THE SYNTHESIS AND OXIDATION OF SOME CYCLOPHOSPHAZANES.

A thesis submitted to the
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for the degree of
DOCTOR OF PHILOSOPHY
by

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To My Mother and Father.

D. A. Harvey.

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D. A. Harvey.

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Abstract

The reactions of a series of cyclic and acyclic phosph(III)azanes with diborane and borane adducts were investigated in an attempt to establish the most reactive nucleophilic sites in the phosph(III)azanes and to gain information relating conformation and reactivity.

Tris(dimethylamino)phosphine, $P(NMe_2)_3$, reacted with triethylamine -borane, Et_3NBH_3, to produce the monoborane adduct, $(Me_2N)_3PBH_3$. Reaction of diborane, B_2H_6, with the acyclic phosph(III)azanes, $\left[(Me_2N)_2P\right]_2NMe$ gave a diborane adduct. In similar reactions of B_2H_6 with a series of phosph(III)azanes $(Ph_2P)_2NR$, (R = Me, Et and Pr^i), the products rapidly decomposed, but evidence was obtained for the formation of a monoborane adduct where R = Me and Et. In all cases where an acyclic phosphazane-borane adduct was obtained it was established that the BH_3 group was bonded to the phosphorus atom.

Analogous reactions with cyclodiphosph(III)azanes have shown that BH_3 groups bond to the P_2N_2 ring through the phosphorus atoms. The reactions of cis and trans $(Me_2NPNBu^t)_2$ with 1 mole equivalent of Et_3NBH_3 produced only cis-$Me_2N(BH_3)\overline{PNBu^t.P(NMe_2)}NBu^t$, with 2 mole equivalents of Et_3NBH_3 a bis borane adduct was obtained, the proportion of the geometrical isomers produced being dependent on the temperature of the reaction.

The reaction of $(Me_2NPNBu^t)_2$ with excess diborane, B_2H_6, proceeded with overall retention of configuration. Analogous reactions using $(MeOPNBu^t)_2$ gave a bis borane adduct, similar to those above but $(MeOPNBu^t)_2$ was less reactive than $(Me_2NPNBu^t)_2$.

An attempted reaction between $(ClPNBu^t)_2$ and Et_3NBH_3 failed to produce a borane adduct, but when the reaction was repeated using tetrahydrofuran-borane, $THF.BH_3$, the monoborane adduct, $Cl(BH_3)\overline{PNBu^tPClNBu^t}$ was formed. Over a period of several weeks cis-$Me_2N(BH_3)\overline{PNBu^tP(NMe_2)}NBu^t$ disproportionated to cis-$(Me_2NPNBu^t)_2$ and cis-$(Me_2N(BH_3)PNBu^t)_2$.

Nmr data indicates that the reaction of $(XPNBu^t)_2$ (X = Cl or NMe_2) and 1 mole equivalent of chlorine gave a product which is either $\overbrace{XPNBu^tPCl_2XNBu^t}$ or the ionic salt $\overbrace{XPNBu^tP^+ClNMe_2NBu^t}\ Cl^-$. When the reaction was repeated using $(ClPNBu^t)_2$ and excess chlorine, ring cleavage occured, the only identifiable product being $Cl_2P(O)N{=}PCl_2N(H)Bu^t$. $(ClPNBu^t)_2$ and bromine resulted mainly in the formation of decomposition products.

Reaction of $\overbrace{ClPNBu^tPClNR}$ (R = Me, Et) with excess of dry chlorine surprisingly gave a zwitterionic product, $Cl_2\overbrace{P^+NBu^tP^-Cl_4}NR$ (R = Me, Et). The reaction of $\overbrace{ClPNBu^tPClNEt}$ with 1 mole equivalent of bromine gave either $\overbrace{ClPNBu^tPClBr_2}NEt$ or $\overbrace{ClPNBu^tP^+BrXNEt}\ Y^-$ (X and Y = Cl or Br). When the reaction was repeated with 2 mole equivalents or excess bromine, a zwitterionic product was obtained.

By contrast, the reaction of $(ClPNPh)_2$ and excess chlorine resulted in the simple oxidation product, $(Cl_3PNPh)_2$.

Reactions of excess chlorine with a series of acyclic phosph(III)azanes of the type $(Cl_2P)_2NR$ (R = Me, Et and Pr^n) gave cyclodiphosph(V)azanes, $(Cl_3PNR)_2$ (R = Me,Et, and Pr^n). These reactions have been shown to proceed via two intermediate compounds, the first is still unidentified but the second has been identified by nmr as the hitherto unknown monomeric species $Cl_3P{=}NR$ (R = Me,Et, and Pr^n), and $Cl_3P{=}NBu^t$.

When the reactions were repeated with bromine the products again included $(Cl_3PNR)_2$, though small quantities of $(BrCl_2PNR)_2$, $(Br_2ClPNR)_2$ and $(Br_3PNR)_2$ were found in small traces along with PCl_3, PCl_2Br, and $PClBr_2$.

The formation of phosph(III)azanes by the reaction of PCl_3 with $EtNH_3Cl$ in refluxing sym-tetrachloroethane has been reinvestigated. It was found that different major products $(Cl_2P)_2NEt$, $(ClPNEt)_3$ and $P_4(NEt)_5Cl_2$ could be obtained by suitable variation of the stoichiometry. However, when the reactions were repeated using $MeNH_3Cl$ instead of $EtNH_3Cl$, only $(Cl_2P)_2NMe$ could be obtained. When $(Cl_2P)_2NR$ (R = Me or Et) was heated, $(ClPNR)_3$ (R = Me or Et) and PCl_3 were produced along with decomposition products. The reverse reaction was also possible; refluxing a solution containing PCl_3 and $P_4(NEt)_5Cl_2$ gave $(ClPNEt)_3$ and, in turn, $(Cl_2P)_2NEt$.

A series of derivatives of $(ClPNEt)_3$ were prepared, $(Me_2NPNEt)_3$ was obtained only as a trans isomer while $(MeOPNEt)_3$ and $(FPNEt)_3$ were present as a mixture of cis and trans isomers. Conformational information for these rings was difficult to establish. The ring compound $(ClPNEt)_3$ was also reacted with a series of monoamines H_2NR (R = Et, Pr^i, and Bu^t) to produce a trans substituted product, $(R(H)NPNEt)_3$ (R = Et, Pr^i, and Bu^t), and a fused ring compound, 2,4-ethylimino-6-ethylamino-1,3,5-triethylcyclotriphosph(III)azane. The ratio of the two types of products varied with the size of R, the larger R the more the fused ring compound was favoured. This proportion of products, as detected by ^1H and ^{31}P nmr, was also affected by heating which favoured the fused ring compound. An adamantane like cage molecule $P_4(NEt)_6$ was also identified.

Fluoro-, alkylamino- and alkoxy- derivatives of $P_4(NEt)_5Cl_2$ were prepared by reaction with SbF_3, Me_2NH, Et_2NH, $C_5H_{10}NH$, MeOH and Bu^tOH. In all cases two isomers were formed, termed 'symmetric' and 'asymmetric' (these terms are based on consideration of the ^{31}P nmr spectra and the resulting structural assignments of the terminal phosphorus atoms.

The reaction of $P_4(NEt)_5Cl_2$ with a series of monoamines RNH_2 (R = Et, Bu^t and H) led to the formation of a series of compounds $P_4(NR)_5(NR')$ (R = Et, R' = Bu^t or H) with an adamantane-like cage structure. In the reaction of $P_4(NEt)_5Cl_2$ with $EtNH_2$ an intermediate with a direct P——P bond was tentatively identified.

Oxidation reactions using S_8, Se_8, Te_8 and Bu^tOOH were carried out on $(ClPNEt)_3$ and $P_4(NEt)_5Cl_2$ and their derivatives. The reaction of $(Me_2NPNEt)_3$ and $(MeOPNEt)_3$ with sulphur and selenium gave the oxidation products $(Me_2N(X)PNEt)_3$ (X = S or Se), and $(MeO(Y)PNEt)_3$ (Y = S or Se). In all cases only a trans isomer was obtained regardless of the structure of the starting material. The reaction of $(ClPNEt)_3$ with three moles of Me_2SO gave only a small amount of the trans mono- and di-oxy derivatives, $Cl(O)\overline{PNEt.P(Cl)NEt.P(Cl)NEt}$ and $Cl(O)\overline{PNEt.P(Cl)(O)NEt.P(Cl)NEt}$ respectively. Dithio-derivatives $P_4(NEt)_5(NMe_2)_2S_2$ and $P_4(NEt)_5(NC_5H_{10})_2S_2$ were also made by reaction with elemental sulphur. Only one isomer was obtained in each case, possibly containing the sulphur atoms bonded to terminal phosphorus atoms. Reactions with elemental Se_8 mainly produced decomposition products.

The oxide, $P_4(NEt)_5Cl_2O$, as a mixture of two isomers, was produced by the reaction of Me_2SO on $P_4(NEt)_5Cl_2$ and it was also found as an impurity in a number of reactions.

CHAPTER 1

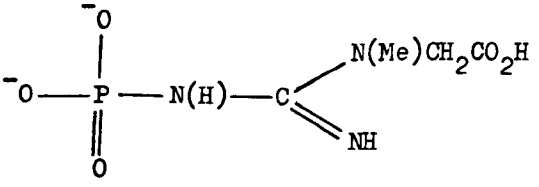
GENERAL INTRODUCTION.

1.1 General.

The element phosphorus, which does not occur free in nature, was first discovered in 1667 by Hennig Brand of Hamburg, who, from his experiments with boiling down of urine, found a substance which glowed in the dark and ignited when exposed to the air. Its "glowing" properties led it to be called phosphorus from the Greek for 'light-bearing'. The product of its combustion with air was investigated in 1694 by Boyle who made an acidic solution which is now known to be phosphoric acid, H_3PO_4. In 1770, phosphorus was recognised as being an important constituent of bones and in 1779 Gahn discovered that phosphorus was present in minerals, the first to be discovered being pyromorphite. In 1812 the first practical use of phosphorus was developed when striking matches were manufactured. In 1842 artificial fertilisers were patented using a process involving sulphuric acid and bones. To this day fertilisers are the single most important commercial application of phosphorus compounds.

From the early 19th century onwards, it has been recognised that phosphorus compounds are important for the growth of plants and animals. Today in biochemistry phosphorus compounds are seen at the heart of many extremely important biological systems. These include adenosine triphosphate (ATP), an energy-transfer agent in nature and nucleic acids which are the basis of all material including DNA. Phosphorus has been found in bones, teeth, blood and nerve functions. It is so important that it constitutes 1% of the weight of the human body. Phosphorus-nitrogen compounds are less common than phosphorus-oxygen compounds in biological systems, but a well known example of the former group is phosphocreatine (A).

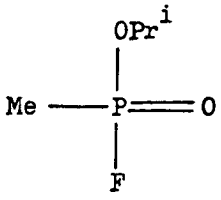
This compound may be an emergency source of phosphate in the production of ATP.



(A)

Today the most common source of phosphorus compounds is from phosphates extracted from sedimentary mineral deposits. Although there are over two hundred phosphate containing minerals only the apatite group, $Ca_3(PO_4)_6X_2$ (where X= F, Cl, or OH) are commercially important. The widespread use of phosphates has led to some problems of sewage disposal. The build up of phosphate concentration in lakes and slow moving rivers causes excessive growth of algae which starve the water of oxygen so killing fish and plant life. However, these lakes and rivers can recover if the phosphate input is stopped since there will be a gradual settling out of the phosphate already present. If effluent is treated with iron or aluminium salts this allows a quicker sedimentation of the phosphate as iron or aluminium phosphate.

The toxicity of phosphorus compounds varies widely. Most inorganic phosphates based on four co-ordinated phosphorus are among the safest compounds known. However, some organo-phosphates are also amongst the most powerful poisons made. These include nerve agents such as sarin (B)[1].

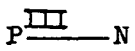


(B)

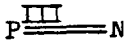
In recent years work on phosphorus compounds has been well documented [2,3].

1.2 Nomenclature.

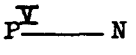
Following the suggestions of Shaw[4] and coworkers phosphorus-nitrogen compounds can conveniently be divided into two categories, phosphazanes and phosphazenes. As in the naming of organic compounds, these categories relate to the type of bonding and unsaturation present in the molecule. Phosphazanes contain phosphorus-nitrogen formal single bonds, while phosphazenes have phosphorus-nitrogen formal double bonds. In both cases the oxidation state of phosphorus is indicated by a Roman numeral as follows, eg. phosph(III)azane or phosph(V)azane, and the types of phosphorus-nitrogen compounds are shown below.



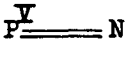
phosph(III)azane



phosph(III)azene

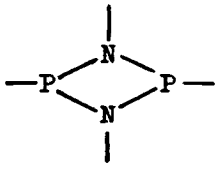


phosph(V)azane

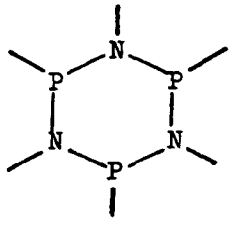


phosph(V)azene

In both phosphazanes and phosphazenes, polymers and cyclic oligomers can be considered to be built up of distinct phosphorus-nitrogen monomer groups. Thus (1) and (2) are cyclodiphosph(III)azanes and cyclotriphosph(III)azanes respectively.

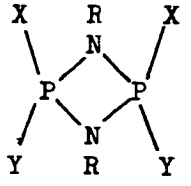


(1)

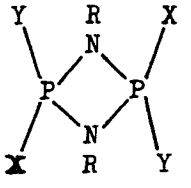


(2)

In this thesis the emphasis is on phosph(III)azanes, where the bond angles at phosphorus are generally less than 100° and the nitrogen has a near planar distribution of bonds. As a result cyclophosph(III)azanes have isomers, the description of which depends on the presence of a four or six membered ring system. In four membered rings (1) geometrical isomerism arises because of the presence of a phosphorus lone pair. These are classified as cis or trans isomers.



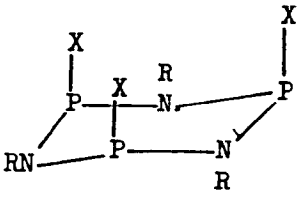
cis



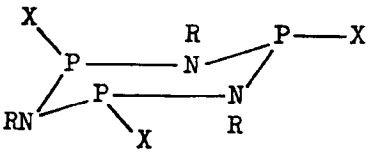
trans

(1) (R = Alkyl groups
X = alkyl, alkoxy, amino, halogen
Y = lone pair.)

In cyclotriphosphazanes (2), the substituents on phosphorus can also adopt cis or trans arrangements, but in addition these substituents can also adopt equatorial or axial positions as in derivatives of cyclohexane. Assuming that a chair conformation is preferred, the positions of the phosphorus substituents can give four isomers, (a,a,a), (e,e,e), (a,e,e) and (a,a,e), where a = axial and e = equatorial.

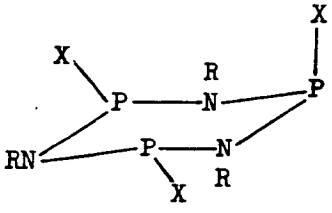


(a,a,a)

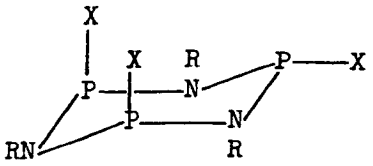


(e,e,e)

cis



(a,e,e)



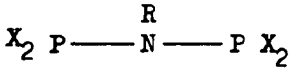
(a,a,e)

trans

(2)

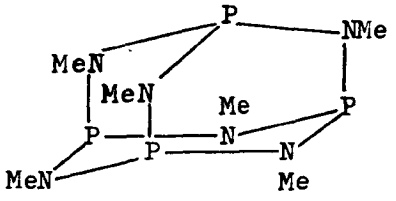
In practice only two isomers have so far been found, one cis and one trans. In the case of (2, R = Me, X = OPr), Zeiss and coworkers have suggested that the cis isomer is (a,a,a) and the trans isomer is (a,a,e).[5]

A number of acyclic phosphazanes containing the P-N-P backbone (3) were also studied in this work and for reasons of convenience these are referred to as bis(phosphino)amines, although formally these would be referred to as 1-phosphinophosphazanes.



(3)

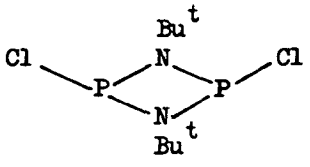
Phosphazanes also exist as cage type molecules, but the systematic name is not normally used as it is very long and inconvenient. Therefore, for convenience $P_4(NMe)_6$(4), has been called phosphorus tri-N-methylimide by its discoverer R.R. Holmes,[6] although here greater uniformity is achieved by naming it as a derivative of cyclotetraphosph(III)azane.

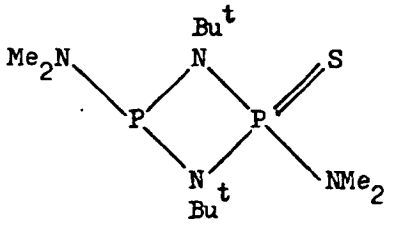


(4)

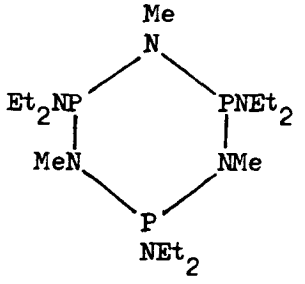
The naming of some examples of phosphazanes, relevant to this thesis are as follows:

(a) $Cl_2P—N(Me)—PCl_2$: bis(dichlorophosphino)methylamine.

(b)  : 2-<u>cis</u>-4-dichloro - 1,3-di-t-butyl cyclodiphosph(III)azane.

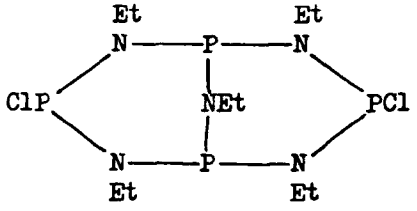
(c) 

: 2-trans-4-bis-dimethylamino-1,3-di-t-butyl-2-thiocyclodiphosphazane.

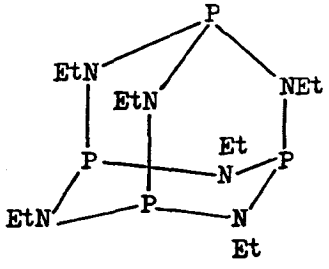
(d) 

: 2,4,6-Trisdiethylamino-1,3,5-trimethylcyclotriphosph(III)azane.

(isomerism ignored)

(e) 

: 2,6-ethylimino-4,8-dichloro-1,3,5,7-tetraethylcyclotetraphosph(III)azane.

(f) 

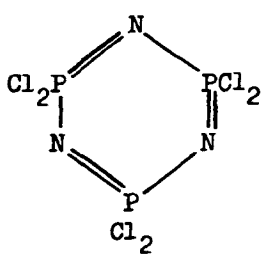
: 2,6-ethylimino-4,8-ethylimino-1,3,5,7-tetraethylcyclotetraphosph(III)azane.

Holmes[6]; phosphorus tri-N-ethylimide.

IUPAC ; 2,4,6,8,10-hexaethyl-2,4,6,8,10-hexaaza-1,3,5,7-tetraphosphatricyclo(3.3.1.1)decane.

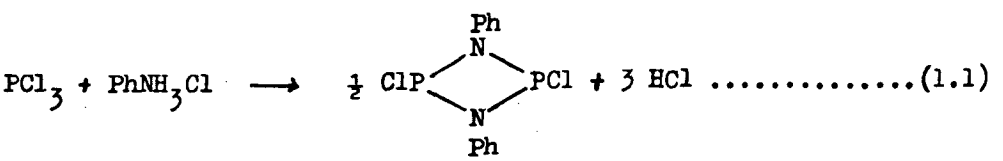
1.3 Historical and Synthesis.

Early work on the formation of phosphorus-nitrogen compounds was carried out by Liebig and Wöhler,[7] and separately by Rose[8] in 1834. They investigated the reaction of ammonia with phosphorus pentachloride and obtained a small quantity of a stable crystalline compound containing nitrogen, phosphorus and chlorine. It was not until 1864 that Gerhardt[9,10] and later Laurent[11] in 1850, established its empirical formula as $NPCl_2$. In 1864 Gladstone and Holmes[12,13,14], and in 1870 Wichelhaus[15], used vapour density measurements to establish the molecular formula as $N_3P_3Cl_6$. In the late 19th century work by Stokes[16-22] showed that this compound had a cyclic structure (C) and went on to identify a general series of compounds of the type $(NPCl_2)_n$ (n:4-7)



(C)

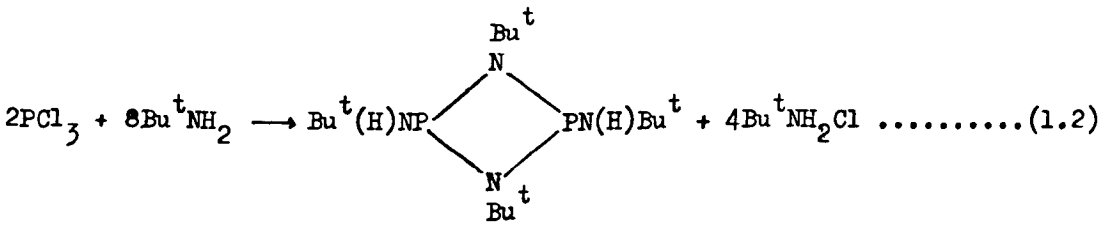
In 1894 Michaelis and Schroeter[23] reported the reaction of phosphorus trichloride with aniline hydrochloride. The product was formulated as a 'phosphazo compound', ClP=NPh, and the dimeric structure was deduced from molecular weight measurements.



(1a)

Several amino derivatives of (1a) were also isolated.

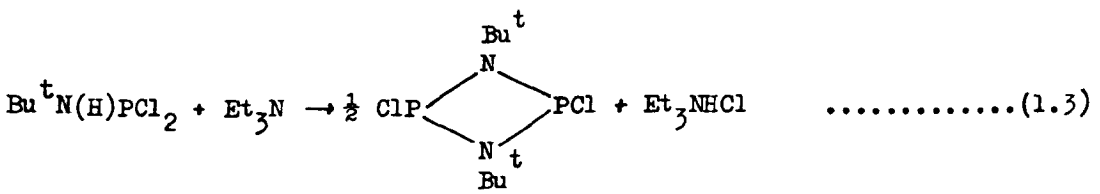
Very little work was carried out on cyclophosph(III)azanes until the early 1960's. In 1961 Holmes[6] reacted phosphorus trichloride with an excess of methylamine, and obtained a reasonable quantity of a phosphazane with the formula, $P_4N_6Me_6$. This was shown to have an adamantane type cage structure, $P_4(NMe)_6$,(4). Holmes and Forstner[24] also synthesised an amino-substituted cyclodiphosph(III)azane (1b), as shown in reaction(1.2)



$$2PCl_3 + 8Bu^tNH_2 \longrightarrow Bu^t(H)NP(NBu^t)_2PN(H)Bu^t + 4Bu^tNH_2Cl \quad \text{.....(1.2)}$$

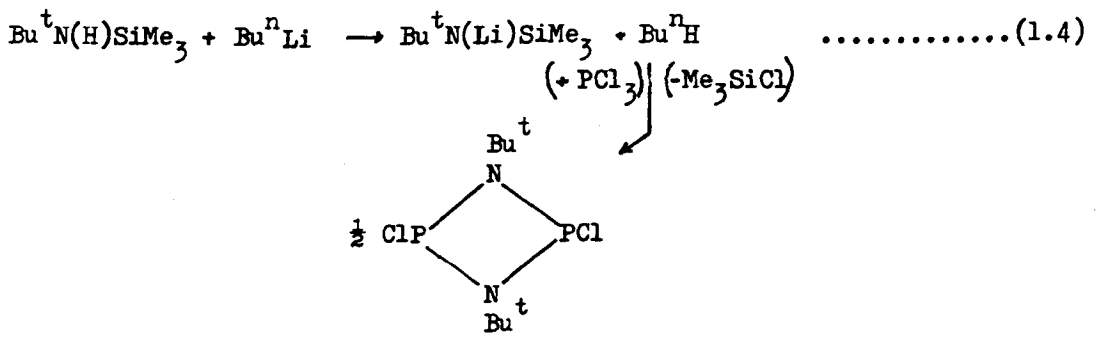
(1b)

More recently a number of alternative routes to the dimeric cyclophosphazanes have been established. Scherer and Klusmann[25] devised the synthesis of the first fully authenticated cyclodiphosph-(III)azane (1c).



$$Bu^tN(H)PCl_2 + Et_3N \longrightarrow \tfrac{1}{2}\,ClP(NBu^t)_2PCl + Et_3NHCl \quad \text{.....(1.3)}$$

(1c)



$$Bu^tN(H)SiMe_3 + Bu^nLi \longrightarrow Bu^tN(Li)SiMe_3 + Bu^nH \quad \text{.....(1.4)}$$

$(+PCl_3)$ $(-Me_3SiCl)$

$\tfrac{1}{2}\,ClP(NBu^t)_2PCl$

(1c)

In 1973 Haszeldine and coworkers, showed that the products of the reaction of phosphorus trichloride and aniline hydrochloride are temperature dependent[26]. At low temperatures the product is bis(dichlorophosphino)aniline (3a), but at higher temperatures the product is the four-membered ring compound (1a). The reaction mechanism they postulated was :

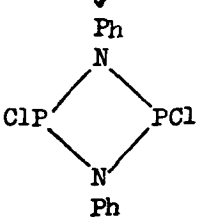
$$PhNH_2 + PCl_3 \xrightarrow{-HCl} (Cl_2P)_2NPh,\ (3a) \quad \text{.....(1.5)}$$

(excess)

$$\downarrow -PCl_3$$

$$ClP{=}NPh$$

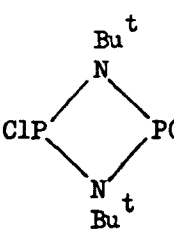
$$\downarrow$$



(1a)

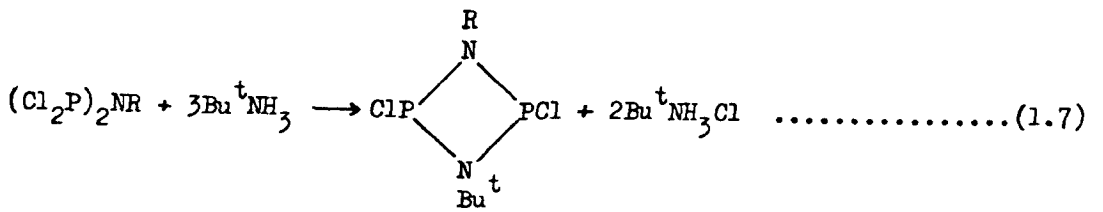
Perhaps the easiest synthetic route to a cyclodiphosph(III)azane developed to date was by Keat, Nixon and coworkers[27]. In this reaction phosphorus trichloride is reacted with three mole equivalents of tert-butylamine to give a 38% yield of (1c).

$$6Bu^tNH_2 + 2PCl_3 \xrightarrow{\text{diethylether}} \text{(1c)} + 4\ Bu^tNH_3Cl \quad \text{.....(1.6)}$$



(1c)

Keat and Bulloch[28] have also established the synthesis of cyclodiphosph(III)azanes with different N-alkyl-sustituents, (1d).

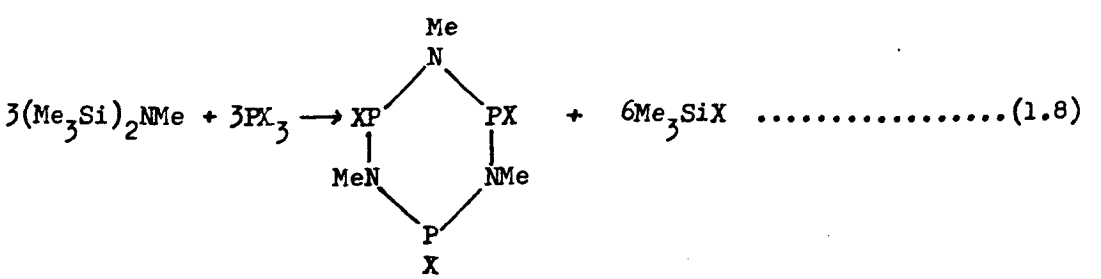


(R = Me, Et)

(1d)

Both reactions (1.6) & (1.7) occur too rapidly for any intermediate species to be identified. In addition, the overall rate is little affected by the type of alkyl group.

Less work has been carried out on the formation of six membered cyclophosphazanes than on the smaller four membered rings. In 1965 Abel and coworkers[29] claimed to have made the cyclotriphosph-(III)azane, $(ClPNEt)_3$, from the reaction of phosphorus trichloride and a silylamine, $EtN(SiMe_3)_2$. However, this work could not be repeated by Nixon in 1970[30] and Keat and Nixon in 1973[27]. More recently this reaction was used successfully for the synthesis of some cyclotriphosph(III)azanes[31].



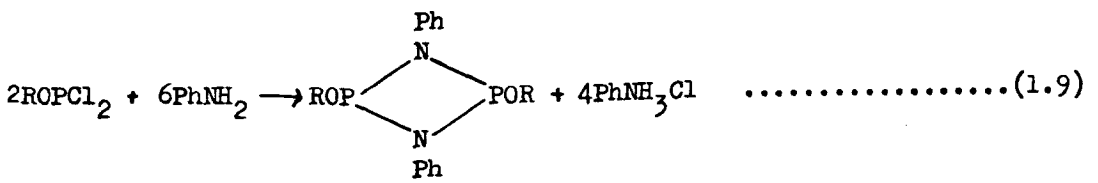
(2) (X = Cl or Br)

Keat and Nixon[27] have also shown that 4 -membered ring, $(ClPNEt)_2$, was a minor product of the reaction of ethylamine and phosphorus trichloride, the major product being bis(dichlorophosphino) ethylamine, $(Cl_2P)_2NEt$.

1.4. Reactions of cyclophosph(III)azanes.

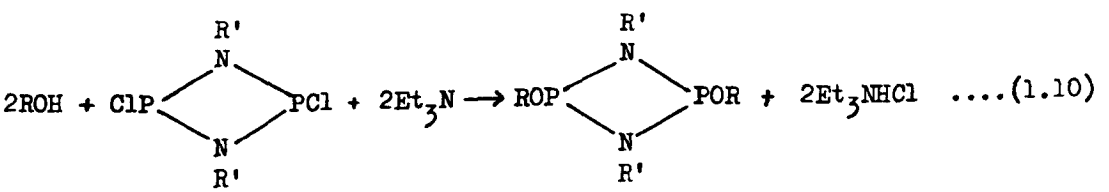
1.4a. Substitution reactions.

In their early work on the formation of cyclophosph-(III)azanes, Michaelis and Schroeter [23] made derivatives of the dichlorocyclophosphazane (1a) using piperidine and aniline. As previously mentioned, little work was carried out after that until the early 1960's. In 1964 Mitsanobu and Mukaiyama prepared alkoxy-derivatives of cyclodiphosph(III)azanes by the reaction of aniline with dichloroalkoxyphosphines [32]. This work was substantiated by Kawashima and Inamoto in 1976 [33].



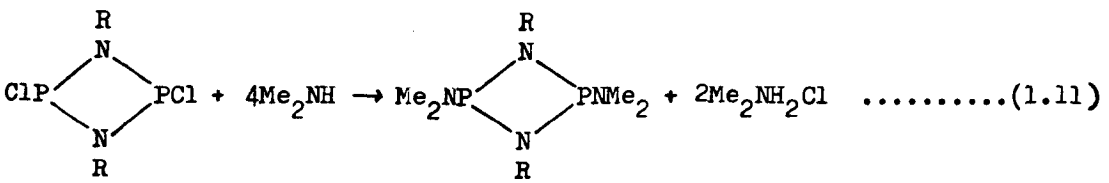
(1e) (R = Me or Et)

Alkoxy and aryloxy-derivatives of cyclodiphosphazanes can also be formed by the reaction of an alcohol or phenol and a base on the cyclodiphosph(III)azane (1) [34,35,36].



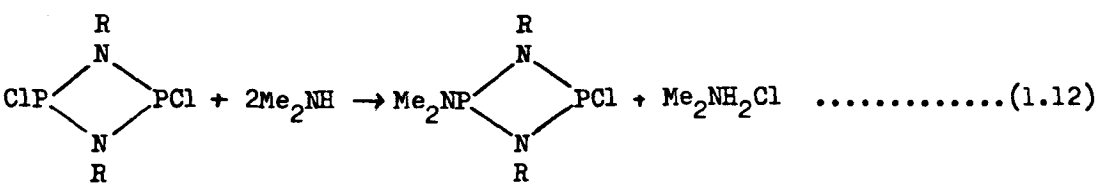
(1c) (1e ; R' = Bu^t)

In general, the preparation of substituted ring products is carried out by the displacement of chlorine or other halogens from cyclophosph(III)azanes. In addition to the synthesis of the alkoxy-derivatives, many amino-derivatives are known[37], eg. (1.11).



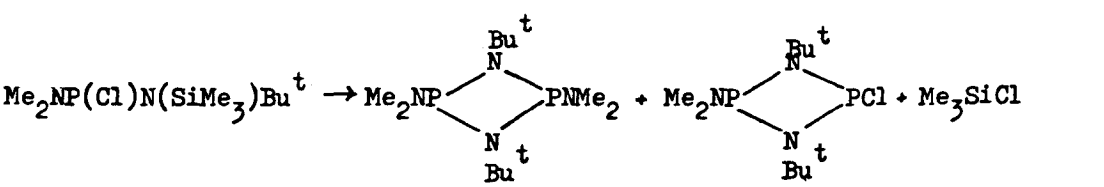
(1) (1f)

A monosubstituted product can also be obtained by adjusting the quantities of reactants used.



(1) (1g)

Mono and di-substituted dimethylamino-derivatives of (1c) can also be synthesised by heating (dimethylamino)(t-butyltrimethylsilylamino) chlorophosphine, $Me_2NP(Cl)N(SiMe_2)Bu^t$ [38]:

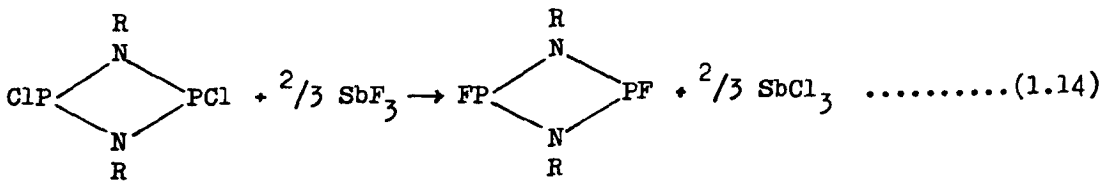


40% 60%

(1f') (1g') .....(1.13)

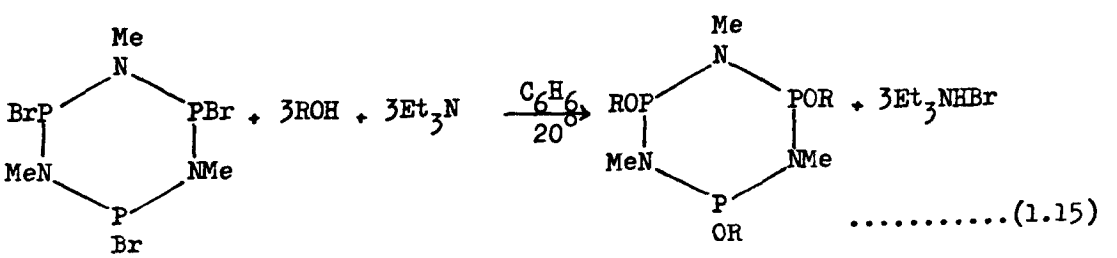
Diethylamine has provided a similar series of products, but di-isopropylamine only results in mono-substitution.

Fluoro-derivatives have been prepared by heating the cyclodiphosph(III)azane (1c) with antimony trifluoride.



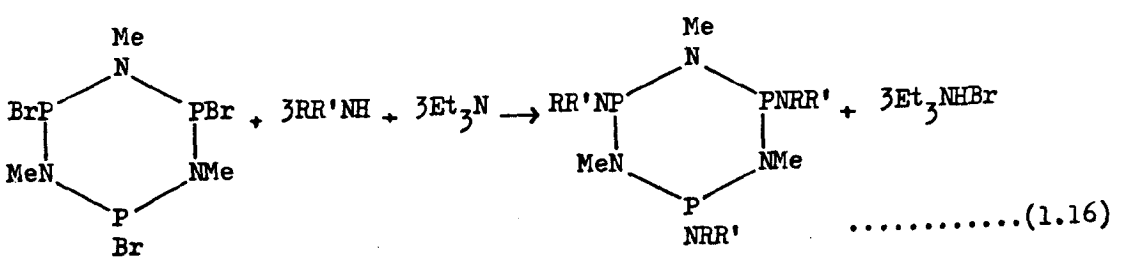
(1c) (1h)

Substitution reactions of cyclotriphosph(III)azanes have also been obtained by reactions analogous to those of cyclodiphosph-(III)azanes [39].



(2a) (2b)

(R = Me,Et,Pr^{i},Bu^{t},Ph,p-Br-C_6H_4)

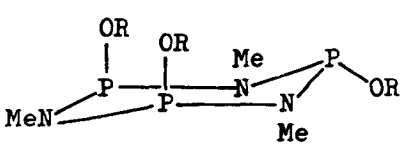


(2a) (2c)

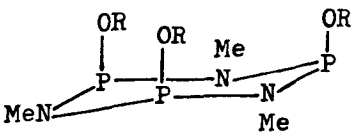
(R = R' = Me,Et ; R = Ph,R' = Me)

In reaction 1.15, in all cases, complete substitution of the halogen atoms was obtained. However, in reaction 1.16, with di-isopropylamine, only the mono substituted product was obtained. This is probably due to steric effects of the di-isopropylamino-group hindering attack at the other two phosphorus atoms in the ring.

The preparation of cyclotriphosphazane-derivatives often yields two isomers, one with all the phosphorus atoms equivalent, the other with two phosphorus signals of intensity ratio 2 : 1. Zeiss and coworkers have tentatively assigned the structures of some of the alkoxy-derivatives to these isomers as shown [39].



(2b,i)



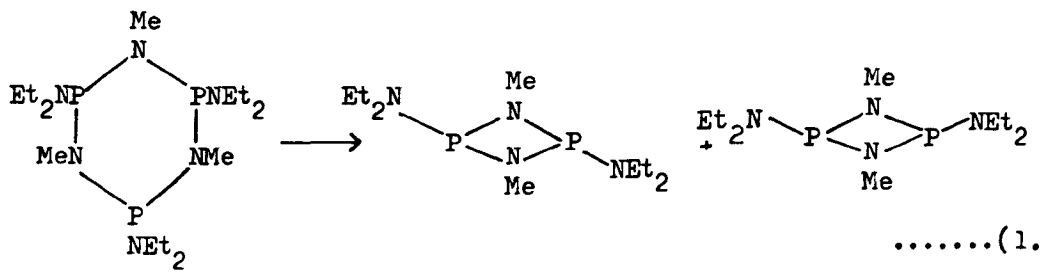
(R = Me)

(2b,ii)

These are readily distinguished by $^{31}P\{^{1}H\}$ nmr spectroscopy which also shows that the concentration of (2b,i) increases on heating relative to (2b,ii).

