THE STRUCTURE AND REACTIVITY OF SOME AMINO PHOSPHINES

by W. Sim.

A Thesis presented to Glasgow University as part fulfilment of the requirements for the Degree of Doctor of Philosophy. This Thesis is the result of my own work and has not been submitted in part or in full to any other University.

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CONTENTS

NOMENCLATURE. i.

CHAPTER 1. GENERAL SURVEY. 1.

CHAPTER 2. SYNTHESIS OF AMINOPHOSPHINES CONTAINING THE N-H LINKAGE. 33.

CHAPTER 3. SYNTHESIS AND PROPERTIES OF BIS(N-DIPHENYL-N-ALKYL)DI(AMINO)PHENYLPHOSPHINES. 40.

CHAPTER 4. THE ^{1}H N.M.R. SPECTRA OF SOME AMINOPHOSPHINES. 70.

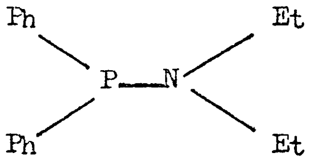
CHAPTER 5. THE MASS SPECTRA OF PHOSPHOBENZENE AND OF SOME METHYLAMINO SUBSTITUTED PHOSPHINES. 87.

APPARATUS AND TECHNIQUES. 105.

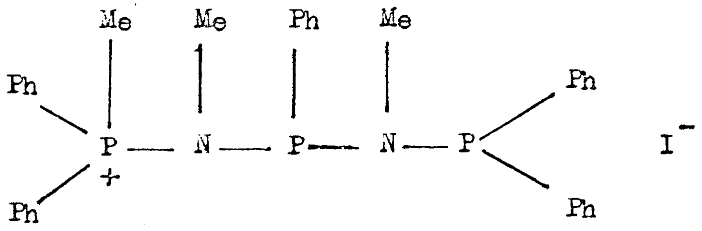
SUMMARY. 106.

NOMENCLATURE

Phosphorus (III)-nitrogen compounds are normally referred to as either amine or phosphine derivatives. For example, the compound:



may be described either as diphenylphosphinodiethylamine or diethylaminodiphenylphosphine. Neither the designation phosph(III)azane (put forward by Shaw as a basis for the nomenclature of these compounds), nor the form of designation (1) based on the original acids has been widely adopted. The phosphine-amine system also has its limitations, especially in the case of longer chain unsymmetrically substituted molecules. For example,



which was one of the compounds prepared in this project,

/is very

is very difficult to describe and it was found convenient to adopt a trivial system of nomenclature. The ever increasing complexity of P(III)-N systems will no doubt involve future authors more and more in the use of trivial names to describe their systems.

CHAPTER 1.

GENERAL SURVEY.

GENERAL SURVEY

The chemistry of phosphorus(III)-nitrogen systems dates back to the end of the nineteenth century, when Michaelis first investigated the reactions of phosphorus trichloride with a number of primary and secondary amines. It is only within the last ten years, however, that these compounds have received any great attention, but during this comparatively short time progress has been extremely rapid due to considerable improvements in handling techniques and the availability of physical methods of investigation.

Compounds containing a P(III)-N bond are generally synthesised by the elimination of hydrogen chloride between an amine and a chlorophosphine, R_2PX, using either excess amine or a tertiary amine as hydrogen chloride acceptor:

$$PhPCl_2 + 4EtNH_2 \longrightarrow PhP(NHEt)_2 + 2EtNH_3^+Cl^- \qquad 2$$

$$(CF_3)_2PNH_2 + (CF_3)_2PCl \xrightarrow{Me_3N} [(CF_3)_2P]_2NH + Me_3NH^+Cl^- \qquad 3$$

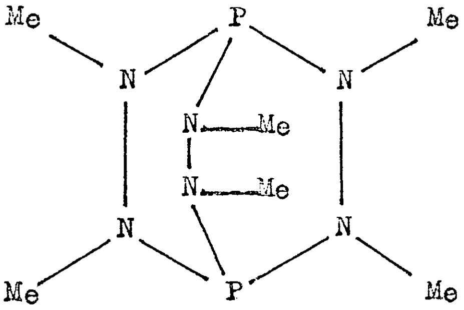
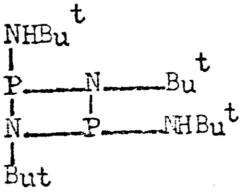
/1a.

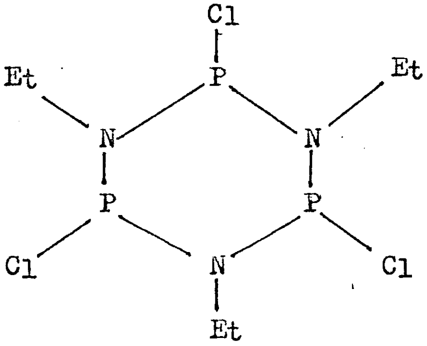
1a. CLASSIFICATION

Previous authors have classified aminophosphines according to the skeletal arrangement of phosphorus and nitrogen atoms. However, this often means placing two compounds of widely differing properties in the same class e.g. Me_2N-PMe_2 and Me_2N-PCl_2, the latter having two reactive chlorine atoms attached to phosphorus. A system of classification has therefore been adopted whereby compounds containing potentially reactive groupings, e.g. RNH- or R_2PCl, have been separated from those which have both the phosphorus and nitrogen atoms fully substituted.[x] In dealing with the preparation of aminophosphines, no strict system will be adhered to, since very often only slight changes in the nature of the reactants, or in the stoichiometry of the reaction mixture, give products which are chemically very unalike or have a different P-N framework. Table I shows examples of the various classes of compounds the properties of which will be discussed later.

[x] The expression "fully substituted" will be used throughout to describe compounds which do not contain either a P-Cl or an N-H linkage.

TABLE I

Fully substituted aminophosphines	Reference
Me_2N-PMe_2	4
$PhP(NMe_2)_2$	5,6
$P(NMe_2)_3$	7
$N[P(CF_3)_2]_3$	3
$(Ph_2P)_2NEt$	8
	9
Aminophosphines containing the NH-linkage	
$(CF_3)_2PNH_2$	10
$PhP(NHEt)_2$	2
$P(NH.CH_2CH{=}CH_2)_3$	11
$(Ph_2P)_2NH$	12
	13

Aminophosphines containing the P-Cl linkage	Reference
$(Me_2N)_2PCl$	14
Cl_2PNEt_2	15
$PhP(Cl)NEt_2$	5
	16,21

1b. FULLY SUBSTITUTED AMINOPHOSPHINES

Fully substituted aminophosphines, on account of their relatively high stability to moisture and heat, are by far the most widely studied of the compounds containing a P(III)-N bond. The simplest members of this class are prepared directly by the elimination of one molecule of hydrogen chloride between a secondary amine and a monochlorophosphine, R_2PCl, using either excess amine or a tertiary amine as hydrogen chloride acceptor. In this way, hydrogen chloride is conveniently removed as the solid amine hydrochloride. It is essential in aminophosphine syntheses to use dry, inert solvents and to carry out the reaction in an inert atmosphere (usually N_2) to reduce the possibility of hydrolysis and oxidation. Benzene, ether and n-pentane have proved useful solvents since they can readily be dried (Na or K wire), are fairly unreactive towards starting materials and products and from which the unwanted amine hydrochloride is precipitated.

In the case of weakly basic and/or highly hindered amines, it is often necessary to react the sodium salt of the amine with the chlorophosphine,[17] e.g.

$$Ph_2NNa + Ph_2PCl \longrightarrow Ph_2P{-}NPh_2 + NaCl$$

/Longer

Longer chain and branched chain aminophosphines can be prepared by similar methods, e.g.

$$(CF_3)_2PNH_2 + (CF_3)_2PCl \xrightarrow{Me_3N} [(CF_3)_2P]_2NH + Me_3NH^+Cl^- \qquad 3$$

$$[(CF_3)_2P]_2NNa + (CF_3)_2PCl \longrightarrow [(CF_3)_2P]_3N + NaCl \qquad 3$$

$$PhPCl_2 + 4Et_2NH \longrightarrow PhP(NEt_2)_2 + 2Et_2NH_2^+Cl^- \qquad 5$$

$$PCl_3 + 6Me_2NH \longrightarrow (Me_2N)_3P + 3Me_2NH_2^+Cl^- \qquad 7$$

Aminochlorophosphines, R_2NPCl_2 and $(R_2N)_2PCl$, have recently proved useful starting materials in the synthesis of fully substituted aminophosphines. Alkylation of the P-Cl bond has been achieved by the use of organometallic reagents such as n-butyllithium,[14,18] aluminium alkyls[19] and alkyl magnesium halides.[20]

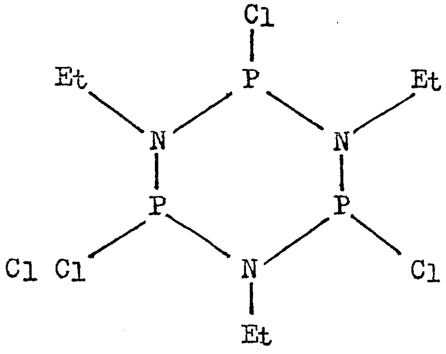
Abel[21] and co-workers have demonstrated the use of silazanes in aminophosphine syntheses, e.g.

$$3Et_2N.SiMe_3 + PCl_3 \longrightarrow (Et_2N)_3P + 3Me_3SiCl$$

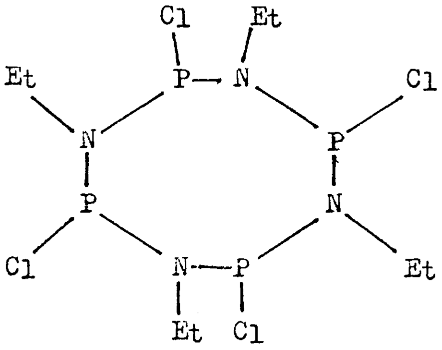
Trimethylchlorosilane is conveniently removed from the reaction mixture by distillation. In the reaction of phosphorus trichloride with $EtN(SiMe_3)_2$, the same workers have succeeded in isolating products of molecular formulae $(PNClEt)_3$ and $(PNClEt)_4$. These are isomeric with the alkyl substituted phosphonitrilic

/trimer

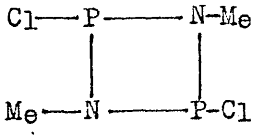
trimer and tetramer respectively, but do not possess the strong band at 1250 cm.$^{-1}$ in the infra-red which is characteristic of the P=N absorbtion. On this basis, they were assigned the structures:



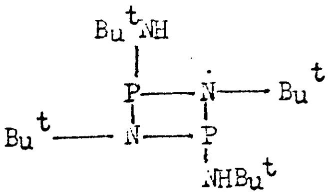
and



The corresponding reaction of PCl_3 with $MeN(SiMe_3)_2$ gave the four-membered ring species:

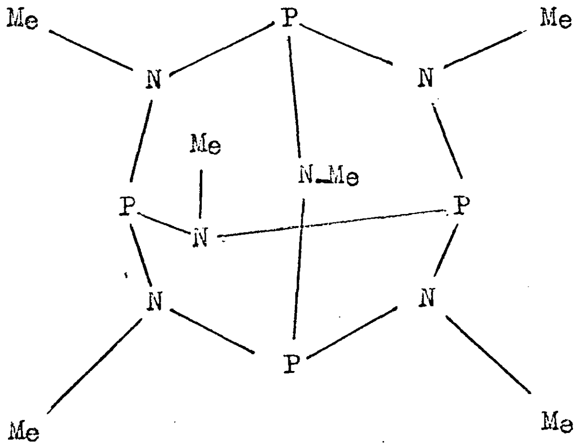


Reaction of PCl_3 with primary amines leads to a variety of products depending on the nature of the amine employed (see Section 1d.). With tertiary butylamine,[13] the product, on the basis of infra-red and molecular weight studies has been assigned the cyclic structure:

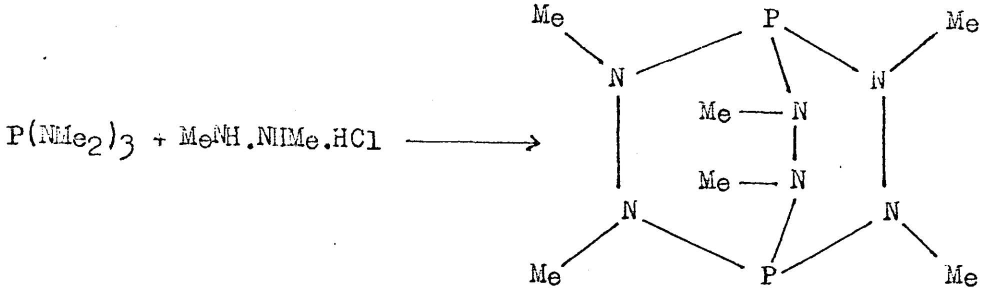


/With

With methylamine,[22,23] however, the product was found to have the composition $P_2N_3Me_3$. Cryoscopic molecular weight measurements in benzene were compatible with the formula $P_4N_6Me_6$ while the ^1H n.m.r. spectrum consisted only of a triplet. All the data are in accord with a structure analogous to that of phosphorus(III) oxide, P_4O_6:



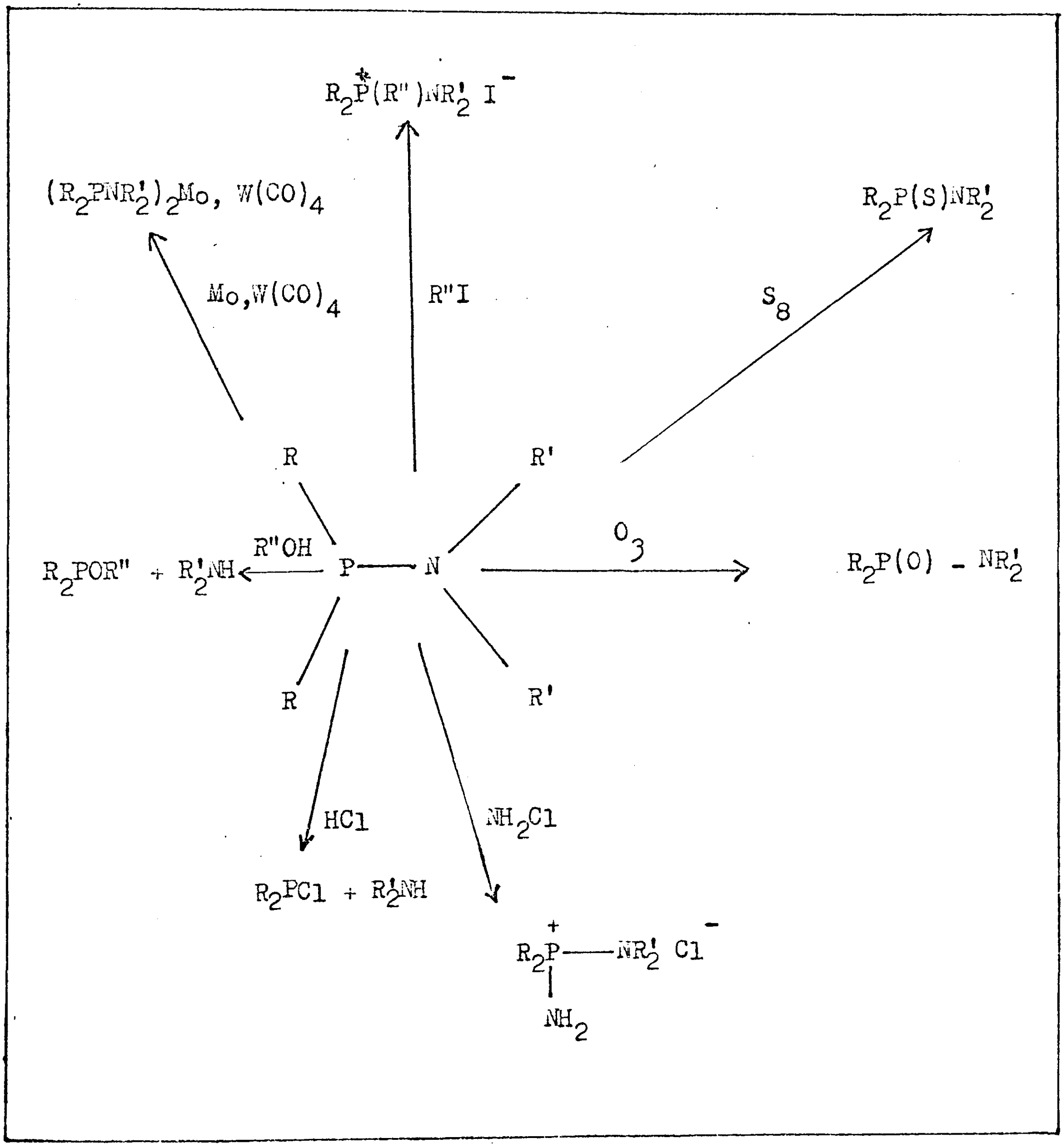
Another type of bridged cyclic structure[9] is obtained by transammination of tris(dimethylamino)phosphine with 1,2-dimethylhydrazone hydrochloride:



1c. GENERAL REACTIONS OF AMINOPHOSPHINES

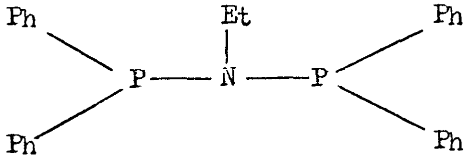
The nucleophilic and electrophilic substitution reactions of aminophosphines are basically those of alkyl or aryl substituted phosphines although the presence of the nitrogen atom(s) does, to some extent, affect the degree of reactivity (see Section 1f.). A summary of their typical reactions is given in Table 2.

TABLE 2.


R2P*(R")NR'2 I-
(R2PNR'2)2Mo, W(CO)4
Mo,W(CO)4
R"I
R2P(S)NR'2
S8
R
R'
P — N
R2POR" + R'2NH
R"OH
O3
R2P(O) - NR'2
R
R'
HCl
NH2Cl
R2PCl + R'2NH
R2P+—NR'2 Cl-
NH2

Aminophosphines are oxidised by a number of oxidising agents (O_3,[25] MnO_2,[24] H_2O_2) and react exothermically with elemental sulphur.[17,26] With alkyl iodides,[5,28] the product is the phosphonium- and not the ammonium- salt. They behave as good σ-donors in complex formation with electron deficient molecules such as boron hydrides.[29] With transition metals there is also the possibility of back donation from the metal d-orbitals to the empty 3d-orbitals of suitable symmetry on phosphorus by a π-type interaction. The P–N bond is also susceptible to cleavage by nucleophilic attack at phosphorus and, as a result, aminophosphines react with aqueous acids,[30] alcohols[19] and halide ion.[29]

When two phosphorus atoms are bridged by nitrogen,[8] e.g.



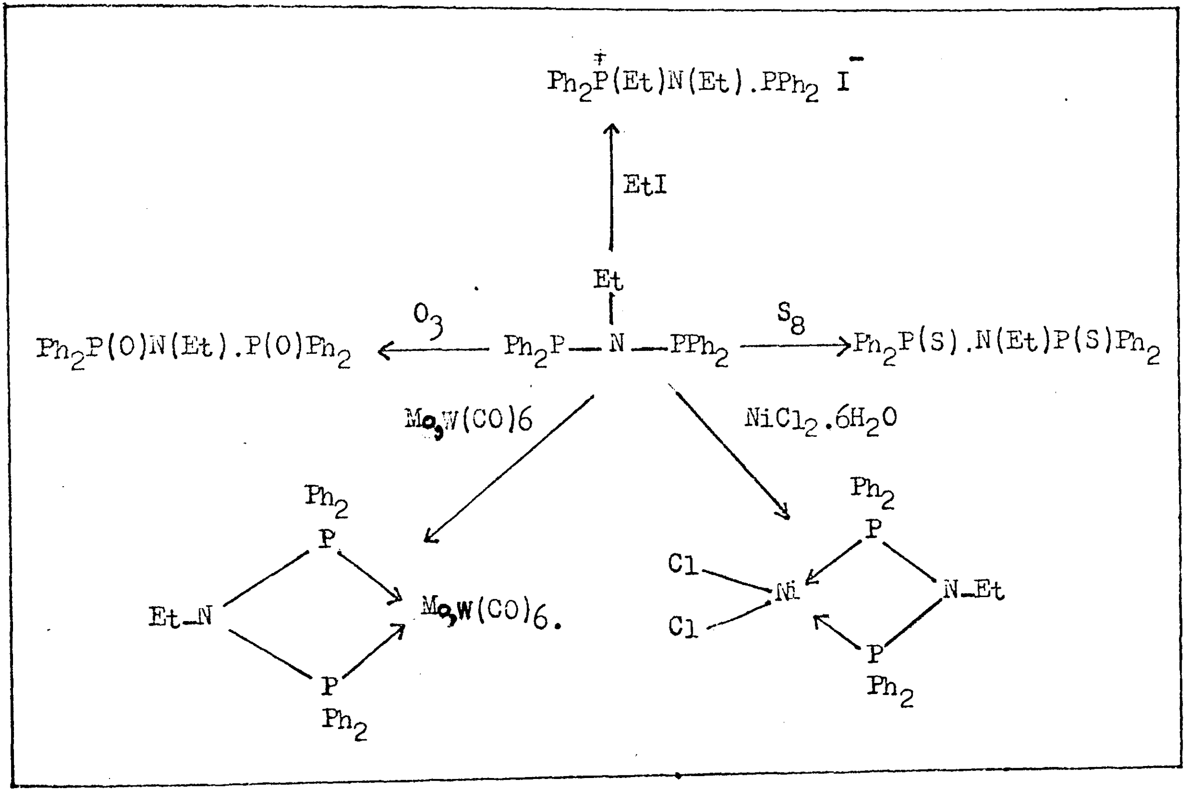
the reactivity at phosphorus is little affected. (Table 3). The one notable exception is the reaction with alkyl iodides which leads to quaternisation of only one phosphorus atom. Theories have been put forward to account for this apparent anomaly and these will be discussed in Section 1f.

At the start of this study, aminophosphines containing three phosphorus atoms alternating with nitrogen in a chain had not been

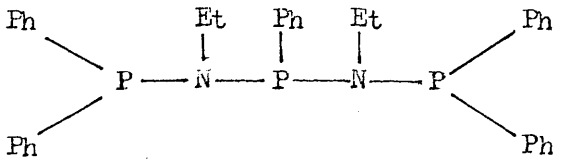
/studied

TABLE 3

SOME REACTIONS OF BIS(DIPHENYLPHOSPHINO)ETHYLAMINE. (8).



studied to any extent although the compound[31]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had been synthesised.

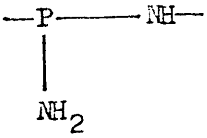
1d. AMINOPHOSPHINES CONTAINING THE N-H LINKAGE

Aminophosphines containing the N-H linkage are prepared by the reaction of chlorophosphines with ammonia or primary amines. They are generally thermally unstable and undergo condensation with elimination of amine and formation of polymeric and cyclic species. For this reason, few compounds in this class are known.

One of the earliest examples of this thermal instability was found in the products of the reaction of phosphorus trichloride with liquid ammonia. Moureu and Wetroff[32] studied this reaction in detail and proposed the following reaction sequence as the reaction mixture was allowed to warm up:

$$PCl_3 + 3NH_3 \longrightarrow P(NH_2)_3 \xrightarrow{-NH_3} P(NH)(NH_2) \xrightarrow{-NH_3} P_2(NH)_3 \quad \text{etc.}$$

$P(NH_2)_3$ has not been isolated free from ammonium chloride although the addition product $(NH_2)_3PBH_3$[33,34] has been well characterised. Phosphorus imide-amide[35] $P(NH)(NH_2)$ has been prepared by the reaction of phosphorus trichloride with liquid ammonia at - 20° in ether. Its properties suggest it to be polymeric with the probable structural unit:



$$-\underset{\displaystyle NH_2}{\underset{|}{P}}-NH-$$

/The

The reaction of PCl_3 with primary amines leads to a variety of products depending on the nature of the amine employed. A summary of these reactions is given in Table 4. Two possible mechanisms can be put forward to account for the formation of the condensed species:

(a) Replacement of three chlorine atoms by amino-groups followed by deamination, or

(b) Replacement of two chlorine atoms followed by elimination of hydrogen chloride.

The nature of the products obtained does not appear to depend on the basicities of the amines employed and hence a mechanism relying mainly on steric factors is proposed to account for the observation.

The process of chlorine replacement may be considered to take place stepwise, i.e.

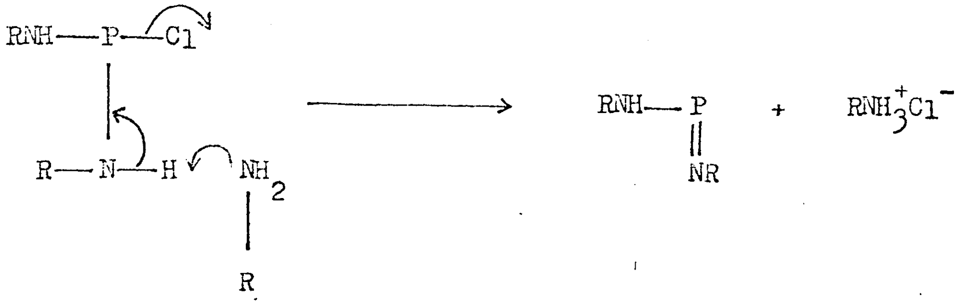
$$PCl_3 + RNH_2 \longrightarrow Cl_2PNHR \xrightarrow{RNH_2} ClP(NHR)_2 \xrightarrow{RNH_2} P(NHR)_3$$

As the steric requirements of the entering amine group increase, so replacement of the third chlorine atom becomes more difficult and a competing reaction involving the amine as hydrogen chloride acceptor sets in, i.e.

