \longrightarrow \mathrm{(PhP)_4} + \mathrm{4RN{=}P(Ph)(NHR)_2} + \mathrm{4RNH_2}$$

thus attaining the correct stoichiometry of the reaction.

Of the three proposed mechanisms, the free radical reaction is most favoured since it accounts for more of the experimental observations. The failure to isolate cyclophenylphosphine from heating the tertiary butylaminophosphine is probably due to steric factors inhibiting ring formation but, instead, giving rise to bi- and triphosphines of the type, $\mathrm{(NHBu^t)(Ph)P{-}P(Ph)(NHBu^t)_2}$ or $\mathrm{(Ph)(NHBu^t)P{-}P(Ph){-}P(Ph)(NHBu^t}$ On refluxing bis(ethylamino)phenylphosphine at 142° under reduced pressure for five days, with removal of the volatile component as formed, no precipitation of the aminophosphazene occurred but ethylamine was isolated from the vacuum cold traps. Therefore, if $\dot{\mathrm{N}}\mathrm{HR}$ radicals are produced in this reaction combination with a hydrogen radical is preferred to self condensation which would give hydrazines.

There is an obvious need for further experimental evidence before any of the above reactions may be adopted as the correct mechanism. The inclusion of a free radical inhibitor during the heating process would establish whether radicals were present but care is needed to ensure that the inhibitor does not react with the aminophosphine. A more convenient method to show the presence of radicals would be the use of E.S.R. techniques. Useful information may also be obtained by carrying out the condensation in a solvent of high dielectric constant such as nitrobenzene although this could give rise to an entirely different class of compound.

In all the experiments where amine was removed from the system, the amount obtained was always greater than that required to satisfy the rearrangement equation and it seems reasonable to suggest that this was due either to further reaction of the phosphazene, involving amine elimination, or to condensation of the aminophosphine. In order to characterise the products resulting from this excess of amine the liquids, isolated after removal of the phosphazene, were investigated.

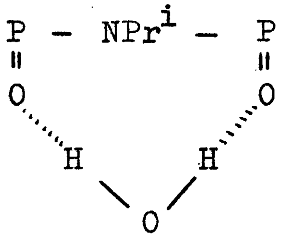
From the total amount of amine isolated in these reactions it was obvious that some of the aminophosphine had not reacted and this was confirmed by isolation of the diethyl ester of phenylphosphonous acid from an alcoholic solution of one of these liquids,i.e.

$$PhP(NHR)_2 + 2EtOH \longrightarrow PhP(OEt)_2 + 2RNH_2$$

A convenient way to remove this unreacted starting material, in view of the sensitivity of these compounds towards moisture, is by conversion into a stable solid adduct such as the oxide or sulphide. Unfortunately no solvent could be found to remove the cyclophenylphosphine from these liquids which did not react with the aminophosphine present and therefore, with excess oxygen or sulphur the polymers $(PhP(O)O)_n$ and $(PhP(S)S)_n$ would be produced(92) but in the reactions described below, these compounds were not isolated.

Refluxing the liquid, obtained after heating bis(ethylamino)phenylphosphine, with sulphur gave the aminophosphine sulphide, corresponding to 16.03% of the starting material, and a brown waxy solid which could not be recrystallised. Although the quantity of ethylamine liberated in this reaction was unknown, a rough estimate could be made by comparison to those reactions in which similar amounts of the phosphazene had been produced and the ethylamine isolated. From this calculation, and assuming that one mole of the excess amine originated from two moles of the aminophosphine, the amount of sulphide isolated should have been equivalent to at least 30.5% of the starting material. In view of this discrepancy, further investigation along these lines was abondoned in favour of the liquids obtained on heating bis(isopropylamino)phenylphosphine since the oxide of this compound is insoluble in cold benzene and could thus be easily isolated.

Treatment of one of these liquids in benzene with excess ozone gave 57.8% of unreacted aminophosphine in the form of the oxide. Removal of the benzene left a brown waxy solid from which a white solid was obtained on treatment with aqueous alcohol. The i.r. spectrum of this white solid showed the presence of bonded and non-bonded NH groups (3206, 3292, 3430 and 3475cm^{-1}), A P=O group (1218 and 1193cm^{-1}.) and water (1659cm^{-1}.) and from the analytical data, this compound was assumed to be bis(isopropylaminophenylphosphinyl) isopropylamine monohydrate $[\mathrm{Ph(NHRr^{i})P(O)}]_2\mathrm{NPr^{i}}\ \mathrm{H_2O}$. Recrystallisation from nitromethane failed to remove the water molecule which must therefore be firmly bound probably due to a favourable orientation of the phosphoryl groups.

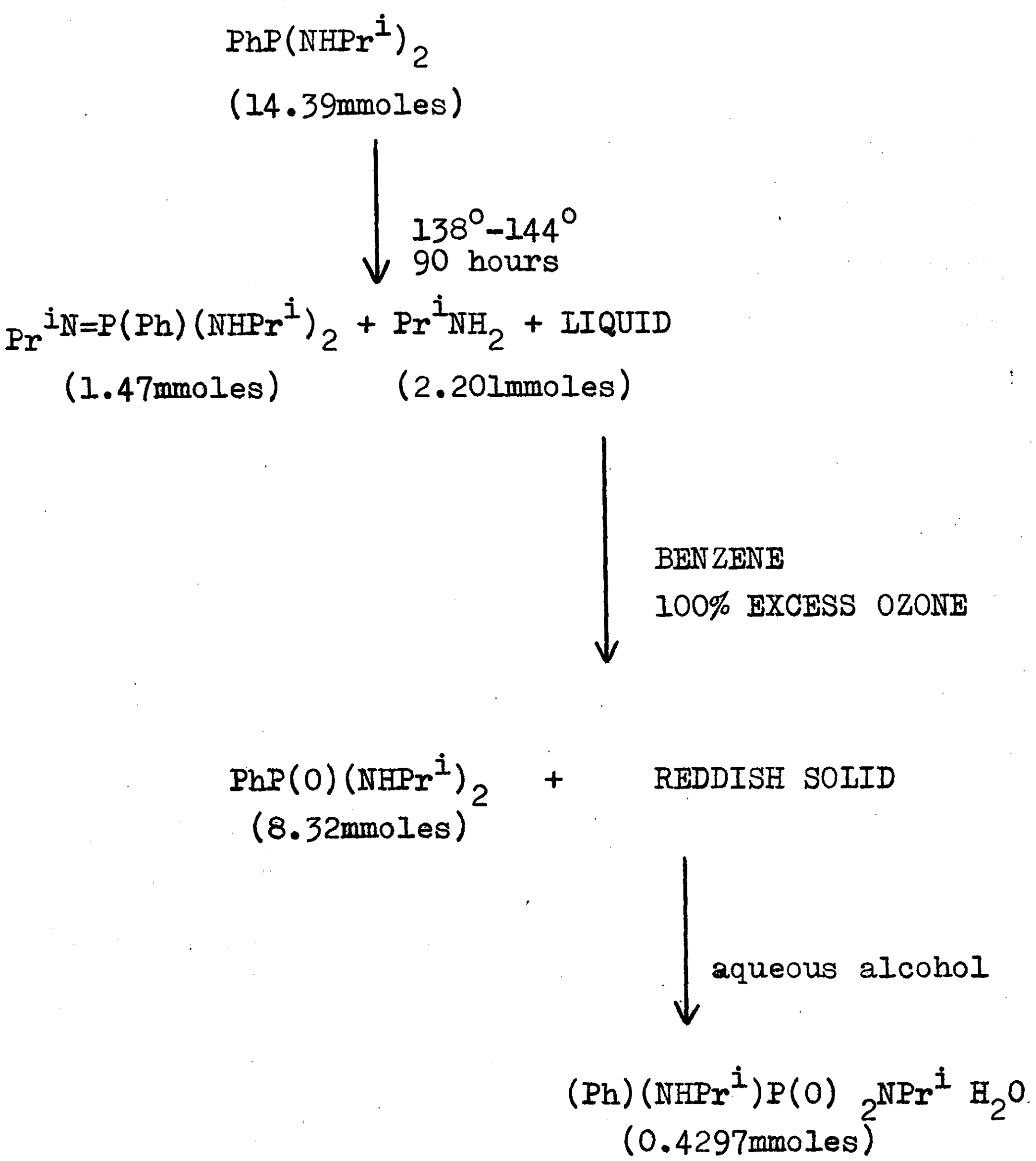


The formation of this compound must arise from the elimination of one molecule of isopropylamine between two molecules of the aminophosphine,

$$2\mathrm{PhP(NHPr^{i})_2} \xrightarrow{\Delta H} \mathrm{(Pr^{i}NH)PhP - NPr^{i} - PPh(NHPr^{i})} + \mathrm{Pr^{i}NH_2}$$

followed by oxidation and hydration. In terms of a free radical mechanism it may be explained by the following scheme,

FIGURE 5.


$PhP(NHPr^i)_2$
(14.39mmoles)
138^o-144^o
90 hours
$Pr^iN{=}P(Ph)(NHPr^i)_2$ + Pr^iNH_2 + LIQUID
(1.47mmoles)
(2.201mmoles)
BENZENE
100% EXCESS OZONE
$PhP(O)(NHPr^i)_2$ + REDDISH SOLID
(8.32mmoles)
aqueous alcohol
$(Ph)(NHPr^i)P(O)\ _2NPr^i\ H_2O$
(0.4297mmoles)

$$\mathrm{PhP(NHPr^{i})_2} \longrightarrow \mathrm{Ph\dot{P}NHPr^{i}} + \mathrm{\dot{N}HPr^{i}}$$
$$\mathrm{PhP(NHPr^{i})_2} + \mathrm{\dot{N}HPr^{i}} \longrightarrow \mathrm{PhP(NHPr^{i})\dot{N}Pr^{i}} + \mathrm{Pr^{i}NH_2}$$
$$\mathrm{Ph\dot{P}NHPr^{i}} + \mathrm{PhP(NHPr^{i})\dot{N}Pr^{i}} \longrightarrow \mathrm{(Pr^{i}NH)PhP\text{-}NPr^{i}PPh(NHPr^{i})}$$

The complete range of products obtained from heating bis(isopropylamine)phenylphosphine is shown in figure 5. The quantity of these products account for all but 2.18mmoles (0.4274g) or 15.2% of the starting material and most of this deficit (ca.1.67mmoles) is probably due to incomplete isolation of the unreacted starting material. The amount of $\left[\mathrm{Ph(NHPr^{i})P(O)}\right]_2\mathrm{NPr^{i}.H_2O}$ isolated was equivalent to 0.4846mmole of the excess amine (0.731mmole) but it is possible that more of this material was present. However, some of this excess amine must be due to a condensation process involving the phosphazene itself since this seems the only way in which to explain the yellow to orange colour observed in these liquids.

A similar reaction pattern to the one above is proposed to account for the excess ethylamine isolated on heating bis(ethylamino)phenylphosphine but with the tertiary butyl analogue the picture is less clear. Ozonisation of the liquid obtained from heating the tertiary butylaminophosphine gave 73.2% of the aminophosphine as the oxide but further investigation was terminated at this point.

Under the conditions studied, two separate reactions take place on heating bis(isopropylamino)-phenylphosphine and bis(ethylamino)phenylphosphine; these are a rearrangement and an aminophosphine condensation with predominance of the former. The original object of this work, which was to prepare condensed aminophosphine systems has therefore been partially attained but the extent is disappointing. However, the results have shown that, unlike the bis(alkylamino)dimethylsilanes, aminophosphines of the type $PhP(NHR)_2$ do not readily undergo thermal self condensation. This difficulty may be due to the phenyl group attached to phosphorus for if these reactions proceed by a free radical mechanism the $Ph\dot{P}NHR$ radical would be highly resonance stablilised and therefore comparatively unreactive. It might be expected that changing the phenyl for a methyl group, where no resonance stabilisation is possible, would facilitate condensation.

The failure to effect complete transformation of aminophosphines into the various reaction products was due to the volume of the reaction vessel employed. This could be overcome by using a vessel of larger capacity and it would be interesting to see the quantitative relationship between the competing reactions.

[illegible] were investigated and it was found that althou [illegible] quantities [illegible] liberated at temperatu low as 60° none of the above products were for 110°. Heating above 170° for prolonged perio red products which were presumed to arise from reaction of the phosphazene but these were not The extent of the phosphazene formation decrea order $Et > Pr^i \gg Bu^t$ and is dependent upon temper time of heating and the volume of the reaction

The rearrangement, where R=Et and Pr^i, is accompanied, to a lesser extent by another rea which involves elimination of one molecule of between two molecules of the aminophosphine to

SUMMARY

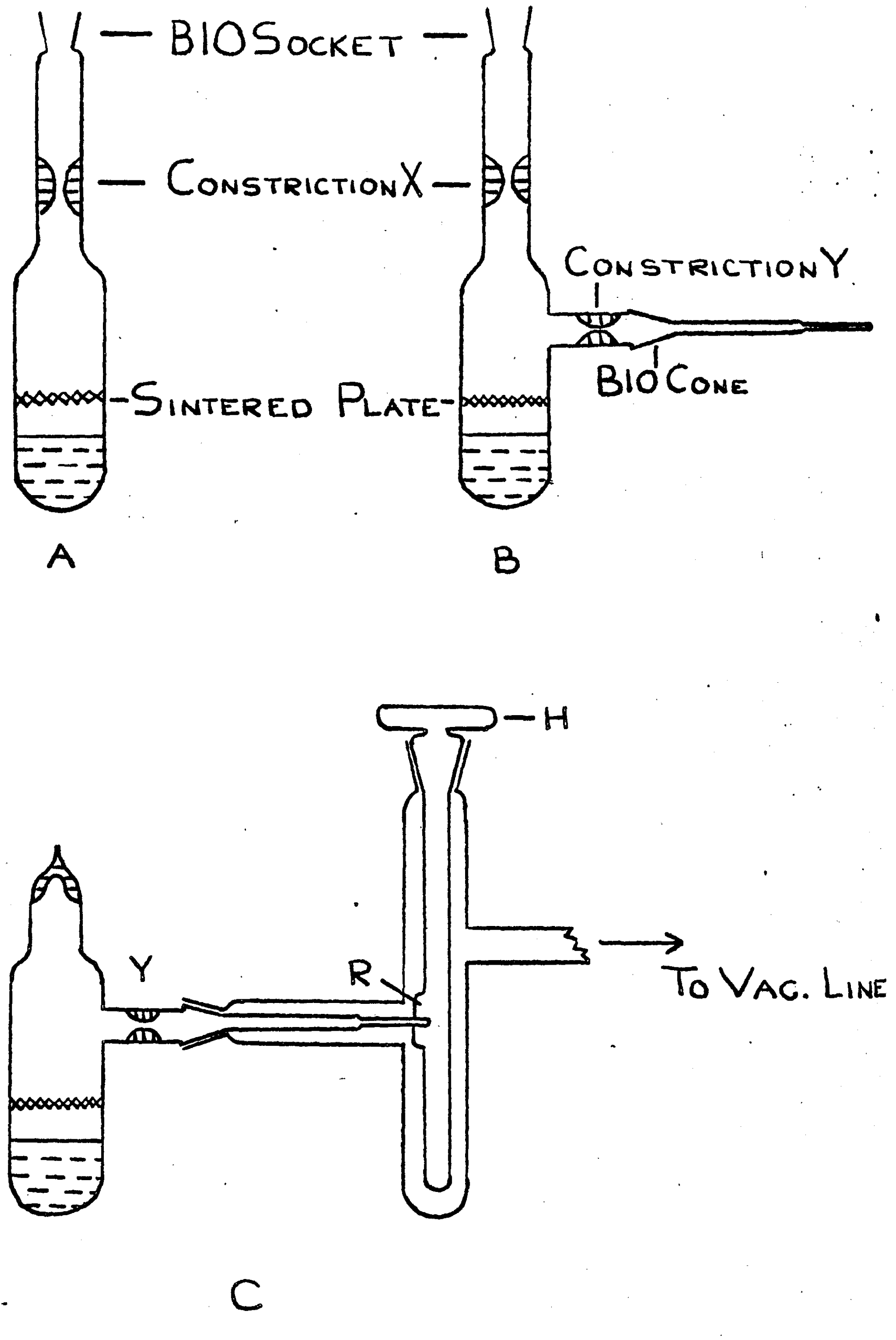
Heating compounds of the type $PhP(NHR)_2$ where $R=Et$, Pr^i and Bu^t in evacuated sealed tubes has given rise to a rearrangement which may be represented by the following equation.

$$2PhP(NHR)_2 \xrightarrow{\Delta H} {}^1/_n(PhP)_n + RN{=}P(Ph)(NHR)_2 + RNH_2$$

but where $R=Bu^t$, no cyclophenylphosphine was isolated. The conditions under which this rearrangement occurred were investigated and it was found that although small quatities of amine were liberated at temperatures as low as 60° none of the above products were formed below 110°. Heating above 170° for prolonged periods gave red products which were presumed to arise from further reaction of the phosphazene but these were not investigated The extent of the phosphazene formation decreases in the order $Et > Pr^i \gg Bu^t$ and is dependent upon temperature, time of heating and the volume of the reaction vessel.

The rearrangement, where $R=Et$ and Pr^i, is accompanied, to a lesser extent by another reaction which involves elimination of one molecule of amine between two molecules of the aminophosphine to give the compound $((NHR)\ PPh)_2NR$.

FIGURE 6.


B10 Socket
Constriction X
Constriction Y
B10 Cone
Sintered Plate
A
B
H
Y
R
To Vac. Line
C

EXPERIMENTAL

Preparation of samples prior to heating:- Bis(ethylamino)phenylphosphine was distilled under reduced pressure using a 7" Vigreux column and a fraction, b.p. 53-56°/10^{-3}mm. was collected in the reaction vessel which consisted of a tube containing a sintered glass plate (porosity 2). When this tube, shown in figure 6A, was a quarter full, it was sealed off at the constriction x while still under vacuum and weighed in order to obtain the amount of aminophosphine. The same procedure was adopted for bis(isopropylamino)phenylphosphine (b.p.52°/10^{-3}mm.) and bis(*tert*. buyylamino)phenylphosphine (64-65°/10^{-3}mm.).

Procedure for the removal of amine:- To remove the amine, the reaction vessel was modified as shown in figure 6B. After heating, the tube was attached to the apparatus shown in figure 6C and the whole system evacuated. The tube was then cooled to -180° and the rotating handle H turned until the raised piece of glass R broke the thin seal on the side arm. The tube was allowed to reach room temperature and then carefully heated to 60° to ensure complete removal of the amine which was condensed into a storage vessel. Constriction Y was now sealed and from the weight of this tube and the storage vessel, and average weight of the amine liberated was obtained.

The amines were identified by comparison of their i.r. spectra, taken in a 10cm. path length gas cell, to those of the known compound at the same pressure.

Isolation of the 2.2 bis(alkylamino)2phenyl 1.alkylphosphazenes

Immediately after heating, the tubes were centrifuged for half an hour to ensure that all the liquid was at one side of the sintered plate. In cases where the amine had been removed, the tubes were reheated till all the solid had dissolved and then centrifuged. When completely cool, the tubes were upended and centrifuged for two hours after which they were broken between the liquid and the sintered plate. The part containing the phosphazene was quickly weighed and then broken to remove the phosphazene. The weight of the empty pieces gave the amount of phosphazene produced.

Purification of the 2.2 bis(alkylamino)2phenyl 1.alkylphosphazenes:

On removal of the phosphazenes from the tubes, they were transferred to a dry box through which a stream of dry

TABLE 5:- Analytical and physical details of the 2.2 bis(alkylamino)2phenyl 1 alkylphosphazenes.

COMPOUND		EtN=P(Ph)(NHEt)	$Pr^iN=P(Ph)(NHPr^i)_2$	$Bu^tN=P(Ph)(NHBu^t)_2$
STATE		AMORPHOUS WHITE SOLID	WHITE CRYSTALLINE SOLID	WHITE CRYSTALLINE SOLID
SUBLIMATION TEMP.°/10^{-3}mm.		90-100	110-115	
m.p.°(SEALED TUBE)		110-122	135-138	299
CARBON%	FOUND	57.6	63.9	
	CALC.	60.3	64.0	
HYDROGEN%	FOUND	8.6	10.1	
	CALC.	9.6	10.0	
NITROGEN%	FOUND	16.3	15.0	11.2
	CALC.	17.6	15.0	13.3
PHOSPHORUS%	FOUND		11.0	
	CALC.		11.0	
MOLEC.WT.	FOUND	221		
	CALC.	239		

nitrogen was passing and thereafter, all operations involving transfer of these compounds from one vessel to another took place in the dry box. Purification of the phosphazenes was achieved by a series of sublimations in which any coloured residues were discarded. Analytical and physical details are given in table 5.

Hydrolysis of 2.2bis(ethylamino)2phenyl 1.ethylphosphazene with water and 2M sodium hydroxide:- The ethylphosphazene (0.1565g.,0.6488mmole) was added to water (25ml.) to give a cloudy solution of pH.10. On boiling the solution it became clear and an alkaline vapour was liberated (pH.10). Boiling was continued till the solution was neutral when it was evaporated to dryness under reduced pressure leaving a white solid (0.1408g., required 0.1375g.). Recrystallisation from petroleum ether 60-80 gave white needles m.p.70-72^{o} (Found: N 12.8. $C_{10}H_{17}N_2OP$ requires N, 13.2%; 13.2%; m.p.72-73^{o}). The i.r. spectrum of this compound was identical with that of bis(ethylamino)phenylphosphine oxide.

With cold 2M sodium hydroxide, the ethylphosphazene was initially insoluble but on standing turned into a colourless oil and then dissolved. After a period of time, white crystals precipitated from the solution which were identical with the oxide.

Ethylamine was isolated by steam distillation onto concentrated hydrochloric acid. The acid solution was then evaporated to dryness under reduced pressure and the white solid obtained recrystallised from an alcohol-ether mixture to give white crystals. These were identified by their i.r. spectrum and m.p.107° as ethylammonium chloride.

The same procedure of hydrolysis was adopted for the isopropyl and tertiary butylphosphazenes but in the later compound, hydrolysis was more difficult as has already been described in the text.

Isolation of cyclophenylphosphine:- The filtered liquid from the tubes was added to ethanol (30ml.). After about a minute, a pale yellow solid precipitated and was removed by filtration under a stream of dry nitrogen. The solid was recrystallised from methyl cyanide to give yellow crystals m.p.152-154° (Found: M(cryoscopically in benzene)462. $C_{24}H_{20}P_4$ requires M 432). The i.r. spectrum of this compound was identical to that given by Henderson et.al.(93) for cyclophenylphosphine.

The quantitative results obtained from heating bis(ethylamino)phenylphosphine and bis(isopropylamino) phenylphosphine are given in tables 6 and 7 respectively.

Bis(<u>tert</u>.butylamino)phenylphosphine (5.9532g., 23.74mmoles) was heated for 307 hours at 142-144° and gave 0.0761g.of a volatile compound which was identified as tertiary butylamine from its i.r.spectrum. The molar ratio of the aminophosphine to the amine was 22:1.