1.4b. Oligomerisation.

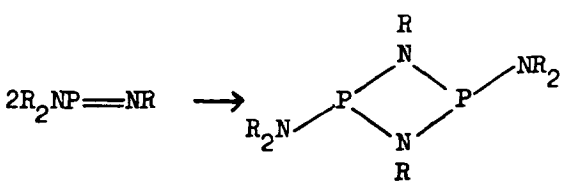
An indication that dimeric and trimeric rings have comparable thermodynamic stabilities comes from the observation that the diethylamine-derivatives (2c) can be converted to the analogous four membered rings, obtained as both cis and trans isomers [39].



(2c) (1i) .....(1.17)

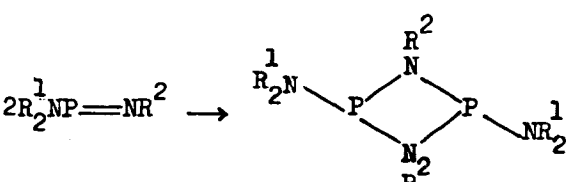
It has been shown by two groups of workers that phosph(III)azenes can be converted to cyclodiphosph(III)azanes on standing.

Niecke et al :



(R = $SiMe_3$) (1j) (ref.40) .....(1.18)

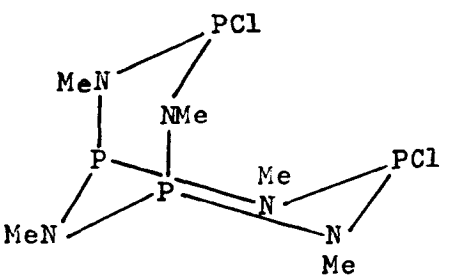
Scherer and Glassel :



($R^1 = Pr^i, R^2 = Bu^t$) (1k) (ref.38) .....(1.19)

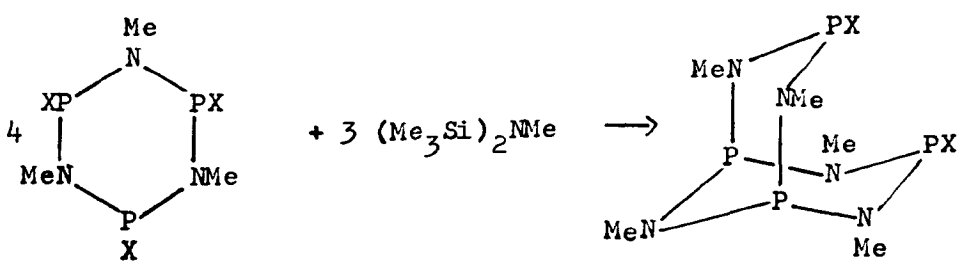
1.4c. Reactions leading to fused rings and cages.

Although the adamantane-type compound $P_4(NMe)_6$, (3a), is well known, being obtained from the reaction of phosphorus trichloride or of bis(dichlorophosphino)methylamine with methylamine, the latter reaction also gives another product which has been identified as having a partial cage structure (4a) [41].



4(a)

Most of the recent work on cage and fused ring phosphazanes has been carried out by Zeiss and coworkers [39,41]. The 'half cage' compound (4a) can be obtained pure from the reaction of heptamethyldisilazane with the cyclotriphosphazane (2a).



(2a)

(4a) (X = Cl or Br)

+ 6 Me_3SiX

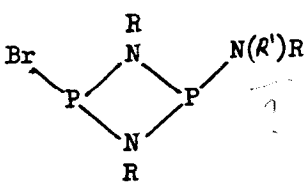
Scherer and Glassel [38] showed that the product of the reaction of phosphorus tribromide and the lithiated amine, R^1RNLi, is dependent on the solvent, see reactions 1.20a and 1.20b. with ether as solvent it gave a monomer, while with n-pentane it gave the dimer rings (1ℓ) and (1m).

$$2R^1RNLi + PBr_3 \xrightarrow{\text{ether}} R^1RNP{=}{=}N{-}R + 2LiBr + R^1Br \quad \text{.....(1.20a)}$$

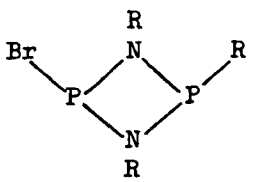
$R = SiMe_3$

$R^1 = Bu^t$ (5)

$$5R^1RNLi + 4PBr_3 \xrightarrow{\text{n-pentane}}$$



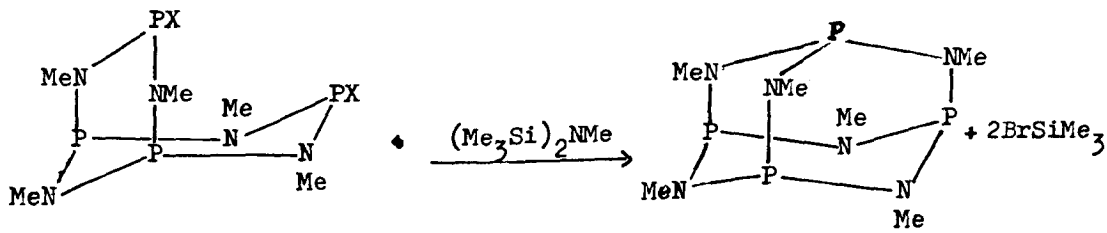
(1ℓ)



(1m)

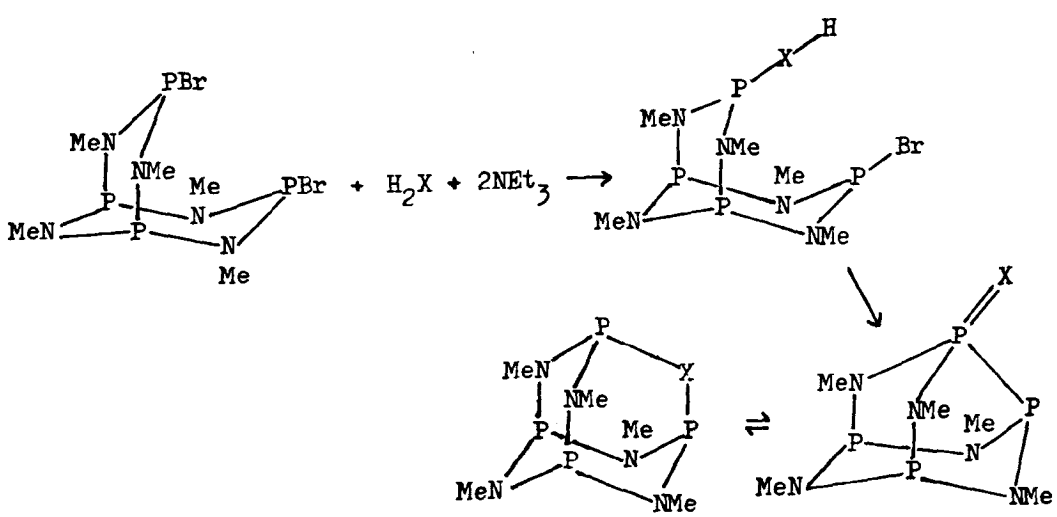
$$+ 5LiBr + 5R^1Br \quad \text{.....(1.20b)}$$

Several substitution products of (4a) have also been prepared. The cage compound (4) can also be prepared from the reaction of the bromo-derivative with heptamethyldisilazane :



(4a)(X = Br) (4) .....(1.22)

A related reaction also produces an interesting cage-product containing a phosphorus-phosphorus bond[42].

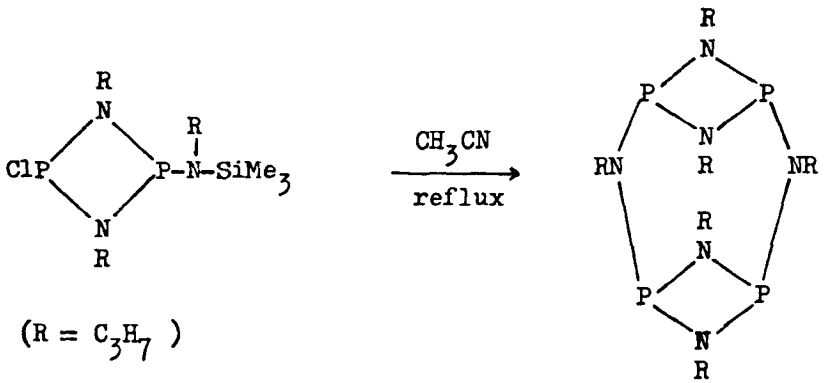


(4b) (6)

(X = O, S, NBu^t)

.....(1.23)

Recent work by Scherer and coworkers [43], has resulted in the synthesis of a related cage compound (7) :



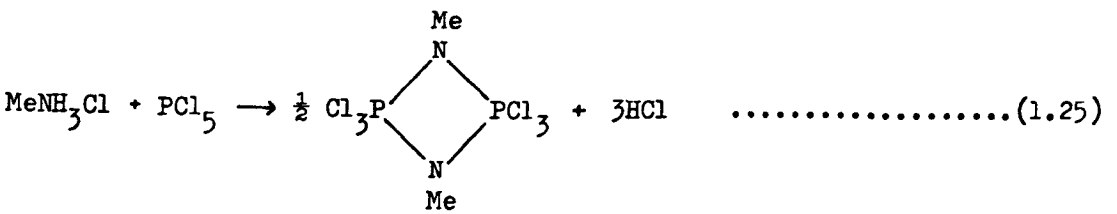
(R = C_3H_7)

(7) .....(1.24)

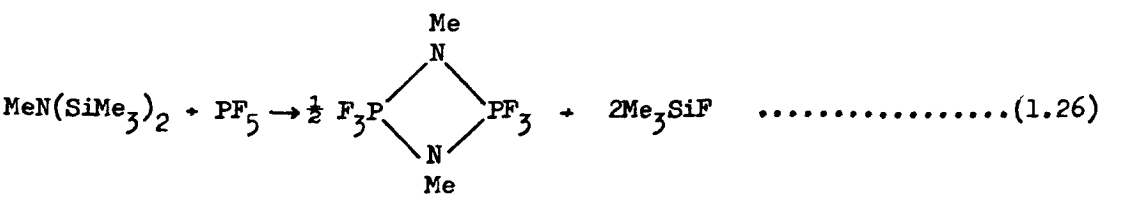
If heated to 156 - 158°C for 12 days, (7) is converted to the thermodynamically favoured adamantane structure, $P_4(NPr^i)_6$.

1.4d. Synthesis of cyclodiphosph(V)azanes.

The formation of cyclophosph(V)azanes containing five co-ordinated phosphorus has been achieved by the reaction of phosphorus pentahalides with amine hydrochlorides [44,45,46] or disilazanes[47].

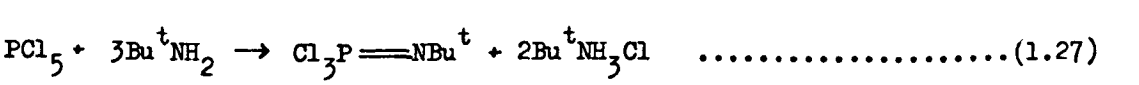


(8a)



(8b)

These rings are formally derived from phosph(V)azenes, $X_3P{=}{=}NR$, and if the R - group is bulky enough the phosph(V)azene can be isolated [48].

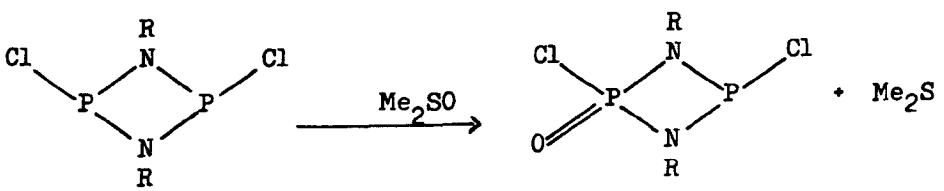


(5a)

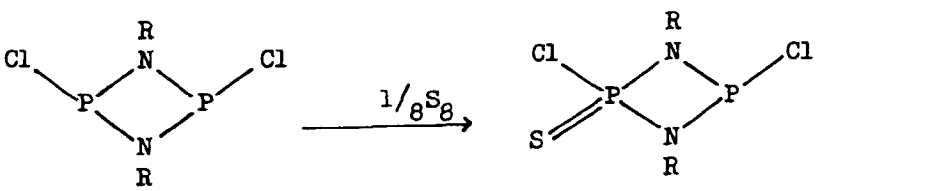
Further work showed that the reaction of phosphorus pentachloride with various aromatic amines gave monomers or dimers, depending on the basicity of the amine. In general the more basic amines gave dimers while those with $k_b = 10^{-13}$ gave monomers.

Numerous routes to cyclodiphosph(V)azanes containing four co-ordinated phosphorus are known. These include (a) oxidation of cyclophosph(III)azanes by sulphur, selenium or oxygen, and (b) ring formation from acyclic reactants.

The investigation of oxidation reactions of cyclophosph(III)azanes was first carried out by Keat, Nixon and coworkers in 1973 [27]. In this work they showed that a monoxide and a monosulphide of the dichlorophosph(III)azane, $(ClPNR)_2$ ($R = Pr^i$ or Bu^t) could readily be formed by reaction with dimethylsulphoxide and elemental sulphur respectively, see reactions (1.28) and (1.29). These reactions were stereospecific.



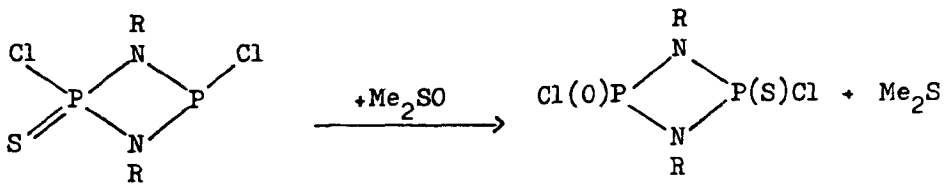
(1) (9a) .....(1.28)



(1) (9b) .....(1.29)

However, reaction of the monosulphide (9b) with dimethyl sulphoxide resulted in an oxide-sulphide as a mixture of cis and trans-isomers.

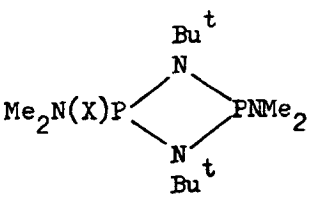
The more forceful conditions needed to react dimethylsulphoxide with (9b) also effects isomerisation.



(9b) (10a) - cis and trans isomers

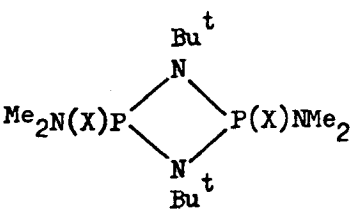
.....(1.30)

Other oxidation reactions were studied by various groups since the early '70's [34,49,50], when they reacted aminocyclodiphosph(III)azanes with t-butylhydroperoxide, sulphur, selenium, tellurium and methyl iodide to give a series of products (9c) and (10b).



(X = S,Se,Te and MeI)

(9c)



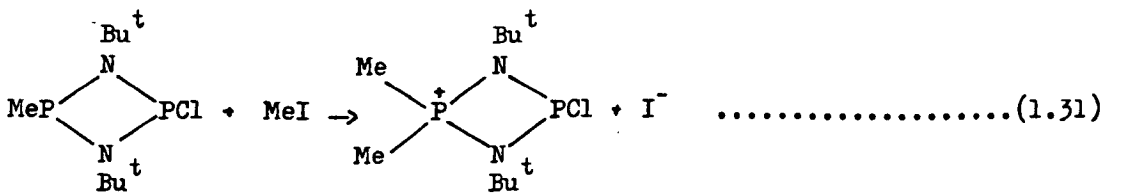
(X = S, and Se)

(10b)

With the exception of the telluride, cis and trans isomers were obtained in each case.

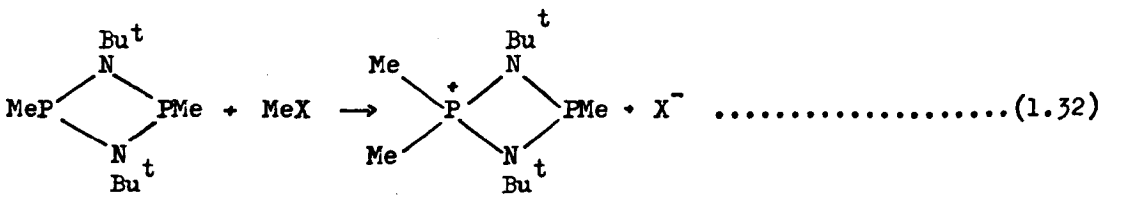
The reaction of (1)($R = Bu^t, X = NMe_2$) with sulphur and selenium yielded products with retention of configuration at phosphorus. However, in analogous reactions with tellurium only a mono-telluride product was obtained, and in this tellurium is readily replaced by sulphur or selenium. In some examples exchange of tellurium between the phosphorus atoms has been observed, and at elevated temperatures, some selenium derivatives will also show this exchange. The preparation of (10b)($X = O$) was carried out with t-butylhydroperoxide since dimethylsulphoxide had proved unreactive in this case. This was stereospecific with retention of configuration at phosphorus.

Scherer and Schnabl[50] also carried out similar oxidation reactions on cyclophosphazanes confirming the retention of configuration at phosphorus. They also examined the reaction of cyclodiphosph(III)-azanes with methyl halides and aluminium trichloride, reactions (1.31-33).



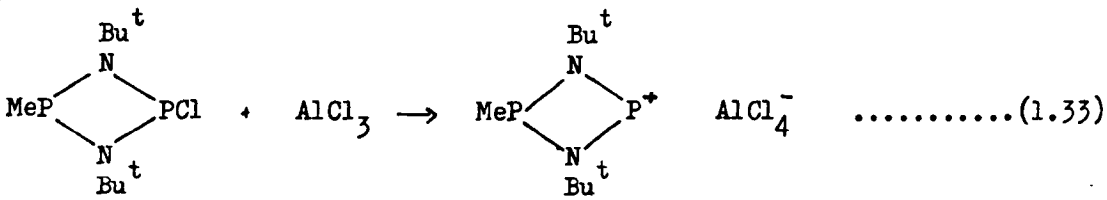
.....(1.31)

(11a)



.....(1.32)

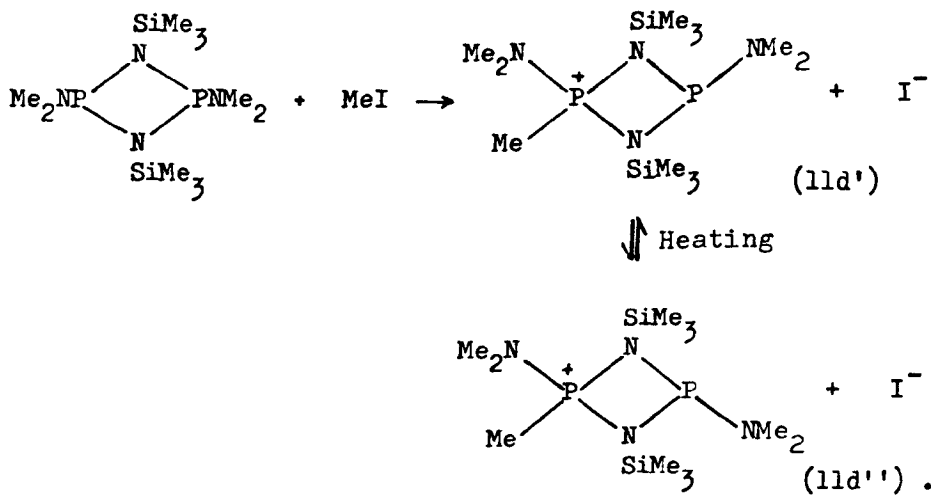
(11b) X = Br or I



.....(1.33)

(11c)

Oxidation reactions were also studied by Zeiss, Feldt Weiss and Dunkel[51] who confirmed the stereospecific nature of the reactions and also showed that isomer interconversion was readily carried out by heating, see reaction 1.34.

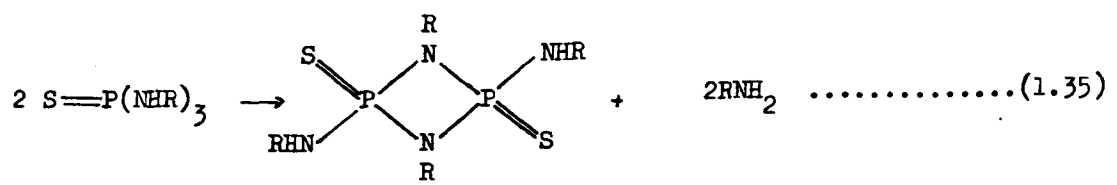


.....(1.34)

The reaction of (9c)(X = S) with a second equivalent of sulphur was slower than the addition of the first sulphur atom.

This reflects a general phenomenon where mono-oxidation products of cyclodiphosphazanes are less reactive to attack by chalogens than the analogous cyclodiphosph(III)azanes. Aminocyclotriphosph-(III)azanes have also been shown to undergo similar reactions with sulphur, giving tri-sulphides [52].

An alternative method of obtaining cyclophosph(V)azanes containing four co-ordinated phosphorus is to produce them directly from acyclic reactants. For example, dithiocyclodiphosph(V)azanes can be prepared by the thermal condensation of tris(amino)phosphine sulphides [53-56].

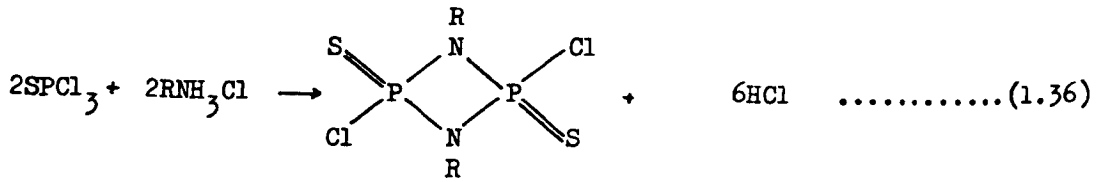


(10c)

(R = Me, Et, Pr^n, Bu^i, $C_5H_{11}{}^i$, Ph, $PhCH_2$)

When alkyl-substituted bis and mono(amino)phosphine sulphides are used the products obtained are similar to those obtained from the analogous reactions using tris(amino)phosphine sulphides. An exception to this is the bis(amino)alkyl phosphine sulphide, $PhP(S)(NHR)_2$(R = H). In this case the product is the trimeric ring $(Ph(S)PNH)_3$ [57].

Another method of preparing dithiocyclophsoph(V)azanes is by the reaction of thiophosphoryl chloride with amine hydrochlorides [58].



(1.36)

(10d)

(R = Ph,4-Cl-C_6H_4)

Analogous dioxycyclodiphosphazanes have also been produced [53,59,60] by the same type of route.

1.4e. Reactions of phosph(III)azanes with boranes and boron trifluoride adducts.

(i) BH_3 adducts

Over the past 25 years a number of workers have studied the formation and properties of BH_3-adducts of amines and phosphines to assess the relative nucleophilic character of these bases see refs. 61 - 70 .. All these studies have shown that unless there are special (including conformational) factors operative, phosphorus forms stronger adducts with borane, BH_3, than nitrogen. In 1960 Reetz [71] demonstrated that trimethylphosphine will displace BH_3 from trimethylamine-borane to form trimethylphosphine-borane. This was confirmed by Holmes and Carter[72] .

Further work by Reetz[62] and others[65,72] has also shown that this greater reactivity of phosphorus persists in molecules which contain both tervalent phosphorus and nitrogen atoms. However steric factors can play an important part in the determination of the most reactive site in these molecules. Jugie and coworkers[65] reacted $Et_3N.BH_3$ with a series of phosphines, Me_2NPMe_2, $(Me_2N)_2PMe$ and $(Et_2NCH_2)_3P$. In the first and second examples they found one phosphorus bonded BH_3 group in the product. However in the third example they found three BH_3 groups in the product, all bonded to nitrogen. In this case steric congestion around the phosphorus atom resulted in greater reactivity at nitrogen. Similar reactions using trisdimethylaminophosphine, $(Me_2N)_3P$, and dimethyl(dimethylamino) phosphine, Me_2NPMe_2, with borane and ethylborane, $B(Et)H_2$, showed the products to contain phosphorus-boron dative bonds[63].

In general coordination by phosphorus or nitrogen in phosphazanes depends on the reference acid. The reaction of the phosphorus trifluoride-borane adduct, $F_3P.BH_3$ with ammonia gives the triaminophosphine-borane and ammonium fluoride as products[62].

This shows that the cleavage of the phosphorus-fluorine bonds and subsequent formation of phosphorus-nitrogen bonds was preferred to the cleavage of the phosphorus-boron bond and the formation of a nitrogen-boron bond.

$$F_3P.BH_3 + 6\ NH_3 \longrightarrow (NH_2)_3P.BH_3 + 3\ NH_4F \quad .....(1.37)$$

The reaction of sodium borohydride with trisdimethylaminophosphine gives the adduct $(Me_2N)_3P.BH_3$[63].

$$NaBH_4 + P(NMe_2)_3 \longrightarrow (Me_2N)_3P.BH_3 + NaNMe_3H \quad .....(1.38)$$

In related reactions where bonding can occur to phosphorus or oxygen, the product still contained phosphorus-boron bonds[62].

$$2\ P(OR)_3 + B_2H_6 \longrightarrow 2\ (RO)_3P.BH_3 \quad .....(1.39)$$

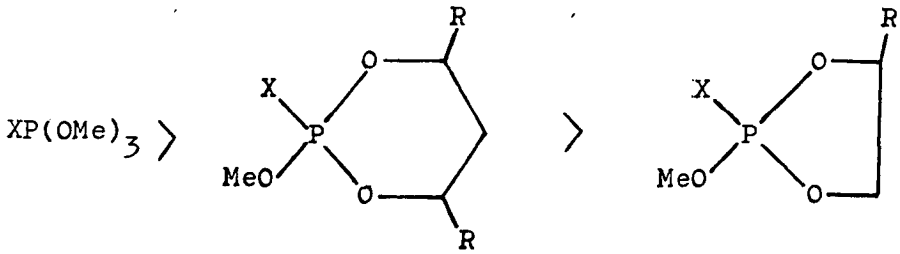
The formation of BH_3 adducts has also been used to establish the dependence of the nucleophilic character of the phosphorus with changes of its substituents. Rodgers, White and Verkade[67] compared variations in the phosphorus-boron length as shown in Table 1.1 below,

Table 1.1 Variations in phosphorus-boron bond lengths

Compound	P-B Bond length (Å)
$H_3B.P_2Me_4$	1.951
$H_3B.PH_3$	1.93
$H_3B.PMe_3$	1.93
$H_3B.P(NH_2)_3$	1.887
$H_3B.PF_3$	1.836

The shorter phosphorus-boron bonds were related to the extent of nucleophilic character of the phosphorus atoms. Therefore, phosphorus

trifluoride demonstrates, as expected, that the strong electron withdrawing power of the fluorine decreases the nucleophilic character of the phosphorus through electron inductive effects. Verkade has also shown that the conformations of the bonds to phosphorus also affect its nucleophilicity[73,74,75]. In a series of ring and cage compounds the nucleophilic character of phosphorus (X = lone pair) is decreased in the order;[74]



(I) (II) (III)

(IV) (V)

In the chair-type ring compound (II) the conformer with X (lone pair) in an axial position is a stronger nucleophile than that with X in an equatorial position. The trend in nucleophilicity can be followed by observation of the B-H stretching frequencies, see Table 1.2. The slight reversal of order as shown by (II) (X = lone pair axial) is explained by the fact that the general order was established by protonation studies and that the proton has a stronger polarising power than BH_3.

Table 1.2. BH_3 stretching frequencies [73,74,75].

Compound	$\nu BH_3/cm^{-1}$ Asym.	Sym.	Weighted Average $/cm^{-1}$
(I)	2397.5	2352.0	2382.3
(II) lone pair axial	2392.5	2342.0	2375.7
lone pair equatorial	2410.0	2354.0	2391.3
(III)	2412.0	2354.0	2392.7
(IV)	2421.5	2363.5	2402.2
(V)	2432.2	2365.5	2410.2

Recent work by Paine and coworkers has led to the successful preparation of some borane adducts of 2,4-difluoro-1,3-ditert-butylcyclodiphosph(III)azane (1h), and the X-ray crystal structure of a bis-borane adduct [76]. In this work mono- and bis-borane adducts of (1h)(R = Bu^t) were readily prepared by reactions with diborane, B_2H_6. The bis-borane adduct $(FPNBu^t)_2(BH_3)_2$, (19a) was found to have a cis structure. The analogous chloro-compound of the starting material, $(ClPNBu^t)_2$ (1c) also has a cis structure but its oxidation product, $(Cl(O)PNBu^t)_2$, has a trans structure as shown by X-ray crystallography [77].

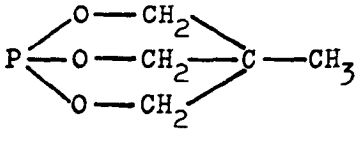
The order of basicity of a series of phosphines to borane was established using the exchange reactions [57]:

$$PR_3 + Me_3N.BH_3 \rightleftharpoons R_3P.BH_3 + Me_3N \qquad .....(1.40)$$

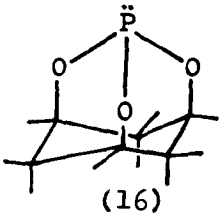
This gave the order as :-

$$PR_3 = PMe_3 \rangle P(NMe_2)_3 \rangle NMe_3 \gg PF_3$$

It was also established that borane adducts of cage compounds, $C_5H_9O_3P$ (15) and $C_6H_9O_3P$ (16) gave high melting solids while trimethylboron adducts are easily dissociable solids. Analogous reactions with boron trifluoride resulted in decomposition.



(15)



(16)

(ii) $\underline{BF_3}$ adducts

Reactions producing phosphine-BF_3 adducts have been carried out by a number of groups [64,78], for example Beg and Clark [78] successfully obtained $Me_3P.BF_3$. However, when there are phosphorus and nitrogen atoms within the same molecule the BF_3 group is seen to bond to the nitrogen rather than to the phosphorus. Fleming and Parry[64] have suggested that this may be due to the formation of a co-ordinated ring intermediate of the type -

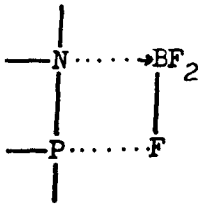


fig. 1.

Unfortunately the reaction of a phosphorus compound with BF_3 often results in cleavage products [61].

In 1962 the reaction of trisdimethylaminophosphine, $P(NMe_2)_3$, and boron trifluoride gave phosphorus trifluoride and boron trisdimethylamine [50]. This showed that boron trifluoride attacked the nitrogen atom. Nöth and Vetter subsequently investigated the reaction of boron trifluoride with trisdimethylaminophosphine, and obtained a series of substituted derivatives of the type, $P(NMe_2)_{3-n}X_n$ (X = Cl) (n = 1,2) [61]. These experiments confirmed the previous findings and suggested that the phosphorus-nitrogen bond was cleaved by the boron trifluoride.

N.m.r. and i.r. data have indicated that boron has co-ordinated to nitrogen and not phosphorus in a series of nickel complexes, $NiL_2(CO)_2.BF_3$ where L = $Me_2N.PF_2$ [80].

$$NiL_2(CO)_2 + (\text{excess})BF_3 \longrightarrow NiL_2(CO)_2.nBF_3 \quad (n = 1.11\text{-}1.44) \quad .....(1.41)$$

$$NiL_4 + (\text{excess})BF_3 \longrightarrow NiL_4.nBF_3 \quad (n = 1.24\text{-}2.6) \quad .....(1.42)$$

In difluoro(dimethylamino)phosphine-borane, $H_3B.P(NMe_2)F_2$ n.m.r. and i.r. data provides evidence for the presence of a phosphorus-boron bond. However in the analogous boron trifluoride adduct, $F_3B.P(NMe_2)F_2$, a boron-nitrogen bond was indicated [64].

(iii) P—B bonding

It has been suggested that the phosphorus-boron dative bond is supplemented by a π-interaction between the boron-hydrogen σ-bond electrons and the phosphorus 3d-orbitals in

borane adducts[60]. This explains the base strength reversal towards boron trifluoride of the first row donors such as nitrogen and oxygen which show greater Lewis basicity than second row donors such as phosphorus and sulphur. The order towards boron trifluoride is :

$$N < P, O < S$$

But with borane the order is :

$$P < N, S < O$$

1.5. Bonding, Structure and Reactivity.

1.5a. General.

Phosphorus has five valence shell electrons, $(Ne)3s^2 3p^3$, and exhibits two oxidation states, phosphorus (III) and phosphorus(V). Tervalent phosphorus generally has a trigonal pyramidal distribution of bonds, with a bond angle of $\sim 100^\circ$, see fig.2.

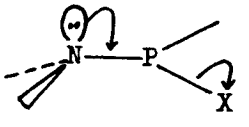
fig.2

In cyclic phosph(III)azanes the nitrogen atom generally has a planar, or near planar, distribution of bonds, and therefore the nitrogen lone-pair is confined to a p-orbital perpendicular to this bonding plane [81,82]. The phosphorus-nitrogen bond lengths in these compounds are shorter than might be expected from the sum of the single-bond covalent radii. The latter would suggest that the 'normal' single bond is approximately 1.77Å (as in the ion $H_3N\ PO_3^{2-}.Na$) [83], whereas the bond lengths in phosph(III)azanes vary between 1.65 and 1.75 Å, see Tables 1.4 and 1.5. The phosphorus-phosphorus distance in cyclodiphosph(III)-azanes is approximately 2.5 - 2.6 Å and is considerably shorter than 3.6 Å of the sum of the Van der Waals radii. This may allow some form of direct phosphorus-phosphorus bonding interaction.

The relatively short phosphorus-nitrogen bond lengths, 1.66 - 1.69 Å, have been attributed to a form of (p-d)π-bonding [84], although this should not be confused with the formal π-bonding found in phosphazenes.

These (p-d) π interactions assume that the phosphorus 3d-orbitals are of a configuration and energy suitable for interaction with the nitrogen lone-pair.

Recent Ab initio molecular orbital calculations indicate that a second π -bond type interaction may be more important than the (2p - 3d) π type interactions [85]. This involves the nitrogen lone-pair and the antibonding orbital associated with the P-X bond (see fig.3)



(X = halogen, alkyl, amino or alkoxy group)

fig.3a.

This interaction is particularly important when the nitrogen lone-pair and the P-X bond lie in the same plane. This is equivalent to emphasising a canonical form of the type, fig 3b.

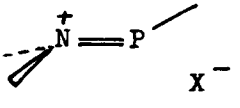


fig.3b.

In phosphorus (V) compounds the multiple bond effects may also arise from the interaction of lone-pair electrons on nitrogen or oxygen, with a vacant π -type orbital on phosphorus. The latter could be a 3d orbital or a σ^*(antibonding) orbital. In the $n \rightarrow \sigma^*$ interaction, an antiperiplanar arrangement is preferred. In phosphoric acid, H_3PO_4, there are a large number of possible configurations, one of which is shown below, fig.4 :

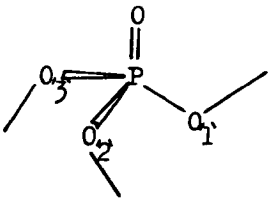


fig.4.

The phosphorus-oxygen double bond and the oxygen ('1', '2' or '3') lone-pairs can adopt antiperiplanar arrangements. However many conformers are populated and the effect is not very specific.

In P_4O_{10} however, the arrangement is such that it allows the $n \rightarrow \sigma^*$ interactions to be maximised. This results in a weakening of the phosphorus-oxygen 'single' bonds. These interactions apparently provide a rationalisation of the electrophilic properties of phosphorus in the molecule.

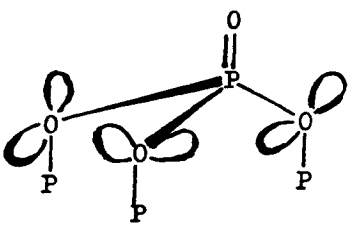


fig.5.

Note : The oxygen lone-pairs are in sp^3 hybridised orbitals.

1.5b. Evidence for Multiple Bonding in P(III) - N compounds.

As previously mentioned, one of the principal sources of evidence in support of π - bonding in phosphorus-nitrogen compounds is the comparatively short bond lengths for the phosphorus-nitrogen bonds. Examination of the data in Table 1.4 shows that not only the short phosphorus-nitrogen bond lengths, but also the sum of the bond angles at the nitrogen supports the notion of a π-bond interaction. A planar or near planar arrangement of bonds around the nitrogen requires the lone pair to be confined to a p-orbital perpendicular to the plane containing the bonds to nitrogen, where it is available for π -type interactions. Therefore compounds with the sum of angles at nitrogen approximating to 360° will exhibit relatively short phosphorus-nitrogen bonds. The compound $P\left[N(CH_2)_2\right]_3$, however, has a sum of angles at nitrogen of only 303.5° and has a mean phosphorus-nitrogen bond length of 1.75Å. This is one of the longest known P-N bonds and approaches the 1.77Å expected of a formal single bond length. In this compound the nitrogen atoms are constrained by the three membered rings.

Infra-red spectroscopic studies of the phosphorus-nitrogen stretching 'frequencies' have also provided evidence for multiple bonding. In phosphazenes the P-N stretching 'frequency' is found in the range 1240 - 1330 cm^{-1} [86,87]. The P-N single bond stretching 'frequency' has been found in the region 650 - 850 cm^{-1} [88], at considerably lower 'frequency' than that found in the phosphine imines. Strongly electronegative substituents on phosphorus increase the extent of π -bonding between phosphorus and nitrogen and this results in an increased P-N stretching 'frequency'[87].

The overall range for P-N double bond stretching frequencies is 1055 - 1500 cm^{-1} [2].

Photoelectron spectroscopy, p.e.s., has been used to identify the mutual relationships between adjacent phosphorus and nitrogen lone pairs, and this can give information on π -bonding effects. Cowley and coworkers used p.e.s. to show that in $P(NMe_2)_3$, two of the nitrogens have lone pairs orthogonal to the phosphorus lone pair, while the third nitrogen had its lone pair eclipsed to that on phosphorus, fig.6, [89,90,91,79].

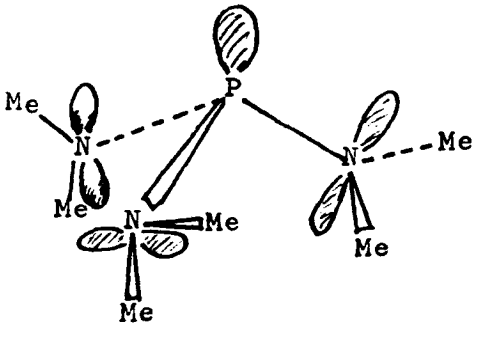


fig.6

This does not provide direct evidence for any π -bonding, but it does show that the phosphorus and nitrogen atoms are in optimum positions for n→σ* interactions.

In phosphorus-nitrogen compounds both the phosphorus and the nitrogen atoms are potential Lewis base sites. However, the phosphorus is generally found to be the more reactive site to electrophiles and this is believed to be due to the electron donation from the nitrogen to phosphorus.