TABLE 4.

REACTIONS OF PRIMARY AMINES WITH PCl_3

				Reference.
PCl_3 +	$MeNH_2$	→	$P_4N_6Me_6$	22,23
	$EtNH_2$	→	$(PNEt.NHEt)_2$?	13
	Bu^tNH_2	→	$(PNBu^t.NHBu^t)_2$	13
	$Ph\ NH_2$	→	$(PNPh.NHPh)_2$	36,37
	<u>o</u> - and <u>p</u> - $MeOC_6H_4NH_2$	→	$(PNR.NHR)_2$	37
	$PhCH_2NH_2$	→	$P(NHCH_2Ph)_3$	15
	$CH_2{=}CH.CH_2NH_2$	→	$P(NH.CH_2CH{=}CH_2)_3$	11
	$Me(CH_2)_{11}NH_2$	→	$P(NH(CH_2)_{11}Me)_3$	38



Thus amines with bulky groups at the nitrogen atom, like Ph, o- and p-$MeOC_6H_4$ and Bu^t react by mechanism (b) to give the imide-amide system, whereas methylamine, benzylamine, allylamine, and dodecylamine totally replace three chlorine atoms to give species of the type $P(NHR)_3$. With the exception of $P(NH.CH_2CH{=}CH_2)$, the latter group undergo thermal decomposition with amine elimination.

No pure compound has been obtained from the reaction of ethylamine with phosphorus trichloride but the analysis figures suggest the imide-amide structure.

In an attempt to prepare cyclic aminophosphines by the action of heat on di(alkylamino)phenylphosphines ($PhP(NHR)_2$), Lane and Payne[2] observed instead the interesting rearrangement process:

$$2PhP(NHR)_2 \xrightarrow[>24\text{ hr.}]{140\text{-}160^\circ} \tfrac{1}{4}(PhP)_4 + PhP(NR)(NHR)_2 + RNH_2.$$

Condensed species were also formed but as yet their compositions

/are

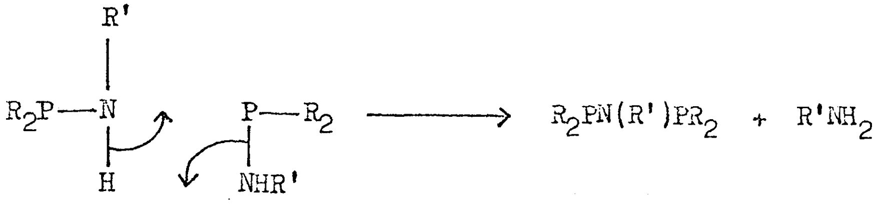
are unknown. A radical mechanism has been proposed to account for the rearrangement reaction. Aminophosphines of the type $PhP(NHR)_2$ are generally more thermally stable than the $P(NHR)_3$ species and can be distilled without a great deal of change at temperatures in the region of 80° (10^{-2} mm.).(present work).

Diphosphinoamines of the type $(Ph_2P)_2NR$[8] have been synthesised by the action of heat on alkylaminodiphenylphosphines (Ph_2PNHR).

$$2Ph_2PNHR \xrightarrow[10^{-2}\text{ mm.}]{200^{\circ}} (Ph_2P)_2NR + RNH_2$$

Again, purification of the starting materials can readily be achieved by distillation in vacuum at temperatures below 120°.

The thermal stability of P-NH compounds appears to depend to a great extent on the number of NHR groups attached to phosphorus (see above) and also on the electronegativity of the substituents. Thus the compound $(CF_3)_2PNH_2$[10] is one of the few aminophosphines known containing the $P-NH_2$ grouping. In its preparation from $(CF_3)_2PCl$ and NH_3 it shows no tendency to react with further molecules of $(CF_3)_2PCl$ and can be distilled unchanged at 67°. This would suggest a mechanism of condensation involving attack by nitrogen on the amino-hydrogen of a second molecule of aminophosphine:



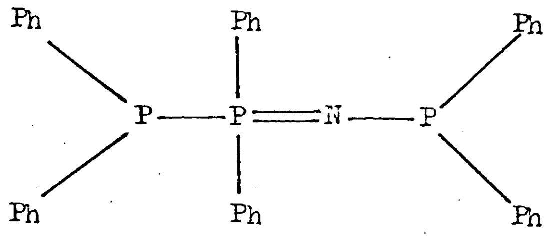
An increase in the electronegativity of the groups attached to nitrogen would thus tend to inhibit condensation provided attack by nitrogen is the rate determining step. Electron withdrawal from nitrogen in the case of $(CF_3)_2PNH_2$ is attributed to lone pair delocalisation into the phosphorus d-orbitals which have been contracted sufficiently (see Section 1f.) by the influence of the highly electronegative CF_3 groups to overlap with the nitrogen p_z-orbital.

The inability of $(CF_3)_2PNH_2$ to react with more $(CF_3)_2PCl$ could be explained in an analogous manner. It is also possible[10] that the non-reactivity of the amino hydrogen atoms is simply due to the presence of strong F...H...N hydrogen bonds which are thought to be present in the vapour phase.

The reaction of bis(diphenylphosphino)amine with diphenylchlorophosphine[39] does not lead to the expected product as predicted by the following equation:

$$(Ph_2P)_2NH + Ph_2PCl \xrightarrow{Et_3N} (Ph_2P)_3N + Et_3\overset{+}{N}H\,Cl^-$$

Instead, the rearrangement product:



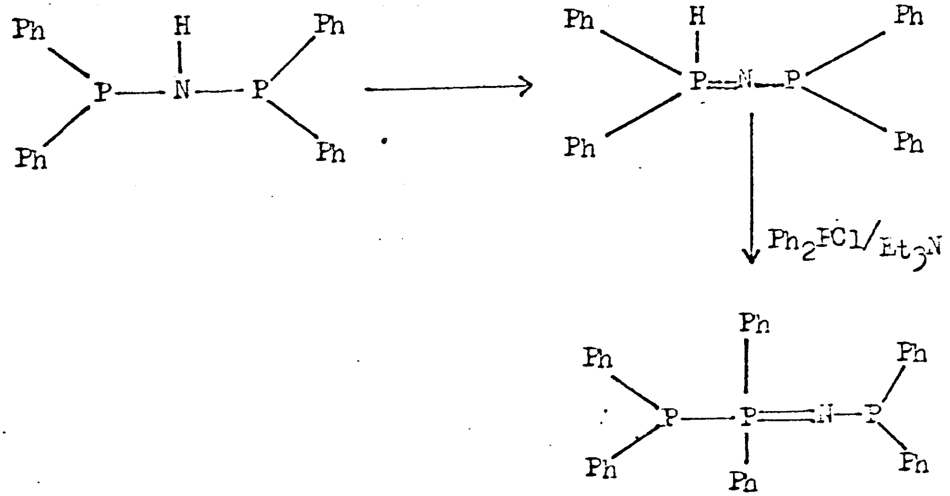
is obtained and the mechanism is probably analogous to that put forward to account for the formation of tetraphenyldiphosphine monoxide from diphenylchlorophosphine and water in the presence of triethylamine:[40]

viz.

$$Ph_2PCl + H_2O \xrightarrow{(1)} Ph_2P{-}OH \xrightarrow{(2)} Ph_2P(O)H$$

$$Ph_2P(O)H + Ph_2PCl \xrightarrow{Et_3N} Ph_2P(O)PPh_2 + Et_3NH^+Cl^-$$

The proton migration (2) from oxygen to phosphorus is an established phenomenon[41] and it would appear that the same can apply to the P—NH system:



1e. HALOGENO(AMINO)PHOSPHINES.

Halogenoaminophosphines, R_2NPX and $(R_2N)_2PX$, are prepared by the reaction of phosphorus(III) halides with amines in stoichiometric proportions, e.g.

$$PCl_3 + 4R_2NH \longrightarrow (R_2N)_2PCl + 2R_2\overset{+}{N}H_2\,Cl^-$$

Dimethylaminochlorophosphines have also been prepared by the action of hydrogen chloride[14] or phosphorus trichloride[42] on tris(dimethylamino)-phosphine, e.g.

$$(Me_2N)_3P + PCl_3 \longrightarrow Me_2NPCl_2 + (Me_2N)_2PCl$$

The halogen substituents in halogenoaminophosphines are readily displaced in nucleophilic attack at phosphorus by e.g. CN^-,[14] H_2O and amines. Replacement of chlorine (or bromine) by fluorine can be achieved with a number of fluorinating agents such as zinc fluoride,[44] antimony trifluoride and sodium fluoride.[45,46,47] Halogen addition reactions may also take place,[14] e.g.

$$(Me_2N)_2PBr + Br_2 \longrightarrow \left[(Me_2N)_2PBr_2\right]Br.$$

The nucleophilic character of the phosphorus atom in halogenoaminophosphines is somewhat diminished, presumably as a result of the electron withdrawing effects of the attached halogen atoms. Thus, tris-(dimethylamino)phosphine reacts exothermically with sulphur[48] whereas Me_2NPCl_2[49] and $(Me_2N)_2PCl$[50] require to be warmed with the reagent before sulphuration occurs. Reactions with methyl iodide[14] follow the same pattern.

The usefulness of halogenoaminophosphines in the synthesis of fully substituted aminophosphines has already been discussed.

/1f.

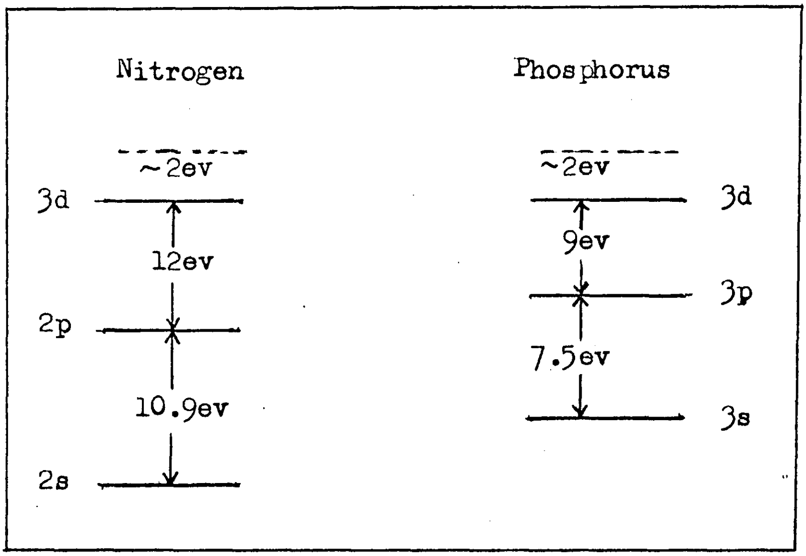

Nitrogen
Phosphorus
~2ev
3d
12ev
2p
10.9ev
2s
~2ev
3d
9ev
3p
7.5ev
3s

Fig. 1.

1f. BONDING IN TERVALENT PHOSPHORUS-NITROGEN SYSTEMS

A consideration of the outer electronic configuration of phosphorus $(3s^2, 3p^3)$ and Hund's rules suggests that three p-bonds are readily formed leading to stable tervalent derivatives. Bond angles of between 90° and 100° (approximately) suggest that there is less hybridisation in phosphorus(III) compounds than in amines which generally have bond angles close to tetrahedral. Formation of a σ-bond between phosphorus and nitrogen using sp^3 hybrid orbitals of varying s-character will thus lead to the interesting situation whereby both phosphorus and nitrogen possess a lone pair of electrons.

In order to decide which of these lone pairs will participate in nucleophilic reactions it is necessary to consider first the atomic energy levels of phosphorus and nitrogen (Fig. 1).[51]

The fact that the 3s-3p promotional energy is less than the 2s-2p suggests immediately that phosphorus rather than nitrogen will participate in nucleophilic reactions leading to 4-coordination using stable sp^3 hybrid orbitals in bonding. Furthermore, the lower 3s-3d promotional energy of phosphorus means that the contribution of higher energy levels will be greater than in nitrogen and hence the phosphorus atom is more polarisable. This, coupled with the greater covalent radius of phosphorus (1.10 Å as

/against

against 0.70 Å for nitrogen) leads to a considerable reduction in the repulsion energy on the approach of a nucleophile and consequently nucleophilic substitution reactions at phosphorus will be facilitated.

In other words, the chemical reactions of aminophosphines parallel to a great extent those of, say, alkyl or aryl substituted phosphines. A striking example of this is the reaction of dimethylamino-dimethylphosphine with methyl iodide[20] which leads to formation of the phosphonium rather than the ammonium salt:

$$Me_2NPMe_2 + MeI \longrightarrow [Me_2N - \overset{+}{P}Me_3]\ I^-$$

The exact nature of the bonding in aminophosphines is for the present a matter of some conjecture, although it has been proposed[4,5,27,70] that there may be some degree of $(p \rightarrow d)\pi$ bonding involving the vacant 3d- orbitals on phosphorus and the p_z orbital on nitrogen. Calculations have shown that 3d orbitals are too diffuse for significant overlap although the overlap integral increases with increasing positive charge on phosphorus.[52] Hence the presence of highly electronegative groups attached to phosphorus confers conditional stability on the 3d-orbitals and the π-character of the P-O bond in, for example, the PO_4^{3-} ion,[53] although less than in the C=C bond, is well established. Nitrogen, being one of the most electronegative elements, might well be expected to participate in π-bonding with phosphorus and there is considerable evidence

/for

for $(p \longrightarrow d)\pi$ bonding in cyclic phosphazenes and in phosphinimines, $R_3P{=}NR'$.[54]

However, the position is by no means so clear in aminophosphines due mainly to the lack of P(III)–N bond length data. Bond energy data[55] are also rather limited and not entirely conclusive, but perhaps the main difficulty lies in the complex nature of the molecules which have been studied.

In contrast, the extent of $(p \longrightarrow d)\pi$ bonding in silicon-nitrogen chemistry has received a great deal of attention recently and has been the subject of some controversy. Randall and co-workers[56] have related $^{15}N-^{1}H$ coupling constants to the amount of s-character of the nitrogen bonding orbitals and make the assumption that this s-character should increase with $(p \longrightarrow d)\pi$ bonding between nitrogen and silicon since this interaction requires the use of a nitrogen orbital with larger, perhaps pure, p-character. Experimental observations on N-trimethylsilylaniline led to the conclusion that the geometry around nitrogen was approximately tetrahedral, which on the above assumption suggests little $(p \longrightarrow d)\pi$ character.

However, Ebsworth[57] has proposed that significant overlap between the lone pair of electrons on nitrogen and the silicon d-orbitals is possible even when the nitrogen atom is sp^3 hybridised.

Cowley and Pinnell[70] have noted that the coupling constant over three chemical bonds (J_{PNCH}) is larger than the coupling constant over two chemical bonds (J_{PCH}) in compounds of the type $RP(CH_3).N(CH_3)R'$ and have put forward one possible explanation involving ($p \longrightarrow d)\pi$ overlap between a filled nitrogen 2p orbital and an empty phosphorus 3d orbital. They also point out that this effect may be due to the higher electronegativity of nitrogen inducing more s-character in the C–H bonds of the methyl group than does phosphorus.

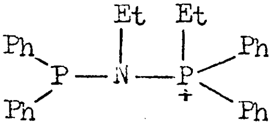
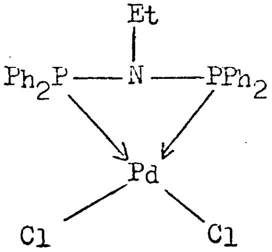
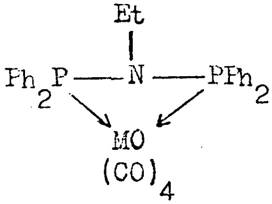
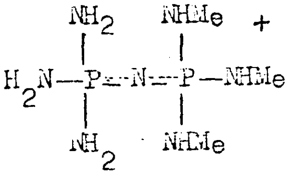
It is perhaps worthwhile to examine the structures of a few aminophosphines containing 4-coordinated phosphorus since the possibility of ($p \longrightarrow d)\pi$ interactions is increased by increasing the positive charge on phosphorus. A list of such compounds is given in Table 5.

Compound I[28] is of greatest interest since it contains both a P(III) and a P(IV) centre. The P(III)–N bond distance of 1.88 ± 0.03 Å is close to the theoretical sum of the covalent radii of phosphorus and nitrogen (1.85 Å). That this bond has less s-character than the P(IV)–N bond is shown by the smaller angle at P(III) ($102^\circ \pm 0.7^\circ$). The angle at nitrogen of $111.1^\circ \pm 1.6^\circ$) is close to the tetrahedral value and as such would tend to rule out ($p \longrightarrow d)\pi$ character in the P(IV)–N and the P(III)–N bonds, but as has already been pointed out by Ebsworth, non-planarity at nitrogen does not necessarily prohibit ($p \longrightarrow d)\pi$ interactions. It might also

/be

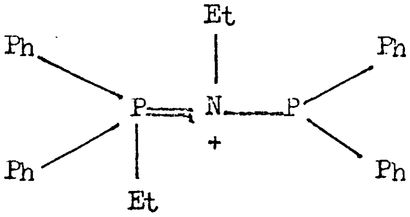
TABLE 5.

SOME P(IV)–N BOND DISTANCES

	Compound	P–N dist. (Å)	Angle at N	Angle at P(mean)
I		1.75 ± 0.03 (P(IV)–N). 1.83 ± 0.03 (P(III) – N	111.0 ± 1.6°	109.5 ± 0.7°. P(IV) 102.0 ± 0.7° P(III)
II		1.72 ± 0.01	97.7°	109°
III		1.71 ± 0.01	103.8 ± 1°	109°
IV	$Ph_2P(O)\ N\ Me_2$	1.67	120°	109°
V	$(NH_2)_3P\text{–}BH_3$	1.65		
VI	 I^-	1.61.	(P–NH bond length)	

be argued that the difference in P–N bond lengths in this compound can be attributed to the differences in hybridisation at the two phosphorus atoms though this seems unlikely in view of the magnitude of the effect.

Evidence in favour of $(p \longrightarrow d)\pi$ interactions comes from the fact that whereas in this compound only the mono-alkyl iodide adduct is formed, the methylene bridged diphosphine, $(Ph_2P)_2CH_2$,[58] can readily add two moles of alkyl iodide. One explanation is that the 4-coordinate phosphorus is stabilised to some extent by contributions from the following resonance hybrid:



The introduction of a second positive charge at P(III) would thus be electrostatically unfavourable. It is unlikely that the effect of positive charge delocalisation is carried directly to the second phosphorus atom in view of the long P(III)–N bond. However, it is possible that in this case the high electronegativity of nitrogen decreases the reactivity at P(III) by a purely inductive effect.

The relatively small angles at nitrogen in compounds II and III[28] suggest that the lone pair of electrons have considerably more s-character than in compound I, and $(p \longrightarrow d)\pi$ interactions with the 3d-orbitals on phosphorus would therefore seem an unlikely proposition. This observation is in accord with the results of Payne

/and

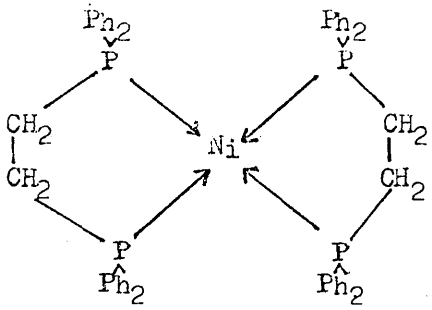
and Walker[59] who recorded little difference between the carbonyl absorption frequencies of $(Ph_2P)NEt.Mo(CO)_4$ and $(Ph_2P)_2CH_2.Mo(CO)_4$.

However, the P–N bond distance in II and III is comparable with the P(IV)–N distance in compound I and it would appear that nitrogen bond angle data alone cannot be used to predict the nature of the P–N bonding.

In compounds IV,[60] V[33] and VI[61] the P–N bond distance tends towards the value found in cyclic phosphazenes[54] (1.5-1.6 Å). It is doubtful whether P(V)–N distances can be related directly to P(IV)–N distances but to a first approximation, the extent of $(p \rightarrow d)\pi$ interactions in compounds I, II and III must be considered to be small. In view of this it seems likely that $(p \rightarrow d)\pi$ interactions in the free aminophosphines will be slight. However, it must be emphasised that any deductions made at the moment regarding the nature and extent of $(p \rightarrow d)\pi$ bonding in aminophosphines must be highly speculative.

AMINOPHOSPHINE COMPLEXES

Compounds of phosphorus(III) generally behave as quite strong Lewis bases in complex formation with electron deficient molecules such as boron hydrides or halides.[29] With transition metals, there is also the possibility of back donation from the metal d-orbitals to the vacant 3d-orbitals of suitable symmetry on phosphorus by a $(d \rightarrow d)\pi$ interaction. The availability of the 3d-orbitals appears to depend to a great extent on the electronegativity of the groups attached to phosphorus. Thus, only PF_3 appears to compare with carbon monoxide in its acceptor capacity and complete substitution of carbon monoxide has been achieved with molybdenum hexacarbonyl[62] and nickel carbonyl.[46] The strongly electron withdrawing fluorine substituents have the effect of reducing the donor properties of phosphorus and increasing the acceptor capacity. Complete substitution of CO can also be achieved in nickel carbonyl using the bidentate ligand, ethylenebis (diphenylphosphine).[63]



It is not entirely clear why the properties of this ligand should differ so much from Ph_3P which forms only the dicarbonyl complex $(Ph_3P)_2Ni(CO)_2$.[64] In general alkyl and aryl substituted monophosphines can replace up to two molecules of carbon monoxide from nickel carbonyl and three from Group VIb carbonyls. This may be due to either (a) the poorer acceptor capacity of the phosphorus 3d-orbitals in these compounds as compared to the $p\pi$ orbitals in CO, or (b) the steric requirements of the ligands, or (c) a combination of both.

In the reactions of aminophosphines with Group VIb carbonyls, only di-substitution appears to be possible, e.g.

$$2(Me_2N)_3P \;+\; Mo(CO)_6 \longrightarrow [(Me_2N)_3P]_2Mo(CO)_4. \qquad 65$$

$$(Ph_2P)_2NEt \;+\; Mo(CO)_6 \longrightarrow (Ph_2P)_2NEt.Mo(CO)_4 \qquad 59$$

Replacement of amino groups by chlorine[66] or fluorine[46] can often result in further substitution even although the electronegativity of chlorine and nitrogen are comparable. It has been suggested[67,68]

/that

that the acceptor capacity of the phosphorus 3d-orbitals towards the central metal atom in aminophosphine complexes is diminished by participation of the nitrogen p_z orbital in $(p \rightarrow d)\pi$ interaction with phosphorus. This is in part supported[68] by the fact that the carbonyl absorption frequencies in the complex $[(Me_2N)_2PCl]_2Ni(CO)_2$ are appreciably higher than in the tris(dimethylamino)phosphine complex $[(Me_2N)_3P]_2Ni(CO)_2$.

Payne and Walker,[59] in an attempt to detect $(p \rightarrow d)\pi$ interactions in the complex $(Ph_2P)_2NEt.Mo(CO)_4$ compared CO absorption frequencies with those of $(Ph_2P)_2CH_2.Mo(CO)_4$[69] and found that there was no significant difference. This would suggest that the acceptor capacity of the two phosphorus atoms has not been greatly affected by the presence of the nitrogen atom. However, in this particular example, there is competition for the lone pair of electrons on nitrogen between two phosphorus atoms and the effect of overlap with the 3d-orbitals is probably too small to be detected in the carbonyl absorption frequency.

Aminophosphine complexes of mercury (II),[5,68] cadmium (II)[68] nickel (II), palladium (II) and cobalt (II)[5,67] are readily prepared by mixing solutions of the reactants. Heating is not normally required and in the case of the transition metal complexes the preparations are carried out at low temperatures since the products tend to decompose on standing in their solutions at temperatures

/greater

greater than 0°. The ready formation of and thermal instability of these complexes is again attributed[67] to the competition between nitrogen and metal for the phosphorus d-orbitals. Thus, whereas conjugation effects in the free ligand make aminophosphines good donors, they decrease the acceptor capacity of the phosphorus 3d-orbitals in their complexes.

Diphosphinoamine complexes of the type $(Ph_2P)_2NR.MX_2$ (R = H, Me, Et) with nickel (II), palladium (II) and platinum (II) are also reported[8] and the bidentate nature of these ligands has been confirmed[28] by X-ray analysis of the complex $(Ph_2P)_2NEt.PdCl_2$. With molybdenum and tungsten hexacarbonyls[59] they give the cis-disubstituted products $(Ph_2P)_2NR$, Mo, $W(CO)_4$. Forcing conditions failed to achieve further substitution.

At the start of this project, few complexes of triphosphines had been studied. Chatt and Watson[69] have prepared complexes of $PhP(o\text{-}C_6H_4PEt_2)_2$, $PhP(C_2H_4.PPh_2)_2$ and $MeC(CH_2PPh_2)_2$ with the carbonyls of Group VI b. These have been shown by i.r. spectroscopy to be cis-trisubstituted complexes. Replacement of three molecules of carbon monoxide is readily achieved.

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CHAPTER 2.

