SOME ASPECTS OF THE CHEMISTRY OF NITROGEN-BRIDGED DIPHOSPHORUS COMPOUNDS

A thesis submitted to the
University of Glasgow
in fulfilment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

by

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March 1976.

ACKNOWLEDGEMENTS

I wish to express my gratitude to my supervisor Dr. R. Keat for his most valuable advice and interest throughout the preparation of this thesis. Thanks are also due to my colleagues in the Chemistry Department for many helpful discussions.

I also wish to thank my wife Catherine for help with proofreading, and Mrs. E. McBain for typing.

Finally, I am indebted to the S.R.C. for the receipt of a research studentship.

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ABSTRACT.

The aminolysis of a number of acyclic and cyclic compounds containing P-NR-P or P-CH_2-P skeletons have been studied.

The reaction of $[Cl_2(S)P]_2NMe$ with excess dimethylamine gives the tetrakisdimethylamino-derivative $[(Me_2N)_2(S)P]_2NMe$. By contrast, the unusual ring compounds $Me_2N(S)\overline{P\cdot NR\cdot P(S)(NMe_2)S}$ (R=Me or Et) have been isolated from the reactions of $[Cl_2(S)P]_2NR$ with six mol equiv. of dimethylamine. The reaction of $Cl_2(O)P\cdot NMe\cdot P(S)Cl_2$ with dimethylamine initially occurs at the phosphinothioyl centre in non-donor solvents, but in diethyl ether solution, dimethylaminolysis preferentially occurs at the phosphinoyl centre. It is argued that this solvent dependent reactivity may be due to aminolysis being anchiomerically assisted by the phosphinoyl oxygen in non-donor solvents. By contrast, dimethylaminolysis of the cyclodiphosphazane $Cl(O)\overline{P\cdot NMe\cdot P(S)Cl\cdot NBu^t}$ occurs exclusively at the phosphinoyl centre in donor and non-donor solvents. Nongeminal bis- and tetrakisdimethylamino-derivatives of $Cl_2(O)P\cdot NMe\cdot P(S)Cl_2$ have been isolated. Attempts to synthesise dimethylamino-derivatives of $[Cl_2(S)P]_2NMe$ and $Cl_2(O)P\cdot NMe\cdot P(S)Cl_2$ by a number of other methods were unsuccessful.

The compounds, $[Cl_2(X)P]_2NR$ (X=lone pair, R=Me, Et or Bu^t; X=O, R=Me or Et; X=S, R=Me) undergo reactions with three mol equiv. of t-butylamine to give cyclodiphosphazanes $Cl(X)\overline{P\cdot NR\cdot P(X)Cl\cdot NBu^t}$. Products of the more complex reactions

of $(Cl_2P)_2NMe$ with methylamine and $(Cl_2P)_2NEt$ with ethylamine have been identified. The reaction of $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$ with three mol equiv. t-butylamine gives the cyclodiphosphazane $ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$, whereas $Bu^tNHP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$ was the only product isolated from the analogous reaction with $Cl_2P{\cdot}NMeP(S)Cl_2$. No cyclic products were identified from the reactions of $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ or $Cl_3P{=}N{-}P(O)Cl_2$ with t-butylamine, the latter compound giving mono- and nongeminal-bis-t-butylamino derivatives. Possible reasons for the ease of cyclodiphosphazane formation in many of these reactions and the dependence of the reaction on the primary amine involved are discussed.

Similar reactions of $[Cl_2(O)P]_2CH_2$ with t-butylamine and i-propylamine gave a new class of ring compound, $Cl(O)P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NR$ (R = Bu^t or Pr^i) (1,2,4-azadiphosphetanes), but no cyclic products were obtained from analogous reactions with $Cl_2(O)P{\cdot}CH_2CH_2{\cdot}P(O)Cl_2$. Attempts to prepare pure samples of $(Cl_2P)_2CH_2$ as a substrate for cyclisation reactions from the reaction of phosphorus trichloride with $(Ph_2P)_2CH_2$ were unsuccessful, and some of the products of this reaction are described. Both mono- and nongeminalbisdimethylamino derivatives of $[Cl_2(O)P]_2CH_2$ are obtained on reaction with dimethylamine, although the former derivative was not isolated. Attempted cyclisation of the bisdimethylamino derivative $[Me_2N(Cl)(O)P]_2CH_2$ by t-butylamine gave the acyclic product, $[Bu^tNH(Me_2N)(O)P]_2CH_2$, rather than $Me_2N(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2){\cdot}NBu^t$. The latter cyclic derivative, obtained by heating

$(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)NHBu^t$, was resistant to ring opening by dimethylamine, whereas ring opening occurred in the attempted dimethylaminolysis of $Cl(O)\overline{P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t}$. Cyclodiphosphazanes $Cl\overline{P{\cdot}NMe{\cdot}P(X)Cl{\cdot}NBu^t}$, $Cl(X)\overline{P{\cdot}NMe{\cdot}P(X)Cl{\cdot}NBu^t}$ (X = O or S) and $Cl(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$ can be formed from reactions of $Cl\overline{P{\cdot}NMe{\cdot}PCl{\cdot}NBu^t}$ with dimethyl sulphoxide and sulphur. Aminolysis of cyclodiphospha(III)zanes $Cl\overline{P{\cdot}NR{\cdot}PCl{\cdot}NBu^t}$ (R= Me, Et or Bu^t) results in the formation of mono- and diamino derivatives, while cyclisation of $[Me_2N(Cl)P]_2NMe$ with three mol equiv. t-butylamine provides a second route to the 2,4-bisdimethylamino-derivative, $Me_2N\overline{P{\cdot}NMe{\cdot}P(NMe_2)NBu^t}$. Dimethylaminolysis of the mixed oxidation state cyclodiphosphazanes $Cl\overline{P{\cdot}NMe{\cdot}P(X)Cl{\cdot}NBu^t}$ (X = O or S) is found to occur initially at the phosphorus(III) atom. Slow rotation about the phosphorus(III)-nitrogen bonds of dimethylamino-substituted cyclodiphosphazanes has been detected by ^1H n.m.r. spectroscopy and the barriers to rotation about these bonds have been measured and discussed.

CHAPTER 1

GENERAL INTRODUCTION

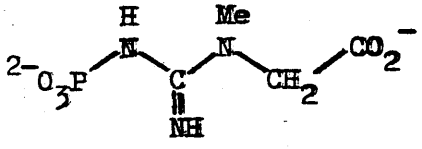
HISTORICAL

Although Schiff[1] was one of the first to report the preparation of a number of phosphorus-nitrogen compounds, it was Michaelis who was responsible for most of the work conducted before 1915 (which he also adequately surveyed[2,3]). These early investigations centred round reactions between fairly simple compounds, mainly simple chlorophosphorus compounds and amines or ammonia, but in many cases the products isolated from these reactions were discovered to be quite complex, as is exemplified by the formation of cyclic phosphorus-nitrogen products in reactions involving primary amines or ammonia.

Very little further work involving phosphorus-nitrogen compounds was reported until the 1950's when interest in this area of chemistry was renewed. Since then much of the early work has been reinvestigated and greatly extended by a number of workers in Britain, Continental Europe (notably West Germany), the U.S.A., and the U.S.S.R. Undoubtedly the development of modern spectroscopic techniques - notably nuclear magnetic resonance - has greatly aided, and even encouraged, recent investigations.

A variety of fairly minor industrial uses have been found for phosphorus-nitrogen compounds, the more important of these being their action as flameproofing agents, polymer plasticisers, and antioxidants. Also there has been considerable interest in the insecticidal and herbicidal activity possessed by a number of phosphorus-nitrogen compounds. The formation and cleavage of

phosphorus-nitrogen bonds is of great importance in some biological processes. For example, the maintenance of adenosine triphosphate (ATP) levels, during periods when ATP is required as a source of energy for muscular activity, is achieved by the phosphorylation of adenosine diphosphate (ADP) by phosphoryl creatine (I). The facile cleavage of the



(I)

phosphorus-nitrogen bond in (I) plays an integral part in this important phosphorylation process.

AMINOLYSIS OF CHLOROPHOSPHORUS COMPOUNDS

The aminolysis of chlorophosphorus compounds has proved to be a most useful route to the formation of phosphorus-nitrogen bonds. Aminolysis can be effected by a number of means, but the most widely used and investigated are reactions involving primary and secondary amines or their hydrochlorides. These reactions have the general form:

$$\geq NH + ClP\lessgtr \longrightarrow \geq N\text{-}P\lessgtr + HCl$$

or

$$-NH_2 + Cl_2P\lessgtr \longrightarrow -N{=}P\lessgtr + 2HCl$$

The hydrogen chloride produced in these reactions is either, liberated from the reaction as a gas, or, as is usual in reactions involving free amine, trapped and precipitated from the reaction by excess amine (or added tertiary amine) as an amine hydrochloride. The reactions with amine hydrochlorides are normally slow and require heating, whereas reactions with free amines can be very vigorous and exothermic.

Trimethylsilylamines are often used as alternatives to free amines.

$$\geq NSiMe_3 + ClP\lessgtr \longrightarrow \geq N\text{-}P\lessgtr + Me_3SiCl$$

The trimethylsilylamines react less vigorously than free amines (often useful in avoiding side reactions), and volatile trimethylsilylchloride is easily removable from the reaction. Metalated amines are occasionally employed in reactions with chlorophosphorus compounds, and often produce cleaner reactions when sterically

hindered amines or chlorophosphorus compounds with low electrophilicities are involved.

$$>NM + ClP\lesssim \longrightarrow >N\text{-}P\lesssim + MCl \quad (M = Li, Na \text{ or } K)$$

There are three general factors which can exert a strong controlling influence on the course of aminolysis of chlorophosphorus compounds,

1. the nature of the chlorophosphorus compound
2. the nature of the amine
3. the reaction conditions employed.

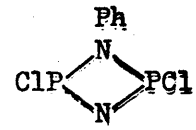
In the following survey only reactions between amines and simple chlorophosphorus compounds will be examined with the aim of illustrating the varying relative importances of these factors.

Aminolysis of three-coordinate chlorophosphorus compounds.

The reactions of phosphorus trichloride with primary aromatic amines or their hydrochlorides have been the subject of a number of conflicting reports. Early work[4,5] claiming the formation of bis(anilino)chlorophosphine, $(PhNH)_2PCl$, and tris(anilino)phosphine, $(PhNH)_3P$, has been questioned[6], and has not been substantiated by other workers.[7-10] Instead Michaelis and Schroeter reported[7] that the reaction of phosphorus trichloride with excess aniline hydrochloride gave a product of the formula $(PhNPNHPh)_n$ - which was found to be a dimer.

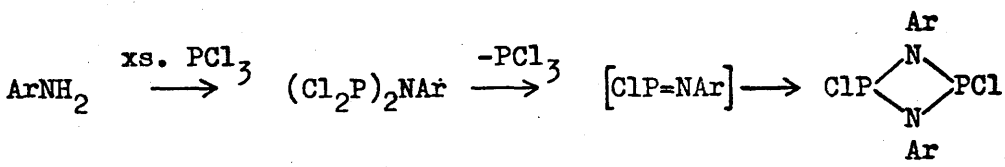
$$2\ PCl_3 + 4\ PhNH_3Cl \longrightarrow PhNHP\underset{\text{Ph}}{\overset{\text{Ph}}{\langle N_N \rangle}}PNHPh + 10\ HCl$$

This was later corroborated by the reaction of phosphorus trichloride with excess aromatic amine.[8,9] The report[7], that reaction of aniline hydrochloride with excess phosphorus trichloride yields the similar compound 2,4-dichloro-1,3-diphenylcyclodiphosphazane (II), was challenged by



(II)

Goldschmidt and Krauss[9], who isolated bis(dichlorophosphino)aniline, $(Cl_2P)_2NPh$, as the product. This apparent conflict was resolved by Haszeldine and co-workers[10] who showed that $(Cl_2P)_2NPh$ is isolated under low temperature work up conditions, whereas (II) is isolated under high temperature work up conditions by thermal decomposition of $(Cl_2P)_2NPh$. Other primary aromatic amines behave similarly. The reaction scheme proposed for the formation of these 1,3-diaryl-2,4-dichlorocyclodiphosphazanes involves the phosphorus imide intermediate ClP=NAr:



The reactions of phosphorus trichloride with primary aliphatic amines and their hydrochlorides, although exhibiting some similarities to reactions with aromatic amines, seem to be more dependent on the nature of the amine. An early report[2] showed that dichlorophosphinoalkylamines, $Cl_2P{\cdot}NHR$ (III), are the products of the reactions of primary aliphatic amines with excess phosphorus

trichloride. The corresponding reactions with primary amine hydrochlorides do not yield compounds (III), but instead form bis(dichlorophosphino)alkylamines, $(Cl_2P)_2NR$ (R = Me or Et).[11] These compounds show no tendency to decompose thermally to form cyclodiphosphazanes. The products of the reactions of phosphorus trichloride with three mol equiv. of primary amines vary depending on the amine.[12] These reactions can be summarised as follows:

$$PCl_3 + 3\ MeNH_2 \longrightarrow (Cl_2P)_2NMe + \text{other products} \qquad 1$$

$$PCl_3 + 3\ EtNH_2 \longrightarrow (Cl_2P)_2NEt + (ClPNEt)_n \quad (n = 2,3)$$

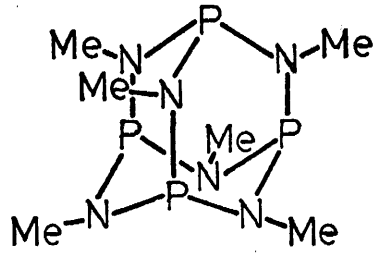
(IV)

$$PCl_3 + 3\ RNH_2 \longrightarrow ClP\langle N(R)\rangle PCl \quad (R = Pr^i \text{ or } Bu^t)$$

(V)

Because of the thermal stability of bis(dichlorophosphino)alkylamines, the mechanism of formation of (V) is almost certainly different from that of (II). Here the reaction scheme proposed[12] involves the self-condensation and cyclisation of (III) (R = Pr^i or Bu^t). (V) (R = Bu^t) is also formed in the reactions of phosphorus trichloride with $Bu^t(Me_3Si)NLi$, and (III) (R = Bu^t) with triethylamine.[13] Reaction with greater proportions of t-butylamine results in aminolysis of the ring compound.[12,14] (IV) (n = 3,4) was reported[15] to be the product of the reaction of phosphorus trichloride with bis(trimethylsilyl)ethylamine, $(Me_3Si)_2NEt$, while reaction with excess ethylamine yields an oil which analyses as $(EtNHPNEt)_n$.[14]

Although no cyclic product could be characterised from reaction 1, reaction with excess methylamine yields the 'cage compound' $P_4(NMe)_6$(VI).[14]



(VI)

The cyclodiphosphazane (V)(R=Me) was reported[15] to be formed by the reaction,

$$2\ PCl_3 + 2(Me_3Si)_2NMe \longrightarrow (V)(R=Me) + 4\ Me_3SiCl$$

but this has proved to be unrepeatable by other workers,[12,16] their findings confirming earlier work[17] which claimed the formation of dichlorophosphino(trimethylsilyl)methylamine, $Cl_2P{\cdot}NMe{\cdot}SiMe_3$. Reaction of a 2:1 mol ratio of phosphorus trichloride to heptamethyldisilazane, $(Me_3Si)_2NMe$, was shown to yield bis(dichlorophosphino) methylamine, $(Cl_2P)_2NMe$.[16]

In contrast, aminolysis reactions of phosphorus trifluoride and aryl or alkyldichlorophosphines show little tendency to form cyclic products. Phosphorus trifluoride reacts with primary aliphatic amines[18] to give difluorophosphinoalkylamines, $F_2P{\cdot}NHR$, plus $(RNH)_2PF_2H$, except with t-butylamine when bis(t-butylamino) fluorophosphine, $(Bu^tNH)_2PF$, is the product of further aminolysis. Similarly diamino-derivatives $(RNH)_2PAr$ are the reported products

of the reactions of dichlorophenylphosphine and dichloro(pentafluorophenyl)phosphine with excess primary aliphatic amines[19-21] or aniline,[22] and dichloro(t-butyl)phosphine, Cl_2PBu^t,[23] and dichloro(trifluoromethyl)phosphine, Cl_2PCF_3,[24] react with excess methylamine yielding bis(methylamino)alkylphosphines, $RP(NHMe)_2$ ($R=Bu^t$, CF_3). Also alkyldichlorophosphites, $Cl_2P{\cdot}OR$, are found to react with two mol equiv. heptamethyldisilazane forming $RO{\cdot}P(NMe{\cdot}SiMe_3)_2$,[25] and a Russian report[26] suggests that dichlorophenylphosphite, $Cl_2P{\cdot}OPh$, reacts with excess aniline analogously.

It would seem therefore that in these cases substitution of the second halide atom occurs more readily than either condensation with another chlorophosphine species or loss of hydrogen chloride (or fluoride). This behaviour is further displayed[13] in compounds $XP(Cl)NHBu^t$. When X=Me or Bu^t the chlorine can be easily substituted, but no dehydrochlorination occurs with triethylamine, whereas when X=Cl reaction with triethylamine yields (V) $R=Bu^t$.

Chlorodiphenylphosphine exhibits a greater tendency than dichlorophenylphosphine to form condensation products on aminolysis by primary aliphatic amines or their trimethylsilyl analogues. Reaction of the former phosphine with primary amines yields a mixture of diphenylphosphinoalkylamines, $Ph_2P{\cdot}NHR$, and bis(diphenylphosphino) alkylamines, $(Ph_2P)_2NR$[27] - the greatest proportion of condensation product being formed when R=Me. This difference in the reactivities of these phenyl and diphenylphosphines is also seen in their reactions with heptamethyldisilazane,[12,28]

$$Ph_2PCl + (Me_3Si)_2NMe \longrightarrow (Ph_2P)_2NMe + 2\ Me_3SiCl \qquad 2$$

$$PhPCl_2 + (Me_3Si)_2NMe \longrightarrow PhP(Cl)\cdot NMe\cdot SiMe_3 + Me_3SiCl$$

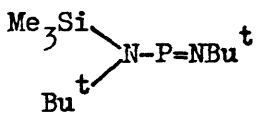
(VII)

No trimethylsilyl intermediate could be isolated in reaction 2, whereas (VII) only reacts at higher temperatures with a further mol of dichloro$\left[Ph(Cl)P\right]_2NMe$ine forming bis[chloro(phenyl)phosphino] methylamine, $\left[Ph(Cl)P\right]_2NMe$.[12] Diaminochlorophosphines[29] and dialkylchlorophosphites[25] also form condensation products on reaction with methylamine and heptamethyldisilazane respectively.

The formation of phosphorus-nitrogen formal double bonds involving tervalent phosphorus is very rare. Many compounds originally thought to contain double bonds have later been shown to be dimers or polymers - although monomeric tervalent phosphazenes have been postulated as intermediates in cyclodiphosph(III)azane formation.[10] Only recently have a few tervalent phosphazenes(VIII, IX) been isolated using lithiated trimethylsilylamines.[30-33]

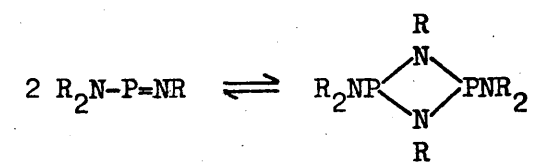
$(Me_3Si)_2N\text{-}P\text{=}NR$

(VIII) R=Me_3Si or Bu^t.



(IX)

The steric bulk of the nitrogen substituents and the possible lower basicity of the two coordinate nitrogen in (VIII) (R=$SiMe_3$) probably prevent a dimerisation, similar to that found for



phosphine imines (see later), occurring.

Michaelis[2] fairly thoroughly investigated the reactions of phosphorus trichloride with secondary amines and their hydrochlorides. Using excess phosphorus trichloride dialkyl/diarylamino (dichloro)phosphines, $R_2N{\cdot}PCl_2$, are formed, whereas using excess amine tris(dialkyl/diarylamino)phosphines, $(R_2N)_3P$, are produced. The corresponding compounds where R=Me were not prepared until much later.[34,35] Michaelis did not report the preparation of any bis(dialkylamino)chlorophosphines, $(R_2N)_2PCl$, although these rather pyrophoric compounds were again later prepared using methods similar to those employed by him.[36,37] Mixed dimethylamino/chlorophosphines can also be easily prepared via redistribution reactions[36] involving phosphorus trichloride and tris(dimethylamino) phosphine.

Alkyl and aryldichlorophosphines and dialkyl and diarylchlorophosphines react straight forwardly with secondary amines.[35,36,38-43]

$$RPCl_2 + 2\,R_2'NH \longrightarrow RP(Cl)NR_2' \xrightarrow{2R_2'NH} RP(NR_2')_2 + 2\,R_2'NH_2^+Cl^-$$

$$R_2PCl + 2\,R_2'NH \longrightarrow R_2P{\cdot}NR_2' + R_2'NH_2^+Cl^-$$

Phosphorus trichloride, dichlorophenylphosphine, and chlorodiphenylphosphine also react with diethyl(trimethylsilyl)amine, $Et_2N{\cdot}SiMe_3$ to form fully and partially aminolysed products.[15]

Aminolysis of four-coordinate chlorophosphorus compounds

The aminolysis of phosphoryl chloride and thiophosphoryl chloride has been fairly systematically investigated by Michaelis.[2] Aminolysis using both free amine (at low temperatures) and amine hydrochloride (on heating) is possible, although preparation of the triamides normally requires the use of free amine and higher temperatures. Reaction proceeds stepwise, further aminolysis becoming progressively slower, due mainly to the reduced electrophilicity of the aminolysis product - although sometimes difficulties are encountered in preparing pure diamides by direct aminolysis.

Reactions of phosphoryl chloride and thiophosphoryl chloride with primary amines are typically less complicated, by dehydrochlorination or condensation side reactions, than the corresponding reactions with phosphorus trichloride, forming mono-, bis- and tris(alkyl/arylamino)-derivatives

$$P(X)Cl_3 + 2\ RNH_2\ (\text{or } RNH_3^+Cl^-) \longrightarrow Cl_2(X)P{\cdot}NHR^{2,44,45}$$

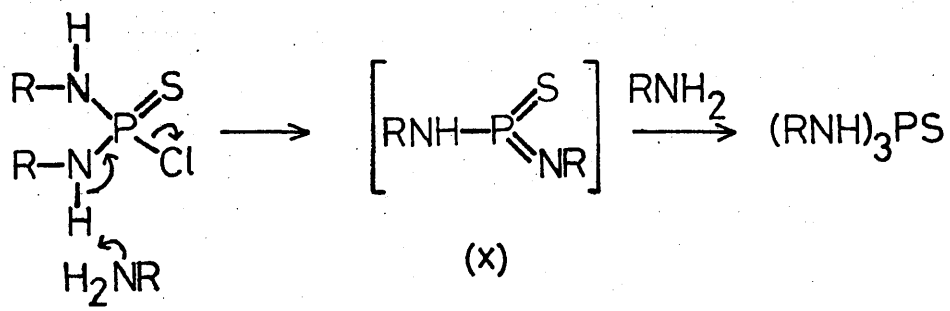
$$P(O)Cl_3 + 4\ RNH_2\ (\text{or } 2\ RNH_3^+Cl^-) \longrightarrow (RNH)_2P(O)Cl^{2,45}$$

$$P(X)Cl_3 + 6\ RNH_2 \longrightarrow (RNH)_3P^{1-3,45,48}$$

X=O or S R=alkyl or aryl

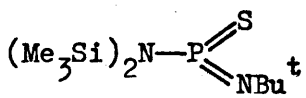
Many of these primary aminophosphinoyl and aminophosphinothioyl derivatives on prolonged heating condense to form cyclodiphospha(V)zanes, eliminating hydrogen chloride or amine[46,47] (see later). Remarkably no bis(alkyl or arylamino)phosphinothioyl chlorides, $(RNH)_2P(S)Cl$, have been reported - possibly due to an accelerated rate of substitution of the last chlorine atom via an ElcB mechanism

involving the metaphosphorimidothiate intermediate(X),



(X)

as suggested by Gerrard and Hamer.[49] Interestingly, compound (XI), possessing the metaphosphorimidothiate structure of intermediate(X) has recently been prepared[32] by sulphuration of the tervalent phosphazene $(Me_3Si)_2NP{=}NBu^t$.



(XI)

Reaction of phosphoryl chloride and thiophosphoryl chloride with secondary amines, or their hydrochlorides, was shown by Michaelis[2] to result in the formation of mono or tris(dialkyl/diarylamino) derivatives, $R_2N{\cdot}P(X)Cl_2$ or $(R_2N)_3PX$ (X=O or S), depending on the reactant mol ratio employed. The simplest members of the triamides, $(Me_2N)_3PO$[50] and $(Me_2N)_3PS$[6], were not reported until much later. Bis(dialkyl/diarylamino)phosphinoyl or phosphinothioyl chlorides, $(R_2N)_2P(X)Cl$ (X=O or S) also can be prepared by direct aminolysis,[50-53]

$$P(X)Cl_3 + 4\,R_2NH \longrightarrow (R_2N)_2P(X)Cl + 2\,R_2NH_2^+Cl^-$$

although Michaelis reported only two such compounds. A route to

bis(dimethylamino)phosphinoyl chloride, $(Me_2N)_2P(O)Cl$, avoiding formation of aminolysis by-products involves the redistribution reaction[54]

$$2\ (Me_2N)_3PO\ +\ P(O)Cl_3 \longrightarrow\ 3\ (Me_2N)_2P(O)Cl$$

Compounds of the general type $XP(O)Cl_2$ and $XP(S)Cl_2$ (X=F,[55-57] OR,[2,3,48,58] alkyl,[59-64] or aryl[65-67]) similarly react with primary and secondary amines yielding both amides and diamides. Many of the primary amino products also condense at higher temperatures, eliminating hydrogen chloride or amine.[46,47]

Most trichloro-derivatives of phosphine imines, $Cl_3P{=}NR$, preferentially exist in dimeric form as cyclodiphosphazanes.[68] The position of the monomer-dimer equilibrium,

$$2\ X_3P{=}NR \rightleftharpoons X_3P\begin{array}{c}\diagup\ R\ \diagdown\\ \diagdown\ N\ \diagup\end{array}PX_3$$

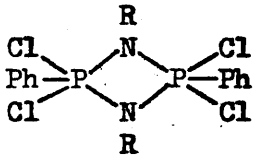
is very dependent on the nature of both substituents X and R, although the influence of the latter is more dominant. Evidence of the influence of phosphorus substituents is found in a study[69] of the diethylaminolysis of hexachlorocyclodiphosphazane, $(Cl_3P{=}NPh)_2$, in which it was shown that reaction initially leads to the formation of the monomer $Et_2N(Cl_2)P{=}NPh$, which undergoes further aminolysis, like chlorophosphinoyl or chlorophosphinothioyl compounds, forming $(Et_2N)_2ClP{=}NPh$ and $(Et_2N)_3P{=}NPh$.

Very extensive investigations have been conducted into aminolysis of the analogous cyclophosphazenes, $(Cl_2P{=}N)_n$ and their derivatives,[70] in which much interest has been devoted to aminolysis substitution patterns. It is found that the majority of amines give rise to predominantly nongeminal substitution patterns, although a few amines, notably t-butylamine, form preferentially geminal isomers. Reasons for these differing substitution patterns have been discussed.[70,71]

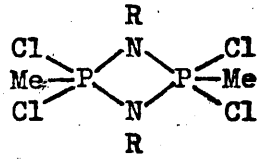
Aminolysis of five coordinate chlorophosphorus compounds.

Phosphorus pentachloride reacts with primary arylamines,[68,72-74] alkylamines[75,76] or their hydrochlorides, in a 1:1 mol ratio, yielding compounds of the type $(Cl_3PNR)_n$ (R=aryl or alkyl; n=1 or 2). The majority of the aryl derivatives formed are dimers (cyclodiphosphazanes). Monomeric products are only isolated from reactions involving arylamines of low basicity, although in many cases dimers are reversibly converted to monomers in solution on heating.[68] Both monomers and dimers are found for $(Cl_3PNR)_n$ (R=alkyl), the degree and position of branching in the alkyl groups influencing the relative stabilities of the two forms.[76] Zhmurova and Kirsanov[72] reported evidence for the transient formation of $Cl_4P{\cdot}NHAr$ in reactions with arylamines, but this has been challenged recently by Klein and Latscha[74] who found no evidence for this intermediate. A similar reaction between phosphorus pentachloride and lithiated hexamethyldisilazane, $(Me_3Si)_2NLi$, yielding $Cl_3P{=}NSiMe_3$, has also been reported.[77] Reactions between

arylamines or their hydrochlorides with tetrachloro(phenyl) phosphorane, $PhPCl_4$,[78] and tetrachloro(methyl)phosphorane, $MePCl_4$,[79] and between alkylammonium chlorides and $PhPCl_4$[80] proceed analogously yielding (XII) (R=alkyl or aryl) or (XIII) (R=aryl),



(XII)



(XIII)

some of the latter compounds forming monomers in solution on heating. Dichloro(triphenyl)phosphorane, Ph_3PCl_2,[81] and dichloro(triphenoxy)phosphorane, $(PhO)_3PCl_2$,[82] similarly form triphenyl- or triphenoxyphosphine imines, $X_3P{=}NAr$ (X=Ph or OPh), on reaction with primary arylamines.

Reactions[83] between compounds R_nPCl_{5-n} (n=0,1,2) with excess primary or secondary amines lead to the formation of quasi-phosphonium compounds. $[R_nP(NHR')_{4-n}]^+Cl^-$ or $[R_nP(NR_2')_{4-n}]^+Cl^-$, the initial products of phosphorus pentachloride with secondary amines being 'adducts' of R_2NPCl_4 with PCl_5 (probably $[R_2NPCl_3]^+PCl_6^-$). On the other hand, tris(trifluoromethyl)dichlorophosphorane, $(F_3C)_3PCl_2$,[84] and aryl(chloro)trifluorophosphoranes, $ArPF_3Cl$,[85] behave like fluorophosphoranes, R_nPF_{5-n},[86] in their reactions with secondary amines - forming five coordinate aminophosphoranes.

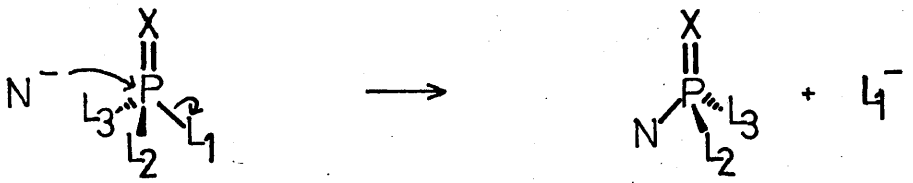
$$(F_3C)_3PCl_2 \xrightarrow{2\ Me_2NH} (F_3C)_3P(Cl)NMe_2 \xrightarrow{2\ Me_2NH} (F_3C)_3P(NMe_2)_2$$

$$ArPF_3Cl + 2\ R_2NH \longrightarrow ArP(F_3)NR_2 + R_2NH_2^+Cl^- \quad (R=alkyl)$$

Mechanisms.

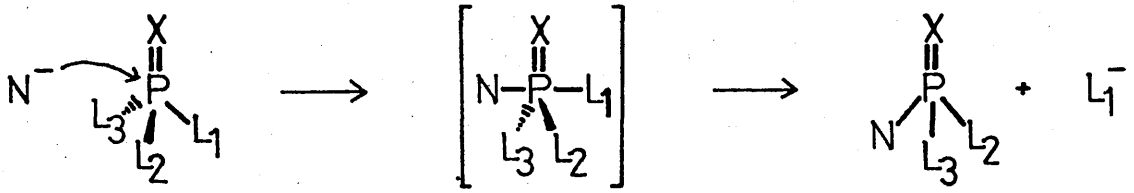
Mechanisms of nucleophilic attack on phosphorus compounds and evidence for these, with reference to a variety of examples, have been amply discussed elsewhere.[87-89] Briefly, the major mechanistic types possible for nucleophilic attack on three and four coordinate phosphorus can be summarised as:

(a) direct displacement with inversion of configuration - $S_N2(P)$



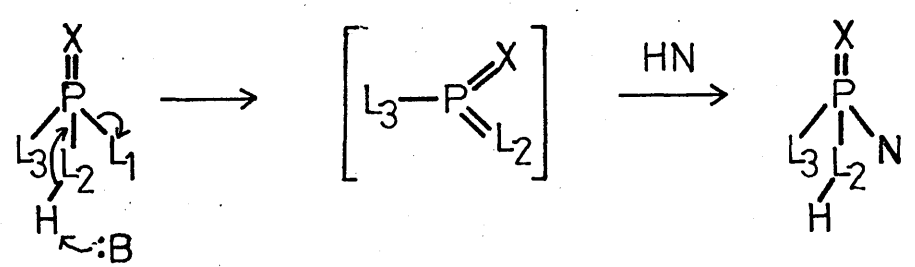
(X=lone pair, O,S,N etc. - throughout (a), (b) and (c))

(b) addition-elimination

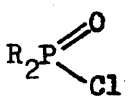


in this case the trigonal bipyramidal intermediate may pseudorotate, leading to a racemic product.

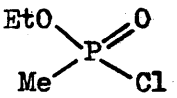
(c) elimination-addition - $S_N1(P)$ - examples known generally involve base catalysed elimination (ElcB)



Although mechanistic studies are rather sparse, some insight has been gained into the mechanisms of the reactions of chlorophosphorus compounds with amines. Reactions of (XIV)[90] and (XV)[91]

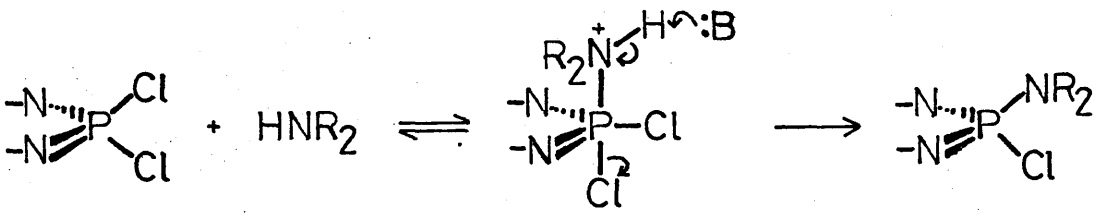


(XIV) (R=alkyl)



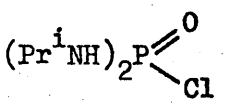
(XV)

with a number of primary and secondary amines were reported to follow second order kinetics - consistent with an $S_N2(P)$ mechanism. More detailed kinetic data on reactions of amines with chloro-derivatives of cyclotriphosphazenes have been interpreted in terms of a five coordinate intermediate (formed in a rapid pre-equilibrium) undergoing dehydrochlorination assisted by amine[92] or solvent.[93,94]

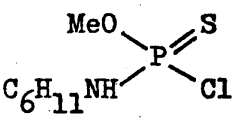


(B = amine or T.H.F.)

Although there has been no clear evidence of an $S_N1(P)$ type mechanism in aminolysis reactions, it has been suggested[49] that substitution of the last chlorine in the reaction of thiophosphoryl chloride with primary amines involves a mechanism similar to the ElcB mechanism thought to operate in the base hydrolysis of (XVI)[95] and (XVII).[96]



(XVI)

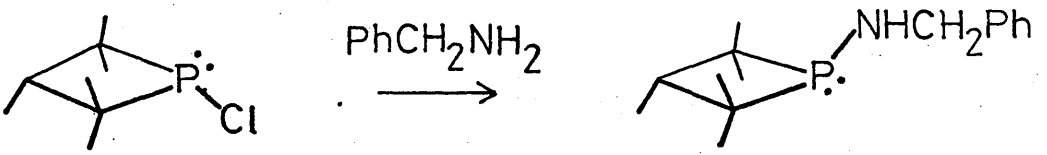


(XVII)

The major evidence used in support of hydrolysis by this mechanism is,

1) loss of optical activity in the product
2) greatly enhanced rates of hydrolysis (compared with other chlorophosphorus compounds) in basic media only.

Almost nothing is known about the mechanism of reaction of three coordinate chlorophosphorus compounds with amines. One of the few mechanistic indications is found in the reaction of 1-chloro-2,2,3,4,4,-pentamethylphosphetan(XVIII) with benzylamine, which was shown[97] to proceed with inversion of configuration - consistent with a $S_{N}2(P)$ mechanism,



(XVIII)

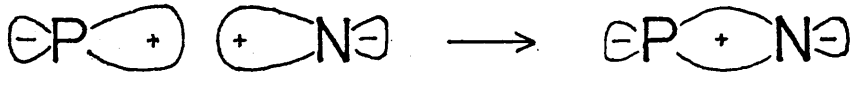
whereas aminolysis of the 1-oxide derivative of (XVIII) proceeds with retention of configuration,[98] implying pseudorotation of the trigonal bipyramidal intermediate.

PHOSPHORUS-NITROGEN BONDING

Considerable interest has centred around phosphorus covalent bonding, and in particular, the possible participation and importance of phosphorus 3d-orbitals. Experimental results from a number of sources have been used as evidence of 3d-orbital participation, especially in π-bonding, but in some cases these results are open to other interpretations.

σ-bonding.

Treating the molecular orbital bonding system in covalent phosphorus compounds as a combination of suitably hybridised atomic orbitals, the formation of a phosphorus-nitrogen single bond involving tervalent or four-coordinate, quinquevalent phosphorus can be naively described as a combination of a phosphorus $\underline{sp}^3$ hybrid orbital and a nitrogen $\underline{sp}^2$ hybrid orbital.



Use of an $\underline{sp}^2$ hybridised nitrogen orbital (or one approximating to $\underline{sp}^2$ hybridisation) is supported by aminophosphorus compound structural data, which indicate planar or near planar geometry about nitrogen (Table 1).

TABLE 1

Selected structural data for phosphorus-nitrogen compounds

Compound	Sum of N bond angles	P-N bond length (Å)	Source
$(Me_2N)_3P$	$352\frac{1}{2}^\circ$	1.700(5)	e.d.[99]
$(Me_2N)_2PCl$	360°	1.730(5)	" [100]
$Me_2N{\cdot}PCl_2$	360°	1.69(3)	" [99]
$Me_2N{\cdot}PF_2$	$348\frac{1}{2}^\circ$	1.684(8)	" [99]
"	360°	1.66	m.w. [99]
"	360°	1.628(5)	X-ray[99]
$Me_2N{\cdot}P(O)Cl_2$	348°	1.67(4)	e.d. [99]
$Ph_2P{\cdot}NMe{\cdot}P(S)Ph_2$	353°	1.719(4) P^{III}	X-ray[101]
		1.680(4)	
$Cl_2(O)P{\cdot}NPh{\cdot}P(S)Cl_2$	360°	1.651(6) P(O)	" [101]
		1.690(6)	
$F_2P{\cdot}NMe{\cdot}PF_2$	360°	1.680(6)	e.d. [102]

e.d. = electron diffraction

m.w. = microwave

The geometry around phosphorus approximates to tetrahedral (sp^3 hybridisation) in four coordinate phosphorus, while in the corresponding tervalent compounds the bond angles are smaller - indicative of more p-character in the sp hybrid orbitals involved in bonding (Table 2).

TABLE 2

Bond angles around phosphorus

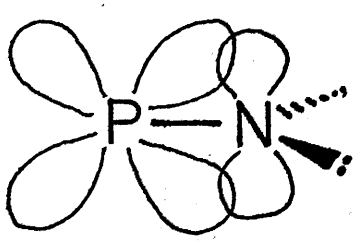
Compound	X-$\hat{P}$-X	Source
PCl_3	100.2°	e.d.
$P(S)Cl_3$	101.8°	"
$P(O)Cl_3$	103.3°	"
PF_3	97.8°	"
$P(S)F_3$	100.3°	"
$P(O)F_3$	101.3°	"
PMe_3	98.6°	"
$P(O)Me_3$	106°	"
$Me_2N{\cdot}PCl_2$	98°;100°	"
$Me_2N{\cdot}P(O)Cl_2$	102°;102°	"

(ref.99, e.d. = electron diffraction)

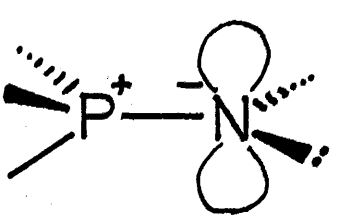
Also the sign of the $^{1}J(^{31}P-^{15}N)$ spin-spin coupling has been used[103] as an indication of the presence of greater p-character in the phosphorus-nitrogen bonds of aminophosphines compared to their phosphorus(V) analogues. The trigonal bipyramidal σ-bond framework around five coordinate phosphorus can be described in terms of phosphorus sp^3d hybridisation - although a description involving the use of s and p-orbitals only (in which sp^2 hybrid orbitals bond equatorially, and a three centre, two electron bond, involving a phosphorus p-orbital, bonds axially) is possibly preferable[104] as this overcomes the problem that phosphorus 3d-orbitals may possess energies too high to participate in σ-bonding.

π-bonding.

The involvement of 3d-orbitals in π-bonding is also a subject of some controversy. In compounds such as phosphine imines and cyclodiphosphazenes there is evidence, mainly from bond length data and infra-red spectroscopy, which points to the phosphorus-nitrogen bonds resembling formal double bonds in which the filled p-orbital on sp^2 hybridised nitrogen overlaps with a vacant 3d-orbital on phosphorus (form a), rather than a zwitterionic description (form b).



a



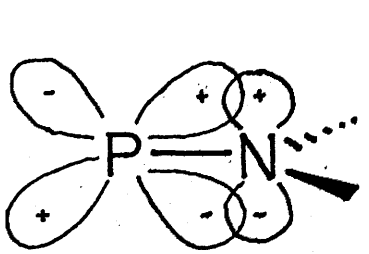
b

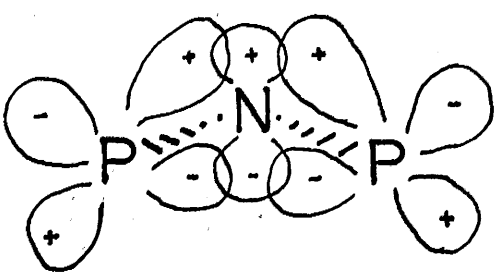
π-donor substituents on phosphorus are expected to decrease the amount of π-character in the phosphorus-nitrogen bond, whereas the presence of electronegative substituents is expected to contract the phosphorus 3d-orbitals, facilitating increased π-overlap. Also overlap with a second 3d-orbital can occur by rotation of the phosphorus-nitrogen bond through 90°, providing possible means of lowering the electronic barrier to bond rotation. In comparison, carbon-nitrogen and nitrogen-nitrogen double bonds[105] (in which d-orbitals are not energetically significant) are best described as being double bonds with a small amount of zwitterionic character,

$$C{=}N \longleftrightarrow \overset{+\ -}{C{-}N} \qquad -N{=}N- \longleftrightarrow \overset{+\ -}{-N{-}N-}$$

the zwitterionic form being comparatively more important in the carbon-nitrogen bond due to electronegativity differences.

Unlike the analogous bonds between first row elements and nitrogen, π-bonding is also possible between formally single bonded phosphorus and nitrogen. Here a degree of π-bonding can be achieved by overlap of the nitrogen lone pair, occupying a p-orbital, with phosphorus 3d-orbitals.

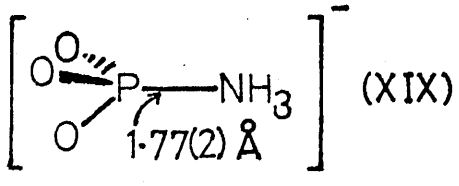




Again more than one 3d-orbital is available for π-bonding, and the amount of π-bonding should be dependent on the effects of electronegativity and of π-donor properties of the phosphorus substituents. In compounds such as cyclodiphosphazanes and nitrogen-bridged diphosphorus compounds, in which the nitrogen is bonded to two phosphorus atoms, a competition should exist between the 3d-orbitals of the two phosphorus atoms for overlap with the nitrogen lone pair.

Evidence for π-bonding.

(1) Bond lengths:- These provide the major evidence for phosphorus-nitrogen $p\pi$-$d\pi$ bonding. The phosphorus-nitrogen bond length in the anion (XIX)[106,107] is generally accepted as approximating closely to a pure phosphorus-nitrogen single bond length.



(XIX)

The much shorter phosphorus-nitrogen bond lengths found in cyclophosphazene rings (generally between 1.53 Å and 1.62 Å [46]) and in phosphine imines (between 1.56 Å and 1.64 Å [99]) strongly indicate the presence of a considerable amount of π-bonding in these formally double bonded compounds. Values for many phosphorus-nitrogen single bonds lie between those found in phosphazenes and 1.77 Å (Table 1), explainable in terms of a smaller degree of $p\pi$-$d\pi$ bonding.

Phosphinoyl compounds (for which a considerable amount of structural data are available[99]) illustrate best the effects of electronegative and π-donor substituents on bond lengths (Table 3).

TABLE 3

The variation of P=O bond length with phosphorus substituent

Compound	P=O bond length (Å)
Me_3PO	1.479
Cl_3PO	1.449(5)
F_3PO	1.436(6)
$MeP(O)Cl_2$	1.448(5)
$Me_2NP(O)Cl_2$	1.47(2)
$PhP(O)Cl_2$	1.47(1)

Clearly, electronegative substituents reduce the phosphorus-oxygen bond length, whereas π-donor substituents increase the phosphorus-oxygen bond length - consistent with the trends expected if $p\pi$-$d\pi$ bonding is present in the phosphorus-oxygen bond.

(2) Planarity at nitrogen:- Planar geometry about nitrogen (in conjunction with bond length data) has been interpreted as evidence of $p\pi$-$d\pi$ bonding in silicon-nitrogen[108] and phosphorus-nitrogen[101,109] bonds, as this geometry provides greater π-overlap. On the other hand other possible reasons have been proposed to explain why nitrogen adopts a trigonal planar geometry. Glidewell[108] (using interatomic distances between substituents) argued that planarity at nitrogen can be equally well explained by steric interactions between substituents, causing the bond angles at nitrogen to open out. As bond lengths and substituent sizes are

similar, the arguments used may be equally applicable to many aminophosphorus compounds. Also an ab initio molecular orbital calculation on $H_2N{\cdot}PH_2$[110] indicates that planarity at nitrogen is due to an electron releasing inductive effect of the $-PH_2$ group, and not to $p\pi-d\pi$ bonding (- although another recent calculation[111] on the same compound predicted a slightly non-planar geometry about nitrogen). It should be noted that neither of these reasons precludes $p\pi-d\pi$ bonding, but only indicate that it may not be responsible for planarity at nitrogen.