This increases the phosphorus base strength while it decreases the nitrogen base strength [47]. Thus in the reaction of $P(NMe_2)_3$ with halogens[92] or sulphur[93] the reaction site has been positively identified as the phosphorus atom.

$$P(NMe_2)_2 + {}^1/_8\ S_8 \longrightarrow (Me_2N)_3P{=}S \qquad \text{.....1.43}$$

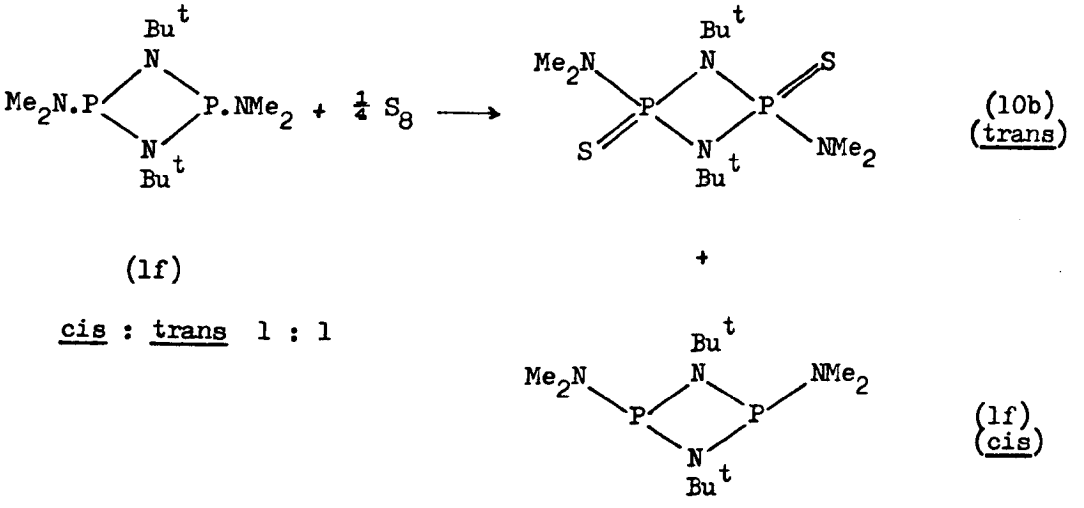
(17a)

$$P(NMe_2)_3 + X_2 \longrightarrow (Me_2N)_3\overset{+}{P}X.\ X^- \qquad \text{.....1.44}$$

(17b)(X = Cl, Br or I)

1.5c. Effects of Geometrical Isomerism.

The addition of elemental sulphur or selenium to a 1 : 1 mixture of *cis*-and *trans*-isomers of $(Me_2N.PN.Bu^t)_2$, (1f), gives only a *trans* disulphide (1b) and demonstrates the greater nucleophilic reactivity of *trans*-isomers relative to the *cis*-isomers [49].

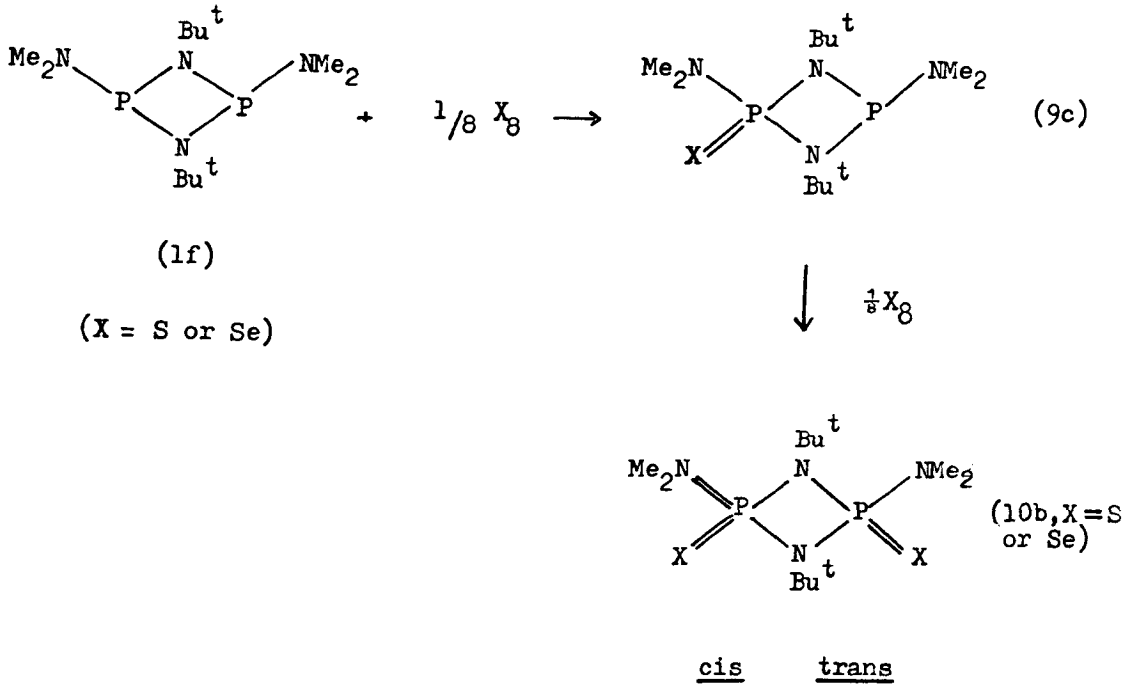


(1f)

cis : *trans* 1 : 1

.....1.45

The oxidation reactions of cyclophosph(III)azanes with sulphur, selenium and methyl iodide are stereospecific with retention of configuration at phosphorus [49]. These reactions proceed with relative ease, with the phosphorus effecting nucleophilic attack on X_8.

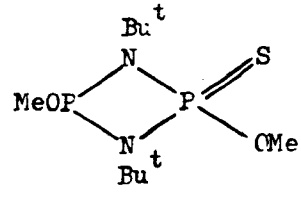


However, with tellurium only a trans-monotelluride (9c, X = Te) is obtained [49]. Examination of the ^{31}P nmr spectrum of this compound shows that the tellurium is exchanging between a number of sites. The exchange process is concentration dependent, suggesting an intermolecular component. These effects show the greater lability of the phosphorus-tellurium bond compared with either the phosphorus-sulphur or phosphorus-selenium bonds. The phosphorus-selenium bond in (9c)(X = Se) shows similar effects, but only when heated to 160°C. The lability of the phosphorus-tellurium bond also means that the tellurium can be readily displaced by sulphur or selenium.

The reactivity of a phosphazane to electrophiles relates to the electron donor powers of the phosphorus substituents. The nitrogen lone pair is not readily available for reaction with electrophilic species, and this is consistent with its being involved in multiple bonding with phosphorus.

Without doubt the most useful analytical tool to be applied to the study of cyclophosphazanes has been ^{1}H and ^{31}P nmr spectroscopy The basic principles of ^{1}H nmr spectroscopy are well known and do not need repeating here. The technique, in conjunction with $^{1}H - \{^{31}P\}$ double resonance experiments, was widely used for routine identification of compounds. By examining the ^{1}H spectrum, with, and without, ^{31}P decoupling, one can correlate various hydrocarbon groups with particular phosphorus atoms, so gaining more structural information than is possible from a single resonance ^{1}H spectrum. This technique also gives the phosphorus shift without the need to obtain a ^{31}P nmr spectrum, but only if spin coupling between the ^{1}H and ^{31}P nuclei is present.

In ^{31}P nmr spectroscopy both the phosphorus chemical shift (δ_P)† and the phosphorus-phosphorus coupling constant $(J_{PP'})$ can be used to characterise isomeric cyclophosphazanes. Phosphorus(III) shifts are generally at a lower field than the analogous phosphorus (V) shifts. This is particularly true of the cyclophosphazanes, for example, in the monosulphide (9d), shown below, the phosphorus(III) shift is 110.0 while the phosphorus(V) shift is 75.7 [25].



(9d)

Also for $(ClPNBu^t)_2$ $\delta_P = 207.3$ and for $(Cl(O)PNBu^t)_2$ $\delta_P = 0$

† The convention adopted here is one in which low field shift, relative to 85% H_3PO_4, are positive.

Phosphorus shifts are also dependent on the type of phosphorus substituent. Strongly electron withdrawing groups such as a halogens will result in a shift to lower field, e.g. cis-$(Cl.PN.Bu^t)_2$, $\delta_p = 207.3$ [25], while an electron donating group such as an amino-group gives a higher field shift, cis-$(Me_2N.PN.Bu^t)_2$, $\delta_p = 95.0$ [37b]. The phosphorus shift is also dependent on the type of nitrogen substituent, with smaller N-alkyl groups giving lower-field shifts. For example, cis $(ClPNEt)_2$ has $\delta_p = 227.3$ while cis $(ClPNBu^t)_2$ has $\delta_p = 207.3$.

Exceptionally large differences in phosphorus shifts are exhibited by geometrical isomers [25], these being the largest in any phosphorus containing ring systems. In cyclodiphosph(III)azanes the isomers show shift differences of the order of 60 - 100 ppm. This large seperation makes for easy distinction of isomers (see Table 1.6). In cyclodiphosph(V)azanes, isomers can still be distinquished, but in this case the shift difference is generally <10 ppm.

As with chemical shifts, the coupling constants in cyclophosph(III)azanes are affected by the type of phosphorus substituents and by geometrical isomerism. The P.....P spin couplings for cis and trans-isomers of cyclophosph(III)azanes often have different signs [94, 95], the former positive and the latter negative. Relative sign determination is not straightforward and there is relatively little information on this point. The modulus of the P.....P spin coupling is generally less than 30 Hz. In cyclotriphosph(III)azanes these couplings are even smaller [96]. It is difficult to obtain P..... P couplings from symmetrical compounds since the two phosphorus atoms are magnetically equivalent when proton decoupled.

A number of P.....P spin couplings are also available for cyclodiphosph(V)azanes and they are generally ~ 50Hz, with significant differences between geometrical isomers.

The trans-isomer of $(Me_2NPNBu^t)_2$ (1f) is more reactive to electrophilic species than the cis isomer, see p.9. This is paralleled by infra-red and ^1H nmr studies of the bonding of (1f) and (1n) to $CDCl_3$ and $CHCl_3$ respectively [97], see Table 1.2

Table 1.2. I.R and ^1H nmr Studies of (1f)(X = NMe_2 and (1n)(X = OMe) (hydrogen bonding to $CDCl_3$ and $CHCl_3$).

Compound	$\Delta\nu$ /cm^{-1} (a)	$\Delta\nu$ /Hz (b)
$(Me_2NPNBu^t)_2$ cis	22	21
trans	42	42
$(MeOPNBu^t)_2$ cis	10	17
trans	13	18

(a) I.R. shift of ν(C - D) for $CDCl_3$(0.04 M)/1M (mixture in hexane), relative to pure $CDCl_3$.

(b) ^1H nmr shift, 60MHz, of $CHCl_3$ (0.02M in hexane), relative to the same solution with added compound (0.5M)

The trans-isomers of both (1f) and (1n) show greater shift differences than the cis-isomer, indicating stronger hydrogen bonding between the chloroform (or deuterochloroform) and the former isomer.

Cyclic voltammograms of cis and trans-$(Pr^i_2 NPNPr^i)_2$ have shown that only the trans-isomer undergoes a one-electron oxidation reaction producing a stable radical cation [98]. The trans-isomer undergoes a one-electron reversible reaction while the cis-isomer undergoes a irreversible oxidation reaction. This difference may be due to the trans-isomer having a planar ring, and the cis-isomer having a non-planar ring [99].

The photoelectron spectra (p.e.s.) of cyclodiphosph(III)-azanes, (1f) and (1n) show differences of approximately 0.5eV between cis and trans isomers for the lowest energy ionisations from nitrogen or phosphorus lone-pairs.

Table 1.3 Photoelectron Data for Cyclodiphosph(III)azanes (1f) and (1n)

Compound (1)		Photoelectron bands (eV)			
$(Me_2NPNBu^t)_2$	cis	7.5	8.2	8.8	
	trans	7.1	7.5	8.5	10.0
$(MeOPNBu^t)_2$	cis	8.4	10.1		
	trans	7.7	8.3	10.1	

The p.e.s. of $P_4(NMe)_6$ shows a series of broad bands above 8 eV [100]. The phosphorus ion pairs give a doublet at 10.2 eV. The nitrogen $p\pi$ -electrons show a broad absorption band at 7.7 - 9.7 eV, suggesting that these electrons are stabilised by some bonding interaction since non-bonding nitrogen $p\pi$ -electrons would show ionisation energies of less than 7 eV.

In summary, the reasons for these marked differences between geometrical isomers have yet to be clearly identified. In addition to ring puckering effects, it has been noted that cross-ring $n_p \longrightarrow \sigma^*_{N-p}$ bonding interactions might be particularly favourable in stabilising <u>cis</u> isomers relative to <u>trans</u> isomers.

1.5d. Conformational Effects.

Compounds containing nitrogen-nitrogen (hydrazines) or phosphorus-phosphorus (diphosphines) bonds are well known. Their conformations and element-element bond lengths have been studied in some detail. The dominant factors determining their conformations appear to be steric and lone pair interactions. For example, a series of biphosphines shows dihedral angles of 90 - 100° between the lone pairs of the phosphorus atoms[101,102,103], see fig. 7, for P_2H_4

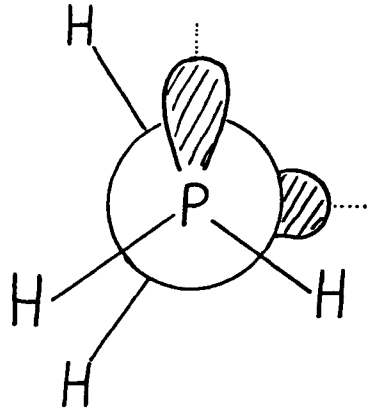
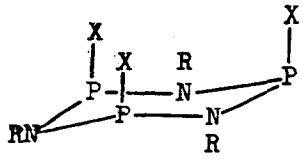


fig. 7

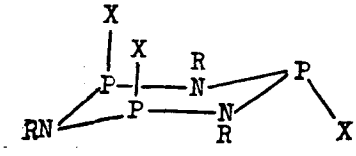
These structures have been rationalised in terms of the gauche effect[104] where the lowest energy configuration is one in which there is a gauche relationship between the lone pairs on adjacent phosphorus or nitrogen atoms. The gauche effect can also be used to rationalise the conformations of tervalent phosphorus-nitrogen compounds.

In alkoxy and amino-cyclodiphosph(III)azanes there are marked differences in properties between geometrical isomers. These phenomena may also exist in cyclotriphosph(III)azanes, where no more than two isomers have been found[40].

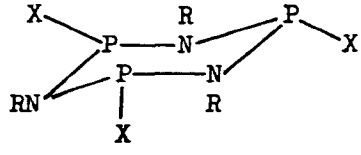
One isomer shows all three phosphorus atoms to be magnetically equivalent in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum, while the other isomer shows two chemically shifted phosphorus signals in the ratio 2 : 1. On the basis of the gauche effect, one might expect that the properties of the phosphorus atoms will depend on the relative orientation of the lone pairs. Assuming a chair conformation for cyclotriphosph-(III)azane ring, the lone pairs can be in an axial or equatorial position on each phosphorus. This leads to four possible arrangements.



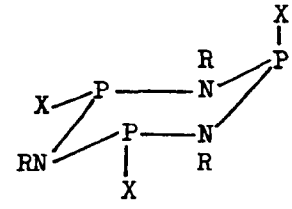
(i) 3 lone pairs equatorial



(ii) 2 lone pairs equatorial
1 lone pair axial



(iii) 3 lone pairs axial



(iv) 1 lone pair equatorial
2 lone pairs axial

fig.8.

Therefore the two isomers obtained for cyclotriphosph(III)azanes are (i) or (iii) and (ii) or (iv), see fig.8.

It is evident from studies on dioxaphosphorinanes and related compounds which generally adopt chair conformation that the phosphorus is more nucleophilic if it has an axial lone pair. This can be rationalised by consideration of the relative orientations of adjacent phosphorus and oxygen lone pairs [105].

axial lone pair equatorial lone pair

Newman projections along the endo -P—O bond.

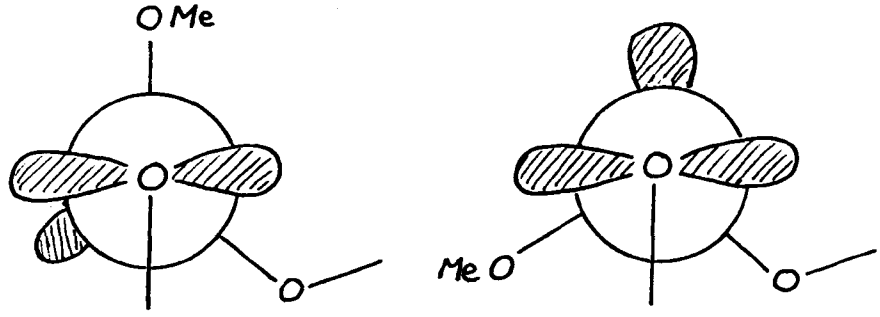


fig.9.

In these examples the oxygen is considered to be approximately sp^2-hybridised with the remaining lone pair in a higher energy p-orbital. The latter is more important in a consideration of interactions with the phosphorus lone pair [106] The near eclipsed arrangement of lone pairs in the first (axial) case, results in a repulsive interaction between the oxygen and phosphorus lone pairs and this increases the nucleophilic character of the phosphorus atom. The second (equatorial) arrangement leads to an orthogonal relationship between the phosphorus and oxygen lone pairs, so making phosphorus relatively less nucleophilic. An analogous effect might be expected

in the cyclotriphosph(III)azanes if it is assumed that the distribution of bonds about nitrogen is planar and the ring adopts the chair conformation., then the corresponding Newman projections are shown.

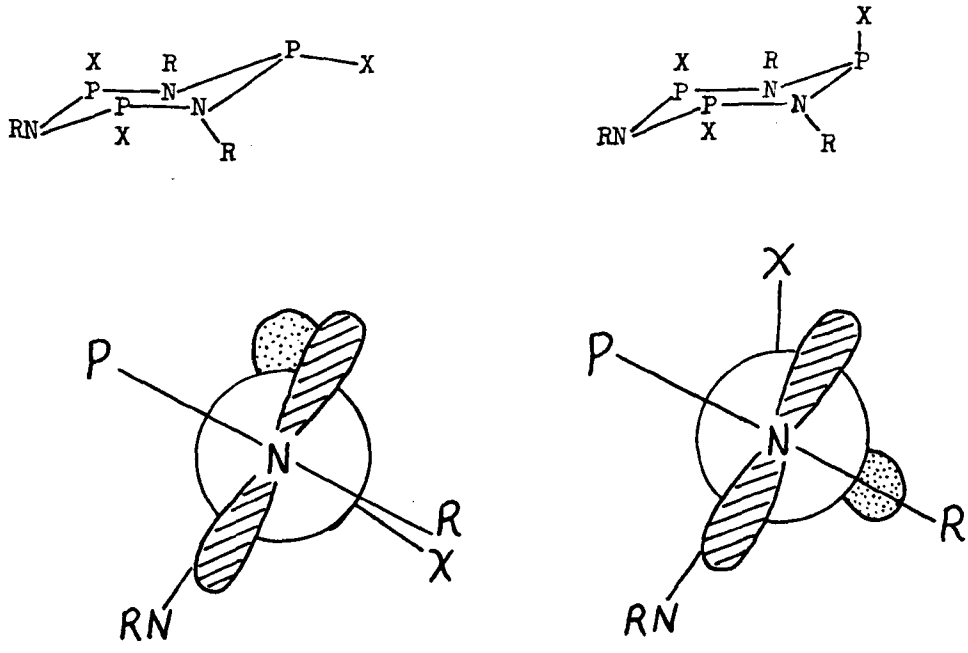


fig. 10.

Related effects are also apparent in trimethylphosphite, $P(OMe)_3$, where the phosphorus oxygen bonds are essentially free to rotate and so able to attain a conformation with relatively strong lone pair-lone pair interaction (fig.11). This raises the phosphorus lone pair energy so increasing its Lewis base properties.

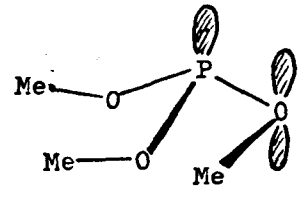


fig.11.

However, in the cage structure, $P(OCH_2)_3CR$,[106] the oxygen lone pairs are constrained to lie orthogonal to the phosphorus lone pairs, and which makes it a poor Lewis base. The greater Lewis base properties of tris(dimethylamino)phosphine, $P(NMe_2)_3$, relative to the cage compound, $P_4(NMe)_6$, can be related in a similar way [24].

1.5e. X-Ray Crystallographic Studies.

X-ray crystallography has been widely used for the determination of detailed structural features of cyclophosphazanes.

(i) Cyclodiphosph(III)azanes :

In 1975 Muir showed that cis-$(ClPNBu^t)_2$ had a slightly puckered ring [95]. Since then numerous studies have shown that cis-isomers exhibit this puckering effect, while trans-isomers have planar rings, Table 1.6. This puckering is most evident in the piperidine derivative, $(C_5H_{10}NPNBu^t)_2$ [97], where phosphorus and nitrogen atoms show a displacement from the mean plane by approximately 0.138 Å, (fig.12) compared with the 0.045 Å in $(ClPNBu^t)_2$. In $(C_5H_{10}NPNBu^t)_2$ the piperidino-rings are also twisted slightly, presumably to reduce cross ring steric interaction see fig. 12

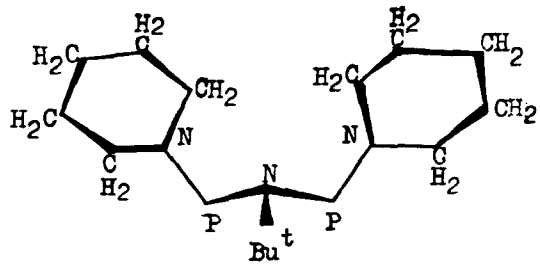


fig.12.

All cyclodiphosph(III)azanes contain endo phosphorus-nitrogen bonds which are shorter than the sum of the covalent radii (for phosphorus and nitrogen, 1.77 Å). For example, $(ClPNBu^t)_2$ has an endo P-N bond length of 1.69 Å [107], and in $(C_5H_{10}NPNBu^t)_2$ these bonds alternate in length between 1.72 Å and 1.75 Å [97]. It is generally assumed that the shorter phosphorus-nitrogen bonds are associated with more multiple bond character, see Tables 1.4 - 1.7.

(ii) Cyclodiphosph(V)azanes :

Generally the oxidation of a phosphorus(III) compound to a phosphorus(V) compound gives rise to a shortening of the phosphorus-nitrogen bonds and an increase in the $\hat{NPN}$ angle. In the phosphorus(V) compound, cis-$(Me_2N(S)PNBu^t)_2$, there is a puckering in the plane of the ring by 4° from planarity[108], see fig.13. In the phenyl derivative $(Ph(S)PN.Et)_2$, this angle is increased to 8°[109].

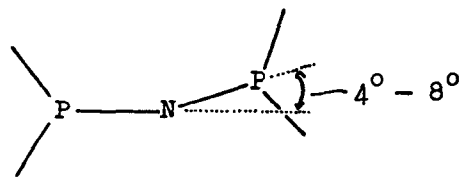


fig.13.

In the cyclodiphosph(V)azanes with five co-ordinate phosphorus, there is a distorted trigonal bipyramidal arrangement of bonds with endo N-P-N approximately 80°. An example is provided by $(Cl_3PNMe)_2$ where the P_2N_2 ring itself contains bonds of differing lengths since the phosphorus-nitrogen bonds are alternately axial and equatorial, see fig.14.

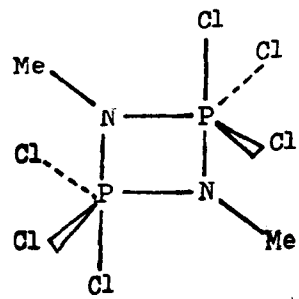


fig.14.

(iii) Cyclotriphosph(V)azanes :

In their work on $(MeO(O)PNMe)_3$, Bullen and Ansell showed the ring to have a twisted boat conformation [110]. The average phosphorus-nitrogen bond length of 1.66Å is considerably shorter than the single bond length and this has been taken as evidence for strong π —interaction in the ring. The average phosphorus-oxygen (OMe) bond length is 1.56 Å, which is shorter than the 1.71 Å of a normal single bond phosphorus-oxygen bond length [111]. This has been interpreted as indicating further π —interactions between the phosphorus and the oxygen atoms at the methoxy-groups. The methoxy groups take up the configuration shown in fig.15.

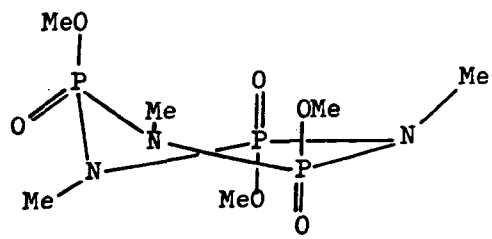


fig.15.

In the salt $Na_3(NHPO_2)_3 \cdot 4H_2O$ there is a cyclotriphosph(V)azane type ring which has the ionic form $(^-O_2.PN.H)_3$ [100] see fig.16.

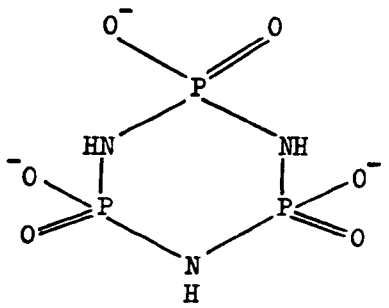


fig.16.

This ring has a chair configuration with short phosphorus-nitrogen bonds averaging 1.68 Å and short phosphorus-oxygen bonds averaging 1.49 Å.

(iv) Cyclotetraphosph(III)azanes :

The only known crystal structure of a cyclotetraphosph-(III)azane is of $(MePNMe)_4$ [113]. The ring has a crown conformation and is the first example of such in any eight membered phosphorus-nitrogen ring. The nitrogen atoms have a planar distribution of bonds and the phosphorus-nitrogen bond lengths average 1.720 Å.

(v) Cyclotetraphosph(V)azanes :

The crystal structures of a number of cyclotetraphosph-(V)azanes have been studied [114-118]. All show the expected short phosphorus-nitrogen bond lengths. The structures obtained for $K_4(PO_2NH)_4 \cdot 4H_2O$ and $Cs_4(PO_2NH)_4$, $6\ H_2O$ [116,117], and $(NH)_4P_4O_8H_4 \cdot 2H_2O$ [118] are similar, the basic phosphorus-nitrogen skeleton of which is shown in fig.17.

The rings adopt twisted conformations , Berking and Mooty [116,117] found isomers of $K_4[PO_2NH]_4 \cdot 4H_2O$ and $Cs_4\ PO_2NH\ _4 \cdot 6H_2O$ to have two conformations, chair or saddle (see fig. 17).

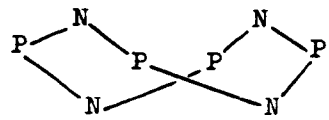


fig.17.

Bullen, Paddock and coworkers examined the crystal structures of two isomers of $(MeO(O)PNMe)_4$ and showed that while the major isomer had a boat conformation [114], as in fig.17 the minor isomer had a chair conformation [115], see fig. 18 . The boat configuration is described as having a cis-trans-cis-trans arrange of bonds in the ring ; the chair conformation is described as cis-cis-trans-trans.

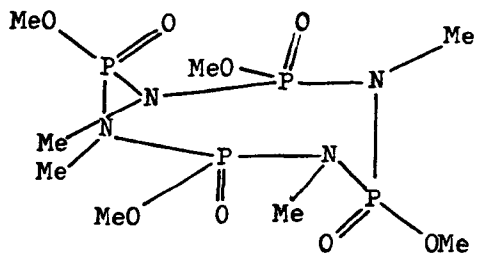


fig.18.

This chair conformation has a near planar arrangement for six atoms of the ring, see fig.18, and does not show any twisting of the structure similar to that found in the boat conformation.

Mullen, Paddock and coworkers[115] have calculated that the energy difference between the boat conformation (cis-trans-cis-trans) and the chair conformation (cis-cis-trans-trans) is 4.2 kJ mol^{-1} in favour of the boat form. The cis-cis-cis-trans isomer would have an energy difference relative to the boat isomer of 10 kJ mol^{-1}, and although this energy difference is not prohibitively large, no such isomer has yet been found.

Cage and fused ring molecules :

The adamantane-type structure, $P_4(NMe)_6$ has short phosphorus-nitrogen bond lengths, 1.69 Å and a near planar arrangement of bonds at nitrogen (sum of bonds angles ca. 356°)[100]. The fused ring structure of $P_4(NPr^i)_6$ has also been studied[43] the phosphorus-nitrogen skeleton is shown in fig.19, this being different from $P_4(NMe)_6$ above.

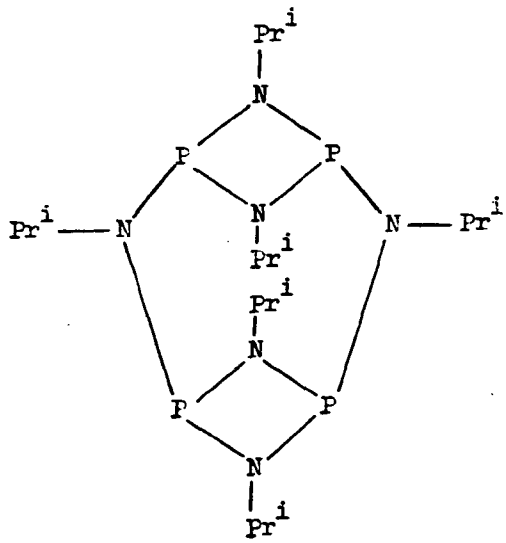


fig.19.

The phosphorus-nitrogen bonds of the four membered rings are 1.70 Å while the phosphorus-nitrogen (bridge bonds are slightly longer at 1.72 Å. The latter two structure determinations were of relatively low accuracy due to disorder effects.

Table 1.4.

Selected structural data for some aminophosphorus compounds.

Compound	Ref.	Sum of N bond angles	P-N bond length (Å)	Source
$P(NMe_2)_3$	119	352.5°	1.700(5)	e.d.
$(Me_2N)_2PCl$	120,121	360°	1.730(5)	e.d.
$(Me_2N)PCl_2$	120,121	360°	1.69(3)	e.d.
$(Me_2N)P(O)Cl_2$	120,122	148°	1.67(4)	e.d.
$P\left[N(CH_2)_2\right]_3$	119	303.5°	1.75(1)	e.d.
Me_2NPF_2	123	360°	1.628(5)	X-ray
Me_2NPF_2	124	348.4°	1.684(8)	e.d.
Me_2NPF_2	125	360°	1.66	m.w.
H_2NPF_2	124	345°	1.661(7)	e.d.
H_2NPF_2	126	360°	1.650(4)	m.w.
$(Cl_2P)_2NMe$	127	360°	1.664(10)	n.m.r.
$(F_2P)_2NMe$	128	360°	1.680(6)	e.d.
$Ph_2P.NMe.P(S)Ph_2$	129	353°	1.719(4)(P(III)) 1.680(4)	X-ray
$P_2(NMe)_6$	130	345°	1.68(3)	X-ray
$P_4(NMe)_6$	131	343°	1.66(3)	X-ray
$P_4(NMe)_6S_4$	132	358°	1.66(3)	X-ray
$P_4(NMe)_6S_4$	133	358°	1.656(14)	X-ray
$P_4(NMe)_6O_4$	133	351°	1.667(20)	X-ray
$P_4(NMe)_6MeI$	134	352°	1.71(3)	X-ray
$P_4(NMe)_6$	100	356°	1.695(10)	X-ray

Table 1.5.

P-N bond lengths and angles in Cyclophosph(III)azanes.

Compound	Ref.	P-N Distance (Å)	Angles(°) ∠N-P-N	∠P-N-P
$(ClPNBu^t)_2$	107	1.689(4)	82.5(3)	97.3(4)
$(Ph_2P(Me)NPNBu^t)_2$	135	1.724 1.691 exo 1.72(P exo- exo)	80.1	96.9(endo) 116.2(exo)
$(H_{10}C_5NPNBu^t)_2$	97	1.75(2) 1.72(2) 1.68(2)	80.3(1) 110.3 105.3	96.8(1)
$\left[(PhN(H)P_2(NPh)_2\right]_2NPPh$ in CH_2Cl_2	136	1.723	79.4	99.9 115.6
$((Me_3Si)_2NPNSiMe_3)_2$	40	1.727 1.712	82.5	97.5

Table 1.6.

Selected structural data of some cyclodiphosph(V)azanes.

(a) Bond distances.

Compound	Ref.	P...N bond lengths (Å)	P...P bond distances (Å)	N...N bond distances (Å)
$(Cl_3PNMe)_2$	137 138	1.769,1.635 1.776,1.629	2.599 2.577	2.202 2.230
$(F_3PNMe)_2$	139	1.74, 1.60	2.59	2.09
$(PhF_2PNMe)_2$	140	1.78, 1.64	2.61	2.21
$\left[(Cl_3C)F_2PNMe\right]_2$	141	1.742,1.621	2.579	2.159
$\left[(C_6F_5)F_2PNMe\right]_2$	142	1.750,1.631	2.594	2.169
$(Ph_2FPNMe)_2$	143	1.780,1.652	2.659	2.169
$(Cl(O)PNBu^t)_2$ ....trans	144	1.661	2.439	2.255
$(Ph(S)PNPh)_2$ ....trans	145	1.695	2.562	2.221
$(Ph(S)PNMe)_2$ ....trans	146 147	1.69	2.50	2.26
$(Ph(S)PNEt)_2$ ....trans	146 148	1.686	2.518	2.241
$(Ph(S)PNEt)_2$ ....cis	146 109	1.687	2.491	2.261
$(Cl(S)PNMe)_2$ ....trans	149	1.67	2.48	2.23
$(C_{15}H_{15}N_2PS)_2$ ....trans	150	1.74, 1.80 endo 1.75 exo	2.53	2.48

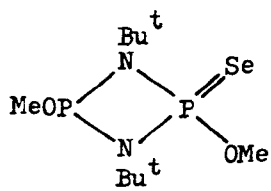
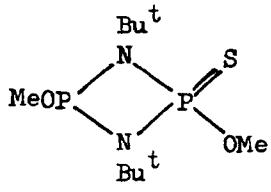
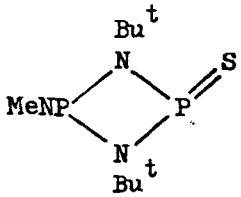
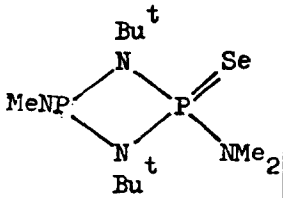
Table 1.6.

(b) Bond angles

Compound		Ref.	$\hat{PNP}$(°)	$\hat{NPN}$(°)
$(Cl_3PNMe)_2$		137 138	99.5 98.3	80.5 81.7
$(F_3PNMe)_2$		139	102.0	78.0
$(PhF_2PNMe)_2$		140	99.4	80.6
$[(Cl_3C)F_2PNMe]_2$		141	100.1	79.9
$[(C_6F_5)F_2PNMe]_2$		142	100.2	79.8
$(Ph_2FPNMe)_2$		143	101.6	78.4
$(Cl(O)PNBu^t)_2$	...trans	144	94.5	85.5
$(Ph(S)PNPh)_2$	...trans	145	98.1	81.9
$(Ph(S)PNMe)_2$	...trans	146 147	96.0	84.0
$(Ph(S)PNEt)_2$	...trans	146 148	96.7	83.4
$(Ph(S)PNEt)_2$	...cis	146 109	95.2	84.2
$(Cl(S)PNMe)_2$	...trans	149	96.0	84.0
$(C_{15}H_{15}N_2PS)_2$	...trans	150	91.0	89.0

Table 1.7.

Comparison of ^{31}P n.m.r. data for geometrical isomers.

Compound	Ref.	Isomer			
		trans		cis	
		δ_P(ppm)	J_{PP},(Hz)	δ_P(ppm)	J_{PP},(Hz)
$(ClPNEt)_2$	115			227.3	
$(ClPNBu^t)_2$	115			207.3	
$(MeOPNBu^t)_2$	115 34	202.4	-9.5	133.7	15.9
$(Me_2NPNBu^t)_2$	49	184.7	-10.0	95.0	14.0
$(Me(H)NPBu^t)_2$	49	172.4		98.1	
$(H_{10}C_5NPNBu^t)_2$	49	182.3		91.9	
$(MeO(S)PNBu^t)_2$	115	56.6	20.8	51.6	28.5
$(Me_2N(S)PNBu^t)_2$	49	53.8	20.2	44.8	41.2
$(Me_2N(Se)PNBu^t)_2$	34 49	48.9	6.2	39.8	33.1
	115	119.3 (PIII) 72.3	-11.1	96.2 P(III) 53.8	-17.3
	115	110.0 (PIII) 75.7	12.6	94.2 P(III) 60.2	14.7
	49	103.6 (PIII) 68.0	11.2	91.4 (PIII) 49.0	11.2
	49	111.7 (PIII) 61.0	-10.1	90.0 36.2	9.4

Chapter 2.

Reactions of phosphazanes with diborane, B_2H_6, and boron trifluoride-diethylethanoate, $Et_2O.BF_3$.

2.1. Introduction.

Reactions of various phosph(III)azanes with diborane, triethylamine-borane and boron trifluoride-diethyletherate were carried out to investigate the nucleophilic characteristics of the phosphorus and nitrogen atoms. In this respect the work was a development from that described in Chapter 1 Section 1.4e., see page 30. In general the investigations confirmed the trends established in the previous works; there were no major disagreements

2.2. Results.

2.2a. Reactions of acyclic phosph(III)azanes with borane adducts.

The reaction of tris(dimethylamino)phosphine, (3a), with 1 mole equivalent of triethylamine-borane readily gave the tris(dimethylamino)phosphine-borane (12a), $\delta_{P(III)}$ = 104.7, $J_{P}{}^{11}{}_{B}$ = 98.5Hz , $J_{P}{}^{10}{}_{B}$ = 50.0Hz, see also ref. 63.

$$P(NMe_2)_3 + Et_3N,BH_3 \xrightarrow{100^{\circ}C} (Me_2N)_3P.BH_3 + Et_3N. \qquad .....(2.1)$$

(3b) (12a)

Bis[(dimethylamino)phosphino]methylamine, $((Me_2N)_2P)_2NMe$ (3c) and diborane, B_2H_6, gave a bis-borane product, (17a), δ_P = 104.1

$$[(Me_2N)_2P]_2NMe + B_2H_6 \xrightarrow[\text{amb. temp.}]{\text{pet. ether}} (Me_2N)_2P(BH_3)N(Me)P(BH_3)(NMe_2)_2 \qquad .....(2.2)$$

(3c) (12b)

Consistent with this formulation, the ^{1}H n.m.r. spectrum of (12b) gave a triplet δ = 2.44, J_{PH} = 5.4 Hz. Interestingly the mass spectrum showed an ion-*parent* for the mono-borane adduct, m/e = 281, but not for the bis-borane adduct. The ^{31}P n.m.r. spectrum gave δ_P = 104.1, J_{PB} = 96.7 Hz.