SYNTHESIS OF AMINOPHOSPHINES CONTAINING THE N-H LINKAGE.

INTRODUCTION.

Di(alkylamino)phenylphosphines of the type $PhP(NHR)_2$ where $R = Et, Pr^n, Pr^i$, and Bu^t have been prepared by the reaction of dichlorophenylphosphine with the required primary amine. e.g.

$$PhPCl_2 + 4EtNH_2 \longrightarrow PhP(NHEt)_2 + 2EtNH_3^+Cl^-.$$

At room temperature they are all colourless liquids and they may be distilled in vacuo in the region 50 - 100° (10^{-3}mm). Yields of pure material from these syntheses were generally very low (ca.25%) and a number of possible explanations have been put forward to account for this. From the nature of the by-products, it has been proposed that deamination and rearrangement reactions are largely involved in side reactions. The rearrangement reaction has been investigated in some detail by Lane and Payne[1] who found that in sealed tubes at temperatures in excess of 140°, di(alkylamino)-phenylphosphines give a mixture of products which have been identified as polyphenylphosphine, $(PhP)_n$, a monophosphazene of the type $PhP(NR)(NHR)_2$, and a primary amine.

$$2PhP(NHR)_2 \longrightarrow PhP(NR)(NHR)_2 + \frac{1}{n}(PhP)_n + RNH_2.$$

Quantitative conversion into the monophosphazene has not been achieved and it is thought that an equilibrium exists, between the products and the di(alkylamino)phosphine. In some cases, the amount of amine produced was greater than required by the stoichiometry and it has been proposed that straightforward

/deamination

deamination leading to condensed aminophosphine systems takes place to a small extent.

It was the aim of this work to investigate these side reactions further with a view to minimising them. Since di(alkylamino)-phenylphosphines are intermediates in the syntheses of diamino-triphosphines of the type $PhP(NR.PPh_2)_2$, it was considered essential that a convenient synthesis giving good yields was available.

RESULTS AND DISCUSSION.

In view of the elevated temperatures and lengths of time required to effect the rearrangement reactions, it was considered unlikely that such a process would affect the yields of pure products to any great extent during distillation. It was decided therefore to vary the initial reaction conditions and the reaction:

$$PhPCl_2 + 2EtNH_2 \xrightarrow{2B} PhP(NHEt)_2 + 2BH^+Cl^-$$

where the base was either triethylamine or excess ethylamine, was carried out in a variety of solvents. The results are given in Table 1.

TABLE 1

Solvent.	Base.	Typical yield of $PhP(NHEt)_2$ %.
benzene	$EtNH_2$	28
benzene	Et_3N	26
ether	$EtNH_2$	28
ether	Et_3N	23
n-pentane	$EtNH_2$	62
n-pentane	Et_3N	57

It can be seen that the use of the tertiary amine, triethylamine, as hydrogen chloride acceptor has little effect on the final yield and an excess of the reacting amine is all that is required to remove hydrogen chloride from the reaction. The change of solvent from ether or benzene to n-pentane has striking results and yields of over 70% of di(ethylamino)phenylphosphine have been obtained on several occasions.

It is believed that the reason for the low yields in the cases of benzene and ether as solvent, is the retention of small quantities of ethylamine hydrochloride in the crude product after filtration and removal of solvent. Some impetus is given to this theory when one considers that silylamines can be more readily thermally deaminated with the formation of condensed species by refluxing with ammonium sulphate.[2] The latter is believed to catalyse the deamination by protonation of the nitrogen atom and facilitating nucleophilic attack at silicon by a second molecule of silylamine.

There is some evidence from n.m.r. studies (see chapter 4) that amine hydrochlorides do in fact protonate the nitrogen atom in aminophosphines which, by analogy with silylamines, would then undergo thermal condensation during distillation. The gummy residues obtained after distillation of di(alkylamino)phenylphosphines are believed to contain condensed species but their exact nature is as yet uncertain.

/Attempts

Attempts have been made in the course of this work to chromatograph these residues on silica gel using benzene as eluent but the only products which have been identified are cyclopolyphenylphosphine, $(PhP)_n$, presumably formed in the thermal rearrangement reaction and the aminophosphine oxides $PhP(NHR)_2O$. The latter probably arise by hydrolysis of the phosphazene $PhP(NR)(NHR)_2$. Reddish coloured oils were also obtained at all stages of the separation, but these have not been identified.

Some evidence for the deaminating effect of amine hydrochlorides has been obtained by heating di(ethylamino)phenylphosphine with a small quantity of ethylamine hydrochloride (purified by sublimation) in a stream of nitrogen at 120°. After 1 hour, one mole of aminophosphine was found to lose approximately one mole of ethylamine. A pure sample under the same reaction conditions gave only ca. 0.2 moles of amine per mole. It was not possible to separate the products from the amine hydrochloride in the former case. However, even this semi-quantitative approach gives some indication of the need to exclude amine hydrochlorides before distillation of crude products.

The use of n-pentane as solvent in the preparation of di(alkylamino)phenylphosphines is best exemplified by the synthesis in 74% yield of di(methylamino)phenylphosphine. Attempts to prepare this compound using benzene as solvent have previously failed to yield the desired product. The preparation of pure,

/bis(diphenylphosphino

bis(diphenylphosphino)methylamine using n-pentane is also reported in this section. This compound had previously been reported[3] to undergo rapid deamination such that acceptable analyses were never obtained. It is believed that amine hydrochlorides may also play an adverse part here, although this has not been tested experimentally.

EXPERIMENTAL.

Diphenylchlorophosphine and dichlorophenylphosphine obtained commercially were distilled under reduced pressure immediately before use. Methylamine was purified by passing it through a tube packed with potassium hydroxide pellets. n-Pentane was dried over calcium hydride and distilled immediately before use.

Di(methylamino)phenylphosphine.

Dichlorophenylphosphine (60.0g; 0.334 mole) was added dropwise to a solution of methylamine (ca.50g.) in n-pentane (1000ml.) at -78°. Entry of air to the mixture was prevented by the use of a nitrogen stream. Reaction was exothermic and a white solid precipitated immediately. The mixture was stirred for 2 hrs.at room temperature to coagulate the precipitate, after which the solution was suction filtered directly into a rotary evaporator to yield on evaporation of solvent 52.2g.of pale yellow liquid. Vacuum distillation yielded a clear liquid (39.8g., 71%) b.p. 79-80°/10^{-3}mm., m.p. ca. 22°.

[Found: C, 57.0; H, 7.4; P, 19.0; N, 16;5%; M (mass spectrum) 168. $C_8H_{13}N_2P$ requires C, 57.1; H, 7.7; P, 18.5; N, 16.7%; M, 168.]

Methylaminodiphenylphosphine.

Methylamine (ca. 5g.) was bubbled into a solution of diphenylchlorophosphine (11.2g; 4.1 m.mole) in n-pentane (250 ml).

/Filtration

Filtration and evaporation of solvent gave 10.1 g. pale yellow liquid which was distilled *in vacuo* to yield a clear liquid (4.1g; 47%), b.p. 111 - 115°.

[Found. C, 72.4; H, 6.4; N, 6.7; P, 14.5%; M (mass spectrum) 215
$C_{13}H_{14}NP$ requires C, 72.6; H, 6.5; N, 6.5; P, 14.4%; M, 215.]

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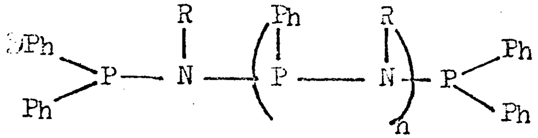
CHAPTER 3.

SYNTHESIS AND PROPERTIES OF BIS(N-DIPHENYL-N-ALKYL)DI(AMINO)PHENYLPHOSPHINES.

INTRODUCTION.

The chemistry of aminophosphines of the structural type:



where R = H, Me, Et and n = 0 is fairly well established (Chapter 1), each phosphorus atom acting as a nucleophile in reactions with sulphur and in donation to transition metals, but behaving independently in quaternisation reactions with alkyl iodides. The preparation of one member of the class of compounds where n = 1 has been reported[1], but at the start of this work little of the chemistry was known.

Aminophosphines of this type present an interesting problem in that one of the phosphorus atoms is in an environment which is chemically different from that of the other two. The central phosphorus atom (P_c) is flanked by two highly electronegative, potentially conjugating nitrogen atoms (as in di(alkylamino) phenylphosphines) while the terminal atoms (P_T) are in an environment which is more like that in bis(diphenylphosphino)alkylamines. $(Ph_2P)_2NR$. It was the aim of this work to

(a) investigate the relative reactivities of P_T and P_c.

(b) examine the effect of changing the coordination number at one (or two) phosphorus atom(s) on the reactivity of the remainder.

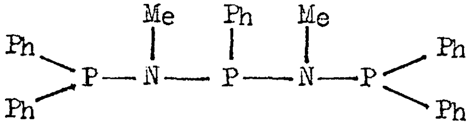
(c) investigate possible $(p \longrightarrow d)\pi$ interactions in the P—N chain.

/The reactions

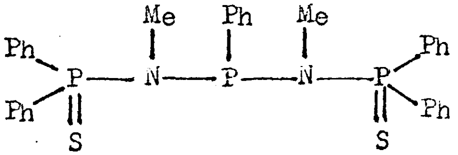
The reactions studied were sulphonation, quaternisation, and replacement of carbon monoxide in Group VIb carbonyls, and in one instance, complex formation with anhydrous nickel(II)chloride.

NOMENCLATURE.

Rigid application of the phosphine - amine system of nomenclature has led to the adoption of di(amino)phenylphosphine, $PhP(NH_2)_2$, as the basis for nomenclature in aminophosphines of the skeletal type P - N - P(Ph) - N - P. For example, the compound:



is strictly referred to as bis(N - diphenylphosphino - N - methyl)-di(amino)phenylphosphine. However, for convenience in writing, the phosphorus atoms will simply be labelled (from left to right) P_1, P_2 and P_3 or, in some cases, P_T, P_C and P_T respectively. For example, the compound:



will be referred to as the 1,3 - disulphide of the parent aminophosphine. In the discussion of the ^1H n.m.r. spectra it has been found more convenient to employ the P_T - P_C terminology.

RESULTS.

The triphosphines, bis-(N-diphenylphosphino-N-ethyl)di(amino)-phenylphosphine (I) and bis-(N-diphenylphosphino-N-methyl)di(amino)-phenylphosphine (II) were prepared by the reaction of diphenylchlorophosphine with the corresponding di(alkylamino)phenylphosphine in the presence of triethylamine as hydrogen chloride acceptor:

$$2Ph_2PCl + PhP(NHR)_2 + 2Et_3N \longrightarrow (Ph_2PNR)_2PPh + 2Et_3NH^+Cl^-$$

They are both white, highly crystalline solids and may be stored indefinitely in air without change. In solution and especially in the presence of amine hydrochloride, they tend to undergo decomposition. For example, ethanolic solutions of (I) in the presence of triethylamine hydrochloride rapidly turn orange in colour and on removal of solvent, the compounds $Ph_2P(O)OEt$, Ph_2POEt and $(Ph_2PO_2)^-(EtNH_3)^+$ can be isolated indicating that ethanolysis and hydrolysis has occurred. In the absence of amine hydrochloride, (I) can be recrystallised from ethanol in good yield.

Attempts to extend the triphosphine series to the isopropyl analogue were unsuccessful. The products obtained from a variety of reaction conditions including refluxing the reactants in benzene were viscous yellow oils which possessed a strong band in the NH region of the infra-red suggesting that replacement of hydrogen by diphenylphosphino groups was not complete. In view of the possible steric hindrance in (I) (see later) formation of the isopropyl analogue could well be sterically difficult.

(I) reacts with sulphur in 1:1 mole ratio to give a product which has been shown by elemental analysis and by mass spectroscopy to be the 1-sulphide, the mass spectrum showing a metastable for the loss of $Ph_2P(S)^+$ from the parent ion.

In the reaction of (II) with sulphur in 1:1 mole ratio, only the disulphide can be isolated even when the reactants are shaken in the cold in benzene solution. Attempts to separate out further products by crystallisation or by chromatography have not been successful.

Both (I) and (II) react with sulphur in 1:2 mole ratio to give good yields of the corresponding disulphides after only ca.1 hr. in refluxing benzene solution. The disulphide of (II) has been shown by ^1H n.m.r. spectroscopy to be the 1,3-disulphide but the exact nature of the disulphide of (I) is not so clear. A peak is observed in the mass spectrum of this material corresponding to the loss of $(Ph_2P)^+$ from the parent ion which suggests the presence of the 1,2-disulphide. The complexity of the ^1H n.m.r. spectrum has precluded ready interpretation.

Both the disulphides of (I) and (II) are highly crystalline white solids which are stable to further atmospheric oxidation and to hydrolysis. Sulphuration of the remaining phosphorus atom takes place only on prolonged heating under reflux in benzene (24 hr.) with excess sulphur. The melting points of the sulphides of (I) and (II) are given in Table 1.

/TABLE 1

TABLE 1.

Sulphides of I and II.

Compound	S_1 m.p.°	S_2 m.p.°	S_3 m.p.°
I	ca.118	217-221	194-198
II	---	191.5-194	181.5-183

In reactions with methyl iodide in ether at room temperature, (I) and (II) form only a mono-adduct, quaternisation taking place at a terminal phosphorus atom. The products are very susceptible to hydrolysis and attempts to crystallise the adduct of (I) have yielded only the hydrolysis product $Ph_2P(Me)NHEt^+ I^-$. This material can, in fact be detected in the n.m.r. spectrum of the initial reaction product. If the reaction is carried out in an n.m.r. tube in $CDCl_3$ as solvent, hydrolysis is avoided and the formation of only the undissociated mono-adduct is observed. When these reactions are carried out in the absence of solvent, there is evidence from weight increases for quaternisation at a second phosphorus atom.

However, the products appear to be extremely sensitive to hydrolysis and have not been characterised.

Replacement of three molecules of carbon monoxide from Group VIb carbonyls by (I) and (II) is readily achieved by refluxing the reactants in acetonitrile or diglyme.

Tris(acetonitrile)tungsten tricarbonyl has proved to be a very useful reagent in the formation of tungsten tricarbonyl derivatives of the triphosphines and crystalline products may be observed in the refluxing reaction mixture after only 15 mins. The products are all yellow, highly crystalline solids, stable to atmospheric oxidation and hydrolysis but tending to decompose in solution or in contact with their solutions. Apart from the chromium complexes, they are very insoluble in the cold in a wide variety of organic solvents but may be dissolved in hot nitromethane, acetonitrile, dimethyl formamide etc. Melting points are listed in Table 2.

TABLE 2.

Group VIb carbonyl complexes of (I) and (II).

$(Ph_2PNR)_2PPh.M(CO)_3$

R		M=Cr m.p.°	M=Mo m.p.°	M=W m.p.°
Me	II	263-265	260 (decomp).	303-305
Et	I	258-260	265 (decomp).	296 (decomp).

Infra-red data suggest that the three phosphorus atoms occupy cis-positions[2] in the octahedron. X-ray analysis of the molybdenum tricarbonyl derivative of (I) is at the moment being carried out.[3]

(I) reacts slowly with anhydrous nickel chloride in refluxing benzene to give a red crystalline solid (m.p.256° on recrystallisation from nitromethane) which has been shown by n.m.r. and elemental analysis to be the diphosphinoamine complex, $(Ph_2P)_2NEt.NiCl_2$. This compound had been previously[4] prepared by the reaction of bis-(diphenylphosphino)ethylamine with nickel chloride in ethanol. In the present work, the yield of this complex was only ca.15% after 5 days' refluxing of the reactants in benzene. No other complexes were isolated; the residue consisted of unreacted (I) and nickel chloride. The formation of further products cannot be excluded, but attempts to separate them by chromatography on silica gel were not successful. When no precautions were taken to exclude moisture from this reaction, the reaction rate is somewhat faster but the compound obtained is the hydrolysis product, $Ph_2P.NEt.PPh.NHEt.NiCl_2$. (m.p.249°). The ultra-violet spectrum of this complex suggests that it is of the low spin type L_2MX_2. Again, no further products were isolated from this reaction.

DISCUSSION.

The properties of (I) and (II) parallel to some extent those of the diphosphinoamines, $(Ph_2P)_2NR$.[4,5] Each phosphorus atom may act as a nucleophile in reactions with sulphur and in complex formation

/with

with Group VIb carbonyls. In quaternisation reactions with methyl iodide, only the mono-adduct is formed under mild reaction conditions. From the evidence available, the terminal phosphorus atoms are initially the more reactive towards sulphur and methyl iodide. There are two possible explanations for this:

(a) the nucleophilicity of the central phosphorus atom is relatively less than the terminal phosphorus atoms by virtue of the presence of the two highly electronegative nitrogen atoms.

(b) the central phosphorus atom is more sterically hindered.

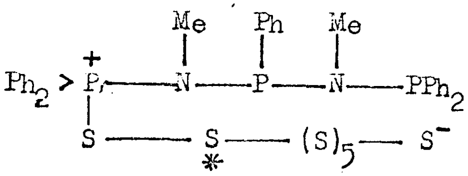
In view of the fact that di(alkylamino)phenylphosphines, $PhP(NHR)_2$, react rapidly with sulphur at room temperature, explanation (a) is not considered to be of great importance. Construction of models of (I) and (II), on the other hand, shows that the central phosphorus atom is more sterically hindered than the other two and hence explanation (b) is favoured.

The course of the addition of sulphur to (I) and (II) is of some interest, especially in view of the fact that the only product isolated in the reaction of (II) with sulphur in 1:1 mole ratio was the 1,3-disulphide. It does not seem likely that sulphuration of P_1 should increase the reactivity of P_3 to such an extent that further sulphuration takes place in the same molecule in preference to a free aminophosphine molecule. Bartlett and Meguerian[6] have studied the kinetics of the sulphuration of triphenylphosphine and have proposed the following mechanism:

$$Ph_3P + S_8 \longrightarrow Ph_3\overset{+}{P}\text{-}S\text{-}(S)_6\text{-}S^-$$

$$Ph_3\overset{+}{P}\text{-}S\text{-}\overset{*}{S}\text{-}(S)_5\text{-}S^- + Ph_3P \longrightarrow Ph_3P{=}S + Ph_3\overset{+}{P}\text{-}S\text{-}(S)_5\text{-}S^-$$

The second stage involves nucleophilic attack by a second molecule of triphenylphosphine on S(*). Applied to sulphuration of the triphosphine (II), the initial stage would be formation of the intermediate:



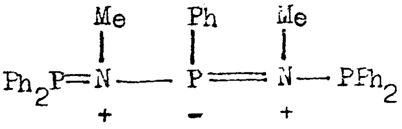
Construction of a model of this intermediate shows that P_3 is in a favourable position for nucleophilic attack at S(*) with formation of a cyclic transition species. Such a process might be expected to be energetically more favourable than attack by a second molecule of (II) at S(*). Since initial cleavage of the S_8 ring is usually the rate determining step in sulphuration reactions, the 1,3-disulphide should be readily formed.

The same principles cannot be applied to the sulphuration of (I) where a monosulphide can be isolated. It is possible that the greater steric hindrance in this molecule prevents the formation of a cyclic transition species so that the second stage of the sulphuration reaction involves attack by a second molecule of (I). The course

/of

of further sulphuration is not clear. The mass spectrum of the disulphide of (I) shows peaks corresponding to the loss of $(Ph_2P)^+$ and $[Ph_2P(S)]^+$ from the parent ion (m/e628). From this it can be concluded that one of the terminal phosphorus atoms has not been sulphurated. However, the presence of the 1,3-disulphide cannot be excluded since $[Ph_2P(S)]^+$ may be lost either from the 1,3- or the 1,2-disulphide, the resultant daughter ion having the same mass number (m/e411). The complexity of the ^{1}H n.m.r. spectrum (see later) of this material would suggest that it may not be a pure 1,2- or a pure 1,3-compound.

The formation of only a mono-adduct in the reaction of (I) and (II) with methyl iodide in ether is somewhat surprising. Again, quaternisation at P_1 is not considered to directly affect the reactivity at P_3 by a process of electron withdrawal involving, for example, the following extreme canonical form:



$$Ph_2P{=}\overset{Me}{\underset{+}{N}}-\overset{Ph}{\underset{-}{P}}{=}\overset{Me}{\underset{+}{N}}-PPh_2$$

In view of the available bond angle and bond length data[7] for the alkyl iodide adduct of $(Ph_2P)_2NEt$, $(p\rightarrow d)\pi$ overlap involving P_2 must be considered to be slight. Inductive effects over four bonds are also likely to be small. Two further explanations are probably of greater validity - (a) steric hindrance at P_3 and (b) the possible proximity of positive charges in the 1,3-diadduct

/if

if formed; However, since no structural data are available for the triphosphines, the real explanation must remain a subject for speculation. There is evidence that further quaternisation may occur when the reactions are carried out in the absence of solvent. However, the products are extremely susceptible to hydrolysis and have not been characterised.

Both (I) and (II) readily replace three molecules of carbon monoxide in reactions with Group VIb carbonyls. The products are the cis-trisubstituted carbonyls with charactoristic bands in the carbonyl region of the infra-red[2] at ca.1940 and 1840cm.$^{-1}$ A comparison of these values (Table 3) with those of some tridentate phosphines not containing a P–N bond shows that they are not significantly different. $(p \longrightarrow d)\pi$ overlap between nitrogen and phosphorus should have the effect of reducing $(d \longrightarrow d)\pi$ back bonding between the metal atom and phosphorus with a resultant decrease in the carbonyl stretching frequencies in the infra-red. The high electronegativity of nitrogen should have the opposite effect. If anything, the latter is the more important in the carbonyl complexes of (I) and (II). These observations are in agreement with the results of Payne and Walker[5] on Group VIb carbonyls of diphosphinoamines.

The slight increase in the carbonyl stretching frequencies is accompanied by a significant lowering of the P–N absorption frequencies as compared to the free ligands (Table 4). This could

/be

TABLE 3.

CO stretching frequencies of some cis-Trisubstituted Group VIb carbonyls (cm.$^{-1}$).

Compound	M=Cr	M=Mo	M=W
$^{(a)}$(I) $M(CO)_3$	1932, 1841	1943, 1848	1938, 1842
$^{(a)}$(II) $M(CO)_3$	1935, 1842	1945, 1851	1938, 1843
$^{(a)}$$PhP(C_2H_4PPh_2)_2M(CO)_3$[8]		1937, 1848	
$^{(a)}$$MeC(CH_2PPh_2)_2M(CO)_3$[8]	1905, 1830	1930, 1834	1930, 1834
$^{(b)}$$(Ph_3P)_3M(CO)_3$[9]		1934, 1835	

(a) 1,2-dichloroethane solution.

(b) chloroform solution.

TABLE 4.

P–N stretching frequencies of complexed Ligands. (cm.$^{-1}$).

$(Ph_2PNR)_2PPh.M(CO)_3$ (Nujol)

R	M=Cr	M=Mo	M=W
Me (845, 814)	818, 793	822, 795	822, 795
Et (875, 852)	860, 842	862, 842	862, 842

be interpreted in terms of a reduction in $(p \rightarrow d)\pi$ overlap between nitrogen and phosphorus due to competition from the central metal atom for the phosphorus d-orbitals. Several further changes in the spectrum of (I) and (II) on complexing occur in the region 700 - 400 cm.$^{-1}$. It has not been possible to assign the bands in this region although the band at 672±2 cm.$^{-1}$ in the spectra of the chromium complexes may be attributed to Cr-C stretching.[10]

In the reaction of (I) with nickel chloride, no product containing the triphosphine skeleton has been isolated. A u.v. spectrum of the red solution obtained on mixing alcoholic solutions of the reactants in 1:1 mole ratio showed a band in the region 25,000 cm.$^{-1}$ which is characteristic of low spin Ni(II) complexes of the type L_2NiX_2. It would appear that only two phosphorus atoms are involved initially in coordination. The reactivity of the third appears to be increased and the products isolated from the reactions carried out under strictly anhydrous conditions and in the presence of water are the rearrangement product $(Ph_2P)_2NEt.NiCl_2$ and the hydrolysis product $Ph_2P.NEt.PPh.NHEt.NiCl_2$ respectively. The other fragments in these reactions have not been isolated.

INFRA -RED SPECTRAL DATA.

The P(III)-N stretching frequency has been variously assigned to be between 800 and 1000 cm^{-1}.[4,5,11,12] (II) shows two bands in this region. Their positions appear to be fairly sensitive to the nature of the groups attached to phosphorus and this is illustrated by reference to the spectra of (II) and some of its compounds (Table 5). The shift to lower wavenumbers on complexing has already been discussed. Sulphuration and quaternisation result in a shift to higher wavenumbers and this is in accord with the view that the degree of π - character in the $=P(S)-N$ bond and in the $\overset{+}{P}-N$ bond is greater than in the P(III)-N bond. It has been pointed[10] out that the position of the P-N bond is not subject to any simple relationship involving electronegativity and the increase in the P-N stretching on frequency on going from (II) to (I) cannot be explained in such terms. (I) shows four bands in the region 800 - 1000 cm.$^{-1}$. These consist of a medium intensity doublet at 936 and 917 cm.$^{-1}$ and a further two strong bands at 875 and 852 cm^{-1}. The latter are more sensitive to changes at phosphorus and their positions vary in a manner analogous to those of (II) (with the exception of the disulphide of (I) where one of the bands moves to a lower frequency). The other doublet tends to broaden on complexing and moves slightly to higher wavenumbers. In the spectra of the sulphides and methiodide of (II) it shifts very slightly to higher frequencies and loses the doublet structure. Thus the bands at lower wavenumbers (875 and 852 cm^{-1}) are more characteristic of the P-N stretching frequencies.