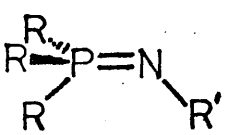
(3) Infra-red spectroscopy:- Probably the most reliable evidence using this technique, is work by Goldwhite and coworkers[112,113] in which they assigned the P=N stretch vibration of a number of phosphine imines to bands in the range 1330-1230 cm^{-1}, and argued that, as phosphorus-nitrogen single bond vibrations are generally assigned to bands in the region 850-650 cm^{-1}, the P=N bond could be regarded as a multiple bond.

(4) Barriers to phosphorus-nitrogen bond rotation:- Substantial rotational barriers about phosphorus-nitrogen single bonds (mainly in aminophosphines) have been observed and measured using variable temperature n.m.r. A number of factors have been suggested as possible contributors to these rotational barriers, including $p\pi-d\pi$ bonding.[109,114,115] Steric factors have been demonstrated to be important - rotational barriers increasing with increasing bulk of substituents on nitrogen,[109,116] although unexpectedly the opposite trend is observed on increasing the bulk of the R-group in compounds $RP(Cl)NMe_2$.[116] Evidence which has been used to support $p\pi-d\pi$ bonding as a possible contributor to phosphorus-nitrogen rotational barriers includes -

(a) the higher barriers to rotation found in unsymmetrical compounds $RP(Cl)NMe_2$, compared to the symmetrical compounds $R_2P{\cdot}NMe_2$ and $Cl_2P{\cdot}NMe_2$[109] (- due possibly to unsymmetrical substitution causing assymetry in the phosphorus 3d-orbitals);

(b) the lower barriers found in compounds $XP(R)NMe_2$ (X=F or Ph) compared to $ClP(R)NMe_2$.[114] (Both fluorine and phenyl groups are greater potential π-donors than chlorine - the latter also having a lower electronegativity - possibly leading to less $p\pi$-$d\pi$ bonding between phosphorus and nitrogen). The same argument has also been suggested as an explanation of the lower barrier to rotation in $Ph_2(S)P{\cdot}NPr^i_2$ compared to $Ph(S)P(Cl)NPr^i_2$.[115]

On the other hand there are indications that $p\pi$-$d\pi$ bonding, although probably present, makes little contribution to rotational barriers. Firstly the magnetic equivalence of the R-groups in phosphine imines (XX) even at low temperatures[112,113] has been used to show that a very low barrier to rotation exists in these formally phosphorus-nitrogen double bonds. This is probably due to the availability of more than one phosphorus 3d-orbital for π-bonding, whereas in the corresponding C=N- and -N=N- bonds the barrier to bond rotation can only be lowered by stabilisation of the zwitterionic



(XX)

R'=Me; R=Me, OMe or NMe_2

resonance forms. Secondly it has been suggested[117] that the observed phosphorus-nitrogen bond rotational barriers in compounds $Me_2NPCl_n(CF_3)_{2-n}$ (n=0,1 or 2) can be explained by a combination of steric effects and lone pair-lone pair repulsion only, (the difference in ionisation potential of the phosphorus and nitrogen lone pairs, measured from photoelectron spectra, being used as an inverse measure of lone pair-lone pair repulsion). It should be noted however that this method of estimating the magnitude of lone pair-lone pair repulsion has since been disputed.[118]

NOMENCLATURE.

A number of different nomenclature systems for phosphorus compounds are in common use. The following systems will be used here in the naming of compounds containing the P-NR-P and $\overline{\text{P-NR-P-N}}$ units.

(1) P-NR-P compounds:- The general name for compounds containing the monomeric P-NR-P unit will be nitrogen-bridged diphosphorus compounds. Individual compounds for nomenclature purposes are best classified as derivatives of amines. The type of phosphorus substituent are named as follows:

P-	phosphino	e.g. Cl_2P- dichlorophosphino
P(O)-	phosphinoyl	e.g. $(Me_2N)_2P(O)$- bisdimethylamino-phosphinoyl
P(S)-	phosphinothioyl	e.g. $Me_2N(Cl)P(S)$- chlorodimethyl-aminophosphinothioyl

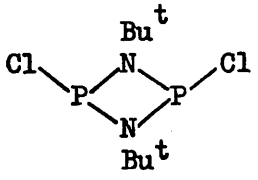
The phosphorus substituents are added as prefixes in alphabetical order e.g.

$Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$	dichlorophosphino(dichlorophosphinoyl) methylamine
$(Me_2N)_2(S)P{\cdot}NMe{\cdot}P(S)(NMe_2)$	bis(bisdimethylaminophosphinothioyl) methylamine
$Cl_2P{\cdot}NMe{\cdot}PPh_2$	dichlorophosphino(diphenylphosphino) methylamine.

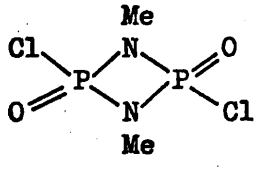
(2) $\overline{\text{P-NR-P-N}}$ compounds:- Two nomenclature systems are in current use for these compounds. The basic four-membered ring, from which the compounds are derived can be named as a cyclodiphosphazane (as proposed by Shaw and coworkers[119]) or, according to the

Chemical Abstracts system, as a 1,3,2,4-diazadiphosphetidine. The former system will be used here.

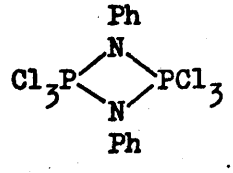
Compounds can be named as derivatives of cyclodiphospha(III)zane or cyclodiphospha(V)zanes, depending on the oxidation state of the ring phosphoruses. Nitrogen and phosphorus substituents are added as prefixes in alphabetical order, and the ring geometry can also be indicated e.g.



1,3-di(t-butyl)-2-cis-4-dichloro-cyclodiphospha(III)zane



2-trans-4-dichloro-1,3-dimethyl-2,4-dioxocyclodiphospha(V)zane



2,2,2,4,4,4 hexachloro-1,3-diphenyl-cyclodiphospha(V)zane.

NITROGEN-BRIDGED DIPHOSPHORUS COMPOUNDS.

Until the 1950's reports concerning the preparation of nitrogen-bridged diphosphorus compounds were very rare - the few compounds known having been prepared from cyclodiphosphazanes[3] or $[(HO)_2(O)P{\cdot}NH]_3$[120] by controlled alcoholysis or hydrolysis. In the last twenty years a number of new preparative routes to these compounds have been developed (notably by Russian workers, who have shown interest in nitrogen-bridged diphosphorus compounds as potential insecticides) resulting in a wide range of compounds now being known. Preparative routes to nitrogen-bridged diphosphorus compounds fall into several categories:

1. Various condensation reactions - which essentially involve the formation of the P-N-P unit from two mono-phosphorus compounds.
2. Rearrangements of phosphazenes containing the P=N-P unit.
3. Interconversion reactions of amino-bridged diphosphorus compounds.

Condensation reactions leading to nitrogen-bridged diphosphorus compounds.

Reactions of chlorophosphines with primary amines, their hydrochlorides, or their trimethylsilyl analogues lead often preferentially to condensed products such as cyclodiphospha(III)zanes or nitrogen-bridged diphosphorus compounds (see pp5-10). The reactions leading to the later compounds directly are summarised in Figure 1. The compounds formed by these reactions are normally thermally stable, one notable exception being bis(dichlorophosphino) aniline, $(Cl_2P)_2NPh$ which on heating[10] eliminates phosphorus

$$2\,PCl_3 + RNH_3^+Cl^- \longrightarrow (Cl_2P)_2NR + 3\,HCl$$

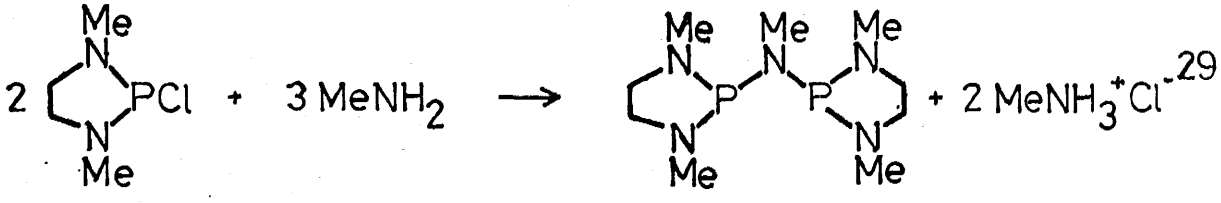
R = Me, Et[11] or Ph[9,10]

$$2\,PCl_3 + 3\,RNH_2 \longrightarrow (Cl_2P)_2NR + \text{other products}$$

R = Me or Et[12]

$$2\,Ph_2PCl + 3\,RNH_2 \longrightarrow (Ph_2P)_2NR + 2\,RNH_3^+Cl^-$$

R = Me, Et or Pr^n [27]



$$2\,X_2PCl + (Me_3Si)_2NMe \longrightarrow (X_2P)_2NMe + 2\,Me_3SiCl \qquad 3$$

X_2 = Cl_2[16]; Ph_2[28]; $(OR)_2$[25]; Ph,Cl[12]

$$2\,Ph_2PCl + (Me_3Si)_2NH \longrightarrow (Ph_2P)_2NH + 2\,Me_3SiCl + \text{other products}^{121}$$

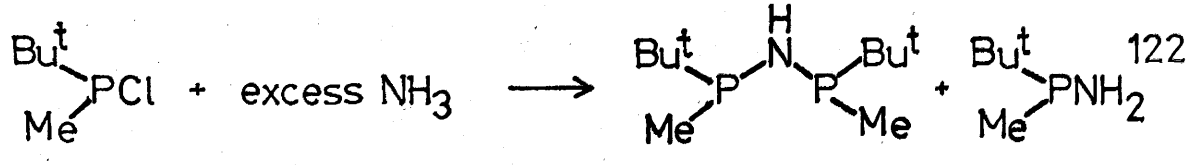


Figure 1

trichloride forming 2,4-dichloro-1,3-diphenylcyclodiphospha(III)zane. The formation of bis[chloro(phenyl)phosphino]methylamine, $[Ph(Cl)P]_2NMe$,[12] from dichlorophenylphosphine by direct aminolysis can only be accomplished using heptamethyldisilazane, as reaction using the free amine (as with other mono-substituted dichlorophosphines) does not lead to condensed products.[20] The intermediate in reaction 3 ($X_2=Ph_2$), $Ph_2P{\cdot}NMe{\cdot}SiMe_3$ obtainable by the reactions

$$\left.\begin{array}{l} Ph_2P{\cdot}NMeLi + Me_3SiCl \\ Ph_2PCl + LiMeN{\cdot}SiMe_3 \end{array}\right\rbrace \rightarrow Ph_2P{\cdot}NMe{\cdot}SiMe_3 + LiCl$$

has been shown[28] to be a useful substrate for condensation with chlorophosphorus electrophiles,

$$Ph_2P{\cdot}NMe{\cdot}SiMe_3 + ClP(X)Ph_2 \xrightarrow{-Me_3SiCl} Ph_2P{\cdot}NMe{\cdot}P(X)Ph_2$$

(X=lone pair or S)

$$Ph_2P{\cdot}NMe{\cdot}SiMe_3 + P(X)Cl_3 \xrightarrow{-Me_3SiCl} Ph_2P{\cdot}NMe{\cdot}P(X)Cl_2$$

(X=lone pair or O)

providing a preparative route to the formation of unsymmetrical nitrogen-bridged diphosphorus compounds containing tervalent phosphorus.

Unlike the analogous reactions with chlorophosphines, few aminolysis reactions of chlorophosphinoyl or chlorophosphinothioyl compounds lead directly to the formation of nitrogen-bridged diphosphorus compounds. Bis(dichlorophosphinoyl)aniline, $[Cl_2(O)P]_2NPh$, has been reported[123] to be the product of the reaction of a 1:1 mixture of aniline and triethylamine with excess phosphoryl chloride. Also hexamethyldisilazane reacts with two mol equiv. of dimethylphosphinothioyl bromide, $Me_2P(S)Br$, yielding bis(dimethylphosphinothioyl)amine, $[Me_2(S)P]_2NH$.[124] Interestingly the dimethyl hydrazine derivative, $Me_2NN(SiMe_3)_2$, reacts with two mol equiv. of phosphoryl chloride forming $[Cl_2(O)P]_2NNMe_2$,[125] whereas the corresponding reaction with heptamethyldisilazane yields the polymer $[MeNP(O)Cl]_n$[15].

A wide variety of nitrogen-bridged diphosphorus compounds containing quinquivalent phosphorus (including unsymmetrical derivatives) can be obtained from condensation reactions with disubstituted aminophosphorus compounds ($Y_2(X)P{\cdot}NHR$, X=lone pair, O or S; R=alkyl, aryl or $SiMe_3$) with halophosphorus compounds - the preparation of tetrahalo-substituted nitrogen-bridged diphosphorus compounds (Figure 2) being a prime example. These reactions are often very dependent on the relative nucleophilicities and electrophilicities of the aminophosphorus and chlorophosphorus substrates. By comparison of reaction conditions, the relative electrophilicities of chlorophosphorus compounds in reactions 4 were found[126] to decrease in the series $PCl_3 > P(O)Cl_3 > P(S)Cl_3$, the latter compound remaining unreactive. Also $Cl_2(S)P{\cdot}NMe{\cdot}SiMe_3$

$$Cl_2(X)P{\cdot}NMe{\cdot}SiMe_3 + PCl_3 \longrightarrow Cl_2(X)P{\cdot}NMe{\cdot}PCl_2 + Me_3SiCl$$

X = O or S [126]

$$Cl_2(X)P{\cdot}NMe{\cdot}SiMe_3 + P(O)Cl_3 \longrightarrow Cl_2(X)P{\cdot}NMe{\cdot}P(O)Cl_2 + Me_3SiCl$$

4 X = O or S [126]

$$Cl_2(O)P{\cdot}NHR + P(O)Cl_3 \xrightarrow{Et_3N} [Cl_2(O)P]_2NR$$

R = Me [126], Et or Ph [127]

$$Cl_2(S)P{\cdot}NHR + P(X)Cl_3 \xrightarrow{Et_3N} Cl_2(S)P{\cdot}NR{\cdot}P(X)Cl_2$$

X = O or S ; R = Me or Ph [128]

$$F_2(X)P{\cdot}NHMe + ClP(X)F_2 \xrightarrow{Me_3N} [F_2(X)P]_2NMe$$

X = O or S [129]

$$F_2P{\cdot}NMe{\cdot}SiMe_3 + PF_5 \longrightarrow F_2P{\cdot}NMe{\cdot}PF_4 + Me_3SiF$$ [130]

$$F_2(O)P{\cdot}NHR + ClP(X)F_2 \xrightarrow{Et_3N} F_2(O)P{\cdot}NR{\cdot}P(X)F_2$$

X = lone pair ; R = Me [130]

X = O ; R = Me, Et or Ph [127]

Figure 2

$$X_2(S)P{\cdot}NHMe + BrP(S)F_2 \xrightarrow{Et_3N} X_2(S)P{\cdot}NMe{\cdot}P(S)F_2$$

$X_2 = Cl_2$; F,Cl [131]

$$X_2(O)P{\cdot}NHMe + BrP(S)F_2 \xrightarrow{Et_3N} X_2(O)P{\cdot}NMe{\cdot}P(S)F_2 \qquad 5$$

$X_2 = Cl_2$; F,Cl [131]

$$Cl_2(O)P{\cdot}NHR + ClP(O)X_2 \xrightarrow{Et_3N} Cl_2(O)P{\cdot}NR{\cdot}P(O)X_2 \qquad 6$$

R = Me, Et or Ph

$X_2 = F_2$; F,Cl [127]

$$F_2(O)P{\cdot}NHMe + P(O)Cl_3 \xrightarrow{Et_3N} F_2(O)P{\cdot}NMe{\cdot}P(O)Cl_2$$

+ other products [127]

Figure 2 contd.

was found to be a poorer nucleophile than $Cl_2(O)P{\cdot}NMe{\cdot}SiMe_3$ towards the above electrophiles. The greater electrophilicity of difluorophosphinothioyl bromide, $F_2P(S)Br$, (reaction 5) compared with thiophosphoryl chloride towards $Cl_2(O)P{\cdot}NHMe$ is the probable reason why reaction only occurs with the former electrophile.[128,131] Finally $Cl_2(O)P{\cdot}NHMe$ (reaction 6) was shown[127] to be a better nucleophile than $F_2(O)P{\cdot}NHMe$ towards dichlorophosphinoyl fluoride, $Cl_2P(O)F$, and phosphoryl chloride, the latter nucleophile forming product mixtures with these phosphinoyl chlorides.

Several dimethylamino-derivatives of bis(dichlorophosphinoyl)-methylamine, $[Cl_2(O)P]_2NMe$,[132] and dichlorophosphino(dichloro-phosphinoyl)methylamine, $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$,[133] have been synthesised by similar condensation reactions using triethylamine (as an HCl trap) or trimethylsilylaminophosphinoyl substrates. A number of the reactions attempted did not yield the expected condensation product due probably to the lower electrophilicities associated with dimethylamino-substituted chlorophosphinoyl compounds. The tetrakisdimethylamino-derivative, $[(Me_2N)_2(O)P]_2NMe$, was prepared[134] earlier by a condensation route.

$$(Me_2N)_2(O)P{\cdot}NHMe + ClP(O)(NMe_2)_2 \xrightarrow{\text{pyridine}} [(Me_2N)_2(O)P]_2NMe$$

Analogous alkoxy-derivatives can be prepared similarly (Figure 3).

Predating most of the above work on condensation reactions involving dehydrochlorination and loss of trimethylsilylhalide, a large number of condensation reactions using metallated aminophosphorus compounds were investigated by some Russian

$$MeO(Cl)(O)P{\cdot}NMe{\cdot}SiMe_3 + PCl_3 \xrightarrow{-Me_3SiCl} MeO(Cl)(O)P{\cdot}NMe{\cdot}PCl_2 \quad ^{133}$$

$$(RO)_2(O)P{\cdot}NHR' + ClPX_2 \xrightarrow{Et_3N} (RO)_2(O)P{\cdot}NR'{\cdot}PX_2$$

$R = R' = Me$; $X_2 = Cl_2$ or MeO,Cl [133]

R = alkyl ; $R' = Et$; $X_2 = Cl_2$ or $(OEt)_2$ [135]

$$\left.\begin{array}{l} Me(RO)(O)P{\cdot}NHR' + ClP(O)(OR'')_2 \\ (R''O)_2(O)P{\cdot}NHR' + ClP(O)(OR)Me \end{array}\right\} \xrightarrow{Et_3N} Me(RO)(O)P{\cdot}NR'{\cdot}P(O)(OR'')_2$$

R, R' and R'' = alkyl [136]

$$Me(R_2N)(O)P{\cdot}NHR' + ClP(O)(OR)_2 \xrightarrow{Et_3N} Me(R_2N)(O)P{\cdot}NR'{\cdot}P(O)(OR)_2 \quad ^{137}$$

R = Me or Et ; R' = alkyl

$$(MeO)_2(S)P{\cdot}NHMe + PCl_3 \xrightarrow{Et_3N} (MeO)_2(S)P{\cdot}NMe{\cdot}PCl_2 \quad ^{138}$$

$$(MeO)_2(S)P{\cdot}NHMe + ClP(O)X_2 \xrightarrow{Et_3N} (MeO)_2(S)P{\cdot}NMe{\cdot}P(O)X_2$$

$X_2 = (alkoxy)_2$, Pr_2 or OPr, NEt_2 [138]

$$(RO)_2(O)P{\cdot}NHMe + ClP(O)(OR)_2 \xrightarrow{pyridine} [(RO)_2(O)P]_2NMe$$

R = alkyl [134]

$$(RO)_2(X)P{\cdot}NHR' + ClP(Y)(NR''_2)_2 \xrightarrow{pyridine} (RO)_2(X)P{\cdot}NR'{\cdot}P(Y)(NR''_2)_2$$

$X = Y = O, S$; $X = S, Y = O$

R, R' and R'' = alkyl [134]

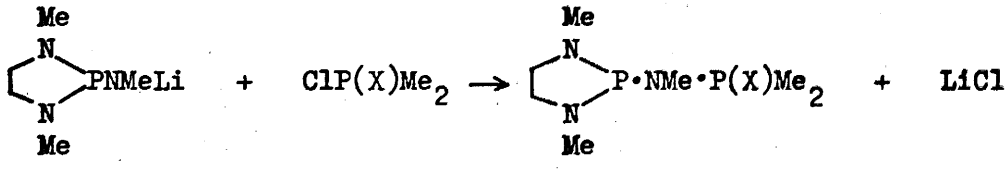
Figure 3

workers,[135,139-141] the bulk of the reactions being of the type

$$(RO)_2(O)P{\cdot}NR'Na + ClP(X)(OR)_2 \rightarrow (RO)_2(O)P{\cdot}NR'{\cdot}P(X)(OR)_2 + NaCl$$

(R=alkyl; R'=alkyl or aryl; X=lone pair, O or S)

Similar reactions with chlorophosphinoyl compounds $ClP(O)(NMe_2)_2$, $ClP(O)(OR)(NMe_2)$, and $ClP(O)(OR)R$ were also reported. Reactions closely related to these, using sodium metal or sodium hydride to effect condensation, have also appeared in the patent literature.[142-145] Similar condensation reactions in which alkoxy or aryloxy groups are not involved have also been reported,



X=lone pair or S[29]

$$Ph_2(O)P{\cdot}NPhK + ClP(O)Ph_2 \longrightarrow [Ph_2(O)P]_2NPH + KCl^{146}$$

A variety of condensation routes to the formation of nitrogen-bridged diphosphorus compounds, containing an NH-bridging unit, involving metals and their salts are known.[147-152]

Nitrogen-bridged diphosphorus compounds can also be formed from condensation reactions in which alkylchlorides are eliminated. These mainly involve reactions of chloraminophosphinoyl compounds

$$X_2(O)P{\cdot}N(Cl)R + (R'O)_3P \longrightarrow X_2(O)P{\cdot}NR{\cdot}P(O)(OR')_2 + R'Cl$$

R and R' = alkyl: X_2=$(OR)_2$; Me,OR[136,153]

$$(RO)_2(O)P{\cdot}N(Cl)Me + Cl_2PX \longrightarrow RO(Cl)(O)P{\cdot}NMe{\cdot}P(O)(Cl)X + RCl$$

X = Cl or Ph[154]

Similarly reaction of the chlorosulphenylamino compound, $(EtO)_2(O)P{\cdot}NMe{\cdot}SCl$, with chlorophosphites was shown[155] to provide a novel pathway to the formation of phosphinothioyl(phosphinoyl) methylamines.

$$(EtO)_2(O)P{\cdot}NMe{\cdot}SCl + 2\ ClP(OR)X \xrightarrow{-RCl} (EtO)_2(O)P{\cdot}NMe{\cdot}P(S)(OR)X + Cl_2P(O)X$$

(X=Cl or OR)

Lastly ethylchloride is eliminated in some condensation reactions of ethoxy-substituted phosphine imines with chlorophosphinoyl compounds[156]

$$(EtO)_3P{=}NR + ClP(O)(OEt)_2 \longrightarrow [(EtO)_2(O)P]_2NR + EtCl$$

(R=Me or Ph)

$$Ph_2(EtO)P{=}NPh + ClP(O)Ph_2 \longrightarrow [Ph_2(O)P]_2NPh + EtCl$$

Reactions of phosphazenes containing the P=N-P unit

A number of phosphazenes (mainly chloro-derivatives) containing the monomeric P=N-P unit can be easily converted into nitrogen-bridged diphosphorus compounds containing NH-bridging units by hydrolysis and closely related reactions (Figure 4). Whereas the reactions of H_2O and HCl with phosphazenes containing groupings of the type $-N{=}PX_2Cl$ and $-N{=}PX_2OR$ respectively provide general routes to these amino-bridged diphosphorus compounds,

$$Ph_2(S)P{-}N{=}PPh_2Cl + H_2O \longrightarrow Ph_2(S)P{\cdot}NH{\cdot}P(O)Ph_2 + HCl$$ [157]

$$Cl_2(O)P{-}N{=}PPh_2Cl + 3\,H_2O \longrightarrow (HO)_2(O)P{\cdot}NH{\cdot}P(O)Ph_2 + 3\,HCl$$ [158]

$$(RO)_2(O)P{-}N{=}PCl_3 + 3\,H_2O \longrightarrow (RO)_2(O)P{\cdot}NH{\cdot}P(O)(OH)_2 + 3\,HCl$$

R = alkyl [159]

$$X_2(O)P{-}N{=}PY_2OR + HCl \longrightarrow X_2(O)P{\cdot}NH{\cdot}P(O)Y_2 + RCl$$ [160,161]

X and Y = alkyl or alkoxy

$$(RO)_2(S)P{-}N{=}P(OR)_3 + HCl \longrightarrow (RO)_2(S)P{\cdot}NH{\cdot}P(O)(OR)_2 + RCl$$

R = alkyl [161]

$$Cl_3P{=}N{-}P(O)Cl_2 + Me_2SO \longrightarrow [Cl_2(O)P]_2NH + ClCH_2SMe$$ [169]

$$Cl_3P{=}N{-}P(O)Cl_2 + \text{excess ROH } Et_3N \longrightarrow [(RO)_2(O)P]_2NH$$ [170]

R = alkyl

Figure 4

$Cl_3P{=}N{-}P(X)(OPh)_2 + HCO_2H \longrightarrow Cl_2(O)P{\cdot}NH{\cdot}P(X)(OPh)_2 + CO + HCl$

X = O or S[162]

$Cl_3P{=}N{-}P(O)X_2 + HCO_2H \longrightarrow Cl_2(O)P{\cdot}NH{\cdot}P(O)X_2 + CO + HCl$

X = Cl[163] or F[164]

$ClF_2P{=}N{-}P(S)X_2 + HCO_2H \longrightarrow F_2(O)P{\cdot}NH{\cdot}P(S)X_2 + CO + HCl$ 7

X_2 = Cl_2, F_2 or F,Cl[165]

but $Cl_3P{=}N{-}P(S)X_2 + HCO_2H \longrightarrow$ no reaction[166] 8

$Cl_3P{=}N{-}P(O)(R)X + HCO_2H \longrightarrow Cl_2(O)P{\cdot}NH{\cdot}P(O)(R)X + CO + HCl$

R = Me or $ClCH_2$; X = aryloxy[167]

R = Cl_3C ; X = Cl[168]

but $X(R)(Cl)P{=}N{-}P(O)Cl_2 + HCO_2H \longrightarrow X(R)(Cl)P{=}N{-}P(O)(Cl)OH + CO + HCl$

R = Me or $ClCH_2$; X = Cl or OAr[168]

Figure 4 contd.

not all reactions of formic acid with phosphazenes of the former type proceed as expected. Compounds $Cl_3P{=}N{-}P(S)X_2$ are much less reactive than $ClF_2P{=}N{-}P(S)X_2$ to formic acid (reactions 7 and 8), remaining unreactive at 60°C,[166] whereas the latter react smoothly at ambient temperatures.[165] Also whereas phosphazenes $Cl_3P{=}N{-}P(O)(R)X$ react with formic acid as expected[167,168] the related compounds $X(R)(Cl)P{=}N{-}P(O)Cl_2$ undergo hydrolysis at the phosphinoyl centre[168] (reactions 9 and 10). The reasons for these differing reactivities are not as yet clear.

Several methoxy- and ethoxy-phosphazenes undergo rearrangement at high temperatures forming methylamino- and ethylamino-bridged diphosphorus compounds,[171]

$$(RO)_3P{=}N{-}P(O)(OMe)_2 \xrightarrow{\Delta} (RO)_2(O)P{\cdot}NR{\cdot}P(O)(OMe)_2 \quad (R{=}Me \text{ or } Et)$$

It was later shown that the course of thermal rearrangement of similar phosphazenes was temperature dependent:[157]

$$(RO)_3P{=}N{-}P(O)(OEt)Me \xrightarrow{170^\circ} (RO)_2(O)P{\cdot}NR{\cdot}P(O)(OEt)Me$$
$$\xrightarrow{130^\circ} (RO)_2(O)P{-}N{=}P(Me)(OEt)(OR) \qquad (R{=}Me,Et)$$

Reactions of nitrogen-bridged diphosphorus compounds.

Included here are reactions of cyclodiphosphazanes which lead to the formation of nitrogen-bridged diphosphorus compounds. Michaelis showed[3] that hydrolysis and alcoholysis reactions of cyclodiphosphazanes $(ArP(O)NAr)_2$ and $(PhNHP(O)NPh)_2$ lead initially to nitrogen-bridged diphosphorus compounds, and this reaction has

been extended[47] to include a number of other nucleophiles. Reactions normally require high temperatures to cleave the ring phosphorus-nitrogen bond. Two notable exceptions involve reactions of (XXI) and its 2,4-dioxo analogues, (XXII) (R=Me or aryl).

$$[Cl(S)PNMe]_2 \quad (XXI) \quad + \text{ excess } MeNH_2 \longrightarrow [(MeNH)_2(S)P]_2NMe^{173}$$

$$[Cl(O)PNR]_2 \quad (XXII) \quad + \; HCl \longrightarrow Cl_2(O)P{\cdot}NR{\cdot}P(O)(Cl)NHR^{174}$$

which both proceed at ambient temperatures.

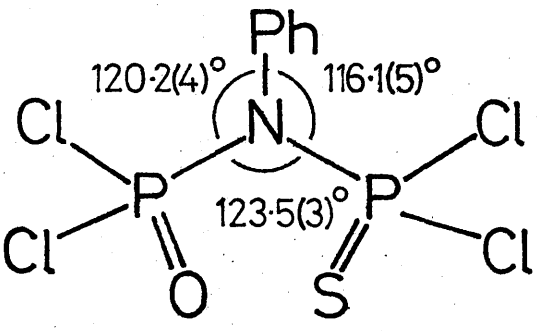
Tervalent phosphorus in nitrogen-bridged diphosphorus compounds can undergo a number of oxidation reactions. Reaction with elemental sulphur, on heating, or occasionally at ambient temperatures, yields the corresponding phosphinothioyl compound.[29,126,135,140] Sulphuration of diphosphorus(III) nitrogen-bridged diphosphorus compounds occurs in a stepwise manner, a similar behaviour being found with bis(diphenylphosphino-methylamino)phenylphosphine, $(Ph_2P{\cdot}NMe)_2PPh$.[175] Formation of a phosphinoyl group by oxidation of tervalent phosphorus can be effected by nitrogen dioxide,[135] or activated manganese dioxide.[20] Apparently oxidation by dimethyl sulphoxide[176] has not been reported in nitrogen-bridged diphosphorus compounds, although oxidation of cyclodiphosphazanes containing tervalent phosphorus has been reported[12] by this method. Lastly reaction of bis(diphenylphosphino) alkylamines, $(Ph_2P)_2NR$[27], and bis(diphenylphosphinoalkylamino)-phenylphosphines, $(Ph_2P{\cdot}NR)_2PPh$,[175] with alkyl iodides yields only

mono-quaternised products.

A number of substitution reactions, mainly involving chlorophosphorus amino-bridged diphosphorus compounds have been reported. Aminolysis[138,162,163,177] (using excess amine) and alcoholysis[135,162] (using excess ROH/Et_3N or NaOR) of chlorophosphorus centres have been used to prepare amino- and alkoxy-derivatives, but of more interest are studies of the substitution patterns of aminolysis in bis(dichlorophosphinoyl)-methylamine, $[Cl_2(O)P]_2NMe$,[132] and of aminolysis and alcoholysis in dichlorophosphino(dichlorophosphinoyl)methylamine, $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$[133] (see Chapter 2). Fluorination of bis(dichlorophosphino)amines, $(Cl_2P)_2NR$ (R=Me, Et or aryl) with antimony trifluoride[11,12] yields the tetrafluoro-derivatives $(F_2P)_2NR$, although reaction of $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$[178] and $[Cl_2P(O)]_2NMe$[127] with sodium fluoride gave only low yields of their tetrafluoro-derivatives. Lastly a few substitution reactions of alkoxy-derivatives of amino-bridged diphosphorus compounds are known[135,155,179,180] many of which involve simultaneous oxidation.

Structural Data.

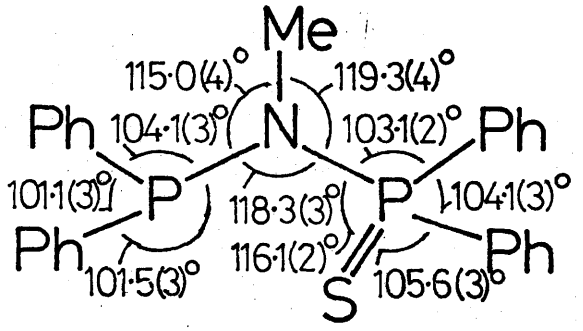
Little structural data on nitrogen-bridged diphosphorus compounds is currently available. Data from X-ray crystal structure investigations of $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$, $Ph_2P{\cdot}NMe{\cdot}P(S)Ph_2$,[101] and $(H_2N)_2(S)P{\cdot}NMe{\cdot}P(S)(NH_2)NHMe$,[181] and from an electron diffraction study of $F_2P{\cdot}NMe{\cdot}PF_2$[102] are shown in Figure 5.



(O)P—N 1·651(6) Å

(S)P—N 1·690(6) Å

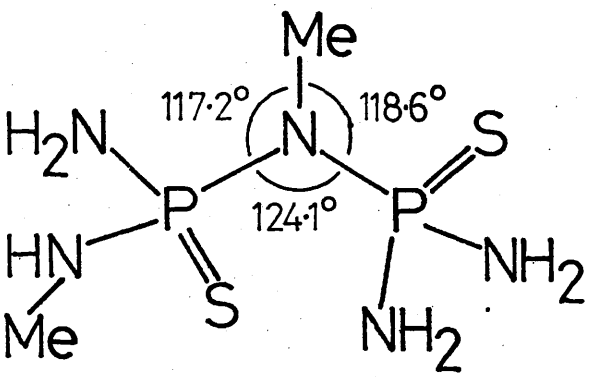
P.....P separation 2·94(2) Å



Ph_2P—N 1·719(4) Å

$Ph_2(S)P$—N 1·680(4) Å

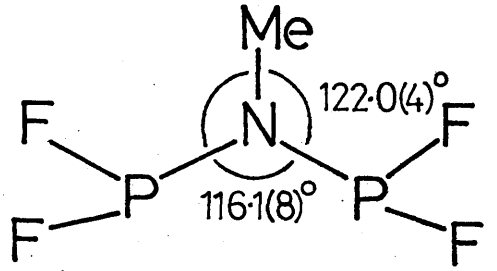
P.....P separation 2·92(1) Å



MeNH(H_2N)P—N 1·689(11) Å

$(H_2N)_2$P—N 1·727(14) Å

P.....P separation 3·02(4) Å



P—N 1·680(6) Å

P.....P separation 2·85(3) Å

Figure 5.

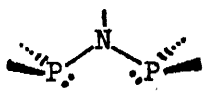
Planar distribution of bonds about nitrogen are found in all these compounds except $Ph_2P{\cdot}NMe{\cdot}P(S)Ph_2$ where the sum of angles around nitrogen is ca 353°. All intramolecular P.....P interatomic distances are less than twice the phosphorus Van der Waal's radius (3.60 Å) suggesting that steric factors may at least be partially responsible for the planar or near planar geometry around nitrogen, although as Glidewell pointed out[108] such conclusions have greater reliability if based on structural data obtained from compounds in the gas phase. Another possible reason for the tendency of the bridging nitrogen to adopt a planar geometry in these compounds is that this geometry leads to an optimisation of $p\pi$-$d\pi$ bonding in the P-N bonds.

All P-N bond lengths are considerably shorter than the generally accepted P-N single bond length (1.77 Å),[106,107] implying that some degree of $p\pi$-$d\pi$ bonding is present. Significant differences in the P-N bond lengths are found in the unsymmetrical compounds $Cl_2(O)P{\cdot}NPh{\cdot}P(S)Cl_2$ and $Ph_2P{\cdot}NMe{\cdot}P(S)Ph_2$, from which it was suggested that variations in theP-N bond lengths are largely dependent on variations in the formal positive charge on phosphorus, which may be expected to increase in the orders

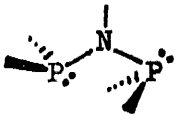
$$N\text{-}PX_2 < N\text{-}P(S)X_2 \text{ and } N\text{-}P(S)X_2' < N\text{-}P(O)X_2'$$

Increased positive charge on phosphorus is therefore expected to result in increased $p\pi$-$d\pi$ overlap, although it should be noted that differences in P-N bond lengths will also be dependent on differences in phosphorus hybridisation, this being more evident in $Ph_2P{\cdot}NMe{\cdot}P(S)Ph_2$ (cf. phosphorus bond angles[182] in Figure 5).

It has been suggested that temperature dependent variations in $^{2}J(P\text{-}N\text{-}P)$ in $(F_2P)_2NR$ (R=Me or Et)[183,184] may be due to variations in rotamer populations, thus it is interesting to discover that the gas phase electron diffraction study of $(F_2P)_2NMe$ shows that the major conformer is a.



a



b

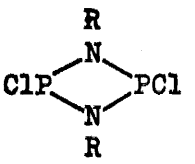
It is possible that, as the presence of a second rotamer (b) (formed from a by rotation of one P-N bond through 180°) in amounts <15% could not be ruled out,[102] the variable temperature n.m.r. data is due to slight variations in the relative populations of rotamers a and b. Recently conformations similar to rotamer a have been suggested for $(F_2P)_2NH$[185] on the basis of infra-red data.

CYCLODIPHOSPHAZANES.

Although cyclodiphosphazanes were first reported at the end of the last century,[7] most of the chemistry of these compounds has only been unfolded in the last twenty years. Reviews describing the chemistry of cyclodiphosphazanes have also recently appeared.[46,47] The following survey outlines synthetic routes to these small ring compounds and describes some of their structural features.

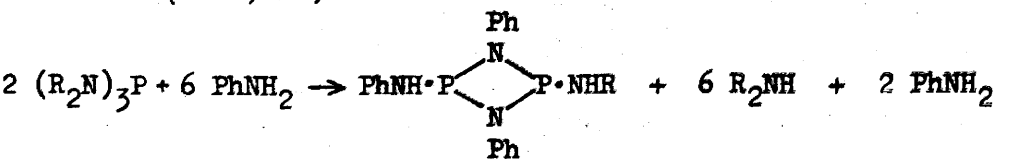
Cyclodiphospha(III)zanes (three coordinate phosphorus).

Relatively few compounds of this type have been reported, the major route to these compounds being the reaction of phosphorus trichloride with primary amines (see pp.5 - 8). Thus 2,4-dichlorocyclodiphospha(III)zanes (V) R=aryl are formed in reactions of primary aromatic amines[10] or their hydrochlorides[7,10] with excess phosphorus trichloride, while (V) R=Et, Pr^i or Bu^t can be prepared using phosphorus trichloride and three mol equiv. of the corresponding primary amine.[12] A report[15] that (V) R=Me is the product of the reaction of phosphorus trichloride with heptamethyldisilazane has not been substantiated by other workers.[12,16] The reactions of phosphorus trichloride with $Bu^t(Me_3Si)NLi$ and of (dichlorophosphino)t-butylamine, $Cl_2P{\cdot}NHBu^t$, with triethylamine also lead to (V) R=Bu^t.[13] This compound can be fluorinated by antimony trifluoride[186] yielding 1,3-di(t-butyl)2,4-difluoro-cyclodiphospha(III)zane, $(FPNBu^t)_2$. Fully aminolysed derivatives $RNHP{\cdot}NR{\cdot}P(NHR)NR$ (R=aryl or Bu^t) can also be prepared from phosphorus trichloride and excess primary alkylamine[14] or arylamine.[7-9]



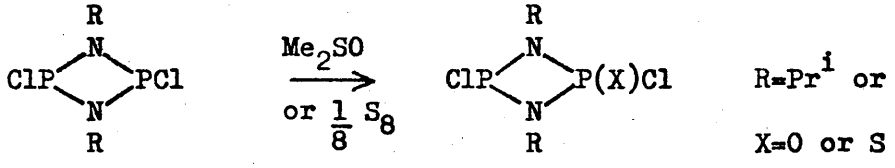
(V)

The reaction of tris(dimethylamino)phosphine[6] or tris(diethylamino)phosphine[187] with aniline provides another route to $PhNHP{\cdot}NPh{\cdot}P(NHPh)NPh$,



whereas reaction of aromatic sulphonylamines, $ArSO_2NH_2$ with chlorophosphino diamides, $(RR'N)_2PCl$ (R=Me, R'=Me or Ph) in the presence of tertiary amine yields $(RR'N)\overline{P{\cdot}N(SO_2Ar){\cdot}P(NRR'){\cdot}}NSO_2Ar$.[188] Bis(benzylamino)pentafluorophosphine, $(PhCH_2NH)_2PC_6F_5$, unlike other bis(alkylamino)arylphosphines, decomposes thermally to give $PhCH_2NH\overline{P{\cdot}NCH_2Ph{\cdot}P(NHCH_2Ph)}NCH_2Ph$ and C_6F_5H.[21]

The controlled oxidation and sulphuration of (V) (R=Pr^i or Bu^t) provide as yet the only reported routes to mixed oxidation state cyclodiphosphazanes.[12]



Cyclodiphospha(V)zanes (four coordinate phosphorus).

An extensive range of compounds of this type is known. The major route to their formation is the thermolysis of primary aminophosphinoyl and aminophosphinothioyl derivatives[46,47] (Figure 6) - many of which are formed as reaction intermediates, which, under the conditions employed, further react to give cyclodiphospha(V)zanes (for example the prolonged heating of primary amines or their hydrochlorides with chlorophosphinoyl or chlorophosphinothioyl substrates). In all these reactions some polymerisation can occur, especially when more forcing conditions are necessary. Reactions in which hydrogen chloride is evolved can only in a few cases be aided by the use of tertiary amines,[47,189] and one instance of the use of Grignard reagents as dehydrochlorinating

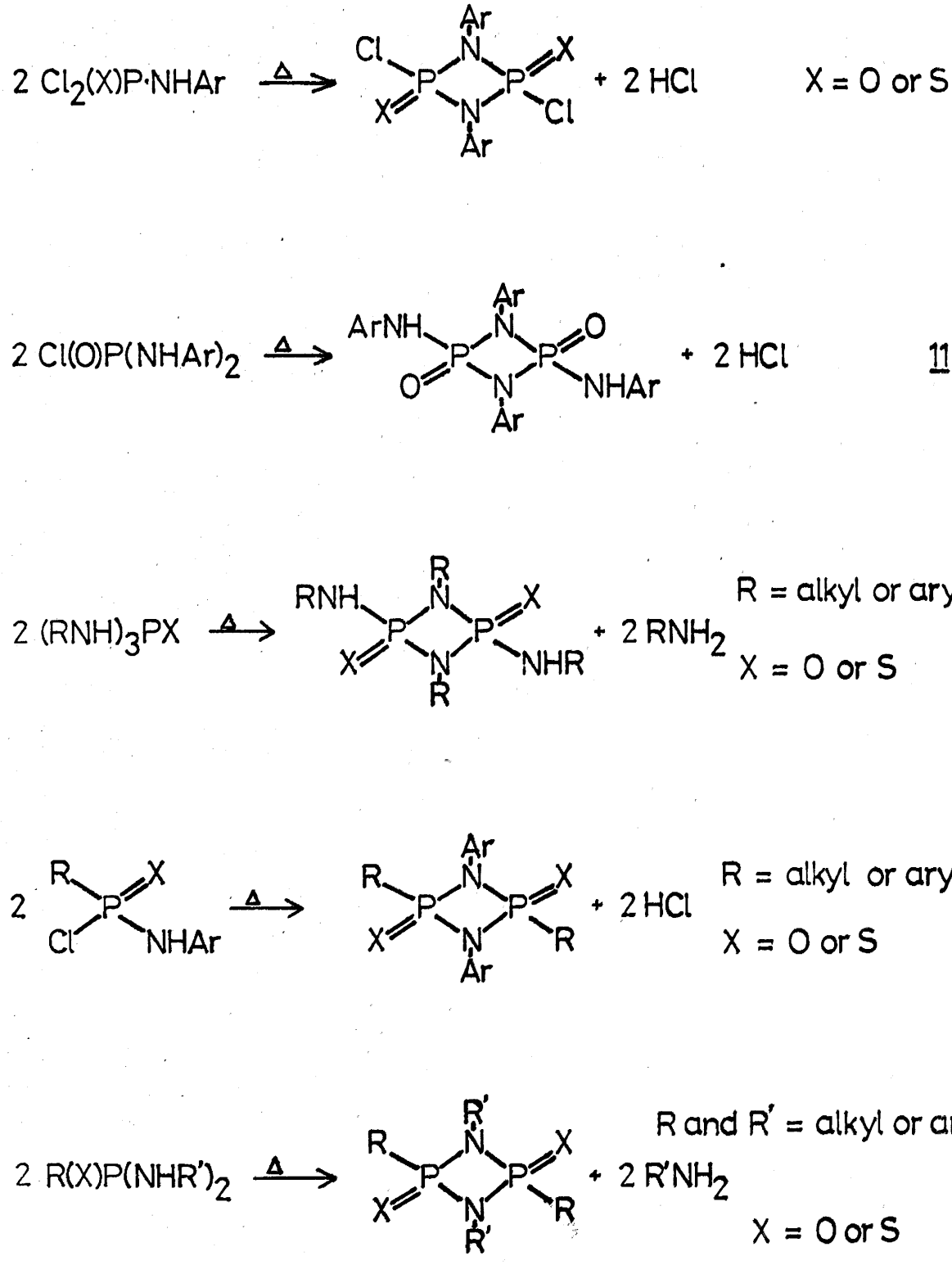
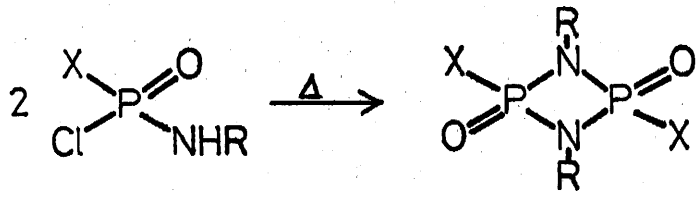

2 Cl2(X)P·NHAr
Δ
Cl
Ar
N
X
P
P
X
N
Cl
Ar
+ 2 HCl
X = O or S
2 Cl(O)P(NHAr)2
Δ
ArNH
Ar
N
O
P
P
O
N
NHAr
Ar
+ 2 HCl
11
2 (RNH)3PX
Δ
RNH
R
N
X
P
P
X
N
NHR
R
+ 2 RNH2
R = alkyl or aryl
X = O or S
2
R
X
P
Cl
NHAr
Δ
R
Ar
N
X
P
P
X
N
R
Ar
+ 2 HCl
R = alkyl or aryl
X = O or S
2 R(X)P(NHR')2
Δ
R
R'
N
X
P
P
X
N
R
R'
+ 2 R'NH2
R and R' = alkyl or aryl
X = O or S

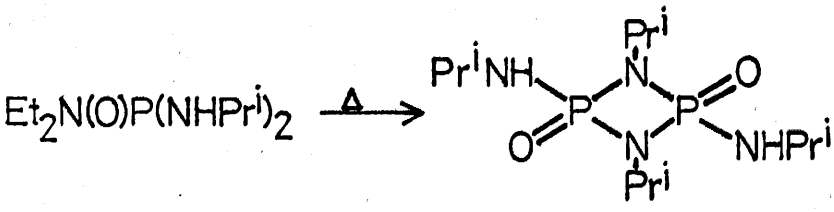
Figure 6.