The reactions of diborane with a series of bis(diphenyl phosphino)amines, (3d,e,f), $(Ph_2P)_2NR$, (R = Me, Et and Pr^i) respectively, were carried out under conditions similar to that of Reaction 2.2. Unfortunately, the products (12, R = Me(c), Et (d) and Pr^i(e)) all readily decomposed and no ^{31}P n.m.r. nor microanalytical data could be obtained. In the case of (12c and d, R = Me and Et), ^{31}P n.m.r. shifts of 76.5 and 78.5 respectively were obtained by double resonance and may be compared with the ^{31}P n.m.r. shift for the respective starting materials of 74.0 and 62.2. The ^1H n.m.r. spectrum of (12c) gave doublet of doublets with a shift δ = 2.67 and phosphorus-proton couplings of 1.8 Hz and 10.5 Hz, which is consistent with reaction of diborane at one phosphorus atom only. Although only one major phosphorus shift was obtained for (12b), a weak signal corresponding to δ_P = 107.7 was also observed in the same spectrum. The ^1H n.m.r. spectrum of (12d, R = Et) is more complex but the CH_2 region showed a doublet of quartets which on ^{31}P irradiation gave a quartet. The reaction of the compound (3c) with triethylamine-borane gave a product with a ^1H spectrum and phosphorus shift identical to that obtained in the reaction with diborane.

Table 2.2. ^{31}P n.m.r. shifts of some acyclic phosph(III)azanes and their borane adducts.

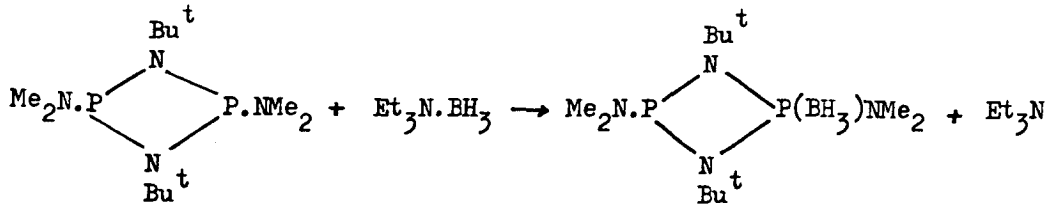
Compound		δ_P (ppm)	Borane adduct	Compound number	δ_P (ppm)	$\Delta\delta_P$
$P(NMe_2)_3$	(3b)	122.2	$(Me_2N)_3P.BH_3$	(12a)	107.9	14.3
$[(Me_2N)_2P]_2NMe$	(3c)	119.0	$[(Me_2N)_2P(BH_3)]_2NMe$	(12b)	104.1	14.9
$(Ph_2P)_2NMe$	(3d)	74.0	$Ph_2P(BH_3)NMePPh_2$	(12c)	76.5 &(107)	-1.5
$(Ph_2P)_2NEt$	(3e)	62.2	$Ph_2P(BH_3)NEtPPh_2$	(12d)	78.5	-16.3

The mass spectra of (12c,d and e) all clearly show the presence of the mono-borane adducts, and of the starting materials, presumably formed by fragmentation in the spectrometer.

It was not possible to obtain complete analytical data for any of those adducts except $(Me_2N)_3P\text{-}BH_3$. However, the ^{31}P n.m.r. spectrum suggests that coordination occurred from phosphorus to boron as expected. The ^{31}P n.m.r. spectrum gave a quartet (1:1:1:1) δ_P 104.7 and $J_{(^{11}BP)}$ = 98.5Hz . An underlying heptet (1:1:1:1:1:1:1) gave $J_{(^{10}BP)}$ = 50.0Hz.

2.2b. Reactions of cyclophosph(III)azanes with borane adducts.

2-cis-4-Bis(dimethylamino)-1,3-di-t-butylcyclodiphosph(III)-azanes, (1f), forms a mono-borane adduct(18a) with one mole equivalent of triethylamine-borane. This adduct has ^{31}P n.m.r. shifts of δ_P 91.4 and 79.1.

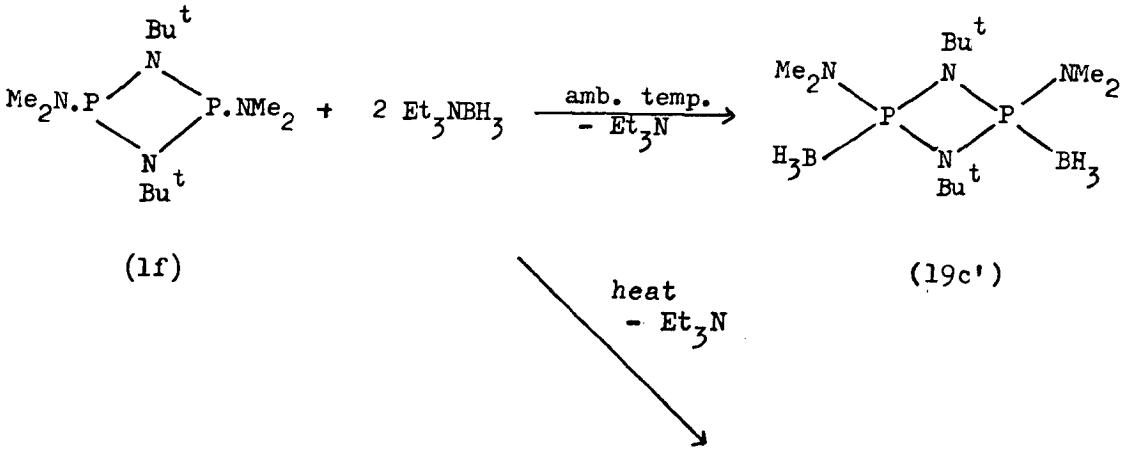


(1f) (18a) 2.3

Compound (18a) was isolated as a crystalline solid after distillation of triethylamine. ^{1}H n.m.r. spectroscopy established that the reaction was almost complete prior to distillation. The analogous trans-cyclophosphazane (1f) gave a product identical to that obtained from the cis-isomer. The adduct (18a) is believed to be a cis isomer. This assignment is based on consideration of the ^{31}P n.m.r. shifts where it has been found that for cyclodiphosph(III)azanes large chemical shift differences exist between cis and trans isomers and that the 'low field' isomer has a cis conformation. This also holds for cyclodiphosph(V)azanes but the shift difference between isomers is considerably smaller [151].

Bis-borane adducts of (1f) could also be prepared using triethylamine-borane, the product being dependent on the conditions. If cis (1f) and two mole equivalents of triethylamine-borane are mixed without heating, then the product is the cis-isomer (19b) .

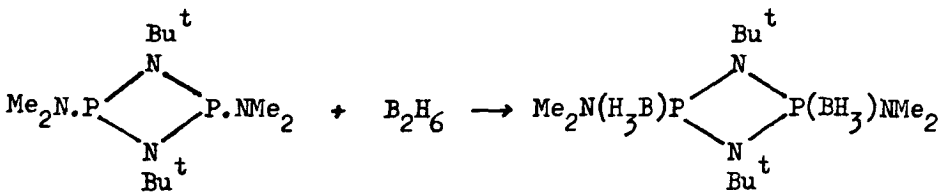
Distillation of the triethylamine gives the trans-isomer (19c)



(1f) (19c') (19c")

.....2.4

On passing diborane through a solution of cis and trans (1f) in light petroleum, the bis-borane cyclodiphosphazane adduct (19a) is immediately formed.



(1f) (19c)

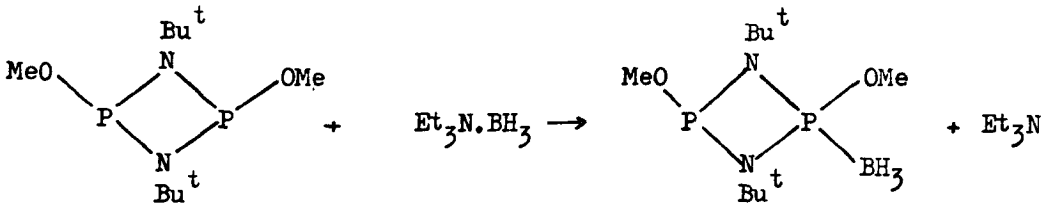
cis and trans isomers

.....2.5

The monoborane adduct (18a) was left for two weeks in methylene chloride solution when n.m.r. spectroscopy showed that it had disproportionated to the cis-cyclodiphosph(III)azane (1f) and a cis-bisborane adduct (19c).

On mixing tris(dimethylamino)phosphine-borane (12) and (1f) in 1 : 1 mole ratio, the monoborane cyclodiphosphazane (18a) and tris(dimethylamino)phosphine were formed.

The cis-bismethoxy-derivative $(MeOPNBu^t)_2$, (1n), shows a similar series of reactions with diborane to that of the bisdimethylamino-derivative (1f), the bisborane adduct being isolated. However, reactions of (1n) with 1 and 2 mole equivalents of triethylamine-borane gave the monoborane adduct (18b).

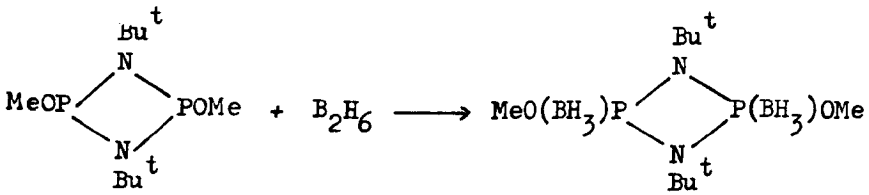


(1n) (18b)

.....2.6

The trans isomer of (1n) also gives a cis-mono-borane adduct (18b) from the reaction with triethylamine borane. The assignment of structures is based on the criteria discussed in pages 43 - 49.

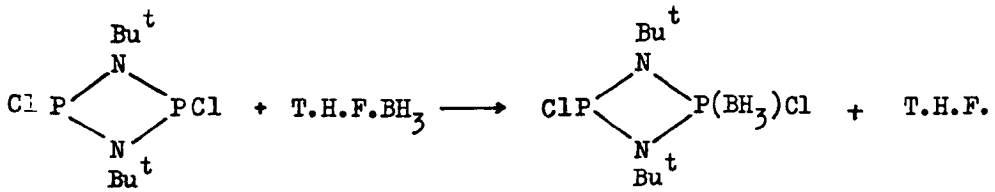
Bis-borane adducts of (1n) are formed by reactions with diborane :



(1n) cis and trans (19b)

.....2.7

The cis-dichloro derivative, $(ClPNBu^t)_2$, (1c) reacts with 1 mole equivalent of tetrahydrofuran-borane to give a product which was not formally identified, but is probably a monoborane adduct.



(1c) (18c)

.....2.8

A similar reaction using triethylamine-borane gave a product with an identical shift, δ_P = 130.5, to that obtained for the reaction of (1c) with triethylamine. This suggests that the product in this case may be a triethylamine adduct.

A related reaction has previously been observed by Holmes [152]. Thus phosphorus trichloride and trimethylamine form an adduct in both the solid and liquid phase at low temperature (-46.5°C).

$$PCl_3 + NMe_3 \rightleftharpoons PCl_3.NMe_3$$

When heated to 0 °C complete dissociation to PCl_3 and NMe_3 occurs.

2.2c. Reactions of phosphazanes with boron trifluoride-diethyletherate.

The preparation of mono-boron trifluoride adducts of the bisdimethylamino-(1f) and bismethoxy-(1n) derivatives of the cyclodiphosph(III)azanes was attempted by the reaction of boron trifluoride-diethyletherate with the appropriate cyclodiphosph(III)azane. The results were ambiguous in both cases, the products gave a ^{31}P n.m.r. spectrum which displayed no phosphorus-boron or phosphorus-fluorine couplings, but showed ^{31}P signals that suggest two main products from each reaction. The reaction with (1n)* gave products with ^{31}P n.m.r. signals of 168.05 and 128.0, ($J_{PP'}$= 20.7Hz) and 138.05 and 128.0 ($J_{PP'}$= 21.1Hz). This may indicate two distinct compounds or isomers of a single compound. The analogous reaction with (1f) gave a similar ^{31}P spectrum with ^{31}P shifts of 160.1 and 116.4 ($J_{PP'}$ = 13.8Hz), and 131.8 and 116.4 ($J_{PP'}$ = 13.9Hz). The ^{19}F n.m.r. spectrum of the product of this reaction gave a 1:1:1:1 quartet at δ_F = 160 (J_{BF} = 17Hz), and a broad 'hump' at (δ_F = 150.2).

The mass spectra of the product of the reactions of (1f) and (1n) with 1 mole equivalent of boron trifluoride show no indication of any ring adduct or of any unreacted starting material.

*(1n) = $(MeOPNBu^t)_2$

2.3. Discussion.

2.3a. Reactions of acyclic phosph(III)azanes with borane adducts.

Investigations into the products of the reactions of acyclic phosph(III)azanes (3b-d) with diborane and triethylamine-borane have confirmed earlier reports that the BH_3 group bonds to the phosphazanes through the phosphorus atoms [64,65,153]. The borane adducts of (3b) and (3c) gave shifts upfield of the starting material, see Table 2.1. This was expected for the borane adducts and has also been observed in the products of oxidation reactions [27]. However, in the case of (3d, e) with diborane, the products (12c,d) have a downfield phosphorus shift relative to the starting material.

The formation of a mono-borane adduct (17b) is surprising in view of the reactivity of diborane towards phosphazanes. The ^1H n.m.r. data and the fact that only mono-borane adducts were observed in the mass spectra suggest that (12c,d) are mono-borane adducts of (3d and e), though this does not explain why only one strong phosphorus shift was obtained by double resonance for the compounds. The problem could not be resolved by ^{31}P n.m.r. spectroscopy as the compounds decomposed too readily before the samples could be examined. It is possible that the products (12c & d) each had two phosphorus shifts in close proximity, ca. 2ppm and that they were mistakenly identified as a single shift. In the analogous fluoride $FPNBu^tPF(BH_3)NBu^t$, Paine and coworkers found phosphorus shifts of 139.8 (P III) and 134.6 ($P(BH_3)$). The $\underline{P}(BH_3)$ signal may also have been broadened by rapid ^{11}B relaxation, and this could have contributed to any misidentification of the two phosphorus signals.

The fact that no bis-borane adducts of (3d-f) were observed is in line with the observation of Paine et al[76] that only mono MeI adducts of diphosphinoamines are formed.

It is probable that the presence of a borane group at one of the phosphorus atoms of the acyclic phosph(III)azane reduces the nucleophilic character of the remaining phosphorus by an inductive effect.

2.3b. Reactions of cyclophosph(III)azanes with borane adducts.

It is surprising that there was no reaction between tetrahydrofuran-borane and the dimethylamino-derivatives (1f) or the methoxy-derivative (1n). By contrast the reaction of triethylamino-borane with the dimethylamino-derivative (1f) gave both mono-(18a) and bis-(19a) adducts. The fact that the methoxy-derivative (1n) gave only a mono-borane adduct (18b), even under forcing conditions indicates that the reactivity of the cyclodiphosph(III)azanes is related to the electron supply to phosphorus. This is expected to be related to the exo-substituents in the order $Cl < OMe < NMe_2$.

By comparison with P(V) compounds of known structure the ^{31}P chemical shifts suggest that the compounds above are cis-isomers. However, when two mole equivalents of triethylamine-borane are mixed with cis-(1f) and the reaction mixture is heated then the product is the trans-isomer. Presumably the trans-isomer is thermodynamically more stable than the cis-isomer.

A similar reaction with trans-(1f) gave the same products as obtained from cis-(1f). As yet it has not been established whether isomerisation occurred before or after reaction with the borane. The reactions of (1f) and (1n) with diborane constituted the only method for the direct formation of trans-(18a,b) and for the preparation of the bis-boranes of (1n), (19b). Diborane is extremely reactive towards cyclodiphosph(III)azanes forming the bis-borane adducts (19a) and (19b) instantly. There is no indication of any mono-boranes (18a) and (18b) being present in the reaction products. The reactions with (1f) and (1n) are stereospecific, although it was not possible to distinguish the relative reactivity of cis and trans-isomers towards diborane.

The disproportionation of (18a) to (1f) and (19a) clearly implies that the mono-borane adduct is relatively unstable with respect to both the bis-borane adduct and the cyclodiphosph(III)azane. The reaction of tris(dimethylamino)phosphine-borane with (1f) results in the formation of the monoborane (18a). The reaction is not reversible implying that the cyclodiphosph(III)azane (1f) is a stronger base towards borane than the acyclic tris(dimethylamino)phosphine. This is probably due to the conformations of the adjacent phosphorus and nitrogen lone pairs (see Chapter 1; p50). In the acyclic tris(dimethylamino)phosphine there is relatively free rotation about the phosphorus-nitrogen bonds and so conformations with a minimum interaction between adjacent phosphorus and nitrogen lone-pairs is possible. However, in the ring compound (1f) there is a fixed arrangement of atoms which leads to a near eclipsed relationship between phosphorus and nitrogen lone-pairs and so increases the basic character of the phosphorus atoms.

The reaction of (1c) with 1 mole equivalent of tetrahydrofuran-borane is believed to form the mono-borane adduct (18c), see Reaction 2.8. If triethylamine-borane is used in a similar reaction, the resulting product appears to be an adduct between the triethylamine and the cyclodiphosphazane. Phosphorus shifts of 190.1 and 137.8 with a phosphorus-phosphorus coupling of 39Hz were obtained from (18c), however, the ^{31}P n.m.r. spectrum did not show any phosphorus-boron coupling, although this may be due to ^{11}B nuclear spin relaxation effects. No bis-borane adducts of the cyclodiphosphazane (1c) were prepared.

The ^{31}P n.m.r. parameters obtained for (18c) differ markedly from those obtained for the analogous fluoro-derivative, as found by Paine and coworkers [76], where the ^{31}P n.m.r. shifts for the two different phosphorus atoms were reasonably close at δ_P =139.8 and 134.6. In the fluoro derivative a strong phosphorus-boron coupling of 55Hz was observed. The bis-borane adduct of (1h; R = Bu^t) was shown, by x-ray crystallography, to have a cis-structure and it seems probable that the mono-borane adduct of (1h; R = Bu^t) would also be the cis-isomer particularly since the starting compound is cis-isomer [34]. However, it is worth noting that dimethylsulphoxide oxidises cis (1c) to trans $(Cl(O)PN.Bu^t)_2$, an arrangement which reduces the P.....P distance and shortens the P—N bonds [77].

^{31}P n.m.r. spectroscopy has proved to be very useful in the identification of the various borane adducts of the cyclodiphosphazanes. In the case of the mono-borane adducts, the ^{31}P n.m.r. shifts of the different types of phosphorus atoms distinguishes between those with and those without an attached borane group, see Table 2.3.

Table 2.3. ^{31}P n.m.r. data for $(XPNBu^t)_2BH_3$

X	δ_P(III)(ppm)	δ_P,(-BH_3)(ppm)	J_{PB}(Hz)	$J_{PP'}$(Hz)	ΔP^{III}*	$\Delta P(BH_3)$*
Cl	190.07	137.8	-	39.0	17.3	69.5
MeO	118.05	109.5	78.8	-	15.7	24.2
Me_2N	91.4	79.1	91.4	-	3.6	15.9

*: Δ P is the upfield ^{31}P shift of the borane adduct relative to the analogous precursor, $(XPNBu^t)_2$

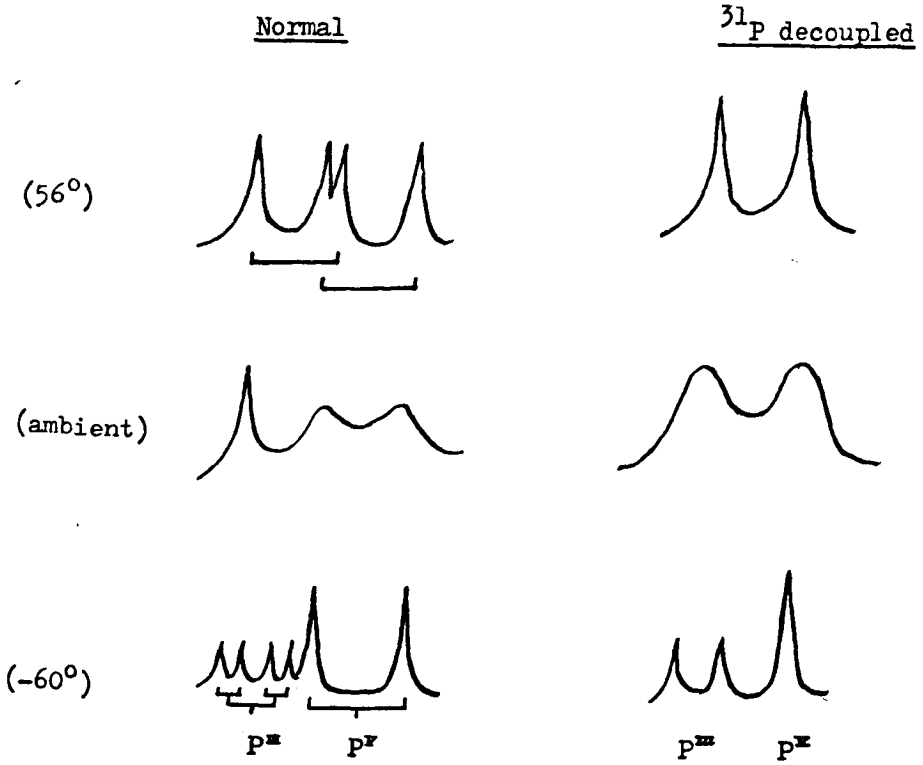
Using empirical relationships ^{31}P n.m.r. spectroscopy can also be used to distinguish cis-and trans-isomers of the bis-borane adducts, see Table 2.4. The cis-isomers have ^{31}P signals upfield of the trans-isomer and have smaller phosphorus-boron couplings. The determination of the structures of the two isomers is based on a comparison of the ^{31}P n.m.r. shifts with analogous oxidation compounds of known structure [49].

Table 2.4. ^{31}P n.m.r. data for bis borane adducts $(X(BH_3)PN.Bu^t)_2$

X	δ_P (ppm) cis	J_{PB} (Hz)	δ_P (ppm) trans	J_{PB} (Hz)
MeO	108.5	81.0	132.2	85.0
Me_2N	85.7	71.4	115.3	80.6

Variable temperature ^1H n.m.r. experiments on both mono- and bis-borane adducts of the bisdimethylaminocyclodiphosph(III)azane (1f) are of interest. Heating the cis bis(borane)adduct (19a') between 30° and 90°C had no appreciable effect on the spectra. However, when the mono-borane adduct (18a) was heated from -60° to 56°C there was a marked change in the ^1H n.m.r. spectrum over this temperature range. This is summarised in fig. 2.2.

Fig. 2.2. Variations in ^{1}H n.m.r. spectrum of (18a) with temperature.



The spectrum and ^{31}P decoupling frequencies indicate that there is non-equivalence of the two methyl groups on the P^{III} NMe_2 group the latter comprising a pair of doublets in the single resonance spectrum.

The dimethylamino-derivatives (18a) and cis and trans (19a) were cooled to -60°C and the effects on the ^{1}H n.m.r. spectra (^{31}P decoupled) were followed. These experiments gave the coalescence temperature for each sample, Tc; that is the temperature at which the individual N-methyl signals, associated with the phosphorus(V) atom, coalesce. Approximate values for the free energy of activation, at the coalescence temperature, for the rate process can be calculated using the formula

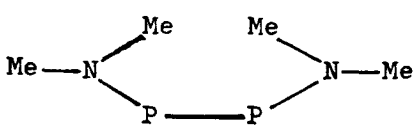
$$\Delta G^{\ddagger} = Tc\left[45.63 + 4.58 \log \frac{Tc}{\Delta\nu}\right]$$

where $\Delta\nu$ = shift (Hz) in absence of exchange.

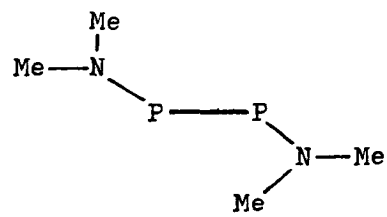
Table 2.5. $\Delta G^{\ddagger}_{Tc}$ for Borane Adducts of $(Me_2N.PN.Bu^t)_2$

Compound	Tc (K)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger}_{Tc}$ (kcal.mol^{-1})
(18a)	283	11.2	14.7
(19a)cis	288	5.0	15.5
(19a)trans	315	2.0	16.9

By analogy with analogous chalcogen derivatives it seems likely that $\Delta G^{\ddagger}_{Tc}$ is a measure of the activation energy of rotation of the phosphorus-nitrogen (exo) bond and from this one can gain information on the configuration of the compound. Table 2.5 correlates the order of $\Delta G^{\ddagger}_{Tc}$ for cis and trans isomers as discussed earlier, see Ch.1 Section 5d, Conformational Effects. The higher value for $\Delta G^{\ddagger}_{Tc}$ obtained for the trans isomer of (19a) confirms this arrangement. The trans isomer has less interaction in the ground state between the exocyclic groups - see fig. 2.3. This leads to higher rotational barriers than the cis isomers. The close proximity of the $-NMe_2$ groups in the cis isomer gives an interaction which destabilises the ground state.



cis



trans

(the ring nitrogen atoms and substituents have not been shown for reasons of clarity).

fig.2.3.

The infrared spectra of the borane adducts of both (1f) and (1n) show that the P-N-P asymmetric stretching mode gradually moves to higher energy as borane groups are added to the cyclodiphosphazane. In this the mono-and bis-borane adducts show that they follow opposite general trends as related oxidation products with chalcogens, see Table 2.6. The fact that mono-and bis-borane adducts have higher energy P-N-P stretching modes than their precursors, and this is possibly indicative of stronger phosphorus-nitrogen bonds being present in the adducts. This is consistent with crystal structural data which shows that phosphorus(V)-nitrogen bonds are generally shorter than analogous phosphorus(III)-nitrogen bonds (see chapter 1.)

badly written

The cis-isomers of the bis adducts (19a,b) have P-N-P asymmetric stretching modes which are at a higher energy than the analogous trans isomers, (ca.5 cm^{-1} in both cases).

The mass spectra of the mono-and bis-borane adducts show that removal of BH_3 groups from the adducts in the spectrometer is generally relatively easy. The mono-borane adducts show a parent ion but have even larger signals for parent - 14, that is the loss of a BH_3 group. The bis borane adduct (19a) shows only a slight trace of a parent ion and a small signal for the parent - 14. In the case of (19b) neither cis or trans isomers show any parent ion. By contrast the analogous fluoro-derivatives of mono- and bis-borane adducts prepared by Paine and coworkers [76] both gave relatively strong parent ions.

Table 2.6. P-N-P (asym) Stretching Modes in Borane, Thio and Oxo Derivatives, $X(Y)P(NBu^t)_2P(Y')X\,NBu^t$

Compound				P-N-P (asym)/cm^{-1}	
X	Y	Y'	ref.	cis	trans
Me_2N	-	-	37b	872/862 870	880
Me_2N	BH_3	-	-	887	-
Me_2N	BH_3	BH_3	-	910	905
Me_2N	S	-	154	884	897
Me_2N	S	S	154	905	912
Me_2N	O	O	154	915	930
MeO	-	-	34	897	890
MeO	BH_3	-	-	910	-
MeO	BH_3	BH_3	-	920	915
MeO	S	-	154	903	902
MeO	S	S	154	922	921

Note: all spectra obtained from Nujol Mulls.

Table 2.7. B - H Stretching Modes in Borane adducts of some Phosphazanes.

Compound		ν (B—H)/cm^{-1}		
		Asym	Sym	Others ‡
$(Me_2N.PN.Bu^t)_2.BH_3$		2380(s)	2350	
$(Me_2N.PN.Bu^t)_2(BH_3)_2$	cis	2405(s)	2380(s)	(2357),(2425)
	trans	2408(s)	2385(s)	(2360),(2420)
$(MeO.PN.Bu^t)_2.BH_3$		2395(s)	2360	
$(MeO\ PN.Bu^t)_2(BH_3)_2$	cis	2415(s)	2408(s)	(2365),(2370)
	trans	2415(s)	2408(s)	(2368)
$(Ph_2P)_2NMe.BH_3$		2400	(v,broad)	
$(Ph_2P)_2NEt.BH_3$		2415(s)	2385(s)	(2448)
$(Me_2N)_2P\ _2NMe.(BH_3)_2$		2390(s)	2350(s)	(2430)(m)

Note: All spectra obtained from Nujol Mull

‡, shoulders in square brackets

There is no appreciable difference in B — H stretching modes between cis and trans isomers of the cyclodiphosphazane diborane adducts (see Table 2.7). This is surprising in view of the difference in chemical and physical properties of cis and trans isomers, (see page 84) B - H stretching modes can also be used as an indication of relative base strengths of a series of derivatives[65,73].

2.3c. Reactions of Phosphazanes with Boron Trifluoride-Etherate.

This series of experiments has not given any clearly identifiable products. In most reactions the addition of the boron trifluoride appears to have resulted in the fragmentation (or decomposition) of the phosphazane. Presumably the boron trifluoride attacks at the nitrogen atom [64] and this results in the phosphorus being more susceptible to hydrolysis.

The cyclodiphosphazanes (1f) and (1n) both gave two sets of phosphorus shifts from the ^{31}P n.m.r. spectra (Section 2.2c). There was no phosphorus-boron coupling and so no evidence to support the presence of a phosphorus-boron bond. The ^{31}P n.m.r. signals that were obtained were present along with those from a large proportion of unidentified decomposition products.

2.4 Experimental.

Preparation of 2,4-bisdimethylamino-1,3-ditert-butylcyclodiphosph(III)-azane-borane.

(a) Attempted preparation using tetrahydrofuran-borane.

Tetrahydrofuran-borane (1.5g, 17.4 mmol) in diethylether (10 ml) was added dropwise to a rapidly stirred solution of 2-cis-4 bisdimethylamino-1,3-ditert-butylcyclodiphosph(III)azane (1f), (2.5g, 8.6 mmol) in diethylether (50 ml) at 0°C. ^{1}H n.m.r. spectroscopy indicated that no reaction occurred despite refluxing the solution (4hrs

(b) Using triethylamine-borane.

(i) 1 : 1 mole ratio;

A mixture of 2-cis-4-bisdimethylamino-1,3-ditert-butyl cyclodiphosph(III)azane (1.4g, 4.8 mmol) and triethylamine-borane (0.6g, 5.2 mmol) was heated to distil off the triethylamine (b.p. = 90°C). The residue was then distilled under reduced pressure to give a clear liquid (b.p. = 92°C at 0.1mm Hg) which, on standing, gave small white crystals of 2-cis-4-bisdimethylamino-1,3-ditert-butylcyclodiphosphazane-borane, (m.p., ca. 170°C) , see Table 2.8 for microanalysis and mass spectroscopy data.

(ii) 1 : 2 mole ratio;

2-cis-4-bisdimethylamino-1,3-ditert-butylcyclodiphosph(III) azane (1.55g, 5.3 mmol) and triethylamine-borane (1.22g, 10.6 mmol) were reacted together as in (i). In this case purification was by recrystallisation giving fine white crystals (m.p. = 192°C) of 2-trans-4-bisdimethylamino-1,3-ditert-butylcyclodiphosphazane-diborane (0.78g, 46% yield) , see Table 2.8 for microanalysis and mass spectroscopy data.

When the product was allowed to stand overnight, crystals were produced which proved (by $^{1}H-\{^{31}P\}$ n.mr.) to be the cis-isomer of the diborane adduct, see Table 2.8a for microanalysis data.

(c) Using diborane.

Excess diborane was bubbled through a solution of 2-cis-4-bisdimethylamino-1,3-ditert-butylcyclodiphosph(III)azane (1.0g, 3.4mmol) in light petroleum (b.p. 40-60°C), (15ml). This gave a white crystalline product sparingly soluble in petrol which proved to be 2-cis-4-bisdimethylamino-1,3-ditert-butylcyclodiphosphazane-diborane, identified by ^{31}P n.m.r. With 2-trans-4-bisdimethylamino-1,3-ditert-butylcyclodiphosph(III)azane, the product was a mixture of cis and trans diborane adducts.

Preparation of 2,4-dimethoxy-1,3-ditert-butylcyclodiphosphazane-boranes.

(a) Using triethylamine-borane.

2-cis-4-dimethoxy-1,3-ditert-butylcyclodiphosph(III)azane, (1n),(1.49g, 5.6 mmol) and a slight excess of 2 mole equivalents of triethylamine-borane were mixed and heated to 60°C for 4 hours. The triethylamine was then distilled off leaving a solid product which proved to be the cis mono-borane adduct, identified by microanalysis and ^{31}P n.m.r. The bis-borane adduct was not formed even after heating over a longer period of time.

The mono-borane adduct was distilled under vacuum to give a clear liquid (b.p. = 90°C at 0.1 mm Hg) which crystallised on standing, m.p. = 55°C (0.6g, 38.2% yield). See Table 2.8a for microanalysis.

(b) Using diborane.

Excess diborane was bubbled through 2-cis-4-bis-dimethoxy-1,3-ditert-butylcyclodiphosph(III)azane (1.0g, 3.76 mmol) in light petrol (bp. 40-60°C) (40 ml). This immediately gave a white precipitate which proved to be the diborane product. ^{31}P n.m.r. spectroscopy suggested that this was the cis isomer. This was recrystallised from light petroleum (b.p 40 - 60°C) to give white crystals, m.p = 110° - 120°C of 2-cis-4-bisdimethoxy-1,3-ditert-butylcyclodiphosphazane-borane.

A similar reaction with 2-trans-4 bisdimethoxy-1,3-ditert-butylcyclodiphosph(III)azane produced a diborane product which gave thin sheet like rhombic crystals, m.p = 183° - 185°C. This is believed to be the trans isomer of the product, 2,4-bisdimethoxy-1, 3-ditert-butylcyclodiphosphazane-diborane.

Reactions of 2-cis-4-dichloro-1,3-ditert-butylcyclodiphosph(III)azane.

(a) With tetrahydrofuran-borane.

2-cis-4 Dichloro-1,3-ditert-butylcyclodiphosph(III)azane (1c) (1.2g, 4.4m mol) was mixed with tetrahydrofuran-borane (0.38g, 4.4 m mol) and after 1 hour a fine white precipitate appeared ^{31}P n.m.r. spectroscopy showed the mixture to contain unreacted starting material and a product which gave a simple AB spectrum (δ_P=190.1 and 137.8 J_{PNP} 39 Hz). This may be a mono-borane adduct of the ring although no P - B coupling was observed.

(b) With triethylamine-borane.

2-cis-4-Dichloro-1,3-ditert-butylcyclodiphosph(III)azane (0.78g, 2.84 mmole) was slowly mixed with triethylamine-borane (0.33g, 2.86 mmol) in light petroleum (b.p 40° - 60°) (10 ml). The solution was heated to 65 °C for 4 hours. This gave an orange-brown crystalline solid which $^{1}H\{^{31}P\}$ n.m.r. spectroscopy showed to contain a large quantity of unreacted cyclodiphosph(III)azane and a small quantity of a product (10%) which gave a phosphorus shift of 130.5. This shift was also obtained from the spectrum from the reaction of (1c) with triethylamine. This suggested that it may be a triethylamine adduct. Satisfactory spectroscopic or microanalytical data could not be obtained.

Reaction of 2,4-bis(dimethylamino)-1,3-ditert-butylcyclodiphosph(III)-azane with boron trifluoride-etherate.

2,4-bis(dimethylamino)-1,3-ditert-butylcyclodiphosph-(III)azane (1.1g, 3.76 m mole) was mixed with boron-trifluoride-etherate in diethylether (15 ml). This gave an immediate exothermic and effervescent reaction, and a fine white precipatate settled out. Under magnification it was seen to have fine elongated crystals, m.p 105° - 108°C). As with the analogous methoxy-compound, the ^{31}P n.m.r. spectrum gave two pairs of doublets, possibly cis and trans isomers of a boron trifluoride adduct (δ_P = 160.1, 116.4; J_{PNP}= 13.8 Hz and δ_P = 131.8, 116.4; J_{PNP}=13.9 Hz). These crystals also proved too unstable to obtain mass spectroscopic or microanalytical data.

The reaction of 2,4-bis(dimethylamino)-1,3-ditert-butylcyclo-diphosph(III)azane with 2 mole equivalents of boron trifluoride-etherate gave no identifiable products.

Reaction of 2,4-dimethoxy-1,3-ditert-butylcyclodiphosph(III)azane with 1 mole equivalent of boron trifluoride-etherate.

Boron trifluoride diethyletherate was added to 2-cis-4-dimethoxy-1,3-ditert-butylcyclodiphosph(III)azane (1.0g, 3.76 mmol) in diethylether (10 ml) and shaken for 1 hour. Thin plate-like crystals were obtained from the solution (m.p. = 35 - 38°C and 48 - 53°C) along with a small quantity of an oil. The oil was distilled under reduced pressure to give two fractions, a clear liquid (b.p. = 40°C at 0.35 mm Hg) and a thick oil (b.p. = 120°C at 0.35 mm Hg). The ^{31}P n.m.r. spectrum of the white solid obtained directly from the reaction showed the presence of unreacted starting material and two pairs of doublets possibly consistent with the presence of cis and trans isomers of a mono-boron trifluoride adduct of the methoxy-cyclophosphazane (δ_P = 168.0, 128.7 J_{PNP} = 20.7 Hz, and δ_P = 138.0, 128.7 J_{PNP} = 21.1 Hz) (see discussion). The crystals quickly decomposed and no microanalytical or mass spectroscopic data could be obtained.

Reaction of 2-4-dimethoxy-1,3-ditert-butylcyclodiphosph(III)azane with 2 mole equivalents of boron trifluoride-etherate.

2-cis-4-Dimethoxy-1,3-ditert-butylcyclodiphosph(III)azane (1.13g, 4.25 mmol) and boron trifluoride-etherate were mixed in diethylether (15 ml), as above. An oily residue was obtained from which the ^{31}P n.m.r. spectrum showed a number of signals, none of which could be identified.

Reaction of 2-cis-4-Dichloro-1,3-ditert-butylcyclodiphosph(III)azane with 1 mole equivalent of boron trifluoride-etherate.

2-cis-4-Dichloro-1,3-ditert-butylcyclodiphosph(III)azane (1.3g, 4.7 m mole) was mixed with boron trifluoride-etherate (0.31g, 2.18mmo and left to stand 24 hours. No reaction was observed, even when later heated to 85°C for 1 hour.

Preparation of Tris(dimethylamino)phosphine-borane.

Tris(dimethylamino)phosphine (4.0g, 24.5 mmol) and triethylamino-borane (3.0g, 26.1mmol) were mixed together under nitrogen and heated to distil off triethylamine. The residue was then distilled under vacumm to yield a clear liquid (b.p. = 50 C at 0.05 mm Hg) (lit:47°C at 0.1 mm Hg)[65]. The product solidified, m.p. = 26-29° C, cf. lit.[65] = 30°C) ^{31}P n.m.r., see Table 2.8.