0.2794g. (1.253mmoles)		
1.3567g. (8.233mmoles)		
1.9621g. (8.210mmoles)	0.7496g. ([illegible]mmoles)	
0.1269g. (0.7669mmoles)		[illegible]g (0.5667 mmoles)
0.3162g. (1.326mmoles)	0.3351g. (2.253mmoles)	0.4035g. (2.936 mmoles)
0.4269g. (2.046mmoles)	0.2118g. (1.361mmoles)	0.4362g. (3.517 mmoles)

rage weight.

TABLE 6.

TUBE NO.	TEMP. °	TIME HOURS	A $PhP(NHEt)_2$	B $EtN{=}P(Ph)(NHEt)_2$	C $(PhP)_4$	D $EtNH_2$	RATIO A : B : C : D
1	157-166	48½	1.4139g. (7.213mmoles)	0.3234g. (1.35mmoles)	0.1430g. (1.324mmoles)		5.33 : 1 : : 5.45 : 1.02: :
2	158-163	72	1.4146g. (7.233mmoles	0.2994g. (1.253mmoles)			5.77 : 1 : :
3	150-170	15	9.4716g. (48.32mmoles)	1.9687g. (8.239mmoles)			5.86 : 1 : :
4	150-170	18	9.5205g. (48.56mmoles)	1.9624g. (8.210mmoles)	0.7496g. (6.942mmoles)		5.92 : 1 : : 6.99 : 1.18: 1 :
5	142	122¼	0.7578g. (3.867mmoles)	0.1609g. (0.7068mmoles)		0.0246g (0.5467 mmoles)	5.45 : 1 : : 7.07 : 1.29: : 1
6	142-148	48	1.7998g. (9.183mmoles)	0.3169g. (1.326mmoles)	0.1353g. (1.253mmoles)	0.1135g.* (2.536 mmoles)	7.23 : 1 : : 7.33 : 1.06: 1 : 2
7	142-148	96½	2.1464g. (10.95mmoles)	0.4889g. (2.046mmoles)	0.2118g. (1,961mmoles)	0.1582g* (3.517 mmoles)	5.56 : 1 : : 5.58 : 1.04: 1 :1.8

* Average weight.

Table 7.

TUBE NO.	TEMP. °C	TIME HOURS	A PhP($NHPr^i$)$_2$	B Pr^iN=P(Ph)($NHPr^i$)$_2$	C (PhP)$_4$	D Pr^iNH_2	RATIO A : B : C : D
1	140-147	116½	4.0682g. (18.17mmoles)	0.5680g. (2.021mmoles)	0.1859g. (1.722mmoles)		9.059: 1 : : 10.6 :1.17: 1 :
2	140-145	163	8.0497g. (35.595mmoles)	1.2594g. 4.480mmoles)			8.1 : 1 : :
3	138-144	90	3.2223g. (14.39mmoles)	0.4130g. (1.470mmoles)		*0.1298g. (2.201 mmoles)	9.788 : 1 : :1.497

*Average Weight.

Investigation of the 'filtered liquid' after heating bis(ethylamino)phenylphosphine.

The term 'filtered Liquid' refers to the liquid obtained after removal of the phosphazene by filtration.

Reaction with sulphur:- The liquid from tube 2 in benzene (40ml.) was refluxed for 14 hours with sulphur (0.2748g.,8.563mmoles) under a stream of dry nitrogen. Removal of the benzene gave a brown waxy solid which on recrystallisation from alcohol gave a white solid (o.3106g.) m.p.84-85°. The i.r. spectrum of this compound was identical to that of bis(ethylamino)phenylphosphine sulphide (m.p.84-85°) and the weight obtained corresponds to 16.03% of the starting material.

Investigation of the 'filtered liquid' after heating bis(isopropylamino)phenylphosphine.

Reaction with alcohol:- After isolating cyclophenylphosphine from tube 1, by the addition of alcohol, the solvent was removed under reduced pressure to leave a pale yellow liquid. Distillation of this liquid gave a colourless fraction bp 44-46°/10^{-3}mm., the i.r.spectrum of which was identical to that of the diethyl ester of phenylphosphonous acid.

Reaction with ozone:- The liquid from tube 2 in benzene (30ml.) was treated with 100% excess of ozone. An exothermic reaction took place and a solid precipitated from the solution which was filtered off to give a white crystalline product (4.5035g.), m.p.158-160°. This solid was identified by its i.r. spectrum as bis(isopropylamino)phenylphosphine oxide and corresponds to 52.7% of the original starting material. On reducing the volume of the orange benzene solution, a further precipitate was obtained (0.5148g.) which recrystallised from alcohol gave a small amount of a white crystalline solid m.p.195-196°. (Found:N 9.3%).

The above procedure was adopted with the liquid from tube 3. The oxide isolated (2.0004g.) corresponded to 57.8% of the original starting material. Removal of the benzene solution under reduced pressure left a reddish-brown waxy solid which was dissolved in alcohol. Addition of water to the alcoholic solution caused a white solid to precipitate (0.1880g.) which was recrystallised from nitromethane to give white crystals, m.p.196°. (Found: C,57.6:H,8.0; N,9.5; P,14.1. $C_{21}H_{35}N_3O_3P_2$ requires, C,57.5; H,8.0; N,9.6; P,14.1%). The i.r. spectrum of this compound was identical to that of the similar compound found in tube 2.

CHAPTER II

Preparations of condensed aminophosphine systems

INTRODUCTION

Since tervalent phosphorus-nitrogen systems of the type (P-N $)_x$ or P-N(P-N$)_x$ -P-N (class III were not effectively produced by thermal condensation of the bis(alkylamino)Phenylphosphines other synthetic routes to these compounds were investigated.

The bis(alkylamino)phenylphosphines have two reactive protons attached to nitrogen and, it is therefore possible to increase the chain length or cause cyclisation by reacting these aminophosphines with mono- or dichloro tertiary phosphines. Thus, with a monochlorophosphine the compounds formed would be R_2P-NR-PPh-NHR or R_2P-NR-PPh-NR-PR_2 while with a dichlorophosphine, cyclic or condensed systems would result. This type of reaction involves the elimination of hydrogen chloride and therefore necessitates the use of a non-protonic base, such as triethylamine, to act as a hydrogen chloride acceptor. Another approach to this reaction would be the formation of the di-sodium or potassium derivative PhP(NRK$)_2$ which could then be reacted directly with the chlorophosphine thus eliminating sodium or potassium chloride.

The work presented in this chapter is a preliminary investigation as to the feasibility of the above synthetic methods for the preparation of condensed aminophosphines.

RESULTS AND DISCUSSION

Reaction of bis(ethylamino)phenylphosphine with elemental potassium:-

Wannagat and Niederprüm (132) found that the proton attached to nitrogen in hexamethyldisilazane could be replaced by an alkalii metal atom by refluxing the compound, in a suitable solvent, with phenyllithium, sodamide or elemental potassium. Using polar solvents such as diethylether, pyridine or tetrahydrofuran, the compounds isolated had associated with them variable quantities of the solvent. An attempt was therefore made to prepare the potassium derivative of bis(ethylamino)phenylphosphine by refluxing the aminophosphine with elemental potassium in tetrahydrofuran, which had been dried by passing it through an alumina column. The reaction was carried out under an atmosphere of dry nitrogen and after refluxing for six hours, the solution was a deep red and nearly all the potassium had disappeared. Removal of the solvent by freeze drying left a pale yellow solid which contained potassium, nitrogen and phosphorus. On exposure to the atmosphere the solid decomposed to an oil and was not investigated further. However, isolation of the derivative is unnecessary and positive results would probably have been achieved by addition of a chlorophosphine to the solution resulting in the elimination of potassium chloride and the production of a condensed aminophosphine.

Reaction of bis(ethylamino)phenylphosphine with Chlorodiphenylphosphine:-

This reaction was carried out in benzene under an atmosphere of dry nitrogen adding the aminophosphine to the chlorodiphenylphosphine in a 1:2 ratio: Excess triethylamine was used as a hydrogen chloride acceptor and filtration of the solution gave a near quantitative yield of triethylammonium chloride on the basis of complete replacement of the nitrogen protons by the Ph_2P- group. Removal of the benzene yielded a white waxy solid whichwas recrystallised from aqueous ethnol to give white crystals m.p.143-144°. This compound was identified as bis(Ndiphenylphosphino Nethylamino)phenylphosphine.

$$PhP(NHEt)_2 + 2Ph_2PCl + 2Et_3N \longrightarrow (Ph_2P(Et)N)_2PPh + Et_3NH^+Cl^-$$

Only a 37% yield of the pure compound was obtained, which was due to hydrolysis of the terminal P-N bonds during recrystallisation since diphenylphosphinic acid was also isolated.

The presence of three donor atoms in this aminophosphine is of interest from the point view of complex formation with transition metal atoms. The tertiary triphosphine $MeC(CH_2PPh_2)_3$ acts as a tridentate ligand replacing three carbonyl groups from molybdenum tungsten and chromium hexacarbonyl to give compounds of the type $M^{VI}(CO)_3\ MeC(CH_2PPh_2)_3$ (M=W, Mo, Cr.). Whether the aminophosphine will show similar behaviour will depend upon its steric arrangement but it could also act as a bidentate or bridging ligand. The possibility of complex formation with this ligand was not fully investigated but on addition of an alcholic solution of the aminophosphine to alcholic solutions of nickel (II) chloride hexahydrate and cobalt (II) bromide hexahydrate, colour changes from green to deep red and from blue to dark green were observed respectively. Although no solids precipitated from these solutions, the colour changes are indicative of complex formation in solution.

Reaction of bis(Ndiphenylphosphine Nethylamino)-

phenylphosphine with methyl iodide:-

Addition of excess methyl iodide to an ethereal solution of the aminophosphine followed by cooling afforded a white solid of formula $(Ph_2P(Et)N)_2PPh.MeI$. Oxidative hydrolysis of this methiodide giving rise to diphenylphosphinic acid would, according to the percentage of the acid obtained, establish the phosphorus atom on which the methyl group resided. Since the compound failed to give diphenylphosphinic acid on hydrolysis with dilute acids or bases the structure was not elucidated but it is likely that the methyl group is symmetrically positioned i.e. $\left[(Ph_2P(Et)N)_2PPhMe\right]^+I^-$

The reaction of bis (ethylamino)phenylphosphine with chlorodiphenylphosphine was repeated, but this time the chlorophosphine was added to the aminophosphine and a 1:1 ratio of the reactants was employed, the intention being to prepare a compound with the P-N-P-N skeleton. The amount of triethylammonium chloride isolated was nearly equivalent to the replacement of one nitrogen proton. Removal of the solvent (benzene) left a pale yellow oil which on distillation gave two fractions, I. a colourless liquid b.p.96-100°/10^{-3}mm. and II. a pale yellow liquid b.p.142-145°/10^{-3}mm. The i.r. spectrum of fraction I was indentical with that of diphenylphosphinoethylamine apart from an additional band at 860cm.$^{-1}$. In view of the similarity between the spectra of the compounds $(Ph_2P)_2$ NEt and $(Ph_2P(Et)N)_2PPh$ (see appendix I) fraction I was assumed to be the required Ndiphenylphosphinoethylamino N'ethylaminophenylphosphine, which had been derived according to the equation

$$PhP(NHEt)_2 + Ph_2PCl + Et_3N \longrightarrow Ph_2P(Et)N\text{-}PPh\text{-}NHEt + Et_3NH^+Cl^-$$

However, analytical data gave an empirical formula of $C_{13}H_{16}NP$ as compared to $C_{11}H_{13}NP$ for the above compound. Unfortunately insufficient material was available for a molecular weight determination but reaction of fraction I with excess methyl iodide yielded a colourless viscous oil which analysed as $C_{14}H_{19}INP$ thus indicating that only one molecule of methyl iodide had been added and also substantiating the empirical formula. This methyl iodide adduct was a methyl phosphonium salt since the i.r. spectrum showed bands at 1307cm.$^{-1}$ (symmetrical CH bending vibration) and 790 cm.$^{-1}$ (P-C assymetric stretch and therefore the molecular formula of fraction I is monomeric or, if dimeric, then the two phosphorus atoms are not joined by nitrogen because P-N-P systems only form mono-methiodides.

Re-examination of the i.r. spectra of the crude reaction product and fraction I showed the presence of a bonded NH group (3360cm.$^{-1}$), N-H deformation (1390cm.$^{-1}$) and mono-substituted phenyl groups. Although the bands in the region 850-980cm.$^{-1}$ were of similar frequency, variations in their intensities were observed which is of interest since this is the region in which the P-N stretching frequency is thought to occur for these compounds. The bands observed from 850-950cm.-1 are given below.

COMPOUND	REGION 850-950cm.$^{-1}$.
Ph PNHet	872 w 935 s
CRUDE PRODUCT	861 s 935 m
FRACTION I	861 m 935 s
FRACTION II	870 s 925 m
METHIODIDE	902 s 850 m (SH)

SH = SHOULDER.

Fraction II was not fully investigated but the nitrogen analysis (9.3%)was higher than fraction I (6.6%) which was surprising since compounds containing a single NHR group would be expected to condense under the conditions employed. Also, the i.r. spectrum showed a low intensity N-H absorption and bands in the region

1150-1250cm.$^{-1}$. It was therefore concluded that on distillation of the crude product, rearrangement had taken place giving fractions I and II either by carbon-carbon fission, if fraction I is monomeric, or by carbon-hydrogen fission resulting in methylene bridged compounds if dimeric. Fraction I was not considered to contain the P=N group on account of the type of methiodide formed.

Despite determined attempts to produce a structure for fraction I from the analytical and infra-red data, no plausible compounds were obtained. The results of this experiment, although inconclusive will serve as a useful guide to subsequent research on P^{III}-N systems of this type since they point to the ease with which rearrangement can take place and how an apparently simple reaction can fail to produce the required product.

The reaction of bis(tert.butylamino)phenylphosphine with chloro-diphenylphosphine:-

This reaction was carried out as with the ethyl analogue using a 2:1 ratio of the chlorophosphine to the aminophosphine. Since a bulky group was attached to nitrogen it was considered expedient to reflux the reaction mixture to ensure complete replacement of the nitrogen protons. Difficulty was experienced in separating the triethylammonium chloride since it passed through a sintered glass filter and a filter paper was used instead. Removal of the benzene left a yellow waxy solid which was recrystallised from ethanol to give a small yield of a white crystalline solid, m.p.183-188°. Attempts to precipitate more solid by the addition of water to the alcoholic solution resulted in the isolation of diphenylphosphinic acid. The i.r. spectrum of the first precipitate was identical to that of tetraphenyldiphosphine dioxide or monoxide but its melting point was different from that reported by Kuchen and Buchwald (133), 167° , for the dioxide and that of the monoxide, 154°(134). The isolation of tetraphenyldiphosphine dioxide (or monoxide) and diphenylphosphinic from this reaction was probably caused by the ingress of moisture to the system and emphasizes the extreme care which must be taken to carry out reactions of this type under completely anhydrous conditions. The formation of $Ph_2P(O)\text{-}PPh_2$ may be explained by the following equation,

$$\mathrm{Ph_2PCl + H_2O \longrightarrow Ph_2P\overset{\curvearrowleft}{O}H \longrightarrow Ph_2P(O)H \xrightarrow{Ph_2PCl} Ph_2P(O)\text{-}PPh_2 + HCl}$$

and atmospheric oxidation would give the dioxide.

Reaction of bis(ethylamino)phenylphosphine with dichlorophenylphosphine

Reaction of $PhPCl_2$ with $PhP(NHEt)_2$ can lead to a variety of condensation products. If intermolecular elimination of hydrogen chloride takes place then linear compounds of formula

$$Z - (Php - NEt)_x - Y$$

where Z = Cl and Y = PPh-NHR when X = 1 and Z = NHEt or Cl and Y= PhPCl or PhpNHEt when $x > 1$. No general equation can be written for this reaction but as x increases the ratio of the reactants approaches unity.

Formation of linear compounds followed by intramolecular elimination of hydrogen chloride or ethylamine would result in cyclic $\overset{III}{P}$ -N systems i.e.

$$Cl(PPh\text{-}NEt)_3\ PPh\text{-}NHEt \xrightarrow{B} (PPh\text{-}NEt)_4 + BHCl.$$

$$EtNH(PPh\text{-}NEt)_2\ PPh\text{-}NHEt \xrightarrow{\Delta H} (PPh\text{-}NEt)_3 + EtNH_2.$$

It is likely that reactions of this type will give rise to both linear and cyclic aminophosphines since the reaction of aniline and dichlorophenylphosphine, already mentioned, gave a mixture of both a cyclic trimer and linear compounds which have not yet been identified.

Addition of dichlorophenylphosphine to bis(ethylamino)phenylphosphine, using a 1:1 ratio of the reactants and triethylamine as a hydron chloride acceptor under the same reaction conditions as before, gave a near theoretical yield of triethylammonium chloride corresponding to the replacement of all the nitrogen protons. Removal of the benzene left a viscous yellow oil of molecular weight 730 which could not be recrystallised. No chlorine was detected but the i.r. spectrum showed the presence of NH groups. The oil was thought to be a mixture containing linear and possibly cyclic P^{III} -N compounds.

In the preparation of tri-N-methylimide, Holmes and Forstner used methylamine itself as both solvent and hydrogen chloride acceptor. The temperature of the reaction mixture was not taken above 50° and high yields of $P_4(NMe)_6$ were obtained. The success of this reaction prompted repetition of their synthetic method using dichlorophenylphosphine and ethylamine. The reaction vessel was kept at -78° but on addition of the phosphine a violent reaction took place and a deep red solution developed. On allowing the reaction mixture to warm up, this red colouration disappeared leaving a pale yellow solution. Excess ethylamine was removed by heating for a week at 50-55° and the pasty solid which was left was extracted with benzene. Removal of the benzene gave a pale yellow oil from which a small yield of bis(ethylamino)phenylphosphine was obtained but no other volatile component could be isolated even when the temperature of the flask was $180^{\circ}/10^{-3}$mm. The residue had a molecular weight of 402 and a nitrogen value of 9,3% (the cyclic trimer, $(PPh\text{-}NEt)_3$, requires N, 9.3%, M=456). However, on standing both the residue and the crude product precipitated cyclophenylphosphine indicating that rearrangement had taken place. The experiment was abandoned but it is worth noting that Ewart, performing the same experiment, achieved similar results.

group.

An attempt was made to prepare the compou
[illegible] using the above method bu
yielded a compound of empirical formula [illegible]
unknown structure. Reaction with Methyl iodi
a viscous liquid of empirical formula $C_{14}H_{19}$

The reaction of bis(ethylamino)phenylph
with dichlorophenylphosphine was unsuccessful
product was not easily identified. However,
rearrangement, giving rise to cyclophenylphos
occurred and the use of more sophisticated se

SUMMARY

By reacting bis(ethylamino)phenylphosphine with chlorodiphenylphosphine, using triethylamine as a hydrogen chloride acceptor, the compound bis(Ndiphenylphosphino Nethylamino)phenylphosphine was prepared. Although a similar reaction using bis(tert.butylamino) phenylphosphine failed to give the tertiary butyl analogue of the above compound, it is thought that vigorous exclusion of moisture and oxygen would give the required compound and that this method of replacing nitrogen protons by a $-PPh_2$ group is applicable tervalent phosphorus-nitrogen systems, containing an $-NHR$ or $-NH_2$ group.

An attempt was made to prepare the compound Ph_2 P-NEt-PPh-NHEt using the above method but distillation yielded a compound of empirical formula $C_{13}H_{16}NP$ of unknown structure. Reaction with Methyl iodide gave a viscous liquid of empirical formula $C_{14}H_{19}INP$.

The reaction of bis(ethylamino)phenylphosphine with dichlorophenylphosphine was unsuccessful in that the product was not easily identified. However, no rearrangement, giving rise to cyclophenylphosphine, occurred and the use of more sophisticated separation techniques could lead to the identification of some

interesting cyclic or linear compounds.

The reaction of dichlorophenylphosphine with ethylamine using the amine as solvent led eventually to a rearrangement and the formation of cyclophenylphosphine.

sodium wire.

Preparation of bis(N-diphenylphosphino-N-ethyla
phenylphosphine)

Bis(ethylamino)phenylphosphine(2.2730g., 11.6
excess triethylamine (14ml.) in benzene (75ml.
added under a stream of dry nitrogen with cons
stirring to chlorodiphenylphosphine (5.2105g.
in benzene (75ml.). A white solid precipitate
and after addition was complete, stirring was
for two hours. The solid was removed by filt
washed with benzene and the washings combined
filtrate. This solid (3.1816g., required 3.17
m.p.249° was identified by its i.r. spectrum
Triethylammonium chloride (m.p.254°). Remov

EXPERIMENTAL

The bis(ethylamino)phenylphosphine used in the following reactions had been freshly distilled and stored in evacuated sealed tubes. Chlorodiphenylphosphine and dichlorophenylphosphine were obtained commercially and distilled before use, fractions being taken at $148^{o}/10^{-1}$mm. and $50-52^{o}/2x10^{-2}$mm. respectively. Triethylamine, ether and benzene were dried over sodium wire.

Preparation of bis(Ndiphenylphosphine Nethylamino) phenylphosphine

Bis(ethylamino)phenylphosphine(2.2738g., 11.6mmoles) with excess triethylamine (14ml.) in benzene (75ml.) were added under a stream of dry nitrogen with constant stirring to chlorodiphenylphosphine (5.21855g., 23.72mmoles) in benzene (75ml.). A white solid precipitated immediately and after addition was complete, stirring was continued for two hours. The solid was removed by filtration, washed with benzene and the washings combined with the filtrate. This solid (3.1816g., required 3.1791g.), m.p.249^{o} was identified by its i,r, spectrum as Triethylammonium chloride (m.p.254^{o}). Removal of the benzene solution at reduced pressure gave a white waxy solid (5.9259g.) which was recrystallised from alcohol to give white crystals (2,4527g., 37.5%), m.p.144-145°. Found: C, 72.4 ; H, 6.1 ; N, 4.9 ; P, 16.5. $C_{34}H_{35}N_2P_3$ requires, C, 72.4 ; H, 6.2 ; N, 5.0 ; P, 16.5%).

Preparation of bis(Ndiphenylphosphino Nethyl) methylphosphonium iodide:-

The above aminophosphine (0.1533g., 0.2717mmoles) in ether (15ml.) with excess methyl iodide gave a white solid (0.1510g., 78.7%, m.p.ca.85°(decomp.). (Found: N, 4.1. $C_{35}H_{38}IN_2P_3$ requires N, 4.0%).