+ 2 HCl 12

R = aryl ; X = alkoxy or 2° amino

R = Pr^i ; X = NEt_2



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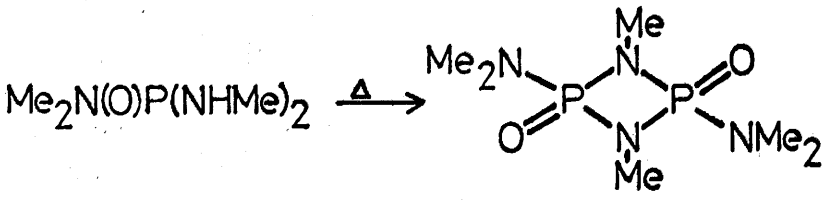
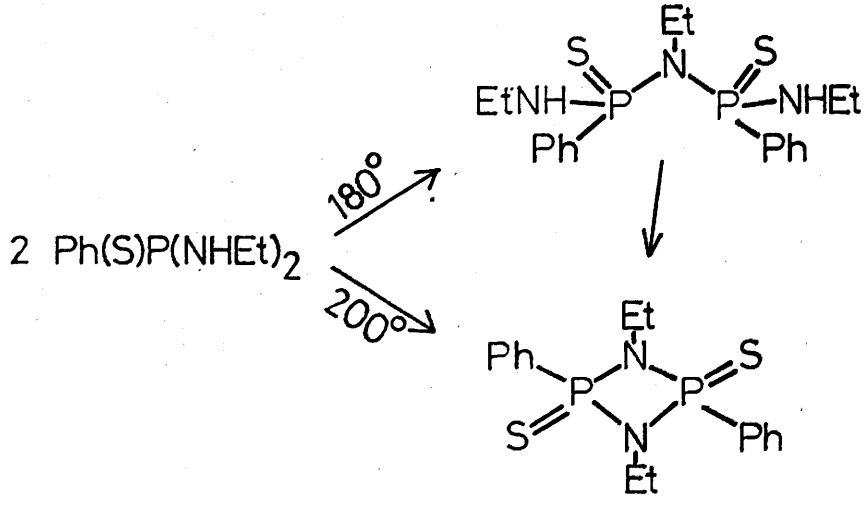
but 

14

Figure 6 contd.

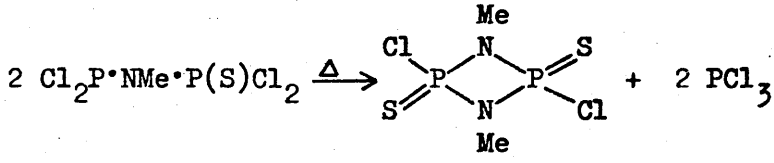
agents has been reported.[190] Reactions (11) and (12) (X= secondary amino) illustrate that hydrogen chloride is eliminated in preference to amine; while in thermolyses of mixed triamino-derivatives $R_2N(O)P(NHR')_2$, in which either the primary or the secondary amine can be eliminated, the more volatile is lost (cf. reactions (13) and (14)). Reaction of $(Me_2N)_3PO$ with primary aromatic amines similarly yields on heating[191] $[Me_2N(O)PNAr]_2$ plus dimethylamine, presumably via the intermediate $(Me_2N)_2(O)P{\cdot}NHAr$.

There is evidence to suggest that at least some of these thermolyses leading to cyclodiphosphazanes may proceed via nitrogen-bridged diphosphorus intermediates. Ibrahim and Shaw[192] found that thermolysis of the diamide $Ph(S)P(NHEt)_2$ yields a nitrogen-bridged diphosphorus compound at a lower temperature than that required for cyclodiphosphazane formation,



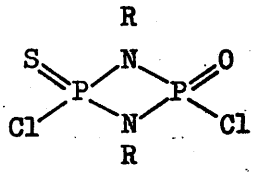
although this behaviour was apparently not observed for diamides $Ph(S)P(NHR)_2$ (R=Me or CH_2Ph).[193] The ability of the analogous nitrogen-bridged compound $[(MeNH)_2(S)P]_2NMe$ to cyclise eliminating methylamine has also been demonstrated.[173]

A few chloro-derivatives of nitrogen-bridged diphosphorus compounds also react to form cyclodiphosphazanes. Kukhar' showed[174] that compounds $Cl_2(O)P{\cdot}NR{\cdot}P(O)(Cl)NHR$ (R=Me or aryl) cyclise with ease in the presence of tertiary amine. Dichlorophosphino-(dichlorophosphinothioyl)methylamine, $Cl_2P{\cdot}NMe{\cdot}P(S)Cl_2$ is thermally unstable and forms the 2,4-dithiocyclodiphosphazane(XXIII) on heating.[128]

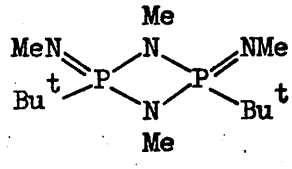


(XXIII)

2,4-dioxo and 2,4-dithiocyclodiphospha(V)azanes can be formed by a number of routes from other cyclodiphosphazanes. Hexachlorocyclodiphosphazanes, $(Cl_3PNR)_2$, can be easily converted into the corresponding 2,4-dioxo compounds $[Cl(O)PNR]_2$ with sulphur dioxide, while reaction with hydrogen sulphide in the presence of tertiary amine forms the 2,4-dithio analogues.[46,47] Reaction of cis$(ClPNBu^t)_2$ with dimethyl sulphoxide led unexpectedly to trans$[Cl(O)PNBu^t]_2$, indicating that oxidation occurs stereospecifically by a mechanism involving both inversion and retention of configuration.[194] Treatment of $(ClPNR)_2$ ($R=Pr^i$ or Bu^t) with $\frac{1}{8}$th mol equiv. S_8 followed by dimethyl sulphoxide yields 2-oxo-4-thiocyclodiphospha(V)zanes(XXIV).[12] Phenyl isothiocyanate,



(XXIV) ($R=Pr^i$ or Bu^t)



(XXV)

PhNCS, converts the diimidocyclodiphosphazane(XXV) into its 2,4-dithio analogue, $[Bu^t(S)PNMe]_2$.[189]

2,4-dichlorocyclodiphospha(V)zanes, $[Cl(X)PNR]_2$ (X=O or S), undergo chlorine substitution reactions with a number of nucleophiles[46,47] - for example primary and secondary amines, trimethylsilylamines and sodium alkoxides. Generally only when excess nucleophile is used, often in conjunction with more forcing reaction conditions, do ring opening reactions occur.

Cyclodiphospha(V)zanes (five-coordinate phosphorus).

In many cases a fine balance exists between the relative thermodynamic stabilities of give coordinate cyclodiphospha(V)zanes and their monomeric form, phosphine imines. Reactions of chlorophosphoranes with aromatic amines of low basicity[68] or highly branched aliphatic amines[76] lead only to the monomeric product. Monomers can often be formed in solution on heating,[68,80] which revert to cyclodiphosphazanes on solvent evaporation. Also substitution reactions of five coordinate cyclodiphosphazanes can lead to monomeric products - for example the reactions of hexachlorocyclodiphosphazanes, $(Cl_3PNR)_2$ with diethylamine, alcohols and chlorine gas.[46,47]

Reactions of acyclic substrates leading to the formation of five coordinate cyclodiphosphazanes are summarised in Figure 7. As discussed previously (page 14) compounds of this type are obtained directly from reactions of chlorophosphoranes with primary amines or their hydrochlorides. Similar methods have been developed

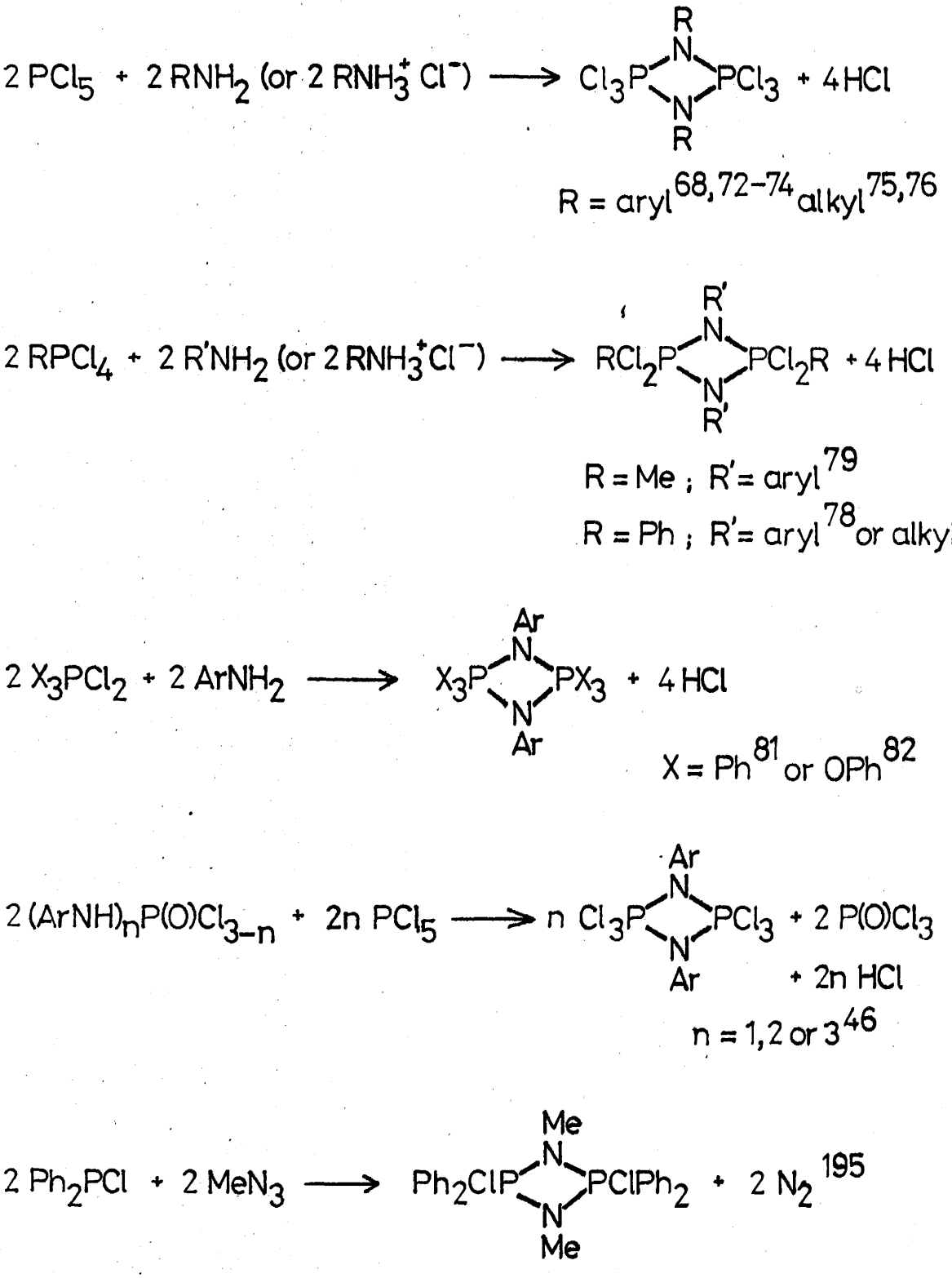
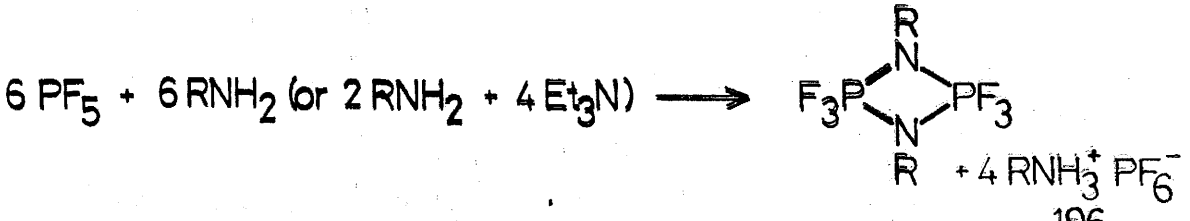
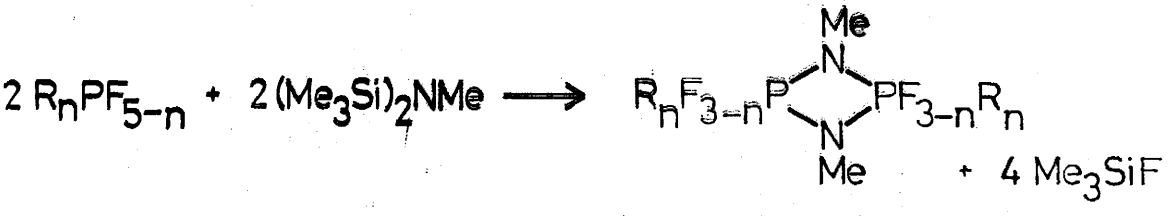
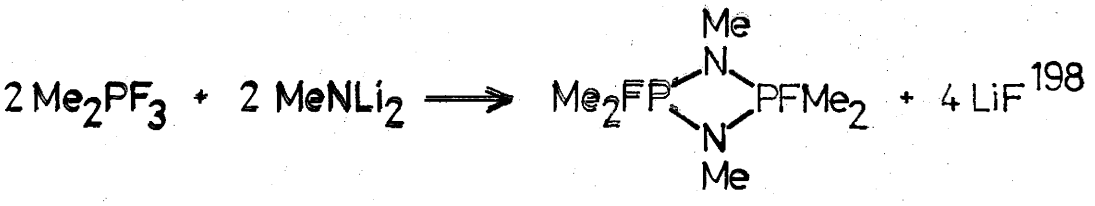

2 PCl5 + 2 RNH2 (or 2 RNH3+ Cl−) ⟶ Cl3P(NR)2PCl3 + 4 HCl
R = aryl[68,72-74] alkyl[75,76]
2 RPCl4 + 2 R'NH2 (or 2 RNH3+Cl−) ⟶ RCl2P(NR')2PCl2R + 4 HCl
R = Me ; R' = aryl[79]
R = Ph ; R' = aryl[78] or alkyl[80]
2 X3PCl2 + 2 ArNH2 ⟶ X3P(NAr)2PX3 + 4 HCl
X = Ph[81] or OPh[82]
2 (ArNH)nP(O)Cl3−n + 2n PCl5 ⟶ n Cl3P(NAr)2PCl3 + 2 P(O)Cl3 + 2n HCl
n = 1,2 or 3[46]
2 Ph2PCl + 2 MeN3 ⟶ Ph2ClP(NMe)2PClPh2 + 2 N2 [195]

Figure 7.







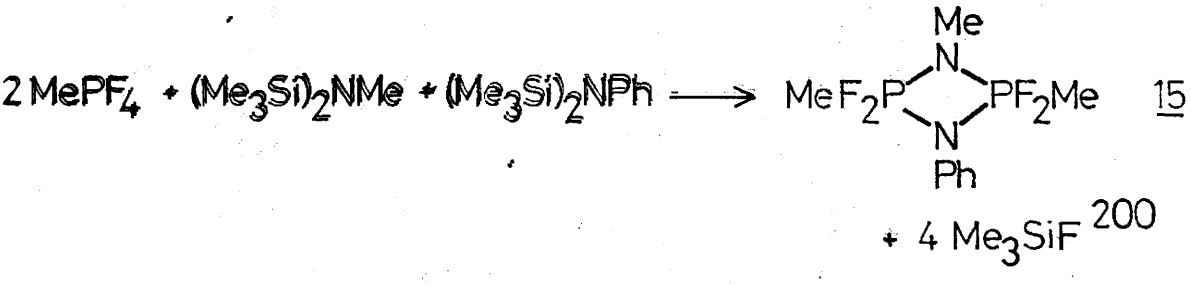
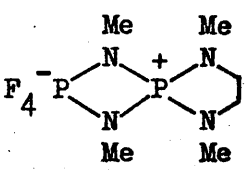


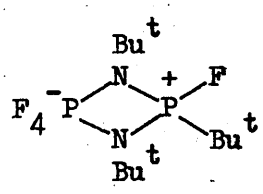
Figure 7 contd.

using fluorophosphoranes as substrates - one of the more versatile routes being reaction with heptamethyldisilazane,[46,197-199] although when the less reactive dialkyl/aryltrifluorophosphoranes are involved, it is preferable to use the more reactive lithiated amine, $MeNLi_2$.[198] Reaction 15 is remarkable in that apparently neither of the symmetrical cyclodiphosphazanes $(MeF_2PNR)_2$ (R=Me or Ph) are formed, although as yet no experimental details have been published.

Until recently, few examples of substitution reactions resulting in the four membered ring being retained, were known. Fluorination of hexachlorocyclodiphosphazanes, $(Cl_3PNR)_2$ by antimony trifluoride yields the hexafluorocyclodiphosphazanes, $(F_3PNR)_2$.[46,47] Halogen exchange, leading to the formation of a range of mixed chloro/fluoro-derivatives, occurs on heating together hexachloro and hexafluoro 1,3 dimethylcyclodiphosphazanes.[201] Recently, however, Harris, Schmutzler and coworkers prepared a number of methyl and methoxy-derivatives of $(F_3PNMe)_2$ (including the first known asymmetrical substituted derivatives) by reaction with MeHgI or LiMe, and LiOMe.[198,200] Also reactions of $(F_3PNMe)_2$ with $LiMeN{\cdot}CH_2CH_2{\cdot}NMeLi$ and $(F_3PNBu^t)_2$ with Bu^tLi unexpectedly led to zwitterionic cyclodiphosphazanes (XXVI) and (XXVII).[202]



(XXVI)



(XXVII)

Structural Features.

Because of the inherent nature of the four membered ring most cyclodiphosphazanes can exist in two possible isomeric forms:

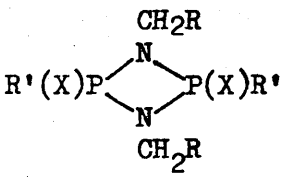
(X=lone pair, O or S etc.)

Isomers have been detected and in many cases structural assignments made using a number of means.

(1) N.m.r.:- The first observation[193] of the existence of two geometrical isomers was made from the ^{1}H n.m.r. of a sample of 1,3-dimethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazane, $[Ph(S)PNMe]_2$, in which two methyl proton triplets in a 10:1 ratio were found. Since then a number of further examples of isomer mixtures have been detected using n.m.r., and in some cases structural assignments have been made. In five coordinate cyclodiphospha(V)zanes of the type $(RF_2PNMe)_2$ it has been shown[198,200,203] that concerted pseudorotation at the phosphoruses can occur leading to gauche $\rightleftharpoons$ trans isomerisation. In some cases this isomerisation can be slowed on

the n.m.r. time scale, allowing the observation of both isomers.

Identification of trans isomers of cyclodiphosphazanes of the general type (XXVIII) has been made[204] using the fact that in the trans isomer the methylene protons are diastereotopic - giving rise to an AB quartet of signals - whereas in the cis isomer the methylene protons are magnetically equivalent, assuming free C-N bond rotation (Figure 8).



(XXVIII)

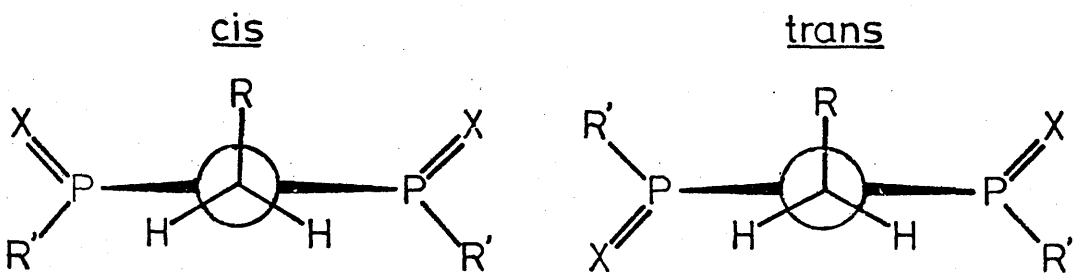


Figure 8.

(2) Vibrational spectroscopy:- Use has been made of the centrosymmetric nature of the trans isomer of $[Ph(S)PNEt]_2$[211] which results in the infra-red and raman spectra being complementary (no coincident bands), whereas for the cis isomer ten coincident bands were found. This structural assignment method can probably be extended to other symmetrically substituted cyclodiphosphazanes.

(3) X-ray crystallography:- Structures of a number of cyclodiphosphazanes have been determined (Table 4) using X-ray crystallography in all cases except in that of $(F_3PNMe)_2$.

Table 4 - Cyclodiphosphazanes, selected structural data.

Compound (ref)	P-N* Å	$\widehat{PNP}$	$\widehat{NPN}$	P...P Å	N....N Å
$[Cl(S)PNMe]_2$ [205]	1.67	96°	84°	2.48	2.23
$(Cl_3PNMe)_2$ [206]	1.769(7);1.635(7)	99.5(4)°	80.5(4)°	2.599	2.202
[207]	1.776(10);1.629(10)	98.3(5)°	81.7(5)°	2.577	2.230
$(F_3PNMe)_2$ [208]	1.74 ;1.60	102°	78°	2.59	2.09
gauche$(PhF_2PNMe)_2$ [209]	1.78(2) ;1.64(2)	99.4°	80.6°	2.61	2.21
trans$[Ph(S)PNPh]_2$ [210]	1.695(4)	98.1°	81.9°	2.562	2.221
trans$[Ph(S)PNMe]_2$ [211]	1.69(1)	96.0(3)°	84.0(3)°	2.50	2.26
trans$[Ph(S)PNEt]_2$ [211]	1.686(6)	96.7(2)°	83.4(3)°	2.518	2.241
cis$[Ph(S)PNEt]_2$ [211]	1.687(10)	95.2(5)	84.2(5)	2.491	2.261
cis$(ClPNBu^t)_2$ [212]	1.689(5)	97.3(4)	82.5(3)	2.540	2.232
trans$[Cl(O)PNBu^t]_2$ [213]	1.661(5)	94.5(2)	85.5(2)	2.439	2.255

* Standard derivations in parentheses.

In the structure investigation of $[Cl(S)PNMe]_2$, the authors did not distinguish between sulphur and chlorine atoms.[205]

All compounds except the two cis isomers possess planar geometry about nitrogen. Petersen and Wagner[210] noted that only small variations occur between different cyclodiphosphazanes in the P...P and N...N interatomic distances across the ring. These distances are all ca 30% shorter than the sum of the respective Van der Waal's radii, and so it was concluded that the ring geometry is probably very dependent on these interactions across the ring. The slight non-planarity of the two cis isomers may be due to phosphorus substituent interactions, although it was suggested[212] that the non-planarity in cis-$(ClPNBu^t)_2$ may be due to crystal packing forces.

The P-N bond lengths in all cyclodiphosphazanes containing three and four coordinate phosphorus are fairly similar and much shorter than the generally accepted P-N single bond length (1.77 Å). Two different P-N bond lengths are found for five coordinate cyclodiphosphazanes as the ring spans axial/equatorial sites, the longer P-N bond, which approximates to the pure single bond length, being axial. An interesting structural comparison can be made between $(ClPNBu^t)_2$ and $[Cl(O)PNBu^t]_2$. On oxidation, the P...P interatomic distance across the ring is reduced by a shortening of the P-N bond length, and an increase in the $\widehat{NPN}$ angle.

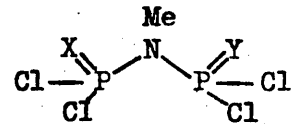
(4) Physical properties:- Two physical properties have been used to distinguish geometrical isomers of cyclodiphosphazanes. If an isomer mixture is present it has been found[211] that the trans isomer is eluted first in column chromatography. Dipole moments have been used[214] with some success in isomer determination employing the fact that the cis isomer should have a larger dipole moment than the trans isomer; but because of inaccuracies in the measurement and calculation of dipole moments this method is best used for cyclodiphosphazanes in which the cis isomer dipole moment is expected to be high.

CHAPTER 2

NITROGEN-BRIDGED DIPHOSPHORUS COMPOUNDS - DIMETHYLAMINOLYSIS OF SOME TETRACHLORO-DERIVATIVES

INTRODUCTION.

The aminolysis substitution patterns of compounds of the general form (XXIX) (X=Y=lone pair, O or S) are of interest as they can provide some information about the mechanism of nucleophilic substitution, as well as giving possible indications and comparisons about the ease with which electronic effects can be transmitted between the phosphorus centres. Furthermore compounds (XXIX) (X ≠ Y) can in principle provide comparisons of the reactivity of phosphino, phosphinoyl and phosphinothioyl groups towards amines and other nucleophiles.



(XXIX)

Reaction of bis(dichlorophosphinoyl)methylamine, $[Cl_2(O)P]_2NMe$, with dimethylamine was shown[132] to proceed by a nongeminal scheme (Figure 9), similar to the dominant substitution pattern found in the dimethylaminolysis of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$.[70] This nongeminal substitution pattern is consistent with initial aminolysis occurring via an associative mechanism. Reaction with two mol equiv. of dimethylamine gave, mixed with the monodimethylamino-derivative, the nongeminal bisdimethylamino-derivative and unreacted starting material suggesting that the deactivating effect of the dimethylamino group exerts little influence on the second phosphinoyl centre. The formation of very small proportions of the trisdimethylamino-derivative parallels the difficulty found in detecting the penta(dimethylamino)cyclotriphosphazene $N_3P_3Cl(NMe_2)_5$, and indicates an enhanced rate of substitution of

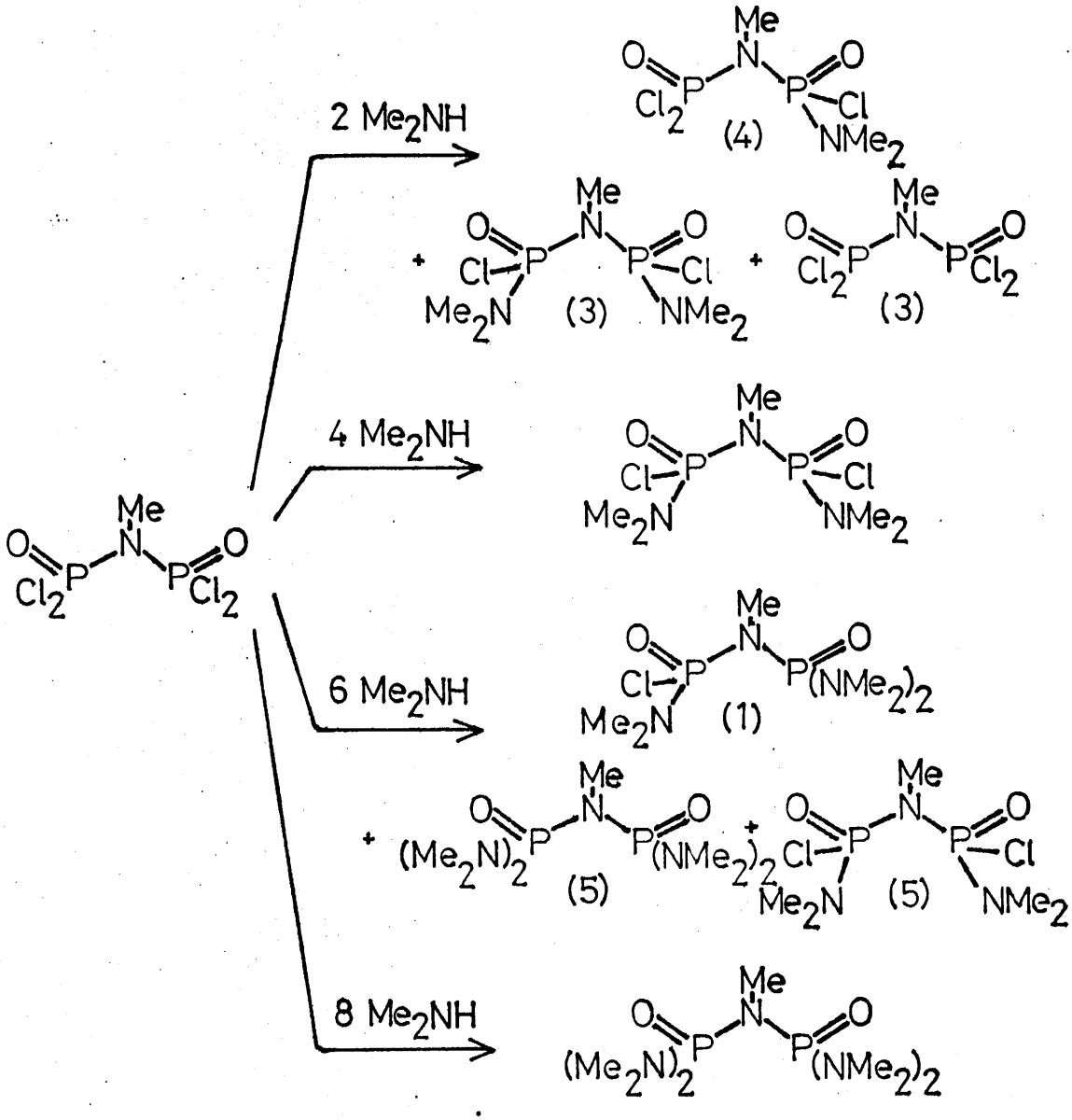


Figure 9

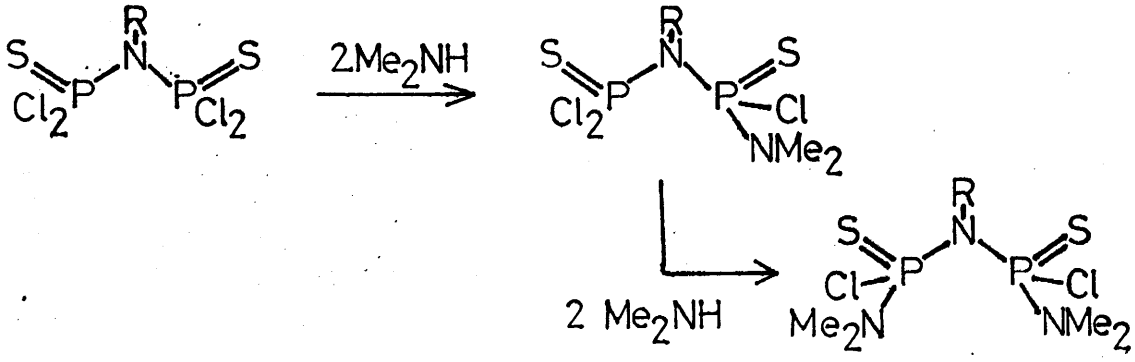


Figure 10

the last chlorine. It was suggested that this may be due to the ease with which this last chlorine heterolyses.

Similarly nongeminal substitution was found in the reactions of bis(dichlorophosphinothioyl)amines $[Cl_2(S)P]_2NR$ (R=Me or Ph) with dimethylamine[215] (Figure 10), formation of the bisdimethylamino-derivative $[Me_2N(Cl)(S)P]_2NPh$ requiring higher reaction temperatures than its methylamino analogue. In contrast to $[Cl_2(O)P]_2NMe$ these bis(dichlorophosphinothioyl)-compounds formed solely monodimethylamino-derivatives on reaction with two mol equiv. of dimethylamine.

The reaction of dimethylaminotrimethylsilane, $Me_3Si{\cdot}NMe_2$, with dichlorophosphino(dichlorophosphinoyl)methylamine, $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$,[133] also gave some interesting results (Figure 11)

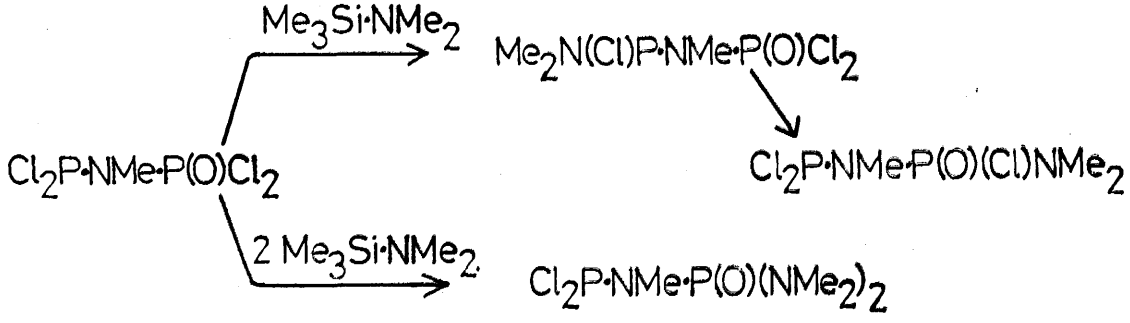


Figure 11.

Aminolysis initially occurs at the phosphino centre (which agrees with qualitative observations on the relative reactivities of tervalent and four coordinate quinquivalent phosphorus halides), but this phosphino-substituted compound rearranges at ambient temperatures to the thermodynamically favoured product $Cl_2P{\cdot}NMe{\cdot}P(O)Cl)NMe_2$. Reaction of $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$ with

methoxytrimethylsilane, Me_3SiOMe, proceeded similarly, although no rearrangement of the methoxyphosphino-derivative, $MeO(Cl)P{\cdot}NMe{\cdot}P(O)Cl_2$, could be detected. The formation of $Cl_2P{\cdot}NMe{\cdot}P(O)(NMe_2)_2$ is surprising as only monosubstitution of the $Cl_2(O)P$- groups in $[Cl_2(O)P]_2NMe$ by $Me_3Si{\cdot}NMe_2$ is possible under similar conditions,[132] suggesting that $Cl_2P{\cdot}NMe{\cdot}P(O)(NMe_2)_2$ may be formed by a facile rearrangement of $Me_2N(Cl)P{\cdot}NMe{\cdot}P(O)(Cl)NMe_2$. This latter compound can be prepared by the condensation reaction:

$$Me_2NPCl_2 + Me_3Si{\cdot}NMe{\cdot}P(O)(Cl)NMe_2 \longrightarrow Me_2N(Cl)P{\cdot}NMe{\cdot}P(O)(Cl)NMe_2 + Me_3SiCl$$

and was found to subsequently isomerise to $Cl_2P{\cdot}NMe{\cdot}P(O)(NMe_2)_2$.

RESULTS.

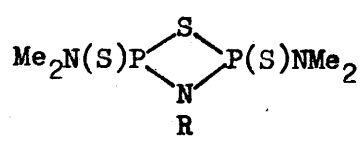
Continuing the investigations into the dimethylaminolysis of compounds of the general type $Cl_2(X)P{\cdot}NMe{\cdot}P(Y)Cl_2$, aminolysis of dichlorophosphinothioyl(dichlorophosphinoyl)methylamine, $Cl_2(S)P{\cdot}NMe{\cdot}P(O)Cl_2$ by dimethylamine was examined, and the latter stages of dimethylaminolysis of bis(dichlorophosphinothioyl) methylamine, $[Cl_2(S)P]_2NMe$, unfolded. Also attempts were made to synthesise some dimethylamino-derivatives of these phosphinothioyl compounds by other means.

(1) Dimethylaminolysis of $[Cl_2(S)P]_2NMe$

It is of interest to examine the latter stages of dimethylaminolysis of $[Cl_2(S)P]_2NMe$ in order to discover whether, like the initial stages, they continue to parallel the substitution pattern found for $[Cl_2(O)P]_2NMe$.[132]

The tetrakisdimethylamino-derivative, $[(Me_2N)_2(S)P]_2NMe$, was readily obtained by reaction of $[Cl_2(S)P]_2NMe$ with excess dimethylamine in refluxing chloroform solution. No reaction of the compound with methyl iodide was detected, unlike $(Me_2N)_3PS$ which forms the quarternised product $(Me_2N)_3PSMe\ ^+I^-$.[216]

Attempts to synthesise the trisdimethylamino-derivative from six mol equiv. of dimethylamine were unsuccessful, an oil consisting of a number of products being obtained, none of which could be identified as the trisdimethylamino-derivative. A crystalline compound separated from the oil was identified as the novel four membered ring compound (XXX) (R=Me).



(XXX)

All the evidence from mass spectroscopy, analysis, and n.m.r. is consistent with this structure. The reaction was repeatable with $[Cl_2(S)P]_2NEt$, but not with $[Cl_2(S)P]_2NPh$, the latter compound yielding mainly $[Me_2N(Cl)(S)P]_2NPh$. In each case apparently only one of the two possible geometrical isomers of (XXX) was formed. Evidence for formation of the trans isomer (or less likely a cis isomer without a plane of symmetry) of (XXX) (R=Et) was obtained from the ^{31}P-decoupled ^{1}H n.m.r. spectrum. This showed two quartets in a 1:1 ratio, assignable to the inner lines of the AB part of an ABX_3 spin system expected for diastereotopic $-CH_2-$ protons. This method has previously been used in the assignment of geometrical isomers of cyclodiphospha(V)zanes.[204]

(2) Dimethylaminolysis of $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$.

$Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ reacts with dimethylamine in non-donor chlorinated solvents, such as methylene chloride or chloroform, to give good yields of mono-, bis-, and tetrakisdimethylamino-derivatives (Figure 12). Nongeminal substitution on reaction with four mol equiv. of dimethylamine was confirmed by $^{1}H\{^{31}P\}$ double resonance (which enabled dimethylamino proton doublets coupled to either phosphinoyl or phosphinothioyl groups to be identified) and also by the presence of a mixture of diastereoisomers. No trisdimethylamino-derivative could be detected, while reaction with excess dimethylamine in refluxing chloroform yields $(Me_2N)_2(O)P{\cdot}NMe{\cdot}P(S)(NMe_2)_2$.

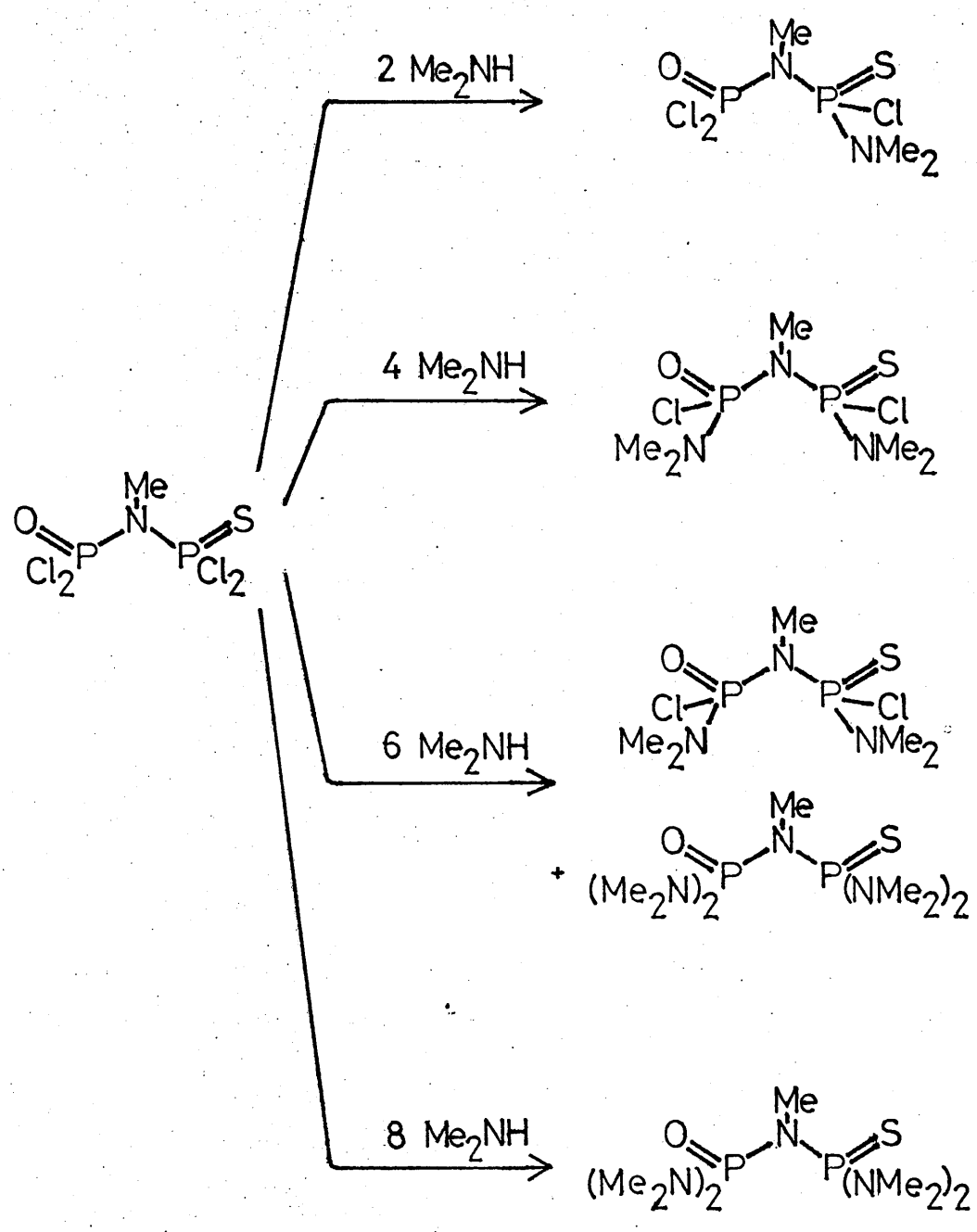

2 Me2NH
4 Me2NH
6 Me2NH
8 Me2NH
Me
O
S
Cl2P
PCl2
Cl
NMe2
Me2N
(Me2N)2P
P(NMe2)2
+

Figure 12

The fact that aminolysis occurs initially at the phosphinothioyl centre was unambiguously established from the multiplicity of the lines associated with the lowfield (phosphinothioyl) signal in the ^{31}P n.m.r. spectrum, and by $^{1}H\text{-}\{^{31}P\}$ double resonance which clearly established that the dimethylamino-proton doublet collapsed on irradiation at the higher ^{31}P frequency (lower field). Preferential reaction at the phosphinothioyl centre also occurs with Me_3SiNR_2 (R=Me or Et) forming $Cl_2(O)P{\cdot}NMe{\cdot}P(S)(Cl)NR_2$ (R=Me or Et).

The use of diethyl ether, however, has a very marked effect on the reaction of $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ with two mol equiv. of dimethylamine. The relative molar proportions of the products (in parentheses), estimated by ^{1}H n.m.r. spectroscopy, were (Figure 13):

$Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ (2) $Cl_2(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$ (1)

$Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$ (3) $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ (3)

All compounds were identified by $^{1}H\text{-}\{^{31}P\}$ double resonance. These results suggest that preferential reaction with dimethylamine now occurs at the phosphinoyl centre. The possibility that the small proportion of $Cl_2(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$ is due to a facile conversion to the bisdimethylamino-derivative $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$ can be discounted using the results of the reaction of $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ with 3.6 mol equiv. of dimethylamine (reaction 16, product ratios in parentheses).

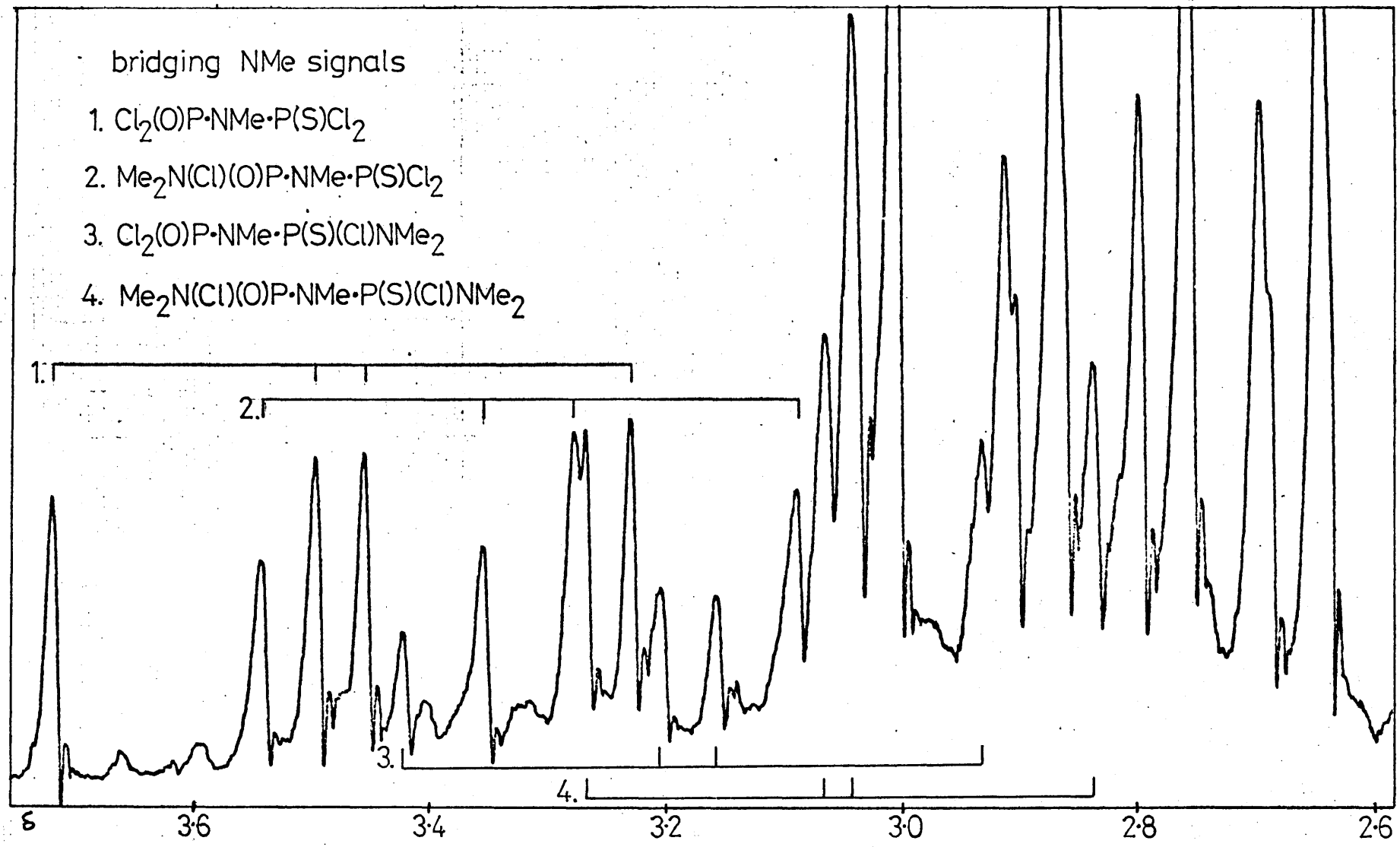


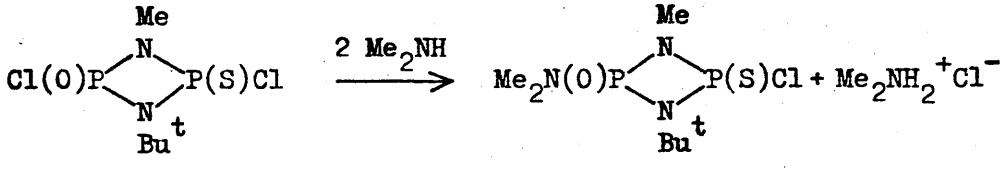
Figure 13 - 60 MHz ^1H n.m.r. spectrum of the products of the reaction of $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ with 2 mol equiv. Me_2NH in diethyl ether solution.

$$Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2 + 3.6\ Me_2NH \xrightarrow{Et_2O} Cl_2(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2 \quad (1) \quad \underline{16}$$

$$+ \ Me_2N(Cl)(O)P{\cdot}NMeP(S)(Cl)NMe_2 \quad (5)$$

The products found apparently indicate that $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ is more reactive than $Cl_2(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$ towards dimethylamine in diethyl ether solution - suggesting that in fact a greater preference for initial reaction at the phosphinoyl centre exists than is indicated by the 2:1 ratio of monodimethylamino-derivatives found on reaction with 2 mol equiv. of dimethylamine. It was not possible to separate $Me_2N(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ from the reaction mixture.