The P=S frequencies in phenyl substituted phosphines have been reported to occur in the region of 616 cm^{-1}.[4,13] A band of weak intensity occurs in this region in all of the sulphides studied.

/However

TABLE 5.

P-N stretching frequencies of (II) and derivatives. (Nujol).

Compound	P-N stretching frequency (cm^{-1}).
$(Ph_2PNMe)_2PPh$	845, 814
$(Ph_2PNMe)_2PPh.S_2$	875, 820
$(Ph_2PNMe)_2PPh.S_3$	870, 833
$(Ph_2PNMe)_2PPh.MeI$	873, 822

However, the main differences in the spectra of the sulphides as compared to the free ligands occur in the region 650 - 750 cm.$^{-1}$, which is in accord with the observations of Thomas and Chittenden[14] on a variety of aminophosphine sulphides. The sulphides of the diphosphinoamines, $(Ph_2P)_2NR$, also showed changes in this region with a strong band appearing at 642 ± 1 cm^{-1}.

'H N.M.R. SPECTRA.

In recent years, detailed analyses of the 'H n.m.r. spectra of organophosphorus compounds has provided a great deal of structural information which could only have been obtained previously by more time consuming chemical methods. J_{PNCH} coupling constant data have been reported for a number of aminophosphines and derivatives.[15-18] In the free aminophosphine, J_{PNCH} is usually of the order of 10c/sec., increasing slightly on the addition of oxygen or sulphur to phosphorus. The smallest values of J_{PNCH} so far reported have been in compounds of the structural type

$$=P-\overset{\overset{Me}{|}}{N}-P=$$

19,20.

For example, in the diphosphinoamine, $(Ph_2P)_2NMe$, it is 2.9 c/sec. increasing to 11.2 c/sec. on sulphuration of both phosphorus atoms. This large difference has been of considerable use in elucidating the structures of the sulphides and the methyl iodide adduct of (II).

'H n.m.r. spectrum of (II).

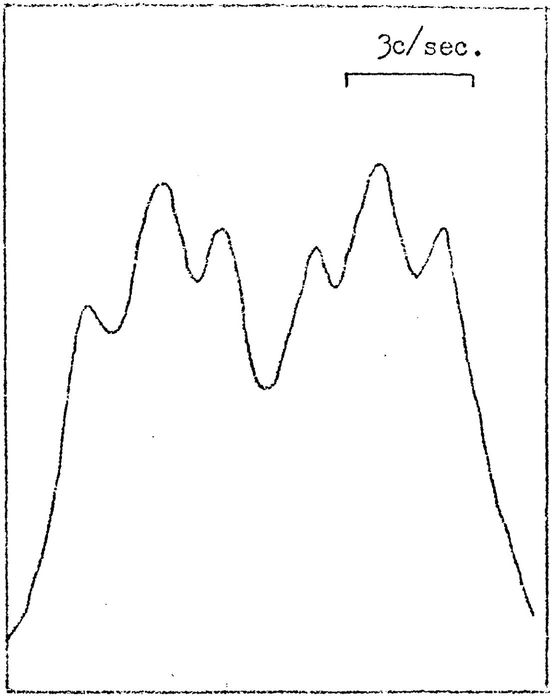


Fig.1. $PhP(NMePPh_2)_2$

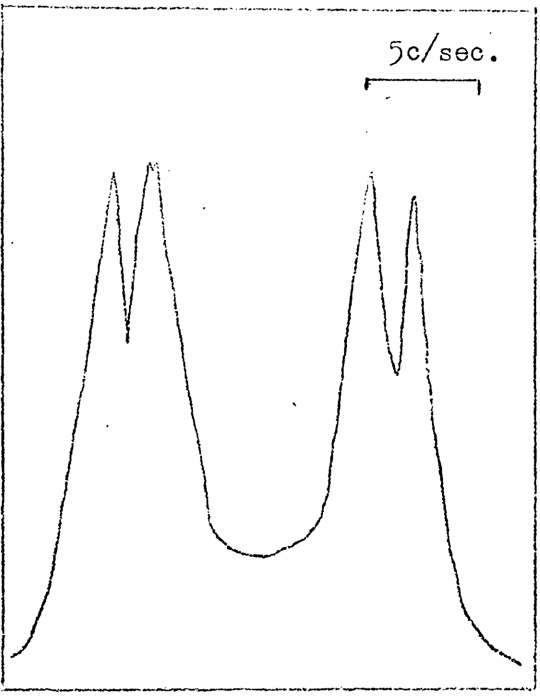


Fig.2. $PhP(NMePPh_2)_2\ S_2$

H_o →

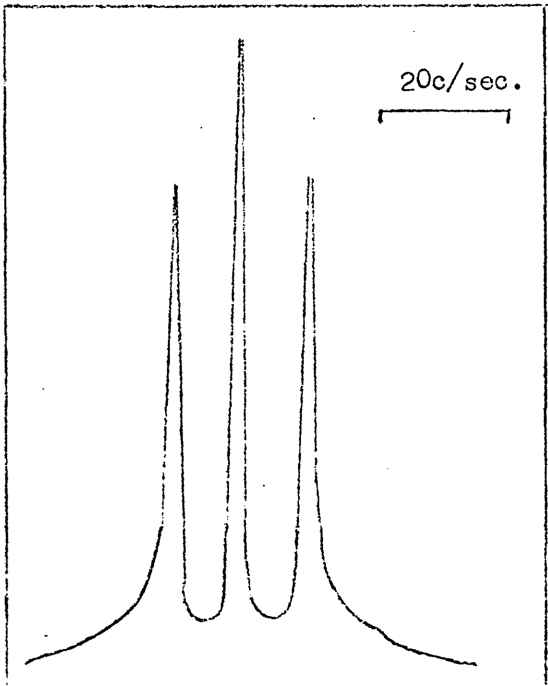


Fig.3. $PhP(NMePPh_2)_2\ S_3$

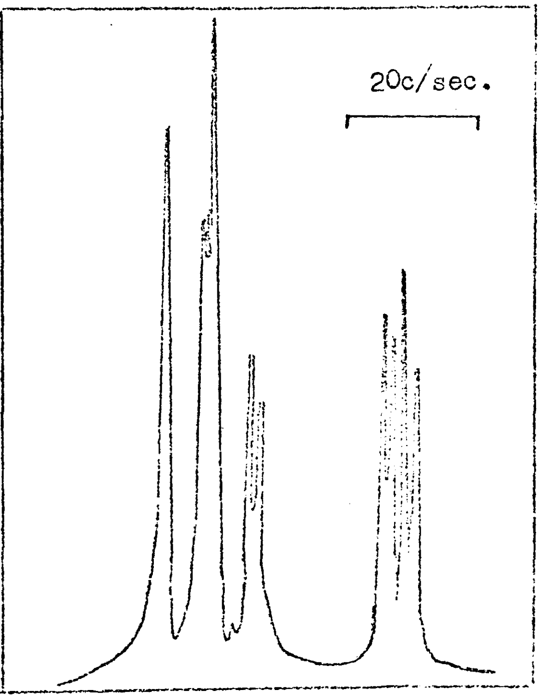


Fig.4. $PhP(NMePPh_2)_2\ MeI$

Methyl-proton resonance signals of II and derivatives (100Mc/sec.)

TABLE 6.

'H n.m.r. data for $(Ph_2PNMe)_2PPh$, $(Ph_2P)_2NMe$ and derivatives.

	τ Values ($CDCl_3$)		Coupling Constants (c/sec).			
Compound	$\tau\ CH_3N$	$\tau\ CH_3P$	J_{PCH}	J_{P_CNCH}	J_{P_TNCH}	$J_{P(+)NCH}$
$(Ph_2PNMe)_2PPh$	7.27	—	—	3.0	4.6	—
$(Ph_2PNMe)_2PPh\ S_2$	7.17	—	—	1.5	12.2	—
$(Ph_2PNMe)_2PPh.S_3$	6.93	—	—	11.0	11.0	—
$(Ph_2PNMe)_2PPh\ MeI$	7.32, 6.88	6.76	12.6	2.0	5.0	12.6
$(Ph_2P)_2NMe$	7.60	—	—	—	1.9	—
$[Ph_2P(S)]_2NMe$	7.29	—	—	—	11.0	—
$(Cl_2P)_2NMe$		—	—	—	3.0	—

The spectra of (II) and derivatives are given in Figs. 1 - 4 and the spectral data in Table 6. The methyl-proton signal in the ^{1}H n.m.r. spectrum of (II) consists of two triplets separated by 4.6 c/sec. and centred at τ 7.27. The same separations are observed on varying the field strength indicating that the triplets are spin-coupled. This observation of a doubled triplet suggests that the methyl-protons are interacting not only with the phosphorus atoms 3 bonds distant (i.e. J_{PNCH}) but with the phosphorus atoms 5 bonds distant. It is unlikely that direct coupling occurs over such a distance. However, effective coupling (or virtual long-range coupling)[21,22] can occur when certain conditions are satisfied. Consider the hypothetical system:

$$CH_3-N-P_A-N-P_B$$

When the chemical shift difference between P_A and P_B is small compared with $J_{P_AP_B}$, the methyl-proton signal might well be a triplet even when J_{P_BNPNCH} is zero. The characteristics of such ABX_3 spin systems are well known and Abraham and Bernstein[23] have shown that a triplet structure will be observed if,

$$(J_{AX} - J_{BX})^2 / 2J_{AB} < \Delta\nu_{\frac{1}{2}}$$

where $\Delta\nu_{\frac{1}{2}}$ is the resolving power of the spectrometer given by the half-height half-width of a single line (<u>ca</u>. 0.5 c/sec.) The separation of the outer lines of the triplet is given[24] by $|J_{AX}+J_{BX}|$

/and

and in the case where $J_{BX}=0$, the lower limit of the coupling constant J_{AB} can easily be calculated by measuring $\Delta\nu_{\frac{1}{2}}$.

In the spectrum of (II), the methyl-proton signal is considered to be doubled by coupling with the near, terminal phosphorus atom (P_T) (J_{P_TNCH} = 4.6 c/sec.) When equation (1) holds, each component of the doublet will show a triplet structure. Now, assuming that $J_{BX} = 0 = J_{P_TNPNCH}$, then

$$(J_{P_CNCH})^2 / 2J_{AB} < 0.5$$

or $$(J_{P_CNCH})^2 < J_{AB}$$

(where P_C refers to the central phosphorus atom).

Now the separation of the outer components of the triplets = 3.0 c/sec. $= |J_{AX}| = |J_{P_CNCH}|$. Hence, the lower limit of $J_{AB} = J_{P_TP_C}$ can be calculated to be about 9 c/sec. This compares with a lower limit of about 30 - 40 c/sec.[25] for J_{PNP} in aminophosphazenes and if J_{PNP} can be taken as an approximate measure of conjugative effects, then conjugation in the aminophosphine system is, as expected, much weaker.

1,3-DISULPHIDE OF (II).

The methyl-proton signal of this compound is effectively that of an A_3MX spin system i.e. a pair of spin-coupled doublets. The larger splitting is attributed to J_{P_TNCH} = 12.2 c/sec. and the lower to coupling with the central phosphorus atom (J_{P_CNCH} = 1.5 c/sec).

/These

These assignments are in accord with the observation that J_{PNCH} increases considerably when the diphosphinoamine $(Ph_2P)_2NMe$ is sulphurated. The failure to observe virtual long-range coupling is attributed to an increase in the chemical shift difference between P_T and P_C (phosphorus(V) and phosphorus(III) respectively). It is difficult to rationalise the low values for J_{P_CNCH} in this compound and in the spectra of methylamino bridged diphosphines in general, in terms of s-character in the P-N bonds, since J_{PNCH} in the compound $(Ph_2P)_2NEt$[19] (Table 7) has the more 'normal' value of 9.7 c/sec.

1,2,3-trisulphide of (II.)

The methyl-proton signal of this compound is a triplet centred at τ6.93 i.e. $J_{P_TNCH} = J_{P_CNCH}$ = 11.0 c/sec. Again, no virtual long-range coupling is observed suggesting that δP_TP_C is much larger than in the free aminophosphine.

Methyl iodide adduct of (II).

The ^1H n.m.r. spectrum of the methyl iodide adduct of (II) consists of three sets of chemically shifted multiplets which have been assigned in order of increasing τ value to 5 phenyl groups, a P-methyl group overlapping with an N-methyl group and an N-methyl group. The non-equivalence of the N-methyl groups suggests immediately that a terminal phosphorus atom has been quaternised. The high field multiplet consists of a doublet of separation 5.0 c/sec. (J_{P_TNCH}) which is further doubled by coupling to the central phosphorus atom

TABLE 7.

'H n.m.r. data for $PhP(NEt.PPh_2)_2$, $(Ph_2P)_2NEt$ and derivatives.

Compound	τ Values. (CDCl$_3$)		
	τ CH_3-C	τ CH_3-P	τ CH_2
$PhP(NEt.PPh_2)_2$	9.17		ca.6.8
$PhP(NEt.PPh_2)_2S_2$	8.92		ca.6.2
$PhP(NEt.PPh_2)_2MeI$	9.19	6.94	ca.6.5
$(Ph_2P)_2NEt$	9.27		6.65
$(Ph_2P)_2NEt.S_2$	9.15		6.35

(J_{P_CNCH} = 2.0 c/sec). These assignments to the N-methyl group which is not adjacent to a quaternised phosphorus atom are in agreement with the assignments in the free aminophosphine. Furthermore, the high field N-methyl group shows no significant change in chemical shift as compared to (II) itself.

The low field methyl-proton signal consists of a doublet (separation = 12.6 c/sec.) overlapping with a pair of spin-coupled doublets (doublet separations = 12.6 c/sec. and 2.0 c/sec.) The former is assigned to the P-methyl group (J_{PCH} = 12.6 c/sec.) and the latter to the adjacent N-methyl group (J_{P_TNCH} = 12.6 c/sec.) and J_{P_CNCH} = 2.0 c/sec). No virtual coupling is observed.

The ^{1}H n.m.r. spectra of (I) and its derivatives do not lend themselves to ready interpretation. At 60 Mc/sec, the methylene-resonance signal of (I) itself is a very broad multiplet which separates out into two distinct multiplets at a field strength of 100 Mc/sec. suggesting that the protons in the methylene group are magnetically non equivalent. This effect may be due to asymmetry at the central phosphorus atom, slow inversion at nitrogen, or hindered rotation in the molecule. Unfortunately, limited access to variable temperature equipment has precluded the solution of this problem. For a reason which is not entirely clear, double resonance techniques have not yet succeeded as an aid to the interpretation of the methylene-resonance signal of (I). However, in the case of the disulphide of (I), where magnetic nonequivalence of the methylene-proton signal is also observed, irradiation of the methyl signal at its resonance frequency causes the low field methylene multiplet to collapse into what can be recognised as a pair of overlapping doublets. The high field multiplet is resolved into 6 lines which are composed of a pair of doublets overlapping with two broad signals. It has not been possible to assign these lines to any particular structure. The problem may be finally resolved by removing the nonequivalence of the methylene-protons (possibly on raising the temperature) and spin- decoupling the methyl protons, but it has not so far been possible to use this technique.

The spectrum of the methyl iodide adduct of (I) in the region above τ 5.0 consists of a broad multiplet overlapping with a doublet of separation 12.3 c/sec. which is assigned to J_{P-CH}. This doublet shows further fine splitting (ca. 1.5 c/sec) which may be due to longer-range coupling with the central phosphorus atom.

The ethylamino methyl-proton signal occurs at τ 9.19 consisting of a triplet with J_{HH} = 7.8 c/sec. Integrated intensity ratios confirm that this compound is indeed the mono-adduct. Due to the complexity of the spectrum in the methylene region, it is not possible to determine by n.m.r. whether the central or terminal phosphorus atom has been quaternised. However, on hydrolysis of this compound, the species $[Ph_2P(Me)NHEt]^+ I^-$ is obtained which confirms that quaternisation has occurred at a terminal phosphorus atom.

EXPERIMENTAL.

Diphenylchlorophosphine, obtained commercially, was distilled under reduced pressure immediately before use. Triethylamine was dried over calcium hydride and distilled from sodium. n-Pentane and benzene were distilled from calcium hydride and potassium respectively. All operations were carried out under a stream of dry nitrogen.

Bis(N-diphenylphosphino-N-ethyl)di(amino)phenylphosphine (I).

Diphenylchlorophosphine (59.4g; 0.27 mole) was added dropwise to di(ethylamino)phenylphosphine (26.3g; 0.13 mole) and triethylamine (23.9g; 0.24 mole) in n-pentane at 0°. The mixture was stirred for 2 hours after which the solution was suction-filtered directly into a rotary evaporator to yield on evaporation of solvent, 31.5g. of white solid. The precipitated amine hydrochloride was treated with ice-cold ethanol to yield on filtration a further 5.4g. of product. The combined material was recrystallised from ethanol to give lustrous white plates (32.1g; 44%), m.p. 143 - 145°.

Found: C, 72.2; H, 6.2; N, 5.1; P, 16.4%; M(mass spectrum) 564. $C_{34}H_{35}N_2P_3$ requires C, 72.4; H, 6.2; N, 5.0; P, 16.5%; M, 564 .

1-sulphide of (I).

(I) (0.75g; 1.32 m.mole) in benzene (40 ml) was heated under reflux for 20 hours with elemental sulphur (0.05g; 1.56 m.mole). Removal of the benzene left a white solid which was recrystallised from ethanol to give a white crystalline solid, m.p. ca. 118°.

/Found;

Found: C, 68.5; H, 6.0; N, 4.2; P, 15.7; S, 5.6%; M(mass spectrum) 596.

$C_{34}H_{35}N_2P_3S$ requires C, 68.4; H, 5.9; N, 4.7; P, 15.6; S, 5.4%; M, 596.

Disulphide of (I).

(I) (0.56g; 1.0 m.mole), in benzene (40 ml) was heated under reflux for 20 hours with elemental sulphur (0.063g; 2.0 m.mole). Removal of the benzene left a white solid which was recrystallised from acetone to give a white crystalline solid, m.p. 217 - 221°.

Found: C, 64.9; H, 5.6; N, 4.4; P, 15.0; S, 10.1%; M(mass spectrum) 628. $C_{34}H_{35}N_2P_3S_2$ requires C, 65.0; H, 5.6; N, 4.5; P, 14.8; S, 10.2%; M, 628.

1, 2, 3-trisulphide of (I).

(I) (0.56g; 1.0 m.mole) in benzene (40 ml) was heated under reflux for 20 hours with elemental sulphur (0.17g; 5.3 m.mole). Removal of the benzene left a white solid which was extracted with three 20 ml. portions of ether to give on slow evaporation of the ether solution, a white crystalline solid, m.p. 194 - 193°.

Found: C, 62.0; H, 5.4; N, 3.8; P, 14.6; S, 14.7%; M (mass spectrum) 660. $C_{34}H_{35}N_2P_3S_3$ requires C, 61.8; H, 5.3; N, 4.2; P, 14.1; S, 14.6%; M, 660.

Methyl iodide adduct of (I).

(I) (0.20g; 0.36 m.mole) in ether (20 ml.) with an excess of methyl iodide gave a white solid, m.p. *ca.* 85°.

/ Found

Found: N, 3.9%. $C_{35}H_{38}IN_2P_3$ requires N, 4.0% .
Recrystallisation from acetone-ether gave white needles, m.p. 99 - 100°, of ethylaminomethyldiphenylphosphonium iodide.
Found: N, 3.6%. $C_{15}H_{19}INP$ requires N, 3.8% .

Chromium tricarbonyl complex of (I).

(I) (1.12g; 1.98 m.mole) in diglyme (50 ml) was heated under reflux with chromium hexacarbonyl (0.44g; 2.0 m.mole) for 4 hours. Removal of the diglyme left an orange solid which was recrystallised from nitromethane to give orange-yellow needles, m.p. 263 - 265°.
Found: C, 63.1; H, 5.0; N, 4.1; P, 12.5%.
$C_{37}H_{35}CrN_2O_3P_3$ requires C, 63.4; H, 5.1; N, 4.0; P, 13.3% .

Molybdenum tricarbonyl complex of (I).

(I) (0.57g; 1.01 m.mole) in acetonitrile (40 ml) was heated under reflux with molybdenum hexacarbonyl (0.27g; 1.02 m.mole) for 2 hours. On cooling, long yellow needles separated out which were recrystallised from nitromethane to give yellow needles, m.p. 260°. (decomp.)
Found: C, 59.8; H, 4.4; N, 3.6; P, 12.2%. $C_{34}H_{35}MoN_2O_3P_3$ requires C, 60.0; H, 4.7; N, 3.8; P, 12.2% .

Tungsten tricarbonyl complex of (I).

(I) (0.57g; 1.01 m.mole) in diglyme (50 ml) was heated under reflux with tungsten hexacarbonyl (0.35g; 1.0 m.mole) for 3 hours. Removal of the diglyme left a yellow solid which was recrystallised

from nitromethane to give yellow needles, m.p. 303 - 305°.
Found: C, 53.5; H, 4.6; N, 3.2; P, 11.1%. $C_{34}H_{35}N_2O_3P_3W$ requires C, 53.4; H, 4.2; N, 3.4; P, 11.2%.

Reaction of (I) with anhydrous nickel(II) chloride.

Nickel(II) chloride hexahydrate (0.97g; 4.0 m.mole) was heated in *vacuo* at 180° for 4 hours, after which (I), (2.3g; 4.2 m.mole) in benzene (80 ml) was introduced. The mixture was heated under reflux for 5 days after which time the precipitated orange material was filtered off and dissolved in chloroform (20 ml) to remove unreacted nickel chloride. Addition of light petroleum (b.p. > 120°) to the chloroform solution and filtration gave a dark red solid which was recrystallised from nitromethane to give red needles, m.p. 259°, of bis(diphenylphosphino)ethylamine nickel(II) chloride.
Found: N, 2.6%. $C_{26}H_{25}Cl_2NNiP_2$ requires N, 2.6%.

Reaction of (I) with nickel(II) chloride without due regard to exclusion of moisture.

Nickel(II) chloride hexahydrate (0.95g; 4.0 m.mole) was heated at 100° in *vacuo* for ½ hour after which time (I), (2.3g; 4.2 m.mole) in benzene (30 ml) was introduced. The mixture was heated under reflux for 17 hours after which the precipitated reddish-orange solid was filtered off, and dissolved in chloroform to remove unreacted nickel chloride. Addition of light petroleum (b.p. > 120°) to the chloroform solution gave a red solid which was recrystallised from dimethylformamide-ether to give small red needles of N-diphenylphosphino-N-ethyl-'N-ethylaminophenylphosphine nickel(II) chloride ($Ph_2PNEt.PPh.NHEt.NiCl_2$). m.p. 259 - 265°.

Found: C, 51.8; H, 5.2; N, 5.4; P, 12.0%. $C_{22}H_{26}Cl_2N_2NiP_2$ requires C, 51.8; H, 5.1; N, 5.5; P, 12.2%.

Bis(N-diphenylphosphino-N-methyl)di(amino)phenylphosphine(I).

Di(methylamino)phenylphosphine (12.8g; 0.076 mole) in n-pentane (100 ml) was added dropwise to diphenylchlorophosphine (33.8g; 0.15 mole) and triethylamine (30 ml) in n-pentane (1000 ml) at 0°. Filtration yielded 53.4g. of white solid which was dried under reduced pressure and extracted with ether (250 ml). Evaporation of the ether solution to dryness gave 27.4g. of white solid which was recrystallised from nitromethane to give long white needles (22.1g; 54%) m.p. 136 - 138°.

Found: C, 71.5; H, 6.0; N, 5.4; P, 17.1%. $C_{32}H_{31}N_2P_3$ requires C, 71.6; H, 5.8; N, 5.2; P, 17.3%.

1, 3-disulphide of (II).

(I) (1.15g; 2.1 m.mole) in benzene (25 ml) was heated under reflux with elemental sulphur (0.13g; 4.1 m.mole) for 1 hour. Removal of the benzene left a white solid which was recrystallised from nitromethane to white plates m.p. 191.5 - 194°.

Found: C, 63.9; H, 5.0; N, 4.8; P, 15.5; S, 10.6%.

$C_{32}H_{31}N_2P_3S_2$ requires C, 64.0; H, 5.2; N, 4.7; P, 15.5; S, 10.7%.

1, 2, 3-trisulphide of (II).

(I) (3.14g; 5.9 m.mole) was refluxed with sulphur (0.97g; 30.3 m.mole) for 17 hours in benzene (30 ml). Removal of the benzene left a white solid which was recrystallised from dimethylformamide to give white needles m.p. 181.5 - 183°.

Found: C, 60.8; H, 4.9; N, 4.3; P, 15.1; S, 15.4%.

$C_{32}H_{31}N_2P_3S_3$ requires C, 60.8; H, 4.9; N, 4.4; P, 14.7; S, 15.2%.

Methyliodide adduct of (II).

(I) (1.07g; 2.0 m.mole) with excess methyl iodide in ether gave a white solid which was recrystallised from ethanol to give white crystals (1.27g; 94%) m.p. ca. 111° (decomp.).

Found: N, 4.0%. $C_{33}H_{34}IN_2P$ requires N, 4.1%.

Chromium tricarbonyl complex of (II).