Reaction of bis(ethylamino)phenylphosphine with chlorodiphenylphosphine:-

To the aminophosphine (2.2868g., 11.67mmoles)and an excess of triethylamine (3ml.) in benzene (60ml.) under dry nitrogen was added chlorodiphenylphosphine (2.5356g., 11.53mmoles) in benzene (30ml.) with constant stirring. A white solid precipitated immediately which was filtered off giving triethylammonium hydrochloride (1.4865g., required, 1.579g.). Removal of the benzene left a pale yellow oil (4.5987g., required, 4.380g.) which was distilled to give two fractions. Fraction I, a colourless liquid, b.p. 96-100°/10^{-3}mm. (Found: C, 71.9 ; H, 7.3 ; N, 6.6 ; P, 14.2. $C_{13}H_{16}NP$ requires C, 71.9 ; H, 7.4 ;

N, 6.5 ; P, 14.3%). Fraction II, a pale yellow liquid, b.p., 142-146°/10^{-3}mm. (Found N, 9.3%).

Reaction of fraction I in ether with excess methyl iodide gave a viscous colourless oil. (Found: C, 47.0 ; H, 5.5 ; I, 35.2 ; N, 3.9 ; P, 8.8 $C_{14}H_{19}INP$ requires C, 46.8 ; H, 5.3 ; I, 35.4 ; N, 3.9 ; P, 8.6%).

Reaction of bis(ethylamino)phenylphosphine with dichlorophenylphosphine:-

Dichlorophenylphosphine (2.7447g., 15.33mmoles) in benzene (50ml.) was added, under dry notrogen, to the aminophosphine (2.8121g., 14.34mmoles) and an excess of triethylamine (13ml.) in benzene (50ml.). A white solid precipitated immediately and after the addition was complete, the mixture was refluxed for 6 hours. Triethylammonium chloride (3.8209g., required, 3.928g.). was removed by filtration, under nitrogen. Removal of the benzene under reduced pressure left a viscous orange oil. (Found: M, 730).

CHAPTER III

Preparation, Properties and Reactions of the Bis(alkylamino)phenylphosphines

INTRODUCTION

The aminophosphines used as starting materials in Chapters I and II necessitated the preparation and purification of a hitherto unreported type of aminophosphine, the bis(alkylamino)phenylphosphines. These compounds are members of Class II, in the general classification and are the primary amine analogues of the bis(dialkylamino)phenylphosphines reported by Ewart (54).

In view of the importance of these aminophosphines as intermediates in the formation of long chain P^{III}-N compounds of the type $Ph_2P-(NR-PPh)_x-NR-PPh_2$ a detailed investigation was carried out as to their ease of handling, and the reactions which occurred with alkyl iodides, oxygen, sulphur and selenium.

Results and Discussion

Preparation and properties of bis(alkylamino)phenylphosphines, $PhP(NHR)_2$.

All the aminophosphines were prepared by adding dichlorophenylphosphine to an excess of the amine according to the equation

$$PhPCl_2 + 4RNH_2 \longrightarrow PhP(NHR)_2 + 2RNH_3^+Cl^-$$

The amine hydrochloride produced was removed by filtration and the solvent used, either benzene or ether, was distilled off leaving a pale yellow oil. This oil was distilled under reduced pressure to give a colourless product which, in view of the knowledge obtained as to the ease with which these compounds undergo atmospheric oxidation and hydrolysis, was stored in an evacuated sealed tube. All the above operations were performed under an atmosphere of dry nitrogen and a feature of this work was the care taken to exclude oxygen and moisture from these reactions. Yet, despite these precautions, in the reactions involving isopropylamine and tertiary butylamine the oxides $PhPO(NHPr^i)_2$ and $PhP(O)(NHBu^t)_2$ were obtained along with the required aminophosphines but this was probably due to the presence of phenylphosphoryl chloride as an impurity.

In all the reactions studied, the yields of pure aminophosphine were low in the order of 25%. The residue from the distillation was a viscous orange oil from which cyclophenylphosphine precipitated on addition of acetone. It is conceivable that, on the basis of a free radical reaction, this polyphosphine would be produced at the tempratures used in the distillation process (up to 170°). However, Ewart, in attempts to prepare these aminophosphines isolated the polyphosphine before distillation and this feature was also noted in the preparation of the ethyl and n-propyl aminophosphines in which cyclophenylphosphine precipitated out of the crude liquid. The low yields may therefore be attributed to secondary reactions taking place during the preparation and further thermal condensation on distillation.

The bis(alkylamino)phenylphosphines, $PhP(NHR)_2$, isolated were those where R=Et,Pr^n, Pr^i and Bu^t (R=Pr^n was not fully investigated). They are all colourless liquids and their physical properties are given in Table 8.

Table 8

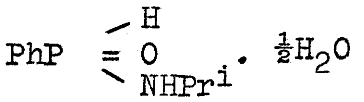
R	b.p./10^{-3}mm.	m.p°	$^{D}_{22N}$
Et	53-56	7.5-7.6	1.5486
Pr^n	100		
Pr^i	52	13.5-14.5	1.5289
Bu^t	64-65	13.5-14.7	1.5198

The aminophosphines were soluble in all the organic solvents investigated but reacted with these containing a hydroxyl group. Thus, bis(ethylamino)-phenylphosphine dissolved in alcohol but on removal of the solvent followed by distillation of the remaining oil, the diethyl ester of phenylphosphonous acid was obtained.

$$PhP(NHEt)_2 + 2EtOH \longrightarrow PhP(OEt)_2 + 2EtNH_2 .$$

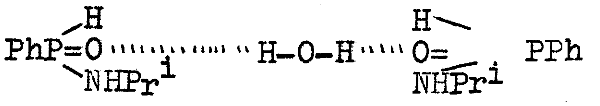
With water, these aminophosphines are initially insoluble but on standing they dissolve to give an alkaline solution.

On leaving the ethyl and isopropyl aminophosphines in contact with the atmosphere, an alkaline vapour was liberated and after a period of about three days, a viscous yellow oil and a white solid were left respectively. Both these products must have resulted from atmospheric hydrolysis of the P–N bond but the process did not go to completion since phenylphosphonous acid or its rearrangement product, $\mathrm{PhP{=}O}\!\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{OH}\end{smallmatrix}$, were not isolated and anslysis gave nitrogen values of up to 8%. The i.r. spectra of these hydrolysis products showed the presence of P–H (2390–2290cm.$^{-1}$), P=O (1190–1160cm.$^{-1}$) and bonded and non-bonded NHR (3420cm.$^{-1}$, 3190cm.$^{-1}$) groups and an element analysis of the product from bis(isopropylamino)phenylphosphine indicated a structural formula of



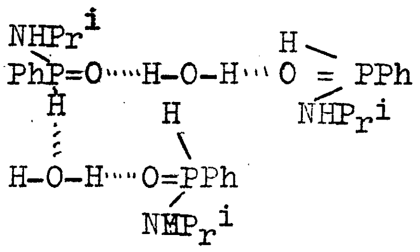
$$\mathrm{PhP} \begin{smallmatrix}\diagup\mathrm{H}\\ =\mathrm{O}\\ \diagdown\mathrm{NHPr^{i}}\end{smallmatrix} \cdot \tfrac{1}{2}\mathrm{H_2O}$$

This formula could not be substantiated by molecular weight determinations carried out ebullioscopically in benzene since values from the graph in a single determination varied from 344 to 579 (Theory, 192). However, it is possible that intermolecular hydrogen bonding is taking place which would account for the increase in molecular weight with concentration. Bonded species of the following types are suggested.

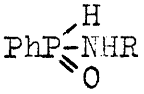


M = 375.

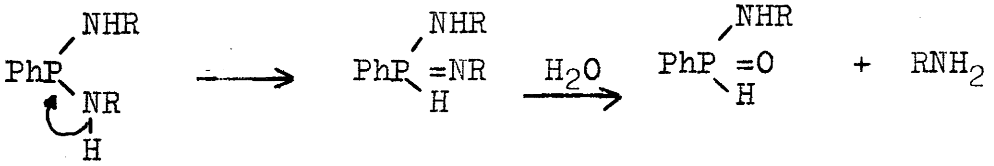
;



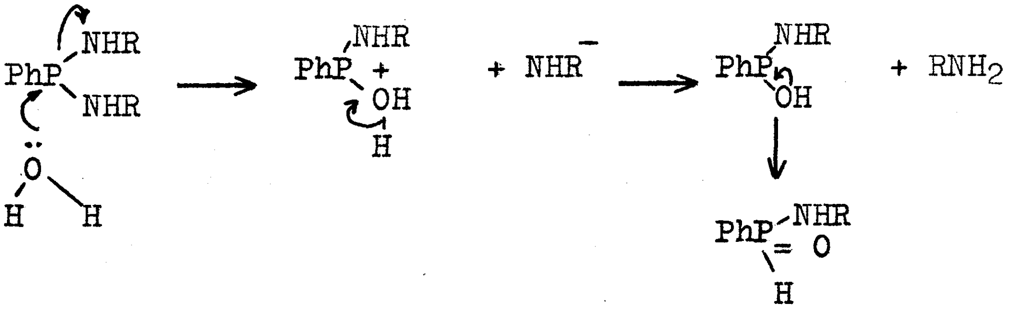
M = 575

On pumping the original compound, the carbon value increases whereas hydrogen decreases indicating the loss of water and therefore giving further confirmation of the proposed structure of a basic  $PhP(H)(=O)NHR$ unit associated with varying quantities of water.

There are two possible reaction mechanisms to explain the atmospheric hydrolysis of these compounds. The first involves initial rearrangement to a phosphazene followed by hydrolysis of the P=N bond.



In the second and more feasible mechanism, attack of water molecule causes the elimination of amine and the formation of a hydroxyaminophosphine which then rearranges to give product.



The latter mechanism is favoured on considering the effect of leaving bis(tert.butylamino)phenylphosphine open to the atmosphere. Although initial liberation of amine occurs, the white solid which formed consisted almost entirely of the oxide $PhP(O)(NHBu^t)_2$. The bulky tertiary butyl groups inhibit the approach of a water molecule to the phosphorus centre and therefore, atmospheric oxidation takes place in preference to hydrolysis. Products arising from the liberation of amine were not isolated but it is possible that the first mechanism may have occurred to a slight extent.

The n-propyl compound was not investigated but is is expected that it would follow the same pattern as the ethyl and isopropyl analogues.

Alkyl iodide adducts of Bis(alkylamino)phenylphosphines.

All these aminophosphines form simple 1:1 alkyliodide adducts with methyl and ethyl iodide to give bis(alkylamino alkylphenylphosphonium iodides. They are easily prepared by adding excess of the alkyl iodide to an ether solution of the aminophosphine from which the solid phosphonium iodide usually precipitates. With the methyl iodide adducts, precipitation occurred almost immediately but with ethyl iodide, the reactions were slower and solid formation had to be induced by cooling the solution. The alkiodides were all white crystalline solids apart from the bis(n-propylamino)-methylphenylphosphonium iodide which was a colourless oil. The compounds isolated and their melting points are shown below.

Table 9:- Alkyliodide adducts. $[PhP(R')(NHR)]^+ I^-$

R' R	Me m.p°	Et m.p°
Et	85-87	62-65
Pr^n	Oil	
Pr^i	165-165.5	110/112
Bu^t	176-178	215-217

The methyl iodide adduct of bis(ethylamino)-phenylphosphine mentioned earlier, which was isolated by Ewart, m.p.75-80° is thus confirmed.

Quaternisation of the phosphorus atom in these compounds leads to enhanced stability of the P-N bond and no decomposition, as noted in the parent ethyl and isopropyl aminophosphines, was observed.

That the alkyl group resides on phosphorus in these compounds was not established chemically but in view of the evidence already quoted for similar aminophosphines it would seem that this would be the correct assumption. Also, examination of the i.r. spectra of the methiodides showed a peak not found in the parent aminophosphines at 1310-1303cm.$^{-1}$ corresponding to the symmetrical C-H bend in the methyl group (94) which is considered as being a reliable correlation band for P-methyl in phosphonium salts. The ethyl iodide adducts do not absorb in this region but bands corresponding to the P-C assymetric stretching frequency (95 were observed at 784-769cm.$^{-1}$ (this absorption occurs at 779cm.$^{-1}$ in$[Ph_3EtP]^+I^-$).

The i.r. data, therefore, confirms that the alkyl group is attached to phosphorus.

Oxides of Bis(alkylamino)phenylphosphines

The oxides of these compounds have been prepared by two synthetic routes. By refluxing aminophosphines of the type R_2NPPh_2 with activated manganese dioxide for two hours in an inert solvent, Sisler and Smith(58) obtained high yields of the corresponding oxides. Application of this method to the bis(alkylamino) phenylphosphines only produced yields of up to 33%, in the case of the ethyl and isopropyl compounds, even after refluxing for 12 hours. A far more efficient method by which to oxidise these compounds was to pass a 100% excess of ozone through the aminophosphine in benzene. An exothermic reaction took place but was easily controlled and the resulting yields of *n*-propyl and *tert*.butylaminophosphine oxides were 100% and 72% respectively. This method of oxidation has many advantages over that used by Sisler and Smith since it reduces the time required to prepare these compounds and also does away with the need of removing the oxidising agent.

The oxides isolated were all stable white crystalline solids. The isopropyl and *tert*.butyl oxides being insoluble in cold benzene and it is interesting to note that the ethyl oxide is soluble in water, a phenomena not usually associated with tertiary phosphine oxides. The melting points and yields of these compounds are given in Table 10.

Table 10:- Oxides of bis(alkylamino)phenylphosphines

$PhP(O)(NHR)_2$

R	m.p.°	Yield%
Et	73(72-74)	26.4
Pr^n	94-95	33.0
Pr^i	159-160	98.0
Bu^t	190-191(188-189)	72.3

(melting points in brackets are those due to Gutman et.al.

The ethyl, tertiary butyl and other oxides of the type $PhP(O)(NHR)_2$ have been isolated by Gutman et.al.(64) from the reactions of phenylphosphoryl chloride and primary amines.

$$PhP(O)Cl_2 + 4RNH_2 \longrightarrow PhPO(NHR)_2 + 2RNH_3^+ Cl^-$$
$$(R=Et,\ Bu^{\underline{n}},\ C_5H_{11}{}^{\underline{n}},\ C_7H_{15}{}^{\underline{n}}).$$

The presence of an NHR and P=O group in one molecule gives rise to inter- and intra-molecular hydrogen bonding and will be discussed in the appendix dealing with the i.r. spectra of these aminophosphines.

Sulphides and Selenides of bis(alkylamino)phenylphosphines

By refluxing the appropriate aminophosphine with an equimolar quantity of elemental sulphur or selenium (red precipitated allotrope) in benzene, under a stream of dry nitrogen, followed by removal of the benzene and recrystallisation of the remaining solid, good yields of the corresponding sulphides and selenides of these compounds were obtained.

The sulphides and selenides isolated, given in table 11, are all stable white crystalline solids but after about three months, the selenides turn pink due to precipitation of selenium. A similar instability has been observed in the selenide of bis(diphenylphosphino) ethylamine, $(Ph_2P(Se))_2$ NEt(79), and in the case of the telluride of tri-n-butylphosphine (96), rapid decomposition takes place resulting in the precipitation of elemental tellurium.

Table 11:- Sulphides and Selenides of Bis(alkylamino) phenylphosphines, PhP(X)(NHR)

X R	S m.p.°	Se m.p.°
Et	84-85	81-82
Pr^i	49.50	
Bu^t	106-106.5	104.105

One of the sulphides, $PhP(S)(NHEt)_2$, has been prepared before from phenylthiophospheryl chloride and ethylamine (m.p.81-82 and was one of the compounds that were screened for anticancer reactivity(82).

Triphenylphosphine sulphides and selenides form stable 1:1 crystalline complexes with iodine and interhalogens such as iodine monochloride and monobromide(97). Also a stable crystalline solid in which three moles of iodine are complexed to two moles of the selenide was isolated. In view of the stability of these complexes, a preliminary investigation was carried out to see whether the sulphides and selenides of bis(alkylamino)phenylphosphines would form similar compounds with iodine.

The compounds $PhP(S)(NHEt)_2$, $PhP(Se)(NHEt)_2$ and $PhP(S)(NHPr^i)_2$ were added to a molar excess of iodine usin chloroform as solvent, and immediately the colour of the solution changed to a deep red in the case of the ethylaminophosphines and an orange with isopropyl indicating that complex formation had taken place in solution. On leaving overnight in a refridgerator deep red crystals were observed in the solutions containing the ethylaminophosphines (the isopropyl solution showed no sign of crystal formation) but in separating them from the solution by filtration they decomposed turning into purple waxy solids. Further attempts to isolate these halogen complexes were therefore abandoned but it is expected that exclusion of oxygen and moisture from these reactions would facilitate their isolation.

Reaction of dichlorophenylphosphine with methylamine

Numerous abortive attempts were made to prepare bis(methylamino)phenylphosphine. Due to the volatility of methylamine (b.p.-6.5°) these reactions were carried out using high vacuum techniques, excess of the amine being condensed into a vessel containing dichlorophenylphosphine at -180°. On allowing the system to warm up, a violent exothermic reaction occurred at about -40^{o} to give a white solid and a yellow liquid. The ratio of this white solid, which was identified as methylammonium chloride, to dichlorophenylphosphine varied from 1.8-2:1 indicating that most of the chlorine atoms had been replaced by the -NHMe group. However the ratio of methylamine used in the reaction to the chlorophosphine was 4.2-2.7:1 and therefore, it is assumed that in some cases, the initial formation of $PhP(NHMe)_2$ was followed by a secondary reaction involving the elimination of amine.

In order to separate the aminehydrochloride from other reaction products various solvents were used including benzene, methylene chloride, alcohol and tetrohydrofuran. The latter two solvents finally gave compounds which contained no nitrogen. With alcohol, the diethyl ester of phenylphosphonus acid was isolated and using tetrahydrofuran, a colourless oil was obtained, the i.r. spectrum of which showed the presence of OH groups and aliphatic C-H units. It is known that reduction of diphenylphosphinic acid by lithium aluminium hydride using boiling tetrahydrofuran as solvent produces diphenylphosphine and a tertiary phosphine, $Ph_2P(CH_2)_4OH$(98). It is possible, therefore, That a similar reaction has taken place during the separation of aminehydrochloride to give $PhP[(CH_2)_4OH]_2$.

Nitrogen containing compounds were obtained using methylene chloride as solvent but the experiments could not be reproduced and the products, viscous oils, were difficult to handle and purify. Since it was feared that methylene chloride might react with these compounds and analytical data showed the presence of oxygen, the solvent was changed to benzene and apparatus was devised so that the whole reaction procedure including filtration could be carried out under vacuum.

The product of the reaction in which benzene was used as solvent was a pale yellow liquid which gave small amounts of a colourless product on distillation under reduced pressure. Nitrogen analysis of this colourless liquid was well below that of the required aminophosphine and it was assumed that atmospheric hydrolysis had taken place. No further fractions could be distilled even on raising the temperature of the oil bath to 250°. The residue consisted of a brown glass which could not be purified and analytical data indicated a formula of $(C_{7.5}H_{8.2}N_1P_{1.07}O_{0,3})_4$ which is close to the empirical formula required for a cyclic system, $(C_7H_8NP)_x$.

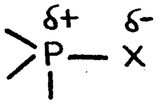
Production of the above compound in which the phosphorus-nitrogen ratio is unity must have involved amine elimination during distillation and a gas i.r. of the volatile compound in the vacuum cold traps showed the presence of methylamine. On repeating this experiment, the glass obtained after attempting to distill the crude product had a molecular weight of 1005 and therefore it was assumed that linear chains of P^{III}-N units were being formed by thermal self condensatio involving methylamine elimination.

No further attempts were made to isolate bis(methylamino)phenylphosphine but application of the techniques used to prepare the other bis(alkylamino)phenylphosphines might prove successful.

Reactivity of the P-N bond in bis(Alkylamino)phenylphosphine

The reactivity of some bis(alkylamino)phenylphosphines to atmospheric hydrolysis is not to be found in the bis(dialkylamino)phenylphosphines which can be recovered unchanged after long exposure to the atmosphere and are, in fact, purified by shaking with water (in order to remove dissolved amine hydrochloride). This difference in reactivity may be due to the two alkyl groups on nitrogen, in the bis(dialkylamino)phenylphosphines, giving rise to complete steric shielding of the phosphorus centre whereas if one of the alkyl groups is replaced by a proton, this shielding is decreased thereby allowing attack on phosphorus by a water molecule. The extent of the steric shielding in the series $PhP(NHR)_2$ going from R=Et to tertiary butyl has already been noted. Thus, on leaving these compounds open to the atmosphere hydrolysis and P-N bond scission occur where R=Et and Pr^i but only oxidation takes place when $R=Bu^t$.

Quaternisation of the phosphorus atom in the bis(alkylamino)phenylphosphines by forming alkyl iodine adducts, oxides sulphides and selenides must lead to a change of symmetry and the formation of an sp^3 hybridised molecule which will cause increased shielding of the phosphorus centre as compared to that of the parent aminophosphine. This will account for the lack of reactivity observed in these compounds, but it may equally be explained by considering the electron distribution in these compounds. With alkyl iodide adducts, a positive centre is formed on phosphorus and with oxides, sulphides and selenides a dipole is set up due to the greater electronegativity of these elements than phosphorus giving a bond of the type



This positive charge will increase the extent to which the lone pair on nitrogen will back donate to the vacant 3d orbitals on phosphorus and thus give rise to a shorter and stronger P -N bond. The electronegativities of sulphur (2.5) and selenium (2.4) are very close to that of phosphorus (2.1) and therefore only a weak dipole will exist which explains the decomposition of the selenides to give elemental selenium. It would be expected that in time the sulphides would undergo a similar decomposition.

SUMMARY

The preparation of a new class of compounds, the bis(alkylamino)phenylphosphines $PhP(NHR)_2$ is reported where $R=Et.Pr^n$, Pr^i and Bu^t . Attempts to prepare the compound $PhP(NHMe)_2$ were unsuccessful These aminophosphines were found to behave as tertiary monphosphines forming 1:1 alkyl iodide adducts, oxides, sulphides and selenides but the presence of two -NHR groups attached to phosphorus caused the original compounds to be very reactive towards oxygen and moisture.

Preparation of other members in this series should be possible using the same synthetic technique but before attempting this, it would be advantageous to isolate and characterise the other compounds which are produced in these reactions.

EXPERIMENTAL

Dichlorophenylphosphine was obtained commercially and was freshly distilled under reduced pressure before use. Anhydrous grade amines were used and dried over sodium wire. Benzene and ether were also dried over sodium wire. Distillations were carried out using a 7" Fenske column incorporating a direct attachment to a high vacuum system.

Preparation of Bis(ethylamino)phenylphosphine:- Dichlorophenylphosphine (149.82g., 0.8370moles) in dry ether (1000ml.) was added drop wise, with stirring, to ethylamine (176.5g., 3.922moles) in ether (1500ml.) at 0°. Entry of air to the mixture was prevented by the use of a nitrogen stream. The reaction was exothermic and a white solid precipitated immediately. The mixture was stirred for three hours after which the solid was removed by filtration under nitrogen, washed with dry ether and the washings combined with the filtra The solid, (128.6g., required 132.6g.) was identified as ethylamine hydrochloride. The ether was removed by distillation under nitrogen giving a pale yellow product (134.3g.) which was distilled and a colourless liquid obtained (45.558g., 28%), b.p.53-56°/10^{-3}mm., ${}^{D}_{22}$n.1.5486, m.p.6.5-7.5° (Found: C,61.4; H,8.8; N,14.1; P,15.8; M(ebullioscopically in benzene), 202; $C_{10}H_{17}N_2P$

requires C,61.2; H,8.7; N,14.3; P15.8%; M,195).