Reaction of bis(diphenylphosphino)methylamine with diborane.

Excess diborane was bubbled through bis(diphenylphosphino) methylamine (0.45g, 1.13 m mole) in diethylether (10 ml). When the solvent was removed the product appeared as a white solid, mp 55° - 60°C. The $^{1}H-\{^{31}P\}$ n.m.r. spectrum suggests the product to be bis(diphenyl-phosphine)methylamine-borane, (ca.0.42g, ca.90% yield). The mass spectrum showed a parent ion at m/e = 413, required m/e = 413. The product decomposed before microanalytical data was obtained.

Reaction of bis[(dimethylamino)phosphino]methylamine with diborane.

Excess diborane was bubbled through bis[(dimethylamino)phosph-ino]methylamine (0.23g, 0.86 m mole) in light petroleum (b.p 40° - 60°C) at ambient temperature. $^{1}H-\{^{31}P\}$ n.m.r. spectroscopy and ^{31}P n.m.r. both indicated the product was a diborane adduct, δ_P 104.1, J_{PB} = 96.7. The mass spectrum gave a parent m/e = 281 which is consistent with a monoborane adduct, but this does not rule out the possibility of a diborane product, The product decomposed before a satisfactory microanalysis could be obtained.

The Reaction of bis(diphenylphosphino)ethylamine with diborane.

Bis(diphenylphosphino)ethylamine (0.27g, 0.67 mmol) and diborane gave a solid product, m.p. = 75 - 85°C. ^{1}H -{ ^{31}P} n.m.r., which suggests that the product was bis(diphenylphosphino)ethylamine-borane, δ_P,(ca.) = 78.5 ppm. The product decomposed before ^{31}P n.m.r. or microanalysis could be obtained. The mass spectrum was not scanned above 340*, the theoretical parent should have m/e = 427, however an ion at m/e = 257 has been tentatively identified as $\left[(Ph_2P)NEt.BH_3\right]^+$. (* : this was due to a machine fault.)

Reaction of bis(diphenylphosphino)isopropylamine with diborane.

Bis(diphenylphosphino)isopropylamine (0.26g, 0.61 mmol) and diborane gave 0.1g. (ca. 40%) of a crude solid product, m.p. = 112 - 120°C. The mass spectrum gave m/e=441 which is the parent ion for bis(diphenylphosphino)isopropylamine-borane. Microanalysis and ^{31}P n.m.r. spectrum could not be obtained because of decomposition.

Preparation of diborane, B_2H_6.

The diborane used in the reactions described previously, was prepared by slowly adding boron trifluoride-diethyletherate in diglyme (ratio 1:15), to a rapidly stirred solution of sodium borohydride in diglyme (ratio 1:15). Only a limited amount of the BF_3-Et_2O was added at any one time; sufficient to make enough B_2H_6 for immediate use. The overall reaction is ;

$$3\ Na^+BH_4^- + 4\ BF_3 \longrightarrow 3\ Na^+BF_4^- + 2\ B_2H_6$$

Moisture was removed prior to the reaction by flushing the apparatus with dry nitrogen.

Table 2.8. Analytical data for some phosphazane-borane adducts.

(a) Microanalysis.

Compound	Expt. (%)			Theory (%)		
	C	H	N	C	H	N
$(MeOPNBu^t)_2BH_3$	42.8	10.06	9.85	42.85	9.64	10.0
$(MeOPNBu^t)_2(BH_3)_2$ cis	40.63	10.69	9.62	40.9	10.2	9.6
trans	40.38	-	9.35			
$(Me_2NPNBu^t)_2(BH_3)_2$ cis	44.75	11.38	-	45.0	11.3	17.5
trans	45.2	11.35	17.59			

(b) Mass Spectra.

Compound	Expt.(m/e)	Theory (m/e)
$(MeOPNBu^t)_2BH_3$	280	280
$(MeOPNBu^t)_2(BH_3)_2$	280 - monoborane	294
$(Me_2NPNBu^t)_2BH_3$	306	306
$(Me_2NPNBu^t)_2(BH_3)_2$	319 - (-H)	320
$(Ph_2P)_2NMe.BH_3$	- not scanned	427
$(Ph_2P)_2NPr^i.BH_3$	441	441
$[(Me_2N)_2P]_2NMe(BH_3)_2$	281 - monoborane	295

Table 2.9 ^{31}P n.m.r. data for some phosph(III)azane-borane adducts.

Compound		δ_P(ppm)		J_{PB}(Hz)
$(Ph_2P)_2NMe.BH_3$		76.5*		-
$(Ph_2P)_2NEt.BH_3$		78.5*		-
$(Me_2N)_3P.BH_3$		107.9		98.5(B^{11}) ca.50.0(B^{10})
$(Me_2N)_2PNMe(BH_3)_2$		104.1		-
$(ClPNBu^t)_2BH_3$		190.1	137.8	-
$(Me_2NPNBu^t)_2BH_3$		91.4	79.1	91.4
$(Me_2NPNBu^t)_2(BH_3)_2$	...cis	-	85.7	71.4
	..trans		115.3	80.6
$(MeOPNBu^t)_2BH_3$		118.05	109.5	78.8
$(MeOPNBu^t)_2(BH_3)_2$	...cis	-	108.5	81.0
	..trans	-	132.2	85.0

* Only 1 phosphorus shift was obtained from the $^{31}P - \{^1H\}$ n.m.r. spectrum. There was no indication of the other phosphorus shift that one would have expected to find.

Chapter 3.

Reaction of Phosphazanes with halogens.

3.1. Introduction.

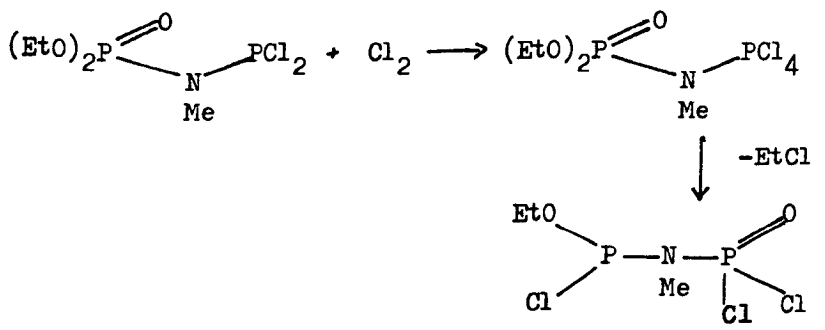
The reaction of halogens with various phosphorus containing compounds has been studied over the past 15 years by various groups[48, 92, 155, 156]. Attempts by some workers to carry out a simple oxidation reaction of phosphazanes using chlorine has failed. The addition of chlorine to these compounds resulted in the formation of ionic intermediates and subsequent N-alkyl bond cleavage[48].

$$(R_2N)_3P + Cl_2 \longrightarrow (R_2N)_3P^{+}Cl\ \ Cl^{-}$$
$$\downarrow$$
$$RN{=}P(NR_2)_2Cl + RCl$$

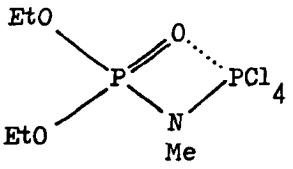
The product was very sensitive to hydrolysis.

$$RP(NR_2)_2 \xrightarrow{Cl_2} RP(NR_2)_2Cl_2 \xrightarrow{H_2O} RP(O)(NR_2)_2$$

In some cases the products of the reaction with chlorine undergo intramolecular rearrangement.



This rearrangement is believed to proceed by the formation of an intermediate of the type:



Interestingly this reaction involves the reduction of $P^{V} \longrightarrow P^{III}$ although the reason for this is not clear.

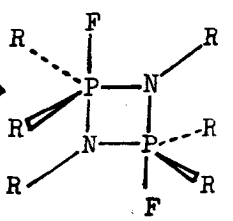
Both the formation of ionic intermediates and the occurence of intramolecular rearrangements (bond cleavage) have important implications in this work, (see discussion).

The preparation of cyclodiphosph(V)azanes containing five-coordinate phosphorus has, until now, involved the reaction of acyclic precursers, for example;

$$MeNH_3Cl + PCl_5 \longrightarrow \tfrac{1}{2}(Cl_3PNMe)_2 + 3\ HCl$$

A number of workers have successfully prepared fluorinated cyclodiphosph(V)azanes and their derivatives [157,158,159].

$$2\ RN(SiMe_3)_2 + 2\ R_2PF_3 \longrightarrow$$

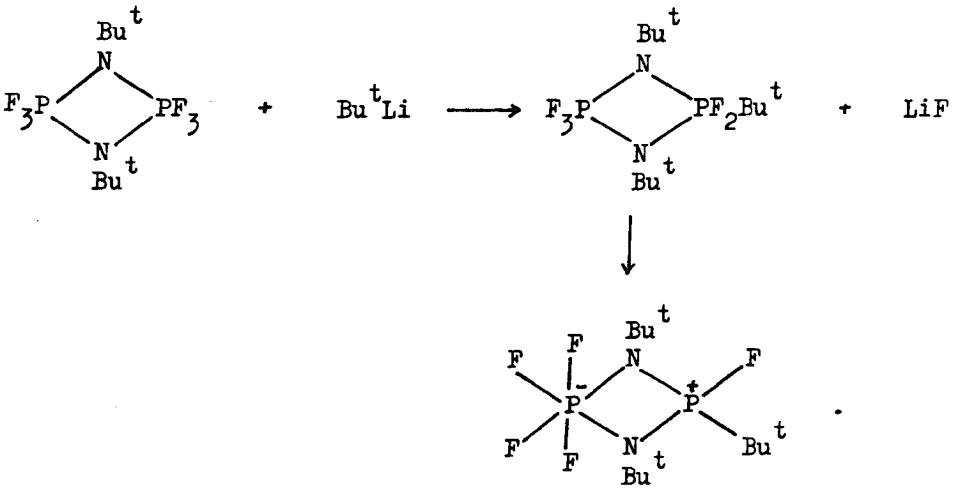


$$+\ 4\ Me_3SiF$$

(R = Me, Et, Ph.)

It has been shown by X-ray crystallography, see Tables 1.4 and 1.5, that the end phosphorus-nitrogen bonds are alternately axial and equatorial with respect to the trigonal bipyramid of bonds about the phosphorus atoms.

Further work by Harris and Schmutzler [160] has shown that reaction of t-butyl-lithium with $(F_3PNBu^t)_2$ can result in zwitterion formation (22).

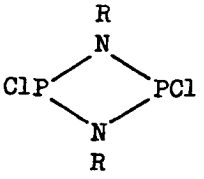


(22)

3.2. Results and Discussion.

3.2a. Reactions of halogens with cyclophosph(III)azanes.

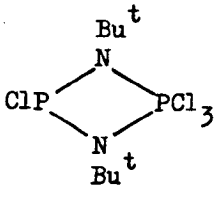
The oxidation reactions of some cyclophosph(III)azanes (1)



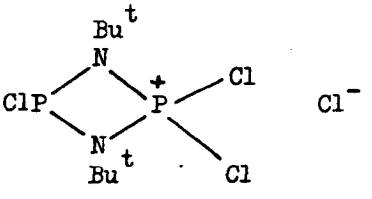
R = Me,Et (1d), Bu^t (1c), Ph (1a).

(1)

with chlorine and bromine were investigated. Reaction of (1c) with one mole equivalent of chlorine at low temperature (-78°C) gave a product with ^{31}P n.m.r. shifts of 183.3 and -51.9 in intensity ratio of 1 : 1. However, the bulk of the material proved to be unreacted starting material. The reaction product (ca.10%) gave ^{31}P shifts consistent with the presence of one phosphorus(III) atom and one phosphorus(V) atom, and could be either a mixed oxidation state covalent compound (20a) or a salt (20b).



(a)



(b)

(20)

The possibility of it being a compound containing PCl_6^- was excluded since this would have given a ^{31}P shift at very high field (ca-200– -230).

When the reaction was repeated using 2 mole equivalents of chlorine this product was not observed. Repeated reactions with 2 mole equivalents of chlorine consistently gave a second product with ^{31}P shifts of -2.1, 8.2 and 23.8. A singlet in the ^{1}H n.m.r. spectrum at $\delta_H = 1.59$ was positively identified as t-butylchloride by addition of some t-butylchloride to the solution.

When excess chlorine was bubbled through a solution of (1c) at ambient temperature, the solution contained three major components as shown in the representation of the spectrum, see Fig. 3.1.

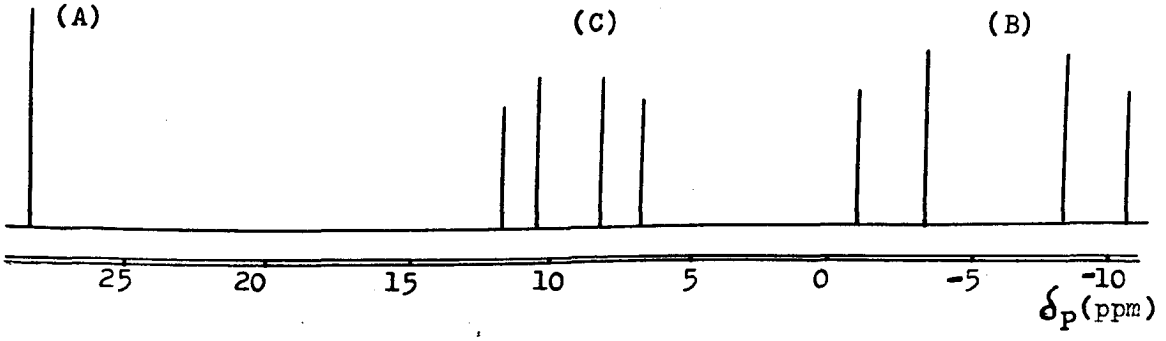


Fig.3.1.

Representation of ^{31}P n.m.r. spectrum of the products of the reaction of $(ClPNBu^t)_2$ and excess Cl_2.

Of the three components, only that labelled 'B' has been positively identified as $Cl_2P(O)N{=}{=}PCl_2N(H)Bu^t$, (21). Its identity was established by its ^{31}P n.m.r. shifts and confirmed by the addition of a small quantity of the authentic compound (21)[161]. The constitution of (21) indicates that in spite of all efforts to keep the reaction conditions dry, water was present in small traces.

Table 3.1: ^{1}H and ^{31}P n.m.r. Data for the Products of the Reaction of $(ClPNBu^{t})_2$ with chlorine.

Compound	Proportion %	δ_P		$^2J_{PNP}$(Hz)	δ_H	$^4J_{PNCCH}$(Hz)
A	20	27.9		-	1.54	1.45
B	40	-2.1	-9.8	27.9	1.48	1.45
C	40	10.8	8.1	38.5	1.42	0.73

The mechanism of N-alkyl group cleavage involved in the formation of 'B' is not clear, but it is worth noting that this also occurs when an acyclic phosph(V)azane is formed in the reaction of tris(dialkylamino) phosphine and chlorine[155], see Reaction 3.1.

$$(R_2N)_3P + Cl_2 \longrightarrow (R_2N)_3P^{+}Cl\ Cl^{-}) \qquad (R = Et, Pr, Bu^{t}, Bu^{i}, Hexyl^{n})$$

$$\downarrow$$

$$RN{=}{=}P(NR_2)_2Cl + RCl \qquad \text{.....3.1}$$

The reaction of (1c) with both one and two mole equivalents of bromine results largely in the formation of unidentified products. Traces of phosphorus tribromide (δ_P = 225) were also found[38].

$^{1}H - \{^{31}P\}$ double resonance experiments gave phosphorus shifts of δ_P 132.7 and 25.8 when 1 mole equivalent or less, of bromine was used. An experiment in which five small portions of bromine, each of 0.2 mole equivalent, were added to (1c), was carried out, and the growth of various signals in the ^{1}H n.m.r. spectrum was observed. Doublets at 1.49 and 1.52 with phosphorus-hydrogen couplings of 1.0 and 1.45 Hz respectively were observed, and double resonance experiments showed they were associated with phosphorus atoms with δ_P = 132.3 and 27.2 respectively. The doublets were of equal intensity and grew with each addition of bromine. When the spectrum was re-run after 20 hours the ratio of the doublets had changed from 1 : 1 to 1 : 2 in favour of the signal at δ_H 1.52, δ_P 27.2. Also a large underlying 'hump' had disappeared and a large signal corresponding to the starting material was observed. This re-appearance of the starting material and the disappearance of the broad 'hump' may suggest that in the initial reaction the starting material reacts with some bromine going possibly to salt, and, with time, gradually releases this bromine again as equilibrium is attained. However, there is no clear indication of what this reaction product is. The presence of the two doublets and the fact that in the ^{31}P n.m.r. the shift of 27.2 is a singlet shows that this corresponds to a compound with a single phosphorus being present and consequently implies P—N bond cleavage.

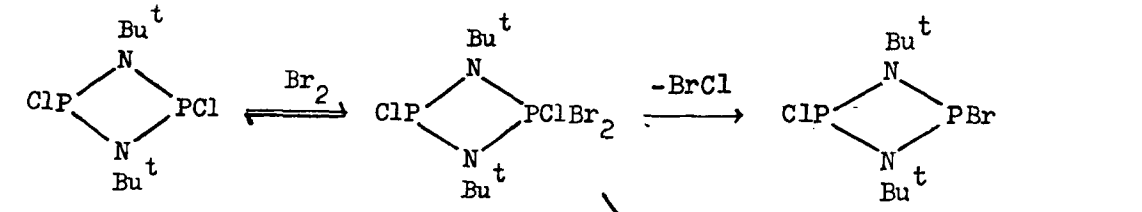
Reaction of (1c) with one and two mole equivalents of bromine has given traces of crystalline material although it very quickly decomposed. The ^{31}P n.m.r. spectrum consisted of a large number of unidentified doublets mainly upfield of H_3PO_4.

The ^{31}P n.m.r. spectrum of the mother liquor from the reaction with one mole equivalent of bromine proved very interesting. It gave signals for the starting material (207.9), phosphorus tribromide (226.1) and at 223.8 a signal from $(BrPNBu^t)_2$ (1q)[38]. Additionally there were two doublets centred at 211.8 and 209.5 both having a phosphorus-phosphorus coupling of 8.7 Hz which may be from a mixed halide derivative (1t), p.108. The existence of the dibromo (1q) and bromo-chloro derivative (1t) coupled with the presence of the phosphorus tribromide would give further credence to the idea that initially bromine reacts with (1c) and then a halide ion is later lost. In some cases the bromine remains and it is the chlorine which is lost, see Reaction 3.3. The dissociation of phosphorus pentahalides to phosphorus trihalide and halogen has been known for some time. In the case of phosphorus pentabromide the dissociation to form phosphorus tribromide and bromine is encouraged by heating[162,163].

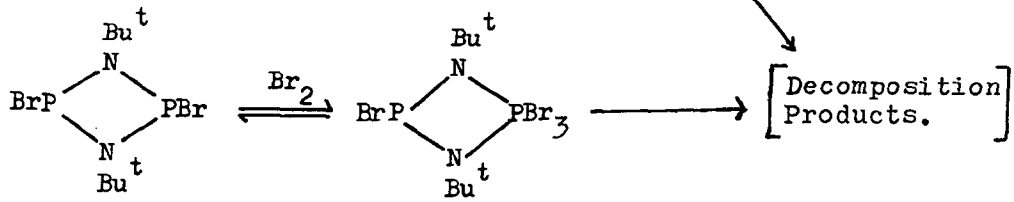
$$PBr_5 \rightleftharpoons PBr_3 + Br_2 \qquad \ldots\ldots(3.2)$$

With phosphorus pentachloride however, the molecule is stable and does not dissociate on heating[162,164].

In the reaction 3.3(a) an intermediate (20c) is believed to be formed. The precise nature of this compoundis uncertain. It is either a mixed oxidation state covalent compound analogous to (20a) or an ionic compound analogous to (20b).



(1c) (20c) (1t) .....(3.3a)

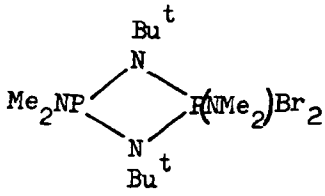


(1q) (20d) .....(3.3b)

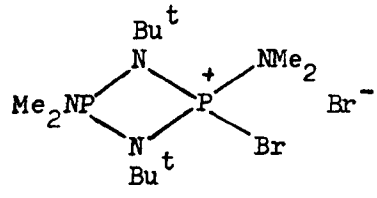
The mother liquor from the reaction with the two mole equivalents of bromine did not show any indication of (1q) or of (1t). It did however give a signal from phosphorus tribromide and a singlet at δ_P 148.1. The corresponding crystalline material showed a general similarity with the product from the analogous reaction with one mole equivalent of bromine, but it also gave a large unidentified singlet at 178.2.

Although the reaction of (1c) with bromine results in products which have only been tentatively identified it would appear that the immediate reaction product is some form of mixed halide compound or salt with stoichiometry similar to (20c) and then either decomposes by phosphoru nitrogen bond cleavage or releases a halide ion to give (1c) or (1t). Increasing proportions of bromine result in extensive phosphorus-nitrogen bond cleavage.

The reaction of one mole equivalent of bromine with cis (1f) was even more exothermic than was the case with (1c). The product of this reaction was less complex than the case with (1c). The ^{1}H n.m.r. spectrum of products gave three doublets with shifts of δ_H 3.20, 2.85 and 2.67 with intensity ratios of 2:1:1 and phosphorus-hydrogen couplings of 14.3, 16.3 and 16.3 Hz respectively. These gave ^{31}P shifts of 0.9 and 84.3 respectively from double resonance experiments. The former ^{31}P shift is at lower field than one might expect for five coordinated phosphorus, suggesting that the phosphorus may be four coordinated as found in a salt. The ^{31}P shifts are generally consistent with compound (20e)



(covalent form)



(ionic form)

(20e)

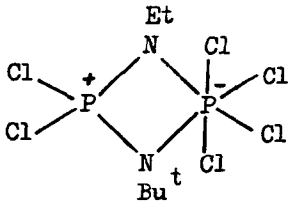
The two smaller doublets in the ^{1}H spectrum may be due to restricted rotation of the exo-phosphorus(III)-nitrogen bond. This type of restricted rotation has been observed in cyclodiphosph(III)azanes[165,166,4c]

Reactions of (1f) with two mole equivalents of bromine did not result in any identifiable products.

The analogous reaction of (1r)* with excess chlorine gave a white solid product, m.p = 65 - 70°C with ^{31}P n.m.r. shifts of 29.5 and -218.1, J_{PNP} = 107 Hz.

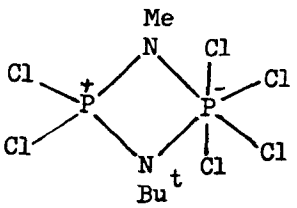
* (1r), ClP.NEt.PCl.NBu^{t}

This product is thought to be the zwitterion (22a) and its composition has been confirmed by microanalysis.

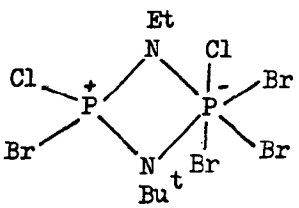


(22a)

The formulation of this compound as a zwitterion is based on the comparison of the ^{31}P n.m.r. shift of the anion PCl_6^-, $\delta_P = -281$[167]. A zwitterionic product has also been obtained from the reaction of chlorine with (1s) $\overbrace{ClP.NMe.PCl.NBu^t}$ giving ^{31}P n.m.r. shifts of 37.9 and -206.2, (22b) and from 2 mole equivalents of bromine with (1r) giving (22c), ^{31}P n.m.r. shifts of 33.6 and -153.2.

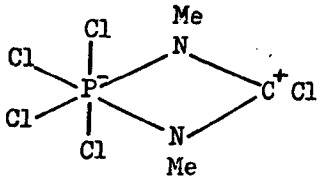


(22b)



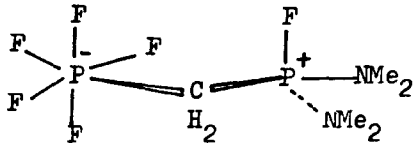
(22c)

Related phosphorus-nitrogen zwitterions have been previously prepared; for example Hormuth and Latscha[168] obtained the compound (23) with a ^{31}P n.m.r. shift of $\delta_P = -202(\pm)$[169].



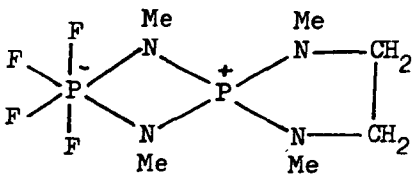
(23)

Cowley and Lee[170] prepared a stable zwitterion (24) based on a P-C-P backbone with ^{31}P shifts of 73.0 and -141.6.

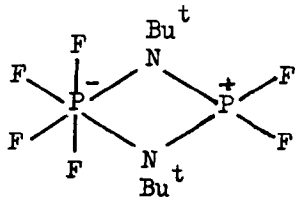


(24)

Other zwitterionic species (25)(26) were reported by Schmutzler and coworkers[160]. Compound (25) was obtained from the reaction of $(F_3PNMe)_2$ with N-lithiated diamines, and (26) from $(F_3PNBu^t)_2$ and tert-butyllithium.



(25)

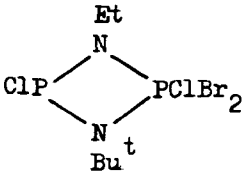


(26)

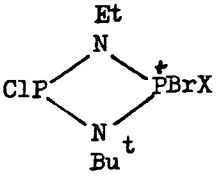
Table 3.2.[157] ^{31}P n.m.r. Data for Zwitterions (25) and (26).

Compound	δ_{PX_6} (ppm)	δ_{PX_4} (ppm)	J_{PNP}(Hz)
(25)	-151.6	33.4	107.5
(26)	-139.0	68.5	54.4

The methylene proton n.m.r. spectrum of the reaction mixture obtained from 1 mole equivalent of bromine and, (1r), $\overline{ClP.NEt.PCl.NBu^t}$, was a doublet of quartets at δ_H 3.8 (couplings of 25.0, 7.3 and 2.0 Hz). $^1H-\{^{31}P\}$ double resonance experiments gave ^{31}P shifts of 163.0 and -47.4. This compound readily decomposed and it was not possible to isolate a pure sample. The ^{31}P shifts and the phosphorus-hydrogen couplings suggest that the product has two types of phosphorus atom, with oxidation states of three and five. This product may have either an ionic or covalent structure (20f), although there is no firm information available on the relative positions of Cl or Br_2.



(covalent form)

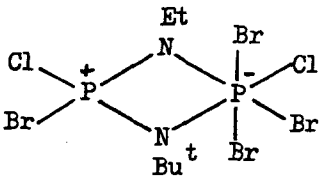


(ionic form)

$[X = Cl \text{ or } Br]$

(20f)

When the reaction was repeated with 2 mole equivalents of bromine, the product was a fine white powder which had phosphorus shifts of 33.6 and -153.2. The ^{31}P shifts suggest that it probably has a zwitterionic structure such as (22c), although the relative positions of the chlorine and bromine atoms are not established.

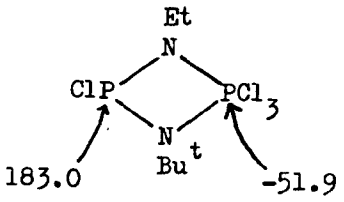


(22c)

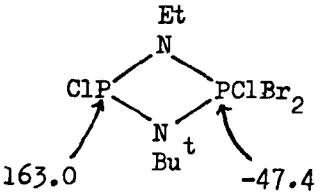
It appears that the products of the reaction of two mole equivalents of chlorine or bromine with $\overline{ClP.NEt.PCl.NBu^t}$ (1r) and $\overline{ClP.NMe.PCl.NBu^t}$ (1s) are zwitterionic. The zwitterions could be formed via a covalent intermediate with two five-coordinated phosphorus atoms which undergo rapid rearrangement. By analogy with $(Cl_3PNR)_2$ (R = Me,Et)[167,171], such a product could be expected to have a phosphorus shift at approximately -80, but so far no such signal has been observed from these reactions.

Comparison of the ^{31}P n.m.r. shifts of the products of reactions of (1r) with 1 mole equivalent of halogen (20a, b and c), with the products of the reactions with 2 mole equivalents of halogen (22a and c) suggest that compounds (20) are covalent in nature at least in methylene chloride or deuterochloroform solution.

From one mole equivalent reaction :

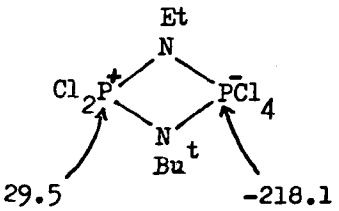


(20a)

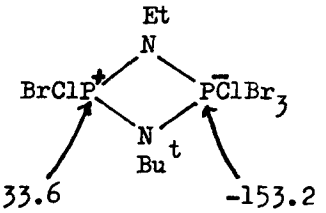


(20c)

From two mole equivalent reation :



(22a)



(22c)

Fig. 3.2.

Comparison of the ^{31}P n.m.r. Shifts of the Products of the Reactions of cis ClP.NEt.PCl.NBu^t(1r) with One and Two Mole Equivalents of Halogen (chlorine and bromine).

In compounds (20a and c) the ^{31}P shifts of -51.9 and -47.4 suggest that they are from five coordinated phosphorus (see Tables 3.3 and 3.6) rather than phosphonium species $\equiv P^+$ (typical shift -55)

Table 3.3. ^{31}P n.m.r. Shifts of $(RN{=}PCl_3)_2$ [167].

R	δ_P (ppm)
Me	-78.2
Et	-78.8
Pr	-78.7
Bu	-79.3
Ph	-80.2
Am	-78.4

Marchenko and coworkers[152] have suggested that the intermediate product of the reaction of chlorine with tris(dialkylamino) phosphines is a phosphonium salt, see Reaction 3.1 page 103 In that case the amino groups would be able to affect conjugative stabilisation of the phosphonium ions, see fig. 3.3.

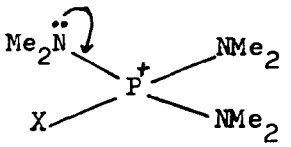


fig. 3.3.

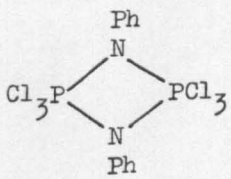
It is not unreasonable to assume that since the reaction of cyclodiphosph(III)azanes with one mole equivalent of halogen produces a covalent product, the corresponding reaction with two mole equivalents may also produce a covalent product, at least initially. This covalent product would then undergo rearrangement (either intra- or intermolecular) to give the zwitterionic products described above.

This process may be encouraged by any excess halide present in the reaction mixture. It should be recalled that phosphorus pentahalide can disproportionate as shown in reaction 3.4 [162].

$$2\ PCl_5 \rightleftharpoons P^+Cl_4 + P^-Cl_6 \qquad \text{.....3.4}$$

This ionic dissociation is encouraged by polar solvents, and in the solid state.

By contrast, the reaction of excess chlorine with (1a), 2,4-dichloro-1,3-diphenylcyclodiphosph(III)azane, gave a fine white crystalline powder, m.p. 138° - 141°C with ^{31}P n.m.r. shift of -79.8. This product was the known cyclodiphosph(V)azane, $(Cl_3PNPh)_2$ (8c) [162,167].

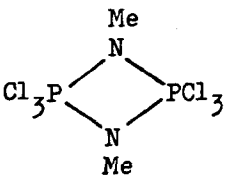


(8c)

There was no indication of any zwitterion formation in this case. The stability of this covalent compound relative to a zwitterionic species may be related to the greater electron withdrawing power of the phenyl groups. This has a stabilising effect on the compound and it hinders the formation of ionic groups. The bulky t-butyl group will also have a destabilising effect on the analogous t-butyl compound, $Cl_3P{=}Bu^t$, which is found as a monomer in preference to a dimeric form.

3.2b. Reaction of halogens with acyclic phosph(III)azanes.

When dry chlorine gas was bubbled through a solution of bis(dichlorophosphino) methylamine, $(Cl_2P)_2NMe$ (27a) in methylene chloride solution, there was an exothermic reaction, and colourless crystals were deposited which proved soluble in larger quantities of methylene chloride. The ^1H and ^{31}P n.m.r. spectra of the crystals in deuteriochloroform solution gave a triplet and heptet respectively. The high field ^{31}P shift of the heptet δ_P =-78.9 suggested that the compound contained five coordinated phosphorus and the n.m.r. parameters are similar to those reported for $(Cl_3PN.Me)_2$, (8a) [167,172] (δ_P =-78.2). Traces of PCl_5 were also found.



(8a)

This identification was confirmed by microanalytical and melting point data. Small quantities of phosphorus pentachloride were also identified in the reaction products (broad signal, δ_P = 81).

The formation of (8a) was followed by n.m.r. examination of the reaction mixture immediately after chlorination at ambient temperature, and at -78°C. The $^{31}P-\{^1H\}$ n.m.r. spectrum obtained after the ambient temperature reaction showed singlets at 219.5 (phosphorus trichloride) 160.2 (unreacted starting material), -78.9 (8a) and a product at -45.5.

This latter signal gradually decreased in intensity as (8a) increased and this with ^{1}H coupling, was shown to be a 1:3:3:1 quartet. This quartet was related to a doublet in the ^{1}H spectrum with the same spin coupling. It is believed that the signal at $\delta_P = -45.5$ is from the previously unidentified monomeric phosphazane, $Cl_3P{=}{=}NMe$ (28a). Its ^{31}P shift is observed to move upfield with increasing temperature, ca. 10 ppm/100°C. Some similar PPP-trichloro-N-alkylmono-phosphazanes, $Cl_3P{=}{=}NR$ have been previously isolated[173], but only where R is a branched alkyl group, or contains electron withdrawing substituents such as halogen atoms. The ^{31}P shifts of some of these N-alkyl compounds are noted in Table 3.4.

Table 3.4. ^{31}P shifts for phosph(V)azenes, $Cl_3P{=}{=}NR$.

R	δ_P (ppm)	Ref.
Bu^{sec}	-38.7 *	174
Bu^{t}	-88.4	48
CEt_3	-98.0	48
$CHEt_2$	-76.5	48
$CHPr_2$	-80.3	48

* The shift of -38.7 for $Cl_3P{=}{=}NBu^{s}$ has been questioned [48].

The fact that the shifts of these monomeric species are close to those reported for the dimers $(Cl_3PNR)_2$ (R = Me (8a), Et (8d), Pr^{n} (8e)), see Table 3.5 might, at first sight, raise some doubts regarding this assignment for $Cl_3P{=}{=}NMe$ (28a) and the analogous ethyl (28b) and propyl (28c) derivatives.

However, it should be noted that increasingly bulky R-substituents result in pronounced upfield shifts and this has been attributed to an opening of the P═N̂—C angle [173]. The shifts attributed to the monomers (28a - c), also follow this trend. The monomer $ClP_3{=}NBu^t$ has been re-prepared and its ^{31}P shift of -85.7 is in reasonable agreement with the literature value of -88.4 [48]. Its ^{31}P shift does not seem particularly sensitive to changes of halocarbon solvents, but it does undergo a low field shift of ca. 4 ppm on going from carbon tetrachloride to acetonitrile solution.

In the reaction of (27a) with chlorine at -78°C in deuteromethylene chloride solution a white solid was immediately formed. The reaction mixture was held at this temperature and the ^{31}P n.m.r. spectrum showed signals at 158.7 (27a) and an unidentified signal at 52.0.On increasing the temperature this latter signal broadened and moved upfield. As the temperature rose the white solid dissolved in the deuteromethylene chloride.On standing at ambient temperature for two hours the solution gave ^{31}P n.m.r. signals at -32 (28a), 219.0 (PCl_3) and -79.1 (8a) which appeared to have replaced the unidentified signal with a shift of 52 ppm.

The chlorination of $(Cl_2P)_2NEt$ (27b) was also carried out in deuteromethylene chloride at -78°C. In this case no immediate precipitate was formed, but two broad equal intensity signals appeared at -6 and -9 in the ^{31}P n.m.r. spectrum. At -103°C these signals broadened and moved to δp = 0 and -10. Traces of phosphorus trichloride were apparent. On raising the temperature to -53°C these two broad signals coalesced to a broad singlet at δp = -22 and the phosphorus trichloride signal increased in intensity.

At ambient temperature the ring compound $(Cl_3PNEt)_2$ (8d) slowly crystallised out. The monophosphazane $Cl_3P{=}NEt$, δ_P -44.6 was readily observed when the reaction was repeated at 0°C. Similarly chlorination of $(Cl_2P)_2NPr^n$ (27c) at 0°C gave $Cl_3P{=}NPr^n$ (28c) (δ_P = -22.8) and the cyclodiphosph(V)azane $(Cl_3PNPr^n)_2$ δ_P -79.1.

In all these reactions other unidentified ^{31}P n.m.r. signals were observed in the region δ_P 0 to 50, though these generally constituted less than 10% of the total signal intensity.

The above result may be summerised as shown in reaction (3.3);

$$(Cl_2P)_2NR + Cl_2 \longrightarrow \text{"X"} \longrightarrow \underset{(8)}{\text{cyclodiphosphazane}} \qquad .....(3.3)$$

The identity of the intermediate(s) "X" is still unresolved, but immediately prior to the formation of (8) there will be the monomer $Cl_3P{=}NR$. Results obtained from the reaction of $(Cl_2P)_2NEt$ with chlorine at low temperature suggests that there is an intermediate containing at least two different types of phosphorus atom. The shifts obtained exclude the possibility that it is $Cl_2PNR.PCl_4$ since tervalent phosphorus would give much lower field signals. The insolubility of this unknown suggests that it is a more polar or ionic species such as $Cl_2PNR.P^+Cl_3\ Cl^-$ or $Cl_4PNR.P^+Cl_3\ Cl^-$. The unidentified intermediate(s) require to be capable of eliminating phosphorus trichloride to give the monomer (28).

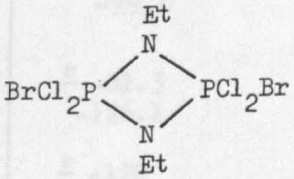
The ^{31}P n.m.r. shifts of the few known PX_4^- species cover a wide range generally to high field of analogous PX_3 compounds[176].

Qualitative observations on the rate of dimerisation of $Cl_3P{=}{=}NMe$ (28a) showed that the rate increased as the temperature was raised from 0°C to ca.25°C, although it is possible that at elevated temperatures dissociation might again be favoured. In view of these findings, it is not surprising that monophosphazenes $Cl_3P{=}{=}NR$(R = Me,Et,Pr) (28a - c) have not been previously identified. Their synthesis is usually accomplished by the reaction of alkylammonium chloride with phosphorus pentachloride in sym-tetrachloroethane solution (b.p. 144°C)[177]. All attempts to trap out $Cl_3P{=}{=}NMe$ (28a) with pyridine were unsuccessful, dimerisation was again favoured over reaction with this base. A feature of the ^1H n.m.r. spectra of (28a - c) is the very large PNCH spin coupling constants, see Table 3.5; they are the largest known of this type. Usually PNCH spin couplings lie in the range 10 - 20 Hz.

Although no ^{14}N spin coupling effects were apparent, the possibility that some of the broadening effects observed in the ^{31}P n.m.r. spectra of (28) and of "X" arise from the quadrupolar nature of the ^{14}N nucleus cannot be excluded.