(II) (1.12g; 2.1 m.mole) in diglyme (50 ml) was heated under reflux with chromium hexacarbonyl (0.46g; 2.1 m.mole) for 24 hours. Removal of the diglyme gave a waxy orange solid which was recrystallised from nitromethane to give yellow needles, m.p. 258 - 260°.

Found: C, 61.5; H, 4.7; N, 4.0; P, 13.0%. $C_{35}H_{31}CrN_2O_3P_3$ requires C, 62.5; H, 4.7; N, 4.2; P, 13.8%.

Molybdenum tricarbonyl complex of (II).

(I) (1.2g; 2.1 m.mole) in acetonitrile (50 ml) was heated under reflux with molybdenum hexacarbonyl (0.51g; 1.9 m.mole) for 1½ hours. Removal of the acetonitrile left an orange-yellow solid which was recrystallised from dimethylformamide to give yellow granular crystals m.p. 265° (decomp.).

Found: C, 58.6; H, 4.5; N, 4.1; P, 12.9%. $C_{35}H_{31}MoN_2O_3P_3$ requires C, 58.7; H, 4.4; N, 3.9; P, 13.0% .

Tungsten tricarbonyl complex of (II).

(I) (1.13g; 2.0 m.mole) in acetonitrile (50 ml) was heated under reflux with tris(acetonitrile)tungsten tricarbonyl (0.78g; 2.0 m.mole) for 1 hour. The precipitated yellow crystals were recrystallised from dimethylformamide to give yellow granular crystals m.p. 296° (decomp.).

Found: C, 52.3; H, 3.7; N, 3.7; P, 11.4%. $C_{35}H_{31}N_2O_3P_3W$ requires C, 52.2; H, 3.9; N, 3.5; P, 11.6% .

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CHAPTER 4.

THE ^1H N.M.R. SPECTRA OF SOME AMINOPHOSPHINES.

INTRODUCTION.

It is well known that the methyl protons in an isopropyl group adjacent to an asymmetric centre will be magnetically nonequivalent as shown by their 'H n.m.r. spectra[1]. Unequal population of the various conformers in such molecules is normally accepted as the cause of nonequivalence[2,3] although Waugh and Cotton[4] have pointed out that when the asymmetry of substitution is sufficiently low, the nonequivalence of the geminal groups or atoms can persist even when the conformers are all accidentally of equal energy or when internal motion is free. Gutowsky[1] has shown that the geminal fluorine nuclei in the molecule $CF_2Br.CFBrCl$ remain nonequivalent over a wide range of temperatures and has attributed this behaviour to the inherent asymmetry of the molecule.

In the event of a change in the magnitude of nonequivalence with temperature, a change in population of the conformers is inferred[3]. Preferred conformations have been attributed to solvent effects,[5,6,7] phenyl substitution[8], hydrogen bonding[9] or to a combination of these factors[10,11]. Slow inversion about nitrogen[12] has also been proposed as a possible explanation for the nonequivalence of the geminal methyl groups attached to nitrogen in the molecule $PhP(Cl)NMe_2$.

Nonequivalence of the methyl protons in the isopropyl groups of the compound di(isopropylamino)phenylphosphine, $PhP(NHPr^i)_2$ has recently been reported[13], and in section 4a, an attempt is made to relate qualitatively the magnitude of nonequivalence in this compound and its derivatives to the structural features of the molecule and to changes in solvent.

Section 4b deals with the ^1H n.m.r. spectra of some methylamino-substituted phosphines which have been interpreted in terms of A_3BX spin systems.

Section 4c deals with aromatic region of phenyl-substituted aminophosphines in general.

4a. MAGNETIC NONEQUIVALENCE IN N-ISOPROPYLAMINO PHOSPHORUS COMPOUNDS.

In deuterochloroform solution at 33°, the isopropyl methyl signals of compounds I - V (Table 1) consist of a doublet by coupling to the methine protons ($J_{H-C-C-H} \sim 6.0 - 6.5$ c/sec.; $J_{P-N-C-C-H}$ and $J_{H-N-C-C-H} \sim 0.5$ c/sec.) which is doubled again due to magnetic nonequivalence. Significant nonequivalence is not observed in the spectra of compounds VI and VII where the phenyl group attached to phosphorus has been replaced by a phenoxy - and a dimethylamino - group respectively; nor is it observed when asymmetry at phosphorus is removed on substitution of one of the isopropylamino - groups by a phenyl group. (Compounds VIII - X).

Nonequivalence of the methyl groups would therefore appear to depend on the presence of an asymmetric phosphorus atom which has a phenyl group directly attached to it. The magnetic nonequivalence of the methyl groups in compound III is strongly temperature dependent (Figs. 1a and 1b.), indicating the presence of an exchange process the rate of which should be measurable on the n.m.r. time scale. This effect is unlikely to be the result of restricted rotation of the isopropyl group relative to the asymmetric centre since Gutowsky has shown that nonequivalence should inherently persist at elevated temperatures in the presence of an asymmetric centre. A more likely explanation is that the relatively high rates of inversion at nitrogen effectively average out chemical

TABLE 1.

Chemical shifts of methyl protons in CDCl of some isopropylamino substituted phosphines.

Compound	τ Values	δ_{CH_3} (c/sec.)
$PhP(NHPr^i)_2$ (I)	8.83, 8.87	2.2
$PhP(NHPr^i)_2O$ (II)	8.89, 8.92	2.3
$PhP(NHPr^i)_2S$ (III)	8.89, 8.90	1.5
$PhP(NHPr^i)_2Se$ (IV)	8.83, 8.91	3.2
$PhP(NHPr^i)_2MeI$ (V)	8.58, 8.68	6.1
$Ph\underset{\overset{\|}{O}}{C}P(NHPr^i)_2$ (VI)	8.86	0.5
$Me_2N\underset{\overset{\|}{O}}{P}(NHPr^i)_2$ (VII)	8.85	*ca.* 0.8
$Ph_2P(NHPr^i)$ (VIII)	8.89	0.5
$Ph_2P(S)NHPr^i$ (IX)	8.85	0.5
Ph_2PNHPr^iMeI (X)	8.66	0.5

δ_{CH_3} refers to chemical shift difference between methyl proton signals.

shift differences. In turn, nitrogen inversion rates appear to be influenced by proton exchange at that centre. Thus, the NH-signal of III at 33° (Fig. 1a) is an exchange-broadened, spin-coupled triplet at τ 7.75 where $J_{P-N-H} \sim J_{H-N-C-H} \sim 9$ c/sec., whereas at -60°, it is quite a sharp triplet.(Fig. 1b).

A correlation between proton exchange rates and the magnitude of nonequivalence is shown in a study of the effect of solvent on this parameter (Tables 2a - 2e). Introduction of small quantities of dry hydrogen chloride into deuterochloroform solutions of III and IV resulted in the removal of nonequivalence. At the same time, the NH - signal moves downfield and coalesces to a sharp singlet resonance (see Fig. 1c). The methine proton signal also sharpens up in each case and may be recognised as two overlapping septets ($J_{P-N-C-H}$ = 11.0 c/sec. for III and 11.2 c/sec. for IV). It is worth mentioning here that at higher concentrations of hydrogen chloride (saturated solution) some P-N bond cleavage occurred with formation of isopropylamine hydrochloride. This observation suggests that protonation does in fact occur at nitrogen.

Proton exchange rates such as those prevailing when small concentrations of acid are present are likely to be accompanied by a relatively high rate of nitrogen inversion cf. the analogous behaviour of dibenzylmethylamine in aqueous acid solution[14]. Hence, in the presence of dry hydrogen chloride, deuterochloroform

/solutions

Fig. 1a. III at 33°

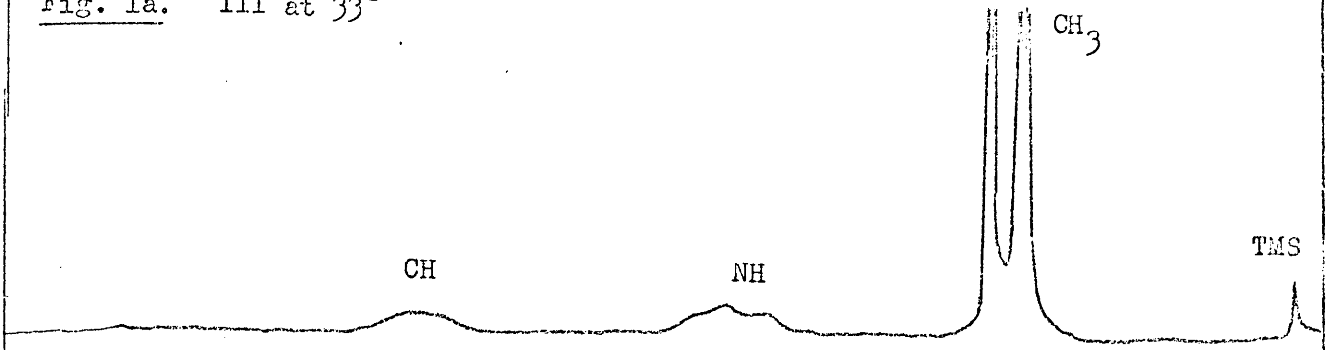


Fig. 1b. III at -60°

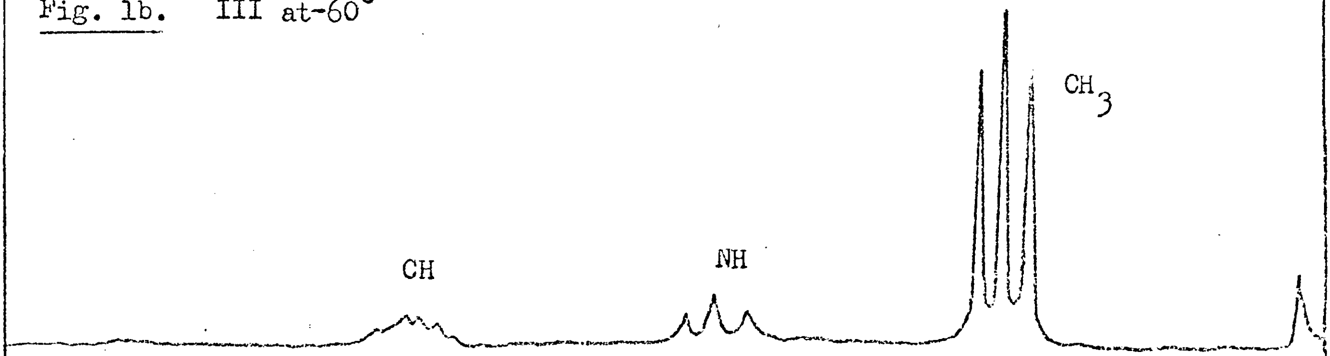


Fig. 1c. III in $CDCl_3$/HCl

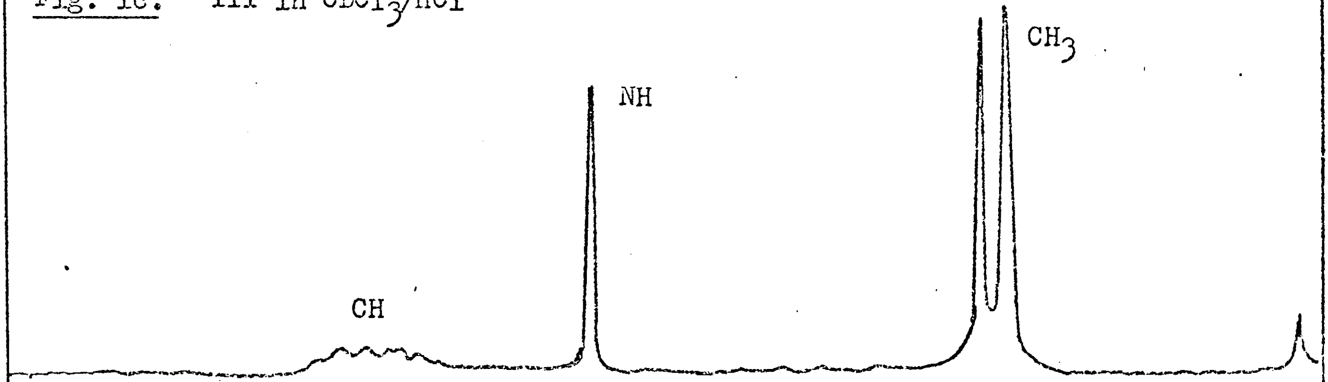
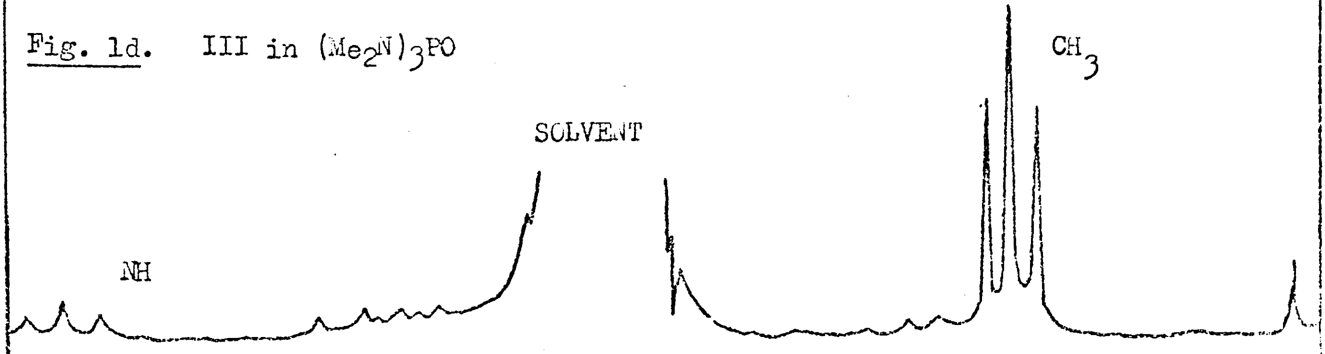


Fig. 1d. III in $(Me_2N)_3PO$



H_o →

TABLE 2.

(a) $PhP(O)(NHP_r^i)_2$(II).

Solvent	δCH_3	τ NH
deuterochloroform	2.3	7.56
deuterochloroform/HCl	1.4	7.37
benzene	3.0	
pyridine	3.9	5.50
hexamethylphosphoramide	8.1	5.51

(b) $PhP(S)(NHP_r^i)_2$ (III).

Solvent	δCH_3	τ NH
deuterochloroform	1.5	7.75
deuterochloroform/HCl		
benzene		8.05
pyridine		5.40
hexamethylphosphoramide	6.6	5.29

(c) $PhP(Se)(NHP_r^i)_2$(IV).

Solvent	δCH_3	τ NH
deuterochloroform	3.2	7.66
deuterochloroform/HCl		5.81
benzene		7.89
pyridine		5.29
hexamethylphosphoramide	6.2	5.23

TABLE 2 (continued).

(d) $PhP(NHPr^i)_2MeI$.(V).

Solvent	δ CH_3	τ NH
deuterochloroform	6.1	4.44
deuterochloroform/HCl	5.4	4.61
benzene	— insoluble —	
pyridine	4.2	—
hexamethylphosphoramide	6.1	—

(e) $PhP(NHPr^i)_2$.(I).

Solvent	δ CH_3	τ NH
deuterochloroform	2.2	8.02
deuterochloroform/HCl	2.6	<u>ca</u>. 6
benzene	3.2	8.25
pyridine	2.4	7.33
hexamethylphosphoramide	2.5	<u>ca</u>.6.65

solutions of III and IV may not exhibit nonequivalence as a result of the increased rate of inversion at nitrogen effectively averaging out the asymmetry effect at phosphorus.

The above arguments have been applied solely to the behaviour of compounds III and IV. Addition of hydrogen chloride to deuterochloroform solutions of I, II and V does not result in disappearance of nonequivalence. It is reasonable to assume that the nitrogen atoms in the methyl iodide adduct (V) are virtually non-basic as a direct consequence of being adjacent to a quaternised phosphorus atom. The failure of added hydrogen chloride to remove nonequivalence by protonation at nitrogen can thus be explained on this basis.

The behaviour of compounds I and II is less readily explained. In the case of the oxide(II), nonequivalence persists not only on addition of dry hydrogen chloride but also at temperatures up to 60° in methylene chloride solution. It has been estimated that nonequivalence disappears around 60° in the case of the sulphide. Although this particular temperature range is rather limited, it is still difficult to understand why the oxide(III) and the sulphide(III) should differ to such an extent.

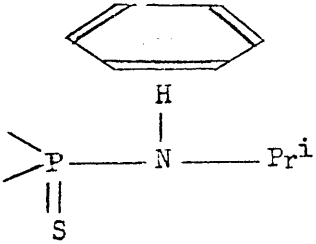
If the rate of inversion at nitrogen is considered to be the main factor in determining the magnitude of nonequivalence, it would appear that the rate of inversion in the case of the oxide is less readily affected.

/There

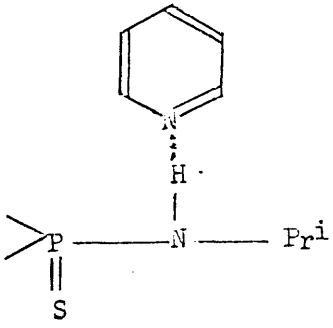
There is some evidence from infra-red studies to suggest that the compound $PhP(O)(NHPr^i)_2$[13] is intramolecularly hydrogen bonded in dilute solution and Nyquist[15] has proposed that the existence of two bands in the NH- region (dilute solution) of the infra-red spectrum of compounds of the type $(RO)_2P(O)NHR$ may be due to cis- and trans-configurations of the NH- group with respect to the phosphoryl group.

The existence of strongly intramolecularly hydrogen bonded species can be used somewhat speculatively to explain certain distinctions between the oxide and the sulphide. There is in fact evidence that phosphine sulphides of the type $(RO)_2P(S)NHR$ are also intramolecularly hydrogen bonded[15]. However, in view of the greater electronegativity of oxygen relative to sulphur, such effects are considered to be less important in solutions of the sulphides.

From Table 2b it can be seen that the methyl proton signal of III is simply a doublet ($J_{H-C-C-H} \sim 6.3$ c/sec.) in benzene or pyridine solution. The large shift to higher field in benzene and the shift to lower field in pyridine of the NH-signal (Table 2b) suggests that the amino-proton is solvated in each case[16,17,18] ie.



and



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This specific solvation by aromatic molecules is considered to average out the anisotropic shielding effect of the phenyl group attached to phosphorus. In pyridine, however, the NH- signal of the oxide does not move downfield to such a great extent suggesting that solvation is not so efficient. The retention of intramolecularly hydrogen bonded species in this case is considered to hinder the solvation of the NH protons with the result that the shielding effect of the phenyl group attached to phosphorus is not effectively averaged out. The same argument may be applied to benzene solutions of the oxide. The chemical shift of the NH protons could not be determined in this case due to the fact that the oxide is fairly insoluble in benzene.

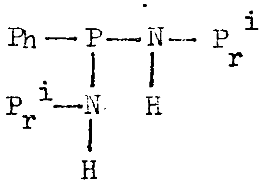
In the hydrogen bonding, non-aromatic solvent, hexamethylphosphoramide, the magnitude of the nonequivalence of the methyl protons of compounds II, III and IV is considerably increased. In this basic solvent, it is reasonable to assume that conditions of slow or no proton exchange occur due to strong intermolecular association. Thus the NH signals are fairly sharp triplets at ca. τ 5.4 (cf.Fig. 1d).

The converse effects of solvation by aromatic molecules have already been discussed in the case of the sulphide III, and the same ideas may be extended to the selenide (IV).

The magnitude of the nonequivalence of the methyl protons in compound (I) is virtually unaffected by change of solvent. It is quite possible that, once again, intramolecularly hydrogen bonded

/species

species of the type



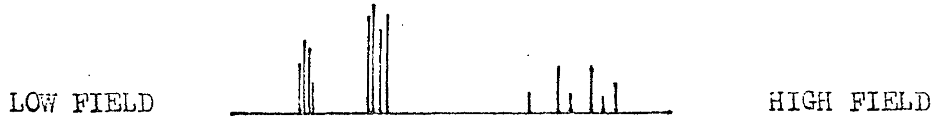
$$Ph-P(NHPr^i)-NH-Pr^i$$

are effective in preventing extensive solvation of the NH protons by all the solvents so far discussed. Four-membered rings containing phosphorus(III) and nitrogen are fairly well known in aminophosphine chemistry. Their ready formation is made possible by the relatively small angle at phosphorus in phosphorus(III) compounds.

4b. ^{1}H n.m.r. SPECTRA OF SOME METHYLAMINO-SUBSTITUTED AMINOPHOSPHINES.

The pure liquid ^{1}H n.m.r. spectra of the compounds $PhP(NHMe)_2$(XI), Ph_2PNHMe(XII) and PhP(Me)NHMe(XIII)(Figs.2a - 2d) have been interpreted in terms of A_3B spin systems which are doubled by coupling of the methyl and amino-protons (A_3B system) with phosphorus (X).[19]

The characteristics of A_3B spin systems are fairly well known[20] and it can be shown that as $\nu_0\delta_{AB}$ decreases relative to J_{AB}, the number of spectral lines may increase to a maximum of 16 in the extreme case. Theoretical spectra have been worked out for a large number of $\frac{\nu_0\delta_{AB}}{J_{AB}}$ values and when $\frac{\nu_0\delta_{AB}}{J_{AB}}$ is in the order of 40 the spectrum has the following appearance:



In practice, this is seen as a broadening of the signals viz.

In view of the fact that the spin systems in compounds XI - XIII are on the borderline between A_3BX and A_3MX spin systems (except a neat sample of XI at 60 Mc/sec.), it is possible to determine coupling constants fairly accurately by inspection. Spectral data and coupling constants are given in Table 3. The N-methyl proton signal in each case consists of a doublet by coupling with the amino-protons ($J_{P-N-C-H}$ = 5.5 c/sec.) which is doubled again by coupling with

/phosphorus

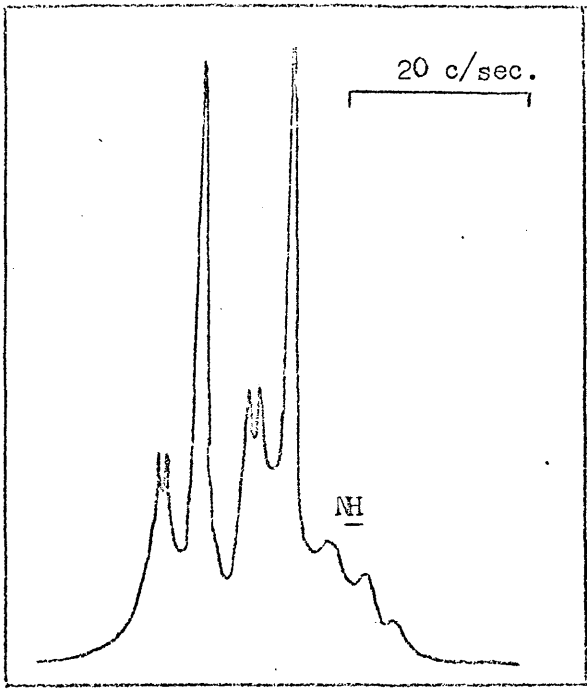


Fig.2a. PhP(NHMe)$_2$ (60Mc/sec.)

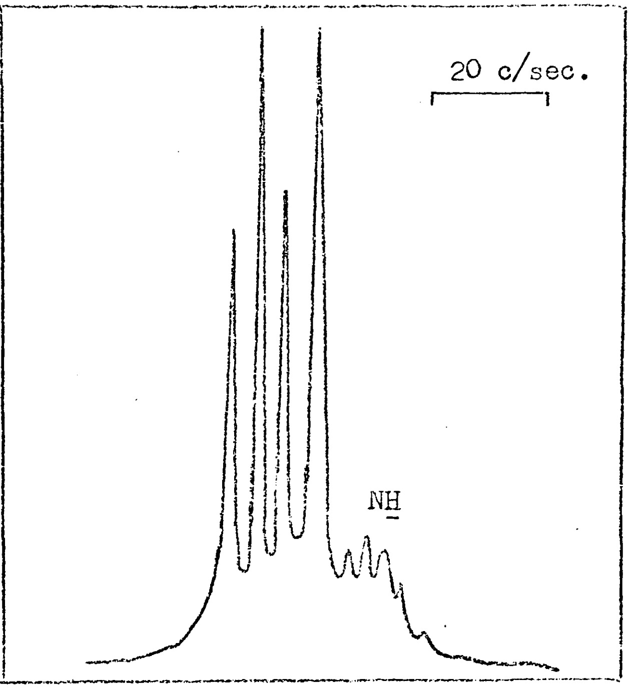


Fig.2b. PhP(NHMe)$_2$ (100Mc/sec.)

H_o →

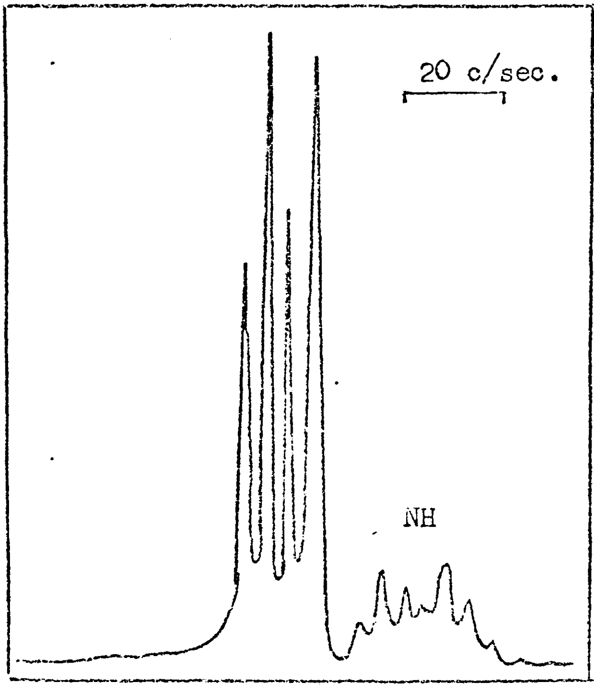


Fig. 2c. Ph_2PNHMe (60Mc/sec.)