Preparation of Bis(ethylamino)methylphenylphosphonium iodide:-
Methyl iodide (0.2846g., 2.004mmoles) in dry ether (5ml.) was added to the phosphine (o.3153g., 1.607mmoles) in ether (5ml.). The solution became cloudy and on cooling a solid precipitated which was filtered off to give a white methiodide (0.3740g., 69%). This solid was recrystallised from an acetone-ether mixture to give white needles, m.p.85-87°. (Found; N,8.4; 1,37.6. $C_{11}H_{20}IN_2P$ requires N,8.3; I,37.6%).

Preparation of Bis(ethylamino)ethylphenylphosphonium iodide:-
Ethyl iodide (0.9029g., 5.788mmoles) in dry ether (25ml.) was added to the phosphine (0.7077g., 3.610mmoles) in ether (5ml.). No reaction was observed but on standing the solution became cloudy and an oil separated out which after a further period of time solidified. This product (0.5470g.,43%) was recrystallised from an alcohol-ether mixture to give white needles, m.p.62-65°. (Found: N,8.0; 1,36.3. $C_{12}H_{22}IN_2P$ required N,8.0; I, 36.1%).

Removal of the ether left a pale yellow oil (0,2451g.) which was not investigated.

Preparation of Bis(ethylamino)phenylphosphine oxide:-
The phosphine (3.0330g., 15.47mmoles) in benzene (100ml.)

was refluxed for 12 hours under a stream of nitrogen with activated manganese dioxide (16.143g., 0.1856 mole). The manganese dioxide was removed by filtration and washed with benzene and the washings combined with the filtrate. Removal of the benzene left a grey solid (0.8640g., 26.4%) which was recrystallised from ether to give white needles m.p.73° (Found: N,13.2. $C_{10}H_{17}N_2OP$ requires N, 13.2%; m.p.72-74°) (64).

Preparation of Bis(ethylamino)phenylphosphine sulphide:- The phosphine (3.1064g., 15.84mmoles) in benzene (100ml.) was refluxed for 12 hours, under a stream of nitrogen, with elemental sulphur (0.6395g., 19.98mmoles). Removal of the benzene left a white solid (3.730g., 100%. Theory required 3.613g. for 100%; excess due to silicone grease and an unreacted sulphur) which was recrystallised from ethanol to give white needles m.p.84-85° (Found: N,12.0. $C_{10}H_{17}N_2PS$ requires N,12.2%; m.p.80-81°)(82).

Preparation of Bis(ethylamino)phenylphosphine selenide:- The phosphine (2.4240g., 12.37mmoles) in dry benzene (50ml.) was refluxed for 12 hours, under a stream of nitrogen, with precipitated selenium (0.9800g., 12.40mmole On removal of benzene, a pink waxy solid was obtained which recrystallised from n-hexane to give a white crystalline product m.p.81-82° (Found: N,10.1. $C_{10}H_{17}N_2PSe$ requires N,10.2%).

Alkyl iodide adducts, oxides, sulphides and selenides of the bis(alkylamino)phenylphosphines to be described below were all prepared in a similar manner to those of Bis(ethylamino)phenylphosphine.

Reaction of Bis(ethylamino)phenylphosphine with ethanol:-

The phosphine (1.187g., 6.061mmoles) was added to ethanol (20ml.) After an hour, the ethanol was removed under reduced pressure to leave a pale yellow liquid (1.1060g.) which was distilled to give a colourless product b.p.44-48°/10^{-3}mm. $^{D}_{20}n$ 1.5097. The diethyl ester of phenylphosphonous acid has $^{D}_{20}$ n 1.51.

Preparation of Bis(isopropylamino)phenylphosphine:-

Dichlorophenylphosphine (70.9g., 0.3983mmoles)in ether(350ml was added drop wise, with stirring, to isopropylamine (116.0g., 1.966moles) at 0° under a stream of dry nitrogen. The mixture was stirred for an hour and the amine hydrochloride was removed by filtration under stream of nitrogen, washed with ether and the washings combined with the filtrate. A quantitative yield of isopropylamine hydrochloride was obtained. Removal of the ether by distillation under nitrogen gave a yellow liquid and a crystalline solid; the solid (4.5856g.) was identified as Bis(isopropylamino)phenylphosphine oxide, m.p.159-160°. (Found: N, 11.7. $C_{12}H_{21}N_2OP$ requires N, 11.7

The pale yellow liquid was distilled to give a colourless product, (49.37g., 55.3%) b.p.52°/10^{-3}mm. $^{D}_{19.5}n$ 1.5298; m.p.13.5-14.5°. (Fouhd C,64.3 ; H, 9.2 ; N, 12.7 ; P, 13.8 ; M(cryoscopic in benzene), 211 ; M(ebullioscopic in benzene), 235 $C_{12}H_{21}N_2P$ requires C, 64.3 ; H, 9.4 ; N. 12.5 ; P, 13.8% ; M, 224).

Preparation of Bis(isopropylamino)methylphenylphosphonium iodide:- The phosphine (1,7024g., 7.598mmoles) and methyl iodide (2,279g., 16.05mmoles) gave a white methiodide (2.781g., 96.5%) which was recrystallised from acetone to give white needles m.p.165-165.5°. (Found: C, 43.3 ; H, 6.8 ; 35.2 ; N, 7.9 ; P, 8.5. $C_{13}H_{24}IN_2P$ requires C, 42.6 ; H, 6.6 ; 1, 34.7 ; N, 7.6 ; P, 8.5%).

Preparation of Bis(isopropylamino)ethylphenylphosphonium iodide:- The phosphine (0.6117g., 2.727mmoles) and excess ethyl iodide gave a white ethiodide (0.7962g., 77%) which was recrystallised from an acetone-ether mixture to give white needles, m.p.110-112° (Found: N,7.2 $C_{14}H_{26}IN_2P$ requires N, 7.4%.

Preparation of Bis(ispropylamino)phenylphosphine oxide:- The phosphine (0.5704g. 2547mmoles) and activated manganese dioxide (3.44g., 39.55mmoles) gave a white crystalline

Product (0.2010g., 33%) which was recrystallised from benzene to give white needles, m.p.159-160°. (Found: C, 59.6 ; H, 8.8 : N, 11.7 ; P, 12.5. $C_{12}H_{21}N_2OP$ requires C, 59.9; H, 8.8 ; N, 11.7 ; P, 12.9%).

Preparation of Bis(isopropylamino)phenylphosphine sulphide:- The phosphine (3,0025g., 13.41mmoles) and elemental sulphur (0.4473g., 13.98mmoles) gave a white solid (3.537g., 100%) which was recrystallised from *n*-hexane to give white needles, m.p. 49.50°. (Found: N,11.0 . $C_{12}H_{21}N_2PS$ requires N, 10.9%).

Atmospheric Hydrolysis of Bis(isopropylamino)phemylphosphine: The phosphine was left in contact with the atmosphere and an alkaline vapor (pH10) was liberated. After several days, solid started appearing in the liquid and rapidly increased till all the liquid had been transformed. (Found: C, 55.6 ; H, 8.4 ; N, 7.0 ; P, 16.1 $C_9H_{15}NO_{1.5}P$ requires C, 56.0 ; H, 7.8: N, 7.3 ; P, 16.1%). The solid was pumped at 2mm. (Found: C, 57.4 ; H, 8.2. $C_9H_{14}NOP$ requires C, 59.0 ; H, 7.7%).

Preparation of Bis(n-propylamino)phenylphosphine:- Dichlorophenylphosphine (105.0g., 0.5899mole) in benzene (250ml.) was added dropwise, with stirring, to *n*-propylamine (345.0g., 5.848moles) in benzene (2500ml.)

under a stream of nitrogen at 0°. The amine hydrochloride was removed by filtration under nitrogen. Removal of benzene by distillation left a viscous yellow oil part of which was distilled to give a colourless liquid (1.1436g.,), b.p.$100^{\circ}/10^{-3}$mm. This liquid was identified as Bis(n-propylamino)phenylphosphine by converting it into a methyl iodide adduct and an oxide.

<u>Preparation of Bis(n-propylamino)methylphenylphosphonium iodide</u>:- The phosphine (0.3630g., 1.621mmoles) and excess methyl iodide gave a viscous colourless oil. (Found: N, 7.
$C_{13}H_{24}IN_2P$ requires N,7.7%).

<u>Preparation of Bis(n-propylamino)phenylphosphine oxide</u>:- The phosphine (0.6132g., 2.738mmoles) in benzene (30ml.) was treated with a 100% excess of ozone. Removal of the benzene left a pale yellow solid (0.6432g., 98%) which was recrystallised from ether to give white needles m.p.94-95.
(Found: C, 60.1 ; H, 8.9 ; N, 11.7 ; P, 12.8 $C_{12}H_{21}N_2OP$ requires C, 59.9 ; H, 8.8 ; N, 11.7 ; P, 12.9%).

<u>Preparation of Bis(tert.-butylamino)phenylphosphine</u>:- Dichlorophenylphosphine (63.7619g., 0.3582moles) in benzen (250ml.) and tertiary butylamine (174g., 2.383moles) in benzen (1000ml.) were reacted as before to give a yellow oil whic was distilled to give a colourless product, b.p.$64-65^{\circ}/10^{-}$

$_{22}n^{D}$ 1.5198 ; m.p. 13.5-14.7°. (Found: C, 66.7 ; H, 9.9 ; N, 11.1 ; P, 12.3. $C_{14}H_{23}N_{2}P$ requires C, 66.7 ; H, 9.9 ; N, 11.1 : P, 12.3%).

Preparation of Bis(tert,butylamino)methylphenylphosphonium iodide:-

The phosphine (1,1327g., 4.495mmoles) and excess methyl iodide gave a white solid (1.1413g., 64.3%) which was recrystallised from acetone m.p.176-178° (Found: N, 6.9. $C_{15}H_{28}IN_{2}P$ requires N, 7.1%).

Preparation of Bis (tert.butylamino)ethylphenylphosphonium iodides:-

The phosphine (1.1125g., 4.416mmoles) with excess ethyl iodide gave a white solid (0.2401g., 13.3%) which was recrystallised from an acetone-ether mixture m.p. 215-217° (Found: N, 7.1. $C_{16}H_{30}IN_{2}P$ requires N, 6.9%).

Preparation of Bis(tert.butylamino)phenylphosphine oxide:-

The phosphine (2.7512g., 10.92mmoles) in benzene (30ml.) was treated with 100% excess of ozone. An exothermic reaction took place and a white solid precipitated (2.1135g., 72.3%) which was recrystallised from Nitromethane to give white needles m.p.190-191° (Found: N, 10.4. $C_{14}H_{25}N_{2}OP$ requires N, 10.6% ; m.p. 188-189°(64)).

Preparation of Bis (tert.butylamino)phenylphosphine sulphide:

The phosphine (3.4187g., 13.57mmoles) and sulphur (0.4386g., 13.71mmoles) gave a white solid (3.89g., 100%)

which was recrystallised from alcohol to give a white crystalline product, m.p. 106-106.5° (Found: N, 9.6. $C_{14}H_{25}N_2PS$ requires N, 9.9%.

Preparation of Bis(tert.butylamino)phenylphosphine selenide:-

The phosphine (2.7629g., 10.9mmoles) and selenium (0.9994g., 12.66mmoles) gave a grey solid (3.214g., 87.3%) which recrystallised from n-hexane to give a white crystalline product m.p. 104-105°. (Found: N, 8.6. $C_{14}H_{25}N_2PSe$ requires N, 8.5%).

CHAPTER IV

Transition metal complexes of bis(diethylamino)phenylphosphine and bis(diphenylphosphino) ethylamine

INTRODUCTION

In any study of compounds containing a tervalent phosphorus atom, investigation of the co-ordinating ability of such compounds with transition metal salts is an essential feature. Transition metal complexes of tervalent phosphorus-nitrogen compounds were almost unknown at the start of this work apart from the mercury (II) iodide adducts of the systems Ph_2PNEt_2, $PhP(NR_2)_2$ and $(Ph_2P)_2NR$ (R = alkyl group) isolated by Ewart.(54) It was therefore of interest to expand this work and prepare aminosphosphine complexes with nickel (II), cobalt (II), palladium (II), platinum (II) and copper (I) and compare the properties of the compounds isolated to those of a similar structure involving tertiary phosphines as ligands.

Two aminophosphines were chosen to act as ligands in the proposed complexes because of their ready availability and the ease with which they could be handled. They were bis(diethylamino)phenylphosphine, $PhP(NEt_2)_2$, and bis(diphenylphosphino)ethylamine, $(Ph_2P)_2NEt$, which may be compared to a tertiary monophosphine and a tertiary diphosphine respectively.

In aminophosphine systems, as already stated, interaction occurs between the lone pair on nitrogen and the vacant 3d orbitals on phosphorous giving rise of $p_{\pi} - d_{\pi}$ back bonding.

Thus in a situation where these compounds are acting as ligands, delocalisation of the high electron density on the central metal atom via $d_{\pi} - d_{\pi}$ bonding, may be difficult since some of the 3d orbitals on phosphorus are already involved in π bond formation. This difficulty is not encountered with tertiary alkylphosphines since the 3d orbitals are fully vacant but in tertiary phosphines having an aromatic group attached to phosphorus, interaction between the π molecular orbital of the benzene ring and the 3d orbitals has been postulated on the evidence of ultra violet absorption spectra.

The effects both $p_{\pi} - d_{\pi}$ bonding and interaction of the aromatic π molecular orbitals with the 3d orbitals are expected to be important factors governing the ease of formation and stability of the aminophosphine complexes.

RESULTS & DISCUSSION

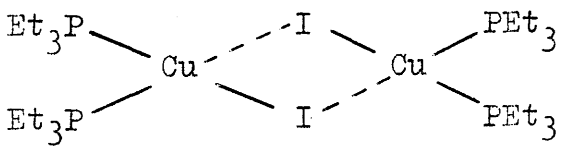
RESULTS & DISCUSSION

Copper (I) iodide adducts of bis(diethylamino)phenylphosphine

One of the recognised methods of characterising tertiary monophosphines and arsines is to prepare their highly crystalline, non-ionic gold (I) chloride complexes having the empirical formula ($R_3P(As)AuCl$). However Mann et.al. (100) found that with copper (I) and silver (I) iodide similar derivatives were formed having the formula ($(R_3P(As)MI)_4$).

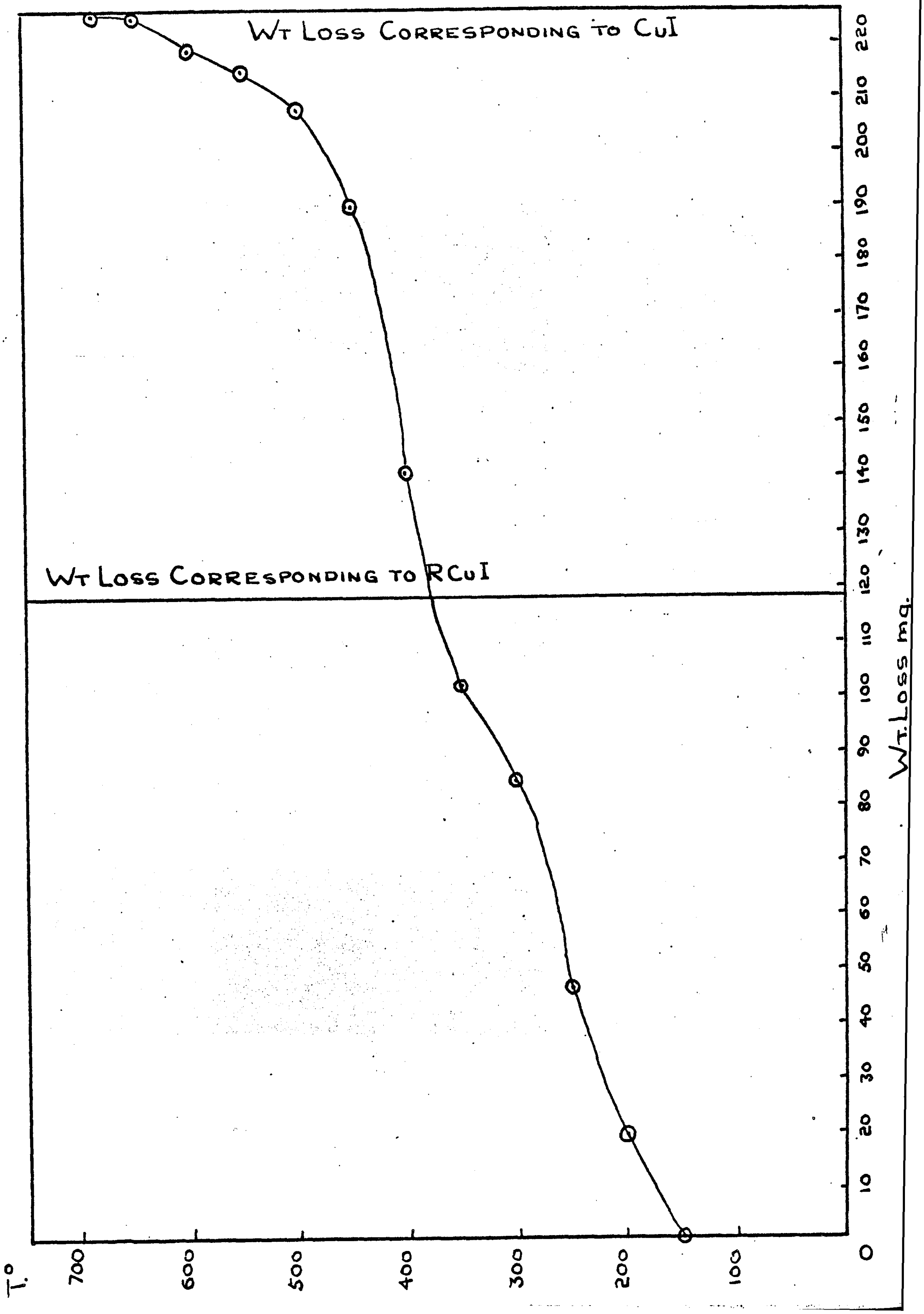
In an attempt to prepare a similar 1:1 copper (I) iodide complex of bis(diethylamino)phenylphosphine, copper (I) iodide dissolved in a saturated solution of potassium iodide was added to an equimolar quantity of the aminophosphine in alcohol giving a white solid. Analysis showed this to be a 2:1 complex of empirical formula L_2CuI ($L = PhP(NEt_2)_2$) and therefore the reaction must have proceeded according to the equation $2L + 2CuI \longrightarrow L_2CuI + CuI$

In 1906, Arbusow (101) reported a compound having an empirical formula of $(Et_3P)_2$ CuI, which on warming readily lost a molecule of triethylphosphine to give the complex $(Et_3P.CuI)_4$. The proposed molecular formula for Arbusow's compound is a dimer $\left[(Et_3P)_2CuI\right]_2$ and its structure may be given as



The complex L_2CuI was found to be monomeric in benzene and nitrobenzene and in the latter solvent is a non-conductor. It is thus the first confirmed case of 3-co-ordination in the chemistry of copper (I). Cass et. al(102) have obtained 2:1 complexes with silver (I) and copper(I) iodide using the ligands p-dimethylaminophenyldimethylphosphine, p-dimethylaminophenyldiethylphosphine and dimethylphenylphosphine but due to the low solubility of the copper (I) complexes molecular weight data was unobtainable. However, the silver (I) iodide complexes are monomeric in benzene over various concentrations and are regarded as examples of 3-co-ordination of the silver (I) atom. It is suggested(103) that this odd co-ordination number is due to the ability of the phosphines to form multiple bonds with the silver atom. By withdrawing one of the 5p orbitals from the hybridised $5s5p^3$ orbitals, used to form σ bonds in 4-co-ordinated compounds, and combining it with two 4d orbitals the silver atom is able to form three strong $\overline{\Pi}$ bonds although electrons are only available to fill two of these $\overline{\Pi}$ type orbitals. However, with two molecules of the phosphine attached to the silver atom, only two such $\overline{\Pi}$ bonds are necessary. The above suggestions appear directly applicable to the 2:1 complexes of copper (I).

FIGURE 7:- WT. LOSS ON HEATING $[PhP(NEt_2)_2]_2CuI$.



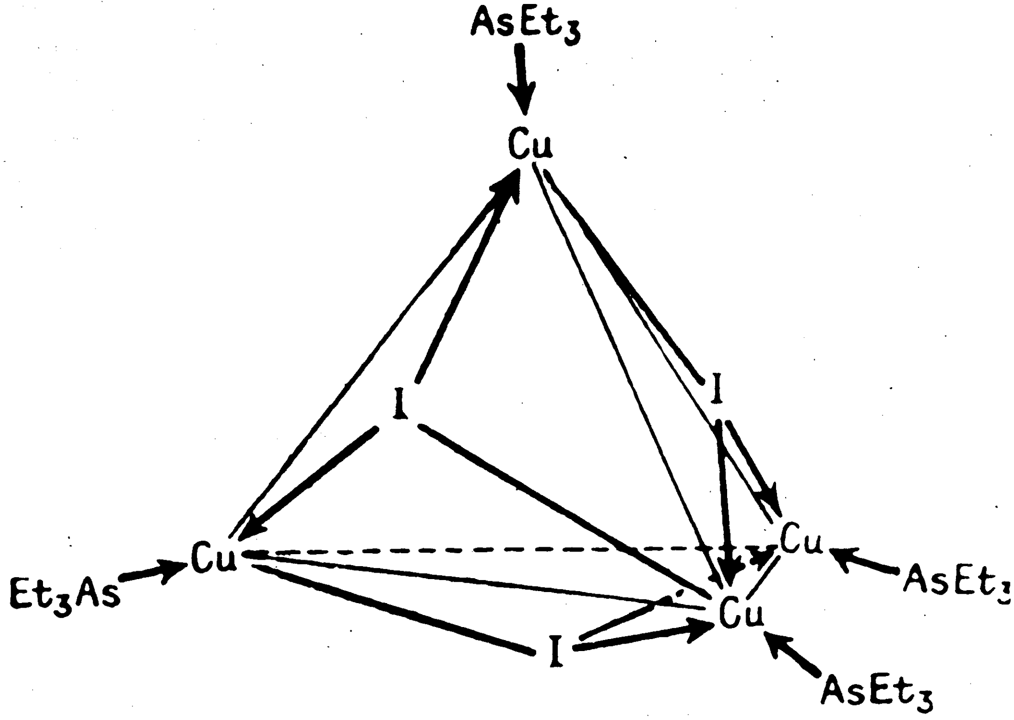
Although the 1:1 copper (I) iodide complex was not isolated on heating L_2CuI, experiments using a thermal balance indicated that such a conversion is possible. The weight loss incurred by heating the 2:1 complex at a steady increase in temperature of 2.76°/min. is shown in figure 7. As can be seen, the complex begins to lose weight at 150° but the rate of weight loss decreases slightly before the point is reached which corresponds to the loss of one aminophosphine molecule. However, there is no definite break at this point and material is again lost steadily till 450° when the rate decreases to a limit at 680° when all the aminophosphine has been removed to leave, presumably, copper (I) iodide. This experiment was repeated without employing a steady increase in temperature and the results are shown in the table below.