The reactions of $(Cl_2P)_2NR$,(R = Me,Et) with bromine at 0°C were also studied. In both cases the addition of two mole equivalents of bromine to a methylene chloride solution of $(Cl_2P)_2NR$ appears to lead to the formation of the appropriate cyclodiphosph(V)azanes (8a and 8d). The monomeric intermediates (28a and b) were also observed soon after mixing the reactants, and when R = Et a triplet at δ_P = -66.3 was also observed.

The position and multiplicity of this latter signal is consistent with the formation of a monophosphazane, $BrCl_2P{=}{=}NEt$ (28d). The ^{31}P n.m.r. spectra of the reaction mixtures showed that small traces of a second product with two spin coupled signals was also formed δ_P -81.3 and -126.1 with P-P coupling of ca. 114 Hz. Since the ^{31}P shifts of these signals were close to the signal from 8f * it seems probable that they arise from an analogous compound such as $Cl_3\overline{P.NEt.PCl_2Br.NEt}$. (8q). However, there were insufficient proportions of this product to allow its isolation. The phosphorus halide ^{31}P n.m.r. signals showed that all members of the series $PCl_{3-n}Br_n$ (n = 1 - 3) were present in the reaction mixtures with the brominated species predominating. A very weak singlet, δ_P -128 may well come from a symmetric mixed halide (8h).



(8h)

* (8f) = $Cl_3\overline{P.NBu^t.PCl_2Br.NBu^t}$

Table 3.5. ^{1}H and ^{31}P n.m.r. data for some monophosphazanes and some cyclodiphosph(V)azanes.[a]

Compound	δ_P (ppm)	δ_{NCH_2} (ppm)	$J_{(PNCH)}$ (Hz)
$Cl_3P{=}NMe$	-45.4	2.98	44.0
$Cl_3P{=}NEt$	-47.8 [b]	3.40	45.3
$Cl_3P{=}NPr^n$	-57.4	3.35	41.6
$Cl_3P{=}NBu^t$	-85.7 [c]	-	-
$BrCl_2P{=}NEt$	[e] -66.3 [d]	-	46.8
$(Cl_3PN.Me)_2$	-78.9	2.98	20.4
$(Cl_3PN.Et)_2$	-79.2	3.50	29.5
$(Cl_3PN.Pr)_2$	-79.1	3.30	30.2
$(Cl_3PN.Ph)_2$	-79.8	-	-
$BrCl_2P.NEt.PCl_3.NEt$	[e] -81.3 -126.1	-	(J_{PNP} ca.114 Hz)
$(BrCl_2PN.Et)_2$	[e] -128		

(a) $CDCl_3$ solution at ambient temperature unless otherwise stated

(b) CD_2Cl_2 at -20°C.

(c) CCl_4 solution, δ_P -82.1 and -84.8 in CH_3CN and C_6H_6 respectively.

(d) $CDCl_3$: CH_2Cl_2 (1:1) at -40°C.

(e) Identification of this compound is tentative.

Table 3.6 ^{31}P n.m.r. shifts of some cyclodiphosph(V)azanes and related zwitterions.

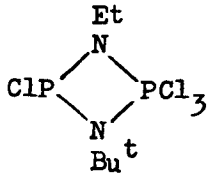
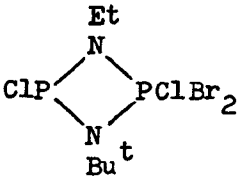
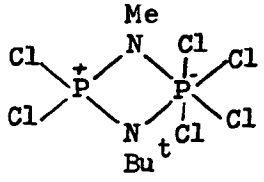
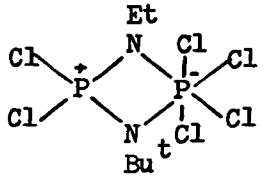
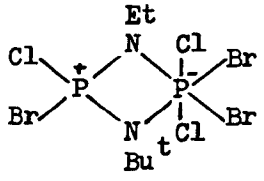
Compound	δ_P(ppm)	
	P(III)	P(V)
	183.3	-51.9
	163.0	-47.4
	P(+ve)	P(-ve)
	37.9	-206.2
	29.5	-218.1
	33.6	-153.2

Table 3.7 Microanalysis data for some phosphazanes.

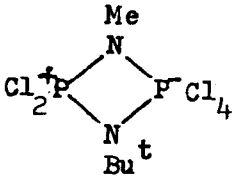
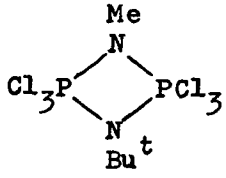
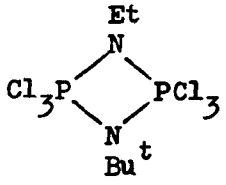
Compound	Expt. (%)			Theory. (%)		
	C	H	O	C	H	O
$(Cl_2P)_2NPr^n$	13.87	3.0	5.38	13.8	2.7	5.37
$(Cl_3PNMe)_2$	7.3	1.4	8.45	7.2	1.8	8.4
$(Cl_3PNPr^n)_2$	18.6	3.9	7.02	18.7	3.7	7.3
	15.85	3.61	7.7	16.0	3.2	7.5

Table 3.8 Mass spectroscopy data for some phosphazanes.

Compound	m/e†	
	Expt.	Theory.
$(Cl_2P)_2NPr^n$	259	259
$(Cl_3PNMe)_2$	330	330
$(Cl_3PNPr^n)_2$	386	386
	372	372
	386	386

†, calculated for ^{35}Cl species.

3.3 Experimental.

Bis(dichlorophosphino)-n-propylamine.

Phosphorus trichloride (115g, 0.84mol) and n-propylamine hydrochloride (20.0g, 0.21mol) were mixed in sym-tetra - chloroethane (300ml) and boiled under reflux for 6 days. Removal of the solvent revealed a dark-brown oil, a part of which was purified by distillation under reduced pressure to give bis(dichlorophosphino)-n-propylamine (8.2g, 15%), a colourless liquid b.p. = 50°C (at 0.005 mm Hg). See Table 3.7 for microanalysis data.

Bis(dichlorophosphino)methylamine and bis(dichlorophosphino) ethylamine were prepared using the literature method[178].

Reaction of bis(dichlorophosphino)methylamine with chlorine.

Chlorine, dried over P_2O_5, was passed through a solution of bis(dichlorophosphino)methylamine (0.5g, 1.97mmol) in methylene chloride (5ml) at 0°C until the solution turned yellow. A similar reaction at ambient temperature was very exothermic. On standing at ambient temperature the solution deposited colourless crystals of 2,2,2,4,4,4-hexachloro-1,3-dimethylcyclodiphosph(V)azane, $(Cl_3PNMe)_2$, (0.42g, 58%) m.p. 160-167°C (c.f. lit.[46] m.p. 160°C). ^{31}P n.m.r. spectroscopy showed that the major component of the remaining solution was phosphorus trichloride, δ_P 218.3. Similar results were obtained by quantative addition of chlorine to bis(dichloro phosphino)methylamine in which chlorine was measured using a vacuum line.

Attempts to trap the intermediate phosphazene, $Cl_3P{=}NMe$, by the addition of pyridine to the reaction mixture were unsuccessful, the dimer, $(Cl_3PNMe)_2$, was again formed. However when the reaction was followed in an n.m.r. tube, ^{31}P n.m.r. spectroscopy gave a shift at δ_P -45.5 which was shown to be the intermediate phosphazene.

Reaction of bis(dichlorophosphino)methylamine with bromine.

Bromine (0.69g, 4.3 mmol) in methylene chloride (3ml) was added dropwise to a stirred solution of bis(dichloro phosphino)methylamine (1.0g, 4.3mmol) in methylene chloride (5ml) at 0°C. On standing 2,2,2,4,4,4-hexachloro-1,3-dimethyl cyclodiphosph(V)azane (0.69g, 48%) crystallised out and was identified by m.p. and ^{31}P n.m.r. chemical shift. The reaction mixture also contained ca. 10% of a product with a ^{31}P n.m.r. spectrum consisting of two doublets, δ_P -80.4, -123.6 ; J_{PNP} = 95Hz., believed to be a cyclodiphosph(V)azane analogous to that above, but containing chlorine and bromine; it was not isolated. The phosphorus(III) halides, PCl_3, PCl_2Br, $PClBr_2$ and PBr_3 (δ_P 218.5, 223.4 226.5 and 227.8 respectively, ratio ca. 1:3:4:3.) were also present.

As with the analogous reaction with chlorine, a phosphazene intermediate, $Cl_3P{=}NMe$, δ_P -45.5, was observed in the ^{31}P n.m.r. spectrum but could not be isolated.

Reaction of bis(dichlorophosphino)ethylamine with chlorine.

Dried chlorine was bubbled through bis(dichloro phosphino)ethylamine (2.15g, 8.1mmol) in methylene chloride (50ml) at 0°C until the solution turned yellow, and then left to sit overnight at ambient temperature. The solvent

was then reduced in volume to ca. 15ml, and from which was deposited small elongated colourless crystals of 2,2,2,4,4,4-hexachloro-1,3-diethylcyclodiphosph(V)azane, $(Cl_3PNEt)_2$, (0.98g 60%)[46] m.p. 130°C. Phosphorus trichloride was again found as a minor product. The intermediate phosphazene, $Cl_3P{=}NEt$, was observed in the ^{31}P n.m.r. spectra (δ_P -47.8) in the reaction mixture at -20°C but it could not be isolated.

Reaction of bis(dichlorophosphino)ethylamine with bromine.

Bromine (0.65g, 4.0mmol) in methylene chloride (3ml) was slowly dropped into a stirred solution of bis(dichlorophosphino) ethylamine (1.0g, 4.2mmol) in methylene chloride (5ml) at 0°C. On standing, colourless crystals of 2,2,2,4,4,4-hexachloro-1,3-diethylcyclodiphosph(V)azane, $(Cl_3PNEt)_2$, (0.29g, 40%), m.p. 130°C. were formed. As in the reaction with bis(dichlorophosphino)methylamine, traces of phosphorus trihalides, PCl_3, PCl_2Br, $PClBr_2$ and PBr_3 were found. ^{31}P n.m.r. spectroscopy gave shifts which have been tentatively assigned to mixed halide derivatives of $(Cl_3PNEt)_2$, δ_P -81.3, -126.1, J_{PNP} = 114Hz for a pentachloro-monobromo derivative, and δ_P -128.0 for a sym-tetrachlorodibromo derivative, both of which constitute less than 20% of the main hexachloro- product. The ^{31}P n.m.r. shift δ_P -66.26, J_{PNCH} =46.8Hz has tentatively been assigned to the intermediate phosphazene $BrCl_2P{=}NEt$.

Reaction of bis(dichlorophosphino)-n-propylamine with chlorine.

Dried chlorine was bubbled through bis(dichlorophosphino) -n-propylamine (0.5g,1.78mmol) in light petroleum, b.p. 40°-60°C, (3 ml) and this immediately formed a white precipitate of 2,2,2,4,4,4-hexachloro-1,3-di-n-propylcyclodiphosph(V)azane (0.61g, 82.3%), m.p. = 104-108°C, δ_P -79.1.

Reaction of 2,4-Dichloro-1,3-di-t-butylcyclodiphosph(III)azane with chlorine.

Dry chlorine was bubbled slowly, for 20 minutes, through a rapidly stirred solution of 2,4-dichloro-1,3-di-t-butylcyclo diphosph(III)azane (0.45g, 1.6mmol.) in methylene chloride (5ml) at ambient temperature. After only 5 minutes the solution had a strong yellow colour due to undissolved chlorine. The solvent was then removed to give a cloudy oil (b.p. = 85°C at 0.02mmHg). ^{31}P n.m.r. spectroscopy of this oil showed it to contain 3 main products -

(i) a singlet δ_P 27.9

(ii) a pair of doublets δ_P 10.8, 8.1 ; J_{PNP} = 38.5Hz

(iii) a pair of doublets δ_P -2.14, -9.81 ; J_{PNP} = 27.9Hz

Only this last product has been positively identified as $Cl_2P(O)N{=}PCl_2N(H)Bu^t$ [16], by the addition of some known compound to the ^1H n.m.r. spectroscopy sample.

When the reaction was repeated and followed by ^1H n.m.r. spectroscopy, the reaction was seen to have gone to completion within 5 minutes. A second re-run of the reaction was carried out with the solution at 0°C and the chlorine bubbled through for 5 minutes until the solution was seen to just start to turn yellow. This, however, made no difference to the result.

The reaction was repeated by the addition of chlorine (0.2g., 2.8mmol)to 2,4-dichloro-1,3-di-t-butylcyclodiphosph(III) azane (0.76g, 2.76 mmol) in deuterated methylene chloride (2ml), on a vacuum line at -78°C, and allowed to stand for 15 minutes. ^1H-$\{^{31}P\}$ n.m.r. spectroscopy of the product solution showed it to contain predominantly unreacted starting material. However doublets which gave phosphorus shifts of -51.9 and 183.3 from double resonance experiments, were observed. The former

shift is possibly from a phosphorus(V) atom but there was no clear identification of the products since they appear to readily decompose.

When this latter experiment was repeated using chlorine (0.1g, 1.4 mmol) and 2,4-dichloro-1,3-di-tert-butylcyclodiphosph(III)azane (0.2g, 0.73 mmol) the ^{1}H n.m.r. spectrum gave a small triplet, J_{PH} = 4.0Hz at δ_H 1.42. This gave, from a double resonance experiment, a phosphorus shift of -40.2. This is of the right order to be from a monomeric species $Cl_3P{=}{=}NBu^t$ but this could not be confirmed.

Reaction of 2,4-Dichloro-1,3-di-t-butylcyclodiphosph(III)azane with bromine.

Bromine (0.46g, 2.9mmol) was slowly added dropwise to a rapidly stirred solution of 2,4dichloro-1,3-di-t-butylcyclodiphosph(III)azane (0.77g, 2.8mmol) in methylene chloride (5ml), giving an exothermic reaction. The reaction solution, when examined by ^{31}P n.m.r. spectroscopy, was shown to contain large quantities of decomposition material. However two compounds were identified, these being phosphorus tribromide, δ_P 226.1 (15%) and 2,4-dibromo-1,3-di-tert-butylcyclodiphosph(III)azane, δ_P 223.8 [38] (5%), but these compounds could not be isolated. When the reaction was repeated with excess bromine no cyclodiphosph(III)azane product could be identified.

The main product obtained with both 1 mole equivalent and excess bromine has a ^{31}P n.m.r. shift of 27.6, and this accounts for approximately 50% of the product material, but it remains unidentified.

Reaction of 2-cis-4-bisdimethylamino-1,3-di-t-butyl cyclodiphosph(III)azane with bromine and chlorine.

Bromine (0.43g, 2.7mmol) in methylene chloride (10ml) was slowly added dropwise to a rapidly stirred solution of 2-cis-4-bisdimethylamino-1,3-di-t-butylcyclodiphosph(III)azane (0.8g, 2.7mmol) in methylene chloride (20ml) at ambient temperature. This produced an exothermic reaction. No precipitate was formed, the solution remained clear. When the solvent was removed, a white solid (m.p. 73-80°C) was obtained (0.8g).

The ^{1}H n.m.r. spectrum of the white solid product showed three doublets, ratio 2 : 1 : 1, with ^{1}H shifts of 3.2, 2.85, and 2.67 respectively and J_{PNCH} of 14.25Hz, 16.3Hz and 4.4Hz respectively Double resonance experiments gave the associated phosphorus shifts of 1.0, 84.3, and 84.4 respectively. This spectrum is consistent with, but not proof of, an ionic species $Me_2N.PNBu^tP^+NMe_2(Br)NBu^t$, Br^- . The product has strong hygroscopic properties and decomposed before microanalysis could be obtained. The mass spectrum did not show any indication of the theoretical parent ion m/e = 452, nor of m/e = 372 (-the loss of Br).

When the experiment was repeated using two mole equivalents of bromine a fine precipitate was formed immediately but it rapidly decomposed and consequently no product could be identified.

Analogous reactions of 2,4-bisdimethylamino-1,3-di-t-butyl cyclodiphosph(III)azane (1.0g, 3.4mmol) with 1 mole equivalent, 2 mole equivalents and excess dry chlorine gave no identifiable products. Decomposition appears to have occurred.

Reaction of 2,4-dichloro-1-ethyl-3-t-butylcyclodiphosph(III)azane with chlorine.

A slight excess of dry chlorine was bubbled through a solution of 2,4-dichloro-1-ethyl-3-t-butylcyclodiphosph(III)azane (2.47g, 10.0mmol) in methylene chloride (20ml) at ambient temperature for 8 minutes. A ^{1}H n.m.r. spectrum of this solution showed that the majority of the starting material had remained unreacted. Additional dry chlorine was bubbled through the solution for a further 10 minutes. The ^{31}P n.m.r. spectrum of this solution showed a strong sharp singlet at δ_P 33.5. The experiment was repeated and the $^{31}P-\{^{1}H\}$ n.m.r. spectrum gave two large signals at 29.5 and -218.1, J_{PNP} = 107.7Hz. This is believed to come from a zwitterion, $Cl_2\overline{P^{+}.NEt.P^{-}Cl_4}.NBu^{t}$. The infrared spectrum of this product showed peaks at 603 and 540cm^{-1} corresponding to that expected for a Cl—P(4 coordinated) bond. The product could not be isolated, since it underwent a slow decomposition. The parent ion was not identified in the mass spectrum and microanalysis data was not acceptable.

Attempts at recrystallisation from dry light petroleum (b.p. = 40-60 °C) did give flat, plate-like, colourless crystals (m.p. 65-70 °C). The suspected zwitterion was formed initially in approximately 80% yield. In all cases the ^{1}H and ^{31}P n.m.r. spectra showed evidence of decomposition.

Reaction of 2,4-Dichloro-1-methyl-3-t-butylcyclodiphosph(III)azane with chlorine

Excess dry chlorine was bubbled through a solution of 2,4-dichloro-1-methyl-3-t-butylcyclodiphosph(III)azane (0.5g, 2.1mmol.) in 50ml of light petroleum (b.p. = 40-60°C). This immediately caused the precipitation of a fine white solid. This was recrystallised from light petroleum (b.p. = 40-60°C) to yield some fine colourless, needle-like crystals. However they very rapidly decomposed to give a pale yellow wax-like product. The experiment was repeated but the initial precipitate was not recrystallised in an attempt to lessen decomposition. $^{1}H-\{^{31}P\}$ n.m.r. spectroscopy gave a triplet at δ_H 3.13 which decoupled to give δ_P 37.9 and -206.2, thus suggesting the presence of a zwitterionic product. Other ^{1}H n.m.r. signals were obtained at δ_H 1.4 and 1.5, and were of comparable intensity to the suspected zwitterion product. Recrystallisation resulted in the disappearance of the triplet at 3.13 and a marked increase in the signal at 1.40.

The ^{31}P n.m.r. spectrum gave a very large singlet at δ_P -36.8 ; this remains unidentified.

The parent ion m/e = 375 was not observed in the mass spectrum, but the microanalysis did support the evidence for a zwitterion. The infra-red spectrum run immediately after the reaction was carried out did show a peak at 595cm^{-1} which corresponds to the region expected for a Cl—P(4 coordinate) bond.

Reaction of 2,4-Dichloro-1-ethyl-3-t-butylcyclodiphosph(III)azane with bromine

Bromine (2.0g, 12.5mmol) in 15ml light petrol (b.p. = 40-60°C) was slowly added to 2,4-dichloro-1-ethyl-3-t-butylcyclodiphosph (III)azane (1.6g, 6.1mmol) in 30ml light petrol (b.p. = 40-60°C) while rapidly stirred under a nitrogen atmosphere. This immediately produced a white precipitate and this quickly turned to a thick oily deposit.

The $^{1}H-\{^{31}P\}$ n.m.r. spectrum gave a doublet of doublets from which double resonance experiments showed δ_P at 33.6 and -153.2. Decomposition, however, resulted in no related signals being detected in the ^{31}P n.m.r. spectrum. However a signal at δ_P 225.9 was found and this suggests that the decomposition material includes a mixed halide, PCl_2Br. Decomposition proved to be too rapid for mass spectroscopy or microanalysis.

2,2,2,4,4,4-Hexachloro-1,3-diphenylcyclodiphosph(V)azane

2,4-Dichloro-1,3-diphenylcyclodiphosph(III)azane (0.25g, 0.82mmol) was dissolved in 25ml of light petrol (b.p. = 40-60°C) and an excess of chlorine gas was bubbled through the solution. A white precipitate was immediately formed. ^{31}P n.m.r. spectroscopy showed this precipitate to have a singlet δ_P -79.8. Its identity was confirmed by the addition of a trace of known 2,2,2,4,4,4-hexachloro-1,3-diphenylcyclodiphosph(V)azane to the sample, see also Table 3.5

Chapter 4.

Formation and reactions of cage and bridged phosphazanes.

4.1. Introduction.

In the formation of cyclophosphazanes, the ring size is largely determined by the steric bulk of the N-alkyl substituents. Sterically bulky groups such as t-butyl readily form dimeric rings. However, small groups such as ethyl do not give dimers in any quantity but have been shown to give rise to various products [27].

$$PCl_3 + 3\ MeNH_2 \longrightarrow (Cl_2P)_2NMe + P_4(NMe)_6$$

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

$$PCl_3 + RNH_2 \longrightarrow (ClPNR)_2 \quad (R = Pr^i,\ Bu^t)$$

In the reaction of $EtNH_2$ and PCl_3, Keat and Nixon showed that the trimer $(ClPNEt)_3$ was present in low yield [30]. A convenient route to the formation of cyclotriphosph(III)azanes is the reaction of $(Me_3Si)_2NMe$ and PX_3, (X = Cl or Br)(1.8) Abel and coworkers claimed that the analogous reaction using $(Me_3Si)_2NEt$ gave $(ClPNEt)_3$ [29] but this could not be substanciated by Nixon et al. in later work [27,179].

A number of groups have also produced larger cage and fused ring compounds, the first from Holmes in 1961 [6], who reported an adamantane structure for $P_4(NMe)_6$ (4) from PCl_3 and $MeNH_2$. Other work has been carried out by Zeiss and coworkers [42] who have also isolated a related cage compound with a direct P-P bond (6). Zeiss has also studied [5,41] possible conformations of the fused ring and six-membered ring compounds, and this will be discussed later in this chapter.

4.2. Results and Discussion.

4.2a. Synthetic Methods.

It has been shown that the reaction of ethylamine hydrochloride with phosphorus trichloride in refluxing sym-tetrachloroethane solution produces bisdichlorophosphinoethylamine $(Cl_2P)_2NEt$, in reasonable yields (ca. 30%) [178].

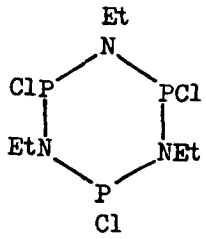
$$2\ PCl_3 + EtNH_3Cl \longrightarrow (Cl_2P)_2NEt + 3\ HCl \qquad \text{.....4.1}$$

During this study, attempts to prepare the latter compound gave a quantity of a residual dark brown oil. When this oil was distilled under reduced pressure, and the distillate crystallised from light petroleum, a pure sample of the cyclotriphosph(III)azane , $(ClPNEt)_3$ (2d), was obtained. This new compound was identified by elemental analysis, mass spectroscopy and ^1H and ^{31}P n.m.r. spectroscopy. It was reported to be formed along with $(ClPNEt)_4$ as an oil by the reaction of phosphorus trichloride with $(Me_3Si)_2NEt$ [28], but clearly a pure sample was not obtained. It was subsequently shown in related work that the ring compound (2d) can be obtained in good yield with a 1:1 mole ratio of ethylamine and phosphorus trichloride[27], see Reaction 4.2

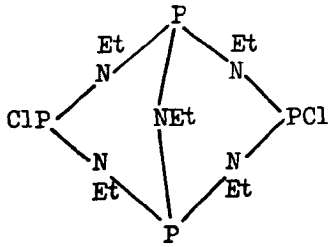
$$3PCl_3 + 3EtNH_2 \longrightarrow \underset{\text{(2d)}}{(ClPNEt)_3} + 6HCl \qquad \text{.....4.2}$$

This suggests that phosphorus trichloride may have been lost from the reaction mixture in the attempt to prepare $(Cl_2P)_2NEt$. These observations led to attempts to prepare other cyclodiphosph(III)-azanes and the bicyclic compound $P_4(NEt)_5Cl_2$, (4a), was obtained, see Reaction 4.3. Purification in this latter case was by recrystallisation alone.

$$4\ PCl_3 + 5\ EtNH_3Cl \longrightarrow \underset{(4a)}{P_4(NEt)_5Cl_2} + 15\ HCl \qquad \text{.....4.3}$$

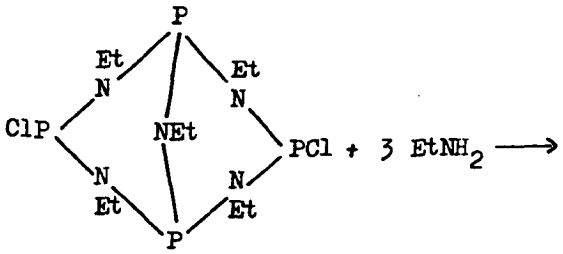


(2d)

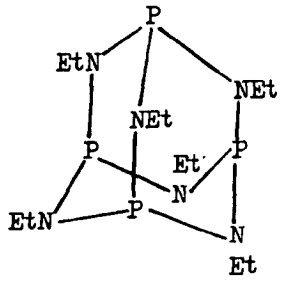


(4a)

Attempts to produce the cage compound $P_4(NEt)_6$, (4c), by this method were unsuccessful, the reaction gave a mixture of the bicyclic compound (4a) and decomposition products ca. 25%. The cage compound (4c) was later successfully prepared by the reaction of (4a) with ethylamine.



$+\ 3\ EtNH_2 \longrightarrow$



$+\ 2\ EtNH_3Cl$

(4a) (4c) 4.4

Minor components ($\sim$ 10%) of the reaction mixture obtained from the synthesis of (2d) gave ^{31}P n.m.r. signals at δ_P 228.0, 145.4, 139.4 and 2.8. The former signal appears to be from cyclodiphosph(III)-azanes, $(ClPNEt)_2$; Lit.[28], δ_P = 227.3, although a pure sample could not be separated. The latter group of three signals, grouped together on the basis of their mutual spin coupling interactions, has been tentatively assigned to a monoxide of (2d). This is consistent with the fact that the same compound could be obtained, although not pure, by the reaction of (2d) with dimethylsulphoxide or oxygen.

The bicyclic compound (4a) can be converted to (2d) and finally to $(Cl_2P)_2NEt$ by refluxing with excess of phosphorus trichloride, although compounds (4a) and (2d) have not been detected in reaction mixtures of ethylamine hydrochloride and excess phosphorus trichloride. This suggests that (2d) and (4a) are more reactive towards phosphorus trichloride than ethylamine hydrochloride.

Attempts to carry out analogous reactions with methylamine hydrochloride were unsuccessful, the only product identified was the diphosphinoamine, $(Cl_2P)_2NMe$. The reason for this difference is not clear, but it is worth noting that the methylamine hydrochloride remains as a solid suspended in refluxing sym-tetrachlorethane, while ethylamine hydrochloride appears to form an oily liquid on the surface of the refluxing solvent. If $(ClPNMe)_3$ and $P_4(NMe)_5Cl_2$ are formed in the reaction, they undergo relatively rapid conversion to the diphosphinoamine $(Cl_2P)_2NMe$.

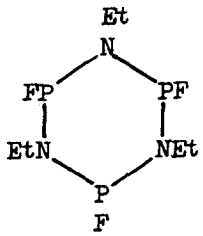
It was found that the cyclotriphosph(III)azanes could be obtained in low yields by prolonged heating of the diphosphinoamines, $(Cl_2P)_2NR$, R = Me or Et.

$$3\ (Cl_2P)_2NR \xrightarrow{\text{ca. } 150^\circ C} (ClPNR)_3 + 3\ PCl_3 \qquad (R = Me, Et) \qquad \ldots\ldots\ldots 4.5$$

The phosphorus trichloride evolved was used as a rough guide to the progress of the reaction. This reaction does not constitute a very useful method of synthesising cyclophosph(III)azanes, because of low yields and the ease of formation of solid orange unidentified decomposition products.

Compound (2d) was converted to the corresponding fluoride (2e) by reaction with antimony trifluoride in refluxing light petroleum solution.

$$(ClPNEt)_3 + SbF_3 \longrightarrow (FPNEt)_3 + SbCl_3 \qquad \ldots\ldots(4.6)$$



(2e)

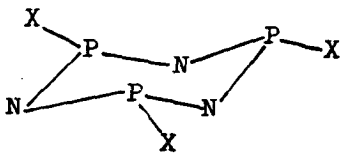
Attempted fluorination of the bicyclic compound (4a) gave a complex mixture of products. Distillation of this mixture under reduced pressure gave a clear oil which gave a series of ^{31}P n.m.r. signals consistent with the presence of two isomers of a fluorinated product (discussed later, see page 153)

Both (2d) and (4a) were readily hydrolysed by water, the reaction with the former being particularly violent.

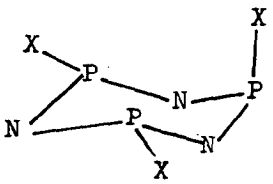
4.2b. Structure of Cyclotriphosph(III)azanes.

The structures of the compounds prepared in this study are of interest, particularly since they may be expected to reflect the conformational constraints of the phosphorus(III)-nitrogen bonds. In considering the solution structures of compounds (2d) and (4a) it is assumed that nitrogen has a planar, or near planar, distribution of bonds, and or a very low barrier to inversion. No crystal structures of cyclotriphosph(III)azanes have yet been reported, but the above assumption is justified in the case of the crystal structure of $(MePNMe)_4$ where the nitrogen atoms have an almost planar distribution of bonds [101]. The bonds to the nitrogen atoms linked to two tervalent phosphorus atoms do deviate significantly from planarity in the adamantane - like structure of $P_4(NMe)_6$ where the average sum of the bond angles at the nitrogen is 356° [100], and $P_4(NMe)_6MeI$ where it is 352° [180].

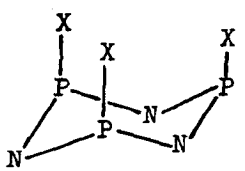
Assuming that (2d,e) and their derivatives are most likely to adopt a cyclohexane chair-type conformation, the structures shown in fig.4.1 show the possible arrangements for the phosphorus substituents, either axial or equatorial (N-ethyl groups omitted for clarity).



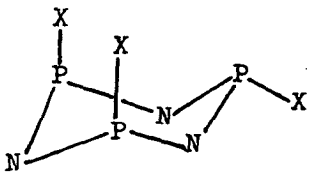
(e,e,e)



(a,e,e)



(a,a,a)



(a,a,e)

Fig.4.1

Since inversion of the cyclotriphosph(III)azane ring in solution is probably fast on the n.m.r. time-scale, a 2-cis-4-trans-6-trichloro-isomer ("trans" isomer) would represent a time average of conformers (a,a,e) and (a,e,e) and the 2-cis-4-cis-6-isomer would be represented by conformers (a,a,a) and (e,e,e). Steric considerations would suggest that (a,e,e) and (e,e,e) conformers might predominate, i.e. where 2, 4-axial-axial interactions are avoided. The ^{31}P n.m.r. spectra of both (2d) and (2e) showed that two forms were present in solution at ambient temperatures. In each case these spectra comprised a singlet and a doublet (relative intensity 2:1) with the latter predominating. These multiplets were further complicated by coupling to the fluorine in the case of (2e). The structures of these isomers must be cis and trans respectively. Unfortunately there is no easy means of distinguishing the possible conformers (fig.4.1), particularly since it is not clear how the solution state relates to any solid state structural information that may emerge. Addition of one mole equivalent of aluminium chloride to (2d) at ambient temperature collapses the three signals from cis and trans isomers into a broad signal at ca, δ_P 126. Presumably chloride ion exchange is promoted under these conditions and the formation of transient species containing the $>N-\overset{+}{P}-N<$ grouping would provide a mechanism for interconverting cis and trans isomers. Although the spectra did not sharpen at low temperatures, the broad signal at ca. δ_P 126 is at lower field than the mean of the cis and trans isomers. It is consistent with the presence of cationic species $=P^+$, which have very low field shifts [170].

On cooling, the ^{31}P n.m.r. signals from (2a) and (2d) sharpened and the proportion of the cis isomers increased. Spin coupling effects were also resolved in the trans isomer (Table 4.1).

The most likely reason for the broad ambient temperature spectra is chloride-ion exchange, since the activation energy for phosphorus inversion (typically $\sim$100 kJ mol) is clearly too high for this process to be feasible at sub-ambient temperatures. Consistent with these suggestions, the temperature dependence of the cis : trans isomer ratio in (2e) was very much less than for the analogous chloride (2d), phosphorus-chlorine bonds being more labile than analogous phosphorus-fluorine bonds.

The ^{31}P n.m.r. spectra of the bicyclic compound (4a) shows that there are two isomers present in solution. The major (symmetric) and minor (asymmetric) compounds give rise to A_2X_2 and AMX_2 spin systems respectively, the structures of which can be considered by reference to fig.4.6.

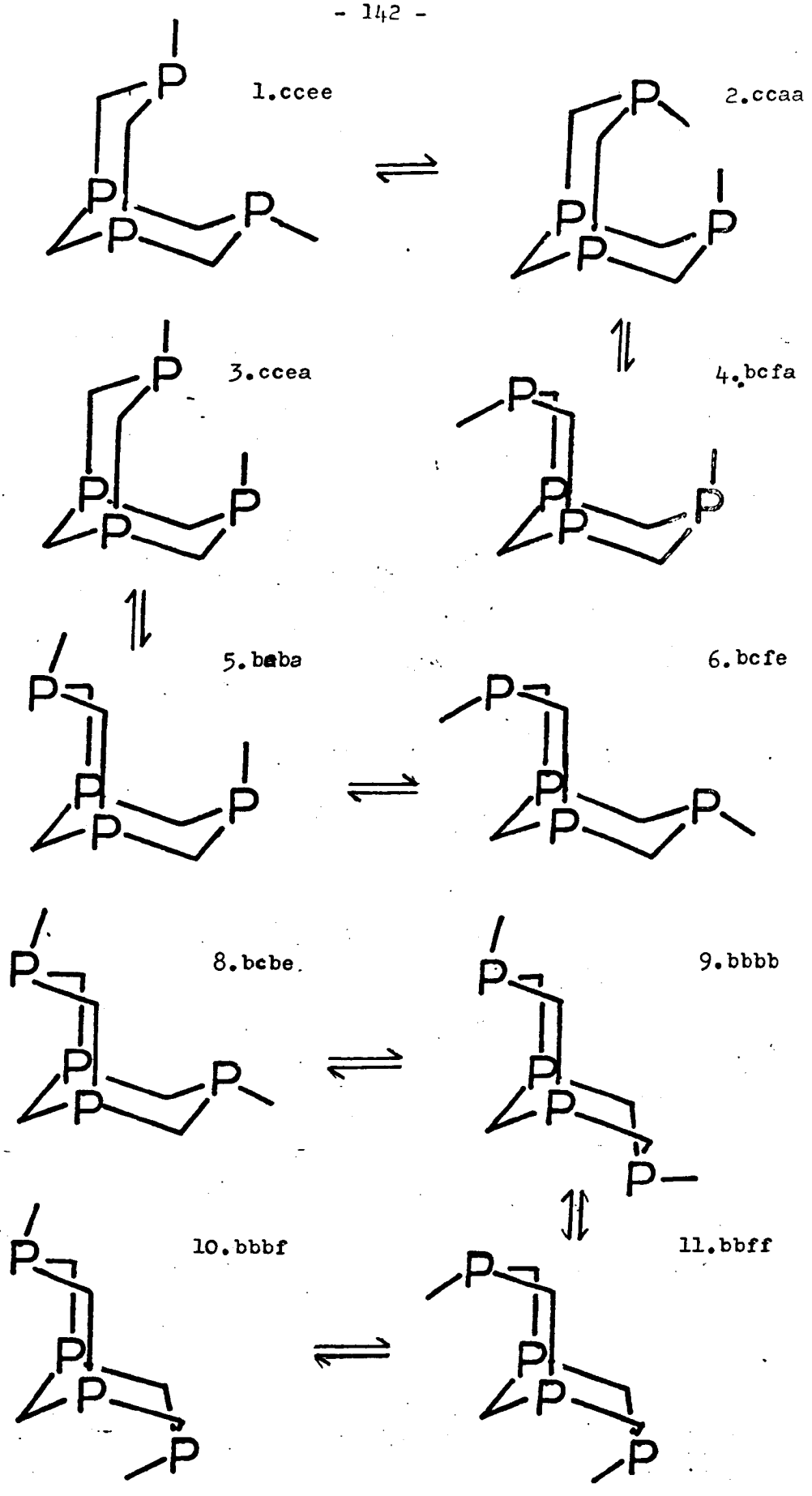
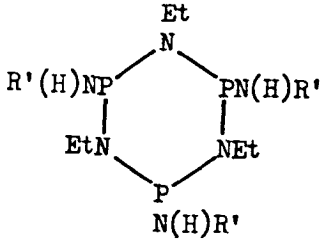


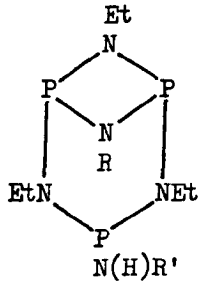
Fig. 4.6 Possible structures for compounds with P_4N_5 skeleton.

The isomers can be interconverted, for at low temperatures the proportion of that isomer giving rise to the A_2X_2 spin system increases. The compound can exist as a series of conformers which are analogous to those possible for bicyclo(3.3.1)nonanes. In the latter system the boat conformation becomes more probable than in the cyclohexane system because of the axial-axial interaction in conformers, analogous to that labelled (c,c,a,a)[180] . Since phosphorus is only three co-ordinated, the conformer (c,c,a,a) is unfavourable, but (c,c,e,e) cannot be excluded. If it is again assumed that ring inversion is fast on the n.m.r. time scale, then the interconversion processes shown are possible. Given that (c,c,a,a) is unlikely, the major isomer can have major contributions from conformers (c,c,e,e), (b,b,b,b) and (b,b,f,f). Any of the remaining conformers could make a significant contribution to the ^{31}P spectrum of the minor isomer.

4.2c. Reactions of cyclotriphosph(III)azanes.

Reaction of cyclotriphosph(III)azanes (2d) with primary alkylamines ($R'NH_2$, R = Et, Pr and Bu^t) gave substitution products (2f - h) and, unexpectedly, a series of bridged ring molecules (29a - c).





(2f, R' = Et

g, " = Pr

h, " = Bu^t)

(29a, R' = Et

b, " = Pr

c, " = Bu^t)

These products were identified by ^{31}P n.m.r. and mass spectroscopy. However, compounds of types (2) and (29) could not be separated by vacuum distillation or recrystallisation.