Finally, dimethylaminolysis of the cyclodiphosphazane $Cl(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$ acted as a useful comparison with the above results. In this case n.m.r. double resonance experiments established that dimethylaminolysis occurred exclusively at the phosphinoyl centre, irrespective of whether the reaction was carried out in methylene chloride or diethyl ether solution.



(3) Attempted preparation of dimethylamino-derivatives by other routes.

Bis(dimethylamino)phosphinothioyl methylamine, $(Me_2N)_2P(S)NHMe$, recently prepared by the reaction of $(Me_2N)_2P(S)Cl$ with methylamine,[217] is also formed in the reaction,

$$Cl_2P(S)NHMe + 4\ Me_2NH \longrightarrow (Me_2N)_2P(S)NHMe + 2\ Me_2NH_2^+Cl^-$$

Interestingly the corresponding reaction with $Cl_2P(S)NHPh$ was shown[215] to proceed differently:

$$2\ Cl_2P(S)NHPh + 7\ Me_2NH \longrightarrow (Me_2N)_2(S)P{\cdot}NPh{\cdot}P(S)(NMe_2)NHPh + 4\ Me_2NH_2^+Cl^-$$

Attempted preparation of a number of geminal bis(dimethylamino)-phosphinothioyl isomers by the following condensation reactions proved to be unsuccessful:

$$(Me_2N)_2P(S)NHMe + P(X)Cl_3 \xrightarrow{Et_3N} (Me_2N)_2(S)P{\cdot}NMe{\cdot}P(X)Cl_2 \quad (X=O \text{ or } S)$$

$$(Me_2N)_2P(S)NHMe + ClP(O)(NMe_2)_2 \xrightarrow{Et_3N} (Me_2N)_2(S)P{\cdot}NMe{\cdot}P(O)(NMe_2)_2$$

Attempted preparation of $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ by similar condensation routes also met with little success.

$$\left.\begin{array}{l} Me_2N(Cl)(O)P{\cdot}NHMe + P(S)Cl_3 \\ Cl_2P(S)NHMe + Cl_2P(O)NMe_2 \end{array}\right\} \xrightarrow{Et_3N} Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)Cl_2 \qquad 17$$

Self-condensation of $Cl_2P(S)NHMe$ may occur in reaction 17, while in the other attempted condensation reactions, hygroscopic precipitates formed which may be adducts of triethylamine with the chlorophosphorus electrophile.

As the trisdimethylamino compound $(Me_2N)_2(O)P{\cdot}NMe{\cdot}P(O)(Cl)NMe_2$ can be formed by heating together bis- and tetrakisdimethylamino-derivatives,[132] similar reactions were attempted with the

corresponding phosphinothioyl compounds, but in both cases no rearrangement occurred,

$$(Me_2N)_2(S)P{\cdot}NMe{\cdot}P(X)(NMe_2)_2 \;+\; Me_2N(Cl)(S)P{\cdot}NMe{\cdot}P(X)(Cl)NMe_2$$

$$\downarrow$$

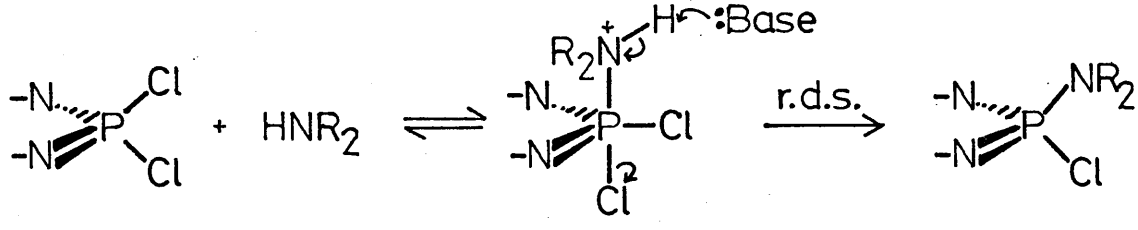
no reaction (X=O or S)

probably indicating lower lability of dimethylamino-groups in these phosphinothioyl compounds.

DISCUSSION.

The observation that $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ undergoes preferential aminolysis reactions at the phosphinothioyl centre in non-donor solvents is totally unexpected, since phosphoryl halides are generally more readily aminolysed than phosphinothioyl halides.[218] In order to explain this unusual reactivity, and the pronounced solvent dependence of the reaction, it is necessary to examine the possible mechanism of nucleophilic substitution in some detail.

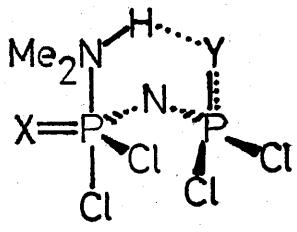
It is not unreasonable to assume that an aminolysis mechanism, similar to that proposed for the aminolysis hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, on the basis of kinetic data,[92-94] operates here. This mechanism involves the dehydrochlorination of a five coordinate intermediate (formed in a rapid pre-equilibrium) as the rate determining step.



Dehydrochlorination has been shown to be assisted by amine[92] or donor solvent (tetrahydrofuran[93,94]).

Applying this mechanism to the dimethylaminolysis of $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ in non-donor solvents, such a rate determining

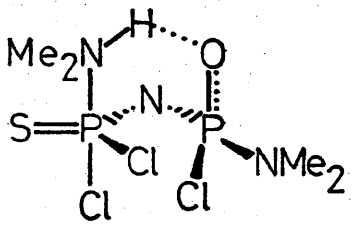
dehydrochlorination could be assisted by an entropy favoured intramolecular association of the type a



a

in which Y acts as a base. As oxygen is likely to be a much better base than sulphur, only aminolysis at the phosphinothioyl centre will be anchiomerically assisted. Donor solvents such as diethyl ether may effectively complete with this intramolecular association in assisting dehydrochlorination, resulting in an aminolysis rate enhancement at both phosphinothioyl and phosphinoyl centres. This would result in the course of reaction being mainly governed by the relative electrophilicities of the two centres, resulting in preferential aminolysis at the phosphinoyl centre in donor solvents. Intramolecular effects of the type discussed would not be possible with the cyclodiphosphazane $Cl(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}N}Bu^t$, which is consistent with the fact that dimethylaminolysis occurs at the phosphinoyl centre in both methylene chloride and diethyl ether. Nucleophilic displacements at phosphorus(V) in 2,2,3,4,4-pentamethyphosphetans generally take place with retention of configuration.[97] Unfortunately it was not possible to determine whether a similar stereospecificity occurs in the formation of $Me_2N(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}N}Bu^t$.

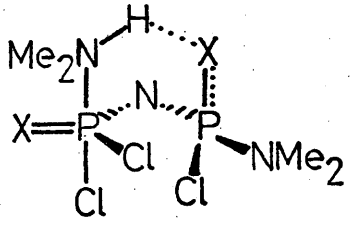
The formation of the bisdimethylamino-derivative $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$ in non-donor solvents is anticipated in terms of the reduced electrophilic nature of the $Me_2N(Cl)P(S)$-group. It is possible that, even in diethyl ether, an interaction of the type b



b

may in part be responsible for the relative ease with which $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ reacts with dimethylamine. It would also be instructive to know the structure of the trisdimethylamino-derivative, but no evidence for its presence in reaction mixtures was obtained.

The difficulties experienced[132] in obtaining pure samples of $Cl_2(O)P{\cdot}NMe{\cdot}P(O)(Cl)NMe_2$ from the dimethylaminolysis of $[Cl_2(O)P]_2NMe$ are also explicable in terms of an intramolecular assisted dehydrochlorination mechanism (c, X=O)



c

This could overcome the 'normal' deactivation effect of the dimethylamino-group on the dichlorophosphinoyl centre. The corresponding intramolecularly assisted mechanism involving c, X=S, would be less favoured due to the lower basicity of sulphur - consistent with the observation that solely monodimethylamino-derivatives are formed in the reactions of $[Cl_2(S)P]_2NR$ (R=Me or Ph) with two mol equiv. of dimethylamine.[215]

The isolation of ring compounds $Me_2N(S)\overline{P\cdot NR\cdot P(S)NMe_2}\cdot S$ (R=Me or Et) during attempts to synthesise trisdimethylamino-derivatives is somewhat surprising since P-S bond formation and cleavage evidently occurs. Although we have no evidence relating to the mechanism of cyclisation, it is interesting to note that formation of this ring system seems particularly favoured in view of the fact that the closely related heterocycle $Me(S)\overline{P\cdot NSiMe_3\cdot P(S)Me}\cdot S$ was recently obtained[219] from the reaction of trimethylsilyl azide with $Me(S)\overline{P\cdot S\cdot P(S)Me}\cdot S$.

N.m.r. discussion.

In Table 5 the ^1H and ^{31}P n.m.r. data for the previously discussed phosphinothioyl compounds are listed. N.m.r. data for the dimethylamino-derivatives of $[Cl_2(O)P]_2NR$ and $[Cl_2(S)P]_2NR$ (R=Me or Ph) have recently been reported,[220] and many of the trends and observations made also apply to the dimethylamino-derivatives of $Cl_2(O)P\cdot NMe\cdot P(S)Cl_2$.

TABLE 5 (contd.)

Compound	^{31}P		^{1}H				
	$\delta(^{31}P)$ p.p.m.	$^{2}J(\underline{P}\text{-N-}\underline{P})$ Hz	δ(NMe) p.p.m.	$^{3}J(\underline{P}\text{-N-C-}\underline{H})$ Hz	$\delta(NMe_2)$ p.p.m.	$^{3}J(\underline{P}\text{-N-C-}\underline{H})$ Hz	$^{5}J(\underline{P}\text{-N-P-N-C-}\underline{H})$ Hz
$Cl_2(O)P\cdot NMe\cdot P(S)Cl_2$	10(PO) 49	3	3.46	13.7(PO) 16.2			
$Cl_2(O)P\cdot NMe\cdot P(S)(Cl)NMe_2$	10(PO) 69	+15.7[g]	3.21	+15.9(PO) +13.2	2.95	14.1	
$Me_2N(Cl)(O)P\cdot NMe\cdot P(S)Cl_2$	16.5(PO) 51	14.5	3.32	11.3(PO) 15.9	2.81	12.9	0.5[b]
$Me_2N(Cl)(O)P\cdot NMe\cdot P(S)(Cl)NMe_2$ (2)[a]	19(PO) 74	+13.9[g]	3.10	+12.1(PO) +13.0	2.79(PO) 2.92	13.3(PO) 14.6	0.3[b]
(1)	[e]	[e]	3.11	12.2(PO) 13.2	2.80(PO) 2.94	13.3(PO) 14.2	
$(Me_2N)_2(O)P\cdot NMe\cdot P(S)(NMe_2)_2$	20(PO) 77	9.7	[e]	[e]	2.72(PO) 2.76	9.5(PO) 10.8	
$Cl_2(O)P\cdot NMe\cdot P(S)(Cl)NEt_2$	9(PO) 67	13.3	3.20	16.0(PO) 13.4	3.43(CH_2)	16.4	

TABLE 5
N.m.r. data.

Compound	^{31}P		^{1}H				
	$\delta(^{31}P)$ p.p.m.	$^{2}J(\underline{P}\text{-}N\text{-}\underline{P})$ Hz	$\delta(NMe)$ p.p.m.	$^{3}J(\underline{P}\text{-}N\text{-}C\text{-}\underline{H})$ Hz	$\delta(NMe_2)$ p.p.m.	$^{3}J(\underline{P}\text{-}N\text{-}C\text{-}\underline{H})$ Hz	$^{5}J(\underline{P}\text{-}N\text{-}P\text{-}N\text{-}C\text{-}\underline{H})$ Hz
$Cl_2(S)P\cdot NMe\cdot P(S)Cl_2$[f]	47.5		3.634	14.75			
$Cl_2(S)P\cdot NMe\cdot P(S)(Cl)NMe_2$[f]	48.9(PCl_2) 70.8	+19.8[g]	3.370	15.62(PCl_2) 12.98	2.900	14.10	0.3
$Me_2N(Cl)(S)P\cdot NMe\cdot P(S)(Cl)NMe_2$[f]	73.5 74.8		3.100 3.190	12.50 12.78	2.890 2.880	15.45[d] 15.35[d]	
$(Me_2N)_2(S)P\cdot NMe\cdot P(S)(NMe_2)_2$[f]	77.7	11.5	2.919	10.48	2.726	11.25	0.2
$Me_2N(S)\overline{P\cdot NMe\cdot P(S)NMe_2}\cdot S$	59	9.8	2.58	15.3	2.97	15.2[d]	
$Me_2N(S)\overline{P\cdot NEt\cdot P(S)NMe_2}\cdot S$	58	9.0	ca 3.15(CH_2)	[e]	2.99	15.2[d]	
$(Me_2N)_2(S)P\cdot NHMe$	79.5		2.63	11.9	2.63	11.9	

TABLE 5 (contd.)

Compound	^{31}P		^{1}H				
	$\delta(^{31}P)$ p.p.m.	$^{2}J(\underline{P}\text{-N-}\underline{P})$ Hz	δ(NMe) p.p.m.	$^{3}J(\underline{P}\text{-N-C-}\underline{H})$ Hz	$\delta(NMe_2)$ p.p.m.	$^{3}J(\underline{P}\text{-N-C-}\underline{H})$ Hz	$^{5}J(\underline{P}\text{-N-P-N-C-}\underline{H})$ Hz
$Cl(O)\overline{P\cdot NMe\cdot P(S)Cl\cdot NBu^t}$ (2)[a]	-1.5(PO) 40	+31.5[g]	2.90	+16.1(PO) +16.9	1.65(Bu^t)		0.7[c]
(1)	-2(PO) 43	43.0	2.92	16.8(PO) 17.2	1.65(Bu^t)		0.7[c]
$Me_2N(O)\overline{P\cdot NMe\cdot P(S)Cl\cdot NBu^t}$	6.5(PO) 46.5	32.8	2.8	e	2.82 1.53(Bu^t)	11.2	

a Figures in parentheses indicate isomer ratios.

b $^{5}J[(S)\underline{P}\text{-N-P-N-C-}\underline{H}]$

c $^{4}J[(O)\underline{P}\text{-N-C-C-}\underline{H}] \approx {}^{4}J[(S)\underline{P}\text{-N-C-C-}\underline{H}]$

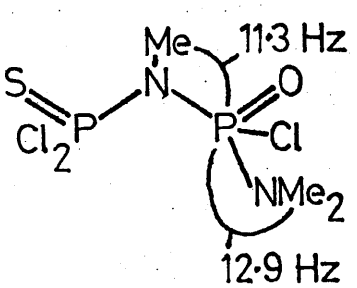
d Strictly speaking this is $\left|{}^{3}J(\underline{P}\text{-N-C-}\underline{H}) + {}^{5}J(\underline{P}\text{-N-P-N-C-}\underline{H})\right|$

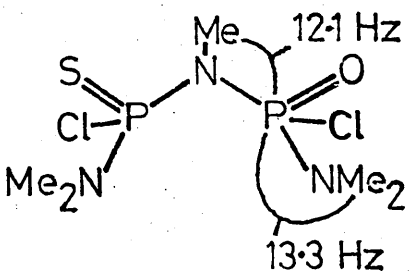
e Not measured.

f Data from ref. 220

g Sign assumes $^{3}J(\underline{P}\text{-N-C-}\underline{H})$ as positive.[231]

Bridging N-methyl protons are found to resonate to low field of terminal dimethylamino-protons, while the δ_{NMe} and δ_{NMe_2} values both decrease on increasing dimethylamino substitution. $^3J(\underline{P}\text{-}N\text{-}C\text{-}\underline{H})$ involving bridging N-methyl protons decrease in the order $PCl_2 > P(Cl)NMe_2 > P(NMe_2)_2$ and terminal dimethylamino-proton couplings show a similar trend - implying that the Fermi contact term is probably dominant in these couplings. A corresponding increase in phosphorus-proton couplings to one phosphorus occurs on aminolysis at the distant phosphorus, as for example is found in the $^3J[(O)\underline{P}\text{-}N\text{-}C\text{-}\underline{H}]$ couplings in $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ and $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$.





As found in the bisphosphinoyl and bisphosphinothioyl compounds, phosphinothioyl-proton couplings are larger than the corresponding phosphinoyl-proton couplings.

The value of δ_P increases in the series $P(X)Cl_2 < P(X)(Cl)NMe_2 < P(X)(NMe_2)_2$ (X=O or S). δ_P is normally also sensitive to aminolysis at the distant phosphorus, and exhibits a similar trend. This increase in δ_P on aminolysis is a general feature of four coordinate phosphorus, and this trend has been accounted for in the semi-empirical approach to phosphorus chemical

shifts proposed by Letcher and Van Wazer.[221] In their treatment the increasing value of δ_P on aminolysis of four coordinate chlorophosphorus compounds is due mainly to an increasing occupation of phosphorus 3d-orbitals involved in $p\pi$-$d\pi$ bonding. An interesting variation in $^2J(\underline{P}\text{-}N\text{-}\underline{P})$ is found in these phosphinoyl (phosphinothioyl) compounds. This coupling decreases in the series mono > bis > tetrakis in the dimethylamino-derivatives, whereas by far the smallest coupling is found in $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ (3 Hz). Although phosphorus-nitrogen bond rotation is almost certainly fast on the n.m.r. time scale in these compounds, this anomalously low value may be due to the tetrachloro-compound possessing a different preferred conformation in solution.

Finally, a characteristic of bridging N-methyl protons which form part of a four membered ring is their low δ_{NMe} value - their resonances being to high field of terminal dimethylamino protons. The bridging N-methyl protons in $Cl(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$ also exhibit greater coupling to the P(S)-centre than to the P(O)-centre.

EXPERIMENTAL.

Methods used in solvent drying and purification of reagents obtained commercially can be found in Appendix A. The compounds $[Cl_2(S)P]_2NMe$,[128] $[Cl_2(S)P]_2NEt$,[128] $[Cl_2(S)P]_2NPh$,[128] $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$,[128] $Cl_2(S)PNHMe$,[128] $Cl_2(O)PNMe_2$,[222] $Cl(O)P(NMe_2)_2$,[54] $Me_2N(Cl)(O)PNHMe$,[132] and Me_2NSiMe_3[223] were prepared by literature methods. Details of the preparation of $Cl(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$ are given in Chapter 5. Instruments used to obtain n.m.r. and mass spectra, and the source of microanalysis results are listed in Appendix B. Analytical data is presented in Table 6.

TABLE 6

Analytical data[a]

Compound	Found					Calc.				
	C	H	N	S	m/e	C	H	N	S	m/e[b]
$[(Me_2N)_2(S)P]_2NMe$	32.7	8.25	21.4		331	32.6	8.2	21.1		331
$Me_2N(S)\overline{P\cdot NMe\cdot P(S)NMe_2}\cdot S$	22.1	5.5	15.5	35.1	275	21.8	5.5	15.3	34.9	275
$Me_2N(S)\overline{P\cdot NEt\cdot P(S)NMe_2}\cdot S$	25.2	5.8	14.95		289	24.9	5.9	14.5		289
$Cl_2(O)P\cdot NMe\cdot P(S)(Cl)NMe_2$	12.5	3.2	9.5			12.4	3.1	9.7		
$Me_2N(Cl)(O)P\cdot NMe\cdot P(S)(Cl)NMe_2$	20.0	5.1	14.2		297	20.15	5.1	14.1		297
$(Me_2N)_2(O)P\cdot NMe\cdot P(S)(NMe_2)_2$	32.9	8.5	20.5		315	34.3	8.6	22.2		315
$Cl_2(O)P\cdot NMe\cdot P(S)(Cl)NEt_2$	20.0	4.1	8.5	32.3[c]	316	18.9	4.1	8.8	33.5	316
$Cl(O)\overline{P\cdot NMe\cdot P(S)Cl}\cdot NBu^t$	20.8	4.7	8.7		280	21.4	4.3	10.0		280

TABLE 6 (Contd.)

Compound	Found					Calc.				
	C	H	N	S	m/e	C	H	N	S	m/e[b]
$Me_2N(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$					289					289
$(Me_2N)_2(S)PNHMe$	33.3	8.95	23.05		181	33.15	8.9	23.2		181

[a] Elemental analyses figures are given in %.

[b] For ions containing ^{35}Cl

[c] Cl analysis

(a) Dimethylaminolyses in chloroform and methylene chloride solution.

Preparation of di [(bisdimethyamino)phosphinothioyl]methylamine, $[(Me_2N)_2(S)P]_2NMe$:- A solution of dimethylamine (20.0g, 0.444 mol) in chloroform (30 ml) was slowly added to a stirred solution of bis(dichlorophosphinothioyl)methylamine, $[Cl_2(S)P]_2NMe$ (7.4g, 0.025 mol) in chloroform (120 ml) at -78°. The solution was allowed to come to room temperature (½h) and then refluxed (24h). The chloroform was evaporated and the product extracted with 5 x 150 ml diethyl ether and filtered to remove the remains of dimethylammonium chloride. The diethyl ether was evaporated to give a yellow solid which on recrystallisation from diethyl ether/ light petroleum b.p. 40-60°(1:1) gave di[(bisdimethylamino) phosphinothioyl]methylamine (3.3g, 40%) a white crystalline solid m.p. 85-86°.

This method was also used in the following preparations and reactions.

1-Methyl-2,4-bisdimethylamino-2,4-dithio-1,3,2,4-azathiadiphosphetane, $Me_2N(S)\overline{P{\cdot}NMe{\cdot}P(S)NMe_2{\cdot}S}$:- Bis(dichlorophosphinothioyl)methylamine (7.1g, 0.024 mol) and dimethylamine (6.6g, 0.146 mol) were refluxed in chloroform (150 ml) for 12h, yielding on work up a yellow oil. On cooling, crystals formed which were filtered and recrystallised from light petroleum b.p. 40-60° giving 1-methyl-2,4-bisdimethylamino-2,4-dithio-1,3,2,4-azathiadiphosphetane, $Me_2N(S)\overline{P{\cdot}NMe{\cdot}P(S)NMe_2{\cdot}S}$ (0.85g, 13%) a white crystalline solid, m.p. 130-150°.

1-Ethyl-2,4-bisdimethylamino-2,4,-dithio-1,3,2,4-azathiadiphosphetane, $Me_2N(S)\overline{P{\cdot}NEt{\cdot}P(S)NMe_2{\cdot}S}$ (0.5g, 5%), a white crystalline solid m.p. 93-97° was similarly prepared from bis(dichlorophosphinothioyl) ethylamine, $[Cl_2(S)P]_2NEt$ (11.4g, 0.0365 mol) and dimethylamine (9.9g, 0.22 mol).

Reaction of bis(dichlorophosphinothioyl)aniline, $[Cl_2(S)P]_2NPh$, with six mol equiv. dimethylamine:- Bis(dichlorophosphinothioyl) aniline (6.5g, 0.018 mol) and dimethylamine (5.0g, 0.111 mol) were refluxed in chloroform (100 ml) for 15h. The solid residue obtained on work up was found to consist mainly of bis(chlorodimethylamino-phosphinothioyl)aniline, $[Me_2N(Cl)(S)P]_2NPh$.

Bisdimethylaminophosphinothioylmethylamine, $(Me_2N)_2(S)PNHMe$:- Dichlorophosphinothioylmethylamine, $Cl_2(S)PNHMe$ (15.1g, 0.092 mol) and dimethylamine (18.0g, 0.40 mol) were refluxed in chloroform (200 ml) for 4h. On work up a white solid was obtained which on recrystallisation from a diethyl ether/light petroleum b.p. 40-60° mixture gave bis(dimethylamino)phosphinothioylmethylamine (12.3g, 74%), a white crystalline solid m.p. 79-80°.

2-Chloro-1-t-butyl-4-dimethylamino-3-methyl-4-oxo-2-thio-cyclodiphosphazane, $Me_2N(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$:- 2,4-Dichloro-1-t-butyl-3 methyl-2 oxo-4-thiocyclodiphosphazane, $Cl(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$ (2.8g, 0.01 mol) and dimethylamine (0.95g, 0.021 mol) were stirred in methylene chloride (100 ml) for 1h after mixing at -78°. On work up a yellow viscous oil was obtained, consisting of mainly $Me_2N(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$. This product could not be purified by vacuum distillation. Similar results were obtained when this reaction was performed using diethyl ether as solvent.

Chlorodimethylaminophosphinothioyl(dichlorophosphinoyl)methylamine, $Cl_2(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$:- Dichlorophosphinothioyl(dichlorophosphinoyl) methylamine, $Cl_2(O)P.NMe{\cdot}P(S)Cl_2$, (2.8g, 0.01 mol) and

dimethylamine (0.95g, 0.021 mol) were stirred in methylene chloride (250 ml) for 1h, after mixing at -78°. The oil obtained on work up was vacuum distilled (68°, 0.05 mm Hg) to give chlorodimethylaminophosphinothioyl(dichlorophosphinoyl)methylamine (1.95g, 68%) as a clear viscous liquid.

Bisdimethylaminophosphinothioyl(bisdimethylaminophosphinoyl)-methylamine, $(Me_2N)_2(O)P{\cdot}NMe{\cdot}P(S)(NMe_2)_2$:- Dichlorophosphinothioyl-(dichlorophosphinoyl)methylamine, $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$, (5.6g, 0.02 mol) and dimethylamine (13.5g, 0.30 mol) were refluxed in chloroform (200 ml) for 10h. On work up a yellow oil was obtained which on vacuum distillation (115°C, 0.1 mm Hg) gave bisdimethylamino-phosphinothioyl(bisdimethylaminophosphinoyl)methylamine (3.5g, 56%), a clear viscous liquid.

Reaction of dichlorophosphinothioyl(dichlorophosphinoyl)methylamine, $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$, with six mol equiv. dimethylamine:- Dichlorophosphinothioyl(dichlorophosphinoyl)methylamine (6.2g, 0.022 mol) and dimethylamine (5.95g, 0.132 mol) were refluxed in chloroform (200 ml) for 15h. A yellowish viscous oil was obtained on work up consisting of a 1:1 mixture of chlorodimethylamino-phosphinothioyl(chlorodimethylaminophosphinoyl)methylamine, $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$, and bisdimethylaminophosphinothioyl (bisdimethylaminophosphinoyl)methylamine, $(Me_2N)_2(O)P{\cdot}NMe{\cdot}P(S)(NMe_2)_2$ - identified by ^1H and ^{31}P n.m.r. spectroscopy. No trisdimethylamino-derivative was detected, even after vacuum distillation (ca 110°, 0.05 mm.Hg).

(b) Dimethylaminolyses in diethyl ether solution.

Chlorodimethylaminophosphinothioyl(chlorodimethylaminophosphinoyl) methylamine, $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$:- A solution of dimethylamine (2.75g, 0.061 mol) in diethyl ether (50 ml) was slowly added to a stirred solution of dichlorophosphinothioyl-(dichlorophosphinoyl)methylamine, $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$, (4.23g, 0.015 mol) in diethyl ether (200 ml) at -78°. The reaction was allowed to come to room temperature (½h) and then stirred for a further 1½h. The dimethylammonium chloride precipitate was then carefully filtered and the diethyl ether evaporated to give a cloudy viscous liquid. This liquid was vacuum distilled (70°, 0.05 mm Hg) giving chlorodimethylaminophosphinothioyl(chloro-dimethylaminophosphinoyl)methylamine (3.0g, 67%) as a mixture of diastereoisomers (ratio 2:1). The major diastereoisomer was isolated as a white crystalline solid (m.p. 54-55.5°) by crystallisation from isopentane solution.

This method was also used in the following:

Reaction of dichlorophosphinothioyl(dichlorophosphinoyl)methylamine, $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$, with two mol equiv. of dimethylamine:- Dichlorophosphinothioyl(dichlorophosphinoyl)methylamine (3.1g, 0.011 mol) and dimethylamine (1.0g, 0.022 mol) were stirred in diethyl ether (300 ml) for 1h after mixing at -78°. The clear viscous liquid obtained on work up was found (using ^1H and ^{31}P n.m.r.) to consist of a mixture of $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$, $Cl_2(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$, $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ and $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$ in a 3:1:2:3 ratio respectively.

Reaction of dichlorophosphinothioyl(dichlorophosphinoyl)methylamine, $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$, with 3.6 mol equiv. of dimethylamine:- Dichlorophosphinothioyl(dichlorophosphinoyl)methylamine (1.4g, 0.0050 mol) and dimethylamine (0.80g, 0.018 mol) were stirred in diethyl ether (250 ml) for 1h after mixing at -78°. A clear viscous liquid was obtained on work up consisting of a mixture of $Cl_2(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$ and $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$ in a 1:5 ratio respectively.

(c) Aminolysis by trimethylsilylamines.

Chlorodimethylaminophosphinothioyl(dichlorophosphinoyl)methylamine, $Cl_2(O)P{\cdot}NMe{\cdot}P(S)(Cl)NMe_2$:- Dimethylamino(trimethylsilyl)amine, Me_3SiNMe_2 (1.8g, 0.015 mol) in methylene chloride (20 ml) was slowly added to a stirred solution of dichlorophosphinothioyl(dichlorophosphinoyl)methylamine, $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ (4.25g, 0.015 mol) in methylene chloride (80 ml) at 0°. After refluxing (1h), the methylene chloride was evaporated off and the trimethylsilylchloride formed in the reaction removed under reduced pressure. The clear yellow oil remaining was vacuum distilled (68°, 0.05 mm Hg) giving chlorodimethylaminophosphinothioyl(dichlorophosphinoyl)methylamine (2.8g, 64%), a clear viscous liquid.

Chlorodiethylaminophosphinothioyl(dichlorophosphinoyl)methylamine, $Cl_2(O)P{\cdot}NMe{\cdot}P(S)(Cl)NEt_2$:- Similarly diethylamino(trimethylsilyl) amine, Me_3SiNEt_2, (1.6g, 0.011 mol) and dichlorophosphinothioyl (dichlorophosphinoyl)methylamine (3.1g, 0.011 mol) refluxed in

methylene chloride (100 ml) for 1h gave a brownish oil on work up. This oil on vacuum distillation (107°, 0.05mm Hg) gave chlorodiethylaminophosphinothioyl(dichlorophosphinoyl)methylamine (2.5g, 72%), a clear viscous liquid.

(d) Attempted condensation reactions.

Attempted reaction of bisdimethylaminophosphinothioylmethylamine, $(Me_2N)_2(S)P{\cdot}NHMe$ with phosphoryl chloride:- Triethylamine (3.0g, 0.030 mol) in benzene (20 ml) was slowly added to a stirred solution of bisdimethylaminophosphinothioylmethylamine (5.1g, 0.028 mol) and phosphoryl chloride (4.3g, 0.028 mol) in benzene (80 ml) at ambient temperature. The solution was refluxed for 24h. The benzene was then evaporated, but extraction of residue with diethyl ether resulted in the near quantitative recovery of bis(dimethylamino)phosphinothioylmethylamine. A thick brownish tar remained which contained triethylamine - possibly in the form of an adduct with phosphoryl chloride.

This method was also used in the following attempted condensation reactions:

Attempted reaction of bisdimethylaminophosphinothioylmethylamine, $(Me_2N)_2(S)PNHMe$, with thiophosphoryl chloride:- Bisdimethylaminophosphinothioylmethylamine (2.5g, 0.014 mol), thiophosphoryl chloride (2.4g, 0.014 mol) and triethylamine (1.5g, 0.015 mol) were refluxed in chloroform (100 ml) for 3h. Work up led to the recovery of bisdimethylaminophosphinothioylmethylamine. A thick yellowish tar containing triethylamine (possibly in the form of an adduct with thiophosphoryl chloride) remained.

Attempted reaction between bisdimethylaminophosphinothioylmethylamine, $(Me_2N)_2(S)PNHMe$, with bisdimethylaminophosphinoyl chloride, $(Me_2N)_2(O)PCl$:- Bisdimethylaminophosphinothioylmethylamine (5.1g, 0.028 mol), bisdimethylaminophosphinoyl chloride (4.75g, 0.028 mol), and triethylamine (2.9g, 0.029 mol) were refluxed in benzene (100 ml) for 15h. No reaction occurred.

Attempted preparations of dichlorophosphinothioyl(chlorodimethylaminophosphinoyl)methylamine, $Me_2N(Cl)(O)P{\cdot}NMe{\cdot}P(S)Cl_2$:-

(1) Chlorodimethylaminophosphinoylmethylamine, $Me_2N(Cl)(O)PNHMe$, (5.45g, 0.035 mol), thiophosphoryl chloride (5.95g, 0.035 mol), and triethylamine (3.55g, 0.035 mol) were refluxed in diethyl ether (150 ml) for $\frac{1}{2}$h after mixing at 0°C. A white precipitate formed containing triethylamine (possibly in the form of an adduct with thiophosphoryl chloride) and unreacted chlorodimethylaminophosphinoylmethylamine was recovered.

(2) Dichlorophosphinothioylmethylamine, $Cl_2(S)PNHMe$ (2.95g, 0.018 mol), dimethylaminophosphinoyl dichloride, $Me_2N(O)PCl_2$ (2.9g, 0.018 mol), and triethylamine (1.8g, 0.018 mol) were refluxed in benzene (75 ml) for 3h. The triethylammonium chloride precipitate was filtered and the benzene evaporated. The residue contained a large amount of unreacted dimethylaminophosphinoyl dichloride. Other products present probably result from the condensation of dichlorophosphinothioylmethylamine molecules.

(e) Attempted thermal rearrangement:- Bis(bisdimethylaminophosphinothioyl)methylamine, $[(Me_2N)_2(S)P]_2NMe$, (4.95g, 0.015 mol) and bis(chlorodimethylaminophosphinothioyl)methylamine, $[Me_2N(Cl)(S)P]_2NMe$, (4.7g, 0.015 mol) were refluxed in chloroform for 24h. No reaction occurred.

(f) Attempted quarternisation of bis(bismethylaminophosphinothioyl)methylamine, $[(Me_2N)_2(S)P]_2NMe$ with methyl iodide:- Bis(bisdimethylaminophosphinothioyl)methylamine (0.7g, 0.002 mol) was added to a solution of methyl iodide (1.6g, 0.011 mol) in nitromethane (25 ml), and the mixture refluxed for 2h. No precipitate formed on the gradual addition of diethyl ether (200 ml). Bis(bisdimethylaminophosphinothioyl)methylamine was recovered almost quantitatively.

CHAPTER 3

NITROGEN-BRIDGED DIPHOSPHORUS COMPOUNDS - REACTIONS WITH PRIMARY AMINES

INTRODUCTION.

It was recently shown[12] that cyclodiphospha(III)zanes (V) ($R=Pr^i$ or Bu^t) are formed in the reactions of i-propylamine and t-butylamine with phosphorus trichloride. A similar reaction is also known to occur with primary aromatic amines, but under more forcing conditions.[10] The reaction scheme proposed[12] for the formation of the aliphatic ring compounds involves the formation and subsequent rapid cyclisation of the intermediate $Cl_2P{\cdot}NR{\cdot}P(Cl)NHR$ (XXXI) (Figure 14).

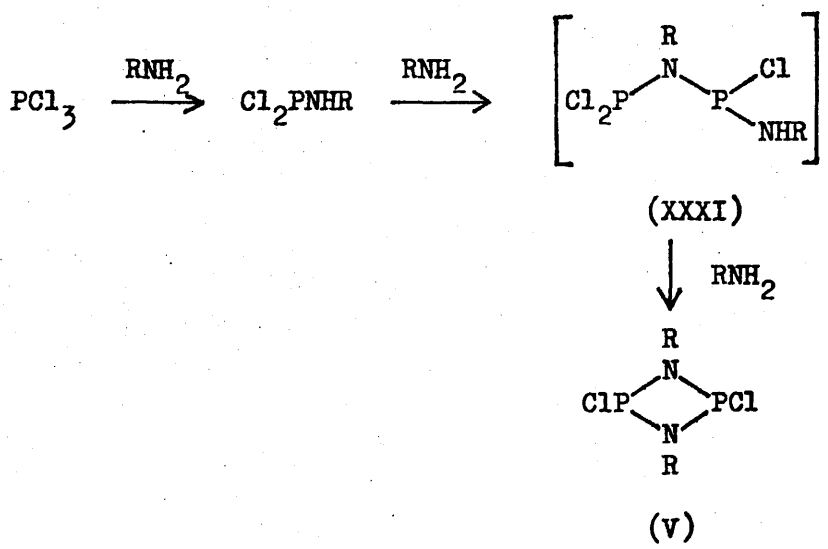


Figure 14 ($R=Pr^i$ or Bu^t)

The cyclodiphosphazane(V) ($R=Bu^t$) can also be obtained by the reaction of Cl_2PNHBu^t with triethylamine,[13] but in neither of these reactions could any direct evidence for the formation of the intermediate (XXXI) be obtained. By comparison, analogous

phosphorus(V) compounds $Cl_2(O)P{\cdot}NR{\cdot}P(O)(Cl)NHR$ (R=alkyl or aryl) are not obtained from the reaction of phosphoryl chloride with primary amines, but can be prepared by the reaction of hydrogen chloride with the corresponding cyclodiphospha(V)zanes. Compounds of the type $Cl_2(O)P{\cdot}NR{\cdot}P(O)(Cl)NHR$ readily cyclise in the presence of triethylamine to reform their parent cyclodiphospha(V)zane.[174]

It is therefore of interest to investigate the reactions of nitrogen-bridged diphosphorus compounds $Cl_2P{\cdot}NR{\cdot}PCl_2$, $Cl_2P{\cdot}NR{\cdot}P(X)Cl_2$ and $Cl_2(X)P{\cdot}NR{\cdot}P(X)Cl_2$ (X=O or S) with primary amines to discover

a) whether monoalkylamino-derivatives similar to intermediate (XXXI) can be isolated.

b) whether these compounds cyclise to form cyclodiphosphazanes.

RESULTS

(1) Reactions of $(Cl_2P)_2NR$ with primary amines.

Bis(dichlorophosphino)amines $(Cl_2P)_2NR$ (R=Me or Et) are best obtained from the reaction of the primary amine hydrochloride salt with phosphorus trichloride, heated under reflux in sym-tetrachloroethane.[11] The corresponding reaction with t-butylammonium chloride however is very slow, and in this case a cyclic rather than an acyclic product is obtained:

$$2\ PCl_3 + 2\ Bu^tNH_3Cl \longrightarrow (ClPNBu^t)_2 + 6\ HCl$$

It was subsequently found that bis(dichlorophosphino)t-butylamine, $(Cl_2P)_2NBu^t$, can be obtained from the condensation reaction

$$Cl_2PNHBu^t + PCl_3 \xrightarrow{Et_3N} (Cl_2P)_2NBu^t + HCl$$

The reactions of $(Cl_2P)_2NR$ (R=Me, Et or Bu^t) with a number of primary amines were investigated.

(a) Reaction with t-butylamine:- Reaction of $(Cl_2P)_2NR$ (R=Me, Et or Bu^t) with three mol equiv. of t-butylamine readily occurs giving cyclodiphospha(III)zanes $ClP{\cdot}NR{\cdot}PCl{\cdot}NBu^t$ (R=Me, Et or Bu^t), and provides the first route to cyclodiphospha(III)zanes containing different nitrogen substituents.

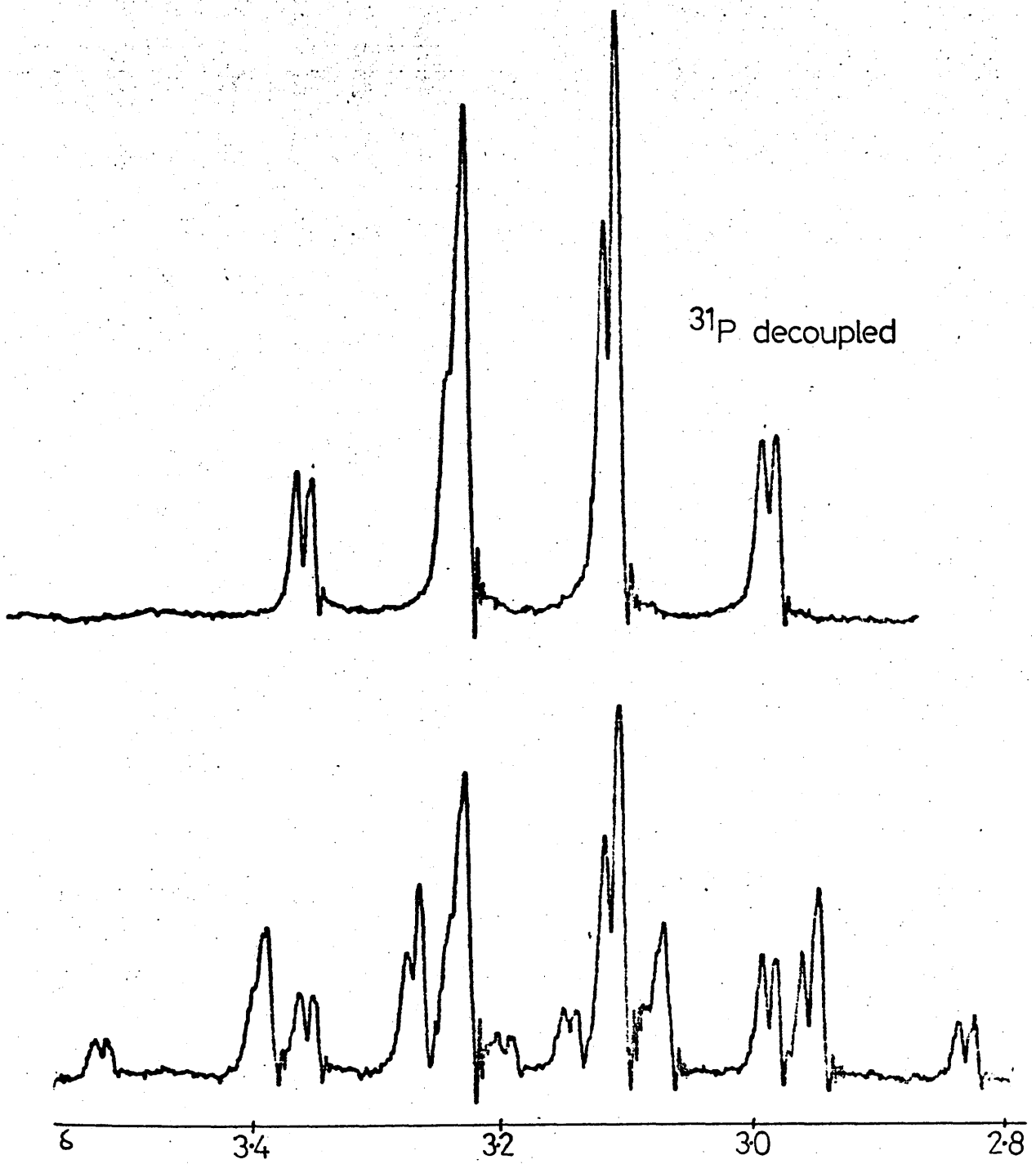
$$Cl_2P{\cdot}NR{\cdot}PCl_2 + 3\ Bu^tNH_2 \longrightarrow \underset{Bu^t}{\overset{R}{\overset{N}{ClP\langle}\rangle\overset{N}{PCl}}} + 2\ Bu^tNH_3^+Cl^- \qquad 18$$

The size of the R-group does not appear to be very important since little difference was observed in the ease with which $(Cl_2P)_2NMe$ and $(Cl_2P)_2NBu^t$ underwent cyclisation. There was no

direct evidence for the presence of intermediates $Cl_2P{\cdot}NR{\cdot}P(Cl)NHBu^t$ even on reaction with two mol equiv. of t-butylamine - a mixture of $(Cl_2P)_2NR$ and $\overline{ClP{\cdot}NR{\cdot}PCl{\cdot}NBu^t}$ only being detected.

^1H and ^{31}P n.m.r. indicate that only one isomer of the cyclodiphosphazanes $\overline{ClP{\cdot}NR{\cdot}PCl{\cdot}NBu^t}$ (R=Me, Et or Bu^t) is formed in each case. The cyclodiphosphazane, $(ClPNBu^t)_2$, prepared via reaction 18, was found to be identical with $(ClPNBu^t)_2$ prepared by other routes.[12,13] An X-ray crystal structure determination has shown this to be the cis isomer.[212] Surprisingly two chemically shifted CH_2-proton signals were found in the ^1H n.m.r. spectrum of $\overline{ClP{\cdot}NEt{\cdot}PCl{\cdot}NBu^t}$ (figure 15). It is unlikely that these arise from a mixture of geometrical isomers as the $^{31}P\{^1H\}$ n.m.r. spectrum consists of a sharp singlet. Instead the observed spectrum is probably due to diastereotopic CH_2-protons of the trans isomer of $\overline{ClP{\cdot}NEt{\cdot}PCl{\cdot}NBu^t}$, in which the outer lines of the AB quartet structure possess negligible intensities.