	Temp. o	Time min	Weight Loss mg.	Total Weight Loss mg.	% Lost*
A	0-150	80	0	0	0
B	150-310	78	44	44	36
C	310-340	123	16	60	49.5
D	340-350	57	19	79	65.1
E	350-360	185	11	90	74.2
F	360-700	131	24	114	94

(* Removal of both aminophosphine molecules is regarded as 100%.)

The weight loss in B was rapid but was not sufficient to correspond to the complete removal of one molecule of the aminophosphine.

FIGURE 8.



During time C, loss of material was slow but at the end, when it was assumed that one ligand molecule had been removed, weight loss was again rapid (D) despite a small increase in temperature. This must be due to the greater ease with which the aminophosphine is removed from (LCuI) as compared to L_2CuI. During time E the temperature was increased at a steady rate from 360-700^{o} (2.6^{o}/min) and at the end, most of the aminosphosphine had been removed. From the results obtained in this experiment, it would appear that a temperature of about 260^{o} would effect the complete removal of one ligand molecule and thus give the tetrameric 1:1 copper (I) iodide complex.

The 1:1 copper (I) iodide complex of bis(diethylamino)-phenylphosphine was prepared by reacting the 2:1 complex with an equimolar quantity of copper (I) iodide or by adding the aminophosphine to copper (I) iodide in equimolar quantities as described previously. The compound was tetrameric in benzene and therefore has the formula $(LCuI)_4$. A complete X-ray analysis(100) on a similar compound, $(Et_3AsCuI)_4$, has established that the copper atoms are positioned at the apices of a regular tetrahedron with the iodine atoms each lying in the centre, but above the plane, of one face of the tetrahedron (figure 8). It is reasonable to suggest that $(LCuI)_4$ and the compound $\left[(Ph_2PNEt_2)CuI\right]_4$ which was prepared by Ewart(59) have the same steric arrangements.

Reactions of bis(diethylamino)phenylphosphine with nickel (II) and cobalt (II) salts

Reactions of tertiary monophosphines with nickel (II) salts have, in general, given rise to complexes of formula $R_2Ni^{II}X_2$. Alkyl, aryl and alkylaryl tertiary monophosphine complexes have been prepared and voluminous data amassed as to their sterochemical arrangement and properties. Tertiary monophosphine complexes of cobalt (II) are less numerous and are all tetrahedral having the formula $R_2Co^{II}X_2$. They also show a tendency to be oxidised by molecular oxygen and hence are more labile than similar complexes of nickel (II).

These complexes are usually prepared by addition of the ligand to an alcoholic solution of the nickel (II) or cobalt (II) salt (employing an inert atmosphere with the latter), but application of this method failed to produce the required aminophosphine complexes. On addition of bis(diethylamino)-phenylphosphine to an alcoholic solution of nickel (II) chloride hexahydrate, a colour change from green to brown was observed and on standing a brown solid precipitated which, due to its small particle size, could only be isolated by centrifuging the solution. Similar reactions occurred with nickel (II) nitrate hexahydrate in (in n butamol) when the colour change was from green to blue and back to to green on standing and with nickel (II) thiocyanate, the solution turned from blue to green; a green and a deep red solid being isolated from the above reactions respectively. All three compounds had nitrogen values far below the theoretical requirements and were therefore not investigated further. However, the colour changes observed in the solutions are a qualitative indication that complex formation did initially take place and subsequent decomposition must account for the failure to isolate the required compounds. This break-down of the complex in solution is not understood but is believed to be due to alcolholysis of the P-N bond when complexed.

A similar lability occurs in the nickel (II) complexes of triphenylphosphine(104) which are not formed in the presence of, and are decomposed by, the lower alcohols and also by all donor solvents.

The nickel (II) thiocyanate complex was successfully prepared, however, by addition of an alcoholic solution of the thiocyanate to the aminophosphine at -50°, the whole reaction being kept under an atmosphere of dry nitrogen to exclude oxygen and water vapour. Attempts to recrystallise the product of this reaction, a red crystalline solid, were unsuccessful since it was soluble in, and in some cases decomposed, all the organic solvents tried, but analytical figures indicated that it was a pure compound of formula $L_2Ni(SCN)_2$ which is in line with the general proposition for tertiary monophosphine complexes of nickel (II).

Isolation of nickel (II) halide complexes of the aminophosphine using a similar procedure failed. This can be attributed to the strong bonding between the nickel atom and the associated water molecule in the complex ion $(Ni(H_2O)_6)^{++}$ and therefore the anhydrous metal halide was prepared. Nickel (II) chloride hexaydrate which has been dehydrated by refluxing it with acetic acid followed by frequent washing with butan-1-ol is reported to be soluble in cold ethanol(105) but attempts to achieve this were unsuccessful. Since refluxing the aminophosphine with anhydrous nickel (II) chloride was not practicable due to the decomposition which occurred with the nickel (II) thiocyanate complex at elevated temperatures, further investigations were not carried out.

As with the mickel (II) complexes, difficulty was experienced in isolating aminophosphine complexes with Cobalt (II) salts. Reactions of alcoholic solutions of the hydrated salts with the aminophosphine at room temperature or above resulted in a colour change of the solution but no solids corresponding to the formula L_2CoX_2 were obtained. These difficulties were overcome, as in the case of nickel (II), by use of the anhydrous cobalt (II) salt and carrying out the reaction at -50° in an inert atmosphere. Three complexes were thus isolated having the formula L_2CoX_2 where X is SCN, Cl and Br. The complexes were all green solids.

Complexes of bis(diethylamino)phenylphosphine with palladium (II) and platinum (II) chloride.

In general, three types of tertiary monophosphine or arsine complexes of palladium(II) and platinum(II) are known and will be described below.

(i) $L_2M^{II}X_2$:- (where $L=R_3P(As)$; $M=Pd^{II}$, Pt^{II};

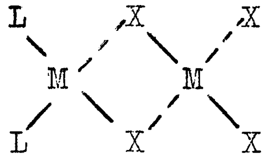
$X=NO_3$, Cl, Br, NCS)

Complexes of this type have been known since the 19th century and are square planar giving rise to cis- and trans-isomerides$^{(106)}$.

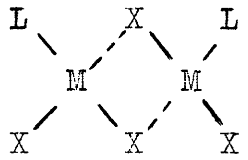
(ii) $(LM^{II}X_2)_2$:- These compounds are prepared$^{(107)}$ by reacting $L_2M^{II}X$ with the corresponding metal halide, e.g.

$$L_2M^{II}X_2 \quad + \quad M^{II}X_2 \quad \longrightarrow \quad (LM^{II}X_2)_2$$

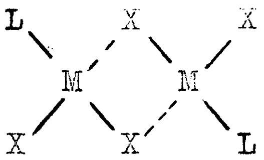
or by heating the compound $L_2M^{II}X_2$ when one molecule of the tertiary monophosphine or arsine is lost. These are square co-planar halide bridged compounds and three geometrical isomers are possible, all of which have been isolated, e.g.,



unsymmetrical



cis-symmetriaal



trans-symmetrical

(iii) $R_3M^{II}X_2$:- Only the palladium (II) and platinum (II bromide complexes of methyldiphenylarsine have been prepared having this formula$^{(108)}$. In solution at room temperature, these compounds are thought to disproportionate giving L_2MBr_2 and L but at -78°, conductance measurements indicate the presence of a uni-univalent electrolyte and the following scheme has been suggested.

$$L_3M^{II}Br_2 \xrightarrow[25^{\circ}]{\text{Acetone}} L_2M^{II}Br_2 + L \underset{}{\overset{-78^{\circ}}{\rightleftharpoons}} L_3M^{II}Br^{+} + Br^{-}$$

Both the palladium (II) and platinum (II) chloride complexes of bis(diethylamino)phenylphosphine which were isolated were of type (i) having the formula $L_2M^{II}Cl_2$. The palladium (II) chloride complex was prepared by shaking an aqueous solution of potassium tetrachloropalladate (II) with an etheral solution of the aminophosphine. The orange ether layer was separated and on slow evaporation gave the required product in the form of yellow crystals. This complex dissolved in all the more common organic solvents but only from low boiling solvents such as acetone and ether could the compound be recovered. With high boiling solvents (alcohol, nitromethane) the solution became a deep brown and a black amorphous precipitate, which was presumed to be elemental palladium, was formed.

The method of preparation used for the palladium(II) complex failed to produce the platinum(II) analogue. However, it was prepared by adding an aqueous solution of the aminophosphine to a similar solution of potassium tetrachloroplatinate(II). Removal of the precipitated potassium chloride followed by slow evaporation of the filtrate gave pale yellow crystals of the platinum(II) complex. This compound did not show the same instability in solution, as noted with the palladium(II) complex, and could be recrystallised from ethanol.

Molar conductances of the transition metal complexes of bis(diethylamino)phenylphosphine

The conductances were measured in pure nitrobenzene at 25° and are given in table 13. The nickel (II) and cobalt (II) thiocyanate complexes give values for Λ_M which, although low compared to other reported values, indicate that they are acting as uni-univalent electrolytes. Dissociation into two ionic species is further confirmed by a molecular weight determination of the nickel (II).

complex in nitrobenzene which gives a value of just over half the formula weight. The ionic species which exist in solution have not been investigated but the following ionisation is suggested.

$$L_2M^{II}(NCS)_2 \xrightarrow{PhNO_2} L_2M^{II}(NCS)PhNO_2^{\;+} + NCS^{-}$$

The complexes of copper (1) and platinum (II) are non-electrolytes but the ΛM values for those of cobalt (II) bromide and chloride and palladium (II) chloride are sufficiently high to warrant very slight dissociation, probably similar to that given above.

Stability of the complexes of bis(diethylamino)phenylphosphine.

The cobalt (II) and nickel (II) complexes decomposed if the solids were left in contact with the solutions at temperatures $> 0^{\circ}$ or if left damp with solvent after filtration. Decomposition was rapid if the solids, when isolated, were left open to the atmosphere and a dark red waxy solid and green oils were produced in the case of the nickel (II) and cobalt (II) complexes respectively. However, these complexes could be stored unchanged indefinitely in evacuated sealed tubes. The nature of these changes was not investigated, the products being sparingly soluble in all solvents apart from dilute aqueous strong acids and of indefinite composition. Hydroxy-, alkoxy or oxy- compounds are possible due to hydrolysis or alcoholysis of the P-N bond leading to a subsequent break-down of the complex. Oxidation of the metal atom is also a possibility.

Qualitatively, the complexes of copper (I), platinum (II) and palladium (II) are far more stable than those already mentioned since they are more easily prepared and can be handled in the atmosphere without immediate decomposition. After a long period of time (ca. 6 months), however, these complexes also decompose losing their crystalline form to give waxy solids.

The instability of the nickel (II) complex is unusual and apart from triphenylphosphine complexes already mentioned, no previous instance of decomposition has been reported. On the other hand, difficulty in preparation and rapid decomposition have been a prominent feature in the chemistry of tertiary phosphine or arsine complexes of cobalt (II). Jensen(109) prepared the compounds $(PEt_3)Co^{II}Cl_2$ and $(PPr_3^{\underline{n}})_2Co^{II}Cl_2$ and found them to be most unstable if left open to the atmosphere. Of eight phosphines studied, Cass et. al.(102) found that only p-dimethylaminophenyldimethylphosphine formed complexes with cobalt (II) salts but these were difficult to isolate and purify. It is possible that this decomposition results in a change of oxidation state of the metal atom for the complex Co(diarsine)$_2$ Cl$_2$ in contact with the atmosphere gives a mixed cobalt (II) - cobalt (III) compound of formula $\left[Co(diarsine)_2\ Cl_2\right]_2^+ CoCl_4^=$ (diarsine = o-phenylenebisdimethylarsine), and it was noted that transformation into the tervalent state was accompanied by an enhanced stability(110). Atmospheric oxidation of the cobalt (II) complexes of ethylene-bis(diethylphosphine in solution also accurred(118) giving compounds of formula $\left[C_2H_4\ (PEt_2)_2Co^{III}X_2\right]$ X (X=Br$_2$Cl). Since the cobalt (II) and nickel (II) complexes of bis(diethylamino)-phenylphosphine decomposed even when kept in a dry box, it was assumed that oxidation was the prime cause of the instability of these compounds.

Structure if the nickel (II), cobalt (II), palladium (II) and platinum (II) complexes of bis(diethylamino)phenylphosphine

Tertiary monophosphine complexes of nickel (II) having the formula $L_2Ni^{II}X_2$ have been assigned a tetrahedral or square co-planar structure. Examples of the former, which are high spin complexes having having magnetic moments in the range 4.1 - 4.9B.M., have until recently been rather uncommon but Venanzi et.al.(104, 105, 111) using the ligands triphenylphosphine and butyldiphenylphosphine have prepared nickel (II) halide complexes which are tetrahedral and pseudo-tetrahedral respectively. The uncertainty with the butyldiphenylphosphine complexes arises from values of magnetic moments obtained in solution which indicate an equilibrium of the following type,

$$\underset{\text{(paramagnetic)}}{(Ph_2BuP)_2NIX_2} \xrightleftharpoons{\text{BENZENE}} \underset{\text{(diamagnetic)}}{(Ph_2BuP)_2NIX}$$

Nickel (II) halide complexes of phenyldibutylphosphine, trialkylphosphines and all nickel (II) thiocyanate complexes are diamagnetic, having a square co-planer structure. With the thiocyanate ion, a low spin complex is formed irrespective of the phosphine ligand due to the large crystal-field splitting caused by the anion. The complex $\left[PhP(NEt)_2\right]_2Ni^{II}(NCS)_2$ was found to be diamagentic and had absorption bands at 35,300cm.$^{-1}$ and 25,800cm.$^{-1}$. Bands in the region 35,500-33,000cm.$^{-1}$ have, in similar complexes, been assigned(112) to the phosphine ligand since they do not later on changing the anion. The band at 25,800cm.$^{-1}$ is attributed to charge transfer from the anion to the central metal atom and absorptions at similar frequencies have been observed in $(Bu_2PhP)_2Ni^{II}(NCS)_2$ (25,770cm.$^{-1}$), $(BuPh_2P)_2Ni^{II}(NCS)_2$

(24,900cm.$^{-1}$) and $(Et_3P)_2Ni^{(II)}(NCS)_2$(27,000cm.$^{-1}$). On the basis of this evidence and previous discussion, the complex is square co-planar and although no dipole moments were measured it probably has a trans-configuration as in $(Ph_3P)_2Ni^{II}(NCS)_2$.

A similar structure is suggested for the Pd(II) and Pt(II) complexes of bis(diethylamino)phenylphosphine since they are diamagnetic and a square co-planar structure is in line with other Pd(II) and Pt(II) complexes of formula $L_2M^{II}X_2$. Complexes of this type are all diamagnetic but it is interesting to note that magnetic measurements on $\left[PhP(NEt_2)_2\right]_2Pd^{II}Cl_2$ using a Gouy type balance gave values of 4-6 B.M. The compound was purified and sent to Professor Lewis in Manchester who established that it was diamagnetic as expected. The nature of the paramagnetic impurity or of an alternative form of the complex was not investigated. The palladium(II) complex gives an absorption at 25,510cm.$^{-1}$.

The cobalt(II) compounds, $\left[PhP(NEt_2)_2\right]_2Co^{II}X_2$ where X=NCS, Cl, Br, have magnetic moments in the range 4.34 - 4.53 B.M., indicative of three unpaired electrons. The spin only value for a complex having three unpaired electrons is 3.88 B.M., but the higher experimental values are attributable to an orbital contribution to the magnetic moment. The absorption spectra of $\left[PhP(NEt_2)_2\right]_2Co(NCS)_2$

show bands at 35,720cm.$^{-1}$ (due to ligand), 13,[illegible] .$^{-1}$ and 15,900cm.$^{-1}$. The last band is found over the range 14,000cm.$^{-1}$ - 17,000cm.$^{-1}$ in all tetrahedral tertiary monophosphine complexes of cobalt (II) salts and is due to the transition from the $^4A_2$ ground state to the $^4T_1$ (P) state. These compounds have magnetic moments of 4.3 - 4.9 B.M. The complex $[PhP(NEt_2)_2]2\ Co^{II}(NCS)_2$ must clearly have a tetrahedral structure and it is assumed that this will also apply to the bromide and chloride complexes but it is expected, in the latter two compounds, that the absorption band around 15,000cm.$^{-1}$ will move to lower wave numbers(113).

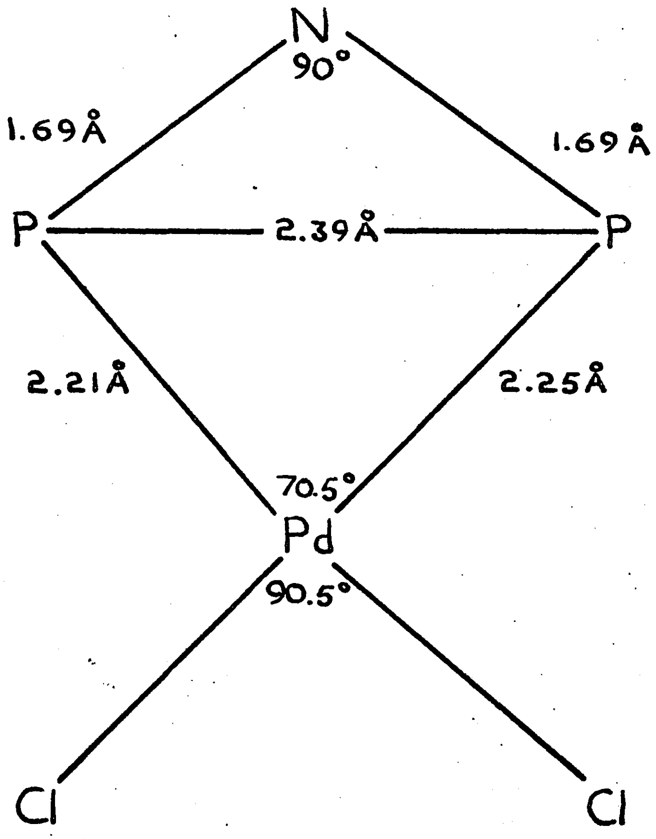
Complexes with bis(diphenylphosphino)ethylamine.

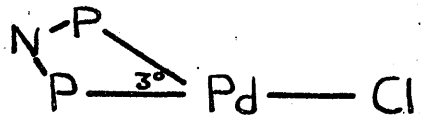
The complexes isolated of nickel (II), palladium (II) and copper (I) with the ligand bis(diphenylphosphino)-ethylamine, $(Ph_2P)_2NEt$, their colour and melting points are given below.

COMPLEX	COLOUR	m.p.°
*R Ni Cl_2	Red	309
R Ni Cl_2	Red	269-270
R Ni Br_2	Dark red	289-291
R Ni I_2	Purple	285-286
R $Ni(NCS)_2$	Brown	252-253
R $Ni(NO_3)_2$	Yellow	160-163
R Pd Cl_2	Yellow	276-278
R Cu I	White	242

$R=(Ph_2P)_2NET$; * $R=(Ph_2P)NMe$.

FIGURE 9:- STRUCTURE OF $(Ph_2P)_2NEt\,PdCl_2$.

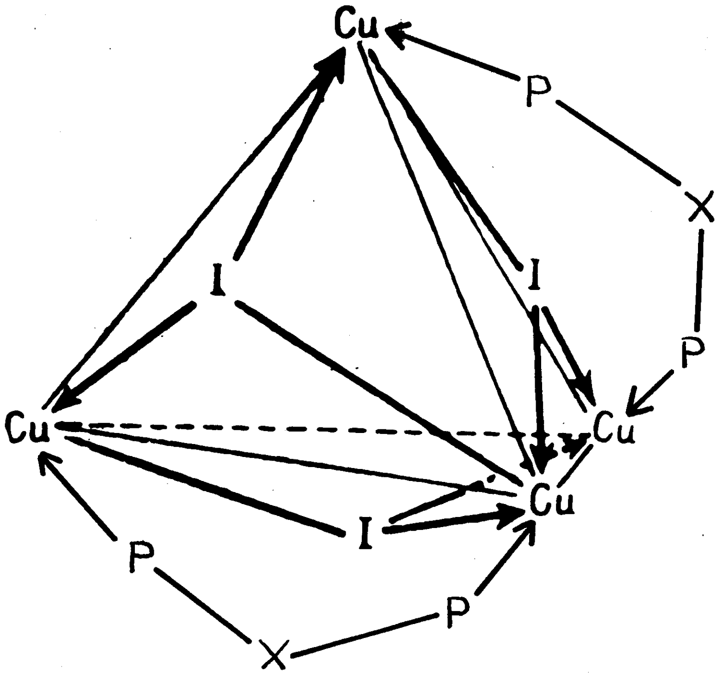




The nickel (II) halide and thiocyanate complexes were easily prepared by adding a boiling ethanolic solution of the aminophosphine to a boiling ethanolic solution of the nickel (II) salt when a crystalline solid precipitated almost immediately. The compound $(Ph_2P)_2NEtNI(NO_3)_2$ was not formed in ethanol and if the solvent used for its preparation, 2-methylpropanol, was heated to above 60^o decomposition appeared to take place resulting in a brown colloidal precipitate. The copper (I) iodide and palladium (II) chloride complexes were prepared in the same way as those of bis(diethylamino) phenylphosphine.

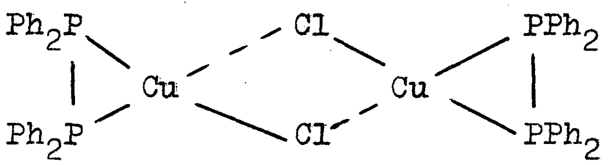
In the survey, it was mentioned that in its reactions with mercuric iodide, bis(diphenylphosphino)ethylamine acted as if it were a bidentate ligand. The nickel (II) and palladium (II) complexes, listed above, of formula $(Ph_2P)_2NEtM^{II}X_2$ give further indication of the aminophosphines bidentate nature and conclusive proof of this has now been obtained from an X-ray structure determination on the complex $(Ph_2P)_2NEtPdCl_2$ carried out by Mr. J. Mokoulo of this department. His results, shown in figure 9, clearly show the four membered ring formed between the complex and the metal atom.

FIGURE 10.