The reaction of ethylamine with (2d) gave mainly the substitution product (2f) and ca. 10% 'bridged' product (29a). There was also a trace of the adamantane cage molecule (4b) δ_P 79.3; this was confirmed by mass spectroscopy. However, with isopropylamine the product was mainly the bridged compound (29b) and only a trace (ca.15%) of the substituted ring (2g). The analogous reaction using tert-butylamine with (2d) gave products similar to the isopropylamine reaction. Reaction with methylamine gave a thick oil which contained a large number of unidentified products (^{31}P n.m.r.).

When heated at 90°C under nitrogen (1 hr.) the product of the reaction of (2d) and ethylamine, showed a marked increase in the amount of cage compound (4b). The proportion of (2f) also decreased relative to (29a). When heated to 90°C in a vacuum (3 hrs.) the reaction products from (2d) and ethylamine were nearly all converted to the cage compound (4b), except for a small amount of (29a) (ca.5%).

The ^{31}P n.m.r. spectra of (2f-h) showed that they were all trans isomers, the spectra each consisted of a doublet and a triplet, ratio 2:1 with phosphorus-phosphorus spin couplings of 12-14 Hz, see Table 4.1. The ^{31}P n.m.r. spectra (29a-c) gave a very low field doublet and a high field triplet, ratio 2:1. The very low field shift of the doublet is consistent with a trans isomer for a cyclophosph(III)-azane ring, as found with $(R_2NPNR')_2$ and is evidence for the presence of a dimer ring structure in the products (29a-c).

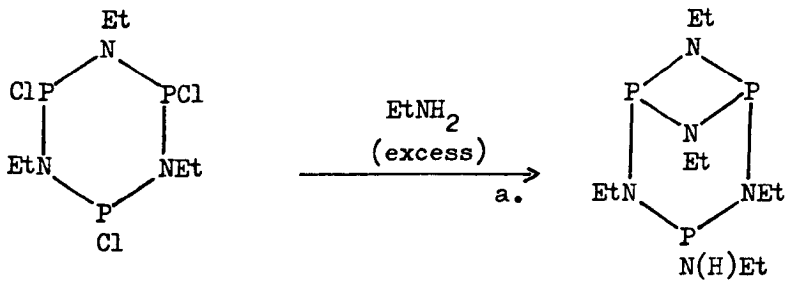
The products of the reactions of (2d) with alkylamines $R'NH_2$ are summarised in Table4.1. As the size of R' increases so the yield of the bridged product (29a-c) relative to the substituted ring compound (2f-h) increases.

Table 4.1: ^{31}P n.m.r. data for the products of the reaction of (2d) with alkylamines RNH_2 (R = Et, Pr^n, Bu^t).

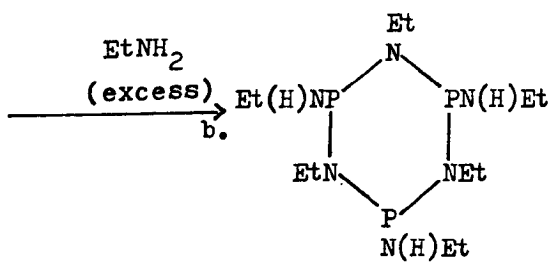
Compound	R	δ_P (ppm)	J_{PP} (Hz)
(2f)	Et	95.9, 107.1	13.8
(2g)	Pr	93.4, 104.2	<13.5
(2h)	Bu^t	92.8, 106.5	12.4
(29a)	Et	97.1, 206.0	5.2
(29b)	Pr	96.0, 199.4	4.0
(29c)	Bu^t	98.9, 201.1	4.0

The products of the reaction of (2d) and ethylamines show a solvent dependence. The work described above is based on the use of diethylether as solvent. When benzene was used as the solvent the cage compound (4c) was the principal product of the reaction at ambient temperature. When the reaction was repeated at higher temperature, ca.75°C, the main product was (2f), (ca.90%) and smaller quantities of (4c) and (29a), each of ~5%. At 0°C, the products from (2d) and ethylamine in methylene chloride solution were mainly (2f) and, to a lesser extent (29a), with a trace of (4c). When the mixture was raised to ambient temperature there was an increase in the quantity of (16a) so that the ratio of (2f): (29a) was 1:1. At 75°C the quantity of (29a) was raised further, so that the ratio of (29a); (4c) was 4:1 with 5% (2f). This would indicate that not only was there conversion of (2f) to (4c) but also an increase in the formation of (29a).

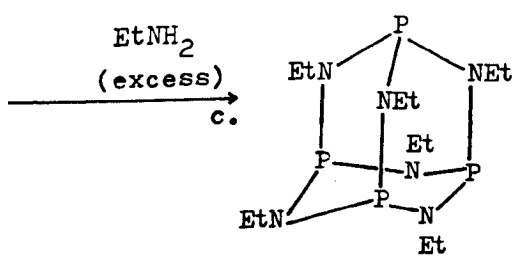
When heated in a vacuum for 1 hour the (29b) : (4c) ratio changed to 2:3 therefore there is also a conversion of (29b) to (4c). The conditions favouring the formation of each product are summarised in Reaction 4.6.



(2a) (29b)



(2h)



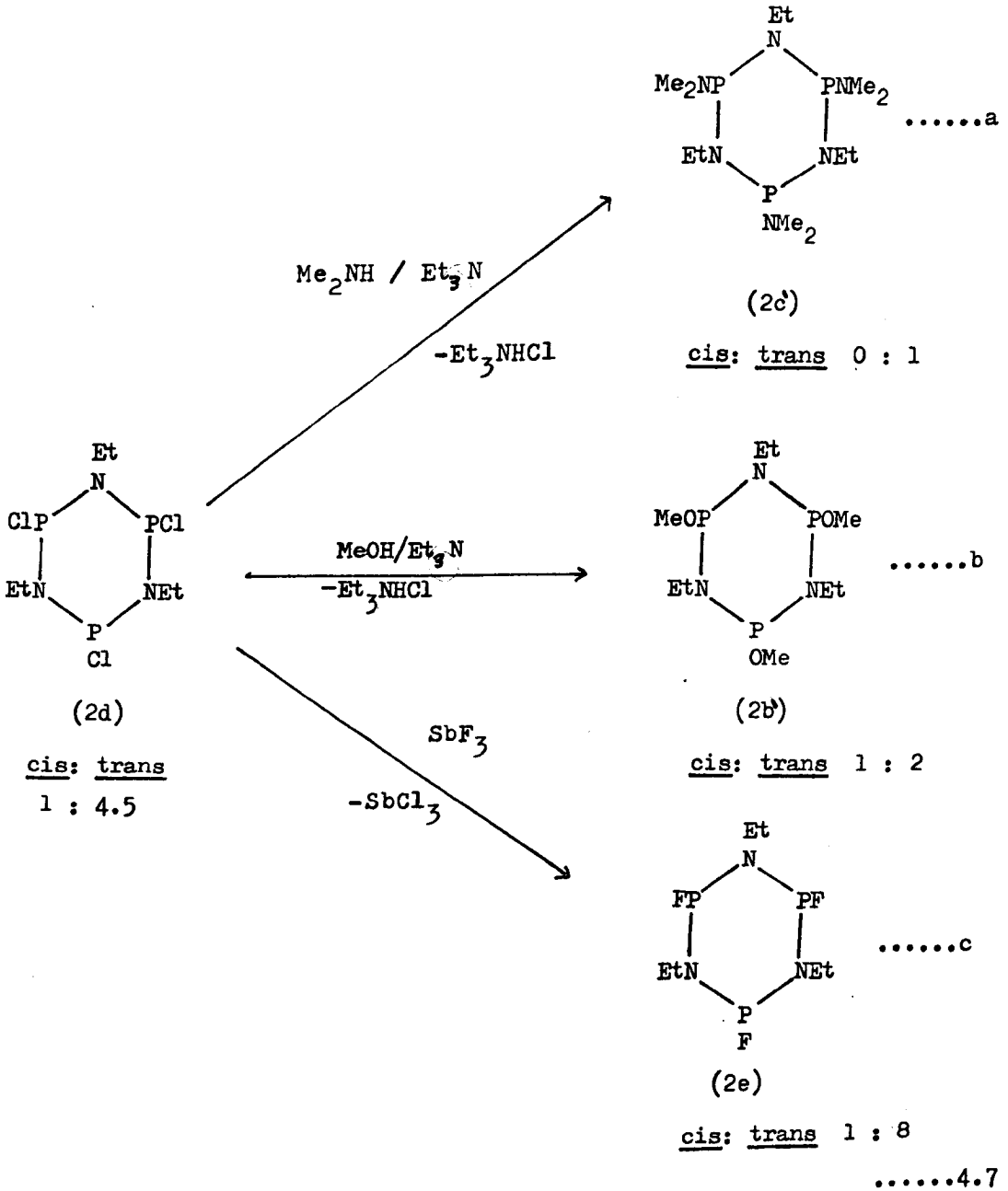
(4c) 4.6

Favoured conditions : a) polar solvent, high temperature (70°C)

b) low polarity solvent, high temperature (75°C)

c) low polarity solvent, ambient temperature

Derivatives of (2d) and (4a) have been prepared by substitution reactions similar to those applied to the cyclodiphosph-(III)azanes [34,49]. With derivatives of (2d), both cis and trans isomers were obtained in most cases, while derivatives of (4a) gave 'symmetric' and 'asymmetric' isomers, see page 142. A brief summary of the reactions involving (2d) and the isomer ratio of the products is given below in Reactions 4.7 a, b and c.



The trans-isomers were generally predominant and their ^{31}P n.m.r. signals always occured at lower field than the corresponding cis-isomers. Trans-isomers of the cyclodiphosph(III)azanes also have lower field signals than cis-isomers [34]. In addition, the phosphorus-phosphorus spin couplings are of a similar magnitude to those in cyclodiphosph(III)azanes, see Table 4.2. (cf. Table 4.12)

Table 4.2: ^{31}P n.m.r. data for $(XPNEt)_3$ derivatives.

X	$\delta_{(ppm)}$(a)			J_{PNP}(Hz)	Ratio
	cis	trans		trans	trans : cis
F	100.3	111.2	117.8	-	8.5 : 1
Cl	102.2	127.2	134.6	6.7(b)	4.1 : 1
OMe	97.7	104.0	113.9	12.7	2.2 : 1
NMe_2	-	107.8	109.2	17.0	100 : 1

(a) $CDCl_3$ solution at ambient temperature

(b) $-60^{\circ}C$

Zeiss and coworkers previously prepared a similar series of derivatives of the analogous methyl compound $(ClPNMe)_3$ [5] .

The infra-red spectrum of trans $(Me_2NPNMe)_3$, (2c) showed a P-N-P asymetric stretching mode at lower energy than any of the other derivatives (2b,d or e) suggesting that the phosphorus-nitrogen (ring) bonds in (2c) are slightly weaker than in (2b,d or e) see Table 4.3.

Table 4.3. P-N-P Asymmetric Stretching Modes in $(XPNR)_3$.

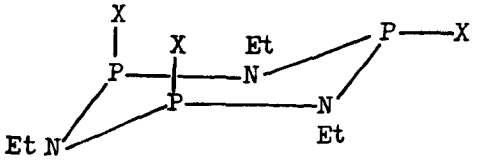
Compound		$\nu_{(PNP)}$ asym cm^{-1}		
$(MeOPNMe)_3$	(2b)	925	(892)*	
$(Me_2NPNMe)_3$	(2c)	915	907	(885)*
$(ClPNEt)_3$	(2d)	950	(912)*	

*, ( ) - indicates that the signal appears as a shoulder.

At ambient temperatures the trans isomers of the above compounds are favoured by the presence of electronegative substituents on phosphorus, in contrast cis isomers of cyclodiphosph(III)azanes are favoured by the same type of substituents, see Table 4.2. The ratios of isomers do not seem to be related in a simple way to the bulk of the phosphorus substituents.

The ^1H n.m.r. spectrum of $(Me_2NPNEt)_3$(2c') shows no indication of restricted rotation about the P-NMe_2 bond. This is in contrast with the case in the analogous cyclodiphosph(III)azanes where the restricted rotation is a feature. In $(Me_2NPNBu^t)_2$ the bulky Bu^t group raises the barrier to rotation.

Zeiss has suggested that the cis $(ROPNMe)_3$ isomers are (a,a,a) and that the trans isomers are (a,a,e) [5], see fig. 4.3 for trans form.



(X = OMe, OEt, OPr^i, OBu^t, OPh, p-BrC_6H_4O)

fig.4.3

The arrangement of axial phosphorus substituents avoids the eclipsing of the adjacent phosphorus and nitrogen lone-pairs, see fig. 4.4 (and page 52).

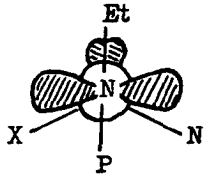
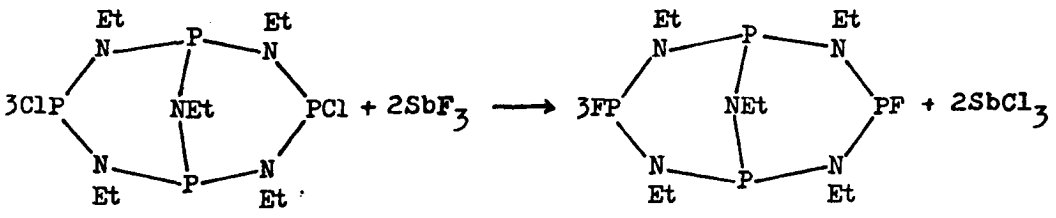


fig. 4.4

However, balanced against this is the steric congestion between the three axial substituents, and it is this steric factor which presumably results in trans isomers being favoured over cis isomers (see page 51-53) In the case of the dimethylamino-derivatives (2c), the bulk of the dimethylamino-group will be a major factor in discouraging cis-isomer formation. It should also be noted however, that this group is the least electronegative of those studied.

4.2d. Reactions of fused ring cyclophosph(III)azanes.

The fused ring compound (4a, X = Cl) also undergoes similar substitution reactions to those of (2e) giving alkoxy-, dialkylamino- and fluoro-derivatives. Compound (4a) is present as two isomers, symmetric and asymmetric, the symmetric form being predominant. At low temperatures the proportion of the asymmetric isomer was considerably reduced. The difluoro-derivatives (4d) was formed together with other unidentified products, by reaction with antimony trifluoride:



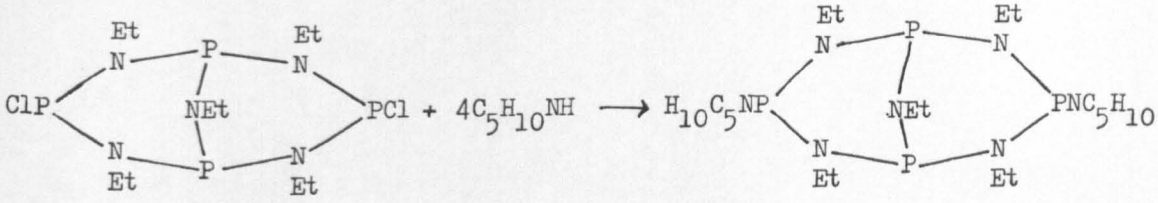
(4a) (4d) 4.8

The ^{31}P n.m.r. spectrum of (4d) at -65°C gave a symmetric : asymmetric isomer ratio of 3 : 2, the asymmetric isomer was absent in the chloro-derivative (4a) at a similar temperature.

In cyclodiphosph(III)azanes, isomer interconversion of chlorides probably proceeds by chloride ion exchange. It is not certain how interconversion would proceed with other types of substituent. It is reasonable to assume that with the fused ring cyclophosph(III)azanes, that isomer interconversion will follow a similar pattern.

4.2e. Amino and alkoxy derivatives of some fused ring cyclophosph(III)-azanes.

The addition of four molar equivalents of piperidine to (4a) produced the piperidino-derivative (4e), which exists in two isomeric forms, symmetrical and asymmetrical.



(4a) (4e)

+ $2C_5H_{10}NH_2Cl$

.....4.9

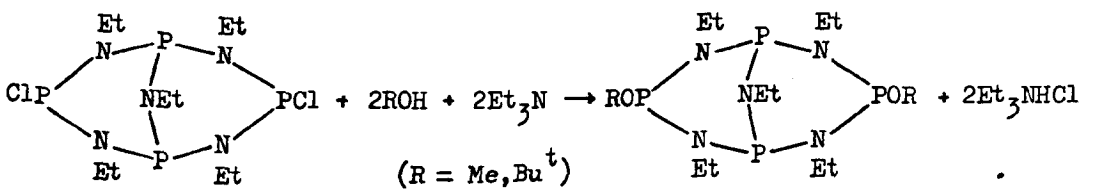
Initially the dominant isomer was the asymmetric form, unlike the starting material (4a) which is predominantly a symmetric isomer. Compound (4e) had symmetric : asymmetric isomer ratio of 1 : $3\frac{1}{2}$, but the proportion of symmetric isomer gradually increased with time. Similar observations were noted with dimethylamino and diethylamino derivatives of (4a). In all three cases the quantity of symmetric isomer increased until it was the dominant isomer, showing that it is the thermodynamically favoured isomer. The initial 'favouring' of the asymmetric isomer may be related to the minimising of steric interaction between the piperidino groups, thereby reducing the strain within the molecule.

? Something wrong with this sentence

Table 4.4. Initial and Final isomer ratios of amino derivatives, $P_4(NEt)_5X_2$.

X	Initial		Final	
	Sym.	Asym.	Sym.	Asym.
NMe_2	1	1.5	1	0.8
NEt_2	1	4.0	1	0.8
NC_5H_{10}	1	3.5	1	1

The alkoxy-derivatives (4f, X = OMe and Bu^t) were prepared as shown below

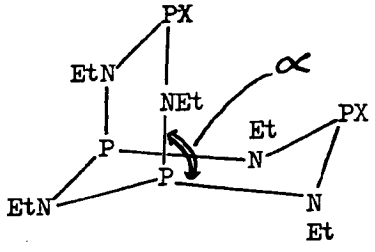


(4f) (R = Me,Bu^t)

.....4.10

However, unlike the alkylamino-derivatives, the alkoxy-derivatives showed a preference for the symmetric isomer,initially (4f , R = Me) exhibited a steady symmetric : asymmetric isomer ratio of 1.5 : 1 and (4f, R = Bu^t) gave an isomer ratio of 2 : 1. This difference in the preferred isomer formed immediately on reaction may be due to the alkoxy-derivatives being able to take up configurations which will minimise steric interactions through rotation about the phosphorus -oxygen bond.

The ^{31}P shifts of the bridging phosphorus atoms of (4a-) can imply some structural information about the isomers, see fig.4.5 and Table 4.5.



∝ = hinge angle

fig. 4.5

Table 4.5: ^{31}P n.m.r. shifts of bridge-phosphorus and shift differences between isomers of $P_4(NEt)_5X_2$.

X	^{31}P shifts Symmetric	Asymmetric	Shift difference (ppm)
Cl	54.3	36.9	17.4
F	46.6	35.4	11.2
NMe_2	82.6	58.5	24.1
NEt_2	85.6	58.3	27.3
NC_5H_{10}	82.0	56.8	25.2
OMe	62.1	43.5	19.6
OBu^t	71.7	50.7	21.0

Strong electron withdrawing species such as the halogen atoms give small shift differences, 11-17 ppm, between isomers, while electron donating groups such as the dialkylamino groups give larger shift differences, 24-27 ppm. This bridge-phosphorus shift difference between isomers may be related to variations in the arrangement and angles of bonds around the bridge phosphorus atom. Recent work by a Russian team has shown that variations in the bond angles at the phosphorus in phosphines leads to dramatic changes in both phosphorus shifts and coupling constants [181]. In general, the valence angles around 3-coordinate phosphorus is of the order of 100°. The exception to this is in the series PR_3 (R = alkyl or hydrogen). In this series changes in the angles around the phosphorus atom have been observed, and have been attributed to the redistribution of s and p character between the phosphorus orbitals involved in the bonding and the lone-pair. The progression down a series of phosphines follows a close curve when graphs are plotted (i) ^{31}P shift *vs.* angle,

(ii) J_{PH} *vs.* angle,

As angles increase, so shifts fall and coupling constants will increase, see table below ;

Table: Variations in ^{31}P shifts and J_{PH} with P bond angles.

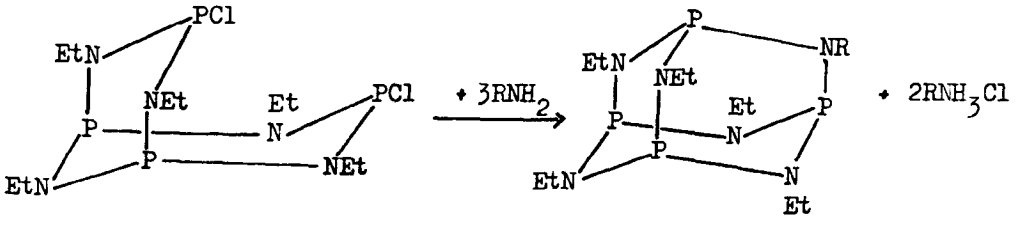
Compound	P bond angle(°)	δ_P(ppm)	J_{PH}(Hz)
PH_3	*ca.* 94	239	182.2
PBu^t	*ca.* 108	-63	196.0

Serious deviations can be observed when phosphines containing electronegative substituents are used. The extent of hybridisation in the phosphorus orbitals was determined by the use of ionisation potentials, n.m.r. shifts and coupling constants, and I.R. stretching vibration frequencies.

As in other phosphorus compounds, in the fused ring cyclo-phosph(III)azanes electronegative substituents give lower field shifts in the ^{31}P n.m.r. spectrum.

4.2f. Formation of cage compounds.

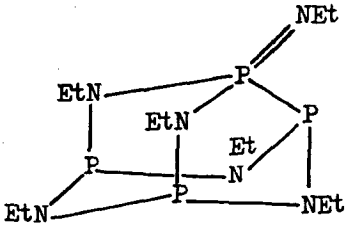
Adamantane-like cage compounds have been prepared from (4a) by reaction with primary amines (RNH_2; R = H, Et or Bu^t)



(4a) (4c, R = Et
g, R = Bu^t
h, R = H) 4.11

A single ^{31}P n.m.r. shift of 79.0 was obtained for (4c) showing that all four phosphorus atoms are identical. With (4g and h) there are two pairs of non-equivalent phosphorus atoms; (4g) gave ^{31}P shifts of 77.6 and 71.8 and J_{PNP} 19.3 Hz. Compound (4h) gave ^{31}P shifts of 86.9 and 69.2 J_{PNP} 18.2 Hz.

In the reaction of (4a) with ethylamine a weak set of signals, intensity ratio 2:1:1 was observed in the ^{31}P n.m.r. spectrum, δ_P 137.15, 56.9 and 4.1 respectively, J(PNP) 166.5 and 17.5 Hz. The large PNP coupling is consistent with a cage structure with a direct phosphorus-phosphorus bond (6) , similar to a compound observed by Zeiss (see page 21).



(6)

A third compound was obtained in similar quantities to (6) δ_P 7.6 and 122.3 (not scanned above δ_P 140), J(PNP) 15.1 Hz. This has been tentatively identified as the monoxide of (4a), (30a) An analogous monosulphide, $P_4(NMe)_6S$ has been prepared by Reiss et al[182] with δ_P 52 (P(III)) and 118 (P(V)). When left in Et_2O solution the proportions of both (6) and (30a) increase as (4c) decreases.

A crystalline product was obtained only in the case of (4c) which is a 'symmetrical' molecule. With (4g) and (4h) the initial product was a thick oil despite numerous attempts at crystallisation. Compound (4g) was distilled under reduced pressure, but when examined by ^{31}P n.m.r. spectroscopy it was shown to be the cage molecule (4f) and some traces of other unidentified materials; (4h) behaved similarly. Final identification of (4g) and (4h) was by mass measurement. The fact that (4g) does not crystallise may be due to adverse crystal packing effects, and is consistent with the fact that $P_4(NMe)_6$ is disordered in the solid state[182].

4.2g. Oxidation reactions of cyclotriphosph(III)azanes.

Some oxidation reactions of cyclotriphosph(III)azanes (2) by sulphur, selenium, tellurium and oxygen have been studied. The reaction of (2i) and (2j) with three mole equivalents of elemental sulphur or selenium results in the formation of the appropriate tris-chalcogen derivatives.

$$(Me_2NPNEt)_3 \xrightarrow{X_8} (Me_2N(X)PNEt)_3 \quad \text{.....4.12}$$

(2i) (31a, X = S; b, X = Se)

$$(MeOPNEt)_3 \xrightarrow{X_8} (MeO(X)PNEt)_3 \quad \text{.....4.13}$$

(2j) (31c, X = S; d, X = Se)

These oxidation products all have trans structures, as shown by ^{31}P n.m.r. (see Table 4.5).

Trans structures were obtained for $(MeO(Se)PNEt)_3$ and an impure sample of $(Me_2N(O)PNEt)_3$. The conformation of these examples may be compared with the twisted boat conformation of $(MeO(O)PNMe)_3$ as found by Bullen[110]. Therefore, based on Bullen's work , the assignments for the phosphorus shifts and phosphorus-phosphorus couplings in $(MeO(Se)PNEt)_3$ are shown in fig. 4.6,

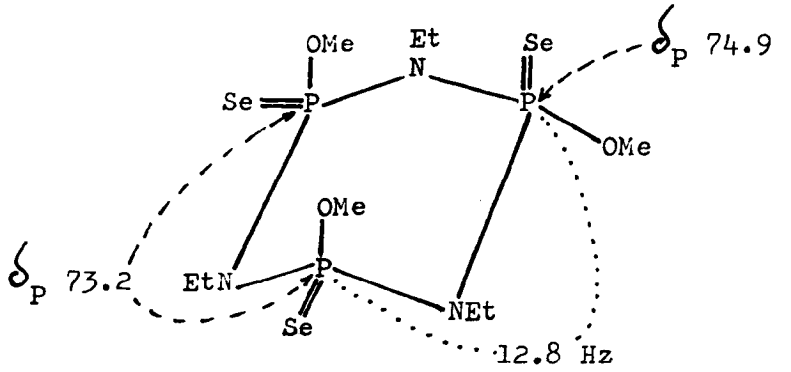


fig. 4.6

A monoxo-derivative, of $(ClPNEt)_3$ may have been made from the reaction of $(ClPNEt)_3$ with one mole equivalent of dimethylsulphoxide. This product gave ^{31}P n.m.r. shifts of 136.9 and 17.0 (ratio 2 : 1), J_{PNP} ca. 25Hz., see fig. 4.7.

A dioxo-derivative of $(ClPNEt)_3$ has been tentatively assigned to signals at δ_P 9.7 and 120. (ratio 2 : 1), J_{PNP} 42Hz. The attempted preparation of $(Me_2N(Te)PNEt)_3$ did not result in any identifiable products.

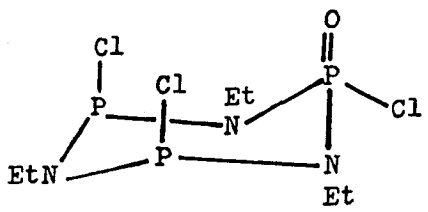


fig. 4.7

In the oxidation reactions described on the previous page, there is a preference for the formation of a trans isomer. Partial oxidation products can exist in numerous isomeric forms depending on the conformation of the ring and the axial or equatorial disposition of the phosphorus substituents.

A related series of oxidation reactions was carried out on the bicyclic compound (4a). The monoxide $P_4(NEt)_5Cl_2O$ (30 a) has been found in two forms. The first type (30 a(i)) gave three ^{31}P shifts 148.0, 123.1, and -5.2 with a ratio of 2 : 1 : 1 and couplings of 25.5 and 8.0 Hz. The other form (30 a(ii)) shows four phosphorus shifts 164.12, 146.7, 122.3 and -12.96, ratio 1 : 1 : 1 : 1, one coupling of 30 Hz was observed. The fact that this second conformer shows four non-equivalent phosphorus shifts suggest that the oxygen is bonded to a bridge phosphorus atom as shown in fig. 4.8.

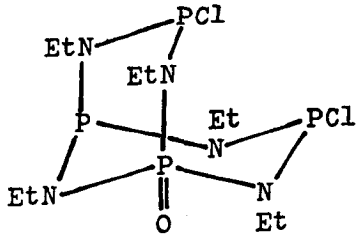


fig. 4.8.

The terminal phosphorus atoms are non-equivalent,(the terminal phosphorus atoms are not common to both 6-membered rings, in fig. 4.8 they are the phosphorus atoms bonded to chlorine). The non-equivalence of the terminal phosphorus atoms is due to either the conformation of the rings or the relative positions of the phosphorus substituents and the lonepairs, see fig.4.6 p.160 for the possible structures for compounds with a P_4N_5 skeleton.

Because of similarities in the shifts exhibited by the two isomers, it is probable that the first isomer also has the oxygen on the bridge phosphorus. When the spectrum was re-run at -65°C only the first conformer (30a(i)) was observed. This suggests that the difference between isomers is conformational rather than structural, ie. both conformers have oxygen on a bridge phosphorus atom.

A dioxo-derivative (30b) was also prepared using dimethylsulphoxide, but it gave little structural information, except to show that it had two pairs of non-equivalent phosphorus atoms. An attempt to form (30b) by bubbling dry oxygen through $P_4(NEt)_5Cl_2$ in petroleum ether failed to produce any (30b).

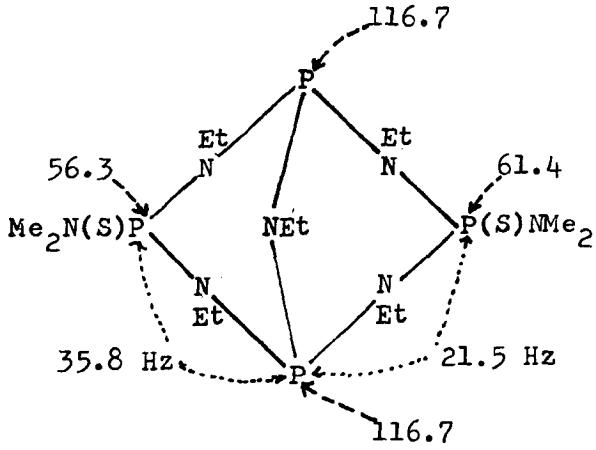
In $P_4(NEt)_6$, phosphorus and nitrogen lone-pairs are orthogonal and therefore not very reactive. In the bridged ring compound $P_4(NEt)_5Cl_2$ the bridging phosphorus atoms should have a near orthogonal arrangement of lone-pairs with neighbouring nitrogen atoms. Therefore these bridging phosphorus atoms are likely to be less nucleophilic than the terminal phosphorus atoms. The formation of 'bridging' oxygen compounds, as shown in fig. 4.8, is surprising.

Two mole equivalents of elemental sulphur were mixed with (4i) and (4e). The subsequent reactions were mildly exothermic and resulted in dithio derivatives being formed.

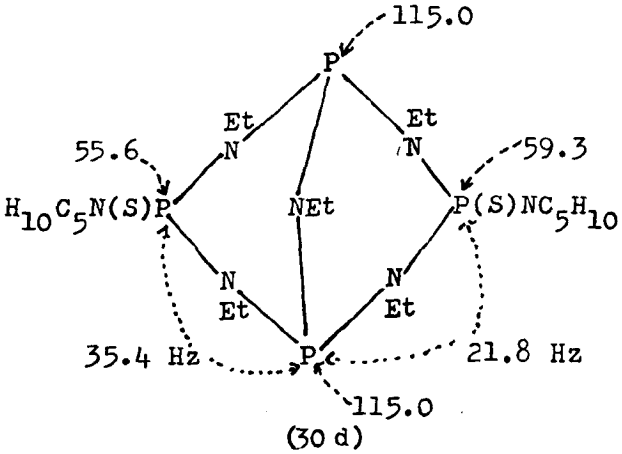
$$\underset{(4i)}{P_4(NEt)_5(NMe_2)_2} + \tfrac{1}{4}\,S_8 \longrightarrow \underset{(30c)}{P_4(NEt)_5(NMe_2)_2S_2} \qquad .....(4.16)$$

$$\underset{(4e)}{P_4(NEt)_5(NC_5H_{10})_2} + \tfrac{1}{4}\,S_8 \longrightarrow \underset{(30d)}{P_4(NEt)_5(NC_5H_{10})_2S_2} \qquad .....(4.17)$$

The ^{31}P n.m.r. spectrum of (29c) showed shifts of δ_P 116.7, 61.4 and 56.3 (ratio 2 : 1 : 1) and J_{PNP} 21.5 Hz and 35.8 Hz. Compound (29d) has a similar spectrum with δ_P 115.0, 59.3 and 55.6 (ratio 2 : 1 : 1) and J_{PNP} 21.8, 35.4 and 2.1 Hz. The starting materials (4e and i) gave high field ^{31}P n.m.r. shifts for the bridge phosphorus atoms and low field shifts for the terminal phosphorus atoms. However, the oxo-derivative (30a) showed that the bridge phosphorus atoms of oxidation products could have a low field shift. The most likely structure for (30c and d), based on the ^{31}P n.m.r. data, is as shown below.



(30c)



(30 d)

In the case of (30c and d), consideration of the phosphorus shifts suggests that the sulphur has reacted with the terminal phosphorus atoms. The identical shifts of the phosphorus(III) atoms and the difference in shifts for the phosphorus(V) atoms is best explained by phosphorus(III) atoms being found in the bridging position. This then requires that the phosphorus(V) atoms are in the terminal position. Some form of non-equivalent configuration between the terminal phosphorus(V) atoms and their substituents, could explain the difference in their phosphorus shifts. Therefore in the compounds $P_4(NEt)_5(NC_5H_{10})_2$, (4e) and $P_4(NEt)_5(NMe_2)_2$, (4i), the terminal phosphorus atoms are the more reactive, being more nucleophilic than the bridge phosphorus atoms. This is in line with the expected situation, see p.162, and is in contrast with that found in $P_4(NEt)_5Cl_2O$.

This difference in the location of the more nucleophilic phosphorus atoms is probably due to the different substituent effects between Cl and NMe_2 or NC_5H_{10}.

A similar reaction to 4.16 was carried out using excess sulphur. However no clearly identifiable product could be obtained. The reaction of (4d) with two mole equivalents of selenium gave fine colourless crystals, m.p. 136-138°C. Microanalysis and mass spectroscopy indicated that this was $P_4(NEt)_5(NC_5H_{10})_2Se_2$, but no satisfactory ^{31}P n.m.r. spectrum was obtained. The mass spectrum indicated a triselenide derivative, m/e = 744.

No reaction was observed between (4e) and excess tellurium the ^{31}P n.m.r. spectrum showed a mass of signals (δ_P 90-130) which proved impossible to analyse.

4.3. Experimental

2,4,6-Trichloro-1,3,5-triethylcyclotriphosph(III)azane.

Phosphorus trichloride (152.1g, 1.11mol), ethylamine hydrochloride (90.0g, 1.10mol) and sym-tetrachloroethane (600 ml) were mixed in a 1 litre round bottomed flask fitted with a 100cm air condenser and paraffin oil bubbler. The mixture was refluxed for 6 days, cooled to ambient temperature, filtered and the solvent removed. The oily brown residue was distilled under reduced pressure, b.p. 115°C (at 0.003 mm Hg) and the distillate recrystallised from light petroleum (b.p. 40-60°C) to give the compound (78g, 64% yield) m.p. 25-30°C. Omission of the recrystallisation step resulted in this product being contaminated with its monoxide.

^{1}H n.m.r. spectroscopy indicated that it was a mixture of cis and trans isomers, with the former being predominant. When left to stand in a small quantity of light petroleum (b.p. 40-60°C) only crystals of the cis isomer were obtained. For microanalysis, see Table 4.6.

2,4,6-Trichloro-1,3,5-tri-n-propylcyclotriphosph(III)azane.

Phosphorus trichloride (66.0g, 482 mmol) and n-propylamine hydrochloride (23.0g, 241 mmol) were refluxed in boiling sym-tetrachloroethane (350 ml) in a 1 litre round bottomed flask fitted with a 100 cm air condenser and paraffin oil bubbler, for 7 days. The solution was then cooled , filtered and the solvent removed to leave a viscous oil. Fractional distillation under reduced pressure gave two products,

(i) a clear liquid, b.p. = 65 °C at 0.01 mm Hg which gave a ^{31}P n.m.r. shift of 163.9 and m/e = 273, $C_4H_9Cl_4NP_2$ requires m/e = 273. This product is bis(dichlorophosphino)-n-propylamine.

(ii) a clear liquid, b.p. 130°C at 0.02 mm Hg which ^{31}P n.m.r. spectroscopy, microanalysis and mass spectroscopy showed to be 2,4,6-trichloro-1,3,5-tri-n-propylcyclotriphosph(III) azane $(ClPNPr^n)_3$, see Tables 4.6 and 4.7 for analytical data.

2,4,6-Trichloro-1,3,5-trimethylcyclotriphosph(III)azane.

Bis(dichlorophosphino)methylamine (100g, 395 mmol) was heated in a sealed container at 150°C for 4 days. Phosphorus trichloride (44.8g, 76% yield) was given off during the course of the experiment and trapped out. A brick-red coloured liquid remained at the end of the 4 days of heating, and this was distilled under reduced pressure to give a few drops of a clear liquid, b.p. = 110°C at 0.15 mm Hg, which on standing crystallised. This gave a ^1H n.m.r. spectrum corresponding to that of $(ClPNMe)_3$ [31].

2,4,6-Trifluoro-1,3,5-triethylcyclotriphosph(III)azane.

Antimony trifluoride (2.8g, 15.6mmol) was added to a solution of 2,4,6-trichloro-1,3,5-triethylcyclotriphosph(III)azane (5.2g, 15.8mmol) in light petroleum (b.p. 40-60° C) (20 ml) and the mixture refluxed for 1 hour. On cooling, the solution was filtered and the solvent removed to give a colourless liquid, which, when distilled under reduced pressure gave the compound (1.5g, 34%) b.p. = 70°C at 1mm Hg. This was confirmed by mass measurement, see Table 4.8.

2,4,6-Tris(dimethylamino)-1,3,5-triethylcyclophosph(III)azane.

Dimethylamine (2.7g, 60 mmol) was mixed with 2,4,6-Trichloro-1,3,5-triethylcyclotriphosph(III)azane (4.0g, 12.2 mmol) in diethyl-ether (50 ml) at 0°C under a nitrogen atmosphere. This immediately produced a white precipitate of dimethylamine hydrochloride which, when the solution was raised to room temperature, was filtered off. The solvent was removed to reveal an oil which was purified by vacuum distillation to give a clear liquid, bp = 110°-120°C at 0.005 mm Hg (2.8g, 65%). Microanalysis showed this to be the compound, 2,4,6-Tris(dimethylamino)-1,3,5-triethylcyclophosph(III)azane, see Table 4.6.

2,4,6-Trimethoxy-1,3,5-triethylcyclotriphosph(III)azane.

To a mixture of 2,4,6-trichloro-1,3,5-triethylcyclotriphosph-(III)azane (5.0g, 15.2mmol) and triethylamine (4.62g, 45.7mmol) in 200 ml light petroleum (b.p. 40-60°C) under N_2, was slowly added methanol (1.47g, 47.5 mmol). This immediately produced a white precipitate of triethylamine hydrochloride. When raised to ambient temperature the precipitate was filtered off and the solvent removed to give an oil which was purified by distillation to give a clear liquid (3.8g, 79.1%) b.p. 90°-100°C at 0.02 mm Hg. Identification was established by microanalysis, see Table 4.6.