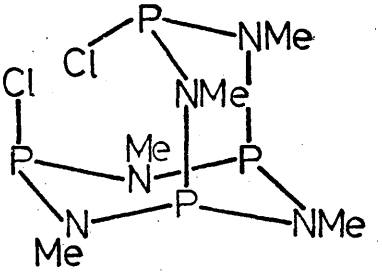
(b) Reactions with other primary amines:- In view of these findings, it seemed possible that cyclodiphospha(III)zanes with small alkyl groups, which have proved difficult to identify,[12] might be prepared by this route.



The CH_2 region of the 60 MHz ^1H n.m.r. spectrum of $ClP(\cdot NEt\cdot PCl\cdot NBu^t)$

Figure 15.

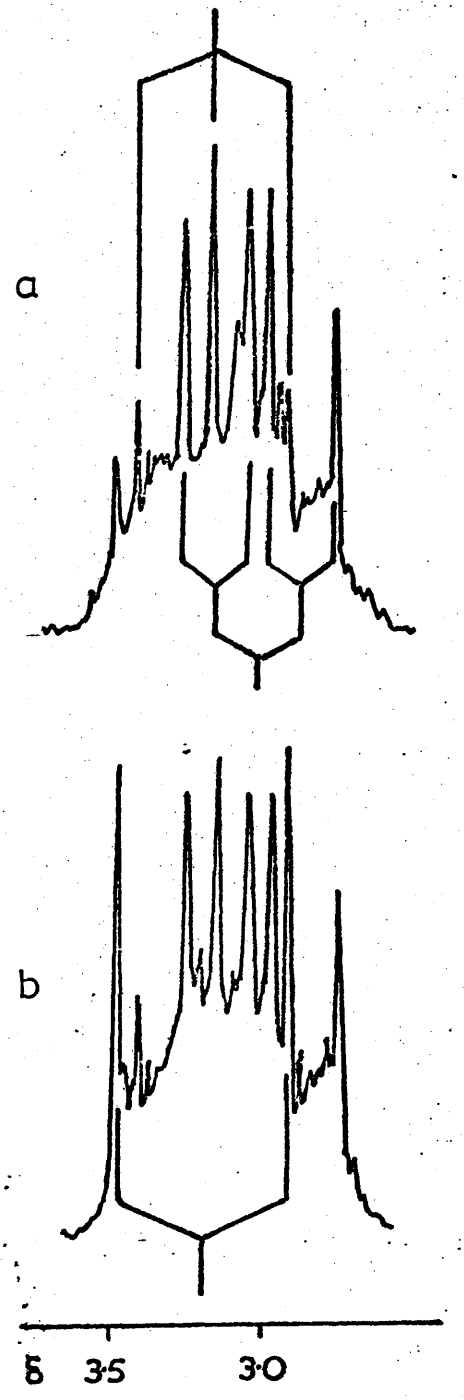
The attempted preparation of $(ClPNMe)_2$ by the reaction of $(Cl_2P)_2NMe$ with three mol equiv. methylamine gave products having the ^1H n.m.r. spectrum shown in Figure 16a. $^1H\{^{31}P\}$ double irradiation n.m.r. experiments showed that this multiplet was connected with ^{31}P signals well out of the range δ200 to δ250 p.p.m. anticipated for $(ClPNMe)_2$ (see Table 7), but nearer the range which may be anticipated for $(ClPNMe)_3$. After several days a new doublet (apparent $J_{(P-H)}$ 34.5 Hz) enclosing a central 'hump' started to appear (Figure 16b) which was connected with a signal at δ 117 p.p.m. in the ^{31}P n.m.r. spectrum. The mass spectrum of both mixtures indicated that ions $(ClPNMe)_n$ (n=2-4) were present, but the most intense molecular ion at m/e 339 had a two-chlorine-isotope pattern. This ion may be identified with compound (XXXII), a probable intermediate in the formation of the cage compound $P_4(NMe)_6$ (^{31}P shift δ 82 p.p.m.), known[14] to be formed from the reaction of phosphorus trichloride with excess methylamine.



(XXXII)

The recent isolation of compound (XXXII)[224] and the observation that its arsenic analogue, $As_4(NMe)_5Cl_2$ is formed[225] in the reaction of $As_4(NMe)_6$ with hydrogen chloride also lend support to its formation here. However, in view of the fact that the reaction mixtures could not be purified and the possibility of

^1H n.m.r. spectra of the products of the reaction of $(Cl_2P)_2NMe$ with 3 mol equiv. of methylamine recorded at 60 MHz.



(a) immediately after mixing the reagents (the triplet arises from coupling to phosphorus at 52 p.p.m. and the doublet of doublets from coupling to phosphorus at 52 and 127 p.p.m.)

(b) after 3 weeks (the new doublet arises by coupling to phosphorus at 117 p.p.m.).

Figure 16.

rearrangements occurring within the mass spectrometer, the presence of $(ClPNMe)_{2-4}$ as reaction products must be regarded as a tentative assignment only.

The analogous reaction between $(Cl_2P)_2NEt$ and ethylamine initially gave the cyclodiphospha(III)zane $(ClPNEt)_2$.

$$(Cl_2P)_2NEt + 3\ EtNH_2 \longrightarrow \underset{\text{Et}}{\overset{\text{Et}}{\text{ClP}\langle\text{N}\rangle\text{PCl}}} + 2\ EtNH_3^+Cl^-$$

The formation of $(ClPNEt)_2$ was indicated by the ^1H n.m.r. spectrum of the reaction mixture which showed a triplet of quartets in the region anticipated for the methylene proton signals. $^1H\{^{31}P\}$ double resonance experiments showed that the ^{31}P chemical shift was δ227 p.p.m. which closely matches the very low field shifts of other cyclodiphospha(III)zanes (Table 7). $(ClPNEt)_2$ may be present as a <u>cis</u> isomer, as the methylene protons appeared to be magnetically equivalent (see page 61). On standing at ambient temperatures, or on vacuum distillation, the original set of methylene proton signals was replaced by a new, more complex, set at lower field. The ^{31}P n.m.r. spectrum of this new product showed two ^{31}P signals at δ129 and 136 p.p.m. in a 1:2 intensity ratio, similar to that obtained from reaction of phosphorus trichloride and ethylamine.[12] Complete ^1H decoupling sharpened up these two signals to well defined singlets. The mass spectrum gave molecular ions corresponding to $(ClPNEt)_n$ (n= 2 or 3), with the latter predominating. The lack of n.m.r. evidence for

$(ClPNEt)_2$ in this second product suggests that its presence results from rearrangements within the mass spectrometer. Furthermore attempts to purify this compound were unsuccessful.

Reactions 19 and 20 both resulted in the formation of complex mixtures;

$$(Cl_2P)_2NBu^t + 3\ MeNH_2 \longrightarrow \text{complex mixture} \qquad 19$$

$$(Cl_2P)_2NMe + 3\ PhCH_2NH_2 \longrightarrow \text{complex mixture} \qquad 20$$

although in the ^1H n.m.r. spectra of both reaction mixtures, triplets coupled to phosphorus nuclei at very low field (δ226 in reaction 19 and δ230 in reaction 20) were detected indicating the presence of small amounts of the cyclodiphospha(III)zanes $ClP\overline{\cdot NMe\cdot PCl\cdot NBu^t}$ and $ClP\overline{\cdot NMe\cdot PCl\cdot NCH_2Ph}$.

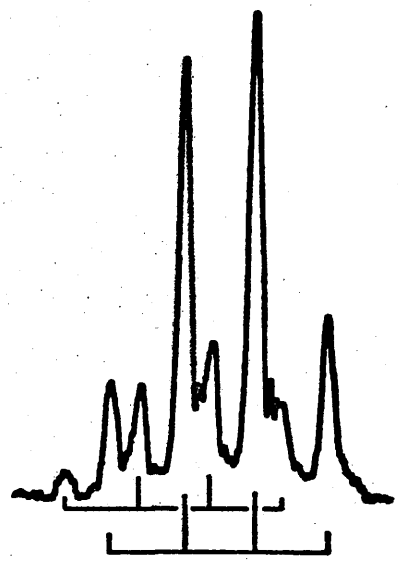
(2) Reactions of $[Cl_2(O)P]_2NR$ with t-butylamine

Bis(dichlorophosphinoyl)alkylamines, $[Cl_2(O)P]_2NR$ (R=Me or Et), react with three mol equiv. of t-butylamine in a similar manner to their tervalent analogues to give good yields of cyclodiphospha(V)zanes $Cl(O)P\overline{\cdot NR\cdot P(O)Cl\cdot NBu^t}$ (R=Me or Et).

$$Cl_2(O)P\cdot NR\cdot P(O)Cl_2 + 3\ Bu^tNH_2 \longrightarrow Cl(O)P\begin{matrix}\diagup N(R)\diagdown\\ \diagdown N(Bu^t)\diagup\end{matrix}P(O)Cl + 2\ Bu^tNH_3Cl$$

Nevertheless, some differences are apparent between the reactions of $(Cl_2P)_2NR$ and $[Cl_2(O)P]_2NR$ with t-butylamine.

The bisphosphinoyl compounds, $[Cl_2(O)P]_2NR$, are less reactive, requiring slight heating (diethyl ether reflux) or prolonged reaction times to effect complete reaction, and in each case the cyclodiphospha(v)zane formed was found to exist as a mixture of geometrical isomers. Structural assignment of the two isomers of $Cl(O)\overline{P{\cdot}NEt{\cdot}P(O)Cl{\cdot}NBu^t}$ (Figure 17) was not possible as the splitting expected from the diastereotopic methylene protons of the <u>trans</u> isomer could not be resolved in the 60 MHz ^1H n.m.r. spectrum.



The ^{31}P decoupled CH_2 region of the 60 MHz ^1H n.m.r. spectrum of $Cl(O)\overline{P{\cdot}NEt{\cdot}P(O)Cl{\cdot}NBu^t}$

The 24.3 MHz ^{31}P n.m.r. spectrum of $Cl(O)\overline{P{\cdot}NEt{\cdot}P(O)Cl{\cdot}NBu^t}$

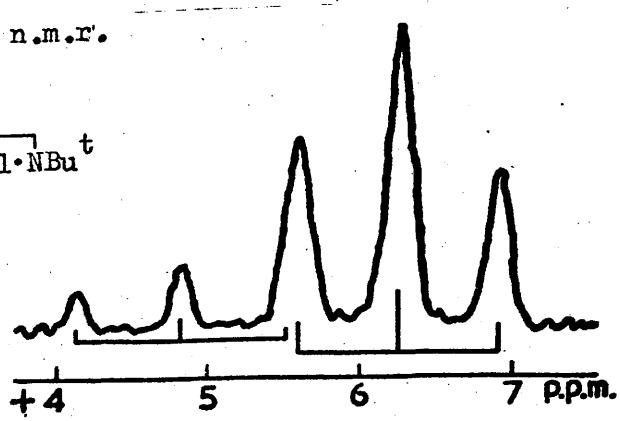
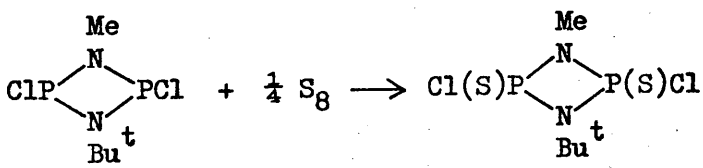


Figure 17.

Further differences were observed on reaction with two mol equiv. of t-butylamine - small quantities of the cyclisation intermediate $Cl_2(O)P{\cdot}NMe{\cdot}P(O)Cl{\cdot}NHBu^t$ being detected, mixed with $Cl(O)\overline{P{\cdot}NMe{\cdot}P(O)Cl{\cdot}N}Bu^t$ and $[Cl_2(O)P]_2NMe$. Cyclodiphospha(V)zanes could not be identified from reactions of $[Cl_2(O)P]_2NMe$ with the more reactive primary amines, methylamine and ethylamine, insoluble products being formed in each case.

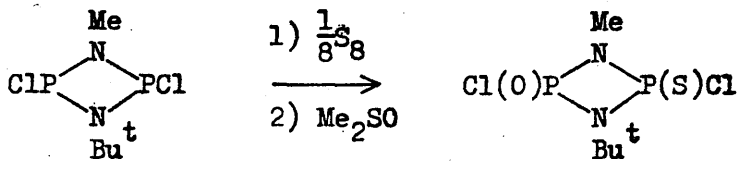
(3) Reactions of $[Cl_2(S)P]_2NMe$ and $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ with t-butylamine

Bis(dichlorophosphinothioyl)methylamine, $[Cl_2(S)P]_2NMe$, reacts with three mol equiv. of t-butylamine in refluxing chloroform to give only a small amount of $Cl(S)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}N}Bu^t$, the reaction mixture consisting mainly of $[Cl_2(S)P]_2NMe$ and unidentified products. The large proportion of these 'side reactions' make the preparation of $Cl(S)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}N}Bu^t$ by this route impractical. A better route to this 2,4-dithiocyclodiphosphazane proved to be the sulphuration of the corresponding cyclodiphospha(III)-zane $ClP\overline{{\cdot}NMe{\cdot}PCl{\cdot}N}Bu^t$ (see Chapter 5)



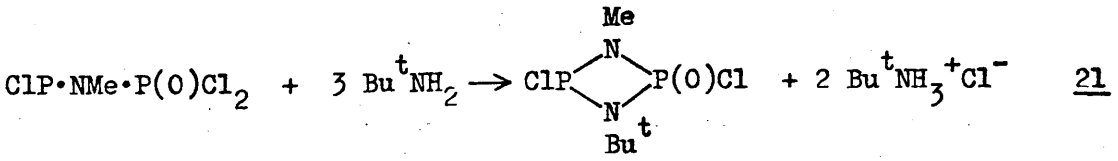
The reaction of dichlorophosphinothioyl(dichlorophosphinoyl) methylamine, $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$, with three mol equiv. of t-butylamine also gave a complex mixture of products, but in this

case no trace of the expected cyclodiphosphazane, $Cl(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$, could be found. Instead, like its 2,4-dithio-analogue this cyclodiphosphazane can also be formed from $ClP\overline{{\cdot}NMe{\cdot}PCl{\cdot}NBu^t}$ - by a stepwise sulphuration and oxidation (see Chapter 5).



(4) Reactions of $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$ and $Cl_2P{\cdot}NMe{\cdot}P(S)Cl_2$ with t-butylamine

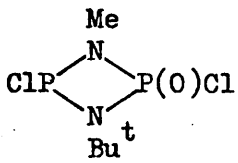
Dichlorophosphino(dichlorophosphinoyl)methylamine, $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$, reacts readily with three mol equiv. of t-butylamine to give on work up the cyclisation product, $ClP\overline{{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t}$.



21

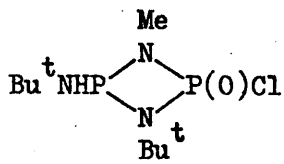
This mixed valence cyclodiphosphazane was initially obtained as a mixture of geometrical isomers, which over a period of days rearranged to give one isomer at ambient temperatures. A ^1H n.m.r. spectrum of the reaction solution, recorded less than 30 mins after mixing the reactants, indicated that this cyclisation is more complex than reaction 21 implies. By the use of $^1H\{^{31}P\}$

tickling experiments it was possible to identify the following components in the reaction solution (relative proportions in parentheses).



1:1 isomer mixture

(6)

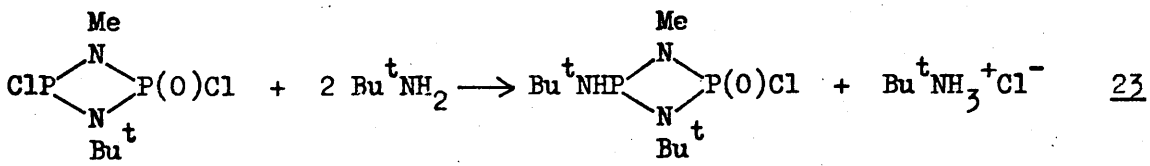


1 isomer

(3)

$Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$ (2) 22

$Bu^tNHP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$ could not be isolated from the solution, but was obtained as the sole product of the reaction:



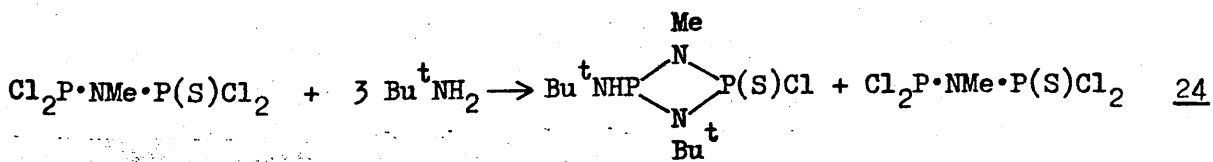
1 isomer

4:1 isomer mixture

23

Interestingly, the isomer of $Bu^tNHP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$ identified in the cyclisation reaction solution was found to be the minor isomer in reaction 23.

The reaction of dichlorophosphino(dichlorophosphinothioyl)-methylamine, $Cl_2P{\cdot}NMe{\cdot}P(S)Cl_2$, with three mol equiv. of t-butylamine initially followed a similar course to that encountered with the phosphinoyl analogue above:

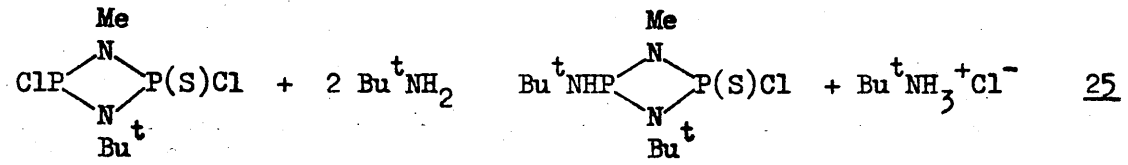


10:1 isomer mixture

(3) (1)

24

but in this case the products did not react further to form $ClP^{\bullet}NMe^{\bullet}P(S)Cl^{\bullet}NBu^{t}$. The formation of $Bu^{t}NHP^{\bullet}NMe^{\bullet}P(S)Cl^{\bullet}NBu^{t}$ was further substantiated by reaction 25:

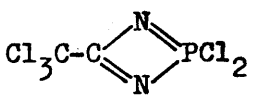


25

5:1 isomer mixture 1:1 isomer mixture

(5) Reaction of N-dichlorophosphinoyl-P,P,P-trichloro-phosphazene, $Cl_3P{=}N{-}P(O)Cl_2$, with t-butylamine.

A report[226] concerning the isolation of (XXXIII), the first four membered ring compound containing a formal phosphorus-nitrogen double bond, prompted the investigation of the reaction of the phosphazene $Cl_3P{=}N{-}P(O)Cl_2$ with t-butylamine. $Cl_3P{=}N{-}P(O)Cl_2$ however reacted stepwise with t-butylamine (figure 18) and showed no tendency to cyclise,



(XXXIII)

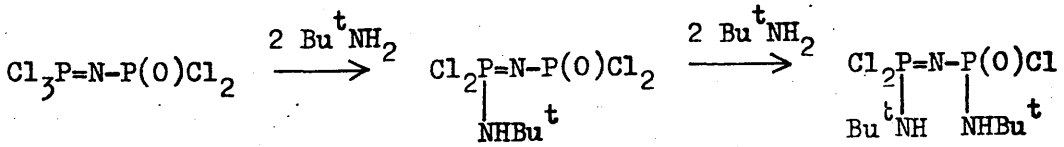
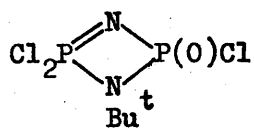


Figure 18

even on reaction of $Bu^{t}NH(Cl_2)P{=}N{-}P(O)Cl_2$ with triethylamine.

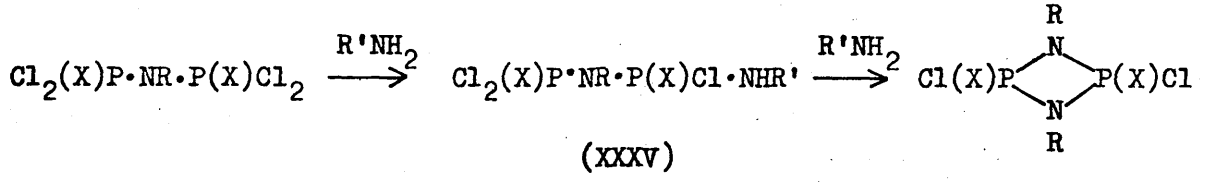
This is probably due to theP-N-P angle in phosphazenes of this type being generally around 140° [227] - much wider than the P-N-P angle in most nitrogen-bridged diphosphorus compounds (see p. 47). Thus greater ring strain in the resulting unsaturated four membered ring compound (XXXIV) would be expected.



(XXXIV)

Discussion.

The formation of cyclodiphosphazanes from the reaction of nitrogen-bridged diphosphorus compounds $[Cl_2(X)]_2NR$ (X=lone pair, O or S) with primary amines (especially t-butylamine) most probably involves the formation and subsequent rapid cyclisation of intermediates (XXXV) - see Figure 19.

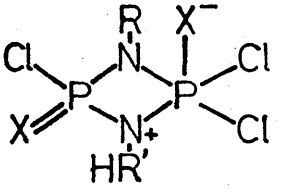


(XXXV)

Figure 19

The instability of intermediates of the general type $Cl_2P{\cdot}NR{\cdot}PCl{\cdot}NHR'$ in the presence of amine was also proposed[12] in the reaction scheme for the formation of cyclodiphosphazanes $(ClPNR)_2$ (R=Pr^i or Bu^t) from phosphorus trichloride and the corresponding primary amine (figure 14).

The ring closure step may be viewed in terms of the formation of the trigonal bipyramidal intermediate (XXXVI). Formation of such an intermediate will be favoured over one formed by an intermolecular aminolysis because of the relatively small loss of (rotational) entropy, any unfavourable enthalpy term reflecting ring strain being overcome by this entropy term. The detection of the cyclisation intermediate $Cl_2(O)P{\cdot}NMe{\cdot}P(O)Cl{\cdot}NHBu^t$ possibly indicates the presence of slightly greater ring strain in



(XXXVI)

(X=lone pair, O or S)

cyclodiphospha(V)zanes. Further evidence for this greater ring strain is also indicated by the larger $\widehat{NPN}$ found in cyclodiphospha(V)zane $[Cl(O)PNBu^t]_2$ (85.5^o)[194] compared with the cyclodiphospha(III)zane $(ClPNBu^t)_2$ (82.5^o)[212].

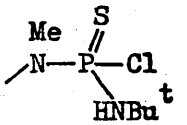
The observation that t-butylamine gives rise to much higher yields of cyclodiphosphazanes than other primary amines indicates that the entropy term is not the only factor controlling cyclisation. The function of the free amine in the cyclisation step is to abstract hydrogen chloride, and the ease with which this happens is clearly dependent on its base strength. t-Butylamine is a relatively strong base, but a poor nucleophile,[228] and, as such, it is likely to be more efficient in abstracting hydrogen chloride than effecting aminolysis at the second - $P(X)Cl_2$ group. On the other hand, methylamine and ethylamine, being stronger nucleophiles, will be more efficient in producing aminolysis products such as R'NH(Cl)(X)P·NR·P(X)(Cl)NHR' - probable precursors of the complex mixture of products generally obtained with these amines. Further evidence of the preferential action of t-butylamine as a base is provided by reaction 26,

$$Cl_2(O)P{\cdot}NMe{\cdot}P(O)Cl{\cdot}NHMe \xrightarrow{Bu^tNH_2} Cl(O)P\begin{smallmatrix} Me \\ N \\ N \\ Me \end{smallmatrix}P(O)Cl \qquad 26$$

where t-butylamine replaces triethylamine[174] as an HCl trap.

This tendency for t-butylamine to act solely as a base is considerably lower on reaction with $[Cl_2(S)P]_2NMe$, while with $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$ t-butylamine apparently shows no preferential

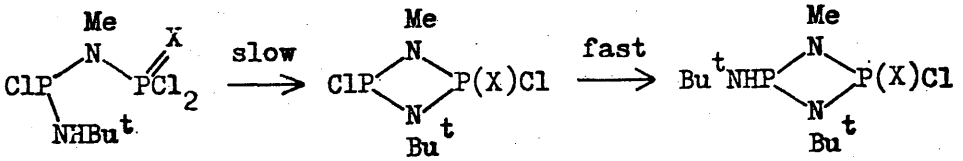
action as a base. Reasons for this differing reactivity of the amine towards these nitrogen bridged diphosphorus compounds containing $-P(S)Cl_2$ groups are not clear, but they may be partially connected with the expected tendency of the group (XXXVII) to undergo nucleophilic attack in basic conditions via a facile $S_N1(P)$ mechanism.



(XXXVII)

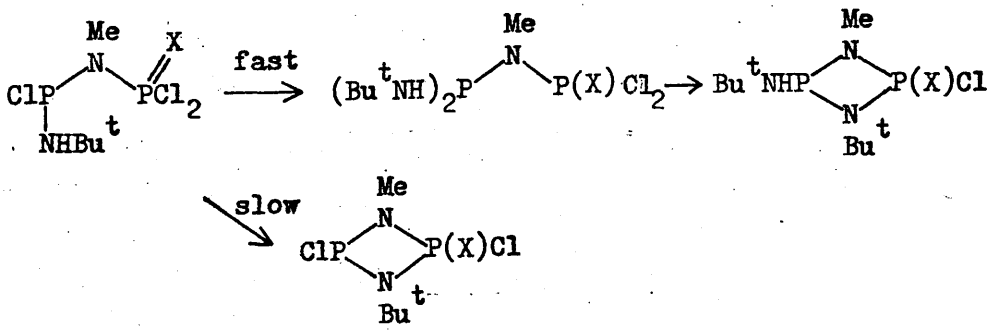
The reactions of $Cl_2P{\cdot}NMe{\cdot}P(X)Cl_2$ (X=O or S) with three mol equiv. of t-butylamine are complicated by the formation of $Bu^tNHP{\cdot}NMe{\cdot}P(X)Cl{\cdot}NBu^t$ (X=O or S). It is not clear whether the formation of these cyclodiphosphazanes is due to:

a) the rate of cyclisation being less than the rate of aminolysis of the first formed cyclodiphosphazane

i.e. 

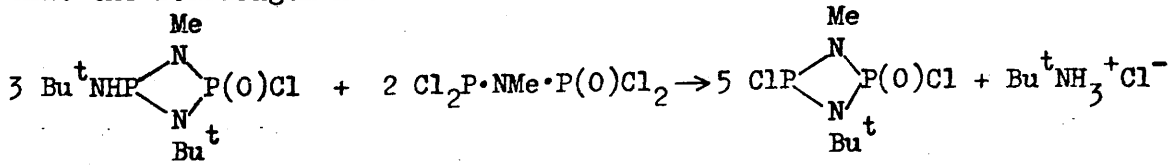
or

b) the rate of cyclisation being less than the rate of aminolysis to form $(Bu^tNH)_2P{\cdot}NMe{\cdot}P(X)Cl_2$ followed by subsequent cyclisation.

i.e. 

(Note that by analogy with the behaviour of $Me_2N{\cdot}SiMe_3$,[133] $Bu^tNH(Cl)P{\cdot}NMe{\cdot}P(X)Cl_2$ is the initial product expected from the reaction of $Cl_2P{\cdot}NMe{\cdot}P(X)Cl_2$ with t-butylamine). The lack of stereospecificity found in the formation of $Bu^tNHP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$ by aminolysis of $ClP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$ (reaction 25) compared with the cyclisation route to this compound (reaction 24), and the observation that the two routes to the formation of $Bu^tNHP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$ (reactions 22 and 23) result in different isomers predominating, are better accommodated by the cyclisation condition (b). On the other hand, it is doubtful whether the dichlorophosphinoyl and dichlorophosphinothioyl groups in the intermediates $Bu^tNH(Cl)P{\cdot}NMe{\cdot}P(X)Cl_2$ (X=O or S) possess low enough electrophilicities to hinder the entropy favoured cyclisation to such an extent as to allow the intermediates $(Bu^tNH)_2P{\cdot}NMe{\cdot}P(X)Cl_2$ (X=O or S) to be formed by futher aminolysis.

The fact that $ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$ can be obtained pure by solvent evaporation from the initial reaction mixture suggests that the rearrangement:



occurs fairly readily. The 3:2 stoichiometry is required to effect complete conversion to $ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$ observed in the reaction of $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$ with three mol equiv. of t-butylamine. The progress of this rearrangement could be followed by monitoring the ^1H n.m.r. of a solution of $Bu^tNHP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$ and $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$ over a period of several days.

It is interesting to note that the formation of cyclodiphospha(III)zanes is invariably stereospecific - only one of the two possible geometric isomers being obtained in every case. Of these, it is known that $(ClPNBu^t)_2$ has a cis structure,[212] and n.m.r. evidence, although not unambiguous, favours cis structures for $(ClPNEt)_2$ and $(ClPNPr^i)_2$.[12] The evidence presented, suggesting a trans structure for $ClP{\cdot}NEt{\cdot}PCl{\cdot}NBu^t$, however, indicates that the isomer obtained seems to reflect a very subtle balance of steric and/or electronic factors. By contrast the cyclodiphospha(V)zanes were obtained as mixtures of geometrical isomers. Unfortunately it is not yet clear whether the isomers of cyclodiphospha(III)zanes and cyclodiphospha(V)zanes obtained reflect thermodynamic or kinetic control.

In this context the observed isomerisation of $ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$ is of particular interest. In this case it appears that both isomers are kinetically almost equally favoured, subsequent isomerisation occurring to give the thermodynamically favoured product. Tervalent phosphorus is known to be configurationally stable at ambient temperatures and it is expected that the constraint of the cyclodiphosphazane ring will increase this stability, relative to analogous acyclic phosphorus(III) compounds. Isomerisation probably occurs by chloride ion exchange at tervalent phosphorus, as isomerisation is faster in the presence of added t-butylammonium chloride, and because phosphorus(III)-chlorine bonds are known to be more labile than phosphorus(V)-chlorine bonds.[229] In view of these results the previous findings

on the cyclisation of $(Cl_2P)_2NMe$ with t-butylamine were re-checked by examining the ^1H and ^{31}P n.m.r. spectra at ca-50°, recorded immediately after mixing the reactants at -78°. No evidence was found for more than one isomer.

EXPERIMENTAL.

Solvents were dried by conventional means. Methods used in the purification of reagents obtained commercially can be found in Appendix A. The compounds $(Cl_2P)_2NMe$,[11] $(Cl_2P)_2NEt$,[11] $[Cl_2(O)P]_2NMe$,[126] $[Cl_2(O)P]_2NEt$,[127] $[Cl_2(S)P]_2NMe$,[128] $Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$,[128] $Cl_2P{\cdot}NMeP(O)Cl_2$,[126] $Cl_2P{\cdot}NMe{\cdot}P(S)Cl_2$,[126] $Cl_3P{=}N{-}P(O)Cl_2$,[230] $Cl_2(O)P{\cdot}NMe{\cdot}P(O)(Cl)NHMe$,[174] and Cl_2PNHBu^t [13] were prepared using literature methods. Information on the instruments used in the measurement of n.m.r. data (see Table 7) and mass spectroscopic data (see Table 8), and the source of microanalyses (see Table 8) can be found in Appendix B.

Preparation of bis(dichlorophosphino)t-butylamine, $(Cl_2P)_2NBu^t$:- To a stirred solution of 17.4 g (0.1 mol) bis(dichlorophosphino) t-butylamine, Cl_2PNHBu^t, and 13.75 g (0.1 mol) phosphorus trichloride in 1000 ml diethyl ether at -78° was slowly added 10.1 g (0.1 mol) triethylamine in 50 ml diethyl ether. The reaction was stirred for a further 1.5h while the temperature rose to ca 20°. The triethylammonium chloride precipitate was removed by filtration and the diethyl ether evaporated to give a white solid. This was recrystallised from light petroleum (b.p. 40-60°) giving 18.5 g (65%) bis(dichlorophosphino)t-butylamine, a white, highly moisture sensitive crystalline solid m.p. ca 55°.

TABLE 7

N.m.r. data

Compound	^{31}P		^{1}H			
	$\delta\,^{31}P$	$^{2}J(\underline{P}\text{-N-}\underline{P})$	$\delta(\alpha\text{-CH})$	$\delta(\beta\text{-CH})$	$^{3}J(\underline{P}\text{-N-C-}\underline{H})$	$^{4}J(\underline{P}\text{-N-C-C-}\underline{H})$
	p.p.m.	Hz	p.p.m.	p.p.m.	Hz	Hz
$(Cl_2P)_2NMe$	160.8		3.32		3.0	
$(Cl_2P)_2NEt$	162.5		3.93	1.53	5.8	<0.3
$(Cl_2P)_2NBu^t$	169.1			1.74		1.0
$ClP{\cdot}NMe{\cdot}PCl{\cdot}NBu^t$	226		2.72	1.37	11.2	1.0
$ClP{\cdot}NEt{\cdot}PCl{\cdot}NBu^t$	219.5		ca 3.17	1.39(Bu^t) 1.26(Et)	9.5	1.0
$ClP{\cdot}NMe{\cdot}PCl{\cdot}NCH_2Ph$	230		2.68(Me) 4.22(CH_2)		ca 11(Me) ca 9(CH_2)	
$(ClPNBu^t)_2$	208.5			1.41		1.0

TABLE 7 (contd.)

Compound		^{31}P		^{1}H			
		$\delta^{31}P$ p.p.m.	^{2}J(P-N-P) Hz	δ(α-CH) p.p.m.	δ(β-CH) p.p.m.	^{3}J(P-N-C-H) Hz	^{4}J(P-N-C-C-H) Hz
$(ClPNEt)_2$		230		3.12	1.27	9.5	<0.3
$(ClPNEt)_3$		136(2)		3.95	1.52	5.5	<0.3
	and/or	129(1)					
$[Cl_2(O)P]_2NMe$		10.3		3.36		13.8	
$[Cl_2(O)P]_2NEt$				3.89	1.51	18.5	<0.3
$Cl(O)\overline{P\cdot NMe\cdot P(O)Cl\cdot NBu^t}$	(3)	-6.4		2.95	1.61	16.3	0.6
	(1)	-4.1		2.99	1.61	15.7	0.6
$Cl(O)\overline{P\cdot NEt\cdot P(O)Cl\cdot NBu^t}$	(4)	-6.2		3.32	1.57(Bu^t)	16.1	<0.5(both)
	(1)				1.41(Et)		
		-4.8		3.40	1.57 1.41	17.0	<0.5(both)

TABLE 7 (contd.)

Compound		^{31}P $\delta^{31}P$ p.p.m.	^{31}P $^{2}J(P\text{-}N\text{-}P)$ Hz	^{1}H $\delta(\alpha\text{-}CH)$ p.p.m.	^{1}H $\delta(\beta\text{-}CH)$ p.p.m.	^{1}H $^{3}J(P\text{-}N\text{-}C\text{-}H)$ Hz	^{1}H $^{4}J(P\text{-}N\text{-}C\text{-}C\text{-}H)$ Hz
$[Cl(O)PNMe]_2$	(4)	-3.0		2.97		17.0	
	(1)	0.0					
$Cl_2(O)P\cdot NMe\cdot P(O)Cl\cdot NHMe$		14.0($POCl_2$) 14.6					
$Cl_2(O)P\cdot NMe\cdot P(O)Cl\cdot NHBu^t$		ca 15		3.18		14.9($POCl_2$) 12.7	
$[Cl_2(S)P]_2NMe$		47.2		3.50		14.9	
$Cl(S)\overline{P\cdot NMe\cdot P(S)Cl\cdot NBu^t}$	(3)	47		2.96	1.73	17.1	0.6
	(2)	49		2.97	1.73	17.1	0.6

TABLE 7 (contd.)

Compound	^{31}P $\delta^{31}P$ p.p.m.	^{31}P $^{2}J(\underline{P}\text{-N-}\underline{P})$ Hz	^{1}H $\delta(\alpha\text{-CH})$ p.p.m.	^{1}H $\delta(\beta\text{-CH})$ p.p.m.	^{1}H $^{3}J(\underline{P}\text{-N-C-}\underline{H})$ Hz	^{1}H $^{4}J(\underline{P}\text{-N-C-C-}\underline{H})$ Hz
$Cl_2P\cdot NMe\cdot P(O)Cl_2$ [b]	170.1(P^{III})	+80±2	3.25		+ 1.5 (P^{III})	
	12.9				+15.5	
$Cl_2P\cdot NMe\cdot P(S)Cl_2$ [b]	167.7(P^{III})	+122±2	2.92		+ 1.2(P^{III})	
	51.4				+15.7	
$ClP(\cdot NMe\cdot P(O)Cl\cdot NBu^t)$ [b]	[a] 134 (P^{III})	-12.0	2.91	1.51	+10.2 (P^{III})	1.2 (P^{III})
	12.5				+18.7	<0.3
	135 (P^{III})	-36.3	3.13	1.34	+ 8.4 (P^{III})	1.9 (P^{III})
	8.0				+17.3	<0.5
$Bu^tNHP(\cdot NMe\cdot P(O)Cl\cdot NBu^t)$ [b]	[a] 85 (P^{III})	-10±3	2.60	1.31	+ 9.0 (P^{III})	1.4
	10			1.44(Bu^tNH)	+19.6	<0.3 (Bu^tNH)

TABLE 7 (contd.)

Compound	^{31}P $\delta^{31}P$ p.p.m.	^{31}P $^{2}J(P\text{-}N\text{-}P)$ Hz	^{1}H $\delta(\alpha\text{-CH})$ p.p.m.	^{1}H $\delta(\beta\text{-CH})$ p.p.m.	^{1}H $^{3}J(P\text{-}N\text{-}C\text{-}H)$ Hz	^{1}H $^{4}J(P\text{-}N\text{-}C\text{-}C\text{-}H)$ Hz
$Bu^tNHP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$ [b]	75.5 (P^{III})	-7.4	2.73	1.31	+ 9.0 (P^{III})	1.4
	3.1			1.44(Bu^tNH)	+17.7	<0.3(Bu^tNH)
[a]	101.5 (P^{III})	-8.5	2.54	1.30	+ 9.0 (P^{III})	1.5
	60.5			1.48(Bu^tNH)	+20.5	<0.3(Bu^tNH)
	107.5 (P^{III})	-8.5	2.68	1.30	+ 8.9 (P^{III})	1.5
	61.5			1.48(Bu^tNH)	+19.2	<0.3(Bu^tNH)
$Cl_3P{=}N{-}P(O)Cl_2$	-0.35	17.0				
	-13.9 (P=O)					
$Bu^tNH(Cl_2)P{=}N{-}P(O)Cl_2$	-1.8	±26.3		1.43	±14.5[c]	1.5
	-10.8(P=O)					
$Bu^tNH(Cl_2)P{=}N{-}P(O)(Cl)NHBu^t$	-3.4	30.2		1.45		
	-6.4(P=O)			1.35		

TABLE 7 (contd.)

a Major isomer in cyclisation reaction.

b Signs of coupling constants assume $^{3}J(P^{V}\text{-N-C-H})$ positive.[231]

c $^{2}J(P\text{-N-H})$; $^{4}J(P\text{-N-P-N-H}) = 4.9$ Hz.

TABLE 8

Analytical data[a]

Compound	Found				Calc.			
	C	H	N	m/e[b]	C	H	N	m/e[b]
$(Cl_2P)_2NBu^t$	18.8	3.2	5.6	273	17.5	3.3	5.1	273
$Cl\overline{P \cdot NMe \cdot PCl \cdot NBu^t}$	25.4	4.9		232	25.8	5.2		232
$Cl\overline{P \cdot NEt \cdot PCl \cdot NBu^t}$	28.8	5.5	28.7[d]	246	29.1	5.7	28.8[d]	246
$Cl(O)\overline{P \cdot NMe \cdot P(O)Cl \cdot NBu^t}$	22.7	5.1	10.8	249[c]	22.6	4.5	10.8	264
$Cl(O)\overline{P \cdot NEt \cdot P(O)Cl \cdot NBu^t}$	26.0	5.1	10.1	263[c]	25.8	5.1	10.0	278
$Cl\overline{P \cdot NMe \cdot P(O)Cl \cdot NBu^t}$	23.85	5.1	10.9	248	24.1	4.9	11.3	248
$Bu^tNH\overline{P \cdot NMe \cdot P(O)Cl \cdot NBu^t}$	37.0	7.8	14.3	285	37.8	7.7	14.7	285
$Bu^tNH\overline{P \cdot NMe \cdot P(S)Cl \cdot NBu^t}$	36.4	8.0	13.9	301	35.8	7.4	13.9	301
$Bu^tNH(Cl_2)P{=}N{-}P(O)Cl_2$	15.4	3.2	9.1	289[c]	15.7	3.3	9.2	304
$Bu^tNH(Cl_2)P{=}N{-}P(O)(Cl)NHBu^t$	28.3	6.7	12.1	326[c]	28.05	5.9	12.3	341

TABLE 8 (contd.)

a Elemental analysis figures are given in %

b For ions containing ^{35}Cl

c Parent -15 ion

d Cl Analysis

Reaction of phosphorus trichloride with t-butylammonium chloride:- To a solution of 413 g (3.00 mol) phosphorus trichloride in sym-tetrachloroethane (200 ml) was added 100 g (0.91 mol) t-butylammonium chloride and the mixture refluxed for 7 weeks during which time hydrogen chloride was slowly evolved. The solution on cooling was then filtered and excess phosphorus trichloride and sym-tetrachloroethane distilled off under reduced pressure. The residue on vacuum distillation (ca 80°, 0.1 mm Hg) gave 118 g (47% based on $Bu^tNH_3^+Cl^-$) 1,3-di-t-butyl-2,4-dichloro-cyclodiphosphazane, $(ClPNBu^t)_2$, a clear, colourless liquid which crystallised on standing.

Preparation of 1-t-butyl-2,4-dichloro-3-methylcyclodiphosphazane, $\overline{ClP{\cdot}NMe{\cdot}PCl{\cdot}NBu^t}$:- To stirred solution of 7.0 g (0.03 mol) bis(dichlorophosphino)methylamine in diethyl ether (125 ml) at -78° was slowly added 6.6 g (0.09 mol) t-butylamine in 25 ml diethyl ether. The reaction mixture was stirred until reaching ambient temperatures (0.5 h). The precipitate of t-butylammonium chloride was then removed by filtration and the diethyl ether evaporated off. The residue was carefully vacuum distilled, the fraction collected at 60-65° 0.05 mm Hg giving 3.7 g (53%) 1-t-butyl-2,4-dichloro-3 methylcyclodiphosphazane, a clear colourless liquid which crystallised on standing.

The following reactions were carried out using similar methods:

Preparation of 1-t-butyl-2,4-dichloro-3-ethylcyclodiphosphazane, $ClP(NEt)PCl(NBu^t)$:- 123.5 g (0.50 mol) bis(dichlorophosphino) ethylamine and 110 g (1.50 mol) t-butylamine were mixed in 1000 ml diethyl ether at -78° and stirred for 2h. The residue after work up gave on careful vacuum distillation (ca80°, 0.1 mm Hg) 75.5 g (61%) 1-t-butyl-2,4-dichloro-3-ethylcyclodiphosphazane, a clear colourless liquid.

Preparation of 1,3-di-t-butyl-2,4-dichlorocyclodiphosphazane, $(ClPNBu^t)_2$:- 2.50 g (0.0091 mol) bis(dichlorophosphino)t-butylamine and 2.0 g (0.027mol) t-butylamine were mixed in diethyl ether (60 ml) at -78° and then stirred (1h). The residue after work up gave on vacuum distillation (ca 80°, 0.15 mm Hg) 2.2 g (88%) 1,3-di-t-butyl-2,4-dichlorocyclodiphosphazane, a clear colourless liquid which crystallised on standing.

Reaction of bis(dichlorophosphino)methylamine with two mol equiv. of t-butylamine:- 4.9 g (0.021 mol) bis(dichlorophosphino)methylamine and 3.14 g (0.043 mol) t-butylamine were mixed in diethyl ether (100 ml) at -78° and then stirred (0.5h). A viscous liquid was obtained on work up which was found (by ^1H n.m.r.) to consist of a 2:1 mixture of $ClP(NMe)PCl(NBu^t)$ and $(Cl_2P)_2NMe$ respectively. No trace of the cyclisation intermediate $Cl_2P{\cdot}NMe{\cdot}P(Cl)NHBu^t$ could be found.

Reaction of bis(dichlorophosphino)methylamine with three mol equiv. of methylamine:- 2.1 g (0.009 mol) bis(dichlorophosphino)-methylamine and 0.95 g (0.031 mol) methylamine were mixed in 20 ml

methylene chloride at -78° and then stirred (0.5h). A viscous liquid was obtained on work up and the products investigated by n.m.r. and mass spectroscopy (see pp. 104-106).

Reaction of bis(dichlorophosphino)methylamine with three mol equiv. of benzylamine:- 9.35 g (0.0401 mol) bis(dichlorophosphino)-methylamine and 12.95 g (0.121 mol) benzylamine were mixed in 15 ml methylene chloride at -78° and then stirred (1h). A yellowish oil was obtained on work up which was shown (by ^{1}H n.m.r.) to conist of a complex mixture of compounds. 1-benzylamino-2,4-dichloro-3-methylcyclodiphosphazane, $\overline{ClP{\cdot}NMe{\cdot}PCl{\cdot}NCH_2Ph}$, was identified as a consitutuent of the mixture, but was not isolated.

Reaction of bis(dichlorophosphino)ethylamine with three mol equiv. of ethylamine:- 6.2 g (0.025 mol) bis(dichlorophosphino) ethylamine and 5.5 g (0.075 mol) ethylamine were mixed in 200 ml diethyl ether (or methylene chloride) at -78° and then stirred (1h). A yellowish oil was obtained on work up which was shown (by ^{1}H n.m.r.) to be mainly 2,4-dichloro-1,3-diethylcyclodiphosphazane, $(ClPNEt)_2$. This compound could not be purified as, on standing at ambient temperatures for over one day, or on vacuum distillation (100-120° 0.1 mm Hg) it rearranged to form a compound tentatively identified as the cyclotriphosphazane $(ClPNEt)_2$. This compound could not be purified by further vacuum distillation.

Reaction of bis(dichlorophosphino)t-butylamine with three mol equiv. of methylamine:- 3.25 g (0.0118 mol) bis(dichlorophosphino) t-butylamine and 1.1 g (0.0355 mol) methylamine were mixed in 80 ml diethyl ether at -78° and then stirred (1h). A viscous opaque

liquid was obtained on work up which was shown (by ^1H n.m.r.) to be a complex mixture in which $ClP{\cdot}NMe{\cdot}PCl{\cdot}NBu^t$ could be identified, but not isolated.