X= O OR NEt

On the basis of its monomeric nature in chloroform, the complex $(Ph_2P)_2NEtCu^II$ is another example of 3-co-ordination in the chemistry of copper (I). A similar complex with tetraphenyldiphosphine of empirical formula Ph_2P-PPh_2CuCl has been prepared(114), but its molecular weight was not measured. This compound could therefore be dimeric.



or more likely, since the biphosphine acts as a monodentate ligand with nickel (II), cobalt (II) and palladium (II) salts, tetrameric having the tetrahedral structure as in figure 8. On the other hand, tetracyclohexyldiphosphine and copper (I) bromide give the complex $[(C_6H_{11})_2P]_2(Cu^IBr)_2$ but again, no molecular weight data was available(115). Bis(diphenylphosphino)ethylamine is reported to give a complex having a similar empirical formula with copper (I) iodide (m.p.165-168°) but this has not been fully substantiated. If these two copper (I) complexes are tetrameric the structure in figure 10 is suggested,

The nickel (II) and palladium (II) complexes are diamagnetic and their absorption bands in the ultra-violet and visible spectrum are given below. Extinction co-efficients are not recorded due to the incomplete solubility of these compounds in the solvents used. These complexes are of the low spin type and have a square co-planar structure.

COMPLEX	SOLVENT	cm.$^{-1}$
R Ni Cl_2	Benzene	34,130 20,620
R Ni Br_2	Benzene	33,780 19,850
R Ni I_2	Benzene	31,850 18,310
RR Ni $(NCS)_2$	Chloroform	30,300 21,800
R Ni $(NO_3)_2$	Chloroform	26,100 22,200

$R = (Ph_2P)_2NEt$

The band around 20,000cm.$^{-1}$ is observed in tertiary monophosphine complexes having a square co-planar structure; so also is the shift to lower wave numbers in going from Cl to 1. In figure 9 it can be seen that there is a slight distortion from the pure square co-planar structure in the case of $(Ph_2P)_2$ $NEtPd^{II}Cl_2$. Whether such a distortion will exist in the nickel (II) complexes is uncertain and could only be established by X-ray techniques. The structure of the nickel (II) nitrate complex is still unknown since some of its physical properties differ from those of the other nickel (II) compounds.

In the preparation of this compound, it was noted that the initial red solution changed on standing to green. Jensen(117) observed a similar transient red colouration in solution during the preparations of the tetrahedral complexes $(PhEt_2P)_2Ni^{II}(NO)_3)_2$ and $(PEt_3)_2Ni^{II}(NO_3)_2$ which he attributed to the formation of an intermediate square co-planar compound. However, $(Ph_2P)_2NEtNi^{II}(NO_3)_2$ is diamagentic thus ruling out a tetrahedral structure. Further, the conductance values in nitrobenzene indicate that it contains two ionic species in solution. $Co^{II}(TEP)Br_2$(118) TEP=ethylenebis(diethylphosphine) in nitrobenzene has the structure $\left[Co^{II}(TEP)_2\right]^{2+}\left[Co^{II}Br_4\right]^{2-}$ although the conductance 16.4 mhos. is far lower than required for a di-divalent electrolyte. This explanation could be applied to the nickel (II) nitrate complex but in view of the doubt which exists, it is obvious that this compound merits further investigation.

It is of interest to compare the co-ordinating ability of bis(diphenylphosphino)ethylamine to that of other tertiary diphosphines and arsines. The compound most closely related to $(Ph_2P)_2NEt$ is methylenebis(diphenyl-Phosphine) in which the - NEt group has been replaced by CH_2. Unfortunately, no complexes with nickel (II) or palladium (II) salts have been reported but with osmium (II) and ruthenium (II) chloride (119) the tertiary diphosphine acts as a bidentate ligand forming octahedral complexes of the type $L_2M^{II}Cl_2$. In diphosphines where the phosphorus atoms are separated by two carbon atoms such as TEP(118) and the o-phenylenebisdialkylphosphines(120) and arsines(121) complexes isolated with nickel (II) and cobalt (II) have the formula

$$\underset{1}{(\text{ P-x-P }) M^{II}X_2} \; ; \; \underset{11}{(\text{ P-x-P })_2 M^{II}X_2}$$

With the o-phenylene compounds, the ease with which complexes of type II are formed is due to their rigid structure which holds the co-ordinating atoms in a favourable position for chelation. With diphosphines where the two phosphorus atoms are joined directly, a marked difference exists between the type of co-ordination found with tetraphenyldiphosphine (114) and tetracyclohexyldiphosphine (115). The former diphosphine acts as a monodendate ligand while the latter is bidentate forming complexes with nickel (II), palladium (II) and cobalt (II) salts of formula $LM^{II}X_2$, no compounds of the form $L_2M^{II}X_2$ being isolated. The complexes isolated with bis(diphenylphosphino)ethylamine indicate, therefore, that its co-ordinating ability is more similar to that of tetracyclohexyldiphosphine than to that of the other tertiary diphosphines discussed. Recent work done in this department by Mr. A. Walker (81) confirms the above statement, since in the reactions of $(Ph_2P)_2NR$ (R=Me, Et.) with molybdenum hexacarbonyl, only two carbonyl groups could be replaced despite vigorous reaction conditions while in similar reactions involving $(Ph_2P)_2CH_2$, $o-C_6H_4(PEt_2)_2$ and $(CH_2PPh_2)_2$, two and four carbonyl groups were replaced by each ligand (122).

The instability in the transition metal complexes of bis(diethylamino)phenylphosphine was not found in those of bis(diphenylphosphino)ethylamine which remained unchanged after exposure to the atmosphere for two years. This difference in stability is thought to be a result of the extent of $d_\pi - d_\pi$ back bonding between the metal atom and phosphorus. Thus, in $PhP(NEt)_2$, the situation arises where the vacant 3d orbitals on phosphorus are so involved with $d_\pi - p_\pi$ bonding with the two nitrogen atoms that they are unable to disperse the excess negative charge on the metal atom which would stabilise the complex. The non-bonded p orbital of the nitrogen atom in $(Ph_2P)_2NEt$

is capable of back bonding with the 3d orbitals on two phosphorus atoms and, it may therefore be stated that quantatively, the extent to which these 3d orbitals are involved with $p_\pi - d_\pi$ bonding is four times less than in $PhP(NEt_2)_2$. Metal to ligand $d_\pi - d_\pi$ bonding will thus occur causing a strong metal-ligand bond and explaining why $(Ph_2P)_2NEt$ stabilises the lower oxidation states of the transition metal atoms discussed to a much greater extent than $Php(NEt_2)_2$. It would also appear that the interaction of the aromatic molecular orbital with the 3d orbitals on phosphorus is small compared to that of the 2p nitrogen orbital.

On the basis of the above argument, it is expected that the stability of similar transition metal complexes of diethylaminodiphenylphosphine, Ph_2P-NEt, will, when prepared, be intermediate between those of the two aminophosphines discussed.

SUMMARY

In the transition metal complexes of bis(diethylamino)-phenylphosphine it was found that the aminophosphine is monodentate thus behaving like a tertiary monophosphine. Compounds isolated had the formula L_2MX_2 ($L=PhP(NEt_2)_2$; M=Ni(II), Co(II), Pd(II), Pt(II)) and from the magnetic moments and absorption spectra of these complexes, those of cobalt(II) (X=NCS, Cl, Br) had a tetrahedral structure while the rest were square co-planar. With copper (I), two complexes were isolated of formula $(LCuI)_4$ and L_2CuI, the latter being regarded, due to its monomeric nature, as the first confirmed example of 3-co-ordination in the chemistry of copper (I).

The complexes of bis(diphenylphosphino)ethylamine have the formula LMX_2 ($L=(Ph_2P)_2NEt$; M=Ni(II), Pd(II)) and are all square co-planar. The aminophosphine is bidentate and its co-ordinating ability was found to resemble that of tetracyclohexyldiphosphine in preference to that of other tertiary diphosphines. The copper(I) complex, LCuI, is monomeric and therefore 3-co-ordinate.

The relative stability of the complexes formed with the two aminophosphines is discussed in terms of the bonding within the aminophosphines themselves.

EXPERIMENTAL

Preparation of bis(diethylamino)phenylphosphine:-

Diethylamine (63.8 g., 0.8724 mole), which had been dried over potassium hydroxide pellets, (63.8 g., 0.8724 mole) in dry benzene (100 ml.) was added with stirring and under a stream of dry nitrogen to dichlorophenylphosphine (36.4 g., 0.2034 mole) in dry benzene (500 ml.) Stirring was continued for 3 hours after addition of the diethylamine and the diethyammonium chloride (43.5 g., required 44.6 g.) removed by filtration. Removal of the benzene under reduced pressure left a brown oil which was distilled to give a colourless product (33.66 g., 65.6%), b.p. $80^{\circ}/10^{-1}$mm. (Found: N, 10.8. $C_{14}H_{25}N_2P$ requires N, 11.1%)

Bisthiocyanatodi(bis-diethylaminophenylphosphine) nickel(II)

Potassium thiocyanate (1.13 g., 11.6 mmoles) dissolved in boiling ethanol (25ml) was added to nickel(II) nitrate hexahydrate (1.73 g., 5.96 mmoles) dissolved in ethanol (25ml). Potassium nitrate was filtered off and the green alcoholic solution of nickel(II) thiocyanate was added dropwise with stirring, under nitrogen, to bis(diethylamino)phenylphosphine (3.28 g., 13.1 mmoles) in ethanol (25ml) and kept at -50°. The resulting red crystalline complex was filtered off under nitrogen and dried in vacuo (1.538 g., 38%),m.p.$99-105^{\circ}$ (Found: N, 12.4; Ni 8.8; M(cryoscopic in nitrobenzene) 355. $C_{30}H_{50}N_6NiP_2S_2$requires N,12.4; Ni, 8.6%; M, 680).

Bisthiocyanatodi(bisdiethylaminophenylphosphine) cobalt(II):-

As described above, potassium thiocyanate (0.424 g.,4.36 mmoles) was added to cobalt(II) nitrate hexahydrate (0.609g., 2.09 mmoles) and the resulting solution of cobalt(II) thiocyanate added to the aminophosphine (0.997 g.,2.09 mmoles). A green crystalline complex (0.447 g., 33%), m.p.98-102° was obtained. (Found: N, 12.2; S, 9.2. $C_{30}H_{50}CoN_6P_2S_2$ requires N, 12.4; S, 9.4%).

Dichlorodi(bisdiethylaminophenylphosphine) cobalt (II):-

Cobalt(II) chloride hexahydrate (0.354 g., 1.49 mmoles) was dehydrated at 180° under a stream of hydrogen chloride and added slowly in ethanol (15 ml) to the aminophosphine (0.780 g., 3.09 mmoles) as described previously. A green crystalline complex (0.475 g., 50.3%), m.p. ca. 70° (decomp.) was obtained. (Found: N,8.5; Cl, 10.9.$C_{28}H_{50}Cl_2CoN_4P_2$requires N, 8.5; Cl, 11.2%)

Dibromodi(bisdiethylaminophenylphosphine) cobalt (II):-

Cobalt(II) bromide (0.4307 g.,1.968 mmoles) which had been dehydrated at 180° under a stream of hydrogen bromide, in ethanol (15ml)and the aminophosphine (1.0342g., 4.097 mmoles) under the conditions described above gave a pale green product (1.1515 g., 84.7%),m.p. 110-112°. (Found: N,7.5. Br, 21.8, $C_{28}H_{50}Br_2CoN_4P_2$ requires N, 7.7; Br, 21.9%)

Dichlorodi(bisdiethylaminophenylphosphine) palladium(II):-

Potassium tetrachloropalladate(II) (0.308 g.,4.01 mmoles in water (25 ml) was shaken with the aminophosphine (2.093 g.,8.30 mmoles) in ether (75 ml.). The ethereal layer was separated, dried over calcium hydride and allowed to evaporate slowly to give a yellow complex (1.611 g., 59%), m.p.109-111°. (Found: N, 8.0; Cl, 10.0. $C_{28}H_{50}Cl_2N_4P_2Pd$ requires N, 8.2; Cl, 10.4%)

Dichlorodi(bisdiethylaminophenylphosphine) platinum(II):-

Potassium tetrachloroplatinate(II) (0.360 g., 0.867 mmoles dissolved in water (7 ml) and acetone (12 ml.) was added to the aminophosphine (0.442 g.,1.75 mmoles). The potassium chloride formed was removed by filtration and on slow evaporation of the yellow filtrate a pale yellow cyrstalline product (0.2567 g., 38.5%) m.p. 100-104° was obtained. (Found: N,7.4; Cl,9.1. $C_{28}H_{50}Cl_2N_4P_2Pt$ require N, 7.3; Cl, 9.2%)

Iododi(bisdiethylaminophenylphosphine) copper (I):-

Copper(i) iodide (1.299g.,6.88 mmoles) in a saturated potassium iodide solution (50 ml), was added to the aminophosphine (3,220 g.,23.8 mmoles) in ethanol (50 ml) and cooled to 0°. The white precipitate (4.290 g.,96.7%) was removed by filtration, washed with water to remove any potassium iodide and recrystallised from ethanol to give a crystalline complex, m.p. 103°. (Found: N,8.3; Cu, 8.9

I, 19.0. $C_{28}H_{50}CuIN_4P_2$ requires N, 8.1; Cu, 9.1; I, 18.3%) The molecular weight of this complex was determined ebullcoscopically in benzene (M, 627), cryoscopically in benzene(M,679) and cryoscopically in nitrobenzene (M,703).($C_{28}H_{50}CuIN_4P_2$ requires M, 695).

<u>Iodobis(diethylamino)phenylphosphine copper(I)</u>:-

Copper (I) iodide (0.285g., 1.50 mmoles) dissolved in a saturated potassium iodide solution (25 ml) was added to iododi(bisdiethylaminophenylphosphine) copper (I) (1.132 g., 1.63 mmoles) in boiling ethanol. A white solid (1.183 g., 89%), m.p. 194-198° was obtained. (Found: N, 6.3; Cu, 14.2; I, 28.8; M, (cryoscopically in benzene) 1669, 1848. $C_{14}H_{25}CuIN_2P$ requires N. 6.3; Cu, 14.3; I, 28.7%; M, 1772).

This complex was also made directly by adding the aminophosphine to copper(I) iodide in equimolar quantities.

<u>Dichlorobis(diphenylphosphino)methylaminenickel(II)</u>:-

Bis(diphenylphosphino)methylamine (1.0524g.,2.608 mmoles) in boiling ethanol (75 ml) was added to nickel(II) chloride hexahydrate (0.6804 g.,28.6 mmoles) in boiling ethanol (25ml). The resulting red solution on standing yielded a red crystalline product (0.8574 g., 62.1%) which recrystallised from nitromethane, m.p. 309°. (Found: N, 2.9; Ni, 11.1. $C_{25}H_{23}Cl_2N\ NiP_2$ requires N, 2.7; Ni 11.1%).

The above method was used to prepare the following complexes.

Dichlorobis(diphenylphosphino)ethylaminenickel(II):-

Bis(diphenylphosphino)ethylamine (0.3936 g., 0.955 mmoles) and nickel(II) chloride hexahydrate (0.251 g., 1.73 mmoles) gave a red crystalline product (0.3013 g., 59%), m.p. 269-270°. (Found: N, 2.6; Cl, 12.9. $C_{26}H_{25}Cl_2N\ NiP_2$requires N, 2.6; Cl, 13.1%).

Dibromobis(diphenylphosphino)ethylaminenickel(II):-

The aminophosphine (0.9908 g., 2.395 mmoles) and nickel(II) bromide (0.7090 g., 3.241 mmoles) gave a dark red crystalline complex (1,2393 g., 81.9%), m.p. 289-291° (Found: N, 2.4; Br 25.5. $C_{26}H_{25}Br_2N\ Ni\ P_2$ requires N, 2.2; Br, 25.3%)

Di-iodobis(diphenylphosphino)ethylaminenickel(II):-

The aminophosphine (0.8211 g., 1.986 mmoles) and nickel(II) iodide gave a purple crystalline complex (1.2030 g., 83.5%), m.p. 285-286° (Found: N, 2.0; 1, 35.0. $C_{26}H_{25}I_2NNiP_2$ requires N, 1.9; 1, 34.7%)

Dithiocyanatobis(diphenylphosphino)ethylaminenickel(II):-

Nickel(II) nitrate hexahydrate (0.7537 g., 2.593 mmoles) in boiling ethanol (15ml) was added to potassium thiocyanate (0.4914 g., 5.058 mmoles) in boiling ethanol (15 ml). The potassium nitrate formed was removed by filtration and the green alcoholic solution of nickel(II) thiocyanate and the aminophosphine (0.8165 g., 1.974 mmoles) gave an orange crystalline product (0.9942 g., 85.6%), m.p. 252-253°. (Found: N, 7.2; S, 10.9. $C_{28}H_{25}N_3NiP_2S_2$ requires N, 7.2; S, 10.7%).

Dinitratobis(diphenylphosphino)ethylaminenickel(II):-

The aminophosphine (0.576 g., 1.39 mmoles) in cold 2 - methylpropanol (10ml.) was added to nickel(II) nitrate hexahydrate (0.434 g., 1.49 mmoles) in 2 - methylpropanel (10ml). The resulting red solution on standing yielded a yellow crystalline product (0.536 g., 65%), m.p. 160-163°. (Found: C, 56.0; H, 5.1; N, 7.1. $C_{26}H_{25}N_3NiO_6P_2$ requires C, 52.4; H, 4.7; N, 7.0%.)

Dichlorobis(diphenylphosphino)ethylaminepalladium(II):-

The aminophosphine (8.268 g., 20.0 mmoles) in warm acetone (120ml.) and water (3ml.) was added dropwise to potassium tetrachloropalladate(II) (3.265 g., 10.0 mmoles) in water (100 ml.) and acetone (4 ml.). The resulting solution on standing gave a pale yellow solid (6.081 g., 67%) which recrystallised from alcohol, m.p. 276-278°. (Found: C, 53.1; H, 4.3; Cl, 10.8; N, 2.7; P, 10.2; M(from unit cell and density measurements), 590. $C_{26}H_{25}Cl_2NP_2Pd$ requires C, 52.8; H 4.3; Cl, 12.0; N, 2.4; P 10.5%; M, 591).

Iodobis(diphenylphosphino)ethylaminecopper(I):-

Copper(I) iodide (0.2244g., 1.175 mmoles) dissolved in a boiling saturated potassium iodide solution (12ml.) was added to the aminophosphine (1.194g., 2.894mmoles) in boiling ethanol (45ml.) On cooling, a white solid precipitated which was removed by filtration, washed with water and dried in vacuo. Recrystallisation from ethanol gave white needles (0.254g., 35.8%), m.p.242° (Found: I,20.9; N,2.2; M(ebullioscopically in chloroform), 586. $C_{26}H_{25}CuINP_2$ requires I, 21.0; N,2.3%; M,604).

Magnetic moments:- Except for the palladium complex, these were measured on a Gouy-type balance and since the complexes had a sufficiently small crystalline size, powdering of the samples was not required. Sample tubes were made of pyrex glass and calibrated by means of mercury (II) tetrathiocyanatocobaltate (II) ($Xg=16.4 \pm 0.08 \times 10^{-6}$) which was prepared according to Nyholm and Figgis(123). AR cobalt (II) sulphate heptahydrate (28g.) and AR ammonium thiocyanate (30g.) each in boiling distilled water (50ml.) were added to AR mercury (II) chloride (27g.) in distilled water (300ml.) The blue crystalline tetracyanato complexprecipitated and was filtered off and dried at 120°.

Conductance measurements:- These were made at 25° in nitrobenzene (which had been purified by storage over a molecular sieve followed by distillation under reduced pressure) at concentrations around 10^{-3}M by means of a Phillips PR 9500 conductance bridge.

Magnetic Moments and conductances of complexes of bis(diethylamino)phenylphosphine are shown in table 13. Complexes of bis(phenylphosphino)ethylamine are all diamagnetic and, apart from $(Ph_2P)_2NEt.CuI$ (Λ=10.1) and $(Ph_2P)_2NEt.\ Ni(NO_3)_2$ (Λ=27.1), non-electrolytes.

Table 13:- Magnetic moments and conductances of complexes of PhP(NEt$_2$)$_2$

COMPLEX	X$_g$10^6	X$_m$10^6	DIAMAG. CORRECTION 10^6	X$_{corr}$10^6	μ_{EFF}BM	EQUIV.COND	
						Λ M	CONC.M10^{3-}
R$_2$Ni(CNS)$_2$	0.09924	67.45	448.6	516.05	1.106 (DIAM.)	17.34	1,000
R$_2$Co(CNS)$_2$	11.00	7477.8	448.6	7926.4	4.339	21.81	1.145
R$_2$CoCl$_2$	12.92	8202.0	433.4	8635.4	4.534	6.407	1.055
R$_2$PdCl$_2$	21.17 9.46	14440.0 6452.0	433.4	14873.4 6885.4	6.184 4.033	4.033	0.9705
R$_2$PtCl$_2$	-0.01945	-14.99	433.4	418.41	1.000 (DIAM)	0.5924	1.003
(RCuI)$_4$					DIAM	0.9346	0.955
R$_2$CuI					DIAM	3.00	1.116
R$_2$CoBr$_2$	10.72	7750.0	455.8	8205.8	4.426	8.067	1.023

R = PhP(NEt$_2$)$_2$

APPENDIX 1.

The Infra-red spectra of some aminophosphines and their derivatives.

The infra-red spectra of some Aminophosphines.

The spectra of these compounds were recorded on either a Unicam SP100 double-beam infra-red spectraphotometer equipped with an SP130 sodium chloride prism-grating monochromator (3000 lines/in (2150-3650cm^{-1}) and 1500lines/in (650-2150cm.$^{-1}$) and a potassium bromide prism grating (375-1150cm.$^{-1}$); or, a Perkin Elmer Model 237 grating spectrophotometer employing two gratings covering the ranges 625-2000cm.$^{-1}$ and 1250-4000cm.$^{-1}$.

Solids were run in the form of potassium bromide discs using 1-2mg. of the substance in 300mg. KBr, or as a nujol mull. Solvents used for solution spectra were of analytical grade and in the case of chloroform, the solvent was passed down a column of silicagel immediately before use. The concentration was 1^{o}/o w/v and the spectra were run in 1mm. sodium chloride cells. The spectra of the liquid bis(alkylamino)phenylphosphines were recorded in 0.025mm. sodium chloride cells.

General Characteristics.

Since the compounds studied all contain the P-phenyl group, characteristic absorptions of this group were always present and assignments have been made on the basis of those given by Deacon et.al(95) for the tetraphenyl phosphonium salts. The CH aromatic stretching vibrations produce weak bands in the region 3080-3030cm.$^{-1}$. In these compounds two bands always occur in this region along with several weaker bands. In the region 1600-1400cm.$^{-1}$ three bands occur at 1590$\pm$7cm.$^{-1}$(W), 1470$\pm$10cm.$^{-1}$(m-s) and 1435$\pm$4cm.$^{-1}$(s) and are due to the C-C aromatic stretching mode. The latter absorption has until recently been attributed to the P-phenyl group. CH in -plane deformation modes are found near 1178cm.$^{-1}$(W) and 1023cm.$^{-1}$(w-m) and were observed in most compounds but were sometimes masked by stronger absorptions. Similarly, the phenyl ring breathing mode was observed near 998cm.$^{-1}$(w-m). In the region 700-800cm.$^{-1}$, the oxides, sulphides and selenides showed a far greater complexity than the parent aminophosphines in which two peaks occur at 699$\pm$2cm. $^{-1}$(s) and 745$\pm$5cm.$^{-1}$(s). The former peak is due to out-of-plane ring deformations while the latter is the CH out-of-plane deformation mode and in the oxides etc.,is often split giving two bands.