2,4,6-Tripiperidino-1,3,5-triethylcyclotriphosph(III)azane.

Piperidine (6.2g, 7.8 mmol) in 15 ml of light petroleum (b.p 40°-60° C) was slowly added to 2,4,6-trichloro-1,3,5-triethylcyclo-triphosph(III)azane (4.0g, 12.2 mmol) in 50 ml of light petroleum (b.p 40°-60°C) at 0°C under a nitrogen atmosphere.

A white precipitate was immediately formed which was then filtered off at ambient temperature. Unfortunately this filtration was difficult. The solvent was removed leaving an oil which failed to crystallise from pentane. Attempts at distillation under reduced pressure produced only limited yields. This gave a pale yellow oil (b.p = 150°C at 0.02 mm Hg) (2.05g, 40%), which was the compound, found m/e = 474 $C_{21}H_{45}N_6P_3$ requires m/e = 474.

2,4,6-Tris(dimethylamino)-1,3,5-triethyl-2,4,6-tri thiocyclotriphosph(V)azane

To 2,4,6 Tris(dimethylamino)-1,3,5-triethylcyclophosph(III)-azane (1.0g, 2.82 mmol) in methylene chloride (10 ml) at 0°C, was added flowers of sulphur (0.28g, 8.75 mmol). The mixture was then shaken at ambient temperature till all the sulphur appeared to have dissolved. Excess sulphur was later filtered off and the solvent removed to give a cloudy oil. This was recrystallised from light petrol, b.p. 40-60°C, to give long thin needle crystals, m.p. 225-228°C, of the compound. The mass spectrum gave m/e = 450, $C_{12}H_{33}N_6P_3S_3$ requires m/e = 450. Microanalysis confirmed the identification, see Table 4.6.

2,4,6-Tris(dimethylamino)-1,3,5-triethyl-2,4,6- triselenocyclotriphosph (V)azane.

2,4,6-Tris(dimethylamino)-1,3,5-triethylcyclotriphosph(III)-azane (1.0g, 2.82 mmol) and finely powdered selenium (0.67g, 8.48 mmol) were refluxed in methylene chloride for 30 minutes. Unreacted selenium was filtered off and the solvent was removed to give an oil which on crystallisation from petrol (b.p. 40-60°C) gave fine white crystals 209-214°C. The mass spectrum gave m/e = 591, $C_{12}H_{33}N_6P_3Se_3$ requires 591. Identification of the compound was confirmed by microanalysis, see Table 4.6.

2,4,6-Tris(dimethylamino)-1,3,5-triethyl-2,4-diselenocyclotriphosphazane.

This was prepared similarly to the method above using 2,4,6-tris(dimethylamino)-1,3,5-triethylcyclotriphosph(III)azane (0.5g, 1.4 mmol) and selenium (0.24g, 3.0 mmol). This gave fine needle crystals (m.p. 165-167°C) in small yield (>5%). Mass spectroscopy gave m/e = 512, $C_{12}H_{33}N_6P_3Se_2$ requires m/e = 512.

2,4,6-Trichloro-1,3,5-triethyl-2-monoxocyclotriphosphazane.

(i) Dimethylsulphoxide (0.56g, 7.2 mmol) in methylene chloride (5 ml) was slowly added to 2,4,6-trichloro-1,3,5-triethyl cyclotriphosph(III)azane (2.3g, 7.0 mmol) in methylene chloride (10 ml) under nitrogen at -70°C. The solution was then raised to ambient temperature and the dimethylsulphide and solvent were removed to leave a yellow oil. This oil was distilled under reduced pressure (b.p. = 115-120°C at 0.002 mm Hg) to give a clear liquid (1.1g, 46.0%). Mass spectroscopy gave m/e = 343, $C_6H_{15}Cl_3N_3P_3O$ requires m/e = 343. The sample contained a quantity of the analogous dioxo-compound and so microanalysis could not be obtained.

(ii) Dry oxygen was bubbled through 2,4,6-trichloro-1,3,5-triethylcyclotriphosph(III)azane (1.0g, 3.0 mmol) in 10 ml methylene chloride for 48 hours. The solvent was removed to reveal a cloudy oil which, ^{31}P n.m.r. spectroscopy showed to be a mixture of unreacted starting material, monoxo- and dioxo-derivatives.

2,4,6-Trimethoxy-1,3,5-triethyl-2,4,6-trithiocyclotriphosph(V)azane

Flowers of sulphur (0.31g, 9.68 mmol) were added to 2,4,6-trimethoxy-1,3,5-triethylcyclotriphosph(III)azane (1.0g, 3.17 mmol) in methylene chloride (10 ml) and allowed to stand for several days. The solvent was then removed to leave a pale oil. Some clear rhombic crystals, m.p. = 79-82°C, were crystallised from light petroleum (b.p. 40-60°C). The mass spectrum gave m/e = 411, $C_9H_{24}N_3O_3P_3S_3$ required m/e = 411. See Table 4.6 for microanalysis.

2,4,6-Tripiperidino-1,3,5-triethyl-2,4,6-triselenocyclotriphosph (V)azane.

2,4,6-Tripiperidino-1,3,5-triethylcyclotriphosph(III) azane (0.42g, 0.88 mmol) and finely powdered selenium (0.21g, 2.7 mmol) were refluxed for 8 hours in 10ml of benzene. However, a large proportion of the selenium did not appear to have reacted. The solution was filtered and the solvent removed to reveal a white solid. A few fine white crystals (>5% yield) (m.p. 102-105°C) of the compound crystallised from light petroleum (b.p. 40-60°C). Identification was made by microanalysis, see Table 4.6.

2,4,6-Trimethoxy-1,3,5-triethyl-2,4,6-triselenocyclotriphosph (III)azane.

2,4,6-Trimethoxy-1,3,5-triethylcyclotriphosph(III)azane (1.0g, 3.17 mmol) and finely powdered selenium (0.76g, 9.62 mmol) were refluxed in methylene chloride (10 ml) for 1 hour. Some selenium was filtered off and the solvent removed. The product was an oil which failed to give any crystals from pentane or light petroleum. ^{31}P n.m.r. however, gave a spectrum which was consistent with $(MeO(Se)PNEt)_3$, although there were other compounds present.

2,4,6-Tripiperidino-1,3,5-triethyl-2,4,6-trithiocyclotriphosph(V)azane.

2,4,6-Tripiperidino-1,3,5-triethylcyclotriphosph(III)azane (0.75g, 1.58 mmol) and flowers of sulphur (0.16g, 0.5 mmol) were mixed together in 10 ml of methylene chloride. There was an immediate exothermic reaction and the solution was then refluxed for 30 minutes. The solution was filtered and the solvent removed to reveal a cloudy oil. Crystallisation from light petroleum (b.p 40°-60°C) gave small white crystals (m.p 65°-70°C) of the compound. Mass spectroscopy gave m/e = 570, $C_{21}H_{45}N_6P_3S_3$ requires m/e = 570. Identification was confirmed by microanalysis, see Table 4.6

3,7 -Dichloro-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane.*

A mixture of phosphorus trichloride (136.0g, 0.99 mol) and ethylamine hydrochloride (100.0g, 1.22 mol) in sym-tetrachloroethane (800 ml) was boiled under reflux (5 days) as in the preparation of 2,4,6-trichloro-1,3,5-triethylcyclotriphosph(III)azane. Removal of the solvent followed by crystallisation from light petroleum (b.p. = 40-60°C) gave crystals of the compound, m.p. 62-65°C ,(46g, 45%). Identification was confirmed by microanalysis and mass spectroscopy, see Tables 4.6and 4.7

* alternate name. - see Chapter 1.

3,7-Dipiperidino-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5-tetraphosphabicyclo-3,3,1-nonane.

An excess of piperidine (3.2g, 37.6 mmol) in diethylether (50 ml) was slowly mixed with a rapidly stirred solution of 3,7-dichloro-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane (2.0g, 4.9 mmol) in 150 ml of diethylether at $0^{\circ}C$. A white precipitate was immediately formed, the solution was allowed to slowly rise to ambient temperature and the white precipitate, which was water soluble, was filtered off. The solvent was removed by evaporation to yield an oil which gave small white crystals, mp. = 62°-$65^{\circ}C$, from crystallisation from pentane. Identification was carried out using microanalysis and mass spectroscopy, see Tables 4.6and 4.7.

3,7-Dimethoxy-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3.3.1-nonane.

Methanol (0.26g, 8.12 mmol) and (0.66g, 6.53 mmol) of triethylamine in 5 ml dry petroleum spirit were slowly added to (1.6g, 3.9 mmol) of 3,7-dichloro-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane in 50 ml dry petroleum spirit, and a white precipitate was immediately produced; this was removed by filtration. The solvent was removed to give a clear liquid which proved to be susceptible to hydrolysis. All attempts at crystallisation from pentane and light petroleum (b.p 40°-$60^{\circ}C$) failed and no sample could be isolated. Identification of the compound was made using mass spectroscopy, see Table 4.7.

3,7-Ditert-butoxy-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5-tetraphosphabicyclo-3,3,1-nonane.

This was produced by the same method as above, using (2.0g, 4.88 mmol) of 3,7-dichloro-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane and (0.59g, 7.97 mmol) of t-butanol and (0.8g, 7.92 mmol) of triethylamine in 60 ml of light petroleum (b.p 40°-60°C) at ambient temperature. The product was a cloudy oil and again purification was unsuccessful. Mass spectroscopy gave a parent ion m/e = 485, $C_{16}H_{43}N_5O_2P_4$ requires m/e = 485. A mass measurement m/e = 371.0939 corresponding to the loss of two t-butyl groups was obtained, however, a machine fault disallowed a scan in the region of m/e = 485.

3,7-Bis(dimethylamino)-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane.

Excess dimethylamine was bubbled through a solution of 3,7-dichloro-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane, (1.0g, 2.44 mmol) in 50 mls of methylene chloride at 0°C under a nitrogen atmosphere. The resulting precipitate, methylammonium chloride, was filtered off and the solvent removed to give an oil, This failed to crystallise from pentane even at -78°C. Identification was by mass measurement, see Table 4.8.

3,7-Bis(diethylamino)-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane.

Diethylamine (3.64g, 49.8 mmol) in 20 ml diethylether was slowly dropped into a rapidly stirring solution of 3,7-dichloro-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane, (5.1g, 12.4 mmol) in 100 ml diethylether at ambient temperature. As found in previous experiments, a white precipitate was immediately formed

This was filtered off and the solvent removed to give a viscous oil. All attempts at purification failed. Mass spectroscopy gave m/e = 483, $C_{18}H_{45}N_7P_4$ requires m/e = 483.

Phosphorus tri-N-ethylimide.

Ethylamine was bubbled through 3,7-dichloro-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane, (1.0g, 2.44 mmol) in 8 ml of diethylether. This immediately gave a white precipitate which was filtered off. The solvent was removed to give a cloudy oil which was distilled under reduced pressure to give a clear oil, bp. 100°C at 0.05mm Hg. This was further purified by sublimation onto a cold finger (-78°C) to give small clear crystals (m.p 40°-42°C). The mass spectrum gave m/e = 382, $C_{12}H_{30}N_6P_4$ requires m/e = 382. See Table 4.6 for microanalysis.

1,3,5,7-Tetraethyl-2,6-hydroimino-4,8-ethyliminocyclotetraphosph(III)azane.

Dry ammonia was bubbled through (2.0g, 4.88 mmol) of 3,7-dichloro-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosph-bicyclo-3,3,1-nonane in 60 ml diethylether while rapidly stirred. The resulting precipitate was removed by filtration and the solvent evaporated to reveal a cloudy oil, purification of which proved unsuccessful. Identification was by mass measurement, see Table 4.8.

1,3,5,7-Tetraethyl-4,8-ethylimino-2,6-t-butyliminocyclotetraphosph(III)azane.

t-Butylamine (1.1g, 15.1 mmol) was added dropwise to (2.0g, 4.88 mmol) of 3,7-dichloro-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane in 15 ml diethylether while rapidly stirred. A white precipitate was formed immediately and was later filtered off. The solvent was removed to yield a thick cloudy oil which was distilled under reduced pressure to give a clear liquid, b.p. 100°C at 0.09 mm Hg. but this was still impure when examined by microanalysis. See Table 4.6.

3,7-Bis(dimethylamino)-3,7-dithio-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane.

Sulphur (0.26g, 8.1 mmol) was slowly added to 3,7-bis(dimethylamine)-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane (1.85g, 4.3 mmol) in methylene chloride (5 ml) and stirred rapidly. The reaction was immediate and strongly exothermic. When cool the solution was filtered and the solvent removed to yield a cloudy oil which would not crystallise from petroleum ether. ^{31}P n.m.r., mass spectroscopy, and mass measurement confirm this product to be the dithio derivative, 3,7-bis(dimethylamino)-3,7-dithio-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane, $P_4(NEt)_5(NMe_2)_4S_2$, see Tables 4.7 and 4.8.

3,7-Dipiperidino-3,7-dithio-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane.

Sulphur (0.14g, 4.4 mmol) was slowly added to 3,7-dipiperidino-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane (1.1g, 2.2mmol) in a rapidly stirred solution of light petroleum (b.p 40°-60°C) (8 ml). The reaction was mildly exothermic. The solution was filtered and the solvent removed to give a thick viscous oil which crystallised from light petroleum (b.p. 40-60°C) to give white crystals m.p 118°-120°C (0.55g, 44% yield). ^{31}P n.m.r. spectroscopy, microanalysis and mass spectroscopy identified this product as 3,7-di piperidino -3,7-dithio-2,4,6,8,9-pentaethyl-2,4,6,8,9-pentaaza-1,3,5,7-tetraphosphabicyclo-3,3,1-nonane, $P_4(NEt)_5(NC_5H_{10})_2S_2$, see Tables 4.6 and 4.7.

The reaction of methylamine with 2,4,6-Trichloro-1,3,5-triethylcyclotriphosph(III)azane.

Dry methylamine was bubbled through 2,4,6-trichloro-1,3,5-triethylcyclophosph(III)azane (3.5g, 10.6 mmol) in light petrol (b.p 40°-60°C) (50 ml). A white precipitate of methylamine hydrochloride was immediately formed. The precipitate was later filtered off and the solvent removed to give a thick oil. No clearly identifiable product could be obtained. However, ^{31}P n.m.r. gave groups of signals which suggested that polymerisation had occurred.

The reaction of ethylamine with 2,4,6-Trichloro-1,3,5-triethylcyclotriphosph(III)azane.

Dry ethylamine was bubbled through 2,4,6-trichloro-1,3,5-triethylcyclophosph(III)azane (1.1g, 3.34 mmol) in light petroleum (40°-60°C) (50 ml) and this immediately produced a white precipitate of ethylamine hydrochloride which was later filtered off. The solvent was removed to give a clear oil which ^{31}P n.m.r. spectroscopy showed to contain;

(i) a substituted ring, 2,4,6-tris(ethylamino)-1,3,5-triethylcyclotriphosph(III)azane.

$(Et(H)NPNEt)_3$, δ_P = 107.1, $J_{PP'}$ = 13.8 Hz (2)

δ_P = 95.9, $J_{PP'}$ = 13.8 Hz (1)

(ii) a bridged compound, 1-ethylamino-2,4,6,7-tetraethyl-1,2,4,6,7-pentaaza-1,3,5-triphosphabicycloheptane

δ_P = 206.0, $J_{PP'}$ = 5.2 Hz (2)

δ_P = 97.1, $J_{PP'}$ = 5.2 Hz (1)

(iii) a small trace of phosphorus tri-N-ethylimide ($P_4(NEt)_6$)

M/e = 382

δ_P = 79.2

Product ratios (i) : (ii), 1:1 with traces of (iii)

Heating the mixture under a nitrogen atmosphere resulted in the increase of (iii) and a decrease of the other products. It proved impossible to separate the products of this experiment.

The reaction of t-butylamine with 2,4,6-Trichloro-1,3,5-triethylcyclotriphosph(III)azane.

Dry t-butylamine (4.36g, 60 mmol) in diethylether (20 ml) was slowly added dropwise, under a nitrogen atmosphere, to a rapidly stirred solution of 2,4,6-trichloro-1,3,5-triethylcyclotriphosph(III)azane (3.25g, 9.9 mmol) in diethylether (60 ml). A white precipitate was immediately formed during the mildly exothermic reaction. The eventual product was a clear oil, b.p 98.0°C at 0.0 mm Hg.

^{31}P n.m.r. spectroscopy, mass spectroscopy and mass measurement identified the product to be a mixture of:

(i) a substituted ring, 2,4,6-tri(t-butylamino)-1,3,5-triethylcyclotriphosph(III)azane

$\delta_P = 106.5, J_{PP'} = 12.5$ Hz (2)

$\delta_P = 92.8, J_{PP'} = 12.3$ Hz (1)

(ii) a 1-t-butylamino-2,4,6-triethyl-7-t-butyl-1,2,4,6,7-pentaaza-1,3,5-triphosphabicycloheptane.

$\delta_P = 201.1, J_{PP'} = 0.1$ Hz (2)

$\delta_P = 98.9, J_{PP'} = 15.6$ Hz (1)

(iii) unidentified large singlets δ_P ca. 122

Initially there was a greater amount of substituted ring product (i), but this quickly decreased as the amount of the bridged product (ii) increased.

The reaction of isopropylamine with 2,4,6-trichloro-1,3,5-triethylcyclotriphosph(III)azane.

Dry isopropylamine (3.58g, 61.7 mmol) in diethylether (50 ml) was slowly dropped into a rapidly stirring solution of 2,4,6-trichloro-1,3,5-triethylcyclotriphosph(III)azane (3.3g, 10.0 mmol) in diethylether (100 ml) under a nitrogen atmosphere. A white precipitate (Pr^iNH_3Cl) was immediately formed, this was filtered off and the solvent removed to give a cloudy oil which distilled under reduced pressure to yield a clear liquid, b.p = 106°C at 0.1 mm Hg (0.56g, 14.1% yield) and this was suggested by ^{31}P n.m.r. spectroscopy and mass measurement to be the bridged compound 1-isopropylamino-2,4,6-triethyl-7-isopropyl-1,2,4,6,7-pentaaza-1,3,5-triphosphabicycloheptane.

The ^{31}P n.mr. spectrum contained signals at δ_P = 199.4, J_{PNP} = 4.0 Hz and δ_P = 201-205, broad ratio 2:: 1. There was no signal corresponding to a cage compound.

Attempted preparation of 2,4,6-tribromo-1,3,5-triethylcyclotriphosph(III)azane.

2,4,6-Trichloro-1,3,5-triethylcyclotriphosph(III)azane (3.2g, 10.7 mmol) and phosphorus tribromide (2.7g, 10.0 mmol) were mixed together in a distillation apparatus and gradually heated under nitrogen to distil off phosphorus trichloride. The product was then recrystallised from light petroleum (b.p. 40-60°C) to give a few crystals, m.p. 43-45°C, believed to be the compound. However the product decomposed before an accurate microanalysis or mass spectrum could be obtained. The ^{31}P n.m.r. spectrum showed a broad band of signals over most of the range 0-200 ppm, though there was a large singlet at δ_P 148.3. The I.R. spectrum showed a signal at 525 cm^{-1} which may be from a P—Br stretching 'frequency'.

Table 4.6 Microanalysis data for some tricyclo- and cage-structure phosphazanes.

Compound	Expt.			Theory.		
	C	H	O	C	H	O
$(ClPNEt)_3$	21.76	5.06	12.9	21.79	4.57	12.79
$(Me_2NPNEt)_3$	40.6	9.25	24.0	40.7	9.33	23.7
$(MeOPNEt)_3$	33.9	7.45	13.6	34.3	7.62	13.35
$(ClPNPr^n)_3$	28.9	6.09	-	29.15	5.7	11.34
$(Me_2N(S)PNEt)_3$	32.27	7.14	18.5	32.0	7.34	18.67
$(MeO(S)PNEt)_3$	26.42	6.12	9.52	26.28	5.84	10.22
$(C_5H_5N(S)PNEt)_3$	44.8	7.25	14.56	44.2	7.9	14.74
$(Me_2N(Se)PNEt)_3$	24.36	5.58	14.23	24.37	5.59	14.22
$(C_5H_5N(Se)PNEt)_3$	36.8	6.5	12.3	35.5	6.3	11.8
$P_4(NEt)_5Cl_2$	28.7	7.1	16.6	29.3	6.1	17.0
$P_4(NEt)_5(C_5H_{10}N)_2$	48.6	8.9	19.05	48.3	9.0	19.7
$P_4(NEt)_5(C_5H_{10}N)_2S_2$	41.54	7.85	17.1	42.0	7.88	17.17
$P_4(NEt)_5(C_5H_{10}N)_2Se_2$	36.4	6.86	14.91	36.1	6.77	14.74
$P_4(NEt)_6$	37.6	7.9	22.3	37.7	7.9	22.0

Table 4.7 Mass spectroscopy data for some tricyclo — and cage-structure phosphazanes.

Compound	Expt.(m/e)	Theory.(m/e)
$(ClPNEt)_3$	329	329
$(Me_2NPNEt)_3$	354	354
$(MeOPNEt)_3$	315	315
$(FPNEt)_3$	279	279
$(C_5H_5NPNEt)_3$	474	474
$(ClPNPr^n)_3$	359	359
$(Bu^tN(H)PNEt)_3$	438	438
$(Me_2N(S)PNEt)_3$	450	450
$(MeO(S)PNEt)_3$	411	411
$(C_5H_5N(S)PNEt)_3$	570	570
$(MeOPNEt)_3S_2$	379	379
$(MeOPNEt)_3S$	347	347
$(Me_2NPNEt)_3S_2$	512	512
$(ClPNEt)_3O$	345	345
$P_4(NEt)_5Cl_2$	410	410
$P_4(NEt)_5(NMe_2)_2$	427	427
$P_4(NEt)_5(NEt_2)_2$	483	483
$P_4(NEt)_5(NC_5H_5)_2$	507	507

Table 4.7 ...(cont.)

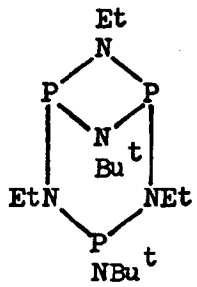
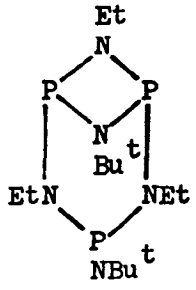
Compound	Expt.(m/e)	Theory.(m/e)
$P_4(NEt)_5(OMe)_2$	401	401
$P_4(NEt)_5(OBu^t)_2$	485	485
$P_4(NEt)_6$	382	382
$P_4(NEt)_5(NH)$	354	354
$P_4(NEt)_5(NBu^t)$	410	410
$P_4(NEt)_5(NMe_2)_2S_2$	491	491
$P_4(NEt)_5(NC_5H_{10})_2S_2$	571	571
$P_4(NEt)_5(NC_5H_{10})_2Se$	665	665
	365	365

Table 4.8 Mass measurement data for some cyclic- and linked ring phosph(III)azanes.

Compound	Expt.	Theory
$(FPNEt)_3$	279.0428	279.0423
$(Bu^t(H)NPNEt)_3$	438.2120	438.2918
$P_4(NEt)_5(OMe)_2$	401.1431	401.1431
$P_4(NEt)_5(NMe_2)_2$	427.2069	427.2063
$P_4(NEt)_5(NMe_2)_2S_2$	491.1494	491.2460
$P_4(NEt)_5(NH)$	354.1178	354.1169
$P_4(NEt)_5(NBu^t)$	410.1837	410.1797
	365.2028	365.2027

Note ; Masses were calculated using ;

^{12}C = 12.000000

^{1}H = 1.0078246

^{14}N = 14.003074

^{16}O = 15.9949141

^{31}P = 30.973764

Table 4.9 ^{31}P n.m.r. data for some cyclotriphosphazanes.†

Compound		δ_P(ppm)	J_{PNP}(Hz)
$(ClPNEt)_3$	...cis	104.1	-
		102.2*	6.7
	..trans	129.0^1 / 135.4^2	
		127.2^1 / 134.6^2 *	6.7
$(ClPNPr^n)_3$	...cis	105.3	
	..trans	130.6^1 / 136.5^2	-
$(ClPNMe)_3$	...cis	101.4	
		99.4*	6.7
	..trans	127.2^1 / 134.6^2	-
		125.8^1 / 131.4^2 *	6.7
$(FPNEt)_3$	...cis	100.4	-
		99.2*	6.2
	..trans	111.2^1 / 117.8^2	-
		108.2^1 / 116.1^2 *	6.2
$(ClPNEt)_3O$		140.6 /148.6 / 2.8	2.0 / 23.9 / 28.5
$(Et(H)NPNEt)_3$		95.9^1 / 107.1^2	13.8
$(Pr(H)NPNEt)_3$		93.4^1 / 104.2^2	<13.5
$(Bu^t(H)NPNEt)_3$		92.8^1 / 106.5^2	12.4

Table 4.9 ...(cont.)

Compound		δ_P(ppm)	J_{PNP}(Hz)
$(MeOPNEt)_3$	...cis	97.7	-
	..trans	104.0[1] / 113.9[2]	12.7
$(Me_2NPNEt)_3$	..trans	107.8[1] / 109.2[2]	17.0
$(MeO(Se)PNEt)_3$	trans	74.9[1] / 73.2[2]	12.8
$(ClPNEt)_3O_2$		9.7[2] / 120.0[1]	42.0
$(ClPNEt)_3O$	(a)	17.0[1] / 136.9[2]	ca. 25
	(b)	140.6 / 148.6 / 2.8	2.0 / 23.9 / 28.5

† Data normally recorded at ambient temperatures.

* indicates data recorded at -65°C.

Table 4.10 ^{31}P n.m.r. data for some bicyclic phosphazanes†

Compound		δ_P (ppm)	J_{PNP} (Hz)
$P_4(NEt)_5Cl_2$	'A'	51.8 *	8.0 *
		130.77*	
	'B'	33.64 (x)	7.5
		120.8	13.0
		132.1	
$P_4(NEt)_5(NC_5H_{10})_2$	'A'	82.0	13.5
		97.0	
	'B'	56.9 (x)	17.4
		71.2	12.1
		81.2	
$P_4(NEt)_5(NMe_2)_2$	'A'	82.7	12.8
		101.8	
	'B'	58.5 (x)	18.5
		76.4	11.7
		85.1	
$P_4(NEt)_5(NEt_2)_2$	'A'	85.6	13.7
		100.4	
	'B'	58.3 (x)	19.6
		74.3	12.4
		81.4	
$P_4(NEt)_5(OMe)_2$	'A'	62.1	9.0
		108.1	
	'B'	43.5 (x)	7.5
		97.5	1.0
		102.2	

Table 4.10 (cont.)

$P_4(NEt)_5(OBu^t)_2$		72.0 103.8	8.0
$P_4(NEt)_5(NMe_2)_2S_2$		116.7 (2) 61.4 56.3	35.8 21.5
$P_4(NEt)_5(NC_5H_{10})_2Se_2$		115.0 (2) 59.3 55.6	35.4 21.8 (J_{PNPNP} = 2.1)
$P_4(NEt)_5Cl_2O$ [a]	(i)	-5.2 123.1 148.0 (2)	25.5 8.0
	(ii)	-12.96 122.3 146.7 164.12	30.0 8.0
$P_4(NEt)_5Cl_2O_2$ [a]		10.95 138.0	30.0
$P_4(NEt)_5F_2$ [a]	'A'	46.6 218.7	8.1
	'B'	35.4 (2) 116.2 119.3	9.2 ca. 5.5

† Data normally recorded at ambient temperature.

* Data recorded at -60 C.

(a) Tentative identification based on the ^{31}P n.m.r. data.

(2) Indicates that this is the shift associated with 2 phosphorus atoms.

Table 4.11 ^{31}P n.m.r. data for some cage phosph(III)azanes.†

Compound	δ_P (ppm)	J_{PNP}(Hz)
$P_4(NEt)_6$	79.0	-
$P_4(NEt)_5(NH)$	70.0 86.9	18.1
$P_4(NEt)_5(NBu^t)$	71.8 77.6	19.3

† Data recorded at ambient temperature.

Table 4.12 ^{31}P n.m.r. shifts for $(XPNR)_2$.

R	X	δ_P(ppm) Cis	Trans
Et	Cl	227.3	-
Bu^t	Cl	207.2	-
Bu^t	NMe_2	95.0	184.7
Bu^t	OMe	133.7	202.4

Appendix A

Purification of solvents and reagents.

Many experiments were carried out under an atmosphere of nitrogen dried by passing the gas through silica gel and phosphorus pentoxide.

Anhydrous solvents were used at all times. These solvents were dried by contact with sodium wire or molecular sieves type 4a.

All amines were distilled from sodium hydroxide pellets with the exception of methylamine and dimethylamine, which were dried by passing the vapours through a sodium hydroxide column. Amine hydrochlorides were dried under reduced pressure.

Phosphorus trichloride was purified by distillation as was sym-tetrachloroethane,

Chlorine was dried by passing the gas through a column of phosphorus pentoxide.

Alcohols, sulphur, selenium, tellurium and boron trifluoride were obtained commercially and used without further purification.

Appendix B

Instrumentation.

(a) N.M.R.

Continuous wave ^{1}H and ^{31}P n.m.r. spectra were obtained using a Jeol C60HL spectrometer at ca. 60 and 24,3MHz respectively. ^{1}H and ^{31}P decoupling were carried out using a Schomandl ND 100M frequency synthesiser and a Jeol SDHC amplifier unit. ^{31}P resonance frequencies were measured by a Racal frequency counter.

Pulsed-Fourier-transform ^{31}P n.m.r. spectra were obtained using a Varian XL-100 spectrometer at ca. 40.5MHz.

(b) I.R.

The infra-red spectra were obtained using a Perkin-Elmer 257 I.R. spectrometer.

(c) Mass Spectroscopy.

The mass spectra were obtained using an A.E.I. MS 12.

(d) Microanalysis.

Microanalysis data were determined by the Microanalysis laboratory, Department of Chemistry, University of Glasgow.

(e) Mass Measurements.

Mass measurements were obtained on an A.E.I. MS 9.

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Compound Reference Numbers

1. Cyclodiphosph(III)azanes

(a) $(ClPNPh)_2$

(b) $(Bu^t(H)NPNBu^t)_2$

(c) $(ClPNBu^t)_2$

(d) $(ClPNR)_2$ R = Me or Et

(e) $(ROPNPh)_2$ R = Me, Et or Bu^t

(f) $(Me_2NPNBu^t)_2$

(g) $Me_2N\overline{PNBu^t.PCl.NBu^t}$

(h) $(FPNR)_2$

(i) $(Et_2NPNMe)_2$

(j) $(R_2NPNR)_2$ R = $SiMe_3$

(k) $(R^1_2NPNR^2)_2$ $R^1 = Pr^i$, $R^2 = Bu^t$

(l) $Br\overline{P.NR.PN(H)R.NR}$ R = $SiMe_3$

(m) $Br\overline{P.NR.PR.NR}$ R = $SiMe_3$

(n) $(MeOPNBu^t)_2$

(p) $(Bu^tPNMe)_2$

(q) $(BrPNBu^t)_2$

(r) $Cl\overline{P.NEt.PCl.NBu^t}$

(s) $Cl\overline{P.NMe.PCl.NBu^t}$

(t) $Cl\overline{P.NBu^t.PBr.NBu^t}$

2. Cyclotriphosph(III)aganes.

(a) $(X\,PN\,Me)_3$ X = Cl or Br

(b) $(RO\,PN\,R')_3$ R = Me or Et, R' = Me or Et.

(c) $(RR'PN\,R')_3$ R = Me or Et, R' = Me or Et.

(d) $(Cl\,PN\,Et)_3$

(e) $(F\,PN\,Et)_3$

(f) $(R(H)N\,PN\,Et)_3$

(g) $(R(H)N\,PN\,Pr^i)_3$

(h) $(R(H)NPN\,Bu^t)_3$

(i) $(Me_2NPN\,Et)_3$

(j) $(MeO\,PN\,Et)_3$

3. Acyclic phosph(III)aganes.

$(X_2P)_2NR$

(a) $(Cl_2P)_2NPh$

(b) $P(NMe_2)_3$

(c) $[(Me_2N)_2P]_2NMe$

(d) $(Ph_2P)_2NMe$

(e) $(Ph_2P)_2NEt$

(f) $(Ph_2P)_2NPr^i$

4. Ethylimino derivatives of some phosphaganes.

(a) $P_4(NEt)_6X_2$ X = Cl or Br

(b) $P_4(NEt)_5X$, X = S, Se or NBu^t

(c) $P_4(NEt)_6$

(d) $P_4(NEt)_5F_2$

(e) $P_4(NEt)_5(NC_6H_{10})_2$

(f) $P_4(NEt)_5(OR)_2$ R = Me or Bu^t

(g) $P_4(NEt)_5NBu^t$

(h) $P_4(NEt)_5NH$

(i) $P_4(NEt)_5(NMe_2)_2$

Note: 4(b), (X = NBu^t) and 4(g) have different structures.

5. Phosph(V)azenes.

$RR'NP{=}NR$ $\quad R' = Bu^t$ $\quad R = SiMe_3$

(a) $Cl_3P{=}NBu^t$

6. Imino-derivative

$P_4(NMe)_6X$ $\quad X = O, S, NBu^t$

7. Linked ring phosph(V)azane

$P_4(NR)_6$ $\quad R = C_3H_7$

8. Cyclodiphosph(V)azanes

(a) $(Cl_3PNMe)_2$

(b) $(F_3PNMe)_2$

(c) $(Cl_3PNPh)_2$

(d) $(Cl_3PNEt)_2$

(e) $(Cl_3PNPr^n)_2$

(f) $Cl_3\overline{P.NBu^t.PCl_2Br.NBu^t}$

(g) $Cl_3\overline{P.NEt.PCl_2Br.NEt}$

(h) $(Cl_2BrPNEt)_2$

9. Mixed oxidation compounds

(a) $(ClPNR)_2O$

(b) $(ClPNR)_2S$

(c) $Me_2N(X)\overline{P.NBu^t.PNMe_2.NBu^t}$

(d) $MeO(S)\overline{P.NBu^t.PO Me.NBu^t}$

10. P(V) compounds

(a) $Cl(O)\overline{P.NR.P(S)Cl.NR}$

(b) $(Me_2N(S)PNBu^t)_2$

(c) $(R(H)N(S)PNR)_2$

(d) $(Cl(S)PNR)_2$ $\quad R = Ph$ or $4\text{-}Cl\text{-}C_6H_4$

11. Ionic derivatives

(a) $Me_2\overline{P^+.NBu^t.PCl.NBu^t}$ $\quad I^-$

(b) $Me_2\overline{P^+.NBu^t.PMe.NBu^t}$ $\quad X^-$

(c) $\overline{P^+.NBu^t.PMe.NBu^t}$ $\quad AlCl_4^-$

(d) $Me_2N(Me)\overline{P^+.N(SiMe_3)_2.P.NMe_2.N(SiMe_3)_2}$ $\quad I^-$

12. Borane adducts

(a) $(Me_2N)_3P.BH_3$

(b) $[(Me_2N)_2P(BH_3)]_2NMe$

(c) $Ph_2P(BH_3).NMe.PPh_2$

(d) $Ph_2P(BH_3).NEt.PPh_2$

(e) $Ph_2P(BH_3).NPr^i.PPh_2$

13. $(RO)_3P.BH_3$

14. $R_3P.BH_3$

15. $C_5H_9O_3P$

16. $C_6H_9O_3P$

17 (a) $(Me_2N)_3P{=}S$

(b) $(Me_2N)_3P^+X$ $\quad X^-$

18. Borane adducts

(a) $Me_2N\overline{P\,NBu^t\,P(BH_3)}NMe_2.\,NBu^t$

(b) $MeO\overline{P\,NBu^t\,P(BH_3)}OMe.\,NBu^t$

(c) $Cl\overline{P\,NBu^t\,P(BH_3)}Cl\,NBu^t$

19. Bis-borane adducts

(a) $(F(BH_3)P\,NBu^t)_2$

(b) $(MeO(BH_3)P\,NBu^t)_2$

(c) $(Me_2N(BH_3)P\,NBu^t)_2$

20. Mixed oxidation states

(a) $Cl\overline{P\,NBu^t\,PCl_3}\,NBu^t$

(b) $Cl\overline{P\,NBu^t\,P^+Cl_2}\,NBu^t.\,Cl^-$

(c) $Cl\overline{P\,NBu^t\,PClBr_2}\,NBu^t$

(d) $Br\overline{P\,NBu^t\,PBr_3}\,NBu^t$

(e) $Me_2N\overline{P\,NBu^t.\,P(NMe_2)Br_2}\,NBu^t$

(f) $Cl\overline{P\,NEt.\,PClBr_2}.\,NBu^t$

21. $Cl_2P(O)N{=}PCl_2N(H)Bu^t$

22. Zwitterions

$F_4\overline{P^-\,NBu^t\,P^+(F)Bu^t}.\,NBu^t$

(a) $Cl_4\overline{P^-\,NBu^t\,P^+Cl_2}.\,NEt$

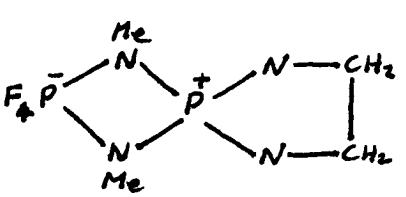
(b) $Cl_4\overline{P^-\,NBu^t\,P^+Cl_2}.\,NMe$

(c) $ClBr_3\overline{P^-\,NBu^t\,P^+ClBr}.\,NBu^t$

23. $Cl_4\overline{P^-\,NMe\,P^+Cl}.\,NMe$

24. $F_5P^-.CH_2.P^+F(NMe_2)_2$

25.



26. $F_4\overline{P^-\,NBu^t\,P^+F_2}\,NBu^t$

27. Acyclic diphosph(III)azanes

(a) $(Cl_2P)_2NMe$

(b) $(Cl_2P)_2NEt$

(c) $(Cl_2P)_2NPr^n$

28. Phosph(V)azene monomers

(a) $Cl_3P{=}NMe$

(b) $Cl_3P{=}NEt$

(c) $Cl_3P{=}NPr^n$

(d) $BrCl_2P{=}NEt$

30. Oxidation products.

(a) $P_4(NEt)_5Cl_2O$

(b) $P_4(NEt)_5Cl_2O_2$

(c) $P_4(NEt)_5(NMe_2)_2S_2$

(d) $P_4(NEt)_5(NC_5H_{10})_2S_2$

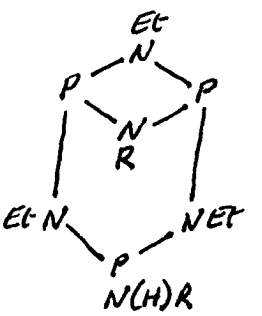
31. (a) $(Me_2N(S)PNEt)_3$

(b) $(Me_2N(Se)PNEt)_3$

(c) $(MeO(S)PNEt)_3$

(d) $(MeO(Se)PNEt)_3$

29.



(a) R = Et

(b) R = Pr

(c) R = Bu^t