Preparation of 1-t-butyl-2,4-dichloro-3-methyl-2,4-dioxocyclodiphosphazane, $Cl(O)P{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$:- To a stirred solution of bis(dichlorophosphinoyl)methylamine (4.50 g, 0.017 mol) in 50 ml diethyl ether at 20° was slowly added 3.75 g (0.051 mol) t-butylamine in 10 ml diethyl ether. The reaction mixture was stirred for 20h at ambient temperatures, after which time the t-butylammonium chloride precipitate was removed by filtration and the diethyl ether evaporated off. The viscous residue consisted almost solely of a 3:1 isomer mixture of $Cl(O)P{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$, which was purified by vacuum distillation (130° 0.1 mm Hg) to give 2.57 g (57%) 1-t-butyl-2,4-dichloro-3-methyl-2,4-dioxocyclodiphosphazane, a clear colourless liquid of unchanged isomer ratio which crystallised on standing. The major isomer was separated by recrystallisation from a diethyl ether/light petroleum (b.p. 40-60°) mixture, giving white crystals m.p.84-86°.

The following reactions were carried out employing similar methods:

Preparation of 1-t-butyl-2,4-dichloro-3-ethyl-2,4-dioxocyclodiphosphazane, $Cl(O)P{\cdot}NEt{\cdot}P(O)Cl{\cdot}NBu^t$:- 3.63 g (0.013 mol) bis(dichlorophosphinoyl)ethylamine and 2.85 g (0.039 mol)

t-butylamine were mixed in 50 ml methylene chloride at 20°. The reaction was refluxed for 24h. Work up gave a viscous oil which consisted of almost solely a 4:1 isomer mixture of $Cl(O)\overline{P{\cdot}NEt{\cdot}P(O)Cl{\cdot}NBu^t}$. A white crystalline solid was obtained on vacuum distillation (ca 70° 0.01 mm Hg) which on recrystallisation from isopentane gave 1-t-butyl-2,4-dichloro-3-ethyl-2,4-dioxocyclodiphosphazane 2.54 g (70%), as clear crystals m.p. 40-55°C (isomer ratio unchanged).

Reaction of bis(dichlorophosphinoyl)methylamine with two mol equiv. of t-butylamine:- 3.18 g (0.012 mol) bis(dichlorophosphinoyl)-methylamine and 1.75 g (0.024 mol) t-butylamine were mixed in 50 ml diethyl ether at 0° and then stirred (10h). Work up gave a viscous oil shown (by ^1H n.m.r.) to consist of a mixture of $[Cl_2(O)P]_2NMe$, $Cl_2(O)P{\cdot}NMeP(O)Cl)NHBu^t$, and $Cl(O)\overline{P{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t}$ in a 10:1:10 ratio respectively. The cyclisation intermediate was not isolated from the reaction mixture.

Reaction of bis(dichlorophosphinoyl)methylamine with three mol equiv. of methylamine:- 1.6 g (0.006 mol) bis(dichloro-phosphinoyl)methylamine and 0.56 g (0.018 mol) methylamine were mixed in 100 ml diethyl ether at -78° and then stirred (1h). Insoluble products were precipitated from the reaction with methylammonium chloride. The small amount of residue remaining on work up was shown by ^1H n.m.r. to be a complex mixture. Similar results were obtained.from the reaction of bis(dichloro-phosphinoyl)methylamine with three mol equiv. of ethylamine, and from the reaction of dichlorophosphinothioyl(dichlorophosphinoyl) methylamine with three mol equiv. t-butylamine, the latter reaction requiring refluxing in diethyl ether for 3h.

Reaction of bis(dichlorophosphinothioyl)methylamine with three mol equiv. of t-butylamine:- 2.46 g (0.015 mol) bis(dichlorophosphinothioyl)methylamine and 3.3 g (0.045 mol) t-butylamine were mixed in 20 ml of chloroform at 20°C. The reaction was then refluxed for 24h. A viscous oil was obtained on work up consisting of mainly (on the basis of ^{1}H n.m.r.) $[Cl_2(S)P]_2NMe$ and $Cl(S)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$ in a 4:1 ratio. The amount of t-butylammonium chloride precipitated was consistent with incomplete reaction having occurred.

Cyclisation of dichlorophosphinoyl(chloro(methylamino)phosphinoyl)methylamine, $Cl_2(O)P{\cdot}NMe{\cdot}P(O)(Cl)NHMe$, by t-butylamine:- To a stirred solution of 0.60 g (0.0025 mol) dichlorophosphinoyl-(chloro(methylamino)phosphinoyl)methylamine in 20 ml of methylene chloride at 20° was slowly added 0.3 g (0.004 mol) t-butylamine in 5 ml methylene chloride. The mixture was stirred for 0.5h. The t-butylammonium chloride precipitate was removed by filtration and the methylene chloride evaporated to give a white crystalline solid shown by ^{1}H n.m.r. to be a 4:1 isomer mixture of 2,4-dichloro-1,3-dimethyl-2,4-dioxocyclodiphosphazane, $[Cl(O)PNMe]_2$.

Preparation of 1-t-butyl-2,4-dichloro-3-methyl-2-oxocyclodiphosphazane, $Cl\overline{P{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t}$:- To a stirred solution of 5.25 g (0.021 mol) dichlorophosphino(dichlorophosphinoyl)methylamine in

methylene chloride (80 ml) at -78° was slowly added 4.6 g (0.063 mol) t-butylamine in methylene chloride (20 ml). The reaction mixture was then stirred (1h) while being allowed to warm up to ambient temperature. The t-butylammonium chloride precipitate was removed by filtration and the methylene chloride evaporated off. The viscous oil remaining was vacuum distilled (102°, 0.6 mm Hg) to give 1-t-butyl-2,4-dichloro-3-methyl-2-oxocyclodiphosphazane, a clear colourless liquid.

^{1}H n.m.r. showed that the reaction residue consisted almost solely of a 4:1 isomer mixture of $ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$, which rearranged at the expense of the minor isomer on vacuum distillation (or after several days' standing) to give only one isomer. The isomer mixture of $ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$ prepared by oxidation of $ClP{\cdot}NMe{\cdot}PCl{\cdot}NBu^t$ (see Chapter 5) was found to remain unchanged over several weeks, but on the addition of finely powdered t-butylammonium chloride a rearrangement with the formation of one isomer occurred after several days.

Reaction of dichlorophosphino(dichlorophosphinothioyl)methylamine with three mol equiv. of t-butylamine:- A similar method to that used in the analogous reaction of $Cl_2P{\cdot}NMe{\cdot}P(O)Cl_2$ with t-butylamine was employed. 2.1 g (0.008 mol) dichlorophosphino-(dichlorophosphinothioyl)methylamine and 1.75 g (0.024 mol) t-butylamine were mixed in 25 ml of methylene chloride at -78°. A viscous oil was obtained on work up which was shown (by ^{1}H n.m.r.) to mainly consist of a 1:3 mixture of dichlorophosphino(dichloro-phosphinothioyl)methylamine and1-t-butyl-2-t-butylamino-4-chloro-3-methyl-4-thiocyclodiphosphazane, $Bu^tNHP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$, respectively.

Preparation of 1-t-butyl-2-t-butylamino-4-chloro-3-methyl-4-thiocyclodiphosphazane, $Bu^tNHP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$:- To a stirred solution of 0.8 g (0.003 mol) 1-t-butyl-2,4-dichloro-3-methyl-2-thiocyclodiphosphazane, $ClP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$ in methylene chloride (10 ml) at -78° was slowly added 0.45 g (0.006 mol) t-butylamine in 5 ml of methylene chloride. The reaction was stirred (2h) while warming up to ambient temperature. t-Butylammonium chloride precipitate was removed by filtration, and the methylene chloride evaporated off. The liquid residue was vacuum distilled (75-80°, 0.03 mm Hg) to give 0.68 g (75%) 1-t-butyl-2-t-butylamino-4-chloro-3-methyl-4-thiocyclodiphosphazane, a clear viscous liquid.

Preparation of 1-t-butyl-2-t-butylamino-4-chloro-3-methyl-4-oxocyclodiphosphazane, $Bu^tNHP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$:- A method similar to that used in the preparation of $Bu^tNHP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$ was employed. 1.25 g (0.005 mol) 1-t-butyl-2,4-dichloro-3-methyl-2-oxocyclodiphosphazane, $ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$, and 0.75 g (0.01 mol) t-butylamine were mixed in 25 ml of methylene chloride at -78°. A white solid was obtained on work up, shown by ^1H n.m.r. to consist almost solely of a 4:1 isomer mixture of $Bu^tNHP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$. The major isomer was separated by recrystallisation in light petroleum (b.p.40-60°) to give 0.85 g (60%) 1-t-butyl-2-t-butylamino-4-chloro-3-methyl-4-oxocyclodiphosphazane.

Reaction of 1-t-butyl-2-t-butylamino-4-chloro-3-methyl-4-oxocyclodiphosphazane, $Bu^tNHP\overline{\cdot NMe\cdot P(O)Cl\cdot NBu^t}$ with dichlorophosphino(dichlorophosphinoyl)methylamine:- Excess dichlorophosphino(dichlorophosphinoyl)methylamine was added to a solution of approx. 0.3 g (0.001 mol) $Bu^tNHP\overline{\cdot NMe\cdot P(O)Cl\cdot NBu^t}$ in deuterochloroform (2 ml). The reaction was monitored by ^1H n.m.r. After two days all the $Bu^tNHP\overline{\cdot NMe\cdot P(O)Cl\cdot NBu^t}$ had reacted to give a mixture of dichlorophosphino(dichlorophosphinoyl)-methylamine and $ClP\overline{\cdot NMe\cdot P(O)Cl\cdot NBu^t}$.

Preparation of N-dichlorophosphinoyl-P-t-butylamino-P,P-dichloro-phosphazene, $Bu^tNH(Cl_2)P{=}N{-}P(O)Cl_2$:- To a stirred solution of 7.4 g (0.028 mol) N-dichlorophosphinoyl-P,P,P-trichloro-phosphazene, $Cl_3P{=}N{-}P(O)Cl_2$ in methylene chloride (90 ml) at -78° was slowly added 4.05 g (0.056 mol) t-butylamine in 20 ml of methylene chloride. The reaction mixture was stirred (2h) while being allowed to warm up to ambient temperature. The t-butylammonium chloride precipitate was removed by filtration and the methylene chloride evaporated off to give a brownish liquid which solidified on standing. Recrystallisation from light petroleum (b.p. 40-60°) gave 4.3 g (72%) N-dichlorophosphinoyl-P-t-butylamino-P,P-dichloro-phosphazene, a white crystalline solid m.p. 60-61°.

Preparation of N-t-butylamino(chloro)phosphinoyl-P-t-butylamino-P,P-dichloro-phosphazene, $Bu^tNH(Cl_2)P{=}N{-}P(O)(Cl)NHBu^t$:- A similar method to that used in the preparation of $Bu^tNH(Cl_2)P{=}N{-}P(O)Cl_2$ was employed. 6.1 g (0.0225 mol)

N-dichlorophosphinoyl-P,P,P-trichloro-phosphazene, $Cl_3P{=}N{-}P(O)Cl_2$ and 6.65 g (0.091 mol) t-butylamine were mixed in 120 ml of methylene chloride at -78° and then stirred (5h). A brownish solid was obtained on work up which proved impossible to purify, but ^1H and ^{31}P n.m.r. and mass spectroscopy all indicated the formation of N-t-butylamino(chloro)phosphinoyl-P-t-butylamino-P,P-dichloro-phosphazene.

Attempted reaction of N-dichlorophosphinoyl-P-t-butylamino-P,P-dichloro-phosphazene, $Bu^tNH(Cl_2)P{=}N{-}P(O)Cl_2$ with triethylamine:- To a stirred solution of 1.5 g (0.0049 mol) N-dichlorophosphinoyl-P-t-butylamino-P,P-dichloro-phosphazene, $Bu^tNH(Cl_2)P{=}N{-}P(O)Cl_2$, in diethyl ether (100 ml) at -78° was slowly added 0.53 g (0.53 mol) triethylamine in 10 ml of diethyl ether. The reaction was allowed to warm up to ambient temperature and then refluxed (3h). N-dichlorophosphinoyl-P-t-butylamino-P,P-dichloro-phosphazene was recovered almost quantatively after filtration and evaporation of diethyl ether.

CHAPTER 4

AMINOLYSIS OF METHYLENE-BRIDGED DIPHOSPHORUS COMPOUNDS

PREPARATION OF TETRACHLORO-DERIVATIVES $[Cl_2(O)P]_2(CH_2)_n$ (n=1 or 2) AND $(Cl_2P)_2CH_2$.

A number of reports concerning the preparation of the methylene-bridged diphosphorus compounds $[Cl_2(X)P]_2CH_2$ (X= lone pair, O or S) have appeared during the last fifteen years. The method generally used in the preparation of bis(dichlorophosphinoyl)methane, $[Cl_2(O)P]_2CH_2$[232] involves the reaction:

$$[(RO)_2(O)P]_2CH_2 + [(HO)_2(O)P]_2CH_2 + 8\ PCl_5 \rightarrow 2\,[Cl_2(O)P]_2CH_2 + 8\ POCl_3 + 4\ RCl + 4\ HCl$$

It was found,[233] however, that inclusion of the acid $[(HO)_2(O)P]_2CH_2$ was unnecessary, chlorination simply occurring by the reaction:

$$[(Pr^iO)_2(O)P]_2CH_2 + 4\ PCl_5 \rightarrow [Cl_2(O)P]_2CH_2 + 4\ POCl_3 + 4\ Pr^iCl$$

Bis(dichlorophosphinoyl)1,2-ethane, $Cl_2(O)P{\cdot}CH_2CH_2{\cdot}P(O)Cl_2$, can be prepared by a similar reaction. Reaction of bis(dichlorophosphinoyl)methane with P_4S_{10} provides a route to its phosphinothioyl analogue $[Cl_2(S)P]_2CH_2$, but unfortunately only low yields are obtained.[234]

Bis(dichlorophosphino)methane, $(Cl_2P)_2CH_2$ is reported to be obtained from the reaction of $(Ph_2P)_2CH_2$ with phosphorus trichloride in a sealed tube at 280°.[235] On attempting to repeat this reaction, no trace of $(Cl_2P)_2CH_2$ was found, instead a mixture possibly containing Cl_2PCH_2Cl, in addition to the expected

chlorodiphenylphosphine and dichlorophenylphosphine, was obtained. However, $(Ph_2P)_2CH_2$ undergoes a ready reaction with refluxing phosphorus trichloride (0.5h):

$$(Ph_2P)_2CH_2 + PCl_3 \longrightarrow Ph_2P{\cdot}CH_2{\cdot}PCl_2 + Ph_2PCl$$

In addition an unidentified orange solid formed. Displacement of diphenylphosphino-groups was complete (indicated by the appearance of a triplet in the ^1H n.m.r. spectrum) after refluxing with phosphorus trichloride for 15h. Difficulties arose in the separation of both $Ph_2P{\cdot}CH_2{\cdot}PCl_2$ and $(Cl_2P)_2CH_2$ from chlorodiphenylphosphine, and all attempts to effect this resulted in decomposition of the desired products. Interestingly the ^{31}P shift reported[235] for $(Cl_2P)_2CH_2$ ($\delta 187\pm1$) is some 13 p.p.m. to low field of that found for the compound giving the triplet in the ^1H n.m.r. spectrum. However, in all other respects the ^1H and ^{31}P n.m.r. spectra (Table 9), obtained from phosphorus trichloride solutions, are consistent with the formation of $Ph_2P{\cdot}CH_2{\cdot}PCl_2$ and $(Cl_2P)_2CH_2$.

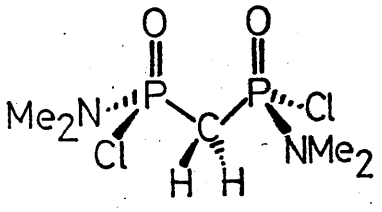
The tetrachloro-derivatives of methylene-bridged diphosphorus compounds provide a possible means of extending the scope of the aminolysis reactions discussed in the preceding two chapters, but, due to difficulties in their preparation, aminolysis reactions of only bis(dichlorophosphinoyl)methane and its 1,2-ethane analogue were investigated.

DIMETHYLAMINOLYSIS OF $[Cl_2(O)P]_2CH_2$.

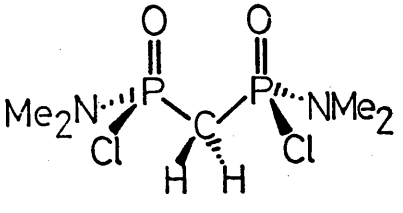
The reaction of bis(dichlorophosphinoyl)methane, $[Cl_2(O)P]_2CH_2$, with dimethylamine follows a similar course to that found[132] for its nitrogen-bridged analogue $[Cl_2(O)P]_2NMe$. Reaction with two mol equiv. of dimethylamine in methylene chloride gave a mixture of $[Me_2N(Cl)(O)P]_2CH_2$, $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)(Cl)NMe_2$ and starting material (reaction 27 - product ratios in parentheses).

$$[Cl_2(O)P]_2CH_2 + 2\ Me_2NH \longrightarrow \begin{cases} Cl_2(O)P{\cdot}CH_2{\cdot}P(O)(Cl)NMe_2 & (1) \\ +[Me_2N(Cl)(O)P]_2CH_2 & (2) \\ +[Cl_2(O)P]_2CH_2 & (2) \end{cases} \quad 27$$

Bis(chlorodimethylaminophosphinoyl)methane, $[Me_2N(Cl)(O)P]_2CH_2$, was obtained as the sole product of reaction with four mol equiv. of dimethylamine. ^1H and ^{31}P n.m.r. spectroscopy indicated that $[Me_2N(Cl)(O)P]_2CH_2$ was formed as a 3:1 mixture of diastereoisomers. Furthermore the 220 MHz ^1H spectrum of this mixture showed that the CH_2-protons of the minor diastereoisomer were magnetically non-equivalent. Only the meso diastereoisomer is expected to show this magnetic non-equivalence,



dl



meso

permitting a meso and dl assignment to be made. As with its nitrogen-bridged analogue $[Me_2N(Cl)(O)P]_2NMe$, a variation in the ratio of diastereoisomers of $[Me_2N(Cl)(O)P]_2CH_2$ occurs on heating. This results in an increase in the relative proportion of the meso isomer of the methylene-bridged compound, probably indicating its greater thermodynamic stability compared with the dl isomers. Further aminolysis, using excess dimethylamine, is reported to give the tetrakisdimethylamino-derivative $[(Me_2N)_2(O)P]_2CH_2$.[236]

The similarities in dimethylaminolysis substitution patterns of $[Cl_2(O)P]_2NMe$[132] and $[Cl_2(O)P]_2CH_2$ indicate that there is little difference in aminolysis mechanism. The formation of nongeminal bisdimethylamino-derivatives points to an associative mechanism being operative, the dimethylamino-group lowering the electrophilic nature of the phosphinoyl centre to which it is bonded. On the other hand the dimethylamino group is ineffective at lowering the electrophilic nature of the second phosphorus in $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)(Cl)NMe_2$. This may be due to an intramolecularly assisted nucleophilic mechanism (figure 20), as discussed in Chapter 2.

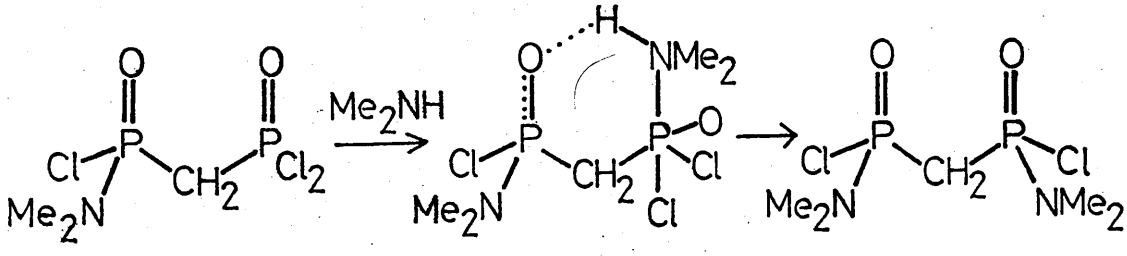


Figure 20.

REACTIONS OF $[Cl_2(O)P]_2CH_2$ WITH PRIMARY AMINES.

The reaction of bis(dichlorophosphinoyl)methane, $[Cl_2(O)P]_2CH_2$, with three mol equiv. of t-butylamine gives the ring compound (XXXVIII), as a mixture of geometrical isomers.

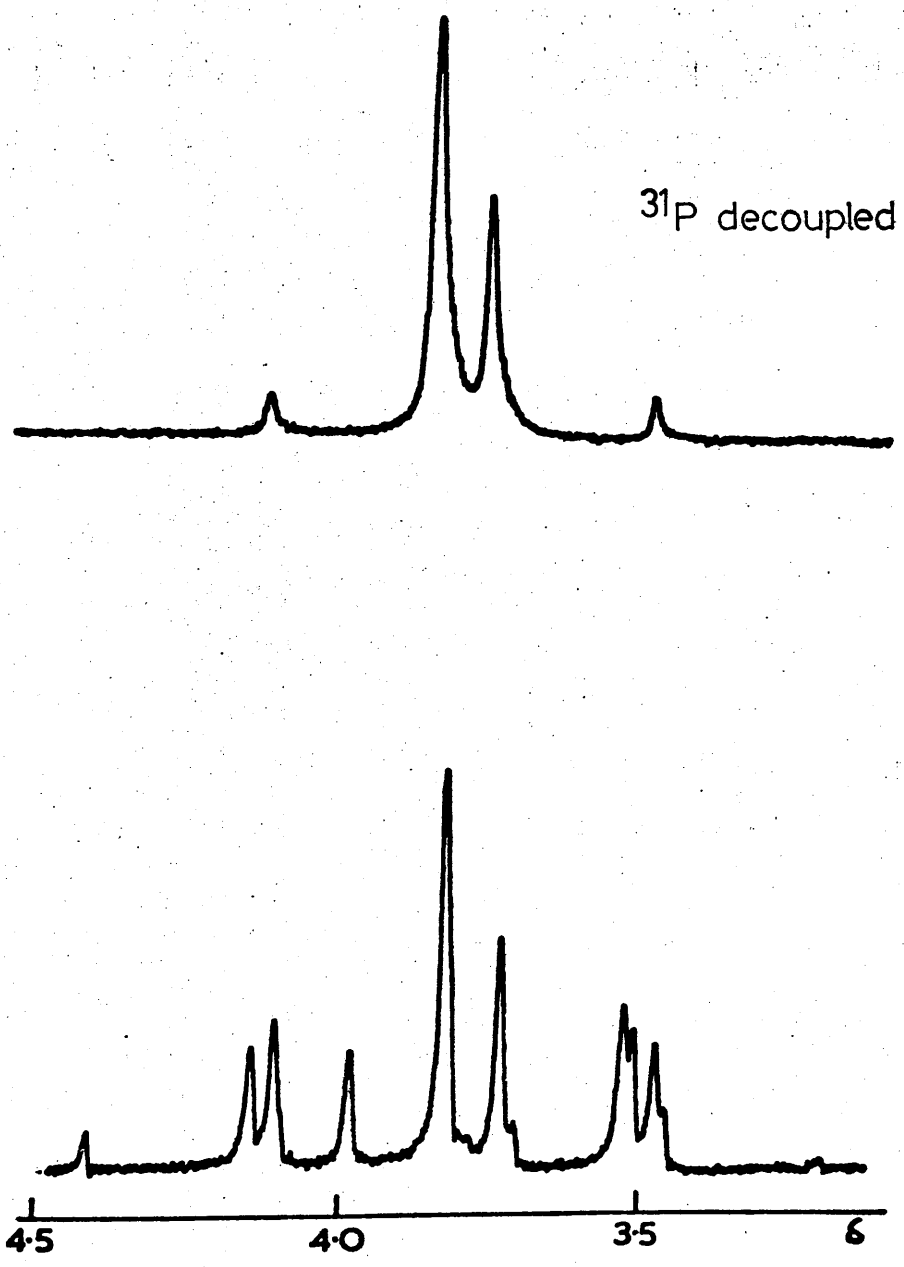
$$[Cl_2(O)P]_2CH_2 + 3\ Bu^tNH_2 \longrightarrow Cl(O)P\begin{matrix}CH_2\\ \diagup\quad\diagdown\\ N\\ |\\ Bu^t\end{matrix}P(O)Cl + 2\ Bu^tNH_3^+Cl^-$$

(XXXVIII)

Compounds belonging to this new class of ring compounds are not easily named using the phosphazane nomenclature, but can be classified as 1,2,4-azadiphosphetanes - thus (XXXVIII) becomes 1-t-butyl-2,4-dichloro-2,4-dioxoazadiphosphetane. A similar reaction with two mol equiv. of t-butylamine left starting material and compound (XXXVIII) only, in a 1:2 mol ratio. The acyclic t-butylamino-derivative $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)(Cl)NHBu^t$ was not detected, unlike the analogous reaction with $[Cl_2(O)P]_2NMe$ from which small quantities of $Cl_2(O)P{\cdot}NMe{\cdot}P(O)(Cl)NHBu^t$ were found (see Chapter 3).

The two isomers of (XXXVIII) were readily identified. The ^1H n.m.r. spectrum of (XXXVIII) is complex in the methylene region, but ^{31}P decoupling showed two groups of signals easily assignable to cis and trans isomers (see figure 21). If the four membered ring is assumed to be planar, then the methylene protons will be equivalent in the trans isomer, but nonequivalent (and therefore form an AB multiplet) in the cis isomer. Integration of these signals shows that the cis:trans isomer ratio is 5:2. The cis isomer can be separated from the mixture by crystallisation from a diethyl ether/petroleum solution.

The CH_2 region of the 60 MHz ^1H n.m.r. spectrum of $Cl(O)\overline{P \cdot CH_2 \cdot P(O)Cl \cdot NBu^t}$



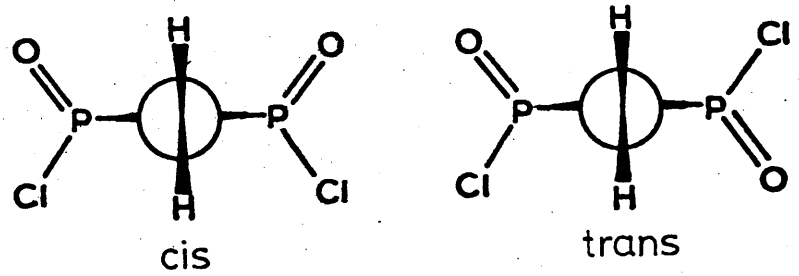


Figure 21

The analogous ring compound $Cl(O)\overline{P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NPr^i}$ was obtained from a similar reaction with i-propylamine with an almost identical cis:trans isomer ratio. However, there was a marked increase in the amount of unidentified insoluble material produced in this reaction, which proved impossible to remove completely. Furthermore attempts to repeat these reactions with aniline and ethylamine were unsuccessful, a complex mixture of products being obtained in each case.

The above reactions of $[Cl_2(O)P]_2CH_2$ with primary amines serve to re-emphasise the importance of the role of the nucleophile. As discussed in Chapter 3, cyclisation only occurs with primary amines which behave preferentially as bases toward intermediates like $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)(Cl)NHR$. i-Propylamine is expected to be a slightly better nucleophile than t-butylamine (due to lower steric bulk) - explaining the lower yields of 1,2,4-azadiphosphetane obtained with the former amine.

Cyclisation of intermediates $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)(Cl)CHR$ (R= Bu^t or Pr^i) is also favoured by the relatively small loss in entropy incurred. It is a feature of the cyclisation of α,ω-halogenoalkylamines, $Hal(CH_2)_nNH_2$[237,238] that the yield of cyclic products, $(CH_2)_nNH$, decreases with increasing n, mainly because of a larger negative entropy change when the larger rings are formed. It is therefore expected that the reactions of t-butylamine and i-propylamine with bis(dichlorophosphinoyl)-1,2-ethane, $Cl_2(O)P{\cdot}CH_2CH_2{\cdot}P(O)Cl_2$, might give reduced yields of cyclic products. It was found that reactions with t-butylamine

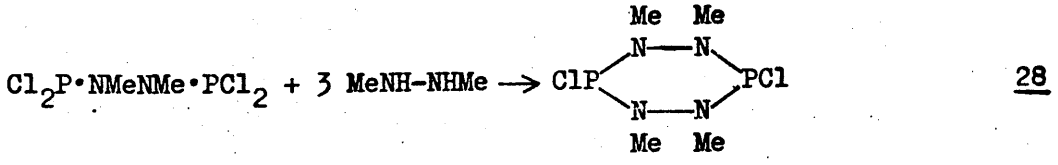
and i-propylamine gave no detectable amounts of ring compounds, instead, in each case, large quantities of an unidentified white solid was precipitated from the reaction, with the amine hydrochloride. N.m.r. spectra of the small amounts of soluble residue remaining were complex, indicating that a mixture of compounds was probably present. Thus it can be seen that the entropy term also has a critical role in the reaction of bis(dichlorophosphinoyl)alkanes with primary amines.

It is worth noting that the high dependence shown by the above reactions on,

a) the entropy term

b) the relative nucleophilicity and basicity of the amine,

is not necessarily of such paramount importance in all cyclisation reactions of this type (see reactions 28[239] and 29[240])



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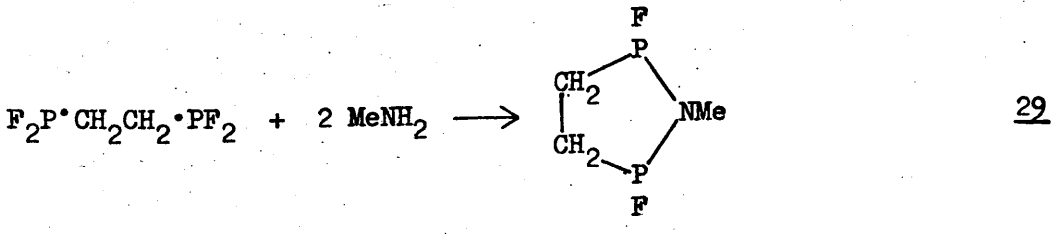


29

In these examples it is possible that factors such as the use of vapour phase reaction conditions in reaction 29, and the oxidation state of phosphorus may be instrumental in modifying the course of the reaction.

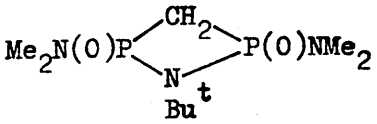
OTHER AMINOLYSIS REACTIONS.

In order to investigate how the electrophilicity of the phosphinoyl centre affects cyclisation, the reactions of the dimethylamino-derivatives $[Me_2N(Cl)(O)P]_2CH_2$ and $[Me_2N(Cl)(O)P]_2NMe$ with t-butylamine were examined. Unexpectedly it was found that the methylene-bridged compound gave an acyclic product in refluxing chloroform solution;

$$[Me_2N(Cl)(O)P]_2CH_2 + 4\ Bu^tNH_2 \rightarrow [Bu^tNH(Me_2N)(O)P]_2CH_2 + 2\ Bu^tNH_3^+Cl^-$$

whereas $[Me_2N(Cl)(O)P]_2NMe$ remained unreactive under the same conditions. The reduced reactivity observed for the latter compound is probably due to the increased degree of amino-substitution about phosphorus lowering the electrophilicity of $[Me_2N(Cl)(O)P]_2NMe$ compared to $[Me_2N(Cl)(O)P]_2CH_2$. This effect is seen to a lesser extent in the preparations of the tetrakisdimethylamino-derivatives $[(Me_2N)_2(O)P]_2NMe$[132] and $[(Me_2N)_2(O)P]_2CH_2$[236], in which refluxing diethyl ether solution is required to give $[(Me_2N)_2(O)P]_2NMe$, whereas the latter is formed on reaction at 0°.

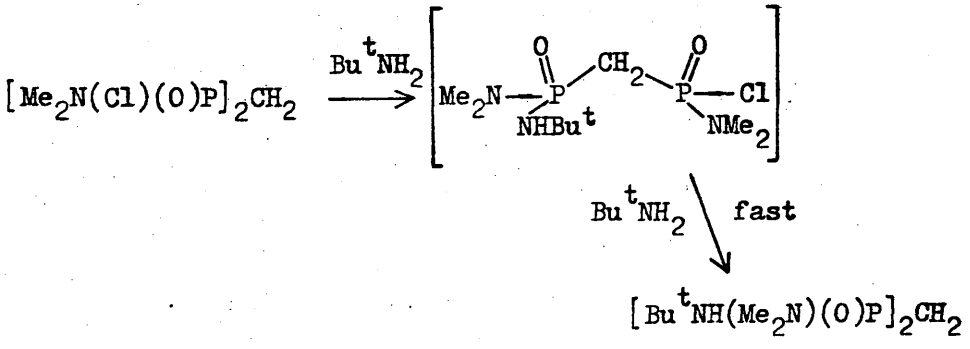
To test the possibility that the acyclic product $[Bu^tNH(Me_2N)(O)P]_2CH_2$ may be formed via a facile ring opening reaction of (XXXIX) with t-butylamine, the synthesis of (XXXIX) from the reaction of $Cl(O)\overline{P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t}$ with dimethylamine was attempted, with the following result.



(XXXIX)

$$Cl(O)P\langle^{CH_2}_{N(Bu^t)}\rangle P(O)Cl + 5\ Me_2NH \rightarrow (Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)(NHBu^t) + 2\ Me_2NH_2^+Cl^- \quad 30$$

However $(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)(NHBu^t)$ on heating cyclised with the elimination of dimethylamine to form (XXXIX). The ^1H n.m.r. spectrum of (XXXIX) showed that the CH_2 protons were magnetically equivalent indicating that a pure trans isomer was obtained. Trans $Me_2N(O)\overline{P{\cdot}CH_2{\cdot}P(O)(NMe_2){\cdot}NBu^t}$ failed to react with t-butylamine or dimethylamine in refluxing chloroform solution. The resistance to ring opening reactions displayed by $Me_2N(O)\overline{P{\cdot}CH_2{\cdot}P(O)(NMe_2){\cdot}NBu^t}$ provides strong evidence that both acyclic amino-derivatives $[Bu^tNH(Me_2N)(O)P]_2CH_2$ and $(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)NHBu^t$ are formed via pathways which do not involve $Me_2N(O)\overline{P{\cdot}CH_2{\cdot}P(O)(NMe_2){\cdot}NBu^t}$ as an intermediate. Thus the reaction of $[Me_2N(Cl)(O)P]_2CH_2$ with t-butylamine must proceed via the reaction scheme:



Further information on the formation of $(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)NHBu^t$ was obtained on repeating reaction 30 using less than five mol equiv. of dimethylamine. Examination of the reaction mixture by ^1H and ^{31}P n.m.r. indicated the presence of the 1,2,4-azadiphosphetane, $Me_2N(O)\overline{P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t}$, showing that at least part of reaction 30 proceeds via a ring opening of this monodimethylamino-derivative of $Cl(O)\overline{P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t}$. The ease with which ring opening occurs

in reaction 30 is unexpected in view of previous studies of the amine induced ring opening of cyclodiphosphazanes, which, with the exception of the cleavage of $[ClP(S)NMe]_2$[173] (or a methylamino-derivative) by methylamine, generally require relatively forcing conditions.[46]

EXPERIMENTAL.

Solvents were dried by conventional means. Methods used in the purification of reagents obtained commercially can be found in Appendix A. The compounds $(Ph_2P)_2CH_2$,[241] $[(Pr^iO)_2(O)P]_2(CH_2)_n$ (n=1 or 2),[242] and $[Me_2N(Cl)(O)P]_2NMe$[132] were prepared by literature methods.

Details of n.m.r. and mass spectroscopic instrumentation and the source of microanalyses can be found in Appendix B. N.m.r. data and analytical data are given in Tables 9 and 10 respectively. The magnitudes and relative signs of $^2J(\underline{P}\text{-}C\text{-}\underline{H})$ in the 1,2,4-azadiphosphetane cis-$Cl(O)\overline{P\cdot CH_2\cdot P(O)Cl\cdot NBu^t}$ were obtained by analysing the CH_2-proton signals as the AB part of an ABX_2 spin system.[243]

TABLE 9

N.m.r. data

Compound		^{31}P		^{1}H				
		$\delta(^{31}P)$ p.p.m.	$^{2}J(\underline{P}\text{-}C\text{-}\underline{P})$ Hz	$\delta(CH)$ p.p.m.	$\delta(NMe)$ p.p.m.	$\delta(Bu^{t})$[b] p.p.m.	$^{2}J(\underline{P}\text{-}C\text{-}\underline{H})$ Hz	$^{3}J(\underline{P}\text{-}N\text{-}C\text{-}\underline{H})$ Hz
$(Ph_2P)_2CH_2$		-22.2		2.74		7.15(Ph)	1.5	
$Ph_2P\cdot CH_2\cdot PCl_2$		-26[a] 189(PCl_2)	±132.5	ca 3.2[a]			± 1.9 ±15.4(PCl_2)	
$(Cl_2P)_2CH_2$		174[a]		ca 3.6[a]			15.6	
$[Cl_2(O)P]_2CH_2$		22.6		4.18			18.3	
$Cl_2(O)P\cdot CH_2CH_2\cdot P(O)Cl_2$		42.5		3.04			4.5[c]	
$Cl_2(O)P\cdot CH_2\cdot P(O)(Cl)NMe_2$		29.2 28.4($P(O)Cl_2$)	11.6	3.92 4.09	2.79		both ca 19 15.3[d]	14.5
$[Me_2N(Cl)(O)P]_2CH_2$	dl	32.0		3.46	2.81		18.1	14.2[e]
	meso	31.8		3.28 3.42	2.80		15.6[d]	14.2[e]

TABLE 9 (contd.)

Compound		^{31}P $\delta(^{31}P)$ p.p.m.	^{31}P $^{2}J(P\text{-}C\text{-}P)$ Hz	^{1}H $\delta(CH)$ p.p.m.	^{1}H $\delta(NMe)$ p.p.m.	^{1}H $\delta(Bu^{t})$[b] p.p.m.	^{1}H $^{2}J(P\text{-}C\text{-}H)$ Hz	^{1}H $^{3}J(P\text{-}N\text{-}C\text{-}H)$ Hz
$[(Me_2N)_2(O)P]_2CH_2$[f]		g		2.38	2.66			
$Cl(O)\overline{P\cdot CH_2\cdot P(O)Cl\cdot NBu^t}$	cis	6.1		3.72 3.92		1.59	±19.8 ±14.4 ‡16.2[d]	
	trans	6.9		3.88		1.59	16.5	
$Cl(O)\overline{P\cdot CH_2\cdot P(O)Cl\cdot NPr^i}$	cis	5.8		3.65 3.85		1.52(Pr^i)	16.3[d]	
	trans	7.3		3.77		1.52(Pr^i)	17.3	
$Cl(O)\overline{P\cdot CH_2\cdot P(O)(NMe_2)NBu^t}$		6.1 11.1	30	g	2.75	1.44	g	10.7

TABLE 9 (contd.)

Compound	^{31}P		^{1}H				
	$\delta(^{31}P)$ p.p.m.	$^{2}J(\underline{P}\text{-}C\text{-}\underline{P})$ Hz	$\delta(CH)$ p.p.m.	$\delta(NMe)$ p.p.m.	$\delta(Bu^t)$[b] p.p.m.	$^{2}J(\underline{P}\text{-}C\text{-}\underline{H})$ Hz	$^{3}J(\underline{P}\text{-}N\text{-}C\text{-}\underline{H})$ Hz
$Me_2N(O)\overline{P{\cdot}CH_2{\cdot}P(O)(NMe_2)}NBu^t$ trans	10.6		2.67	2.78	1.35	15.3	10.5[e]
$[Bu^tNH(Me_2N)(O)P]_2CH_2$	22.9		1.73	2.63	1.28	16.8	9.9[e]
$(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)NHBu^t$	19.2	4.1	g	2.53	1.25	g	10.2
	30.5($P(O)(NMe_2)_2$)			2.65			9.7
				2.61			9.6

[a] Obtained from PCl_3 solutions

[b] All $^{4}J(P\text{-}N\text{-}C\text{-}C\text{-}H)$ couplings <0.5 Hz

[c] $|^{2}J(P\text{-}C\text{-}H) + {}^{3}J(P\text{-}C\text{-}C\text{-}H)|$

[d] $^{2}J(H\text{-}C\text{-}H)$

[e] $|^{3}J(P\text{-}N\text{-}C\text{-}H) + {}^{5}J(P\text{-}C\text{-}P\text{-}N\text{-}C\text{-}H)|$

[f] Data from ref. 236

[g] Not measured

TABLE 10

Analytical data[a]

Compound	Found					Calc.				
	C	H	N	Cl	m/e[b]	C	H	N	Cl	m/e[b]
$Cl(O)\overline{P\cdot CH_2\cdot P(O)Cl\cdot NBu^t}$	24.2	5.1	6.0	27.7	234 (P-15)	24.0	4.4	5.6	28.4	249
$Cl(O)\overline{P\cdot CH_2\cdot P(O)Cl\cdot NPr^i}$	20.3	4.1	5.7		220 (P-15)	20.4	3.8	5.9		235
$Me_2N(O)\overline{P\cdot CH_2\cdot P(O)(NMe_2)NBu^t}$	40.2	8.9	15.6		267	40.5	8.7	15.7		267
$[Me_2N(Cl)(O)P]_2CH_2$	22.2	5.3	9.9	25.1	266	22.5	5.3	10.5	26.6	266
$[Bu^tNH(Me_2N)(O)P]_2CH_2$	46.0	10.0	16.2		340	45.9	10.1	16.5		340
$(Me_2N)_2(O)P\cdot CH_2\cdot P(O)(NMe_2)NHBu^t$					312					312

[a] Elemental analysis figures are given in %

[b] For ions containing ^{35}Cl.

Preparation of bis(dichlorophosphinoyl)methane, $[Cl_2(O)P]_2CH_2$[233]:- 170 g (0.817 mol) phosphorus pentachloride was slowly added (over a period of 0.5h) to 70.0 g(0.203 mol) bis(di-i-propoxyphosphinoyl)methane, $[(Pr^iO)_2(O)P]_2CH_2$. A vigorous reaction initially occurred. After all the phosphorus pentachloride had been added, the mixture was heated to 50-60° for 2h. After cooling to ambient temperature, ca 500 ml light petroleum (b.p.40-60°) was added to the clear liquid, precipitating a white solid. This was separated by filtration and washed in ca 300 ml light petroleum. The solid on recrystallisation from toluene gave 32.0 g (63%) bis(dichlorophosphinoyl)methane, a white crystalline solid m.p. 103-104° (lit.[234] 98-100°).

Preparation of bis(dichlorophosphinoyl)1,2-ethane, $Cl_2(O)P{\cdot}CH_2CH_2{\cdot}P(O)Cl_2$:- A similar method to that used in the preparation of $[Cl_2(O)P]_2CH_2$ was employed. After slow addition of 167.5 g (0.805 mol) phosphorus pentachloride to 71.6 g (0.20 mol) bis(di-i-propoxyphosphinoyl)1,2-ethane, $(Pr^iO)_2(O)P{\cdot}CH_2CH_2{\cdot}P(O)(OPr^i)_2$, the mixture was heated to 50-60° for 2h. Work up gave 37.0 g (70%) of bis(dichlorophosphinoyl)1,2-ethane, a white crystalline solid m.p. 104-110° (decomposition occurring on melting) (lit.[234] 164-165°).

Reactions of bis(diphenylphosphino)methane with phosphorus trichloride:- (a) Following the literature method,[235] 19.2 g (0.05 mol) bis(diphenylphosphino)methane, $(Ph_2P)_2CH_2$, and 48 g (0.35 mol) phosphorus trichloride were heated in a sealed tube

at 250-300° for 5h. The ^{1}H n.m.r. spectrum of the crude reaction product indicated the formation of a mixture from which chloro(diphenyl)phosphine, dichloro(phenyl)phosphine and possibly dichloro(chloromethyl)phosphine, Cl_2PCH_2Cl, could be identified. No trace of bis(dichlorophosphino)methane, $(Cl_2P)_2CH_2$ was found.

(b) 5.0 g (0.013 mol) bis(diphenylphosphino)methane, $(Ph_2P)_2CH_2$, and 18 g (0.13 mol) phosphorus trichloride were refluxed for 0.5h. ^{1}H and ^{31}P n.m.r. indicated the formation of mainly dichlorophosphino-(diphenylphosphino)methane, $Ph_2P{\cdot}CH_2{\cdot}PCl_2$, and chloro(diphenyl)-phosphine. Excess phosphorus trichloride was evaporated under reduced pressure, but on attempted vacuum distillation dichlorophosphino(diphenylphosphino)methane decomposed, and a liquid consisting of mainly chloro(diphenyl)phosphine was obtained.

(c) 5.0 g (0.013 mol) bis(diphenylphosphino)methane and 18 g (0.13 mol) phosphorus trichloride were refluxed for 15h. ^{1}H n.m.r. indicated the formation of mainly bis(dichlorophosphino)methane, $(Cl_2P)_2CH_2$, and chloro(diphenyl)phosphine. Excess phosphorus trichloride was evaporated off, but again on vacuum distillation a liquid mainly containing chloro(diphenyl)phosphine was obtained, bis(dichlorophosphino)methane apparently having decomposed.

Preparation of bis(chlorodimethylaminophosphinoyl)methane, $[Me_2N(Cl)(O)P]_2CH_2$:- To a stirred solution of 6.75 g (0.027 mol) bis(dichlorophosphinoyl)methane in 200 ml of methylene chloride at -78° was slowly added dimethylamine (4.86 g, 0.108 mol) in

20 ml of methylene chloride. The reaction mixture was warmed to ambient temperature and stirred for 15h. The methylene chloride was then evaporated off, and the product extracted with 5 x 50 ml of toluene, giving after filtration and evaporation of toluene 5.9 g (82%) bis(chlorodimethylaminophosphinoyl)methane as a 3:1 dl:meso mixture of diastereoisomers. The major diastereoisomer (dl) was separated by recrystallisation from toluene as a white crystalline solid which decomposed above 90°.

Reaction of bis(dichlorophosphinoyl)methane with two mol equiv. of dimethylamine:- A similar method to that used in the preparation of $[Me_2N(Cl)(O)P]_2CH_2$ was employed. 5.0 g (0.020 mol) bis(dichlorophosphinoyl)methane and 1.8 g (0.040 mol) dimethylamine were mixed in methylene chloride (150 ml) for 15h. A clear viscous liquid was obtained on work up, the ^1H n.m.r. spectrum of which indicated a mixture of bis(chlorodimethylaminophosphinoyl)methane, $[Me_2N(Cl)(O)P]_2CH_2$, bis(dichlorophosphincyl)methane, $[Cl_2(O)P]_2CH_2$, and dichlorophosphinoyl(chlorodimethylaminophosphinoyl)methane, $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)(Cl)NMe_2$, in a 2:2:1 ratio respectively. $[Me_2N(Cl)(O)P]_2CH_2$ was formed as a 4:1 dl:meso mixture, the proportion of the meso diastereoisomer increasing on heating. No other change in the product ratio occurred, and only dl$[Me_2N(Cl)(O)P]_2CH_2$ could be separated from the mixture, by crystallisation from toluene.