In all the compounds, a strong broad absorption band occurred at 1112$\pm$8cm.$^{-1}$ which was assumed to be the 'X-sensitive' frequency referred to by Deacon et.al.(95). Another 'X-sensitive' mode occurs near 720cm.$^{-1}$ but could not be detected in the bis(alkylamino)phenylphosphines. Although in most of the oxides, sulphides and selenides, bands occurred in the range 700-720cm.$^{-1}$ they were too variable to afford definite assignment to this mode. Bis(ethylamino)phenylphosphine was transparent from 375-690cm.$^{-1}$ and the remaining aminophosphines were not investigated in this range. In most of the oxides, sulphides and selenides, three bands were observed in the region 521-442cm.$^{-1}$ and are all assigned to 'X-sensitive' vibrations.

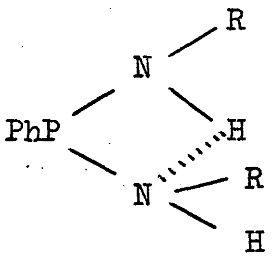
Absorptions due to the alkyl groups attached to nitrogen occurred in the region 2980-2820cm.$^{-1}$(m-s) (CH stretching modes) and near 1470-1440cm.$^{-1}$(w-m) and 1400cm.$^{-1}$(m-s) (CH deformation). Also skeletal vibrations due to the isopropyl and tertiary butyl groups(124) were found at 1163±3cm.$^{-1}$(s) and at 1240cm.$^{-1}$(s), 1231cm.$^{-1}$(s), 1222±2cm.$^{-1}$(s) and 1207±2cm^{-1} respectively.

N-H deformation vibrations in the phosphoramidates have been reported near 1400cm.$^{-1}$. However, assignment of bands in this frequency region is complicated by the presence of other vibrations and therefore this absorption was not investigated.

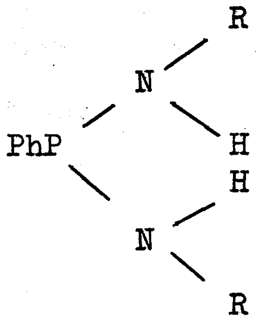
The infra-red spectra of the bis(alkylamino)phenylphosphines.

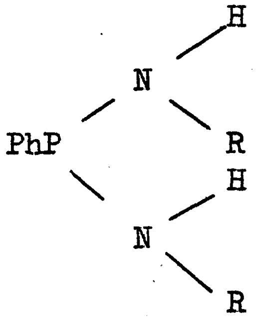
The main bands occurring in the spectra of the bis(alkylamino)phenylphosphines are given in tables 14 and 15; assignments of these bands have been made where possible.

None of these compounds show the presence of free N-H groups and it is assumed that intermolecular hydrogen bonding is taking place between hydrogen and nitrogen. It is also possible that intramolecular hydrogen bonding, resulting from a structure of the type



or from the rotational isomers,





as postulated in the bis(alkylamino)phenylborons(126), is taking place although this could not be established experimentally due to the lability of these compounds.

Since a large number of related compounds, all containing a P-N bond, had been isolated, an attempt was made to assign a frequency to the P-N stretching mode. Reference to the literature on this subject only led to confusion since values of 1155cm.$^{-1}$(67), 850-870cm.$^{-1}$(58), 905-752cm.$^{-1}$ and 773-743cm.$^{-1}$ have been quoted for this frequency. In the bis(alkylamino)-phenylphosphines, a broad strong band in the region 829-929cm.$^{-1}$ is tentatively assigned to the P-N stretching frequency. It would be expected that in the dialkylamino analogues, due to the greater steric forces, the P-N bond would be elongated thus decreasing the P-N stretching force constant and causing a shift to lower frequencies. This is observed and comparison of the spectra of $PhP(NEt_2)_2$ and $PhP(NHEt)_2$ shows bands at 920cm.$^{-1}$ and 929cm.$^{-1}$ respectively. This trend should also be observed in members of the same series so that in the compounds $PhP(NHR)_2$, as R becomes more bulky the P-N stretching frequency will decrease and reference to table 16 shows this decrease in going from R=Et to Bu^t. Similarly formation of a positive charge on phosphorus will decrease the P-N bond length, due to enhanced $p_\pi - d_\pi$ bonding, and thus increases the P-N stretching force constant and also the P-N stretching frequency. Examination of the spectra of the oxides, sulphides and selenides of the bis(alkylamino)phenylphosphines shows that the proposed P-N stretching band has moved to higher frequencies and apart from the sulphide and selenide of bis(tert. butylamino)phenylphosphine appears as two bands of varying intensity separated by about 20cm.$^{-1}$. The values are given in table 16.

Table 16.

COMPOUND	ν P-N cm.$^{-1}$.	ν P-N cm.$^{-1}$.
$PhP(NHEt)_2$	929 s	A 939, 963 m B 947, 963 s C 943, 963 s
$PhP(NHPr^n)_2$	905, 890 m	A 928 s, 938 m
$PhP(NHPr^i)_2$	860 s	A 878, 909 m B 880, 899 m
$PhP(NHBu^t)_2$	829 s	A 837 w 865 m B 842 m C 849 m

A = Oxide; B = Sulphide; C = Selenide.

The occurrance of two bands is probably the result of differing conformations within the molecule which, in the case of the sulphide and selenide of bis(tert.butylamino)-

phenylphosphine, are forced into a single conformation due to the bulky groups attached to phosphorus thus accounting for the single band in these compounds.

The values for the P-N stretching frequency as calculated from Gordy's rule (127) is 735cm.$^{-1}$ and some tervalent phosphorus-nitrogen compounds absorb in the region 750-680cm.$^{-1}$ while others do not. It must therefore be concluded that the P-N stretching frequency is mass sensitive and liable to considerable variation and thus, any assignment of a frequency to this mode is purely speculative.

Infra-red spectra of the alkyl iodide adducts of the bis(alkylamino)phenylphosphines.

The methyl iodide adducts all show a medium absorption at 1307±5cm.$^{-1}$ (m) which only appears as a weak band in the parent aminophosphine. This band is assigned to the symmetrical bending vibration of the CH bonds in the methyl group. The P-C assymetric stretching frequency was found in all the compounds isolated at 775±7cm.$^{-1}$(m-s).

The N-H stretching frequency in these compounds is a broad absorption occurring at 3145±25cm.$^{-1}$. In some cases this absorption is accompanied by a shoulder at a higher frequency of 65±5cm.$^{-1}$. Intermolecular hydrogen bonding is therefore taking place since the solution spectrum of bis(isopropylamino)methylphenylphosphonium iodide in chloroform shows a single peak at 3400cm.$^{-1}$.

The main peaks occurring in the spectra of these compounds are shown in tables 17, 18 and 19.

The oxides, sulphides and selenides of the bis(alkylamino)-phenylphosphines.

The i.r. spectra of some bis(alkylamino)phenylphosphines have already been studied by Gutmann et.al.(128) and their results for the N-H and P=O stretching frequencies along with those isolated by the author are given in the table below.

COMPOUND	N-H stretch cm.$^{-1}$.		P=O stretch cm.$^{-1}$.	
	KBr disc	1%mCCl$_4$	KBr disc	1%in CCl$_4$
PhPO(NHEt)$_2$	3233 (3410,3215)	3402,3183 (3413,3215)	1179 (1180)	1196 (1205)
PhPO(NHPr^n)$_2$	3202	3408,3195	1185	1196
PhPO(NHPr^i)$_2$	3225,3163	3395*	1188	
PhPO(NHBu^t)$_2$	3412,3238 (3410,3240)	3420,3380	1189	1200

*1% in Chcl$_3$; figures in brackets due to Gutmann et.al.

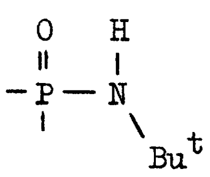
As may be seen, the results are not in complete accordance especially in the case of $PhPO(NHEt)_2$ where no band corresponding to a free N-H group, as reported by Gutmann et.al. ($3410cm.^{-1}$) was observed. Since free N-H groups were also absent from the compounds, $PhPO(NHPr^n)_2$ and $PhPO(NHPr^i)_2$ in which the more bulky alkyl group attached to nitrogen might be expected to give rise to a free N-H group, it must be concluded that Gutmann's observation was incorrect. Also, the values for the N-H stretching frequency of $PhPO(NHEt)_2$ in 1% solution of CCl_4 differ by $10cm.^{-1}$. The values of $340cm.^{-1}$ and $318cm.^{-1}$ were checked against a polystyrene reference ($2850cm.^{-1}$).

It has been found possible to predict (129) the position of the phosphoryl stretching frequency by considering the effect of the substituents V, Y and Z in the molecule VYZP=0. The equation for P=0 is given by

$$\lambda = \frac{39.96 - \Sigma x}{3.993} \ \mu$$

where x is the sum of Xv, Xy and Xz which are the "phosphoryl absorption shift constants" for the substituents V, Y and Z. These shift constants represent an approximate value of the Pauling electronegativity of the groups attached to phosphorus and were derived from compounds containing substituents whose Pauling electronegativities were known (F, Cl, Br). The equation has an average accuracy of ± 0.06µ and the absorption shift constants for the phenyl and alkylamine groups are 2.4 and 3.0 respectively. The value from the equation for the phosphoryl stretching frequency in compounds of the type $PhPO(NHR)_2$ was $1267cm.^{-1}$ ±2 which is far higher than the observed frequencies. The values derived from this equation may only be correlated with experimental frequencies obtained in solution. Since some of the aminophosphine oxides were insoluble in the normal solvents used in infra-red spectroscopy, Gutmann et. al.(128) calculated new values for the shift constants which could be applied to spectra run in KBr discs. The shift constant for the alkylamino group was 2.0, giving a frequency of $1191cm.^{-1}$ for the P=O stretch in close agreement with the values listed in the table.

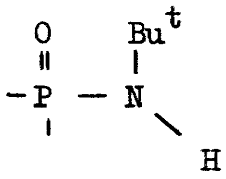
The concentrations employed were too high to eliminate intermolecular hydrogen bonding from the compounds $PhPO(NHEt)_2$ and $PhPO(NHPr^n)_2$ and the ratio of the bonded N-H to the free N-H groups was 6:1. However, in the remaining two oxides, no bonded N-H groups were observed at these concentrations. This was assumed to be the result of the bulky isopropyl and tertiary butyl groups causing steric hinderence to intermolecular hydrogen bonding. In the case of the tertiary butyl oxide, two bands occurred in the free N-H region which, by analogy with the phosphoramidates and phosphoramidothioates$^{(125)}$, were attributed to the presence of cis and trans isomers of the type



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{|}{P}}-\overset{\overset{\displaystyle H}{|}}{N}\diagdown Bu^t$$

cis

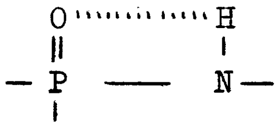
and



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{|}{P}}-\overset{\overset{\displaystyle Bu^t}{|}}{N}\diagdown H$$

trans

The higher frequency band is due to the cis isomer while the lower is the trans and since the former is the stronger absorption it is concluded that there is a greater preponderance of the cis isomer. It has been suggested that the cis isomer is stabilised by a weak electrostatic attraction between the phosphorus oxygen and the N-H proton.



$$-\overset{\overset{\displaystyle O\cdots\cdots\cdots}{\|}}{\underset{|}{P}}-\!\!-\overset{\overset{\displaystyle H}{|}}{N}-$$

In the solution spectra of the compounds $PhPO(NHEt)_2$ and $PhPO(NHPr^n)_2$ a single band was observed at 950cm.$^{-1}$ and 918cm.$^{-1}$ respectively. These bands are thought to be the P-N stretching absorptions.

The values assigned to the N-H, P=S and P=Se stretching frequencies in the sulphides and selenides of the bis(alkylamino)phenylphosphines are given in the table below:

COMPOUND	N-Hcm.$^{-1}$.	P=Xcm.$^{-1*}$.
$PhPS(NHEt)_2$	3282, 3231	615, 604
$PhPSe(NHEt)_2$	3280, 3222	
$PhPS(NHPr^i)_2$	3341, 3199	615
$PhPS(NHBu^t)_2$	3391, 3350	617
$PhPSe(NHBu^t)_2$	3389, 3331	579

* X = S, Se.

The value of the P=S stretching frequency, 616±1cm.$^{-1}$(m) is in agreement with that given by Zingaro(130) for the trialkyl- and triarylphosphine sulphides. It is also possible that the strong absorption at 604cm.$^{-1}$ in the compound $PhPS(NHEt)_2$ is also associated with the P=S bond. Assignment of the P=Se stretching frequency proved impossible since in the region quoted for this band, 473-577cm.$^{-1}$(121), several 'X-sensitive' bands occur. However the strong band at 579cm.$^{-1}$ in bis(diethylamino) phenylphosphine selenide could possibly be attributed to this vibration since none of the other oxides sulphides or selenides show a band at this frequency.

The positions of the N-H stretching frequencies in the sulphide and selenide of bis(ethylamino)phenylphosphi show that in the solid state intermolecular hydrogen bonding is taking place. However, in the compound $PhPS(NHPr^i)_2$ the more bulky groups hinder this bonding to a certain extent and both bonded and non-bonded NH groups are observed. In the solution spectra of $PhPS(NHEt)_2$ and $PhPS(NHPr^i)_2$ (1%w/v in CCl_4) a band is observed at 3404±4cm.$^{-1}$ with a shoulder about 20cm.$^{-1}$ lower in frequency. The occurrence of two peaks, as suggested for the aminophosphine oxides, is due to cis and trans isomers with predominence of the cis form. The steric effect of the tertiary butyl groups does not permit any intermolecular hydrogen bonding in the compounds $PhPS(NHBu^t)_2$ and $PhPS(NHBu^t)_2$ and only free NH groups are observed.

The similarity of the i.r. spectra of the oxide, sulphide and selenide of a particular aminophosphine is shown in tables 20, 21 and 22.

<u>The infra-red spectra of the 2.2bis(alkylamino)2phenyl</u>

1 alkylphosphazenes:

The main absorption bands in these phosphazenes are given in table 23. The spectra of the ethyl and isopropyl phosphazenes were found to resemble closely the spectra of the parent aminophosphine and the aminophosphine oxide while the butylphosphazene did not.

The P=N stretching frequency in the ethylphosphazene (1180cm.$^{-1}$) was easy to assign since bis(ethylamino) phenylphosphine is transparent in this region but with the other phosphazenes, the frequency assigned to P=N is similar to that given for the tertiary butyl and isopropyl skeletal vibrations, and is therefore in doubt.

The infra-red spectrum of bis(NdiphenylphosphinoNethylamino) phenylphosphine (table 24).

The spectrum of this compound is almost identical with that of bis(diphenylphosphino)ethylamine apart from the band at 857cm.$^{-1}$ which in $(Ph_2P)_2NEt$ is at 880cm.$^{-1}$. Compounds of the type $(Ph_2P)_2NR$ ($R=Me,Et,Pr^n$) all have similar absorption bands apart from a variable band in the region 829-880cm.$^{-1}$ which has tentatively been assigned to the P-N stretching frequency (it could,however, be a P-N-P skeletal vibration). A similar assignment is given to the band at 857cm.$^{-1}$ in bis(Ndiphenylphosphino-N ethylamino)phenylphosphine.

It is interesting to note the lower frequency of the 'X-sensitive' vibration near 1100cm.$^{-1}$ in these compounds as compared to the bis(alkylamino)phenylphosphines

Assignment to the absorption bands in the i.r. spectrum of bis(isopropylaminophenylphosphinyl)isopropylamine monohydrate are given in table 25. The phosphoryl stretching frequency occurs as a doublet separated by 21cm.$^{-1}$ and could be due to different conformations of the two phosphoryl groups.

The infra-red spectra of the transition metal complexes.

The infra-red spectra of the transition metal complexes of bis(diphenylphosphino)ethylamine are identical with that of the liquid (table 24) apart from the absence of the band at 924cm.$^{-1}$. In the thiocyanate and nitrate complexes a band at 2090cm.$^{-1}$ and bands in the region 1270-1380cm.$^{-1}$ were observed corresponding to the NCS^- and NO_3^- groups respectively.

Table 14: Infra-red frequencies of the bis(alkylamino)-phenylphosphines.

$PhP(NHEt)_2$	$PhP(NHPr^n)_2$	ASSIGNMENT.
3397,3354 m	3335 m	ν NH
3060,3054 m	3070,3054 m	ν C-H(Argyll)
	2940,2860 s	ν C-H(Alkyl)
1588 w	1583 w	ν C-C
1478 s	1480 s	ν C-C
1449 s	1460 s	
1432 s	1435 s	ν C-C
1399 s	1391 s	
1373 s		
1346 m		
1265 m	1230 m	ν C-N
1178 w	1178 w	β C-H
1110 s	1110 s	X Sens.
1059 s	1085 s	
1017 m	1029 m	β CH
998 w	1000 s	RB*
929 s	905890 m	ν P-N
824 m	810 s	
746 s	743 s	γ C-H
700 s	700 s	Ring Def.

*RB = Ring Breathing; applies to the weak band at 998cm.$^{-1}$.

TABLE 15: Infra-red frequencies of the bis(alkylamino) phenylphosphines.

$PhP(NHPr^i)_2$	$PhP(NHBu^t)_2$
3340 m	3330 m
3067,3052 m	3069,3053 m
2965,2927,2868 s	2955,2900,2864 s
1583 w, 1478 s	1586 w, 1480 s
1466 s	1462 m
1432 s	1436 m
1390 s	1380 s
1378 s	
1360 s	1360 s
1330 s	
1300 m	1300 w
1161 s	1222 s
1130 s	
1096 s	1090 m
1065 w	
1025 m	1030 m
995 s	984 s
911 w	920 m
861 s	829 s
785 m	
741 s	730 s
697 s	699 s

Table 17: Infra-red frequencies of the alkyl iodide adducts of bis(ethylamino)phenylphosphine.

$[PhMeP(NHEt)_2]^+ I^-$	$[PhEtP(NHEt)_2]^+ I^-$
3194m. 3135 s	3130 s
1584 w	1591 w
1436 s	1440 s
1302 m	
1270 m	1274 m
	1168 m
1132 s	1132 s
1110 s	1115 s
1086 s	
1075 m	1075 m
	1030,1012 m
990 s	963 s
960 m	946 m
912 m	
889 s	
854 w	851 s
790 m	
781 m	779 s
753 m	752 s
741 s	742 s, 720 m
691 s	691 s

Table 18: Infra-red frequencies of the alkyl iodide adducts of bis(isopropylamino)phenylphosphine.

$\mathrm{PhMe.P(NHPr^{i})_2\ {}^{+}I^{-}}$	$\mathrm{PhEtP(NHPr^{i})_2\ {}^{+}I^{-}}$
3200 m, 3155 s	3240 m, 3170 s
1592 w	1600 w
1430 s	1435 s
1325 w	1325 w
1311 s	
	1277 w
1172,1161 m	1180 m
1136 s	1139 s
1085 s	1091 s
1070 s	1079 s
1039 s	1040 s
1001 m	1010 m
941 s	930 m
910 m	901 m
889 m	
829 m	843 m
771 s	781 s
751 s	772 s
725 w	746 s
704 s	710 s
699 s	699 w

Table 19: <u>Infra-red frequencies of the alkyl iodide adducts of bis(tert.butylamino)phenylphosphine.</u>

$\mathrm{PhMeP(NHBu^t)_2\ ^+I^-}$	$\mathrm{PhEtP(NHBu^t)_2\ ^+I^-}$
3120 s	3120 s
1588 w	
1436 s	1438 s
1302 s	
1230,1194 s	1226,1190 s
1116 s	1115 s
1082 s	1080 s
1070 s	1068 s
1044, 1028 s	1030, 1016 s
999 m	993 m
935m, 930 s	
890 s	
855 m	868 m
777 m	768 m
741 s	755 m
	732 s
692 s	690 m

Table 20: Infra-red frequencies of the oxide, sulphide and selenide of bis(ethylamine)phenylphosphine.

PhPO(NHEt)$_2$	PhPS(NHEt)$_2$	PhPSe(NHEt)$_2$
3233 s	3282, 3231 s	3280, 3222 s
3081, 3064 w	3082, 3061 w	3081, 3055 w
2971 s	2970 s	2970 s
2931, 2895, 2870 m	2395, 2875, 2823 m	2940, 2876, 2815 m
1592 w	1592 w	1591 w
1459 m	1452 w	1448 w
1439 s	1439, 1406 s	1438, 1402 s
1377 m	1380 m	1379 m
1273 w	1272, 1268 m	1268 m
1179 s	1179 w	1185 w
1129 s		
1110 s	1108 s	1110 s
1070 s	1068 s	1067 s
963 m	963 s	963 s
939 m	947 s	943 s
860,842 w	865,829 w	862m, 825 w
795,781 m	798,782 m	793m, 779 w
748 s	748,715 s	745, 705 s
696 s	691 s	691 s
550 m	659 s	579 s
511 s	615 m	504 m
470 w	512, 496 s	487 w

Table 21: Infra-red frequencies of the oxide, sulphide and selenide of bis(tert.butylamino)phenylphosphine

$PhPO(NHBu^t)_2$	$PhPS(NHBu^t)_2$	$PhPSe(NHBu^t)_2$
3412m, 3238 s	3391m, 3350 s	3389m, 3331 s
3064m, 3030 w	3078, 3055 w	3079, 3055 w
2972 s	2991 m	2971 s
2932,2909, 2871 m	2962s,2910,2872m	2959,2910,2874m
1597 w	1588 w	1590 w
1475 m	1479 m	1478 m
1437 s	1438 s	1436 m
1382 s	1383 s	1385 m
1363 s	1362 s	1365 s
1240,1231,1222 s	1220, 1203 s	1221, 1200 s
1189 s		
1120 s	1108 m	1104 m
1006 s	1018, 1007 s	1005 s
865s, 837 w	849 m	842 m
758 m	762 m	758 m
733 m	736 s	730 m
712 s		
702 s	704 m	702 m
653 m	695 m	693 m
578 s	617 m 604 s	
549 m	546 m	546 m
507 w	521 m	509 m, 521 s
451 w	437 w	479 w

Table 22: Infra-red frequencies of the oxide and sulphide of bis(isopropylamino)phenylphosphine and the oxide of bis(n-propylamino)phenylphosphine.