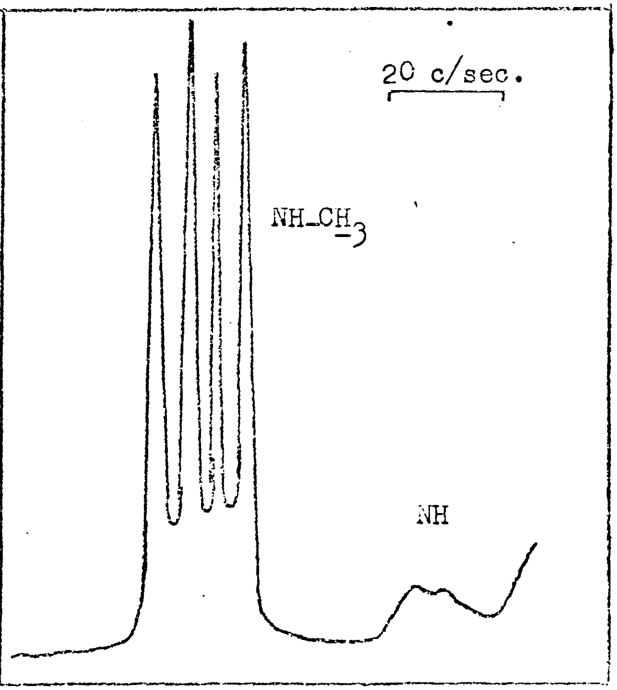


Fig. 2d. PhP(Me)NHMe (100Mc/sec.)

TABLE 3.

Compound	τ values			Coupling constants (c/sec.			
	τ NCH_3	τ PCH_3	τ NH	J_{PNCH}	J_{PCH}	J_{PNH}	J_{HNCH}
$PhP(NHMe)_2$	7.58	—	*ca.* 7.8	10.0	—	*ca.* 13.0	5.5
Ph_2PNHMe	7.62	—	8.18	10.5	—	—	5.6
PhP(Me)NHMe	7.67	8.67	*ca.* 8.4	9.2	5.3	—	5.4

TABLE 4.

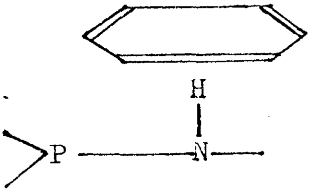
Solvent	Proton Chemical Shifts		τ NH — τ CH_3
	τ NH	τ CH_3	
cyclohexane	7.98	7.54	0.44
benzene	no reference taken		0.73
pyridine	6.97	7.44	-0.47
neat sample	7.30	7.58	0.22

phosphorus ($J_{P-N-C-H}$ = 11 c/sec.)

The NH-proton signal is a broadened multiplet in each case, broadening being attributed to proton exchange and to ^{14}N quadrupolar coupling[21]. In the spectrum of XI at 60 and 100 Mc/sec. it overlaps to some extent with the methyl proton signal. By varying the solvent (Table 4) it is possible to increase δ_{AB} sufficiently to allow measurements to be made on a first order basis. In benzene solution at a field strength of 100 Mc/sec. the NH signal of (XI) can be recognised as a pair of overlapping quartets (J_{P-N-H} = 13 c/sec; $J_{H-N-C-H}$ 5.5 c/sec.)

The large chemical shift difference in benzene as solvent has permitted use of the double resonance technique and the methyl proton signal of XI with the NH protons spin-decoupled is shown in Fig. 3. The doublet separation of 10.0 c/sec. confirms the assignments made in Table 3 to $J_{P-N-C-H}$.

The shift to higher field of the NH proton signal suggests that there is a specific solute-solvent interaction in which the NH-protons are shielded by complexing with benzene[18] i.e.



In the basic solvent pyridine, a characteristic shift of the NH-proton signal to lower field is observed. At the same time the methyl-proton signal shows a reversal in the high field - low field doublet intensity ratios. (AB_3X spectrum).

/The

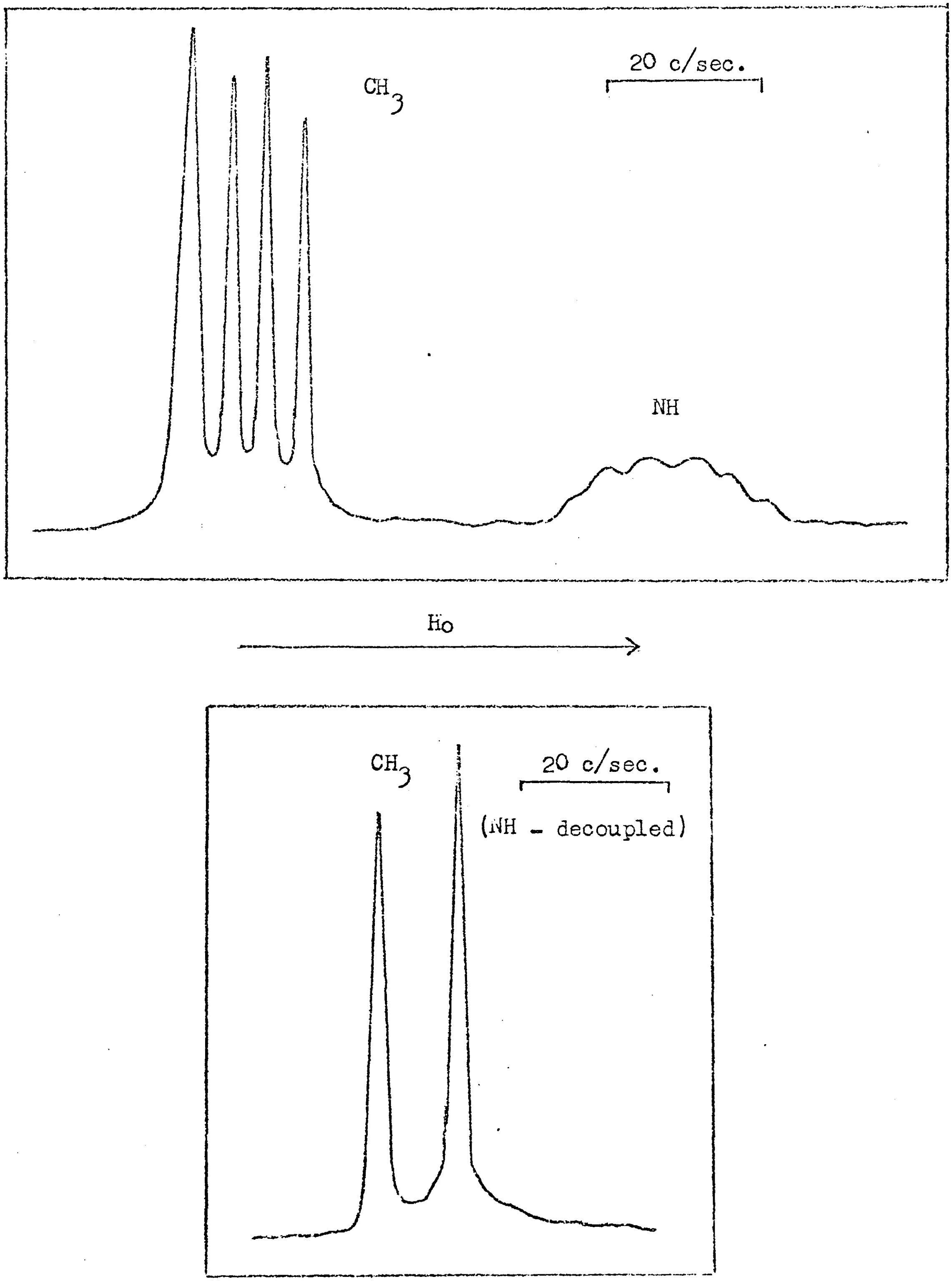


Fig. 3. METHYL-PROTON RESONANCE SIGNAL OF XI (100Mc/sec.)

The pure liquid spectrum of XI at 60 Mc/sec. is fairly far removed from that expected for a first order spectrum ($\frac{\nu_0 \delta_{AB}}{J_{AB}} \sim 2$) and it is not possible in this case to determine accurate values of coupling constants by inspection.

The magnitude of $J_{P-N-C-H}$ in these compounds is comparable with existing data for P(III)-N and P(V)-N compounds. It is interesting to note that in the spectrum of compound XIII $J_{P-N-C-H}$ has almost double the value of J_{P-C-H}. The magnitudes of these coupling constants are very similar to those observed for dimethylaminodimethylphosphine, Me_2NPMe_2,[22] ($J_{P-N-C-H}$ = 9.8 c/sec.; J_{P-C-H} = 5.6 c/sec.) Cowley[23] has suggested that the relatively high value of $J_{P-N-C-H}$ may be due to conjugative or electronegativity effects. However, the observation that J_{P-C-H} is smaller than $J_{P-C-C-H}$ in some ethyl substituted phosphines[24] where such effects are relatively unimportant suggests that the above interpretations may not be valid.

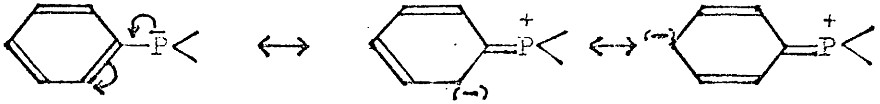
AROMATIC PROTON SIGNALS OF SOME AMINOPHOSPHINES.

The aromatic proton signals in the ^1H n.m.r. spectra of phenyl-substituted aminophosphines are generally rather complex and no attempt is made here to discuss them in any great detail. In the free aminophosphines (phosphorus(III) compounds) the aromatic proton signal is usually (not always) a fairly sharp signal in the region τ2.4 - 2.6. On oxidation or quaternisation, two distinct sets of chemically shifted multiplets are observed. Data obtained from a

/variety

variety of phosphorus(III) and phosphorus(V) compounds (Table 5) show that the high field - low field multiplet intensity ratio is always approximately 3:2 and that the chemical shift difference increases in the order phosphine < phosphine oxide < phosphine sulphide ~ selenide ~ methiodide.

A 3:2 ratio immediately suggests that there is some distinction between the *ortho* and *para*, and *meta* protons, the *meta* protons being deshielded relative to the *ortho* and *para*. Such a distinction obviously cannot be explained for all cases in terms of conjugation involving the phosphorus lone pair and the aromatic ring. i.e.



etc.

A more likely explanation is that only the *ortho* protons are deshielded by a process of induction rather than conjugation. It has in fact been established[25,26] that the phosphoryl group is a moderately strong electron acceptor substituent, and that the deshielding effect on an *ortho* proton may be *qualitatively* related[27,28] to inductive and resonance effects of the substituent.

From Table 5 it would appear that the thiophosphoryl group is a better electron acceptor than the phosphoryl group which suggests that the strong electron withdrawing effect of oxygen is in some way compensated by back bonding to phosphorus [$(p \rightarrow d)\pi$ interaction].

It is of some interest that a significant chemical shift difference is observed for the phosphorus(III) compounds I, XI

TABLE 5.

Aromatic proton chemical shifts of some aminophosphines.

Compound		τ values (approx.) *		$\delta\tau$
$PhP(NHMe)_2$	XI	2.89	3.22	0.33
$PhP(NHPr^i)_2$	I	2.45	2.83	0.38
$PhP(O)(NHPr^i)_2$	II	2.15	2.55	0.40
$PhP(S)(NHPr^i)_2$	III	1.92	2.53	0.61
$PhP(NHEt)_2$	XIV	2.51	2.82	0.31
$PhP(O)(NHEt)_2$	XV	2.14	2.54	0.40
$PhP(S)(NHEt)_2$	XVI	2.00	2.53	0.53
Ph_2PNHMe	XII	2.65	2.88	0.23
Ph_2PNHPr^i	VIII	2.65	2.72	0.07
$(Ph_2P)_2NMe$	XVII	2.65		—
$[Ph_2P(O)]_2NMe$	XVIII	2.20	2.66	0.46
$[Ph_2P(S)]_2NMe$	XIX	1.99	2.72	0.73
$(Ph_2P)_2NEt$	XX	2.65		—
$(Ph_2P)_2NPr^i$	XXI	2.69		—

* taken as mid point of each multiplet.

XIV in which the phosphorus atom is flanked by two nitrogen atoms. For the mono-aminophosphines, XII and VIII and the diphosphinoamine XVII the chemical shift difference is relatively small or zero. One possible explanation is that the presence of two highly electronegative nitrogen atoms in the former compounds has the effect of placing a greater effective positive charge on phosphorus than would a single nitrogen atom in the latter compounds.

EXPERIMENTAL

The compounds of general formula $PhP(X)(NHP_r{}^i)_2$ where X = nothing, O, S, and MeI were prepared by the methods described by Payne and co-workers.[13] Compounds VI and VII were prepared by the reaction of excess isopropylamine with $PhOP(O)Cl_2$ and $Me_2NP(O)Cl_2$ respectively, in benzene as solvent. After filtration and evaporation of solvent, the products were purified by distillation in vacuo. Purity was checked by integration of the respective 'H n.m.r. spectra.

Di(isopropylamino)phenylphosphine selenide (IV).

Di(isopropylamino)phenylphosphine (2.3g; 1.0 m.mole) was heated under reflux for 10 mins. with selenium (0.08g; 1.0 m.mole) in benzene (20 ml). Removal of the benzene left a grey, waxy solid which was recrystallised from n-hexane to give white plates m.p. 45°.

(Found: N, 9.1%. $C_{12}H_{21}N_2PSe$ requires N, 9.2%).

Isopropylaminodiphenylphosphine VIII.

Diphenylchlorophosphine (22.1g; 0.1 mole) was added dropwise to isopropylamine (excess) in n-pentane (200 ml). Filtration and evaporation of solvent left a discoloured white solid which was distilled in vacuo to give a clear liquid (b.p. 97 - 98°/10^{-3}mm.) which solidified on cooling to a crystalline white solid (m.p. ca.30°).

(Found: N, 5.8%. $C_{15}H_{18}NP$ requires N, 5.8%).

Isopropylaminodiphenylphosphine sulphide (IX).

VIII, (0.76g; 3 m.mole) was shaken with elemental sulphur (0.1g; 3 m.mole) in benzene (15 ml). for 5 mins. Evaporation of the solvent left a white crystalline solid which was recrystallised from n-hexane to give white plates, m.p. 75-76°.
(Found: N, 4.9%. $C_{15}H_{18}NPS$ requires N, 5.1%).

Isopropylaminodiphenylphosphine methiodide (X).

VIII, (2.51g; 1.03 m.mole) was shaken with methyl iodide (1.46g; 1.03 m.mole) in ether (30 ml.) Addition of acetone to the resultant solution and cooling yielded lustrous white plates m.p. 119 - 121°.

(Found: N, 3.6%. $C_{16}H_{21}INP$ requires N, 3.6%).

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CHAPTER 5.

THE MASS SPECTRA OF PHOSPHOBENZENE AND OF SOME METHYLAMINO SUBSTITUTED PHOSPHINES.

INTRODUCTION

To date, few publications on the mass spectra of organophosphorus compounds have appeared in the literature. The most detailed investigations have been concerned mainly with the spectra of the esters of phosphorus and phosphoric acids[1] and alkyl substituted phosphines.[2] The following brief account of a variety of phenyl substituted phosphines and aminophosphines is by no means a full treatment of the subject, but it is hoped that it will serve to illustrate the main features of the spectra obtained and as such be of use in future as an aid to structural determination of more complex systems. Furthermore, in view of the current interest in the mass spectra of transition metal carbonyl complexes, it is essential that the cracking patterns of the free ligands are established.

This study is divided into three sections, the first dealing with phosphobenzene (form A) and showing the use of mass spectroscopy in the analysis of this 'compound'. The mass spectrum of phosphobenzene is then dealt with in greater detail together with a number of phosphines which show the same rearrangement process - namely phenyl migrations from one phosphorus atom to another. Finally, the cracking patterns of a variety of aminophosphines

/containing

containing the P-NMe group will be discussed in the light of hydrogen migrations to phosphorus.

A complete mass spectral investigation would, of course, involve the unambiguous assignment of fragment ions by the technique of mass measurement and it must be emphasised that assignments are made here only on the basis of the most probable structures.

EXPERIMENTAL

All spectra were obtained on the A.E.I. MS-9 mass spectrometer with a nominal ionising electron voltage of 70 e.v. and a heated inlet system temperature of 200-250°. Compounds studied were prepared by the methods described in the literature with the exception of XII which was synthesised by the reaction of methylphenylchlorophosphine with excess methylamine. It is a colourless liquid (b.p. 32-35° at 10^{-2} mm.). The preparation of XIII is described elsewhere in this thesis.[3] Phosphobenzene was isolated as a by-product in the distillation of di(ethylamino)phenylphosphine and purification was achieved by crystallisation from acetonitrile. Triphenylphosphine (II) and ethylenebis(diphenyl)phosphine (VI) were obtained commercially.

The partial mass spectra of the compounds studied are given in Figs. 1-13 and the partial cracking patterns with possible assignments in Tables 1-3.

PHOSPHOBENZENE

Phosphobenzene, $(PhP)_n$, was first isolated about one hundred years ago by Kohler and Michaelis[4] who assigned it the formula PhP=PPh by analogy with azobenzene. Since then there has been considerable controversy as to the exact nature of the system of which there are at least four main forms falling into different melting point ranges. Cowley,[5] in a recent review, has detailed the chemical and physical properties of the phosphobenzene system in general, but this discussion will be limited to form A (m.p. 149-156°) which, although the most widely studied, is still the subject of some controversy.

Cryoscopic molecular weight determinations in benzene have always suggested phosphobenzene to be tetrameric $(PhP)_4$, while a variety of reactions carried out under different conditions led to products containing, five, four and three-membered rings. For example,[6] reaction of form A with chromium, molybdenum and tungsten hexacarbonyls in an evacuated sealed tube at 140-150° gave the products $(PhP)_4Cr(CO)_4$, $(PhP)_4Mo(CO)_4$ and $(PhP)_4W(CO)_4$ respectively. With inclusion of solvent,[7] usually benzene, the complexes contained the phosphine as a pentamer. In the absence of solvent, form A reacts with nickel carbonyl in <u>vacuo</u> at 0° to give $(PhP)_5Ni(CO)_3$[8] while in benzene at 15° the product was identified as $(PhP)_4Ni(CO)_3$.[7]

/Furthermore

Furthermore, reaction of form A with boron trifluoride[9] at 0° in benzene solution resulted in formation of a compound with the empirical formula $(PhP)_3BF_3$.

It can be deduced from the above observations that

(a) reaction conditions are very critical, and

(b) some process of ring size interconversion is taking place.

Ring size interconversion was first observed by Burg and Mahler[10] in the $(CF_3)P)_n$ system. They found that trimethylamine or trimethylphosphine speeded up the conversion $(CF_3P)_4 \longrightarrow (CF_3P)_5$ and isolated the intermediate $Me_3P{=}PCF_3$. When $(PhP)_n$ is recrystallised from donor solvents such as acetonitrile[11] or tetrahydrofuran[12] the crystalline solid obtained is found to be pentameric and an X-ray analysis[13] of the material from acetonitrile (m.p.150°) showed it to have an almost planar ring structure.

Ang and West[7] have suggested that ring expansion in the reaction of $(PhP)_4$ with certain transition metal carbonyls may take place via intermediates of the type $PhP{:}M(CO)_n$. However, ring expansion has been observed[7] simply by heating form A in benzene and the production of phenylphosphinidine radicals on heating the solid material was postulated[14] on the basis of trapping experiments with diethyl disulphide:

$$(PhP)_n \xrightarrow{\qquad} PhP{:} \xrightarrow{(Et.S)_2} PhP(SEt)_2$$

/Ring

Ring contraction has been observed by Baudler and co-workers who recorded that the molecular weight of form A (m.p. 150° on crystallisation from tetrahydrofuran) fell over a period of three weeks from around 540 to 320 even when the solid material was stored under nitrogen at -18° (M.W. determinations were carried out cryoscopically in benzene). A mass spectrum of the material with the approximate molecular weight of the tetramer showed the parent ion to be $(PhP)_5^+$. Peaks were also observed corresponding to $(PhP)_4^+$ and $(PhP)_3^+$. That $(PhP)_3^+$ was indeed present in the sample and had not been formed by thermal dissociation of the pentamer in the mass spectrometer was shown by increasing the temperature of the inlet system whereby the peak corresponding to $(PhP)_5^+$ increased relative to $(PhP)_3^+$.

In view of the fact that $(PhP)_4 \longrightarrow (PhP)_5$ ring expansion may take place in the heated inlet system of the mass spectrometer, it cannot be stated with any great certainty that $(PhP)_5$ was a constituent of the original sample. However, by employing comparable inlet system temperatures (200°), both Henderson[15] and Ang[16] recorded $(PhP)_4^+$ as the parent ion in the mass spectrum of samples with a molecular weight in benzene corresponding to the tetramer. This would tend to rule out the possibility of ring expansion in the mass spectrometer.

The mass spectrum of a sample of phosphobenzene (m.p. 147-153° on recrystallisation from acetonitrile; M.W. (cryoscopic in benzene)

/450)

450) run on the A.E.I. MS-9 instrument (heated inlet temperature 200-250°) confirmed the existence of $(PhP)_5^+$ as the parent ion (relative abundance 16.2%). $(PhP)_3^+$ (34.8%) and $(PhP)_2^+$ (8.4%) were also observed. $(PhP)_4^+$, however, was present only to the extent of 2.3%. This result was not expected since the material appeared to be the tetramer on the basis of cryoscopic molecular weight determinations in benzene. (Henderson noted that the abundance of $(PhP)_4^+$ was only 0.4%.

/CONCLUSIONS

CONCLUSIONS

In view of the fact that both Henderson and Ang recorded the mass spectrum of material which had not been recrystallised from donor solvents, it would appear that $(PhP)_5$ is not a constituent of such a sample. This is obtained only by crystallisation from donor solvents such as acetonitrile or tetrahydrofuran or under certain reaction conditions. It would appear that mass spectroscopy can be used to detect the presence of $(PhP)_5$ since this does not seem to be formed by ring expansion in the inlet system.

Furthermore, $(PhP)_n$ appears to exist as pure $(PhP)_5$ only when it is freshly recrystallised from donor solvents. It subsequently undergoes some process of ring contraction to give possibly $(PhP)_4$ and almost certainly $(PhP)_3$. This would account for the fact that all samples of phosphobenzene (form A) appear to be tetrameric in benzene, the molecular weight obtained being an average value for all the species present.

It remains to clarify the processes by which ring expansion and contraction take place.

MASS SPECTRUM OF PHOSPHOBENZENE

The mass spectrum of phosphobenzene is worth further discussion in view of the variety of phenyl migrations which are observed to take place. Such migrations have been observed in the mass spectral cracking patterns of a number of aryl systems e.g.