Preparation of 1-t-butyl-2,4-dichloro-2,4-dioxo-1,2,4-azadiphosphetane, $Cl(O)\overline{P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t}$:- To a stirred solution of 12.75 g (0.051 mol) bis(dichlorophosphinoyl)methane in methylene chloride (300 ml) at -78° was slowly added 11.2 g (0.153 mol) t-butylamine in 50 ml of methylene chloride. The reaction mixture was then refluxed (3h). The t-butylammonium chloride precipitate was removed by filtration and the methylene chloride evaporated to give a cloudy viscous liquid consisting mainly of a 5:2 cis : trans isomer mixture of $Cl(O)\overline{P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t}$. Purification by vacuum distillation (110°, 0.7 mm Hg) gave 6.25 g (49%) 1-t-butyl-2,4-dichloro-2,4-dioxo-1,2,4-azadiphosphetane, a clear colourless liquid which crystallised on standing of unchanged isomer ratio. The cis isomer was separated by recrystallisation from a diethyl ether/light petroleum (b.p. 40-60°) mixture, giving a white crystalline solid m.p. ca 65°C.

The following reactions were carried out using similar methods:

Preparation of 2,4-dichloro-2,4-dioxo-1-i-propyl-1,2,4-azadiphosphetane:- 6.25 g (0.025 mol) bis(dichlorophosphinoyl)methane and 5.5 g (0.075 mol) t-butylamine were mixed in 200 ml methylene chloride at -78°. The reaction mixture was then refluxed (3h). A cloudy viscous liquid was obtained on work up which gave on vacuum distillation (100°, 0.4 mmHg) 2.1 g (35%) 2,4-dichloro-2,4-dioxo-1-i-propyl-1,2,4-azadiphosphetane, a clear colourless liquid.

Reaction of bis(dichlorophosphinoyl)methane with two mol equiv. of t-butylamine:- 2.0 g (0.008 mol) bis(dichlorophosphinoyl)-methane and 1.2 g (0.016 mol) t-butylamine were mixed in 80 ml of methylene chloride at -78°. The reaction mixture was then stirred (15h) at ambient temperature. A viscous liquid was obtained on work up shown by ^{1}H n.m.r. to consist of a 2:1 mixture of $Cl(O)\overline{P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t}$ and $[Cl_2(O)P]_2CH_2$ respectively. No trace of $Cl_2(O)P{\cdot}CH_2{\cdot}P(O)(Cl)NHBu^t$ was detected.

Reaction of bis(dichlorophosphinoyl)methane with three mol equiv. of aniline:- 6.25 g (0.025 mol) bis(dichlorophosphinoyl)methane and 7.0 g (0.075 mol) aniline were mixed in 200 ml methylene chloride at -78°. The reaction mixture was then refluxed (3h). 7.4 g of a white soluble solid was obtained on work up, consisting of a complex mixture of unidentified products.

Reaction of bis(dichlorophosphinoyl)methane with three mol equiv. of ethylamine:- 3.5 g (0.014 mol) bis(dichlorophosphinoyl)-methane and 1.9 g (0.042 mol) ethylamine were mixed in 170 ml of methylene chloride at -78°C. The reaction mixture was stirred for 15h at ambient temperature. A viscous liquid was obtained on work up, consisting of a complex mixture of products of which only bis(dichlorophosphinoyl)methane could be identified.

Reactions of bis(dichlorophosphinoyl)1,2-ethane with three mol equiv. of t-butylamine and i-propylamine:- 5.8 g (0.022 mol) bis(dichlorophosphinoyl)1,2-ethane and 4.8 g (0.066 mol) t-butylamine were mixed in 350 ml of methylene chloride at 0°.

The reaction mixture was then refluxed (4h). A large amount of unidentified insoluble products precipitated from solution with the t-butylammonium chloride. Only traces of a viscous liquid were obtained on work up, consisting of a mixture of unidentified products. Very similar results were obtained from the analogous reaction with i-propylamine.

Preparation of bis(t-butylaminodimethylaminophosphinoyl)methane:- 2.15 g (0.008 mol) bis(chlorodimethylaminophosphinoyl)methane, $[Me_2N(Cl)(O)P]_2CH_2$, and 2.35 g (0.032 mol) t-butylamine were mixed in 100 ml of chloroform at 0°. The reaction mixture was then refluxed (20h). A yellow-orange oil was obtained on work up. On extraction with 5 x 20 ml light petroleum (b.p. 60-80°) a white solid was obtained which gave on recrystallisation from light petroleum (b.p. 60-80°) 2.05 g (75%) bis(t-butylamino-dimethylaminophosphinoyl)methane, a white crystalline solid m.p. 136-149°. The corresponding reaction with three mol equiv. of t-butylamine gave a 3:1 mixture of $[Bu^tNH(Me_2N)(O)P]_2CH_2$ and $[Me_2N(Cl)(O)P]_2CH_2$ respectively.

Reaction of bis(chlorodimethylaminophosphinoyl)methylamine with four mol equiv. of t-butylamine:- 1.4 g (0.005 mol) bis(chlorodimethylaminophosphinoyl)methylamine, $[Me_2N(Cl)(O)P]_2NMe$, and 1.45 g (0.020 mol) t-butylamine were mixed in 100 ml of chloroform at 0° and then refluxed (20h). No reaction occurred and $[Me_2N(Cl)(O)P]_2NMe$ was recovered almost quantitatively.

Preparation of t-butylaminodimethylaminophosphinoyl(bisdimethylaminophosphinoyl)methane, $(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)NHBu^t$:-

To a stirred solution of 1.5 g (0.006 mol) 1-t-butyl-2,4-dichloro-2,4-dioxo-1,2,4-azadiphosphetane, $Cl(O)\overline{P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t}$ in 60 ml of methylene chloride at -78° was slowly added 1.55 g (0.034 mol) dimethylamine in 10 ml of methylene chloride. The reaction mixture was stirred (1h) while warming up to ambient temperature. The methylene chloride was evaporated off and the product extracted with 5 x 50 ml diethyl ether and then filtered. Evaporation of the diethyl ether gave 1.5 g (80%) t-butylaminodimethylaminophosphinoyl(bisdimethylaminophosphinoyl)methane, a clear viscous liquid which decomposed with the loss of dimethylamine on vacuum distillation (160°, 0.01 mmHg) to give 1-t-butyl-2,4-bisdimethylamino-2,4-dioxo-1,2,4-azadiphosphetane, $Me_2N(O)\overline{P{\cdot}CH_2{\cdot}P(O)(NMe_2)NBu^t}$.

Similar decomposition of $(Me_2N)_2(O)P{\cdot}CH_2P(O)(NMe_2)NHBu^t$ (1.55 g, 0.005 mol) occurred on heating the neat liquid to 150° for 0.5h under a nitrogen atmosphere. The solid obtained was recrystallised from a diethyl ether/light petroleum (b.p. 40-60°) mixture to give 0.7 g (53%) 1-t-butyl-2,4-bisdimethylamino-2,4-dioxo-1,2,4-azadiphosphetane, a white crystalline solid m.p. 137-139°.

Reactions of 1-t-butyl-2,4-bisdimethylamino-2,4-dioxo-1,2,4-azadiphosphetane with dimethylamine and t-butylamine:-

In each case an excess of the amine was added to a solution of ca 0.5g (0.002 mol) $Me_2N(O)\overline{P{\cdot}CH_2{\cdot}P(O)(NMe_2)NBu^t}$ in ca 1 ml of deuterochloroform in a n.m.r. tube. The dimethylamine

solution was heated to ca 60° for 1h and the t-butylamine solution for 20h. In each case it was shown by ^{1}H n.m.r. that no reaction had occurred.

Reaction of 1-t-butyl-2,4-dichloro-2,4-dioxo-1,2,4-azadiphosphetane with four mol equiv. of dimethylamine:- A similar method to that used in the preparation of $(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)NHBu^t$ was employed. 1.5 g (0.006 mol) 1-t-butyl-2,4-dichloro-2,4-dioxo-1,2,4-azadiphosphetane, $Cl(O)\overline{P{\cdot}CH_2{\cdot}P(O)Cl{\cdot}NBu^t}$ and 1.1 g (0.024 mol) dimethylamine were mixed in 70 ml of methylene chloride at -78° and then stirred (1h). A viscous liquid was obtained on work up, shown (by ^{1}H and ^{31}P n.m.r.) to mainly consist of a 5:2:1 mixture of $(Me_2N)_2(O)P{\cdot}CH_2{\cdot}P(O)(NMe_2)NHBu^t$, $Cl(O)\overline{P{\cdot}CH_2{\cdot}P(O)(NMe_2)NBu^t}$ and $Me_2N(O)\overline{P{\cdot}CH_2{\cdot}P(O)(NMe_2)NBu^t}$ respectively.

CHAPTER 5

CYCLODIPHOSPHA(III)ZANES - OXIDATION AND AMINOLYSIS PRODUCTS

OXIDATION REACTIONS.

The course of oxidation of cyclodiphospha(III)zanes $(ClPNR)_2$ (R=Bu^t or Pr^i) with dimethyl sulphoxide and elemental sulphur has recently been investigated.[12, 194] A summary of the results obtained is shown in Figure 22.

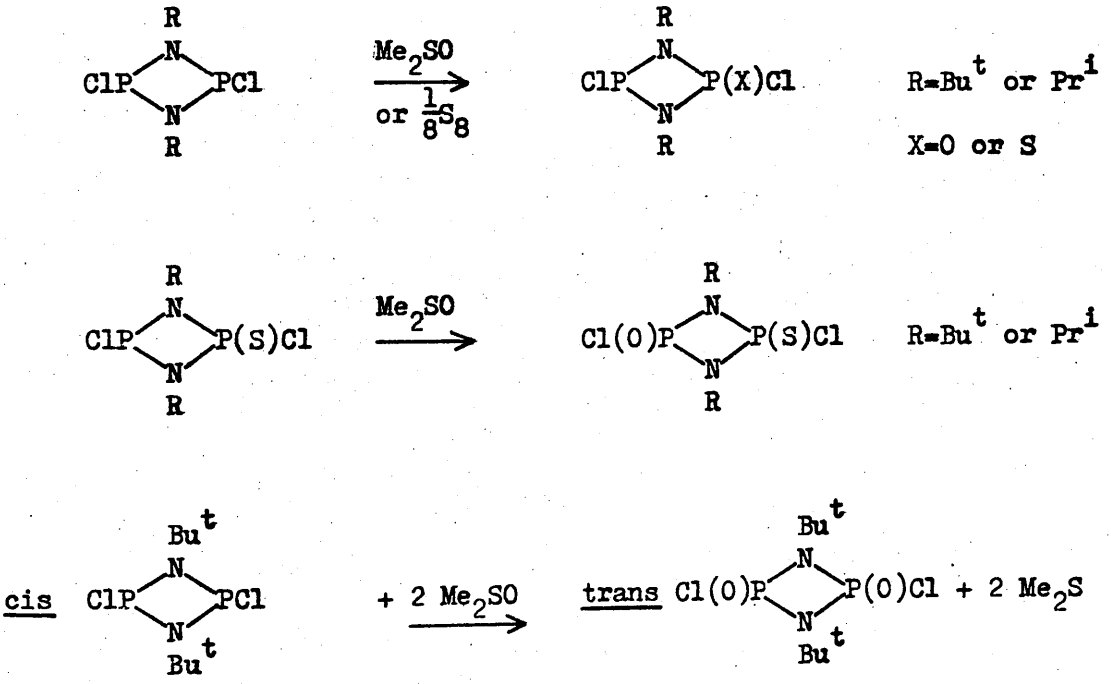
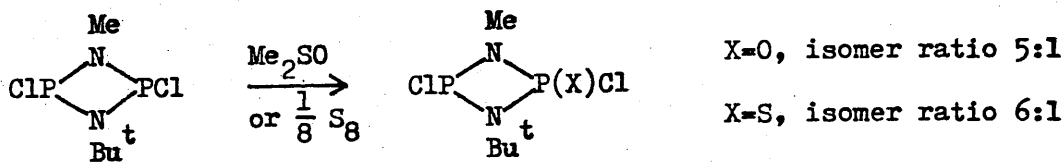


Figure 22.

Only one isomer of each of the cyclodiphosphazanes $ClP{\cdot}NR{\cdot}P(X)Cl{\cdot}NR$ (R=Bu^t or Pr^i; X=O or S) was reported,[12] although since then traces of the other isomers of $ClP{\cdot}NBu^t{\cdot}P(X)Cl{\cdot}NBu^t$ (X=O or S) have been detected,[244] indicating that the partial oxidation of the cyclodiphosphazane cis-$(ClPNBu^t)_2$ by dimethyl sulphoxide or elemental sulphur is not completely stereospecific.

The stereospecific formation of trans-$[Cl(O)PNBu^t]_2$ from cis-$(ClPNBu^t)_2$[194] (reaction 31) implies that a change in mechanism occurs in the two stage oxidation by dimethyl sulphoxide - one stage involving inversion of ring configuration, the other retention. On the other hand a lower stereospecificity in the formation of the oxide-sulphide derivatives $Cl(O)P{\cdot}NR{\cdot}P(S)Cl{\cdot}NR$ ($R=Bu^t$ or Pr^i) results in a mixture of geometrical isomers being detected.

Oxidation of the cyclodiphospha(III)zane $ClP{\cdot}NMe{\cdot}PCl{\cdot}NBu^t$ with dimethyl sulphoxide or elemental sulphur also occurs in a stepwise manner. Reaction with one mol equiv. of dimethyl sulphoxide or elemental sulphur gives the mixed oxidation state cyclodiphosphazanes (XL),

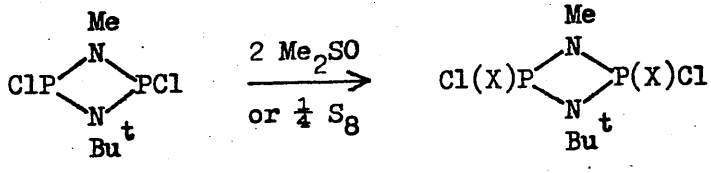


X=O, isomer ratio 5:1

X=S, isomer ratio 6:1

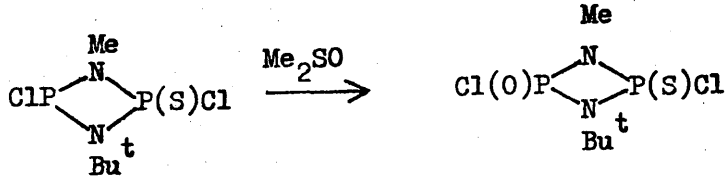
(XL)

while cyclodiphospha(V)zanes are formed on reaction with two mol equiv. of oxidant:



X=O, isomer ratio 5:2

X=S, isomer ratio 3:2



isomer ratio 6:1

isomer ratio 2:1

By contrast, it is found that reaction of the nitrogen-bridged diphosphorus compound, $(Cl_2P)_2NEt$, with one mol equiv. of dimethyl sulphoxide gives mainly the dioxide $[Cl_2(O)P]_2NEt$, plus starting material - indicating an accelerated rate of oxidation of $Cl_2P{\cdot}NEt{\cdot}P(O)Cl_2$.

$$[Cl_2(O)P]_2NEt \qquad (5)$$

$$(Cl_2P)_2NEt + Me_2SO \longrightarrow Cl_2P{\cdot}NEt{\cdot}P(O)Cl_2 \quad (1) + Me_2S$$

$$(Cl_2P)_2NEt \qquad (5)$$

(product ratios in parentheses)

Shaw and coworkers[176] suggested that the reaction pathway for the oxidation of phosphines by dimethyl sulphoxide depends on the electron donating strength of the phosphine. Thus strong electron donors like $(Me_2N)_3P$ react with dimethyl sulphoxide by nucleophilic attack at sulphur, whereas with poor electron donors like phosphorus trichloride the reaction involves the nucleophilic attack of dimethyl sulphoxide oxygen on phosphorus (see figure 23).

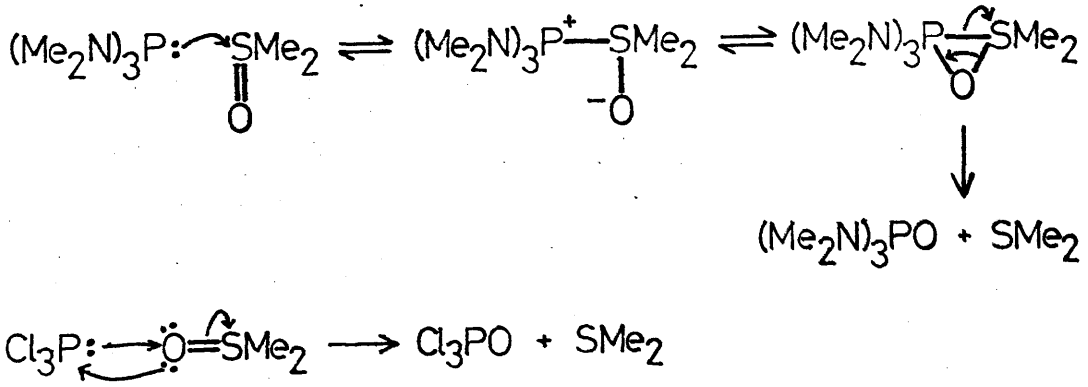


Figure 23.

If it is assumed that cyclodiphospha(III)zanes behave more like $(Me_2N)_3P$ in their reactions with dimethyl sulphoxide, it is expected[89] that an increase in ring strain will occur on formation of the initial four coordinate phosphorus intermediate. The rate of oxidation of cyclodiphospha(III)zanes by dimethyl sulphoxide is therefore expected to be slower than the rate of reaction with acyclic analogues. Unfortunately it is not yet clear why the rate of oxidation of $Cl_2P{\cdot}NEt{\cdot}P(O)Cl_2$ should be greater than that of $(Cl_2P)_2NEt$.

The isomer ratios of $\overline{ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu}^t$ and $Cl(O)\overline{P{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu}^t$ found indicate that both stages of the oxidation of $\overline{ClP{\cdot}NMe{\cdot}PCl{\cdot}NBu}^t$ by dimethyl sulphoxide have a similar degree of stereospecificity. Initial reaction of $\overline{ClP{\cdot}NMe{\cdot}PCl{\cdot}NBu}^t$ with elemental sulphur also gives predominantly one isomer, however in this case a lower degree of stereospecificity is found on further oxidation of $\overline{ClP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu}^t$ by either dimethyl sulphoxide or elemental sulphur. Unfortunately as the ring configurations of the above cyclodiphosphazanes could not be ascertained, no indication as to whether the oxidation reactions of $\overline{ClP{\cdot}NMe{\cdot}PCl{\cdot}NBu}^t$ occur predominantly by retention or inversion of ring geometry could be obtained.

AMINOLYSIS OF CYCLODIPHOSPHA(III)ZANES.

Little is known about the aminolysis of 2,4-dichlorocyclodiphospha(III)zanes, or about the properties of the expected products - aminocyclodiphospha(III)zanes. Evidence for a stepwise aminolysis of the cyclodiphospha(III)zane $(ClPNBu^t)_2$ is provided by the reactions of phosphorus trichloride with several different mol ratios of t-butylamine (see figure 24).

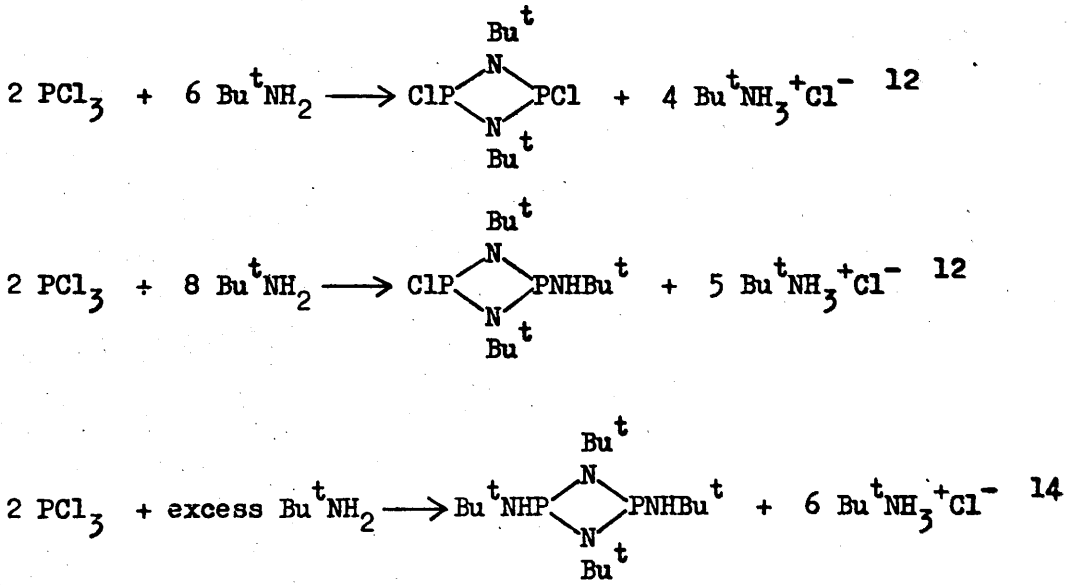


Figure 24

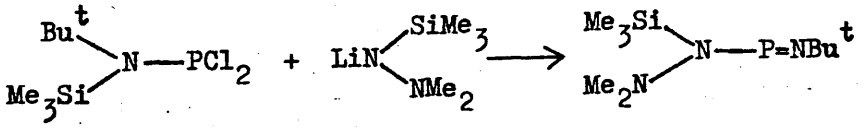
The cyclodiphosphazane $(PhNHPNPh)_2$ is similarly formed from the reaction of phosphorus trichloride with excess aniline[8,9] or its hydrochloride[7] - again almost certainly via the 2,4-dichlorocyclodiphosphazane $(ClPNPh)_2$. Furthermore it is reported[10] that this same 2,4-dichlorocyclodiphosphazane reacts with dimethylaminotrimethylsilane, $Me_2N{\cdot}SiMe_3$, to give the 2,4-bisdimethylamino-

derivative $(Me_2NPNPh)_2$. Reaction of bis(dichlorophosphino)aniline, $(Cl_2P)_2NPh$, with dimethylaminotrimethylsilane also gives the 2,4-bisdimethylaminocyclodiphosphazane $(Me_2NPNPh)_2$, and it is reported[10] that by varying the reaction conditions both geometrical isomers can be obtained. In all other examples of 2,4-diaminocyclodiphospha(III)zanes reported, only one of the two possible geometrical isomers is found.

A number of monomeric analogues of 2,4-diaminocyclodiphospha-(III)zanes (VIII) and (IX) have recently been prepared by the aminolysis of halogenophosphines with certain lithiated secondary amines.[30-33]

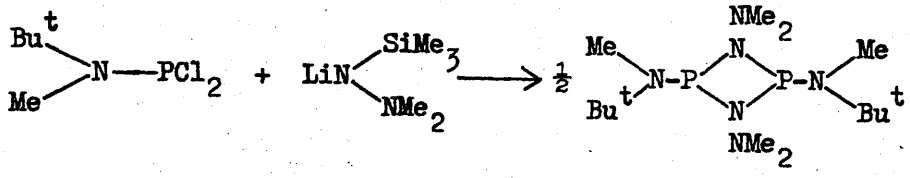
(VIII) R=Me_3Si or Bu^t (IX)

Comparison of reactions 32 and 33[245] provides some evidence to support the theory that these monomers are stabilised by the steric bulk of the nitrogen substituent and by the possible lower basicity of trimethylsilyl-substituted nitrogen.



32

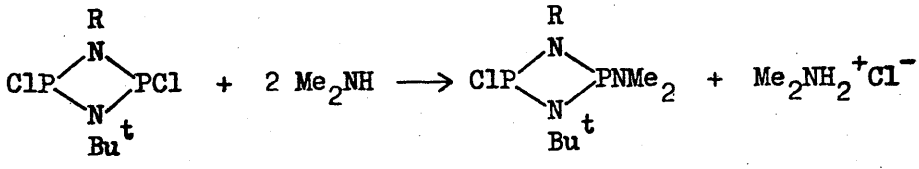
+ LiCl + Me_3SiCl



+ LiCl + Me_3SiCl 33

As yet, however, there are no reports of the cleavage of 2,4-diaminocyclodiphospha(III)zanes to form tervalent phosphazene monomers.

The reaction of the cyclodiphospha(III)zane $(ClPNBu^t)_2$ with dimethylamine was reported[13] to give a complex mixture of products. However, it is now found that the products of dimethylaminolysis of 2,4-dichlorocyclodiphospha(III)zanes, although oxidatively unstable, can be isolated and characterised. Cyclodiphospha(III)zanes $ClP(NR)PCl(NBu^t)$ (R=Me or Bu^t) react with two mol equiv. of dimethylamine to give monodimethylamino-derivatives (XLI).



(XLI)

In both cases only one isomer of the monodimethylaminocyclodiphospha-zanes (XLI) was obtained. However two compounds (indicated by singlets at ca δ100 and δ185 in the $^{31}P-\{^1H\}$ n.m.r. spectrum with relative intensities 2:3 respectively) were formed on reaction

of each of the above 2,4-dichlorocyclodiphospha(III)zanes with four mol equiv. of dimethylamine. ^{1}H n.m.r. (see figure 25) supported by microanalysis and mass spectroscopic data (see Table 19) strongly indicates the formation of cis and trans isomers of the 2,4-bisdimethylamino-derivatives, $Me_2\overline{NP{\cdot}NR{\cdot}P(NMe_2)}NBu^t$ (R= Me or Bu^t). Any possibility that either of the compounds formed could be a tervalent phosphazene monomer is ruled out by the observations that the ring N-methyl protons couple equally to two phosphorus nuclei in both isomers of $Me_2\overline{NP{\cdot}NMe{\cdot}P(NMe_2)}NBu^t$, and the dimethylamino protons in the isomers of both cyclodiphosphazanes, $Me_2\overline{NP{\cdot}NR{\cdot}P(NMe_2)}NBu^t$ (R=Me or Bu^t), exhibit weak virtual coupling.[246] Similar results are also obtained in the reaction of $Cl\overline{P{\cdot}NEt{\cdot}PCl}NBu^t$ with four mol equiv. of dimethylamine. Furthermore, there is no mass spectrometric or n.m.r. evidence to show that either of these ^{31}P signals is connected with the formation of a trimer (e.g. $(Me_2NPNBu^t)_3$) or a tetramer (e.g. $[Bu^tN(Me_2NP)_2NMe]_4$). Therefore these extremely large differences in ^{31}P chemical shifts (ca 85 p.p.m.) found, must reflect considerable differences in the phosphorus chemical environment between geometrical isomers of 2,4-bisdimethylaminocyclodiphosphazanes.

Isomerisation of these 2,4-bisdimethylaminocyclodiphosphazanes is found to occur. The rate of isomerisation increases with increasing steric bulk of the nitrogen substituents - thus while isomerisation of $Me_2\overline{NP{\cdot}NMe{\cdot}P(NMe_2)}NBu^t$ is only apparent after standing for several weeks at ambient temperature, isomerisation of $Me_2\overline{NP{\cdot}NEt{\cdot}P(NMe_2)}NBu^t$ is noticeable after several days, while

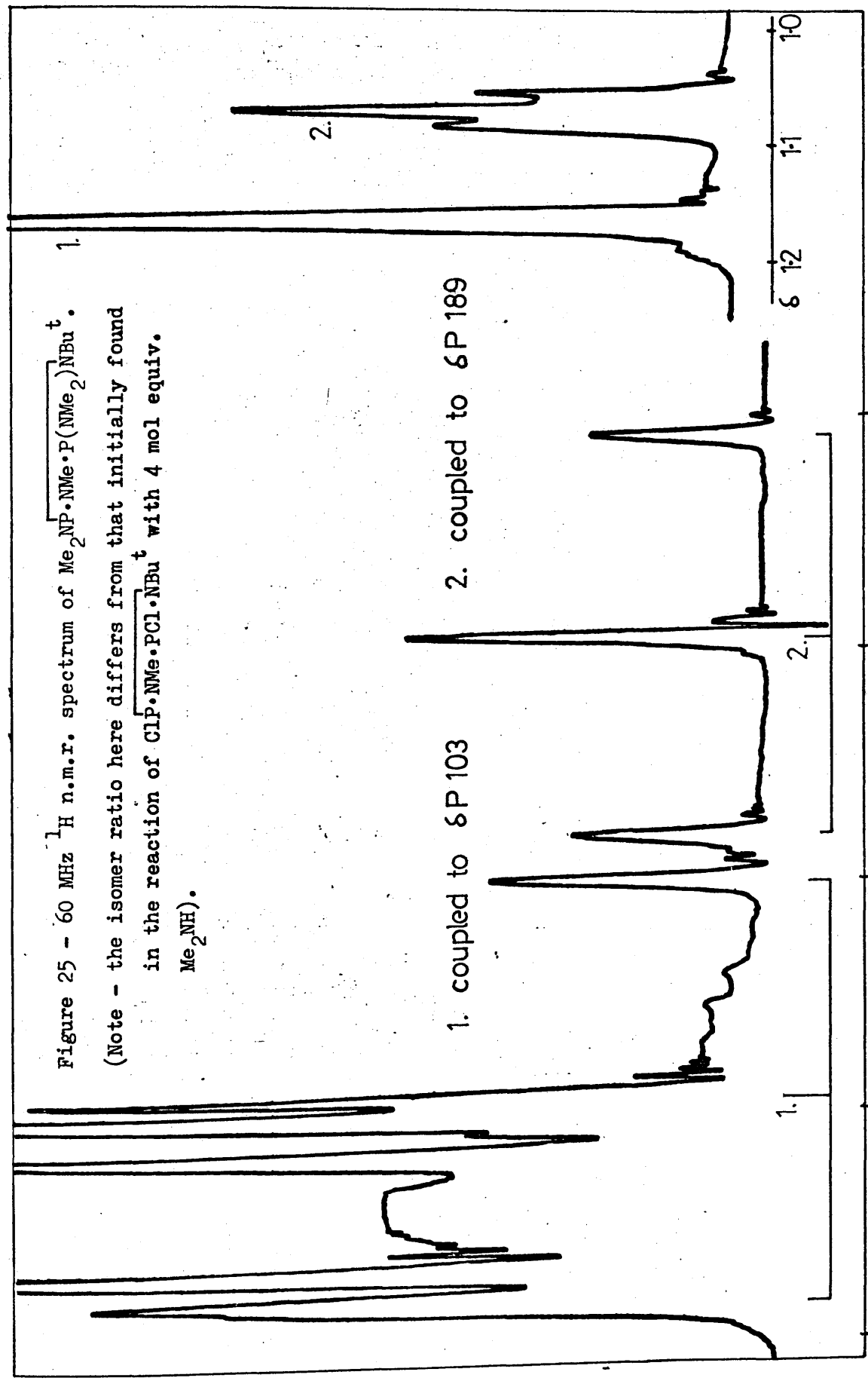


Figure 25 - 60 MHz ^{1}H n.m.r. spectrum of $Me_2NP(NMe_2)NBu^t$.
(Note - the isomer ratio here differs from that initially found in the reaction of $ClP(NMe_2)NBu^t$ with 4 mol equiv. Me_2NH).

$Me_2NP{\cdot}NBu^t{\cdot}P(NMe_2)NBu^t$ isomerises almost completely to one isomer within two days or on vacuum distillation. In every case isomerisation results in an increased proportion of the isomer with the high field ^{31}P signal (ca δ 100 p.p.m.) being formed. Furthermore, in the reaction of $(ClPNBu^t)_2$ with four mol equiv. of ethylamine, only the isomer of $(Et_2NPNBu^t)_2$ with $\delta^{31}P$ = 91 p.p.m. could be detected. Examination of molecular models of these 2,4-bisdimethylamino-cyclodiphosphazanes reveals that considerable steric interaction between dimethylamino substituents appears to be present in these compounds - especially in the cis isomer. Release of the higher steric crowding in the cis isomer would occur on isomerisation to the trans isomer, which is expected to be thermodynamically more stable. The observed isomerisation therefore points to the low field isomers of the 2,4-bisdimethylaminocyclodiphospha(III)zanes having cis configurations. The high steric interaction in the cis isomer could also be partially relieved by puckering of the cyclodiphosphazane ring, or by a slight twisting of the dimethylamino group phosphorus-nitrogen bonds away from the normal lowest energy conformer (see p. 182) in which the plane containing the dimethylamino groups is perpendicular to the plane of the cyclodiphosphazane ring, and the phosphorus and nitrogen lone pairs are orthogonal (see Figure 26).

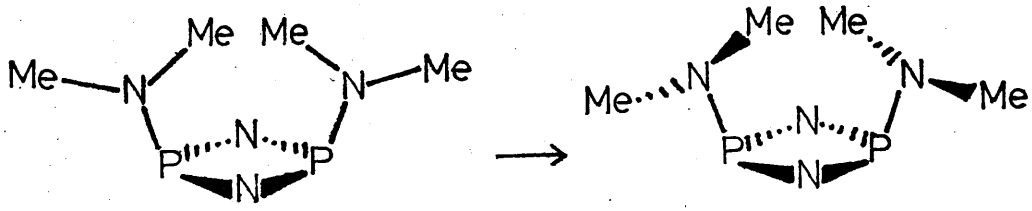


Figure 26.

An alteration in the ground state conformation of this kind will result in a decrease in $p\pi$-$d\pi$ bonding due to increased lone pair-lone pair repulsion, and this may be mainly responsible for the very low field ^{31}P chemical shifts of the cis isomers. The temperature dependence of $\delta^{31}P$ found for these compounds can similarly be interpreted as being caused by variations in the magnitude of $p\pi$-$d\pi$ bonding (see pp.188-190)

It is possible that if steric interaction could be further increased, the cyclodiphosphazane ring may cleave to form a tervalent phosphazene monomer. Unfortunately the attempt to investigate this possibility by preparing $(Pr^{i}_2NPNBu^{t})_2$ from the reaction of $(ClPNBu^{t})_2$ with excess di-i-propylamine gave only the monoamino derivative, $Cl\overline{P{\cdot}NBu^{t}{\cdot}P(NPr^{i}_2)}NBu^{t}$.

Formation of the 2,4-bisdimethylaminocyclodiphosphazane $Me_2N\overline{P{\cdot}NMe{\cdot}P(NMe_2)}NBu^{t}$ was also achieved by the cyclisation of bis(chlorodimethylaminophosphino)methylamine, $[Me_2N(Cl)P]_2NMe$ with three mol equiv. of t-butylamine

$$[Me_2N(Cl)P]_2NMe + 3\ Bu^{t}NH_2 \longrightarrow Me_2NP\begin{array}{c}Me\\N\\N\\Bu^{t}\end{array}PNMe_2 + 2\ Bu^{t}NH_3{}^{+}Cl^{-}$$

(low field:high field isomer ratio 2:3)

Bis(chlorodimethylaminophosphino)methylamine can be prepared in solution by the reaction of bis(dichlorophosphino)methylamine, $(Cl_2P)_2NMe$, with two mol equiv. of dimethylaminotrimethylsilane[133] or four mol equiv. of dimethylamine. Only one diastereoisomer is apparently formed. However it was found that attempts to isolate

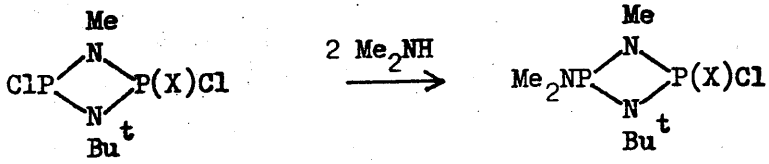
$[Me_2N(Cl)P]_2NMe$ resulted in the compound decomposing on solvent evaporation. Using evidence from n.m.r. and mass spectroscopy, the decomposition may be expressed as:

$$5\ [Me_2N(Cl)P]_2NMe \longrightarrow 4\ (Me_2N)_2PCl + 2\ Me_2NPCl_2 + P_4(NMe)_5Cl_2 \quad \text{(cf.p.104)}$$

(XXXII)

The cyclodiphosphazane, $Me_2N\overline{P{\cdot}NMe{\cdot}P(NMe_2)}NBu^t$, was therefore formed by the reaction of t-butylamine with a freshly prepared solution containing $[Me_2N(Cl)P]_2NMe$.

The reactions of the mixed oxidation state cyclodiphosphazanes, $ClP\overline{{\cdot}NMe{\cdot}P(X)Cl}{\cdot}NBu^t$ (X=O or S), with dimethylamine were also investigated. It was found that, like their reactions with t-butylamine (see Chapter 3), these 2,4-dichlorocyclodiphosphazanes underwent partial dimethylaminolysis exclusively at the phosphorus(III) centre.



34

X = O isomer ratio 5:1 X = O or S isomer ratio 4:1

X = S isomer ratio 6:1

However, unlike the reaction of cyclodiphosphazanes, $ClP\overline{{\cdot}NMe{\cdot}P(X)Cl}{\cdot}NBu^t$ (X = O or S), with t-butylamine, dimethylaminolysis of these cyclodiphosphazanes occurs with a high degree of stereospecifcity.

No direct evidence could be found to indicate whether the mechanism of dimethylaminolysis in reaction 34 (or of other cyclodiphospha(III)zanes) involves inversion or retention of configuration at phosphorus. However, if the aminolysis of cyclodiphospha(III)zanes follows a similar course to that of 1-chloro-2,2,3,4,4-pentamethylphosphetan with benzylamine,[97] then inversion of configuration at phosphorus would be expected to occur.

PHOSPHORUS-NITROGEN BOND TORSIONAL BARRIERS.

Examination of the low temperature ^1H n.m.r. spectra of the dimethylamino substituted cyclodiphosphazanes $ClP(NR)P(NMe_2)NBu^t$, $Me_2NP(NR)P(NMe_2)NBu^t$ (R = Me or Bu^t) and $Me_2NP(NMe)P(X)Cl(NBu^t)$ (X = O or S) in each case indicated that the dimethylamino methyl groups were chemically non-equivalent. On raising the temperature a dynamic process was found to be present which at high enough temperatures caused the methyl groups to become equivalent (see Figure 27). Similar variable temperature n.m.r. effects have previously been reported for a considerable number of other aminophosphines of the types $RP(X)NR_2'$, R_2PNR_2' and X_2PNR_2' (R = alkyl or aryl, R' = alkyl, and X = F, Cl or Br).[109,116,247,248]

There are a number of dynamic processes which could give rise to this observed effect,

i.e. 1) inversion at phosphorus

2) inversion at nitrogen

3) substituent dissociation and recombination

4) hindered rotation of the phosphorus-nitrogen bond.

However there is evidence to show that all but the last process can normally be discounted. Variable temperature n.m.r. spectra of the chiral aminophosphine $Ph(Cl)P(NPr^i_2)$ show that the i-propyl methyl groups remain chemically non-equivalent above the coalescence temperature.[109] Pyramidal inversion at phosphorus would result in all four i-propyl methyl groups becoming chemically equivalent, thus showing that tervalent phosphorus remains

The NMe_2 region of variable temperature ^1H n.m.r. spectra of $ClP{\cdot}NBu^t{\cdot}P(NMe_2)NBu^t$ recorded at 60 MHz.

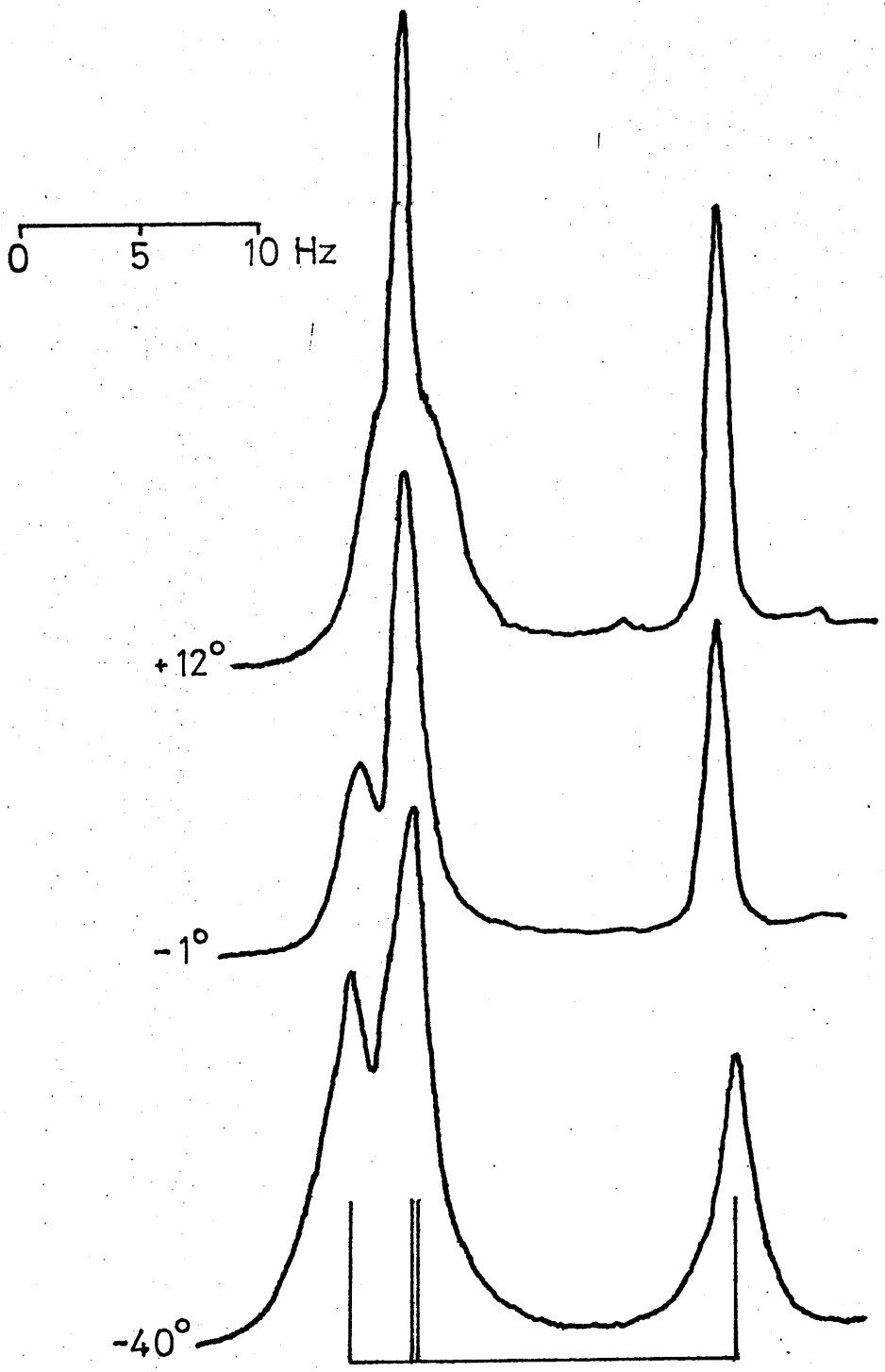


Figure 27.

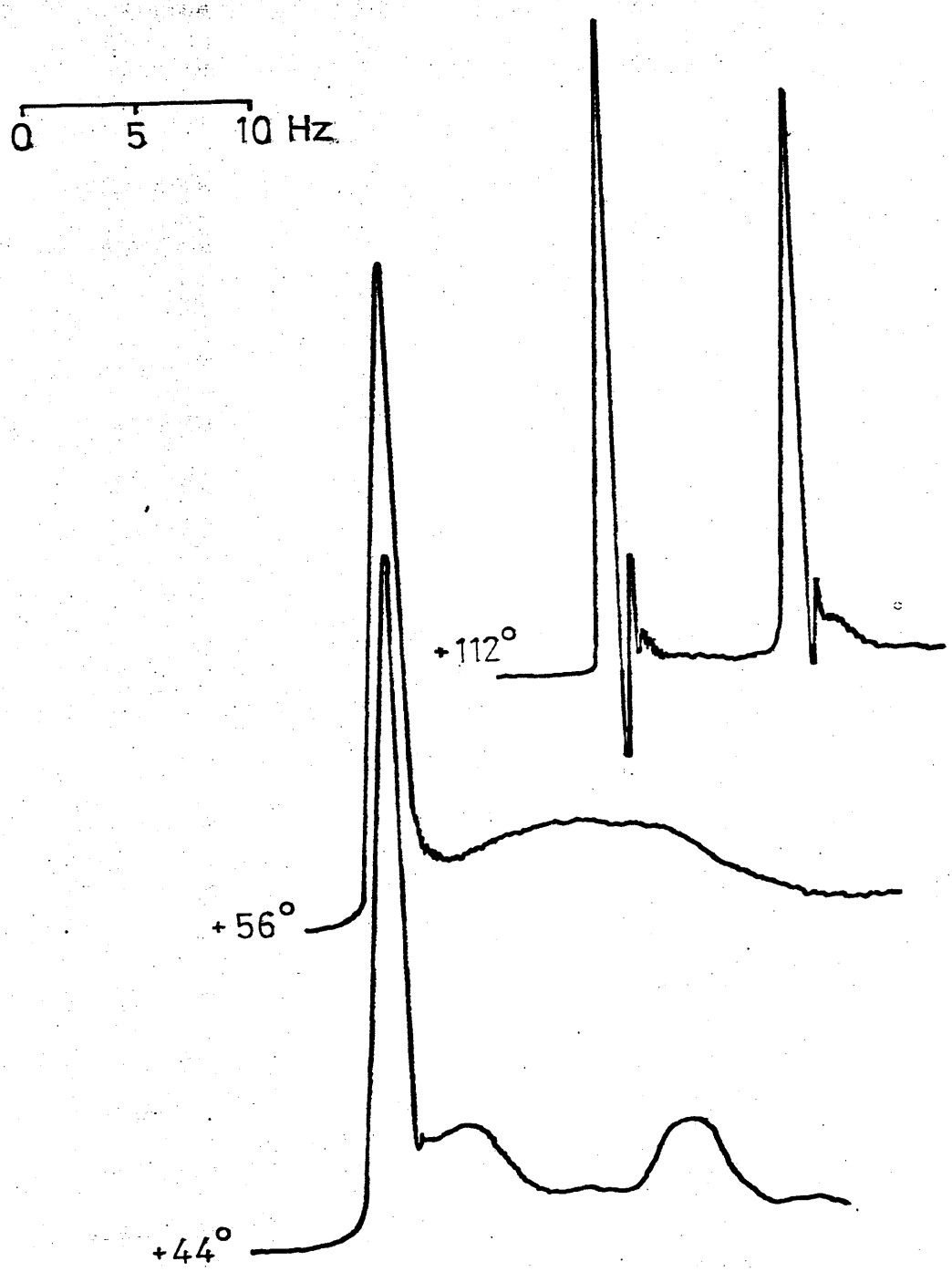
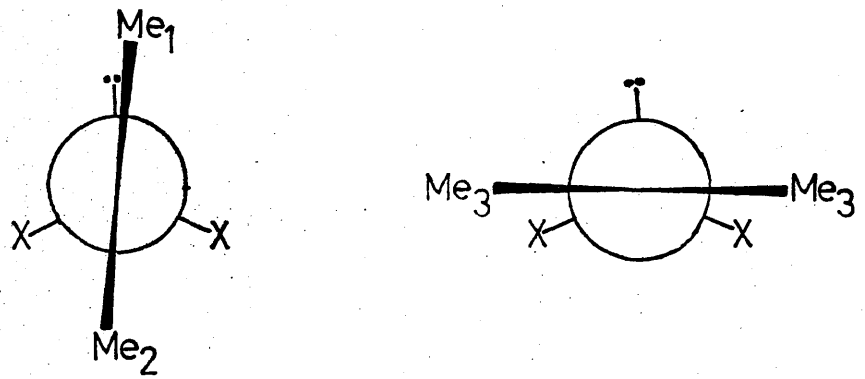


Figure 27 contd.

configurationally stable. In fact barriers to phosphorus(III) inversion are normally too high to be measured by n.m.r. methods.[249] In cyclodiphosphazanes, the constraint of the four membered ring might raise the barrier to inversion still further. Furthermore no isomerisation of the six dimethylamino substituted cyclodiphosphazanes occurred throughout the variable temperature experiments, confirming this configurational stability. On the other hand the barrier to inversion at nitrogen is normally too low to be measured by variable temperature n.m.r. methods.[109] $p\pi$-$d\pi$ Bonding in the phosphorus-nitrogen bond would be expected to reduce this barrier to nitrogen inversion still further - and in fact the geometry at nitrogen in aminophosphines is normally planar or near planar (see p. 21). Furthermore it is found that increasing the bulk of the R-group in compounds $Ph(Cl)P{\cdot}NR_2$ increases the barrier for the dynamic process.[109,116] If inversion at nitrogen was being observed, increasing the bulk of the R-group would increase steric congestion in the pyramidal ground state, leading to lower inversion barriers. The observed dynamic n.m.r. effect both in the above dimethylamino substituted cyclodiphosphazanes and other aminophosphines is independent of solvent and concentration, indicating that a substituent dissociation and recombination process is not involved. There is now general agreement that the dynamic n.m.r. process observed in other aminophosphines is related to hindered rotation about the phosphorus-nitrogen bond, and the results described here lead to a similar conclusion.