*$PhPO(NHPr^i)_2$	$PhPS(NHPr^i)_2$	$PhPO(NHPr^n)_2$
3225, 3163 s	3341 3199	3202 s
3075, 3055 w	3080, 3060	3080, 3050 w
2965 s	2969 s	2960 s
2934, 2869 m	2932,2877,2820 m	2935, 2875 s
1593 w	1591 w	1591 w
1472 m	1478 w 1466 m	1469 s
1437 m	1436, 1417 s	1435 s
1382, 1363 m	1380, 1364, 1306 m	1378 w
1188 s		1185 s
1167 s	1062 m	1173 s
1142 s	1130 s	1141 s
1113 m	1109 s	1114 1110 s
1043 s	1032, 1028 s	
1014 m	1005 s, 996 m	
909, 878 m	899, 880 m	938, 928 m
846 w	829 w	890, 867 m
804 w	796 w	821
750 m	748 s	758 749 s
711 m	714 s	702 s
696 s	692 s 615 w	554 s
	519 m	521 m
	503 m	500 m
	464, 443 w	442 w

*KCl disc

Table 23: Infra-red frequencies of the 2.2bis(alkylamino) 2phenyl lalkylphosphazenes.

$EtN{=}P(Ph)(NHEt)_2$	$Pr^iN{=}P(Ph)(NHPr^i)_2$	$Bu^tN{=}P(Ph)(NHBu^t)_2$
3150 m	3160 m	3150 m
3049 m	3054 m	3020 m
1290 m	1310 w	1302 w
		1230
1180 s	1170 s	1204 s
1067 s	1069 w	1070 w, 1049 s
1023 w	1030 m	1028 s
980 s		1000 w
960 m	917	931 w
865 m	877	890 m
809 w	833	835 w
775 m	775	773 w
744 s	749	756 m
693 s	699	698 m, 710 m

Table 24: Infra-red frequencies of bis(Ndiphenylphosphino Nethylamino)phenylphosphine.

$PhP(N^{Et}_{PPh_2})_2$	$(Ph_2P)_2NEt$
3074, 3055 w	3067,3049 w
2965, 2925, 2867 w	
1586 w	1585 w
1478 m	1474 m
1461 w	
1432 m	1432 m
1371 m	1377, 1369 m
1305 w	
1207, 1180 w	1209, 1180 w
1152 m	1149, 1154 m
1089 s	1187 m
1059 s	1064 s
1026 m	1028 w
1000 w	997 w
926, 917 m	924 m, 908 w
857 s	880 s
760, 742 s	767 m, 751, 745 s
696 s	701, 696 s
620 w	618 w
607 m	596 m
580 w	
526 w	520 m
504 m	509 m
490 m	500
474 m	
446 w	458
426 w	438

Table 25: Infra-red frequencies of bis(isopropylamino-phenylphosphinyl)isopropylamine monohydrate.

	ASSIGNMENT
3475, 3430 m	ν NH (Free)
3292, 3206 m	ν NH(Bonded)
3069 w	ν CH (Arom)
2971 s	ν CH (Alkyl)
2937, 2880 w	ν CH (Alkyl)
1659 w	H_2O
1595 w	ν C-C
1468 m	
1440 s	ν C-C
1405, 1389 m	
1367 m	
1314, 1300 w	
1218, 1193 s	ν P=O
1175 m	Skeletal (isopropyl)
1132, 1121 s	X Sens,
1026, 1010, 998 m	
941 s	
895 m	
862, 825 w	
760, 755 m	γ CH
724 m	X Sens.
715 m	
702 s	Ring Def.

APPENDIX II.

The N. M. R. spectra of some bis(alkylamino)-phenylphosphines and their derivatives.

The proton N.M.R. spectra of some bis(alkylamino)phenylphosphines and their oxides, sulphides, selenides and methyl iodide adducts were recorded by Dr. A. Morton-Blake using an A.E.I. R.S.2 Nuclear Magnetic Resonance Spectrometer operating at 60 Mc/s.

In view of their lability the liquid bis(alkylamino)phenylphosphines were freshly distilled, under reduced pressure, into pyrex sample tubes which were then sealed off while still under vacuum. The solid adducts were recorded as concentrated solutions in deuterochloroform and in all cases, tetramethylsilane (T.M.S) was used as a reference standard.

The chemical shifts (τ-scale) and coupling constants (cycles/s.) are given in tables 27 and 28 respectively.

In the isopropyl derivatives studied, apart from the sulphide, the doublet expected for the methyl protons in the presence of a C-H proton is not observed but instead, two doublets occur. This twin doublet methyl resonance might conceivably arise either from chemically different methyl groups or spin - spin interaction with the nitrogen proton. However since the nitrogen proton signal does not show any extra splitting or broadening due to such a coupling, the latter explanation is untenable.

Different conformations of the isopropyl groups in these molecules will therefore account for this pair of doublets. It should be noted that the separation of these two doublets is greatest in the methyl iodide adduct.

In both the ethyl and isopropyl derivatives there is an increase in the half band width of the low field aromatic proton signal and also a shift to higher τ values of the high field signal in the series aminophosphine, methiodide, oxide, sulphide, selenide. Since the spectra of these compounds were not completely analysed, no valid explanation for these observations can be given but they are probably due to long range coupling of the aromatic protons with the added substituent on phosphorus resulting in a change of the electron distribution over the molecule.

Apart from the two points of interest mentioned above, the N.M.R. spectra of these compounds were as expected for molecules of the type $PhP(NHR)_2$ and $PhP(X)(NHR)_2$ (X = O,S,Se,Me; R= Et, Pr^i, Bu^t.)

Table 27:-

Ethyl Derivatives	Proton Chemical Shifts				
	CH_3-(CH_2)	CH_3-(P)	NH	CH_2	Ph Protons.
$PhP(NHEt)_2$	8.96	-	7.78	7.18	2.65-2.35,2.62
$(PhP(Me)(NHEt)_2)^+I^-$	8.73	7.87	(6.9)		1.7 - 2.1, 2.3
$PhP(S)(NHEt)_2$	8.92	-	(7.2)		1.8 - 2.3, 2.6
$PhP(Se)(NHEt)_2$	8.89	-	(7.2)		1.7 - 2.2, 2.6

Isopropyl Derivatives	Proton Chemical Shifts				
	CH_3-(CH)	CH_3-(P)	NH	CH	Ph Protons
$PhP(NHPr^i)_2$	8.91 8.95	-	8.08	6.8	2.4-2.7, 2.9
$(PhP(Me)(NHPr^i)_2)^+I^-$	8.60 8.70	7.91	-	6.49	1.7-2.1, 2.4
$PhP(O)(NHPr^i)_2$	8.90 8.93	-	7.6	6.58	1.7-2.2, 2.4
$PhP(S)(NHPr^i)_2$	8.9	-	7.45	6.55	1.7-2.2, 2.6

Tert. Butyl Derivatives	Proton Chemical Shifts			
	CH_3-(C)	CH_3-(P)	NH	Ph Protons
$(PhP(Me)(NHBu^t)_2)^+I^-$	8.52	7.63	4.9	1.4-2.0,2.3
$PhP(NHBu^t)_2$	8.78	-	-	-

Table 28.

Ethyl Derivatives	Proton Coupling Constants				
	$C\underline{H}_3C\underline{H}_2$	$C\underline{H}_3\ \underline{P}$	$C\underline{H}_2\text{-}N\underline{H}$	$C\underline{H}_2\ \underline{P}$	$N\underline{H}\ \ \underline{P}$
$PhP(NHEt)_2$	7.00	-	6.8	6.85	6.7
$(PhP(Me)(NHEt)_2)^+I^-$	6.92	13.9	-	-	-
$PhP(S)(NHEt)_2$	6.9	-	-	-	-
$PhP(Se)(NHEt)_2$	6.85	-	-	-	-

Isopropyl Derivatives	Proton Coupling Constants			
	$C\underline{H}_3C\underline{H}$	$C\underline{H}_3\underline{P}$	$C\underline{H}\ \ N\underline{H}$	$N\underline{H}\ \ \ \underline{P}$
$PhP(NHPr^i)2$	5.9	-	1.8	7 7
$(PhP(Me)(NHPr^i)_2)^+I^-$	5.9	13.7	-	- -
$PhP(O)(NHPr^i)_2$	6.4	-	-	- -
$PhP(S)(NHPr^i)_2$	6.1	-	-	- -

Tert.Butyl Derivatives	Proton Coupling Constants	
	$C\underline{H}_3\ \underline{P}$	$N\underline{H}\ \ \ \underline{P}$
$PhP(NHBu^t)_2$	8.80	-
$(PhP(Me)(NHBu^t)_2)^+I^-$	14.0	11.3

APPENDIX III

The Chemistry of Cyclopolyphosphines.

In view of the formation of cyclophenlyphosphine as one of the re-arrangement products from heating bis(alkylamino)phenylphosphine, it is appropriate to summarise briefly some of the aspects in the chemistry of the cyclopolyphosphines.

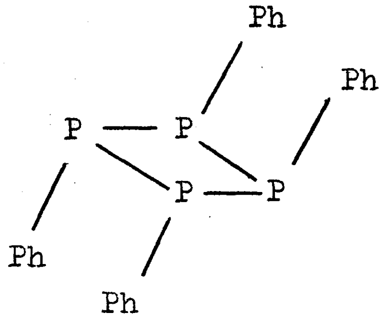
The first reported cyclophenylphosphine was due to Michaelis and Köhler(135) in 1877 who isolated the compound "phosphobenzol", although at that time it was not regarded as a cyclic compound but instead, a dimer of formula PhP=PPh. It is not until 1952 that further reports of the cyclophenylphosphines occur in the literature with the isolation of a compound having the same molecular formula as "phosphobenzol" but a different melting point(136). In the last decade, several publications have appeared concerned with this compound but the conclusions drawn regarding its structure and molecular size have been confusing. The table below surveys the various forms of this compound, (PhP)n, and the values quoted for n which have been reported.

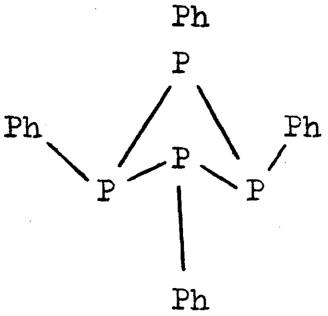
(PhP)n	m.p.°	n	Reference
A	149-150	2	135
B	190	2	136
C	154,5-156	2	137
D	193	4	137
E	252-256	Poly.	137
F	153-155	4	93
G	195-199	4	93

Contd.

(PhP)n	m.p.°	n	Reference.
H	270-285	Poly	93
I	260-285	Poly	93
J	146-150	6.3-7.4.	54

Comparison of the melting points and values for n with the compounds listed in the table show several anomalies which have recently been clarified. "Phosphobenzol", A, has been established as a tetramer(144). A, C and F are thus identical. In the latter case (93) and also compound G, conclusive proof of the molecular formula $(PhP)_4$ was obtained from a mass spectographic analysis. Apart from melting points, F and G only differ with regard to their N.M.R. spectra and it was suggested that they are "stereoconformers", with one a planar ring and the other puckered,





as was found with $(CF_3P)_4$(138) and $(cyclo\text{-}C_6H_{11}P)_4$. Another explanation, given by Burg, was that the two forms of $(PhP)_4$ were due to different rotational conformations of the phenyl rings. B has been proved to be tetrameric and identical with D. The polymeric compounds E and H are also identical but their i.r. spectra differ from that of I.

The complexity of cyclophenylphosphine is more than evident on considering that compounds F to I were all prepared from the same reactants according to the equation

$$PhPCl_2 + PhPH_2 \longrightarrow {}^1/2n(PhP)_{2n} + 2HCl.$$

and to quote Henderson et.al.,"Nor do apparently identical conditions always yield the same results; repetition of conditions yielding F often afforded H and occasionally G". No compounds with an aromatic group other than phenyl have been reported.

In the case of the cycloalkylphosphines, far less ambiguity exists as to the molecular structure and stereochemistry. Until recently, the only cycloalkylphosphines which had been prepared were $(MeP)_5$(139), $(EtP)_4$(140), $(cyclo\text{-}C_6H_{11}P)_4$,(141), $(CF_3P)_4$,(142) and $(Bu^nP)_4$ but now this series has been extended and the compounds $(RP)_4$ where $R=Pr^n$, Pr^i, CNC_2H_4, Bu^i, Am^i and $n\text{-}C_8H_{17}$ have been reported.(93).

It is surprising that in the cyclophenyl- and most of the -alkylphosphines a cyclic P_4 unit exists instead of one involving a P_5 ring because there is considerable strain in a four membered ring which is not alleviated to any great extent by puckering. The stability of the P_4 ring is attributed to extra bonding involving the lone pair of electrons on phosphorus with the vacant 3d orbitals on adjacent atoms resulting in $3d\text{-}3p^{\pi}$ bonding. This concept has been established since the compounds $(CF_3P)_4$ and $(CF_3P)_5$ show an intense absorption in the ultraviolet (2000-2800Å), which is indicative of a high degree of electron delocalisation, while the compounds $(CF_3)_3P$ and $(CF_3)PH_2$ do not absorb in the ultraviolet range.

Several preparative methods, apart from those already mentioned as resulting from rearrangements, have been used to obtain cyclopolyphosphines. The method of Michaelis and Köhler in the preparation of "phosphobenz is still the most widely used procedure for the synthesis of both the phenyl and alkylcyclophosphines. It consists of refluxing a dichlorophosphine and a primary phosphine in an inert solvent such as benzene, hexane or, if there is a bulky substituent on phosphorus, toluene or xylene.

Good yields of cyclophosphines have also been obtained by reducing a dichlorophosphine with lithium, magnesium, sodium, lithium hydride or lithium aluminium hydride. Of the lesser used methods, dehydration of primary phosphine oxides at reduced pressure gave low yields,(93) and the compound $(MeP)_5$ was prepared by heating difluoromethylphosphine at 35-40° for several hours(139). Reaction of di-iodotrifluoromethylphosphine and mercury at room temperature gave a 100% conversion into the tetramer, $(CF_3P)_4$, (60%) and the pentamer (40%). These compounds were also prepared by heating tetratrifluoromethyldiphosphine and bistrifluoromethylphosphine to 350°.

Reactions of tetraphenylcyclotetraphosphine give rise either to adducts where the P_4 ring remains intact or to compounds resulting from ring cleavage. With oxygen or excess sulphur (92) destruction of the ring occurs and polymeric compounds $(PhPO_2)_{ca.5}$ and $(PhPS_2)_x$, are formed but with selenium and equimolar quantities of sulphur (92), the ring remains intact giving the adducts $(PhPSe)_4$ and $(PhPS)_4$. Metallation with sodium under carefully controlled conditions gives the dialkali diphosphide $(PhPNa)_2$ but with excess sodium, all the P-P bonds are broken and $PhPNa_2$ is produced (92). Similar reactions occur with halogens and depending upon reaction conditions either $(PhPX)_2$ or $PhPX_2$ is produced but with excess halogen further oxidation occurs to give tetrahalogenophenylphosphoranes (145). Hydrogen chloride and alkyl iodides cause ring cleavage giving with the former, $PhPCI_2$ and $PhPH_2$, and with the latter, PhR_3Pl and PhR_2Pl_2. However the reaction of methyl iodide with tetraethylcyclotetraphosphine does not cause ring cleavage and quaternisation of one ring phosphorus atom takes place, $\left[(EtP)_4Me\right]^+I^-$.

The cyclophenylphosphine isolated from the reaction,

$$2PhP(NHR)_2 \xrightarrow{\Delta H} RN{=}PPh(NHR)_2 + {}^1/n(PhP)n + RNH_2$$

$$R = Et,\ Pr^i.$$

by addition of alcohol to the 'filtered liquid' was a pale yellow solid. However, if after separation of the phosphazene by filtration, the liquid was allowed to stand for several days in the sealed tube, the cyclophenylphosphine precipitated slowly in the form of large clusters of crystals. Molecular weight determinations on this crude material and also on some which had been recrystallised from acetonitrile (m.p.152-154°) indicated that the compound was tetrameric in benzene. It is therefore identical with compounds A, C and F listed in the above table.

Comparison of the i.r. spectrum of this compound to that published for F(93) is given in table 26. The spectra were almost identical apart from some extra bands which were observed; the spectral range from 625-375cm.$^{-1}$ is also noted.

No molecular weight data was given for the cyclophenylphosphine isolated by Nöth and Vetter (66) from the re-arrangement of the reaction between phenyl-(dimethylamino)iodophosphine and mercury but the melting point (162°) was higher than has been reported for the tetramer of type F. From its melting point, it would be expected that compound J, isolated by Ewart from the reaction of dichlorophenylphosphine with ethylamine, was a tetramer but values for n of 6.3-7.4 were obtained. It is possible that this high value was due to oxidation of the cyclophosphine during storage.

Table 26: Infra-red frequencies of $(PhP)_4$.

$(PhP)_4$	$(PhP)_4$ F	ASSIGNMENT
3065, 3044 w		ν CH
1578, 1576 m	1580 m	ν C-C
1429 s	1432 s	ν C-C
1322, 1313, 1295 w	1300 w	
1184, 1179 w	1182 w	β CH
1158, 1153 w	1158 w	β CH
1084, 1077, 1065 w	1067 m	β CH
1023 m	1030 m	β CH
998 m	1000 m	R.B.
984, 977, 965 w	975 w	
905 w	908 w	γ CH
844, 839, 831 w		
738 s	742 s	
733 s	735 s	
693 u	695 s	Ring Def.
682 s	687 s	
615 w		
495, 484 w		
474 w		
462 w		
448 w		
426 w		
415 w		
397, 393 m		

General Conclusions.

General Conclusions.

Initially, this research study into the Nature of Aminophosphines had certain aims. Some of these have been realised while others, although less fruitful have provided some useful information which should benefit other workers in this field.

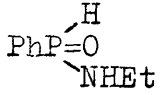
While the original objective in heating the bis(alkylamino)phenylphosphines, namely to produce cyclic and long chain P^{III}——N compounds, was not achieved, discovery of an interesting rearrangement has added a new concept to the chemistry of these aminophosphines. Thus, in future consideration of reactions involving these compounds, the possibility of rearrangement should never be overlooked.Nor is this concept limited to compounds having the NH-P-NH structure since the i.r. spectrum of a solid isolated from the residue left after distilling bis(diethylamino)phenylphosphine was identical to that of cyclotetraphenylphosphine possibly indicating a similar rearrangement. The formation of a monophosphazene as one of the rearrangement products is of particular interest since it demonstrates the ease with which tervalent phosphorus may be converted into the pentavalent form. It is therefore possible that under certain conditions cyclic P^{III}——N compounds would undergo a similar rearrangement and thus provide a direct link with the cyclophosphazenes, i.e.

$$(R\,P - N\,R)_n \longrightarrow (RR\,P - N)_n$$

The rearrangement reaction which occurs on heating bis(ethylamino)phenylphosphine and its isopropyl analogue is well characterised but in the case of bis-(tert. butylamino)phenylphosphine further experimental evidence is needed to determine whether this compound follows the same reaction pattern. In this case the bulky nature of the tertiary butyl group might lead to a different reaction. The extent of the two competing reactions, rearrangement and condensation, and also the nature and origin of the red colouration observed have not been determined. The former problem will necessitate the use of a larger capacity reaction vessel and a quantitative method of separating the various products while with the latter, the visible and ultra-violet absorption spectra might be expected to yield useful results. Again, the need must be stressed for a kinetic study in order to ascertain the mechanism by which these rearrangement products are formed. This information, when available, will undoubtably dictate the synthetic approach to related compounds in the future and generally serve to clarify the present knowledge concerning these P^{III}——N systems.

Although the heating process did produce a condensed aminophosphine which was isolated as an hydrated oxide, $(Pr^{i}NH\ P(O)Ph)_2NPr^{i}.\ H_2O$, the yield was so small as to render this synthetic approach of little value. It is possible that using a different method of heating these compounds, such as refluxing them in an inert solvent or addition of a catalyst, may produce the required condensed systems and is therefore a problem for future research.

The purely chemical approach to condensed P^{III}——N compounds, where hydrogen chloride is eliminated instead of amine elimination as in the heating process, would seem to have great potential in view of the success of increasing the chain length in the reaction of bis-(ethylamino)phenylphosphine with chlorodiphenylphosphine and also the ease with which compounds were isolated from the reaction of aniline with dichlorophenylphosphine (7 Application of advanced separation techniques to the crude product obtained from reacting $PhP(NHEt)_2$ with $PhPCl_2$ could well give rise to some interesting compounds. Even in this method there is the possibility of rearrangement taking place as is exemplified by the as yet unidentified product obtained in the attempt to prepare Ph_2P-NEt-PPh-NHEt.

The use of bis(alkylamino)phenylphosphines as starting materials has enabled much to be learnt about the chemistry of these compounds. In their reactions with alkyl iodides, oxygen, sulphur and selenium these aminophosphines behave simply as tertiary monophosphines. The expected lability of these compounds, due to the presence to protons attached to nitrogen, as compared to the diethyl analogues is observed. However, in comparison to diphenylphosphinoethylamine which on standing, even in the atmosphere, slowly eliminates ethylamine to give bis-(diphenylphosphino)ethylamine, these compounds show a marked difference since they may be stored indefinitely in evacuated sealed tubes and react with atmospheric oxygen and water vapour to give the compound  $PhP(H)(=O)NHEt$ xH_2O due to a rearrangement reaction.

The work on transition metal complexes was limited since only two aminophosphines were studied. However, from the evidence obtained bis(diethylamino)phenylphosphine was found to be a mono-dentate ligand while bis(diphenylphosphino)ethylamine was bi-dentate. The most useful outcome of this work was the preparation and characterisation of two 3-co-ordinated complexes of copper (1) which were hitherto unknown. Although molecular weight data verified this 3-co-ordination an x-ray structure determination is necessary to provide unambiguous proof of the nature of these compounds in the solid state.

The formation of transition metal complexes with linear aminophosphines containing three or more phosphorus atoms and with the cyclic P^{III}——N compounds, when prepared, is an exciting prospect particularly with regard to the type of ligand behaviour they will exhibit. The ring compounds might form sandwich molecules on reaction with molybdenum hexacarbonyl for example.

The aminophosphines studied in this thesis have all contained a phenyl group attached to phosphorus due mainly to the commercial availability of phenyl- and diphenylchlorophosphines. The author feels that a similar study replacing the phenyl group by an alkyl substituent, which at first sight might appear somewhat repetitive, would instead, provide some interesting differences.

The highways of science are boundless and even in the narrow confines of tervalent phosphorus-nitrogen chemistry the paths are endless and new ones are continually appearing Some routes to new compounds are now glaringly obvious and it is hoped that future workers will follow them to some interim conclusion. Ewart considered this subject as one of purely academic interest but suggested the possibility of a commercial or therapeutic utility in the future.

Perhaps his foresight was correct since recent biological tests on aminophosphine oxides, sulphides and selenides prepared in this department have shown the compound bis(tert.butylamino)phenylphosphine oxide to have analgesic activity thus correlating Nature and Aminophosphines.

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