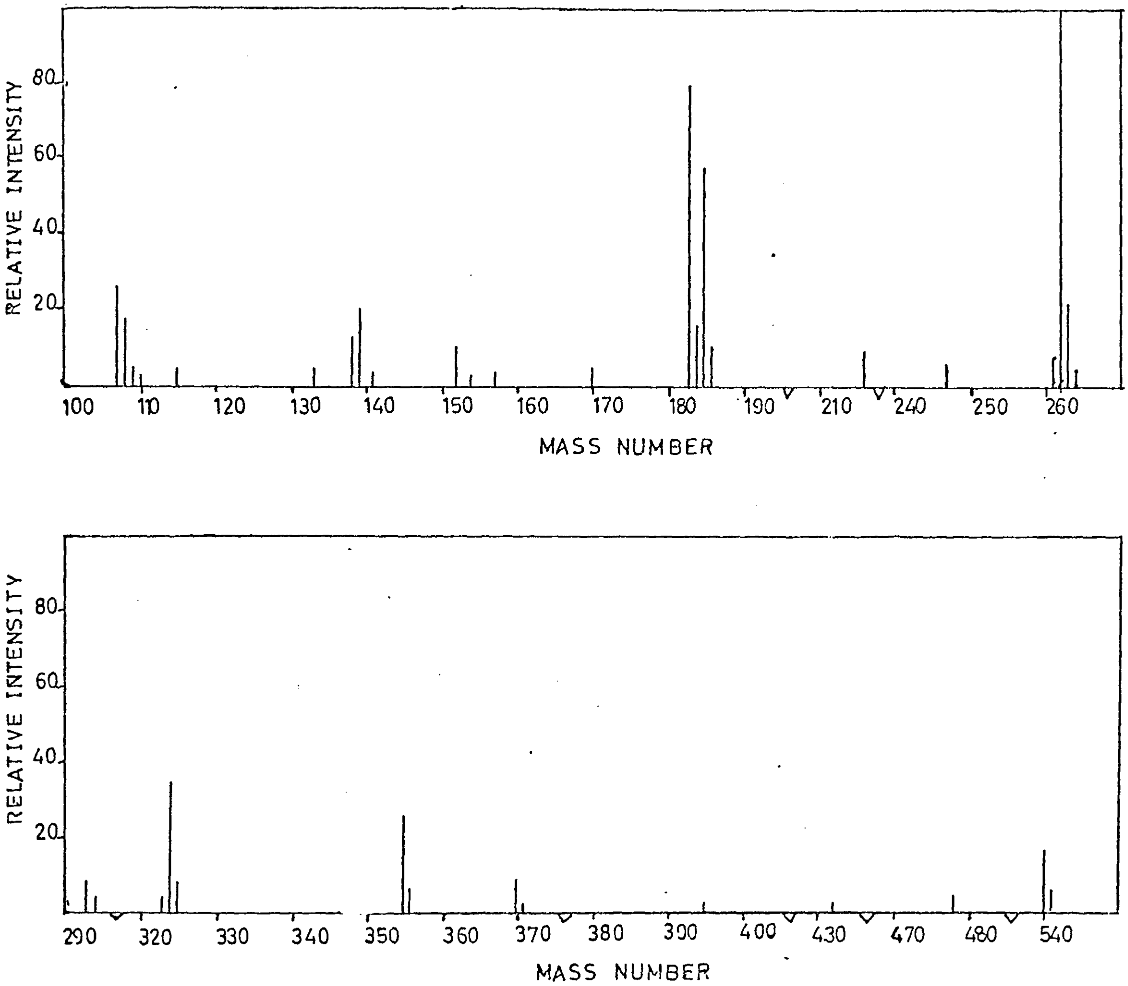


Fig.1 Mass spectrum of Phosphobenzene

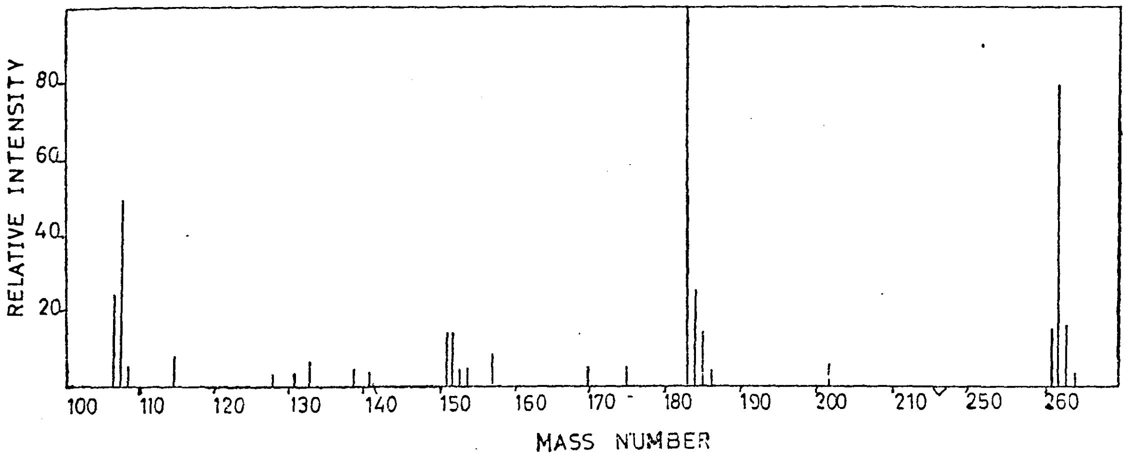


Fig.2 Mass spectrum of Triphenylphosphine

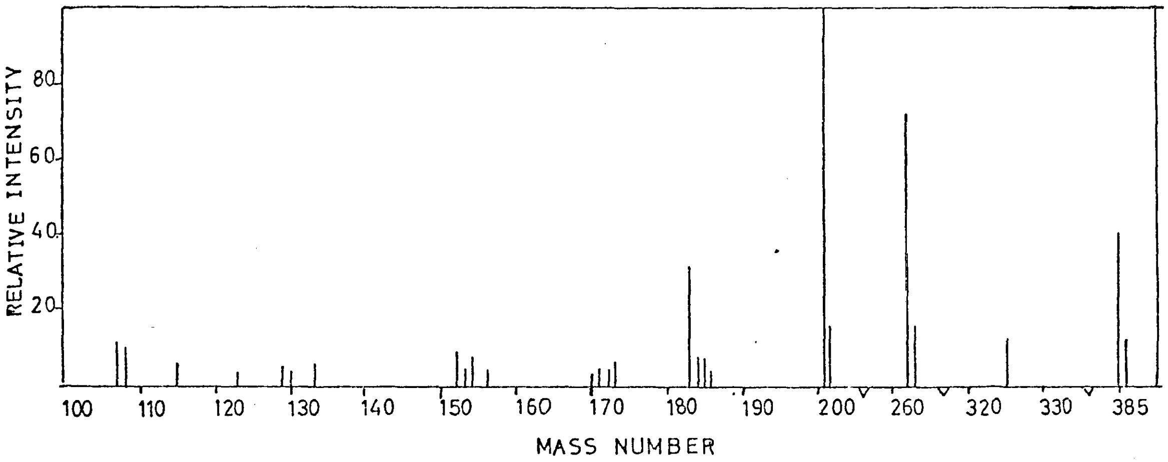


Fig.3 Mass spectrum of Tetraphenyldiphosphine monoxide

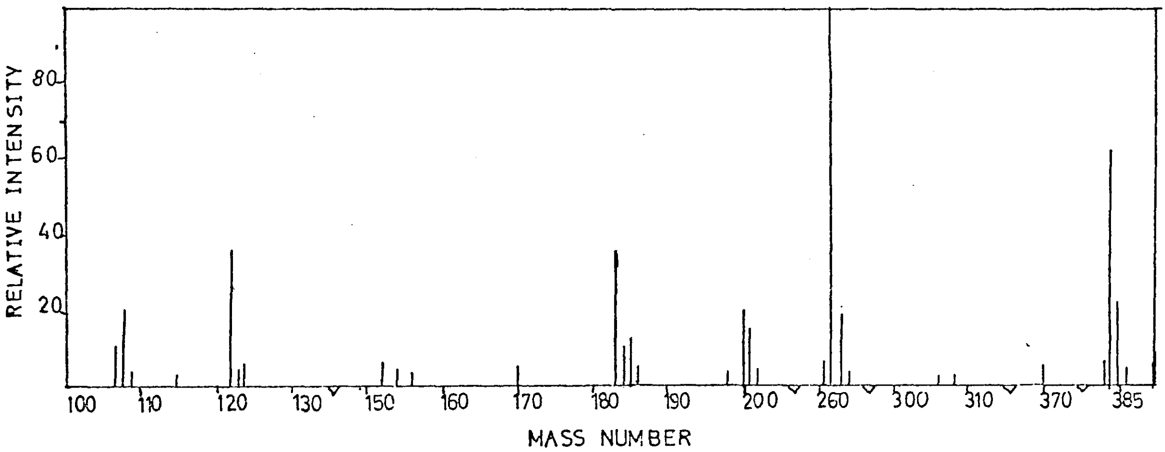


Fig.4 Mass spectrum of bis(Diphenylphosphino)amine

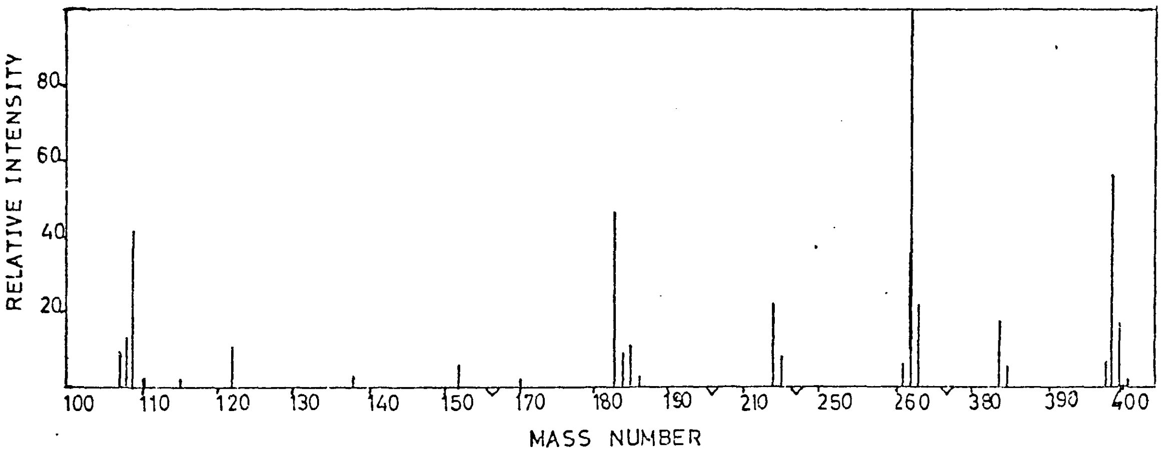


Fig.5 Mass spectrum of bis(Diphenylphosphino)methylamine

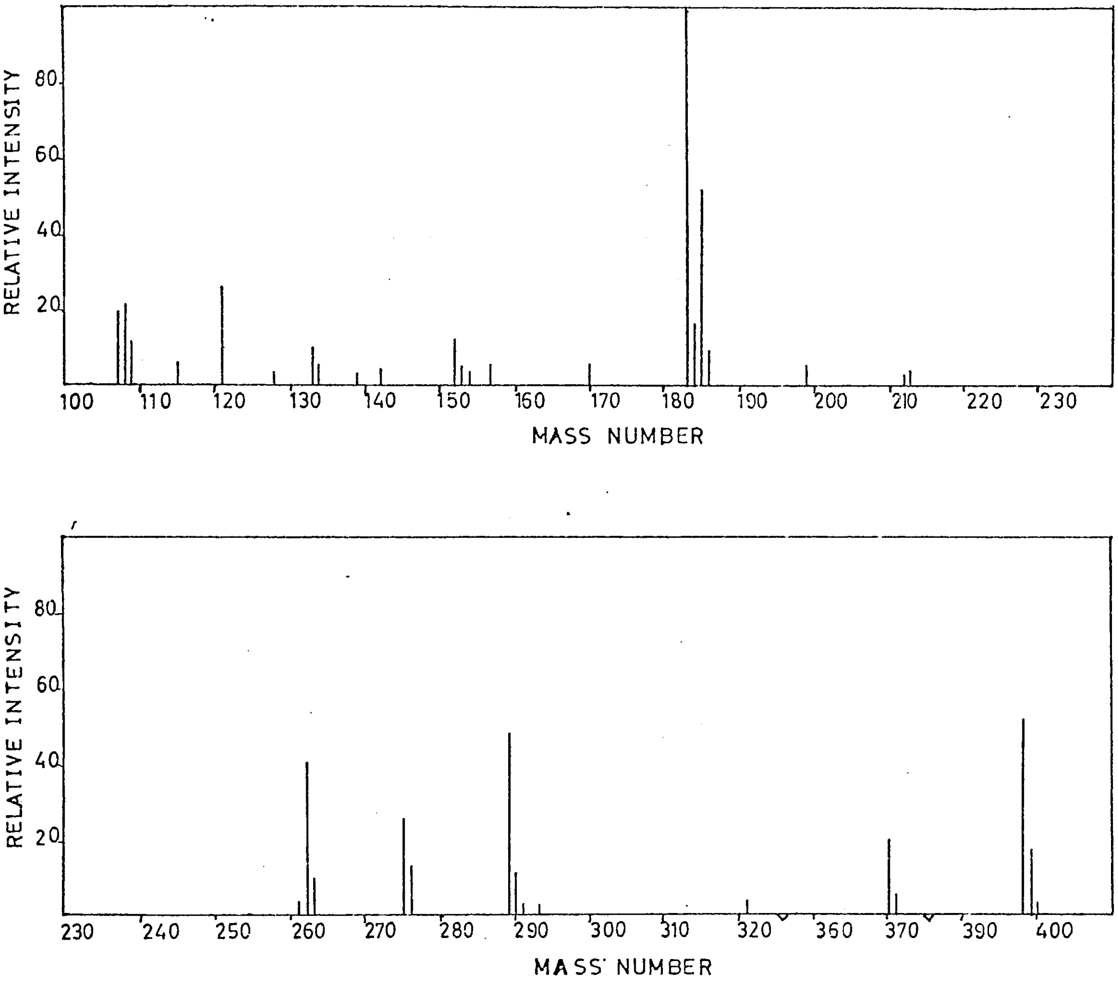


Fig.6 Mass spectrum of Ethylenebis(diphenylphosphine)

TABLE 1.

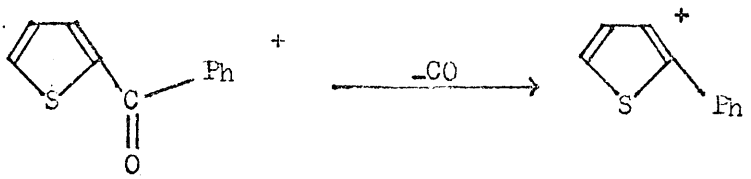
PARTIAL CRACKING PATTERN OF PHOSPHOBENZENE.

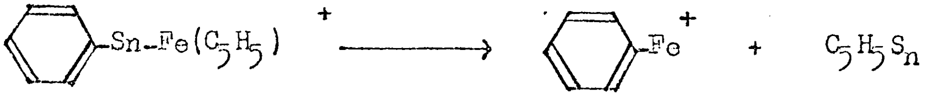
$$\begin{tikzcd}
 & \begin{matrix}\mathrm{Ph_3P_4}^{+}\\ (m/e\ 355)\end{matrix} \arrow[r, "-\mathrm{P_2}"] & \begin{matrix}\mathrm{Ph_3P_2}^{+}\\ (m/e\ 293)\end{matrix} \\
\begin{matrix}(\mathrm{PhP})_5^{+\bullet}\\ (m/e\ 540)\end{matrix} \arrow[ur, "-\mathrm{Ph_2P}^{\bullet}"] \arrow[r, "-\mathrm{P_2}"] \arrow[dr, "-\mathrm{PhP_3}"'] & \begin{matrix}\mathrm{Ph_2P.P(Ph)PPh_2}^{+\bullet}\\ (m/e\ 478)\end{matrix} & \\
 & \begin{matrix}\mathrm{Ph_2P.PPh_2}^{+\bullet}\\ (m/e\ 370)\end{matrix} &
\end{tikzcd}$$

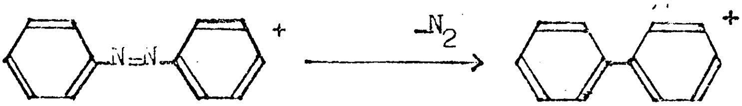
$$\begin{matrix}(\mathrm{PhP})_4^{+\bullet}\\ (m/e\ 432)\end{matrix} \xrightarrow{-\mathrm{P_2}} \begin{matrix}\mathrm{Ph_2P.PPh_2}^{+\bullet}\\ (m/e\ 370)\end{matrix}$$

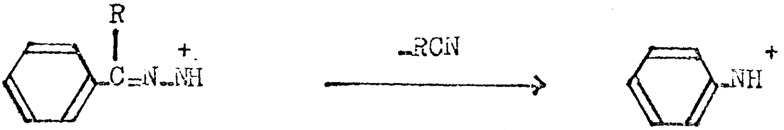
$$\begin{matrix}(\mathrm{PhP})_3^{+\bullet}\\ (m/e\ 324)\end{matrix} \xrightarrow{-\mathrm{P_2}} \begin{matrix}\mathrm{Ph_3P}^{+\bullet}\\ (m/e\ 262)\end{matrix}$$

$$\begin{matrix}\mathrm{Ph_2P}^{+}\\ (m/e\ 185)\end{matrix} \xrightarrow{-\mathrm{H_2}} \begin{matrix}\mathrm{C_{12}H_8P}^{+}\\ (m/e\ 183)\end{matrix}$$

1.  (17)

2.  (18)

3.  (19)

4.  (20)

Decompositions 1 and 2 are considered to be 1,2 - rearrangements while 3 and 4 are 1,3 - rearrangements.

The mass spectrum of phosphobenzene has been interpreted in terms of 1,2-phenyl migrations and the rearrangements for which there is evidence for metastables are given in Table 1. In all but two of these processes the fragment eliminated is the molecule P_2. That all azobenzenes[19] so far studied can decompose by phenyl migration and elimination of N_2 is perhaps of greater historical than mass spectral interest since Michaelis first assigned the phosphobenzene system the formula PhP=PPh by analogy with azobenzene.

From Table 1 it can be seen that no metastables are observed for the transitions $(PhP)_5 \longrightarrow (PhP)_4$, $(PhP)_4 \longrightarrow (PhP)_3$, and $(PhP)_5 \longrightarrow (PhP)_3$. This lends support to, but does not confirm, the idea that $(PhP)_5$, $(PhP)_4$, and $(PhP)_3$ are constituents of the sample

/before

TABLE 2.

OTHER PHENYL MIGRATIONS.

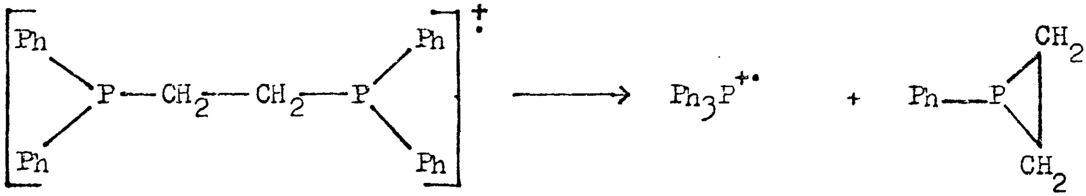
$(Ph_2P)_2NH^{+\cdot}$ [21] (m/e 385)	$\longrightarrow$		$+ PhP = NH$
$(Ph_2P)_2NMe^{+\cdot}$ [22] (m/e 399)	$\longrightarrow$		$+ PhP = NMe$
$(Ph_2P)_2(CH_2)_2^{+\cdot}$ (m/e 398)	$\longrightarrow$	$Ph_3P^{+\cdot}$ (m/e 262)	$+ PhP(CH_2)_2$
$Ph_2P(O)\ PPh_2^{+\cdot}$ [23] (m/e 386)	$\longrightarrow$		$+ PhP = O$

before introduction to the mass spectrometer.

OTHER PHENYL MIGRATIONS.

Tetraphenyldiphosphine monoxide also shows the 1,2-phenyl migration with elimination of the species PhP=O (Table 2), while examples of 1,3- rearrangements are to be found in the series of diphosphinoamines $(Ph_2P)_2NR$. In both the examples cited, the neutral fragment eliminated is the species PhP=NR, where R = H or Me, the daughter ion formed being $(Ph_3P)^+$.

Ethylenebis(diphenylphosphine) shows both a 1,2- and a 1,4-migration in its cracking pattern. The former involves elimination of the phenylphosphinidine radical with phenyl migration to carbon and formation of the species $(Ph_2PCH_2CH_2Ph)^+$ while the latter has been interpreted as follows:



The three membered ring species is proposed as the most likely structure for the fragment $PhP(CH_2)_2$.

Ethylenebis(diphenylphosphine) also shows loss of ethylene from the parent ion. This process has been observed by Lewis[18] and co-workers in the mass spectrum of the complex $(Ph_2P)_2(CH_2)_2Mo(CO)_4$ and is analogous to reaction 3 above and also to the elimination of sulphur from diphenyldisulphide.[24]

TABLE 3.

PARTIAL CRACKING PATTERNS OF SOME AMINOPHOSPHINES CONTAINING THE P–NMe UNIT.

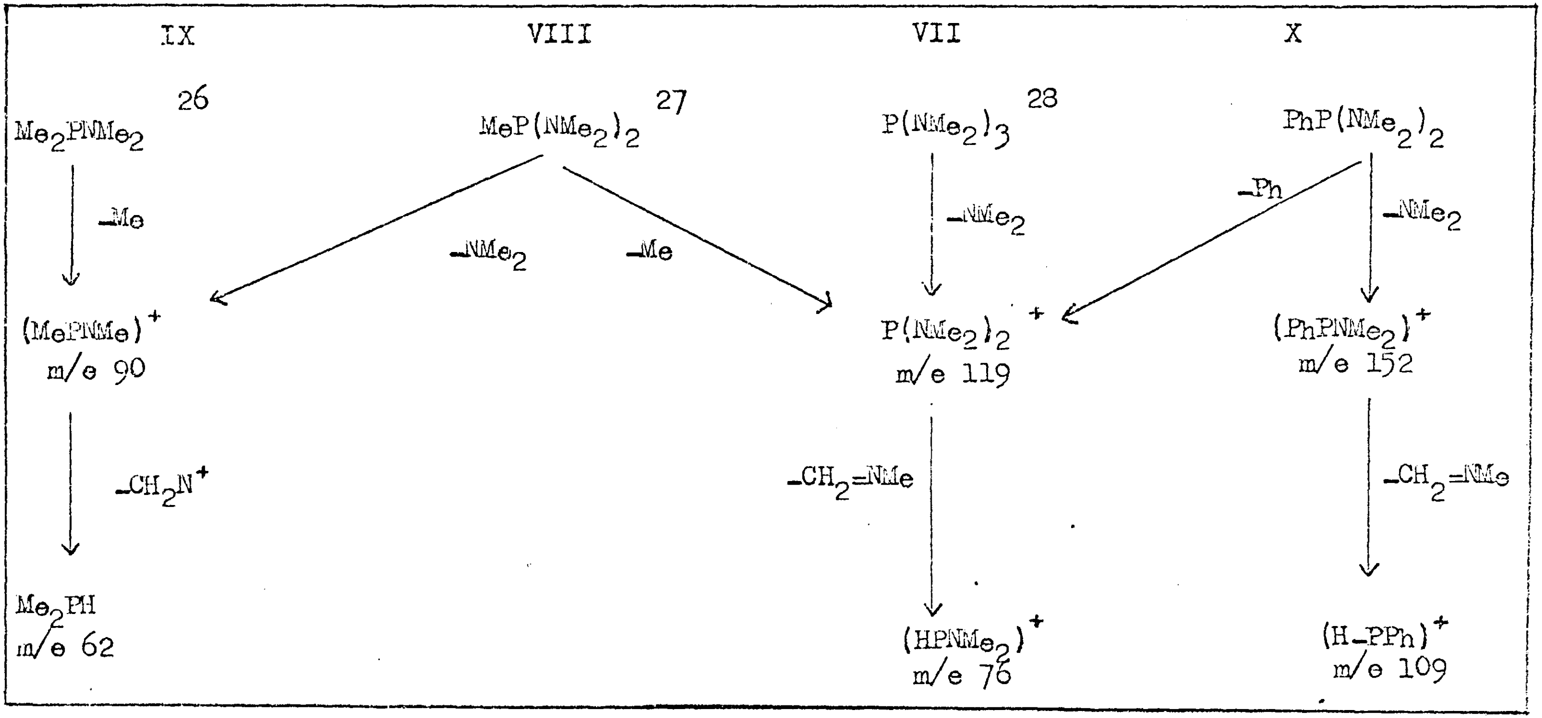
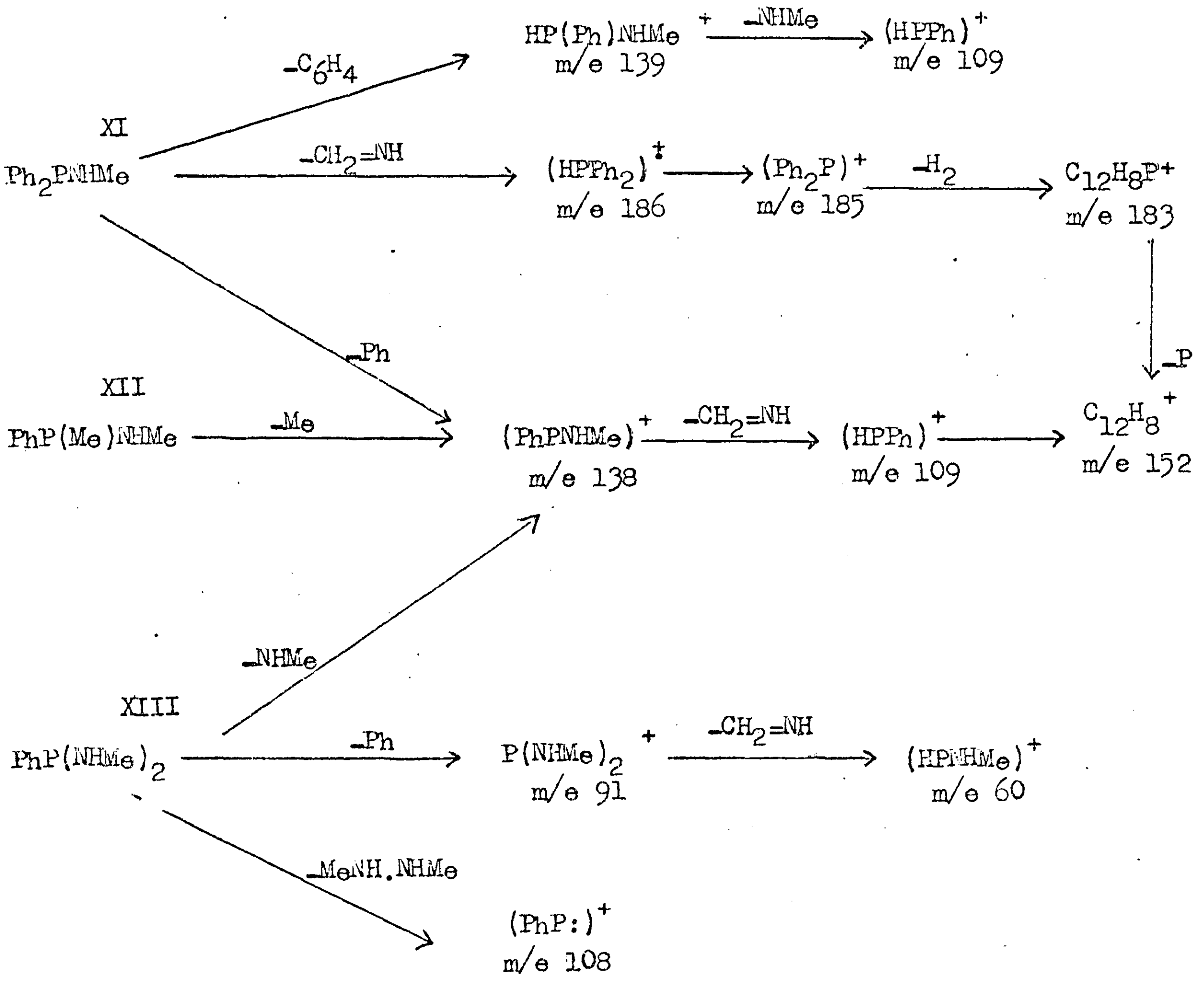
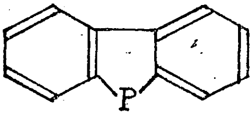


TABLE 3 (contd.)