Assuming that staggered rotamer conformations are more stable than eclipsed conformations, the non-equivalence of the dimethylamino methyl groups found in the low temperature ^1H n.m.r. spectra of compounds X_2PNMe_2 (X=Cl or CF_3) has been used[109] to show that rotamer a possesses the ground state conformation.



a b

(projections assume that the nitrogen atom is planar)

The dihedral angles between the phosphorus lone pair and the methyl groups are:-

Me_1	ca	0°
Me_2	ca	180°
Me_3	ca	90°

Figure 28

It is interesting to note that only in rotamer a are the phosphorus and nitrogen lone pairs orthogonal. From the trend found in the magnitudes of the two $^3J(P-N-C-H)$ coupling constants observed at low temperatures (see Table 11) it can be deduced that

1) similar rotamers are being observed at low temperatures

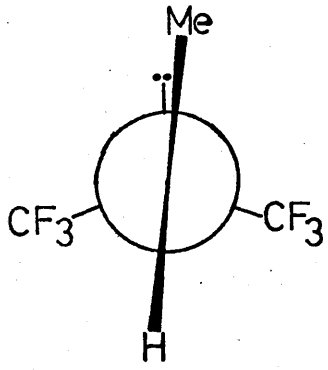
2) there is a dependence of ^{3}J(P-N-C-H) on dihedral angle.

TABLE 11

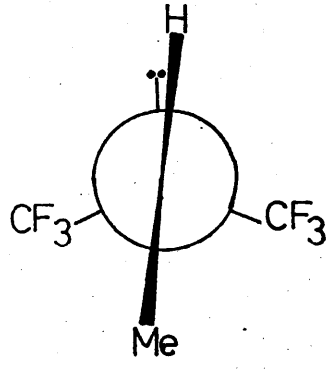
Magnitudes of ^{3}J(P-N-C-H) found at low temperatures.

Compound	^{3}J(P-N-C-H) Hz	$^{3}J'$(P-N-C-H) Hz
Cl_2PNMe_2 [109]	19.2	4.9
$(CF_3)_2PNMe_2$ [109]	ca 14	ca 4
$Ph(Cl)PNMe_2$ [109]	19.2	6.7
$Me(Cl)PNMe_2$ [116]	19.1	8.2
$Bu^t(Cl)PNMe_2$ [116]	18.1	5.8
$ClP(NBu^t)P(NMe_2)NBu^t$	13.2	2.9
$Me_2NP(NMe)P(NMe_2)NBu^t$	13.0	2.3

The low temperature ^{1}H n.m.r. spectrum of $(CF_3)_2PNHMe$ indicates that two unequally populated rotamers are present (see Figure 29)[109]



a



b

major rotamer ^{3}J(P-N-C-H) 13.9 Hz minor rotamer ^{3}J(P-N-C-H) ca 4 Hz

Figure 29.

On steric grounds rotamer a is expected to be the major rotamer (with large $^3J(P\text{-}N\text{-}C\text{-}H)$) indicating that $^3J(P\text{-}N\text{-}C\text{-}H)$ is large for dihedral angles near 0° and small for dihedral angles near 180°. The low temperature ^1H n.m.r. spectrum of Cl_2PBu^t indicates[250] that $^3J(P\text{-}C\text{-}C\text{-}H)$ possesses a similar dependence on dihedral angle.

The variable temperature ^1H n.m.r. data for the dimethylamino substituted cyclodiphosphazanes investigated are shown in Table 12. The Free Energy of Activation ΔG^* was calculated from the Eyring Equation:[251]

$$K = \frac{k T_c}{h} e^{-\Delta G^*/RT} \qquad \left[\Delta G^* = - RT_c \ln \frac{kh}{KT_c}\right]$$

where k = Boltzmann's constant

h = Planck's constant

R = Gas constant

T_c = coalescence temperature ($^\circ K$)

K = rate constant

using the relationship[252] $K = \frac{\pi}{\sqrt{2}} \Delta v_{AB}$

where Δv_{AB} is the chemical shift difference (in Hz) between A and B in the absence of exchange.

Measurement of T_c and Δv_{AB} was carried out using ^{31}P noise decoupled ^1H n.m.r. spectra in order to ensure that the relationship between K and Δv_{AB} was applicable. ^{31}P decoupling also resulted in spectral simplification which aided the measurement of coalescence temperatures.

TABLE 12

Variable temperature ^1H n.m.r. data

Compound	low T. δNMe_2 p.p.m.	low T. ^3J(P-N-C-H) Hz	high T. δNMe_2 p.p.m.	high T. ^3J(P-N-C-H) Hz	T_c °C	$\Delta\nu$ Hz	ΔG^* KJ.mol^{-1}
$ClP[\cdot NMe\cdot P(NMe_2)]NBu^t$	2.72	3.0	2.81	8.0	+7±1.5	12.6	60.7±0.8
	2.80	13.0					
$ClP[\cdot NBu^t\cdot P(NMe_2)]NBu^t$	2.81	2.9	2.80	8.3	+46±1.5	7.4	70.7±0.8
	2.83	13.2					
$Me_2NP[\cdot NMe\cdot P(NMe_2)]NBu^t$			2.68	8.1	ca-80 -85	ca 8	39.7 43.1[a]
	2.63	2.3	2.70	7.6	-34±2	7.9	52.3±1.3
	2.76	13.0					
$Me_2NP[\cdot NBu^t\cdot P(NMe_2)]NBu^t$			2.66	8.4	-57±1.5	5.1	48.1±0.8[a]
		10.5					

TABLE 12 contd.

Compound	low T. δNMe_2 p.p.m.	low T. $^3J(P\text{-}N\text{-}C\text{-}H)$ Hz	high T. δNMe_2 p.p.m.	high T. $^3J(P\text{-}N\text{-}C\text{-}H)$ Hz	T_c °C	$\Delta\nu$ Hz	ΔG^* KJ.mol^{-1}
$Me_2\overline{NP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t}$			2.62	8.7	+24±4	10.8	64.9±1.7[b]
			2.70	8.8	-60°		48
$Me_2\overline{NP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$			2.69	8.4	+28±4	4.6	67.8±1.7[b]
			2.74	8.9	-50°		50

[a] Thermodynamically stable isomer.

[b] Major isomer.

The P-N torsional barrier found for $Me(Cl)P\text{-}NMe_2$ ($\Delta G^* = 49.4$ KJ.mol^{-1})[116] is the largest known for any acyclic dimethylamino substituted phosphine. Comparison of this torsional barrier with the ΔG^* values found in Table 12 emphasises the very high P-N torsional barriers found for some of these dimethylamino substituted cyclodiphosphazanes. In fact the value obtained for $\overline{ClP{\cdot}NBu^t{\cdot}P(NMe_2)}NBu^t$ is only slightly lower than the highest known P-N torsional barrier ($\Delta G^* = 74.5$ KJ.mol^{-1}, obtained for $Br_2P\text{-}NBu^t_2$).[253] Large differences exist between the P-N torsional barriers of cis and trans isomers. As little evidence was found on which to make geometrical assignments, care is necessary when comparing ΔG^* values.

The difference in P-N torsional barrier between the thermodynamically stable isomers of cyclodiphosphazanes $Me_2N\overline{P{\cdot}NR{\cdot}P(NMe_2)}NBu^t$ (R= Me or Bu^t) is approximately 10 KJ.mol^{-1}. As ^1H and ^{31}P n.m.r. data indicate that these isomers possess the same ring geometry, the difference in the magnitude of ΔG^* probably reflects the difference in the steric bulk of the ring N-methyl and N-t-butyl groups. A similar dependence of P-N torsional barriers on steric bulk of ring nitrogen substituents is found for the monodimethylamino derivatives $Cl\overline{P{\cdot}NR{\cdot}P(NMe_2)}NBu^t$ (R = Me or Bu^t) - assuming that both compounds possess the same ring geometry.

The electronic environment of the Me_2NP-group of these dimethylamino substituted cyclodiphosphazanes can be altered by

variation of the substituents on the other phosphorus atom of the cyclodiphosphazane ring, providing a possible means of investigating electronic influences on the P-N torsional barriers. Thus comparison of the ΔG^* data in Table 12 indicates that aminolysis of the other phosphorus atom effectively lowers the P-N torsional barrier. However, the electronic effect of oxidising the other phosphorus atom on the P-N torsional barrier is obscured by the large difference in P-N torsional barriers between isomers of $Me_2\overline{NP{\cdot}NMe{\cdot}P(X)Cl{\cdot}NBu^t}$ (X = O or S). The higher P-N torsional barriers found for monodimethylaminocyclodiphospha(III)zanes compared with their 2,4-bisdimethylamino analogues coincides with a higher $p\pi$-$d\pi$ character expected for the P-NMe_2 bond; but as further electronic comparisons are lacking, and as the magnitude of lone pair-lone pair repulsion between phosphorus and nitrogen lone pairs in these compounds is not known, it cannot be ascertained whether $p\pi$-$d\pi$ bonding or lone pair-lone pair repulsion has the greater influence on P-N torsional barriers.

The ^{31}P chemical shifts of dimethylamino substituted cyclodiphosphazanes are remarkably temperature dependent, compared with their 2,4-dichlorocyclodiphospha(III)zane analogues (see Table 13).

TABLE 13

Temperature dependence of ^{31}P chemical shifts.

Compound	$\delta(^{31}P)$ [a] p.p.m.	(°C)	$\delta(^{31}P)$ [a] p.p.m.	(°C)
$ClP(NMe)PCl(NBu^t)$	226.9	(+107)	225.3	(-56)
$ClP(NMe)P(NMe_2)(NBu^t)$	150.1	($PNMe_2$)	138.6	
		(+60)		(-61)
	197.1	(PCl)	193.3	
$ClP(NBu^t)P(NMe_2)(NBu^t)$	134.1	(+62) ($PNMe_2$)	128.8	(-40)
$Me_2NP(NMe)P(NMe_2)(NBu^t)$	105.7		102.8	
		(+25)		(-56)
	192.3		190.1	

[a] Obtained from $^1H-\{^{31}P\}$ tickling experiments.

Also, the chemical shift temperature dependence of the dimethylamino substituted phosphorus nucleus of $ClP(NMe)P(NMe_2)(NBu^t)$ is greater than that of the chloro substituted phosphorus nucleus. This temperature dependence therefore appears to be associated with the hindered rotation about the P-NMe_2 bond. The conformation stabilised at low temperature probably permits greater $p\pi$-$d\pi$ bonding to occur, as only in this conformation are the phosphorus and nitrogen lone pairs orthogonal. Therefore the observed shifts to high field of the $PNMe_2$ phosphorus chemical shifts on lowering the temperature may be due to increasing $p\pi$-$d\pi$ bonding as the relative population of this rotamer increases. In the mono-dimethylaminocyclodiphosphazane $ClP(NMe)P(NMe_2)(NBu^t)$ such an increase

in $p\pi$-$d\pi$ bonding in the P-NMe_2 bond will cause some increase in $p\pi$-$d\pi$ bonding between the ring nitrogen atoms and the chloro-substituted phosphorus atom, resulting in a similar shift of $\delta^{31}P$ to high field.

A similar temperature dependence of $\delta^{31}P$ may be expected to occur with acyclic aminophosphines which exhibit hindered P-N rotation, but unfortunately this information is not generally available. However, measurements[244] on $Ph(Cl)PNMe_2$ surprisingly show that a slight low field shift of $\delta^{31}P$ occurs on lowering the temperature. It is difficult to reconcile this observation with the data in Table 13, although it is possible that the π-donating phenyl group may in some way be responsible for the slight low field shift of $\delta^{31}P$ found for $Ph(Cl)PNMe_2$.

N.M.R. SPECTRA OF CYCLODIPHOSPHAZANES.

^{1}H and ^{31}P n.m.r. data are given in Table 15.

The ^{31}P chemical shifts of cyclodiphospha(III)zanes are very sensitive to substituent changes. Large shifts to high field occur on oxidation or aminolysis (with the exception of the thermodynamically unstable isomers of 2,4-diamino derivatives). It is also interesting to note the high sensitivity of $\delta^{31}P^{III}$ to changes in substituents on the second phosphorus atom in the same ring (see Table 14). Analogous shift effects are very much smaller in acyclic nitrogen-bridged diphosphorus compounds. This much higher sensitivity of $\delta^{31}P^{III}$ found for the cyclodiphosphazanes probably reflects greater changes in electronic environment caused by the two phosphorus atoms being linked by two N-alkyl groups and by slight variations in ring bond angles and conformation.

TABLE 14

^{31}P chemical shift variations in cyclodiphosphazanes.

Compound	$\delta(^{31}P_{a \text{ or } b})$ p.p.m.	$\Delta\delta(^{31}P_a)^*$ p.p.m.
$ClP_a(NMe)PCl(NBu^t)$	226	
$ClP_b(NMe)P(NMe_2)(NBu^t)$	189	37
$ClP_b(NMe)P(S)Cl(NBu^t)$	164	62
	151	75
$ClP_b(NMe)P(O)Cl(NBu^t)$	135	91
	134	92
$Me_2NP_a(NMe)PCl(NBu^t)$	146	
$Me_2NP_b(NMe)P(NMe_2)(NBu^t)$	103	43
	189	-43
$Me_2NP_b(NMe)P(S)Cl(NBu^t)$	114	32
	111	35
$Me_2NP_b(NMe)P(O)Cl(NBu^t)$	101	45
	81	65
$Cl_2P_a(NMe)PCl_2$	161	
$Cl_2P_b(NMe)P(S)Cl_2$	168	-7
$Cl_2P_b(NMe)P(O)Cl_2$	170	-9

* In each series of compounds this term = $(\delta P_a - \delta P_b)$

TABLE 15

N.m.r. data

Compound	^{31}P		^{1}H			
	$\delta(^{31}P)$	^{2}J(P-N-P)	δ(NMe)[a]	δ Bu^{t}	^{3}J(P-N-C-H)[a]	^{4}J(P-N-C-C-H)[b]
	p.p.m.	Hz	p.p.m.	p.p.m.	Hz	Hz
Cl$\overline{P\cdot NMe\cdot PCl\cdot NBu^{t}}$	226		2.72	1.37	11.2	1.0
Cl$\overline{P\cdot NEt\cdot PCl\cdot NBu^{t}}$	219.5		3.17(CH_2)	1.39	9.5(CH_2)	1.0
				1.26(Et)		<0.5(Et)
$(ClPNBu^{t})_2$	210.9			1.34		1.0
Cl$\overline{P\cdot NMe\cdot P(NMe_2)NBu^{t}}$	189(PCl)	+31.5[c]	2.69	1.32	+11.9(PCl)	0.7(both)
	146				+ 9.8	
Cl$\overline{P\cdot NBu^{t}\cdot P(NMe_2)NBu^{t}}$	178(PCl)	32.5		1.33		0.7(both)
	128					
Cl$\overline{P\cdot NBu^{t}\cdot P(NPr^{i}_2)NBu^{t}}$	184(PCl)	30±2	ca 3.5(CH)	1.37		0.6(both)
	114.5			1.35(Pr^{i})		<0.5(Pr^{i})

TABLE 15 contd.

Compound	^{31}P		^{1}H			
	$\delta(^{31}P)$	$^{2}J(P\text{-}N\text{-}P)$	δ (NMe)[a]	δBu^t	$^{3}J(P\text{-}N\text{-}C\text{-}H)$[a]	$^{4}J(P\text{-}N\text{-}C\text{-}C\text{-}H)$[b]
	p.p.m.	Hz	p.p.m.	p.p.m.	Hz	Hz
$[Me_2N(Cl)P]_2NMe$	144.6		3.10		5.3	
			2.70(NMe_2)		14.2[d](NMe_2)	
$Me_2NP(NMe)P(NMe_2)NBu^t$	103		2.59	1.16	11.3	<0.2
	189		2.19	1.07	10.4	0.8
$Me_2NP(NEt)P(NMe_2)NBu^t$	101			1.28	10.8(CH_2)	<0.3
				1.07(Et)		<0.5(Et)
	187			1.20		0.8
				1.07(Et)		<0.5(Et)
$(Me_2NPNBu^t)_2$	95			1.17		<0.4
	184			1.09		0.8
$(Et_2NPNBu^t)_2$	91		3.13(CH_2)	1.20	6.8(CH_2)[d]	<0.3
				1.05(Et)		<0.5(Et)

TABLE 15 contd.

Compound	^{31}P		^{1}H			
	$\delta(^{31}P)$ p.p.m.	$^{2}J(P\text{-}N\text{-}P)$ Hz	$\delta(NMe)$[a] p.p.m.	$\delta\ Bu^t$ p.p.m.	$^{3}J(P\text{-}N\text{-}C\text{-}H)$[a] Hz	$^{4}J(P\text{-}N\text{-}C\text{-}C\text{-}H)$[b] Hz
$ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$	134(P^{III})	-12.0[c]	2.91	1.51	+10.2(P^{III})	1.2(P^{III})
	12.5				+18.7	<0.3
	135(P^{III})	-36.3[c]	3.13	1.34	+8.4(P^{III})	1.9(P^{III})
	8.0				+17.3	<0.5
$ClP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$	151(P^{III})	-6.0[c]	2.83	1.54	+10.2(P^{III})	1.0(P^{III})
	70				+19.7	<0.4
	164(P^{III})	-36.3[c]	2.86	1.54	+10.0(P^{III})	1.0(P^{III})
	76				+19.1(P^{III})	<0.6
$Me_2NP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$	80.5(P^{III})	-8 ±2[c]	2.68	1.34	+9.1(P^{III})	0.4(both)
	2.4				+17.4	
	101.2(P^{III})	[e]	2.63	1.33	8.5(P^{III})	[e]
	5.3				17.6	

TABLE 15 contd.

Compound	^{31}P		^{1}H			
	$\delta(^{31}P)$	$^{2}J(P-N-P)$	$\delta(NMe)$[a]	δBu^{t}	$^{3}J(P-N-C-H)$[a]	$^{4}J(P-N-C-C-H)$[b]
	p.p.m.	Hz	p.p.m.	p.p.m.	Hz	Hz
$Me_2NP\overline{\cdot NMe\cdot P(S)Cl\cdot NBu^{t}}$	113.9(P^{III})	-12±2[c]	2.68	1.41	+8.7(P^{III})	<0.4(both)
	61.4				+18.6	
	110.9(P^{III})	-10±4[c]	2.73	1.41	+9.0(P^{III})	<0.6(both)
	55.1				+18.8	
$Cl(O)\overline{P\cdot NMe\cdot P(O)Cl\cdot NBu^{t}}$	-6.4		2.95	1.61	16.3	0.6
	-4.1		2.99	1.61	15.7	0.6
$Cl(S)\overline{P\cdot NMe\cdot P(S)Cl\cdot NBu^{t}}$	47		2.96	1.73	17.1	0.6
	49		2.97	1.73	17.1	0.6
$Cl(O)\overline{P\cdot NMe\cdot P(S)Cl\cdot NBu^{t}}$	-1.5(P=O)	+31.5	2.90	1.65	+16.1(P=O)	0.7
	40				+16.9	
	-2.0(P=O)	43.0	2.92	1.65	16.8(P=O)	0.7
	43				17.2	

TABLE 15 contd.

[a] Refers to bridging NMe protons, except where stated otherwise.

[b] Refers to bridging NBu^t protons, except where stated otherwise.

[c] Sign of coupling constant assumes $^3J(P^V\text{-}N\text{-}C\text{-}H)$ is positive.[231]

[d] $\left|{}^3J(\underline{P}\text{-}N\text{-}C\text{-}\underline{H}) + {}^5J(\underline{P}\text{-}N\text{-}P\text{-}N\text{-}C\text{-}\underline{H})\right|$

[e] Not measured.

The ^{31}P chemical shifts of cyclodiphospha(III)zanes are also apparently sensitive to variations in the bulk of ring nitrogen substituents (see Table 16), $\delta^{31}P$ shifting to high field with increasing steric bulk.

TABLE 16

The effect of N-alkyl substituents on the ^{31}P chemical shifts of cyclodiphosphazanes.

Compound		$\delta(^{31}P)$ p.p.m.
$ClP\overline{\cdot NR\cdot PCl\cdot NBu^t}$	R=Me	226
	R=Et	220
	R=Bu^t	211
$Me_2N\overline{P\cdot NR\cdot P(NMe_2)}NBu^t$	R=Me	103;189
	R=Et	101;187
	R=Bu^t	95;184
$(ClPNR)_2$	R=Et	227
	R=Pr^i	222
	R=Bu^t	211

From the limited data available it appears that a similar trend occurs on increasing the bulk of dialkylamino substituents. This parallels the 'γ-effect' found in ^{13}C, ^{15}N and ^{31}P chemical shifts.[254] Applied to the cyclodiphosphazanes in Table 16 this effect results in a shielding of the phosphorus

nucleus by γ-substituted carbon atoms. Thus upfield shifts in $\delta^{31}P$ occur on varying N-alkyl substituents from R=Me (no γ carbon atoms) to R=Bu^t (three γ carbon atoms).

$^1H-\{^{31}P\}$ selective spin decoupling experiments on asymmetrically substituted 1-t-butyl-3-methylcyclodiphosphazanes have revealed interesting changes in the sign of ^2J(P-N-P) which is dependent on the oxidation states of the two phosphorus nuclei. However, no change in sign occurs with the analogous acyclic nitrogen-bridged diphosphorus compounds (see Table 17).

TABLE 17

Absolute signs of ^2J(P-N-P)

Compound		^2J(P-N-P)[a] Hz
$ClP{\cdot}NMe{\cdot}P(NMe_2)NBu^t$		+31.5
$ClP{\cdot}NMe{\cdot}P(X)Cl{\cdot}NBu^t$	X=O	-12.0;-36.3
	X=S	- 6.0;-36.3
$Cl(O)P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$		+31.5; 43.0[b]
$F_2P{\cdot}NMe{\cdot}PF_2$		+437[255]
$Cl_2P{\cdot}NMe{\cdot}P(X)Cl_2$	X=O	+80
	X=S	+122
$Cl_2(O)P{\cdot}NMe{\cdot}P(S)Cl_2$		+3

[a] Signs assume ^3J(P-N-C-H) is positive[231]

[b] Sign not determined.

Due to the rigidity and similarity in structure of the three cyclodiphosphazanes in Table 17, the major factor causing the variation in sign of $^{2}J(P\text{-}N\text{-}P)$ in these compounds is the oxidation state of the phosphorus atoms. Applying the theory used by Jameson[256] to explain the sign of two bond spin-spin coupling constants such as $^{2}J(P\text{-}N\text{-}P)$, the observed variation in the sign of $^{2}J(P\text{-}N\text{-}P)$ can be rationalised if it is assumed that Fermi contact coupling is the dominant nuclear spin-electron spin coupling mechanism associated with the phosphorus(V) nucleus, whereas core polarisation is the dominant coupling mechanism associated with the phosphorus(III) nucleus. The same variation in the sign of $^{2}J(P\text{-}N\text{-}P)$ is not found in acyclic nitrogen-bridged diphosphorus compounds because the magnitude of $^{2}J(P\text{-}N\text{-}P)$ is further dependent to a large extent on the preferred conformation about the phosphorus-nitrogen bonds adopted by each compound. In fact it has recently been shown[257] that the differing signs of $^{2}J(P\text{-}N\text{-}P)$ in compounds $Ph_2P{\cdot}NMe{\cdot}P(Cl)Ph$ ($^{2}J(P\text{-}N\text{-}P)$ positive) and $Ph_2P{\cdot}NPr^{i}{\cdot}P(Cl)Ph$ ($^{2}J(P\text{-}N\text{-}P)$ negative) are almost certainly related to changes in preferred conformation about the phosphorus-nitrogen bonds.

The magnitudes of $^{3}J(P^{III}\text{-}N\text{-}C\text{-}H)$ between the ring N-methyl groups andphosphorus(III) nuclei of 1-t-butyl-3-methyl-cyclodiphosphazanes are invariably considerably larger than those found for their acyclic N-bridged diphosphorus analogues (e.g. $Cl_2P{\cdot}NMe{\cdot}P(X)Cl_2$, X=lone pair, O or S) - see Tables 7 and 15.

The angular dependence of $^{3}J(P^{III}\text{-N-C-H})$ (see pp. 182-184). can be shown to be the major factor causing this difference. Examination of molecular models shows that the dihedral angle between the plane containing the N-methyl group and the plane containing the phosphorus lone pair in cyclodiphosphazanes like $ClP(NMe)PCl(NBu^{t})$ is close to 45° (see Figure 30).

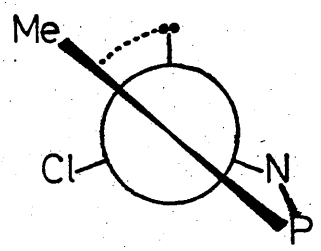
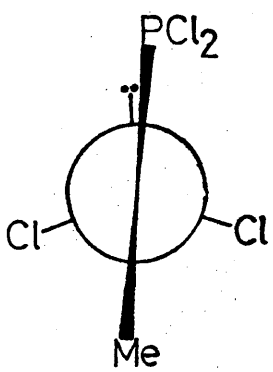


Figure 30.

As this angle is small, $^{3}J(P^{III}\text{-N-C-H})$ is expected to be relatively large (i.e. 11.2Hz). In comparison, the very small value of $^{3}J(P^{III}\text{-N-C-H})$ (3.0 Hz) found for bis(dichlorophosphino)-methylamine, $(Cl_2P)_2NMe$, would seem to indicate that there is a preferred conformation for this compound in which the dihedral angle is close to 180° (see Figure 31)



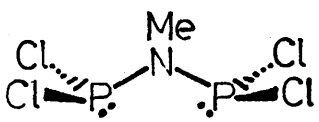


Figure 31.

A gas phase electron diffraction study[102] has established that the related tetrafluoro derivative $(F_2P)_2NMe$ adopts the above conformation. This compound also possesses a low value of $^3J(P^{III}\text{-N-C-H})$ (3.2 Hz)[11], confirming the conformation proposed for $(Cl_2P)_2NMe$.

It is further expected that increasing the temperature should result in an increase in the relative populations of other conformations (all of which will possess larger values of $^3J(P^{III}\text{-N-C-H})$ thus increasing the magnitude of the observed $^3J(P^{III}\text{-N-C-H})$. Such a trend has been observed for $Ph_2P\cdot NMe\cdot P(Cl)Ph$[257] and $(Cl_2P)_2NMe$ (see Table 17). However, as expected, no variation was found in the magnitude of $^3J(P^{III}\text{-N-C-H})$ in the cyclodiphosphazane $ClP\cdot NMe\cdot PCl\cdot NBu^t$.

TABLE 18.

Variation of $^3J(P^{III}\text{-N-C-H})$ with temperature.

Compound	low temp. $^3J(P^{III}\text{-N-C-H})$ Hz	(°C)	high temp. $^3J(P^{III}\text{-N-C-H})$ Hz	(°C)
$Ph_2P\cdot NMe\cdot P(Cl)Ph$	2.2[a] 4.5	(-30)	2.5[a] 4.9	(+105)
$(Cl_2P)_2NMe$	2.6	(-40)	3.6	(+99)
$ClP\cdot NMe\cdot PCl\cdot NBu^t$	11.2	(-40)	11.2	(+99)

[a] Coupling to diphenylphosphino phosphorus.

Similarly, the small dihedral angle between the planes containing the N-t-butyl group and the phosphorus lone pair in cyclodiphosphazanes containing N-t-butyl ring substituents is probably largely responsible for $^{4}J(P^{III}\text{-N-C-C-H})$ being larger than $^{4}J(P^{V}\text{-N-C-C-H})$ in these compounds (see Table 15).

EXPERIMENTAL.

Solvents were dried by conventional means. Methods used in the purification of reagents obtained commercially can be found in Appendix A. The compounds $(ClPNBu^t)_2$[12] and $(Cl_2P)_2NEt$[11] were prepared by literature methods. Details of n.m.r. and mass spectroscopic instrumentation and the source of microanalyses can be found in Appendix B. Analytical data is given in Table 19.

(a) Oxidation reactions of cyclodiphosphazanes.

Preparation of 1-t-butyl-2,4-dichloro-3-methyl-2-thiocyclodiphosphazane, $ClP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$:- A stirred mixture of flowers of sulphur 0.978 g (0.0305 mol) and 1-t-butyl-2,4-dichloro-3-methylcyclodiphosphazane 7.1 g (0.0305 mol) plus a trace of powdered anhydrous aluminium chloride was heated to 150° for 0.5h, when an exothermic reaction took place. The resultant liquid was distilled (62-70°, 0.02 mm Hg) to give 1-t-butyl-2,4-dichloro-3-methyl-2-thiocyclodiphosphazane. (6.2 g, 77%), a clear viscous liquid (isomer ratio 6:1).

Preparation of 1-t-butyl-2,4-dichloro-3-methyl-2,4-dithiocyclodiphosphazane, $Cl(S)P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$:- Similarly a mixture of flowers of sulphur 0.705g (0.022 mol) and 1-t-butyl-2,4-dichloro-3-methylcyclodiphosphazane 2.55 g (0.011 mol) plus a trace of powdered aluminium chloride, heated to 150° for 1h, gave on vacuum distillation (84°, 0.2 mm Hg) 1-t-butyl-2,4-dichloro-3-methyl-2,4-dithiocyclodiphosphazane (1.4 g, 43%), a clear viscous liquid (isomer ratio 3:2).

TABLE 19

Analytical data[a]

Compound	Found				Calc.			
	C	H	N	m/e[b]	C	H	N	m/e[b]
$ClP{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$	21.9	5.1	10.3	264	22.7	4.6	10.6	264
$Cl(S)P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$	21.6	4.4	8.6	296	20.2	4.1	9.4	296
$Cl(O)P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t$	20.8	4.7	8.7	280	21.4	4.3	10.0	280
$ClP{\cdot}NMe{\cdot}P(NMe_2)NBu^t$	34.1	8.5	16.9	241	34.4	8.7	17.2	241
$ClP{\cdot}NBu^t{\cdot}P(NMe_2)NBu^t$	41.7	8.6	15.1	283	42.3	8.5	14.8	283
$Me_2NP{\cdot}NMe{\cdot}P(NMe_2)NBu^t$	43.5	9.7	22.1	250	43.2	9.7	22.4	250
$Me_2NP{\cdot}NEt{\cdot}P(NMe_2)NBu^t$	45.4	10.0	21.4	264	45.45	9.9	21.2	264

TABLE 19 contd.

Compound	Found				Calc.			
	C	H	N	m/e[b]	C	H	N	m/e[b]
$(Me_2NPNBu^t)_2$	49.4	10.7	19.0	292	49.3	10.3	19.2	292
$(Et_2NPNBu^t)_2$	55.0	11.2	15.9	348	55.15	11.0	16.1	348
$Me_2N\overline{P \cdot NMe \cdot P(O)Cl \cdot NBu^t}$				257				257
$Me_2N\overline{P \cdot NMe \cdot P(S)Cl \cdot NBu^t}$	30.6	7.1	14.5	273	30.7	6.6	15.35	273

[a] Elemental analyses figures are given in %.

[b] For ions containing ^{35}Cl (where relevant).

Preparation of 1-t-butyl-2,4-dichloro-3-methyl-2-oxocyclodiphosphazane, $ClP{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$:- To a stirred solution of 1-t-butyl-2,4-dichloro-3-methylcyclodiphosphazane 5.8 g (0.025 mol) in 30 ml methylene chloride at -78° was slowly added dimethyl sulphoxide 1.95 g (0.025 mol) in 20 ml methylene chloride. The reaction was allowed to come to ambient temperatures (1h) after which time the methylene chloride and dimethyl sulphide were evaporated off under reduced pressure and collected in a trap held at -78°. The liquid residue was distilled (67-70°, 0.01 mm Hg) to give 1-t-butyl-2,4-dichloro-3-methyl-2-oxocyclodiphosphazane (4.8 g, 77%), a clear viscous liquid (isomer ratio 5:1).

Preparation of 1-t-butyl-2,4-dichloro-3-methyl-2,4-dioxocyclodiphosphazane $Cl(O)P{\cdot}NMe{\cdot}P(O)Cl{\cdot}NBu^t$:- Using the same method, 6.75 g (0.029 mol) 1-t-butyl-2,4-dichloro-3-methylcyclodiphosphazane and 4.5 g (0.058 mol) of dimethyl sulphoxide in 60 ml methylene chloride gave on vacuum distillation (ca 120°, 0.5 mm Hg) 1-t-butyl-2,4-dichloro-3-methyl-2,4-dioxocyclodiphosphazane (5.7 g, 74%) a clear viscous liquid (isomer ratio 3:2) which slowly crystallised on standing. The major isomer was purified by recrystallisation from a diethyl ether/light petroleum (b.p. 40-60°) mixture, giving white crystals m.p. 84-86°.

Reaction of bis(dichlorophosphino)ethylamine with one mol of dimethyl sulphoxide:- Using the same method, 7.3 g (0.0295 mol) bis(dichlorophosphino)ethylamine and 2.3 g (0.0295 mol) dimethyl sulphoxide in 120 ml methylene chloride gave a clear liquid after evaporation of methylene chloride and dimethyl sulphide. This liquid was shown by ^{31}P n.m.r. to consist of a 5:1:5 mixture of bis(dichlorophosphinoyl)ethylamine, dichlorophosphino-(dichlorophosphinoyl)ethylamine, and bis(dichlorophosphino)ethylamine respectively.

Preparation of 1-t-butyl-2,4-dichloro-3-methyl-2-oxo-4-thiocyclodiphosphazane, $Cl(O)\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$:- A stirred mixture of 1-t-butyl-2,4-dichloro-3-methylcyclodiphosphazane 10.55 g (0.0453 mol), flowers of sulphur 1.450 g (0.0453 mol) and a trace of powdered anhydrous aluminium chloride was heated to 150°for 1h. Without further purification, the residue was dissolved in 80 ml methylene chloride and the solution cooled to -78°. A solution of dimethyl sulphoxide 3.53 g (0.0453 mol) in 30 ml methylene chloride was then slowly added. After warming to ambient temperatures, the methylene chloride and dimethyl sulphide were evaporated under reduced pressure and collected in a trap held at -78°. The residue was distilled (ca 100°, 0.7 mm Hg) to give 1-t-butyl-2,4-dichloro-3-methyl-2-oxo-4-thiocyclodiphosphazane (5.9 g, 46%) a clear very viscous liquid (isomer ratio 2:1).

(b) Aminolysis reactions of cyclodiphosphazanes.

Preparation of 1-t-butyl-2-chloro-4-dimethylamino-3-methyl-cyclodiphosphazane, $ClP{\cdot}NMe{\cdot}P(NMe_2)NBu^t$:- To a stirred solution of 1-t-butyl-2,4-dichloro-3-methylcyclodiphosphazane 6.15 g (0.0264 mol) in 200 ml diethyl ether at -78° was slowly added a solution of dimethylamine 2.4 g (0.053 mol) in 50 ml diethyl ether. The reaction was allowed to warm up to ambient temperature (1h) after which time the dimethylammonium chloride precipitate was removed by filtration and the diethyl ether evaporated under reduced pressure. The liquid residue was distilled (50-56°, 0.02 mm Hg) to give 1-t-butyl-2-chloro-4-dimethylamino-3-methylcyclodiphosphazane (4.3 g, 67%) a clear viscous liquid. Similar methods were used in all of the following preparations.

Preparation of 1,3-di-t-butyl-2-chloro-4-dimethylamino-cyclodiphosphazane, $ClP{\cdot}NBu^t{\cdot}P(NMe_2)NBu^t$:- 1,3-di-t-butyl,-2,4-dichlorocyclodiphosphazane 5.3 g (0.0194 mol) was reacted with dimethylamine 1.75 g (0.0388 mol) in 150 ml diethyl ether at -78°. The liquid residue obtained after work up was distilled (55-65°, 0.03 mm Hg) to give 1,3-di-t-butyl-2-chloro-4-dimethylamino-cyclodiphosphazane (3.7 g, 57%) a clear viscous liquid.

Preparation of 1,3-di-t-butyl-2-chloro-4-di-i-propylamino-cyclodiphosphazane, $ClP{\cdot}NBu^t{\cdot}P(NPr^i{}_2)NBu^t$:- 1,3-di-t-butyl-2,4-dichlorocyclodiphosphazane, 5.6 g (0.0205 mol) was mixed with di-i-propylamine 8.3 g (0.0820 mol) in 170 ml diethyl ether at -78°C. The reaction mixture was then refluxed for 15h.

Work up gave a slightly cloudy viscous liquid which was not purified but shown by ^{1}H and ^{31}P n.m.r. to consist almost completely of 1,3-di-t-butyl-2-chloro-4-di-i-propylamino-cyclodiphosphazane.

Preparation of 1-t-butyl-2,4-bisdimethylamino-3-methylcyclodiphosphazane, $Me_2\overline{NP\cdot NMe\cdot P(NMe_2)}NBu^t$:-

(1) 1-t-butyl-2,4-dichloro-3-methylcyclodiphosphazane 5.25 g (0.0225 mol) was mixed with dimethylamine 4.7 g (0.104 mol) in 180 ml diethyl ether at -78°. The reaction was allowed to warm to ambient temperatures and stirred (3h). The brownish liquid obtained on work up was carefully distilled (60-66°, 0.01 mm Hg) to give 1-t-butyl-2,4-bisdimethylamino-3-methyl-cyclodiphosphazane (3.1 g, 55%) a clear viscous liquid (low field:high field isomer ratio 3:2).

(2) To a stirred solution of bis(dichlorophosphino)methylamine 12.05 g, (0.0517 mol) in 50 ml methylene chloride at -78°C was slowly added a solution of dimethylamine 9.3 g (0.207 mol) in 20 ml methylene chloride. The reaction was stirred (0.5h) while warming slowly to around 0°. A filtered sample of the solution was shown by ^{1}H n.m.r. to consist of a solution of bis(chlorodimethylaminophosphino)methylamine in methylene chloride. To the rest of the solution cooled to -78° was added a solution of t-butylamine 11.3 g (0.155 mol) in 50 ml methylene chloride. The reaction mixture was stirred (2h) after reaching ambient temperatures. The precipitate containing dimethylammonium chloride and t-butylammonium chloride was removed by filtration

and the methylene chloride evaporated under reduced pressure to give a yellowish cloudy liquid. This liquid after further separation from the amine hydrochloride precipitate was carefully distilled (60-66°, 0.01 mm Hg) to give 1-t-butyl-2,4-bisdimethylamino-3-methylcyclodiphosphazane (8.4 g, 64%) a clear viscous liquid (low field:high field isomer ratio 2:3).

Preparation of 1-t-butyl-2,4-bisdimethylamino-3-ethylcyclodiphosphazane, $Me_2NP{\cdot}NEt{\cdot}P(NMe_2)NBu^t$:- 1-t-butyl-2,4-dichloro-3-ethylcyclodiphosphazane 4.8 g (0.0194 mol) was mixed with dimethylamine 4.4 g (0.098 mol) in 170 ml diethyl ether at -78°. The reaction mixture was stirred (2h) after warming up to ambient temperatures. The yellowish liquid obtained on work up was carefully distilled (54-60°, 0.005 mm Hg) to give 1-t-butyl-2,4-bisdimethylamino-3-ethylcyclodiphosphazane (2.7 g, 53%) a clear viscous liquid (low field:high field isomer ratio 2:1).

Preparation of 1,3-di-t-butyl-2,4-bisdimethylaminocyclodiphosphazane, $(Me_2NPNBu^t)_2$:- 1,3-di-t-butyl-2,4-dichlorocyclodiphosphazane 5.3 g (0.0193 mol) was mixed with dimethylamine 4.5 g (0.10 mol) in 180 ml diethyl ether at -78°. The reaction was refluxed (3h) after warming up to ambient temperatures. The yellowish low melting point solid obtained on work up was carefully distilled (85-90°, 0.01 mm Hg) to give 1,3-di-t-butyl-2,4-bisdimethylaminocyclodiphosphazane (2.7 g, 48%) a clear viscous liquid which crystallised on

standing. Isomer rearrangement occurred on vacuum distillation, the low field:high field isomer ratio of 3:2 changing to ca 1:10 after distillation.

Preparation of 1,3-di-t-butyl-2,4-diethylaminocyclodiphosphazane, $(Et_2NPNBu^t)_2$:- 1,3-di-t-butyl-2,4-dichlorocyclodiphosphazane 5.6 g (0.0204 mol) was mixed with diethylamine 6.0 g (0.082 mol) in 170 ml diethyl ether at -78°. The reaction was stirred (15h) after warming up to ambient temperatures. The yellowish liquid obtained on work up was carefully distilled (78-80°, 0.02 mm Hg) to give 1,3-di-t-butyl-2,4-diethylaminocyclodiphosphazane (2.1 g 30%) a clear viscous liquid. ^1H and ^{31}P n.m.r. showed that only one isomer of the product was present before and after vacuum distillation.

Preparation of 1-t-butyl-2-chloro-4-dimethylamino-3-methyl-2-oxocyclodiphosphazane, $Me_2\overline{NP\cdot NMe\cdot P(O)Cl\cdot NBu^t}$:- 1-t-butyl-2,4-dichloro-3-methyl-2-oxocyclodiphosphazane 2.9 g (0.0117 mol) was mixed with dimethylamine 1.10 g (0.0244 mol) in 110 ml diethyl ether at -78°. The reaction was stirred (1h) after warming up to ambient temperatures. The almost clear viscous liquid obtained on work up was not purified further, but ^1H-$\{^{31}P\}$ n.m.r. showed that this liquid almost completely consisted of 1-t-butyl-2-chloro-4-dimethylamino-3-methyl-2-oxocyclodiphosphazane. (isomer ratio 4:1).

Preparation of 1-t-butyl-2-chloro-4-dimethylamino-3-methyl-2-thiocyclodiphosphazane, $Me_2N\overline{P{\cdot}NMe{\cdot}P(S)Cl{\cdot}NBu^t}$:- 1-t-butyl-2,4-dichloro-3-methyl-2-thiocyclodiphosphazane 3.2 g (0.012 mol) was mixed with dimethylamine 1.1 g (0.0244 mol) in 100 ml diethyl ether at -78°. The reaction was stirred (1h) after warming up to ambient temperatures. The liquid obtained on work up was distilled (60-64°, 0.03 mm Hg) to give 1-t-butyl-2-chloro-4-dimethylamino-3-methyl-2-thiocyclodiphosphazane (1.2 g, 36%) a clear viscous liquid (isomer ratio 4:1).

APPENDIX A.

Preparative methods, solvent and reagent purification.

All operations were carried out under a flush of nitrogen (dried by passing through silica gel and phosphorus pentoxide columns) or connected to a conventional vacuum manifold.

Anhydrous solvents were always used and normally kept dry by contact with sodium wire or molecular sieve 4A. The ethanol stabiliser was removed from chloroform before use by contact with basic alumina.

Triethylamine was distilled from sodium and t-butylamine, i-propylamine, di-i-propylamine and diethylamine all distilled from powdered, anhydrous sodium hydroxide before use. Phosphoryl chloride, thiophosphoryl chloride, phosphorus trichloride, dimethyl sulphoxide, aniline, dibromomethane and 1,2-dibromoethane were all purified by distillation. Other anhydrous amines, diethylaminotrimethylsilane, trimethylsilylchloride, methyl iodide, tri-i-propylphosphite, phosphorus pentachloride and triphenylphosphine, all obtained commercially, were used without purification. Methylammonium chloride, ethylammonium chloride, t-butylammonium chloride and ammonium sulphate were all vacuum dried before use.

APPENDIX B.

Instrumentation and analysis.

^{1}H and ^{31}P n.m.r. spectra were recorded on a Jeol C60HL spectrometer at 60 and 24.3 MHz respectively, and selective-noise ^{31}P and ^{1}H decoupling carried out using a Schomandl ND100M frequency synthesiser and a Jeol SDHC unit. ^{31}P resonance frequencies were measured by a Racal frequency counter. ^{1}H n.m.r. spectra at 100 and 220 MHz were recorded on Varian HA100 and HR220 spectrometers respectively. Mass spectra were obtained on an A.E.I. MS 12 spectrometer. C,H,N and Cl analyses were determined by the microanalysis laboratory, Department of Chemistry, University of Glasgow and S analysis by Beller Laboratory.

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