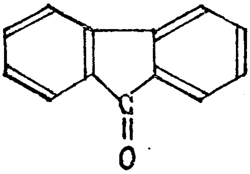


OTHER PROCESSES

A characteristic feature of the mass spectra of polyphenyl substituted phosphines and aminophosphines is the elimination of H_2 from the high abundance ion $(Ph_2P)^+$(m/e185). The resulting high abundance species (m/e183) has been assigned the structure:



on the basis of the behaviour of a number of diphenyl substituted organic compounds eg. benzophenone(25) where elimination of a molecule of hydrogen to give:



is followed by loss of CO to form the biphenylene ion.

AMINOPHOSPHINES CONTAINING THE P-N-Me GROUP.

The partial mass spectra are given in Figs. 7 - 13 and the observed decomposition pathways with possible assignments are outlined in Table 3.

The main decomposition pathway in all cases is loss of a radical (Me_2N, MeNH, Me or Ph) followed by hydrogen migration and imine elimination (except IX) e.g.

$$(Me_2N)_3P^{+\cdot} \xrightarrow{-Me_2N^{\cdot}} (Me_2N)_2P^{+} \xrightarrow{-MeN{=}CH_2} (HPNMe2)^{+}$$

/This

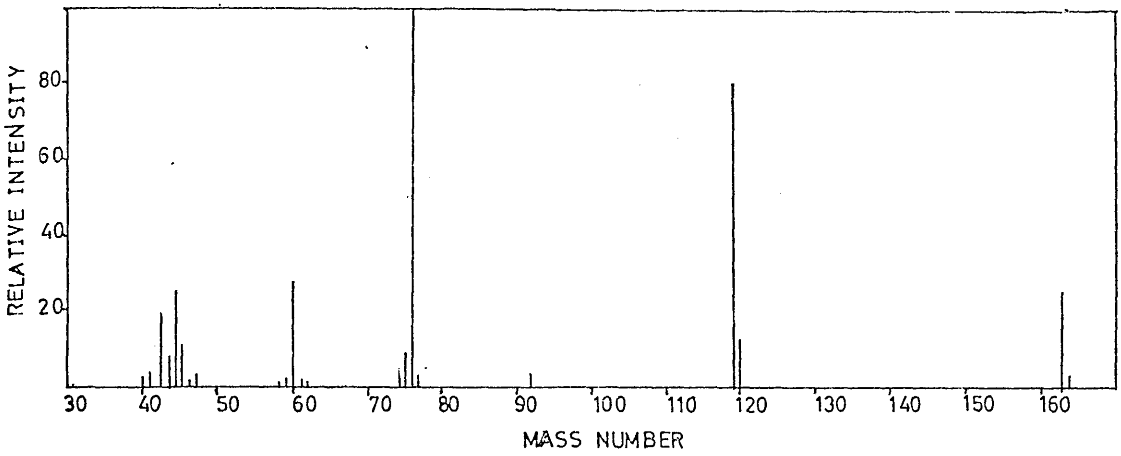


Fig.7 Mass spectrum of tris(Dimethylamino)phosphine

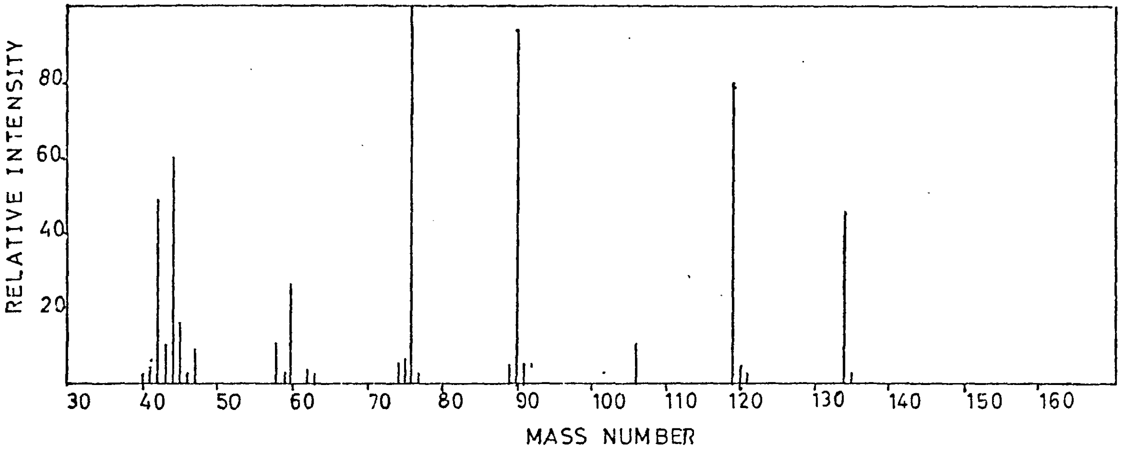


Fig.8 Mass spectrum of bis(Dimethylamino)methylphosphine

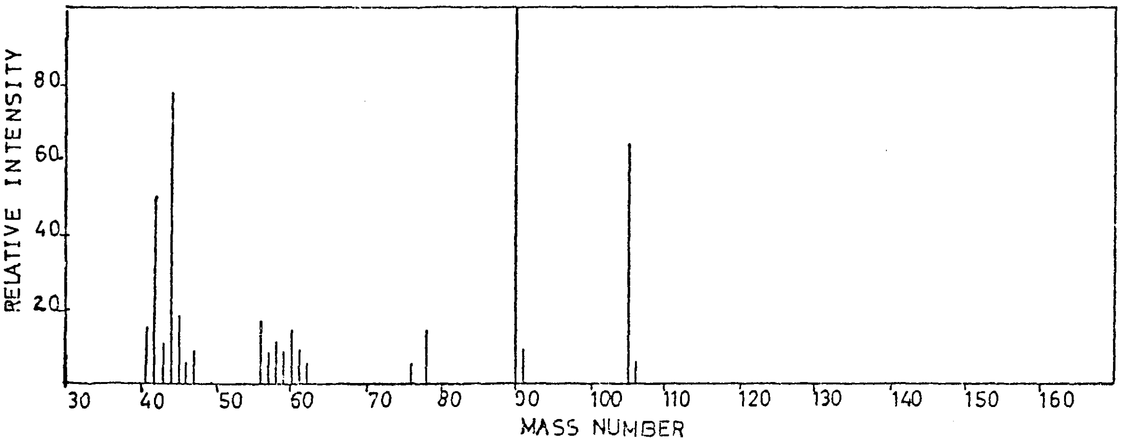


Fig.9 Mass spectrum of Dimethylaminodimethylphosphine

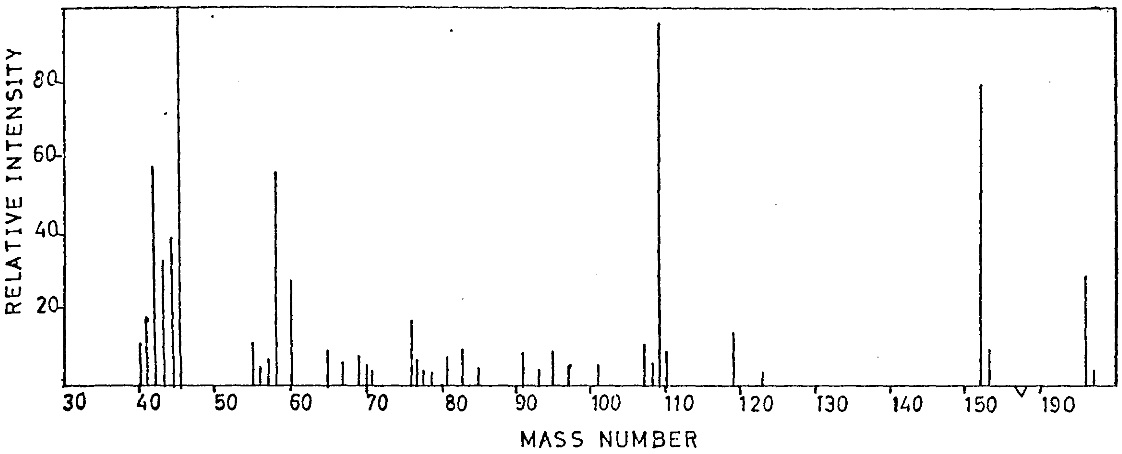


Fig.10 Mass spectrum of bis(Dimethylamino)phenylphosphine

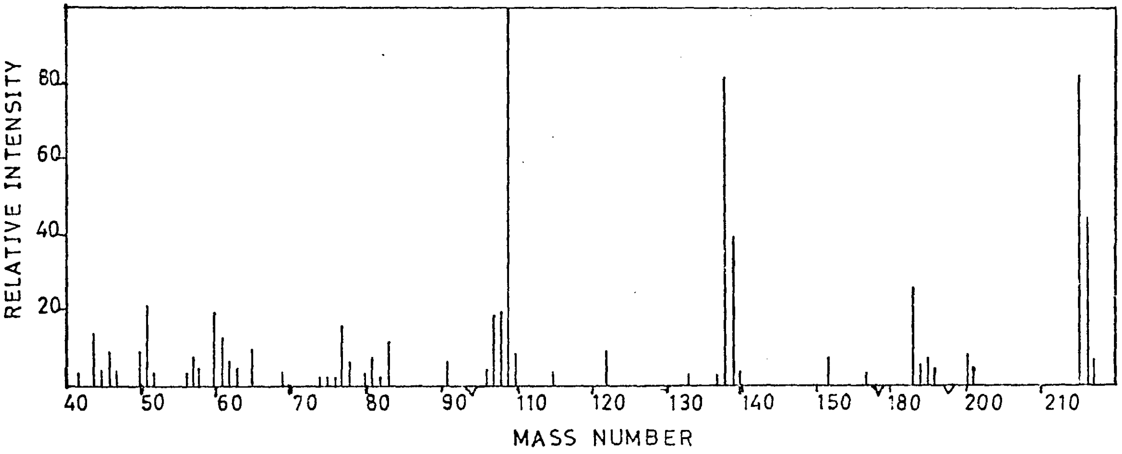


Fig.11 Mass spectrum of Methylaminodiphenylphosphine

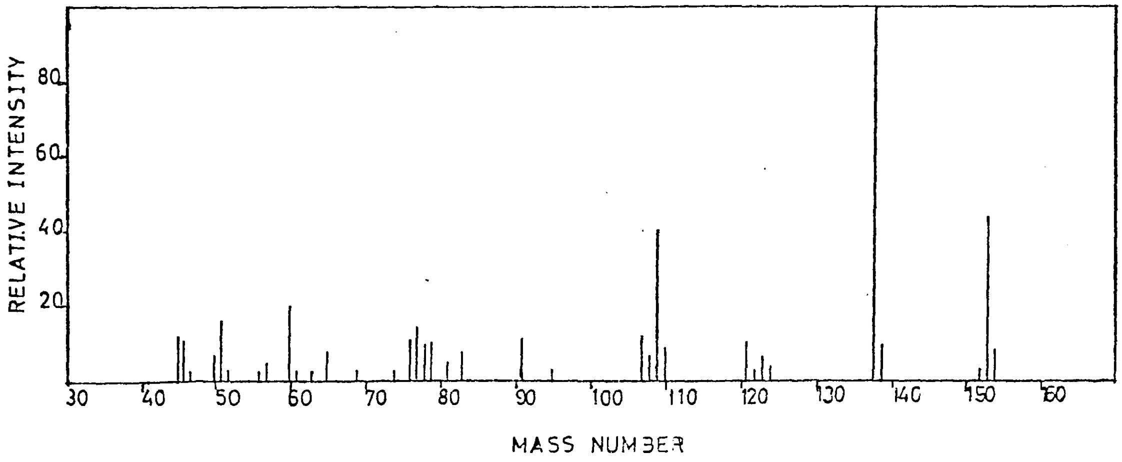


Fig.12 Mass spectrum of methylaminomethylphenylphosphine

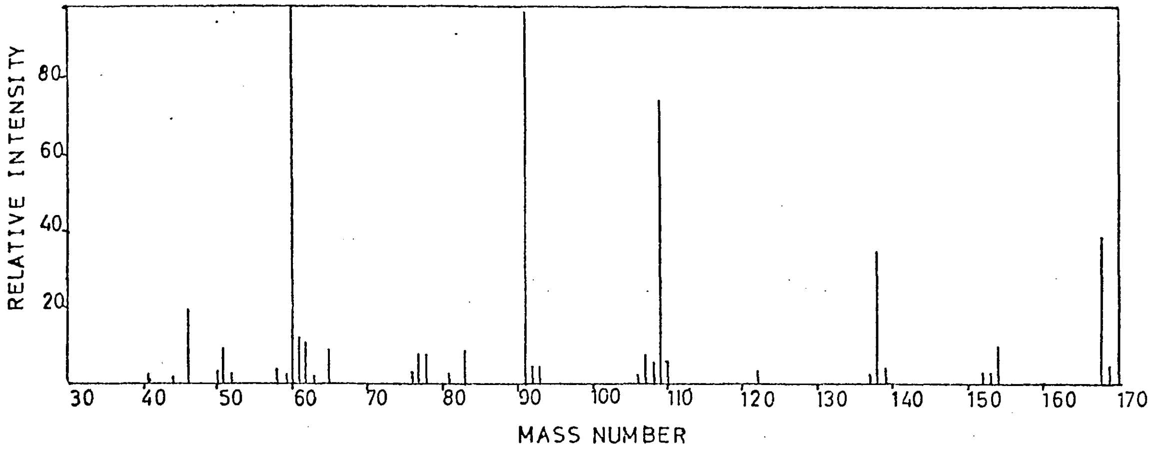
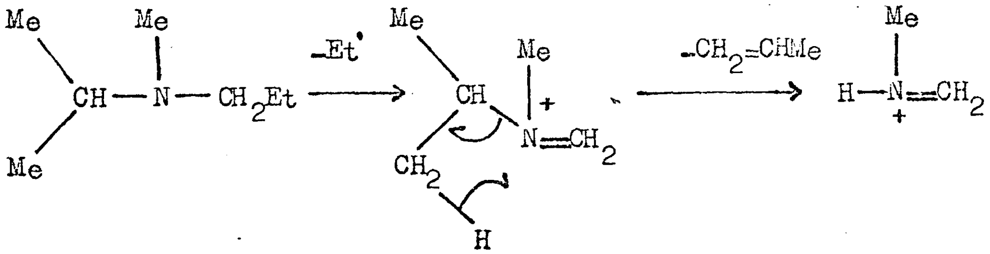
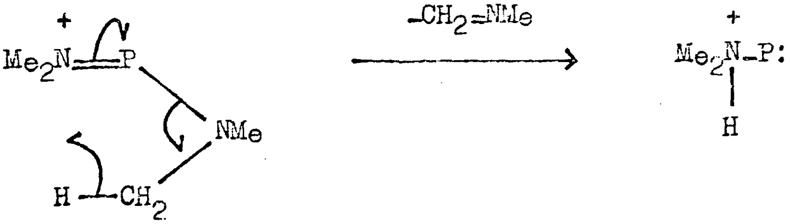


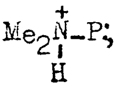
Fig.13 Mass spectrum of Dimethylaminophenylphosphine

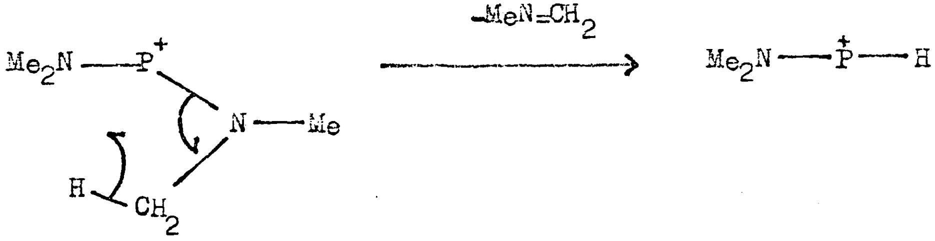
This behaviour is at first sight very similar to the cracking patterns of many secondary and tertiary amines[29] which undergo β-cleavage followed by a 1,3-hydrogen migration to nitrogen and alkene elimination, e.g.[30]



In all the aminophosphines studied, hydrogen migration to nitrogen would involve a 1,4- shift, e.g.



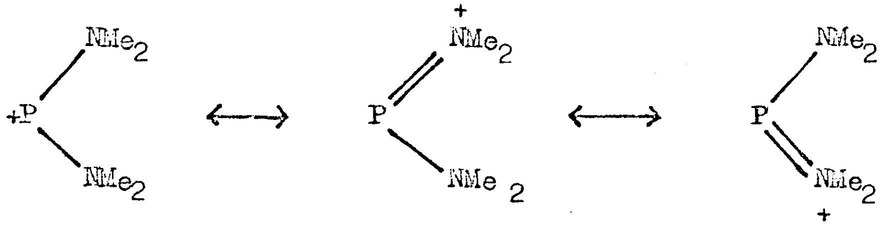
In view of the unlikely existence of the phosphinidine-ammonium cation,  $\mathrm{Me_2}\overset{+}{\underset{\mathrm{H}}{\mathrm{N}}}\mathrm{-P:}$, a mechanism involving hydrogen migration to phosphorus has been invoked:



The ions $(\mathrm{Me_2NH})^+$ (m/e76), and $(\mathrm{Me_2N})_2\mathrm{P}^+$ (m/e119) can be represented

/by

by several resonance forms, e.g.



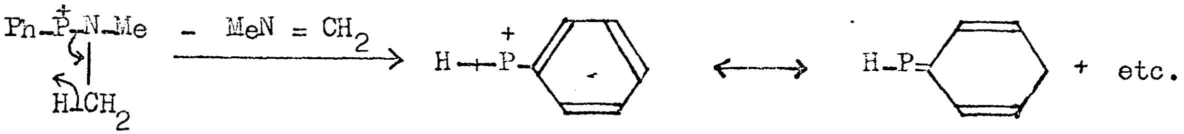
and this may account for their high abundancies. In fact all daughter ions which retain the P–N unit are present in high relative abundance.

Dimethylaminodimethylphosphine (IX) decomposes initially to give the ion $Me.PNMe_2^+$. (The subsequent cracking pattern of this ion is independent of whether it is generated from IX or VIII suggesting that its structure is as written and not the isomeric Me_2PNMe^+.) The product of imine elimination from $MePNMe_2^+$ (relative abundance, 100%) would be the species $MePH^+$ (m/e47). In contrast to the rearrangement ions from VII and VIII, this is present to a comparatively small extent (~10%). It is perhaps significant that this is the only rearrangement ion where stabilisation through conjugation is not possible. No metastable is observed for formation of $MePH^+$ from $MePNMe_2^+$ but there is evidence for the process m/e90 ⟶ m/e62. The latter species has been accurately mass measured to be Me_2PH^+ and hence the fragment eliminated is CH_2N^+, a species isoelectronic with CO.

The phenyl substituted compounds may fragment by loss of either a phenyl or an amino radical. Again, all ions which retain the P–N

/unit

unit are present in high relative abundance. However, P–N bond cleavage may occur without loss of ion stabilisation since the phenyl groups themselves are conjugating e.g.



The rearrangement ion $HPPh^+$ is present in high abundance in all the phenyl compounds cited.

Stabilisation by conjugation has been proposed by Occolowitz and White[1] for the ions $HPOMe^+$ and $P(OMe)_2^+$ observed in high abundance in the mass spectrum of trimethyl phosphite. The cracking pattern of this compound is basically radical loss followed by formaldehyde elimination. However, rearrangement does take place to some extent in the primary process and the ion $HP(OMe)_2^+$ is observed. In the extreme case, triethylphosphine[2] decomposes almost entirely by a series of hydrogen migrations to phosphorus:

$$\overset{+}{\cdot}P(Et)_3 \xrightarrow{-CH_2=CH_2} H^{+\cdot}P(Et)_2 \xrightarrow{-CH_2=CH_2} H_2^{+\cdot}PEt$$

Of the compounds cited here, methylaminodiphenylphosphine is the only compound to show a rearrangement ion in the primary process:

$$Ph_2\overset{+\cdot}{P}\ NHMe \xrightarrow{-CH_2=NH} Ph_2\overset{+\cdot}{P}\ H$$

$$Ph_2\overset{+\cdot}{P}\ NHMe \xrightarrow{-C_6H_4} Ph\overset{+\cdot}{P}\ HNHMe$$

The second process is believed to involve hydrogen migration from a phenyl group to phosphorus with elimination of a benzyne molecule. The daughter ion then loses a methylamino radical to give the ion $H\overset{+}{P}Ph$ (m/e109).

Why the primary process should involve a hydrogen migration only in certain cases must remain a matter of conjecture since insufficient data are available.

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APPARATUS AND TECHNIQUE.

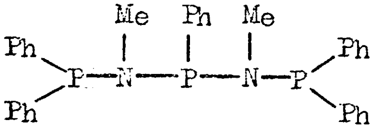
^{1}H n.m.r. spectra were run on the Perkin-Elmer R.10 spectrometer (60 Mc/sec.) and on the Varian Associates HA-100 instrument. Solution concentrations were generally of the order 2 - 5%. Neat liquid samples were prepared by direct distillation into an n.m.r. tube and sealing off in vacuo. τ values were consequently determined by opening the tubes in a dry-box, introducing TMS, and rerunning the spectrum.

Routine infra-red spectra were recorded as Nujol Mulls on the Perkin-Elmer 237 instrument. The frequencies quoted here were measured on the Perkin-Elmer 357 or on the SP-100 instrument.

Nitrogen analyses were carried out by Mr. Cameron (Glasgow) and carbon, hydrogen, and phosphorus etc., by A. Bernhardt, Mulheim, W. Germany.

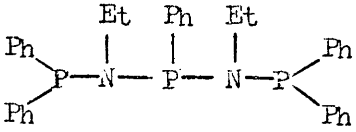
SUMMARY.

The aminophosphines,



(I)

and



(II)

have been prepared by the following reaction scheme:

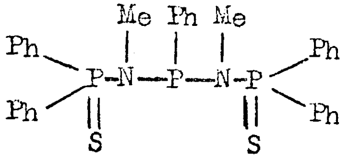
(1) $PhPCl_2 + 4RNH_2 \longrightarrow PhP(NHR)_2 + 2RNH_3^+Cl^-$

(2) $2PhPCl_2 + PhP(NHR)_2 + 2Et_3N \longrightarrow PhP(NR.PPh_2)_2 + 2Et_3NH^+Cl^-$

Using n-pentane as solvent, greatly improved yields of the intermediates $PhP(NHR)$, where R = Me and Et, have been obtained.

Reaction of (I) and (II) with excess methyl iodide in ether yields only a mono-adduct in each case, quaternisation occurring at a terminal phosphorus atom. In the absence of ether, there is evidence for further quaternisation but the ease of hydrolysis of the products has precluded satisfactory analyses.

The stepwise addition of sulphur to (I) has resulted in the isolation of only the di- and the trisulphides, the structure of the disulphide having been shown by 'H n.m.r. spectroscopy to be:



Sulphuration of II proceeds initially at a terminal phosphorus atom but the structure of the disulphide has not been well established.

Both (I) and (II) readily replace three molar equivalents of carbon monoxide in their reactions with Group VIb carbonyls. The products have been shown by infra-red spectroscopy to be the cis-trisubstituted complexes.

A 'H n.m.r. investigation into the source of magnetic nonequivalence of the isopropyl-methyl protons in the series of compounds, $PhP(NHP_r^i)$ X, where X = nothing, O,S,Se and MeI, indicates a relationship between the magnitude of nonequivalence and the rate of proton exchange at nitrogen. This, in turn, appears to affect the rate of inversion at the nitrogen atoms. In the same series of compounds, a relationship appears to exist between the chemical shift of the *ortho*-protons of the phenyl group and the effective positive charge on phosphorus. Reference is made here to the 'H n.m.r. spectra of a variety of aminophosphines prepared in the course of this work.

The mass spectral cracking patterns of a variety of methyl substituted aminophosphines have been elucidated. The

/high

high relative abundance of ions which retain the P–N unit is attributed to resonance stabilisation involving structures of the following type:

$$-\overset{+}{P}-N \longleftrightarrow -P=\overset{+}{N}$$